ADVANCED POLYMERS VIA MACROMOLECULAR ENGINEERING 2023

BOOK OF ABSTRACT

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TBD

Monday, 24th April - 08:50: Plenary Session 1 - Oral

Prof. Christopher Barner-Kowollik [1]

1. *School of Chemistry and Physics, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia*

TBD

Poly(ethylene glycol) isomers (rPEG) as an alternative to PEG: biocompatible, highly water-soluble, non-immunogenic and amorphous polymers

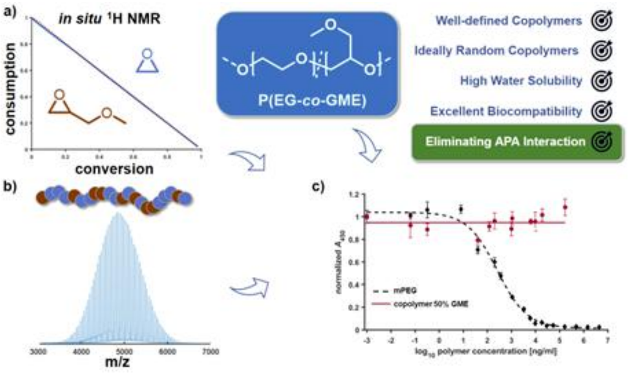
Monday, 24th April - 10:10: Oral Session 1-1 - Oral

Prof. Holger Frey [1], ***Dr. Philip Dreier*** [1], ***Dr. Rebecca Matthes*** [1], ***Mr. Fabian Fuss*** [2], ***Mr. Julian Schmidt*** [2]

1. *University of Mainz*, ***2.*** *Johannes Gutenberg University Mainz*

We are currently witnessing the triumph of nanomedicine, a field that developed rapidly in the 2000s, culminating in the development of the mRNA vaccines against COVID-19, which is enabled by lipid nanoparticles (LNP). Poly(ethylene glycol) (PEG) is at the heart of nanomedicine as a highly biocompatible polymer, which plays a key role in conjunction with many nanotherapeutics due to its high water solubility and excellent biocompatibility, both for the stabilization of LNPs as well as for the widely used “PEGylation” biotherapeutic molecules or by surface coverage of medical nanocarriers. Whereas it was initially believed that PEG is immunologically inert, it has become obvious in recent decades that an increasing number of individuals shows hypersensitivity to PEG and PEGylated pharmaceuticals,[1] ranging from mild symptoms to life threatening anaphylaxis reactions.[2] These adverse reactions are attributed to anti-PEG antibodies (APAs). Consequently, various potential alternatives based on different polymer classes or proteins were investigated as substituents for PEG in the last couple of years, e.g. hydrophilic poly(2-oxazoline)s or polysarcosine.

We introduce a fundamentally different approach to avoid adverse recognition of PEGylated therapeutics and nanomedicines by anti-PEG antibodies. Mimicking nature, the well-defined incorporation of statistically distributed “point mutations” in PEG chains is achieved by anionic random copolymerization of ethylene oxide (EO) with hydrophilic glycidyl ethers, such as glycidyl methyl ether (GME), disabling antibody recognition. We believe that this concept is universally applicable to generate non-immunogenic polymer-conjugated nanotherapeutics. It should be emphasized that any random copolymer of EO and GME is a structural isomer of PEG. Figure 1 shows the structure of copolymers the respective P(EG-*co*-GME) copolymers formed by anionic ROP copolymerization of EO and GME as well as a) *in situ* NMR data, evidencing ideally random copolymerization; b) a typical MALDI-TOF spectrum of a P(EG-*co*-GME) copolymer; c) competitive ELISA data comparing mPEG and 50 mol% GME-containing copolymer with respect to APA interaction, demonstrating that recognition by APA is avoided.



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Sequence control by anionic polymerization

Monday, 24th April - 10:40: Oral Session 1-1 - Oral

Prof. Takashi Ishizone [1]

1. *Tokyo Institute of Technology*

It is known that 1,1-diphenylethylene (DPE) shows a negligible homopolymerizability but undergoes the anionic copolymerization with styrene in the alternating fashion. We found that the anionic polymerization of asymmetric AB-type divinyl monomer, 1-(4-vinyl)-1-phenylethylene having styrene (A) and 1,1-diphenylethylene (B) frameworks in one molecule, proceeds in a “self-alternating manner”. The resultant polymer had almost perfect $(AB)_n$-type alternating sequence, supporting the self-alternating polymerization mechanism. The NMR and MALDI-TOF-MS measurements of the resulting polymer revealed the unique intermolecular cross-propagation behavior. On the other hand, the electrophilicity of DPE derivatives and the nucleophilicity of the corresponding DPE carbanions can be changed by the substituents on the aromatic ring. For example, 1,1-bis(4-cyanophenyl)ethylene (CN2DPE) possessing electron-withdrawing cyano groups shows a higher electrophilicity compared with a parent non-substituted DPE but the resulting CN2DPE anion shows a nucleophilicity lower than that of the DPE anion. A repeating 1:1 addition reaction using 1,1-diphenylethylene (DPE) derivatives, known as “living anionic addition reaction (LAAR),” was performed to construct defect-free DPE sequences composed of non-homopolymerizable vinyl compounds at the polystyrene terminals. In addition to the parent DPE, four functional DPE derivatives possessing electron-donating (*N*,*N*-dimethylamino and trialkylsilyloxy) and electron-withdrawing (bromo and cyano) groups were employed in the LAAR using a living difunctional polystyryl anion. The relative reactivity of the derivatives was predicted by their Hammett substituent constant s_p and vinyl b-carbon chemical shifts. The stoichiometric addition reaction between the resulting DPE anion and more electrophilic derivatives quantitatively proceeded in one direction, even in the presence of residual derivatives. The sequential addition of DPE derivatives in increasing order of their relative electrophilicity to living anionic polystyrene successfully generated a series of AB-, ABC-, and ABCD-type chain-end sequence-controlled polystyrenes with well-defined structures in one-pot reactions.

Design of norbornene–ethylene–vinyl acetate/vinyl alcohol multiblock copolymers: Impact of the chain structure on the copolymer properties

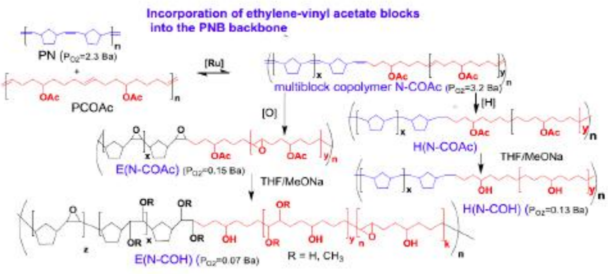
Monday, 24th April - 11:10: Oral Session 1-1 - Oral

***Mr. Alexey V. Roenko* [1], *Ms. Olga A. Adzhieva* [1], *Dr. Roman Yu. Nikiforov* [1], *Dr. Nikolay A. Belov* [1], *Dr. Yulia I. Denisova* [1], *Dr. Maria L. Gringolts* [1], *Dr. Yaroslav V. Kudryavtsev* [2]**

***1.** TIPS RAS, **2.** ESPCI-Paris, PSL University, Sorbonne University, CNRS - UMR7615 - UMR7083 - UMR7167, Paris, France; TIPS RAS, Moscow, Russia*

Multiblock copolymers attract considerable interest due to their ability to combine the properties of individual components [1]. In this work, new norbornene-based functional multiblock copolymers containing ethylene–vinyl acetate/vinyl alcohol sequences are synthesized via the olefin cross-metathesis reaction of polynorbornene with poly (5-acetoxy-1-octenylene) followed by epoxidation, hydrogenation, and deacetylation reactions [2]. The copolymer formation and its gradual randomization by segment reshuffling promoted by Grubbs' catalyst of the 1st generation and polymer-based Ru-carbenes are monitored by in situ ^{1}H NMR and ex situ ^{13}C NMR spectroscopy. The kinetic study reveals that, despite the presence of bulky acetoxy substituents in polyoctenamer chains, Grubbs' catalyst interacts with them more easily than with polynorbornene chains. The rate of the subsequent interchange reaction is controlled by the interaction of [Ru]=poly(5-acetoxy-1-octenylene) carbenes with norbornene units. The chain structure and, therefore, physico-chemical characteristics of multiblock copolymers can be tailored by adjusting the cross-metathesis conditions, such as the polymer concentration, polymer to catalyst ratio, and reaction time. The influence of post-modification on the thermal, mechanical, and gas separation properties of the new copolymers is studied. It is shown that the developed methods efficiently improve the barrier properties, reducing the oxygen permeability up to 30 times in comparison with polynorbornene [3]. The obtained results are promising for various applications and can be extended to a broader family of polydienes and other polymers containing backbone double bonds.

[1] M.L. Gringolts et al. Beilstein J. Org. Chem. 15 (2019) 218
[2] Yu.I. Denisova et al. Polym. Chem. 11 (2020) 7063
[3] A.V. Roenko et al. Polymers 14 (2022) 444



Kudryavtsev apme 23 scheme.png

Polyester and synthetic polypeptide polyHIPEs prepared by ring-opening polymerization

Monday, 24th April - 11:25: Oral Session 1-1 - Oral

Dr. Petra Utroša [1], ***Dr. Ozgun Can Onder*** [1], ***Prof. Sebastijan Kovačič*** [1], ***Dr. Ema Žagar*** [1], ***Dr. David Pahovnik*** [1]

1. National Institute of Chemistry

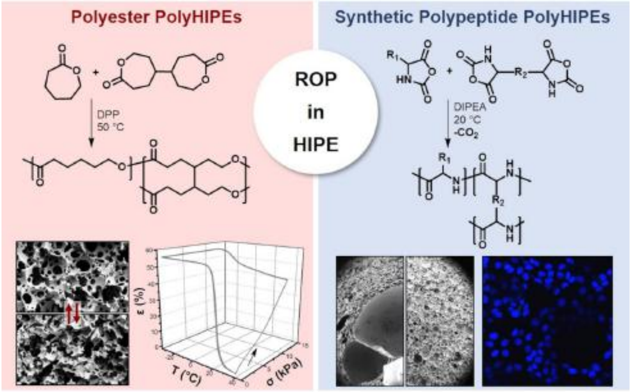
High internal phase emulsion (HIPE) templating is an attractive approach for the preparation of scaffolds with suitable morphology for biomedical applications. Degradable porous materials are often required, which can be prepared by ring-opening polymerization (ROP) of heterocyclic monomers such as lactones for polyesters and *N*-carboxyanhydrides (NCAs) of α-amino acids for polypeptides. We have prepared fully degradable porous materials by ROP directly in the continuous phase of anhydrous HIPEs. PolyHIPEs based on crosslinked polyester, poly(ε-caprolactone) (PCL), were prepared by organocatalytic ROP of ε-caprolactone and show shape memory behavior with excellent shape fixity and shape recovery [1]. We have further extended the synthetic ROP method in HIPE to the polymerization of various types of NCAs to prepare synthetic polypeptide polyHIPEs [2]. The polymerization rate was found to be an extremely important parameter for the successful preparation of polypeptides with typical polyHIPE morphology, as it determines the rate of CO_2 release from HIPE during polymerization. Cell culture studies showed good viability, migration and proliferation of cells on poly(γ-benzyl-L-glutamate) (PBLG) polyHIPE scaffold. By deprotection of the corresponding polypeptide organogels, the stimuli-responsive polypeptide hydrogels with fully preserved polyHIPE morphology were prepared [3]. The hydrogels exhibit pH-dependent behavior, which can be modulated along with their mechanical properties by changing the chemical composition of the polypeptides. We also copolymerized PBLG and PCL allyl-functionalized star macromonomers by thiol–ene photopolymerization in HIPEs to prepare synthetic polypeptide–polyester polyHIPEs [4]. The thermomechanical properties of the polypeptide–polyester polyHIPEs were tuned by varying the PBLG:PCL ratio. Furthermore, we prepared a bilayered PBLG–PCL polyHIPE consisting of two chemically and mechanically different and covalently bonded layers without disturbing the polyHIPE morphology.

[1] P. Utroša, O. C. Onder, E. Žagar, S. Kovačič, D. Pahovnik. *Macromolecules* **2019**, 52, 9291.

[2] O. C. Onder, P. Utroša, S. Caserman, M. Podobnik, M. Tušek Žnidarič, J. Grdadolnik, S. Kovačič, E. Žagar, D. Pahovnik. *Polymer Chemistry* **2020**, 11, 4260.

[3] O. C. Onder, P. Utroša, S. Caserman, M. Podobnik, E. Žagar, D. Pahovnik. *Macromolecules* **2021**, 54, 8321.

[4] P. Utroša, Š. Gradišar, O. C. Onder, E. Žagar, D. Pahovnik. *Macromolecules* **2022**, 55, 5892.



Polyester and polypeptide polyhipes by rop.jpg

Towards fully biodegradable coatings by photo-induced ring-opening polymerization

Monday, 24th April - 11:40: Oral Session 1-1 - Oral

Dr. Julien Pinaud [1], ***Dr. Nicolas Zivic*** [1], ***Dr. Thomas Brossier*** [1], ***Mrs. Floriane Crestey*** [1], ***Dr. Sylvain Catrouillet*** [1], ***Dr. Abraham Chemtob*** [2], ***Dr. Valerie Heroguez*** [3], ***Dr. Patrick Lacroix-Desmazes*** [1], ***Dr. Christine Joly-Duhamel*** [1], ***Dr. Sebastien Blanquer*** [4]

1. *CNRS ICGM,* ***2.*** *UHA,* ***3.*** *Laboratoire de Chimie des Polymères Organiques (LCPO), UMR 5629 CNRS Université de Bordeaux, Pessac,* ***4.*** *Montpellier*

UV-curing is a very effective technique employed both at industrial and academic levels to introduce coatings with specific functionalities (scratch resistance, hydrophobicity, anti-bacterial….) onto various substrates (wood, leather, plastic…).[1] To date, this technology mainly relies on a photo-induced radical polymerization mechanism that limits the range of materials to be employed as coatings but, most importantly, that severely limits the degradability of such coatings by introducing C-C bonds in the polymer backbone. Consequently, like many other plastics, organic coatings also contribute to the global plastic pollution that is now a major concern of our society.[2] The development of a UV-curing technology able to deliver biodegradable coatings is thus necessary. Among the various photopolymerization mechanisms that have been developed over the past ten years, photo-induced ring-opening polymerization (photoROP), using photobase or photoacid generators, has emerged as a powerful technique to prepare biodegradable polymers with well-defined structures and monomer unit sequences.[3] Nevertheless, most of these achievements have been obtained in organic media, which limits the production of biodegradable materials at an industrial level.

Starting from our previous study on the photoROP of cyclic esters and carbonates in solution,[4] this contribution reports on the preparation of biodegradable polyester-carbonate thermosets by UV-induced bulk ROP of a liquid trimethylene carbonate bis-functionalized monomer. In the present study, the influence of various experimental parameters such as initiator type, exposure time, components ratio, and temperature on the progress of the photoROP has been evaluated. Finally, the most promising formulations allowed for the preparation of self-standing films, and for the first time, biodegradable patterned coatings using stereolithography (Figure 1).

Figure 1: Production of biodegradable polyester-carbonate thermosets by UV-induced bulk ROP of a liquid trimethylene carbonate bis-functionalized monomer.

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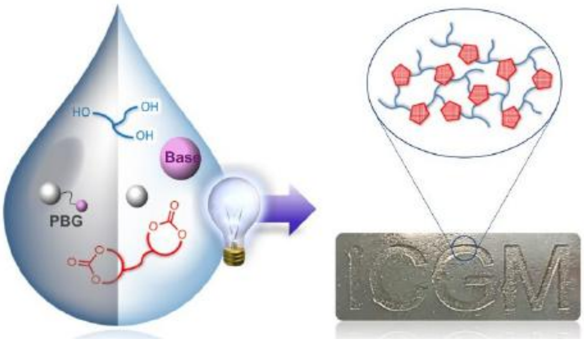

Photorop.jpg

The three C's: Copper, Cobalt, Control' Sustainability and use of flow chemistry

Monday, 24th April - 10:10: Oral Session 1-2 - Oral

Prof. David Haddleton [1]

1. *University of Warwick*

Cobalt(II) mediated catalytic chain transfer polymerisation is one of the most successful yet neglected forms of controlled radical polymerisation. Most of us use commercial products which utilise this chemistry. Certain low spin cobalt(II) compounds based on vitamin B12 undergo reversible chain transfer in a methacrylate polymerisation to give omega-propenyl low molecular weight polymethacrylates, often termed macromonomers. These products themselves are indeed RAFT agents that predate S containing RAFT agents. The chemistry is effective in all solvents from water to cyclohexane and in all types of free radical polymerisation processes including emulsion, suspension, solution and bulk. The so called macromonomers also act as radical chain stoppers leading to block copolymers with other monomers including ethene. The propenyl group can be functionalised by thiol-ene, epoxidation, hydroamination, etc to give alpha functional short chain polymers which are used as dispersants and surfactants in all types of media and polymerisable surfactants. Sequential monomer addition in emulsion can lead to multi block copolymers via sulfur free RAFT. Hyperbranched soluble polymers are easily formed via polymerisation of multifunctional monomers such as EGDMA. Relatively low amounts of catalyst can be used to give dimers and low molecular weight oligomers that contain internal addition fragmentation groups that are currently being used in photo3D printing – adaptive manufacturing. We will also be looking at the use of online monitoring by NMR of polymerisations carried out in flow reactors.

Synthesis of Functional Polyolefin Materials

Monday, 24th April - 10:40: Oral Session 1-2 - Oral

Prof. Eva Harth [1]

1. *University of Houston*

The modification and functionalization of polyolefins is a grant challenge to improve their properties for higher-value products. Interactive properties that can increase adhesion and comparability are some of the main objectives in areas of coating, blending and composites. Fundamental issues exist to incorporate polar monomers during the polyolefin polymerization process or to efficiently post-modify existing polyolefins. We report on the strategies and mechanistic investigations to build di- and multiblock architectures containing segments of polyethylene and polyvinyls, polyacrylates and polyamides. In a one-catalyst strategies we demonstrate (a) a photoinitiated homolytic metal-carbon bond cleavage to form polyolefin macroradicals, (b) radical trapping and (c) fluorinated acrylate chelate complexes which can contribute to the preparation of a divers set of functional polyolefins. The mechanistic features of the Metal-organic light initiated radical polymerization (MILRad) and MILRad functionalization highlight the properties of diimine Pd complexes to form polyolefin macroradicals which can either propagate in a free radical polymerization pathway or are trapped by functionalized TEMPO for controlled radical polymerization. These two methods are employed to prepare block copolymers that contain living ethylene polymerizations and controlled polyacrylate and polyvinyl chains. Diimine Pd(II) fluorinated acrylate chelates provide living polymerization of ethylene and alpha olefins and circumventing the use of chain transfer reagents to result in polyolefins with an active ester chain end. This process allows the introduction of initiation units to give a broad range of block copolymers with high control. The lecture will feature the future possibilities of these approaches to address current challenges in energy conversion and harvesting as well as the upcycling of polymeric materials.

Chemical Upcycling of Polyethylene into α,ω – Functionalized Platform Oligomers

Monday, 24th April - 11:10: Oral Session 1-2 - Oral

Mr. Adamu Aminu Idris [1]***, Dr. Jean Raynaud*** [1]***, Dr. Vincent Monteil*** [2]***, Dr. Véronique Dufaud*** [1]***, Dr. Sebastien NORSIC*** [1]

1. *Université de Lyon, CNRS, Université Lyon 1, CPE Lyon, UMR 5128 - CP2M (Catalysis, Polymerization, Processes & Materials), PolyCatMat team, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne,* ***2.*** *Université de Lyon, CNRS, Université Lyon 1, CPE Lyon, UMR 5128 - CP2M (Catalysis, Polymerization, Processes & Materials), PolyCatMat team, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne, France.*

The strong $C(SP^3) – C(SP^3)$ σ-bonds of polyethylenes are undoubtedly not only the origin for PEs robustness and chemical inertness to many reagents but also hampers their chemical recycling. With a plastic waste generation projected at 1014 million tonnes in 2060 [1] which is seemingly countering the UN 2050 net-zero carbon emission for which plastic production and mechanical recycling contribute significantly, chemical recycling became an additional solution to help tackle the global waste problem [2, 3]. Synthesis of functionalized telechelic oligomers from PEs waste would be a very valuable and viable route to plastic circularity [4]. To carry out precise degradation chemistry with PE, the intermediate introduction of reactive functional groups such as e.g. alkene is advantageous [5]. Herein, we present a two-step process for upcycling polyethylene into α,ω–divinyl, and α,ω–diester oligomers *via;* transition metal–catalyzed partial dehydrogenation and metathesis. We have shown that different levels of internal unsaturation can be installed on the PEs backbone by playing catalyst ligand, loading, or conditions of dehydrogenation. The subsequent cross-metathesis of these internally desaturated polyethylenes with ethylene and *cis*–1,4–diacetoxy–2–butene as chain transfer agents afforded divinyl and diester telechelic with 86 % and 91 % conversions respectively. The products of the two-step process could be used as feed for the synthesis of recycle-by-design polymers, thereby reducing the exploitation of fossils for polymer production and its associated environmental impact.

References

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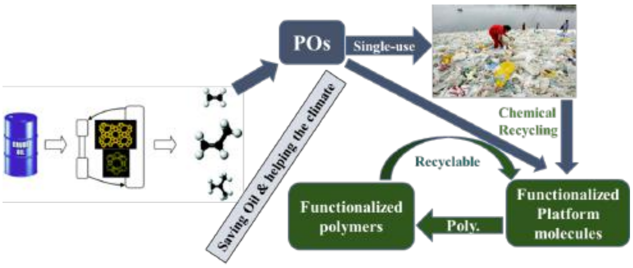

Apme 2023 - graphical abstract.png

Catalytic Chemical Recycling of CO2-Derived Polycarbonates

Monday, 24th April - 11:25: Oral Session 1-2 - Oral

Dr. Thom McGuire [1], ***Dr. Antoine Buchard*** [2], ***Prof. Charlotte Williams*** [1]

1. University of Oxford, 2. University of Bath

Introduction

The chemical recycling of polymers to monomers is important to realizing a truly circular, plastic economy.[1] Polycarbonates derived from CO_2 and epoxides are attracting attention as plastics, elastomers and in higher polymer manufacture,[3] but investigations of their chemical recycling to monomer are limited to bespoke systems in which the epoxide co-monomer has low ring-strain. Here, homogeneous di-nuclear catalysts derived from earth-abundant metals (e.g. Mg(II)) are used to successfully recycle a range of CO_2-derived polycarbonates to epoxides and carbon dioxide. [3,4]

Methods

Depolymerizations were performed in the solid-state using polymer/catalyst films with reactions monitored by TGA, NMR spectroscopy, MS, ATR-IR and SEC. To isolate epoxides on a multi-gram scale, reactions were performed using vacuum transfer apparatus.

Results and Discussion

Using a hetero-dinuclear Mg(II)Co(II) complex, the depolymerizations of CO_2-derived polycarbonates proceeded with excellent efficiency and selectivity at low catalyst loadings (TOF = 25,700 h^{-1}, epoxide selectivity >99%, 0.02 mol%, 140 °C). The Mg(II)Co(II) complex shows metal-metal synergy, giving rise to significantly faster rates than the homo-dinuclear analogues. Kinetic and reactivity investigations suggest that the depolymerization occurs from a metal-alkoxide intermediate at the polymer chain-end and that the reaction is entropically driven. A range of processes for the recovery of the epoxides after depolymerization are discussed and successful repolymerization is demonstrated. Lastly, catalyst recycling is possible over at least four cycles without any compromise in turnover number or purity of the epoxide.

This research shows that CO_2-derived polycarbonates have great potential as chemically recyclable alternatives to polyolefins. Such materials will be particularly beneficial in sectors where demand for recycling is high, such as packaging, consumer goods and the automotive industry.

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4. T. M. McGuire, A. Deacy, F. N. Singer, A. Buchard, C. K. Williams, *J. Am. Chem. Soc.* 2022, 144, 40, 18444–18449

Paris figure-2.jpg

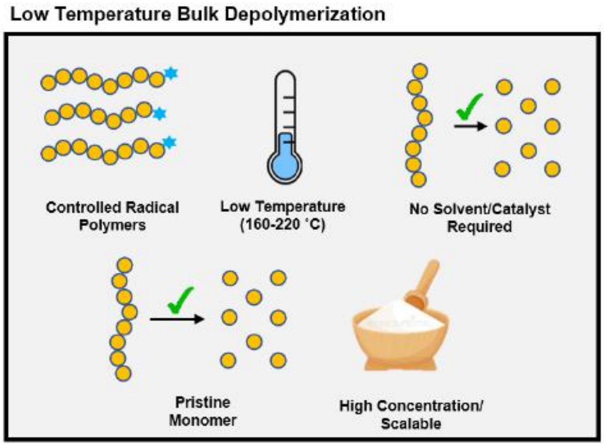
Solvent-Free Depolymerization of Polymers made by ATRP and RAFT Polymerization.

Monday, 24th April - 11:40: Oral Session 1-2 - Oral

Dr. Richard Whifield [1], ***Prof. Athina Anastasaki*** [1]

1. ETH Zurich

Although controlled radical polymerization is an excellent tool to make precision polymeric materials, reversal of the process to retrieve the starting monomer is far less explored despite the significance of chemical recycling. Current depolymerization approaches typically require elevated temperatures (>350 ˚C), high dilutions in specific solvents (typically 0.1-25 mM polymer concentrations), and/or expensive catalysts. Here, we report that RAFT and ATRP synthesized polymers can undergo a low-temperature solvent-free depolymerization back to monomer. The key to the success of the strategy is a facile and quantitative end-group modification step, which yields modified polymers that depolymerize to high conversions at far lower temperatures. In fact, the onset of depolymerization was achieved at 150˚C and more than 90% depolymerization could be obtained at 220 ˚C. The versatility of the methodology was demonstrated by a scalable depolymerization (~10 g of starting polymer) retrieving 84% yield of the starting monomer intact which could be subsequently used for further polymerization. This represents a new low-energy approach for depolymerizing controlled radical polymers and creates many future opportunities as high-yielding, solvent-free and scalable depolymerization methods are sought.



Depolymerization.jpeg

Controlling nanostructure in 3D Printing

Monday, 24th April - 10:10: Oral Session 1-3 - Oral

Prof. Cyrille Boyer [1]

1. *University of New South Wales*

Abstract: Currently, there are no straightforward methods to 3D print materials with nanoscale control over morphological and functional properties. In this talk, a novel approach for the fabrication of materials with controlled nanoscale morphologies using a rapid and commercially available Digital Light Processing 3D printing technique will be presented. The approach uses a controlled/living radical polymerization technique, more specifically, reversible addition-fragmentation chain-transfer (RAFT) polymerization, to control the topologies of the polymers.[1] In this talk, we report a rapid visible light mediated polymerization process and applied it to a 3D printing system. Following the optimization of the resin formulation, a variety of 3D printing conditions will be presented to prepare functional materials.[2] The mechanical properties of these 3D printed materials were investigated under different conditions, showing that the control of the polymer structure can affect the performance of these materials.[3] Finally, by controlling the polymer architecture, we were able to precisely control the nanostructure of these 3D printing materials.[5] The effect of nanostructure of 3D printed materials on their properties will be discussed as well as their potential applications in drug delivery and energy storage, such as their use as solid polymer electrolytes for supercapacitor application.

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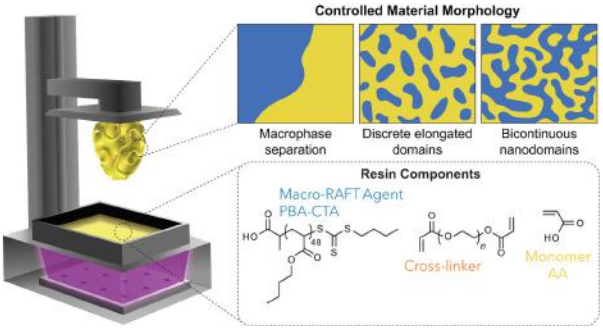


General 3d printing.jpg

Designing New Functional Polymers for 4D Microprinting

Monday, 24th April - 10:40: Oral Session 1-3 - Oral

Prof. Eva Blasco [1]

1. *Heidelberg University*

4D microprinting has become a promising tool for the fabrication of dynamic microstructures opening new opportunities for the additive manufacturing of functional devices with high precision. During the last years, promising examples of defined 4D microstructures employing stimuli-responsive polymers have been shown using two-photon laser printing. Herein, we present our recent work on the field with emphasis on new printable polymeric materials. In particular, shape memory polymers as well as dynamic covalent polymer networks have been demonstrated to be excellent candidates for the preparation of “living” 4D microstructures with potential applications in micro and nanorobotics or biomedicine.

Block copolymers: from well-controlled synthesis to materials with unique properties

Monday, 24th April - 11:10: Oral Session 1-3 - Oral

Dr. Anne-Laure Brocas [1]

1. *Arkema GRL, Lacq, France*

Arkema develops acrylic block copolymers, called Nanostrength, based on a specific technology: synthesis by Nitroxide Mediated Polymerization. This technology enables the synthesis of block copolymers which self-organize at the nanometer length scale. This organization imparts a unique combination of properties such as ductility/softness in materials. Block copolymers are used as additives to improve impact strength without any alteration thermal and any mechanical properties. Nitroxide Mediated Polymerization also offers the possibility to functionalize block copolymers such as amide or acid functions in each block. Recently, new applications have emerged notably due to the functionalization. In epoxy matrix, block polymers are formulated to increase as much as dissolution and mechanical properties. Block copolymers have also a special place in 3D printing applications offering flexibility and expected thermal properties in Fused Deposition Molding technology. Moreover, the rheological properties are controlled by the use of block copolymers while enhancing the mechanical strength in UV formulations.

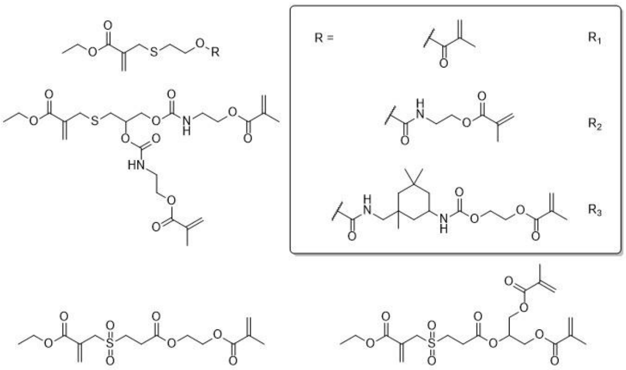
Synthesis and evaluation of polymerizable allyl sulfides and allyl sulfones for the development of low-shrinkage composites

Monday, 24th April - 11:25: Oral Session 1-3 - Oral

Mr. Benajmin Grob [1]***, Mr. Benedikt Frieser*** [1]***, Prof. Robert Liska*** [2]***, Dr. Yohann Catel*** [1]

1. *Ivoclar Vivadent AG,* ***2.*** *TU Wien*

Polymerization shrinkage and the corresponding shrinkage stress in methacrylate-based dental composites are crucial drawbacks for restorative dentistry. It has been shown that polymerization shrinkage and the resulting shrinkage stress may result in marginal leakage which could induce several clinical issues like postoperative sensitivity, marginal staining or the formation of secondary caries. An effective way for the reduction of shrinkage stress is the incorporation of addition fragmentation chain transfer agents (AFCT agents) like allyl sulfides and allyl sulfones. However, the commonly used allyl sulfides are quite flexible due to their thioether structure. Therefore, the mechanical properties (flexural modulus) of the cured composites are reduced. Furthermore, allyl sulfides and sulfones might not be fully incorporated into the polymer network. Consequently, unreacted chain transfer agent (CTA) might leach out. These phenomena prevent the use of AFCT agents in higher concentrations and limit the shrinkage force reduction. Hence, preparation of allyl sulfides and sulfones bearing methacrylate group(s) is an attractive option, as it should compensate the decrease of the mechanical properties and reduce leaching. In this contribution, the synthesis and evaluation of novel polymerizable allyl sulfides and allyl sulfones will be presented (Figure 1). Photo-DSC and DMTA measurements were performed to evaluate the influence of the synthesized CTA on the polymerization rate and on the network homogeneity. Good to excellent shrinkage force values and mechanical properties were obtained for all AFCT based composites. Especially, the incorporation of the allyl sulfides containing multiple urethane and methacrylate moieties improved the mechanical properties. Hence, the incorporation of polymerizable and urethane-based allyl sulfides in dental composite is a promising strategy to obtain low shrinkage materials exhibiting high flexural strength and modulus.



Structures of polymerizable allyl sulfides and allyl sulfones.jpg

Automated, High-Throughput, Digital Solutions for Polymer R&D

Monday, 24th April - 11:40: Oral Session 1-3 - Oral

Dr. Arunraj Chidambaram [1], ***Dr. Amira Abou-hamdan*** [1]

1. *Chemspeed Technologies AG*

This presentation will describe the numerous possibilities of performing automated, high-throughput for the following - Challenging library polymer synthesis
with targeted properties and their characterization, process development from lab-scale synthesis to large scale synthesis in industrial relevant conditions. The above will be substantiated by scientific publications, use-case examples. Finally, the functioning of a federated, closed loop laboratory driven by AI/ML and automated synthesis for polymer research and development will be presented.

Topology and Dispersity: Additional Parameters Regulating the Properties of Functional Polymer Interfaces

Monday, 24th April - 10:10: Oral Session 1-4 - Oral

Prof. Edmondo M. Benetti [1]

1. Laboratory for Macromolecular and Organic Chemistry (MOC), Department of Chemical Sciences, University of Padova, Padova, Italy.

Introduction

In addition to polymer composition, molar mass, and surface coverage, also the architecture (or *topology*) and the *dispersity* of polymer adsorbates have emerged as additional tuning parameters for modulating technologically relevant interfacial properties of polymer brushes.

Methods

Cyclic brushes on macroscopic surfaces are generated by assembling chemically different poly(2-alkyl-2-oxazoline) (PAOXA) adsorbates, which were synthesized by cationic ring-opening polymerization (CROP) of functional monomers. Similar procedures are applied for generating cyclic brush shells on inorganic nanoparticles (NPs).

Polymer brushes presenting different structural dispersity are fabricated by synthesizing poly(methacrylate)s alternatively featuring polydisperse and discrete oligomeric side chains via reversible deactivation radical polymerization (RDRP) methods.

Results

Cyclic polymer brushes provide enhanced steric stabilization and a superlubricious behavior, surpassing the attractive characteristics by commonly applied, linear analogues [1-3]. The steric and conformational constraints introduced during cyclization additionally affect the characteristics of cyclic brushes when these feature a functional character. This is the case for polymer interfaces that are chemically designed to actively interact with proteins present in the medium [4-5].

A variation in dispersity *within* polymer brushes regulates the occurrence of hydrophobic, van der Waals (vdW) interactions between grafts, in turn determining technologically relevant characteristics, such as hydration, adhesive character, lubrication and biopassivity [6].

Discussion

Variation of polymer-brush topology from linear to cyclic broadens the tuning potential for interfacial physicochemical properties, enabling the fabrication of ultra-stable core-shell NPs and superlubricious surfaces. In addition, a modulation of polymer-brush dispersity determines an alteration of hydrophobic, vdW interactions, which permits to tune hydration, adhesion and tribological properties of surfaces.

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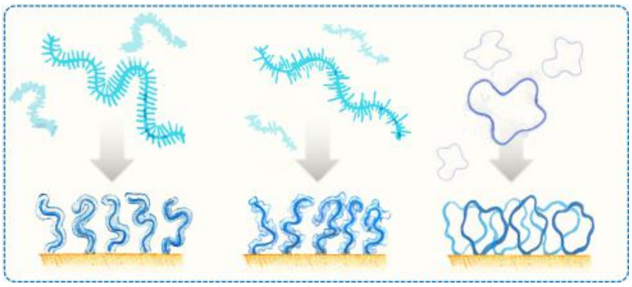


Picture abstract.jpg

Expanding the scope of surface-initiated polymerization

Monday, 24th April - 10:40: Oral Session 1-4 - Oral

Prof. Harm-Anton Klok [1]

1. *EPFL*

Surface-initiated polymerization reactions provide access to chain-end tethered polymer brushes. In particular controlled radical polymerization reactions have proven an extremely powerful tool to generate polymer brush films from a broad range of monomers. Such polymer brushes have attracted interest, for example, as nonfouling biointerfaces or as boundary lubricants. The vast majority of polymer brushes is produced from surfaces that present covalently tethered polymerization initiators using copper catalyzed atom transfer radical polymerization reactions with (meth)acrylate-based monomers.

This presentation will give an overview of examples of recent work from our laboratory in which we have tried to expand the scope of surface-initiated polymerization reactions. Work that will be covered will include the use of supramolecular interactions to grown non-covalently tethered polymer brushes, the use of light-mediated controlled radical polymerizations to facilitate access to brushes generated from “unconventional” monomers as well as polymer brush films that can be produced from very large substrates with extraordinary control over polymer architecture, and synthetic strategies that provide access to all-carbon based polymer brush films.

Hybrid Particles Synthesis by Nitroxide-Mediated Polymerization in Organic Media : a Versatile Route to Colored Electrophoretic Ink Displays

Monday, 24th April - 11:10: Oral Session 1-4 - Oral

Prof. Cyril Brochon [1]

1. *Université de Bordeaux*

Electronic paper based on the controlled motion of electrophoretic particles appears thus promising since it combines the advantages of the usual paper (flexibility, reflective display) and the capacity to refresh information on the same support like the more common LCD or OLED technologies.

In this work the main goal is to rationalize and improve the ink synthesis as well as to design hybrid particles in order to realize the next generation of electrophoretic displays.

For that purpose, we developed a versatile method of hybrid particles synthesis directly in a non-polar organic media. We performed nitroxide-mediated dispersion polymerization of functional monomers, in aliphatic hydrocarbon solvents, in presence of modified inorganic pigments and lipophilic macro-initiator.

This method leads to the design of electrically chargeable particles with a good size control over a large range and a good stability. It is also adaptable to many metal oxide pigments, with various colors. By this way, several inks, specially designed for electrophoretic measurements in organic media have been obtained through one pot synthesis. Finally, different electrophoretic displays, with various colors have been obtained.

Diblock copolymer nanoparticles are effective dispersants for agrochemical formulations

Monday, 24th April - 11:25: Oral Session 1-4 - Oral

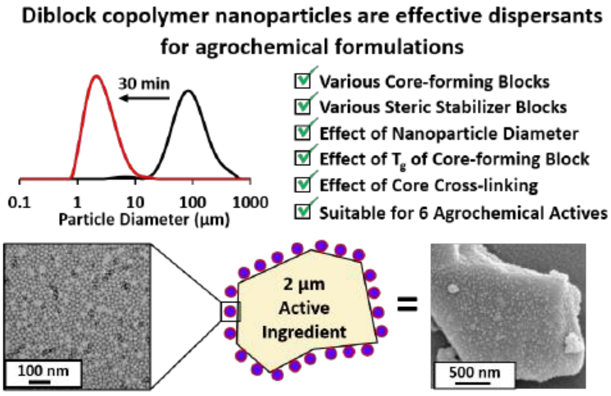
Dr. Derek Chan [1]***, Prof. Steven Armes*** [1]***, Dr. Oliver Deane*** [1]***, Dr. Phil Taylor*** [2]***, Dr. Chris Lindsay*** [2]

1. *University of Sheffield,* ***2.*** *Syngenta*

It is well known that sterically stabilized diblock copolymer nanoparticles can be readily prepared using polymerization-induced self-assembly. Recently, we reported that such nanoparticles can be employed as a dispersant to prepare micron-sized particles of a widely used fungicide (azoxystrobin) via ball milling. Well-defined sterically stabilized diblock copolymer nanoparticles are prepared by RAFT aqueous emulsion polymerization. A poly(glycerol monomethacrylate) precursor was chain-extended with either methyl methacrylate or 2,2,2-trifluoroethyl methacrylate to form spherical nanoparticles of approximately 30 nm in diameter.

These nanoparticles are evaluated as a dispersant for the preparation of azoxystrobin microparticles. Laser diffraction and optical microscopy studies indicated the formation of azoxystrobin microparticles of approximately 2 µm diameter after ball milling. The extent of nanoparticle adsorption on the azoxystrobin was confirmed by electron microscopy studies. It was further quantified using a supernatant assay based on solution densitometry and X-ray photoelectron spectroscopy studies, suggesting a fractional surface coverage of approximately 0.24-0.25. It also appeared that the adsorbed amount was essentially independent of the nature of the core-forming block.

We extended this work further by examining the effect of varying the nature of the steric stabilizer block, the mean nanoparticle diameter, and the glass transition temperature (T_g) of the core-forming block on the particle size and colloidal stability of such azoxystrobin microparticles. In addition, the effect of crosslinking the nanoparticle cores is also investigated. Diblock copolymer nanoparticles prepared using a non-ionic steric stabilizer – rather than a cationic or an anionic steric stabilizer – were demonstrated to be more effective dispersants. Furthermore, nanoparticles of up to 51 nm diameter enabled efficient milling, whereas larger nanoparticles proved to be less effective. This versatile approach was also shown to be applicable to five other organic crystalline agrochemicals, suggesting generic behaviour. Overall, this study suggests that sterically stabilized diblock copolymer nanoparticles may offer a useful alternative approach to traditional soluble copolymer dispersants for the preparation of agrochemical formulations.



D chan diblock copolymer dispersants.png

A polymer prodrug platform for the subcutaneous administration of vesicant anticancer drugs

Monday, 24th April - 11:40: Oral Session 1-4 - Oral

Mr. Lorenzo Tomasini [1], ***Dr. Marianne Ferrere*** [1], ***Ms. Catherine Cailleau*** [1], ***Ms. Stephanie Denis*** [1], ***Dr. Gregoire Gessain*** [2], ***Dr. Julien Nicolas*** [1]

__1.__ Université Paris-Saclay, CNRS, Institut Galien Paris-Saclay, Orsay, France, __2.__ Institut Gustave Roussy, UMR 1015, Villejuif, France

The subcutaneous (SC) route of administration presents key advantages compared to the most used intravenous (IV) route, such as simplicity, reduced costs, and better compliance for the patient.[1] There are only a few examples of SC-injected chemotherapies,[2] because of the irritant/vesicant nature of most anticancer drugs. The development of nanoscale drug delivery systems for cancer has gained considerable interest as a promising strategy to overcome the drawbacks of conventional chemotherapy.[3] However, most of these nanocarriers rely on physical encapsulation of the drug, which precludes their SC administration, as an early release of the drug into the SC tissue is likely to occur, resulting in prohibitive local toxicity.

To tackle this issue, a polyacrylamide (PAAm)-based prodrug strategy has been recently developed by our group, which enables the safe SC administration of paclitaxel (PTX), selected as a model vesicant drug.[4] This approach is based on the ”*drug-initiated*” synthesis of well-defined, water-soluble, PTX-PAAm prodrugs bearing one PTX moiety at each polymer chain end. The drug is therefore inactivated by the covalent linkage to the polymer, thus preventing early PTX release in the SC tissue. The PTX-PAAm prodrug led to higher anticancer efficacy in mice than Taxol, the commercial formulation of PTX.

Herein, we built on this strategy and reported the successful derivatization of this approach: (i) to other hydrophilic polymers well-established in nanomedicine, followed by the comprehensive preclinical development of the corresponding PTX-based prodrugs and (ii) to vinblastine (VLB), a well-known vesicant drug, used in particular in pediatric cancers.

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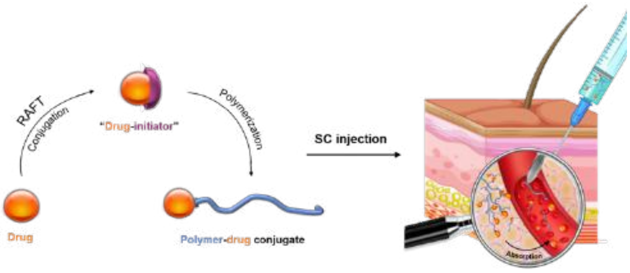

drug-initiated synthesis of polymer prodrugs.png

Tailored Polyvinylamines by raft polymerization

Monday, 24th April - 14:00: Oral Session 2-1 - Oral

Prof. Mathias Destarac [1]

1. Laboratoire des IMRCP, CNRS UMR 5623, Université Toulouse 3 Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

Introduction

Poly(*N*-vinylamides) are water-soluble polymers known for decades as aqueous formulation additives for diverse applications. Cyclic monomer derivatives such as *N*-vinylpyrrolidone (VP) and *N*-vinylcaprolactam (VCL), can be controlled by nearly all Reversible Deactivation Radical Polymerization (RDRP) methodologies. On the other hand, only a few studies reported the successful controlled polymerization of non-cyclic *N*-vinylamides such as *N*-vinylformamide (NVF), N-vinylacetamide (NVA) and *N*-methyl-*N*-vinylacetamide (NMVA), with the works of Debuigne and coworkers using Cobalt-Mediated Radical Polymerization (CMRP) and Yamago and coworkers using Tellurium-mediated Radical Polymerization (TERP). Suprisingly, before this work, suitable RAFT process conditions for controlling homopolymerization and block copolymerization of acyclic *N*-vinylamides could not be found.

Results and discussion

NMVA was successfully controlled by azo-initiated bulk RAFT polymerization at 35°C with xanthate chain transfer agent (CTA).[1] Typical initiator: CTA concentration ratios for RAFT polymerization led to poor monomer conversions due to the combined effects of low initiator efficiency, moderate reactivity of NMVA and RAFT retardation. To counterbalance this effect and obtain satisfactory conversions, an unusually high [initiator]/[RAFT agent] ratio of 1.49/1 was applied. Quite unexpectedly, the selected concentration and temperature conditions allowed a controlled growth of PNMVA chains. Original PEO-*b*□PNMVA and PNIPAAm-*b*-PNMVA double hydrophilic block copolymers (DHBCs) were successfully synthesized.

In the same spirit, the polymerization of NVF was successfully controlled on a wide range of molar masses with low dispersities via RAFT polymerization in DMSO using a xanthate. Here, not only azo initiation[2] at 35°C but also photoiniferter-RAFT (PI-RAFT)[3] polymerization at room temperature were considered. Well-defined PNVF-based homopolymers (Fig. 1) and double hydrophilic block copolymers were synthesized and characterized. Finally, the selective hydrolysis of PNVF block in PVCL-*b*-PNVF block copolymer was performed, thereby giving access to a new dual responsive PVCL-*b*-PVAm copolymer (PVAm=polyvinylamine), marking the starting line for future developments in the synthesis, properties and applications of complex copolymers comprising tailor-made PVAm segments.

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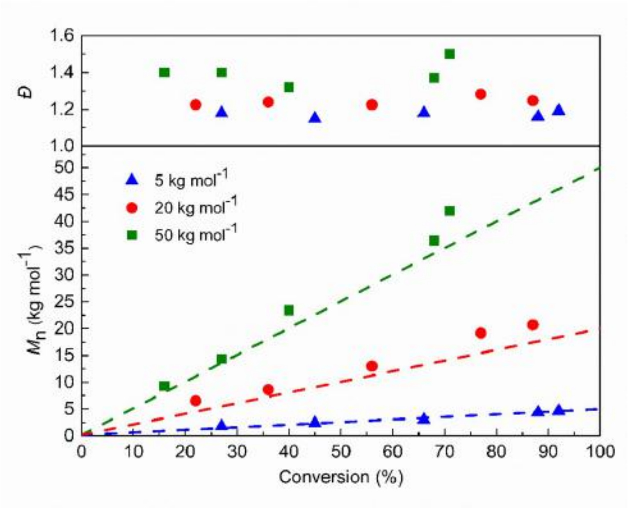

Fig. 1. evolution of mn and during purple led initiated xanthate mediated raft polymerization for different targeted molar masses. conditions rt in dmso..jpg

Synthesis of polysiloxanes via organocatalyzed anionic ring opening polymerization

Monday, 24th April - 14:30: Oral Session 2-1 - Oral

Ms. Alice Corfa [1], *Dr. Vincent Ladmiral* [1], *Dr. Sylvain CAILLOL* [1], *Dr. Julien Pinaud* [1]

1. CNRS ICGM

Polysiloxanes such as polydimethylsiloxanes (PDMS) or polytrifluoropropylmethylsiloxanes (PTFPMS) are high performance polymers, which after formulation and crosslinking, can be employed as sealing or coating pieces in various fields such as automotive or aeronautics.[1] Anionic ring opening polymerization (AROP) of cyclosiloxanes, using organometallic initiators such as butyl lithium, to synthesize PDMS, is well known and allows producing high molar mass polymers. However, this polymerization is mainly performed in bulk at high temperature (>100 °C), providing polymers with relatively high dispersities[1]. Organocatalysis for AROP is of high interest as it occurs under mild and easy conditions and leads to high molar mass, low dispersity polymers (Đ <1.1).

Our work aiming at producing high molar mass and low dispersity polysiloxanes using commercially available compounds, via organocatalyzed AROP of D_3 in the presence of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) as catalyst has thus been studied.

Various initiators (silanols, aliphatic alcohols and phenols) were employed under identical conditions with TBD as an organic catalyst for the AROP of D_3 in THF at 40 °C. The goal was to produce telechelic as well as monofunctional PDMS with reliable methods. Optimization of the experimental conditions by performing a kinetic study of the polymerizations, showed that initiation with a silanol is the best route to reach the target structures and low dispersity (Đ ≈ 1.1) polymers. Although they are not as effective, alcohols are still interesting initiators for producing tunable structures such as block copolymers. As a conclusion, a very easy pathway was optimized to obtain various and precise structures reaching 100,000 g.mol^{-1} under soft conditions. This represents a first step towards the synthesis of various polysiloxanes under soft and easy conditions, such as trifluoropropylmethyltricyclosiloxanes. Further studies are being carried out on the polymerization of F_3 which features much higher reactivity than D_3 and which polymerization behavior is much less known.

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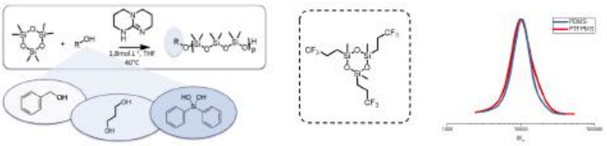

Alice corfa organocatalysis.png

Anionic ring-opening copolymerization of epoxides and thiolactones: a way to synthesize recyclable poly(ester)s

Monday, 24th April - 14:45: Oral Session 2-1 - Oral

Mr. Simon Le Luyer [1]***, Dr. Nicolas Illy*** [2]***, Prof. Philippe Guégan*** [2]

***1.** Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Equipe Chimie des Polymères, 75252 Paris, France,* ***2.** Sorbonne Université*

More than 350 million tons of plastic are produced every year, causing dramatic and global environmental issues and it is urgently necessary to develop more sustainable polymer materials and production processes that are more compatible with a circular and sustainable economy.[1] Among these polymers, poly(ester)s are one of the most commonly used plastics in the world, for example for packaging or in the textile industry.[2] Ester bonds in the repeating unit of such macromolecules allow to consider degrading it and possibly recycle this polymer chemically.[2]

Our group developed the organo-catalyzed alternate copolymerization of epoxides with thiolactones monomers, leading to a new family of functionalized poyesters.[3] This method was applied to a wide range of thiolactones and epoxides monomers, some of which are biosourced such as the N-acetylhomocysteine thiolactone or eugenol glycidyl ether derivatives.[4,5] More, in order to improve the sustainability of this synthesis, solventless polymerization conditions were also tried with positive results, therefore enhancing the green nature of our method.[5]

In the present work, we focus to the recyclability of poly(esterthioether)s structures by studying their depolymerization and their repolymerization. We established that these alternating copolymers can be totally depolymerized in basic or acidic medium, resulting in the α-hydroxy-ω-methyl ester repeating unit. This unit was used as an AB monomer for bulk polycondensation to resynthesize the native poly(esterthioether). Moreover, we studied the cyclability of this process by degrading our repolymerized polymer into the AB unit that was able to polycondensate again. (Figure 1)

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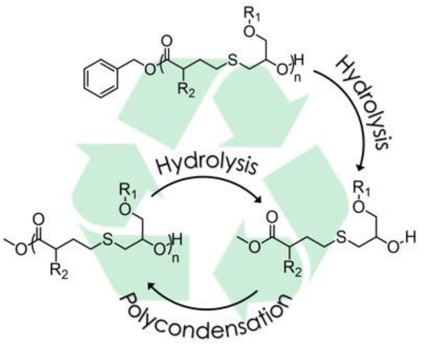

Figure 1 : Polymerization, depolymerization and repolymerization process

Abstract apme.jpg

Synthesis of polycarbonate-based ABA-type triblock copolymers for solid polymer electrolytes

Monday, 24th April - 15:00: Oral Session 2-1 - Oral

Ms. Adriana Saldívar-Martínez [1] ***, Prof. Tim Melander Bowden*** [1]

1. *Uppsala University, Department of Chemistry - Ångström Laboratory*

Solid polymer electrolytes (SPEs) have the potential to replace traditional liquid electrolytes (LEs) in lithium-ion batteries. The utilization of SPEs mitigates the flammability concerns associated with LEs, however, one major drawback of SPEs is their reduced ionic conductivity. Improving their electrochemical properties often means sacrificing mechanical integrity. Micro-phase separated block copolymers are a strategy that combines one block's ability to solvate lithium salts with another block that provides mechanical integrity to attain SPEs that meet all requirements.

The most dominant host material for SPEs is polyethylene oxide (PEO) having an ionic conductivity of 10^{-3}-10^{-4} S cm^{-1} above the melting point (60 °C). However, at higher temperatures, the application of PEO is restricted due to the loss of mechanical properties. Conventional LEs are typically based on organic carbonates, therefore, their polymeric counterparts -polycarbonates- are a promising alternative to PEO in SPEs. Poly(trimethylene carbonate) (PTMC) has excellent ion-solvating capabilities, yet, its ionic conductivity remains relatively low.

In this work, we have developed a material with improved ion-conduction properties by tuning PTMCs properties through the combination of different functionalities in one material, producing a random co-polymer that includes ether in a ratio of 3 to 7 mol%. The material was synthesized via bulk ring-opening polymerization of just one monomer (TMC). By using the metal-free catalyst Diphenylammonium triflate (DPAT), poly(trimethylene carbonate-co-trimethylene ether) (PTMC-co-PTME) copolymer was obtained.

The thermal properties and ionic conductivity of PTMC-co-PTME electrolytes with a fixed content of 30 wt% of LiTFSI were measured by DSC and electrochemical impedance spectroscopy. The most conductive systems showed ionic conductivity of 10^{-5} S cm^{-1} at 60 °C, higher than PTMC homopolymer.

Furthermore, poly(L-lactide) (PLLA) was added to the ion-conducting PTMC-co-PTME to act as a mechanical reinforcement, obtaining PLLA-*b*-PTMC-co-PTME-*b*-PLLA triblock copolymers. The PLLA crystalline phase potentially maximizes mechanical properties and ionic conductivity by promoting full-phase separation. Additionally, PLLA has a high melting temperature (170-180 °C) which allows for a wider range of operating temperatures for batteries. DSC results indicate that in the electrolytes prepared with the triblock copolymers with different LiTFSI concentrations, PLLA crystals are present with melting peaks around 120 °C.

Manipulating controlled and coordination insertion polymerization tools to produce block copolymers based on polyethylene

Monday, 24th April - 15:15: Oral Session 2-1 - Oral

***Dr. Franck D'Agosto** [1], **Dr. Florian Baffie** [1], **Ms. Laura Sinniger** [1], **Dr. Georgios Patias** [2], **Dr. Daniel Lester** [2], **Prof. David Haddleton** [2], **Dr. Vincent Monteil** [1], **Dr. Muriel Lansalot** [3], **Dr. Nicolas Baulu** [1], **Dr. Marvin Langlais** [1], **Dr. Christophe Boisson** [1]*

***1.** Catalysis, Polymerization, Processes and Materials (CP2M), CNRS, Université Claude Bernard Lyon 1, CPE Lyon, **2.** University of Warwick, **3.** Catalysis, Polymerization, Processes and Materials (CP2M), UMR 5128 CNRS, Université Claude Bernard Lyon 1, CPE Lyon*

Introduction. In industry, catalytic coordination-insertion and free radical polymerizations can provide a variety of different materials based on polyethylene (PE). However, more complex macromolecular architectures are difficult to obtain. However, more complex architectures are difficult to obtain.

Methods. To achieve these structures, macromolecular engineering via the use of controlled techniques amenable to ethylene polymerization is investigated.

Results and discussion. Following our initial studies on reversible addition-fragmentation chain transfer (RAFT) polymerization of ethylene,[i] new systems, including those based on iodine transfer polymerization (ITP),[ii] will be presented as they are shown to tackle the detrimental side reactions originally observed with RAFT, and to grant higher extent of living and functionalized chains leading to higher-molar-mass PE. In addition, block copolymers with vinyl monomers are achievable by chain extension of polar polymer chains equipped with the appropriate chain ends to allow controlled polymerization of ethylene.[iii] Original PE-based block copolymers obtained from strategies based on conventional radical polymerization will also be presented.[iv] Eventually, block copolymers incorporating PE segments *via* controlled coordination-insertion polymerization of ethylene alone[v] and *via* an original switch from anionic to coordination-insertion polymerizations[vi] will be discussed.

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Mono-telechelic Polymers from Mechanochemical C-C Bond Activation

Monday, 24th April - 15:30: Oral Session 2-1 - Oral

Mr. Rony Schwarz [1], Prof. Charles E. Diesendruck [1]

[1]. Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 3200003, Israel

Introduction

Selective activation of simple C-C bonds is a highly desirable transformation in organic chemistry. This process can sometimes be achieved under specific conditions using transition metal catalysis.[1] On the other hand, C-C bond scission is the most common outcome in polymer mechanochemistry, where mechanical energy drives chemical reactions in macromolecules. Mechanochemical reactions require a minimal macromolecular length, and typically results in backbone scission and polymer length reduction.[2] In this work, we describe how mechanochemical induced homolytic C-C bond scission in homopolymers can be utilized to introduce functional groups onto the newly formed macroradicals, leading to semi-telechelic chains.

Methods

The process is based on ball-milling the polymer with the adequate small molecule, done using a Retch cryomill under liquid nitrogen flow or at room temperature, depending on polymer chemistry.

Polymer samples were analyzed using a GPC with a triple detector system, which includes a Dionex DAD-3000 PDI UV-Vis Detector, Wyatt OPTILAB T-rEX refractometer, and a Wyatt MALS DAWN HELEOS II 8+TR.

Results and discussion

Ball milling PEG under cryogenic conditions in the presence of 1-(bromoacetyl)pyrene yielded the pyrene terminated PEG. If the PEG has a molecular weight below 20 kDa, no functionalization is seen, supporting a mechanochemical over a thermal mechanism. PEG grinding with pyrene and 1-acetylpyrene showed functionalization to a smaller extant, indicating that macroradical reaction to the bromoacetyl moiety is faster. PEG halogenation was also demonstrated, by milling it with iodine, NBS or NIS. The halogenated PEGs could then be reacted with an amine substituted anthracene to yield an anthracene terminated PEG.

Grinding of additional polymers (polyvinylpyrrolidone, polystyrene, polymethylmethacrylate) with 1-(bromoacetyl)pyrene demonstrated that our functionalization method is general for different polymer chemistries.

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C-c bond activation by polymer mechanochemistry.png

Isomerization of PEG: An efficient approach for the evasion of immune recognition in lipid nanoparticles

Monday, 24th April - 15:45: Oral Session 2-1 - Oral

***Dr. Philip Dreier* [1], *Dr. Rebecca Matthes* [1], *Dr. Dominik Goebel* [2], *Dr. Philipp Heller* [2], *Dr. Thomas Endres* [2], *Prof. Holger Frey* [1]**

***1.** University of Mainz, **2.** Evonik Operations GmbH*

In the last decades, poly(ethylene glycol) (PEG) has been established as the most relevant pharmaceutical polymer in modern nanomedicine.[1] Its attachment, so-called PEGylation, to active pharmaceutical ingredients (API) or the surface of lipid nanoparticles (LNP) facilitates efficient water solubility, increases blood-circulation time (stealth effect) and inhibits aggregation of particles. As an example, PEG lipids are essential stabilizing excipients in LNP formulations to allow for efficient transport and transfection of nucleic acids. Despite these advantages, an increasing number of studies has led to concerns related to the presence of anti-PEG antibodies (APA) in a constantly growing part of the population. The presence of APAs results in the recognition and accelerated blood clearance of PEGylated therapeutics, diminishing the desired effect of PEGylation.[2] This can even lead to anaphylactic shocks in severe cases. As a result, various potential alternatives based on different polymer classes or proteins were investigated as substituents for PEG in the last couple of years.[3]

We present isomerization of PEG as an efficient approach to inhibit APA interaction while preserving PEG´s main advantages and structure. Constitutional isomers of PEG (rPEG) were obtained via living anionic ring-opening (co)polymerization (AROP), offering well-defined structures with tailorable composition profile. Chain end functionalization of rPEGs with lipid anchor groups was conducted to obtain rPEG lipid structures. They were investigated via enzyme-linked immunosorbent assay (ELISA) regarding their interaction with APAs, leading to a detailed picture of the correlation between chain architecture and APA interaction. Further, formulation of various rPEG lipids in LNPs were investigated and compared to established PEG-based LNPs, showing similar particle sizes, transfection efficiencies and cell viabilities *in vitro*. In summary, the presented approach aims at the preservation of the highly efficient and seminal PEG-based nanomedicine for present and following generations.

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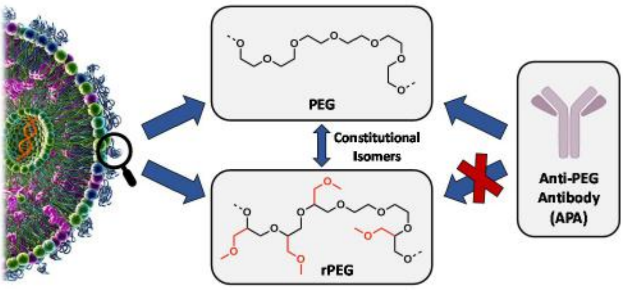


Toc abstract apme 2023 final.jpg

CO2-sourced polyurethanes and polycarbonates for the design of medical devices

Monday, 24th April - 14:00: Oral Session 2-2 - Oral

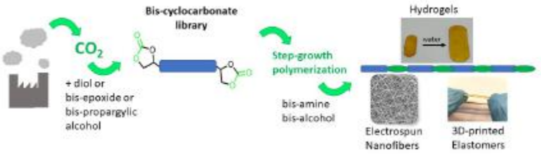
Ms. Anna Pierrard [1]***, Dr. Bruno Grignard*** [1]***, Dr. Christophe Detrembleur*** [1]***, Prof. Christine Jerome*** [1]

***1.** University of Liège*

Today, our modern society is facing climate change and ocean acidification caused by the continuous increase in CO_2 levels within the atmosphere. CO_2 has become a major contributing factor to the greenhouse effect. Traditionally seen as a waste, CO_2 may paradoxically become the key to “greening” our economy. CO_2 is a cheap and renewable carbon source that is regenerated instantaneously and locally. This resource may undergo numerous chemical processes and syntheses to design existing organic molecules and polymers so as new (sophisticated) ones.

In that context, we investigated the synthesis of various CO_2-sourced cyclic carbonates and their valorisation in polymer materials synthesis. The synthesis of non-isocyanate polyurethanes (NIPUs) by step-growth polyaddition of diamines with CO_2-sourced bis(cyclic carbonate)s was especially investigated. We developed novel conceptual routes for the synthesis of such isocyanate-free PUs by valorising different CO_2-sourced building blocks, targeting mild conditions in order to disfavour the occurrence of side reactions. Reactions allowing to introduce CO_2 into various cyclic carbonate monomers were studied and optimized allowing the lab-production up to the kg scale of a set of bis-cyclic carbonate monomers. These monomers were designed for the efficient step-growth synthesis of NIPUs and also of polycarbonates, leading to materials of tuneable properties. Adaptation of the reaction conditions, notably selecting specific catalysts exhibiting no cytotoxicity, allows to produce NIPUs dedicated to biomedical use. The properties of the resulting novel NIPUs materials, e.g. hydroxy-urethane, oxo-urethane, … were then studied and compared to the ones of more conventional PUs.

Biocompatible NIPUs elastomers and hydrogels were developed for biomedical applications. The processing of these NIPUs and polycarbonates by 3D-printing and electrospinning was also investigated, these technologies being of prime interest for the design of biomedical implants and scaffolds for tissue engineering.



From co2 to biomaterials.jpg

Bio-based supramolecular block-copolymers: beyond the barriers of step-growth polymerization

Monday, 24th April - 14:30: Oral Session 2-2 - Oral

Mr. Enzo Pichon [1]***, Dr. Marcin Sleczkowski*** [1]***, Dr. Katrien Bernaerts*** [1]

1. *Maastricht University, Aachen-Maastricht Institute for Biobased Materials, Sustainable Polymer Synthesis Group*

Due to growing environmental concerns in society and the forecasted depletion of fossil fuels, fatty acids have triggered the interest of polymer scientists. After dimerization of C18 fatty acids in vegetable oil and purification, C36 cyclic dimers bearing two carboxylic acid groups are obtained (Pripol®1009). Those dimers are excellent bio-based platform molecules that can be used as monomers. They can be reduced into dimers bearing two primary hydroxyl groups (Pripol®2033) or modified into dimers bearing two primary amine groups (Priamine®1075). A dicarbamate monomer (Priamine®1075-diNHBoc) was also synthesized from Priamine®1075. Using combinations of those four monomers, four different step-growth polymers (polyester, polyurethane, polyamide, and polyurea) were synthesized with two lengths: long polymers using an equimolar ratio of monomers and 5,000 g/mol hydroxyl or amino-terminated pre-polymers using an excess of Pripol®2033 or Priamine®1075.

Those hydroxyl and amino-terminated pre-polymers were then end-capped with ureido-pyrimidone (UPy) moieties that self-assemble into supramolecular dimers interacting via strong quaternized hydrogen bonds[1, 2]. Applied to those pre-polymers, UPy moieties enabled their self-chain extension into long supramolecular polymers (Figure 1).

Properties of both long covalent and supramolecular polymers were compared to prove the presence of strong quaternized hydrogen bonds acting as self-chain-extenders for pre-polymers and assess their influence on the polymer backbone and the material properties. Due to the reversible nature of those supramolecular interactions, the chain-extended polymers can be temporarily broken into pre-polymers by providing enough energy to the system.

First, this enabled easy recycling of the synthesized materials via heating and reprocessing. Second, block copolymers could be obtained by blending different chain-extended UPy terminated pre-polymers. Therefore, another UPy-terminated bio-based semi-crystalline pre-polymer was blended in varying amounts with the fatty-acid-based UPy-terminated urea pre-polymer previously synthesized. This process allows high flexibility in material design and properties. Materials could also be up-cycled by changing their block composition after the synthesis via reblending.

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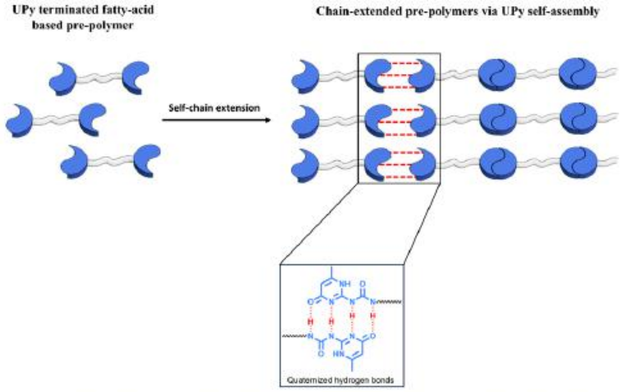

Figure 1 - Schematic representation of UPy terminated pre-polymers self-chain extension

Abstract apme.png

pH-triggered Recovery of Photocatalytic Polymer Particles for Enhanced Efficiency and Recyclability

Monday, 24th April - 14:45: Oral Session 2-2 - Oral

Ms. Rong Li [1], ***Mr. Julian Heuer*** [2], ***Mr. Thomas Kuckhoff*** [2], ***Prof. Katharina Landfester*** [2], ***Dr. Calum Ferguson*** [2]

1. *Max Planck Institute for Polymer Research,* ***2.*** *MPIP*

ABSTRACT

Pseudo-homogeneous polymeric photocatalysts are an emerging class of highly efficient and tunable photocatalytic materials, where the photocatalytic centers are easily accessible towards light penetration and mass diffusion.[1] Recently, stimuli-responsive heterogeneous photocatalytic materials have emerged as a powerful synthetic tool, with simple and rapid recovery.[2,3] Stimuli-responsive polymers are often inexpensive and easy to produce. They can be switched on/off in response to external stimuli, allowing the production of photocatalyst with adaptability, recyclability, and orthogonal control on different chemical reactions.[4] Despite this versatility, the application of stimuli-responsive polymer in the field of heterogeneous photocatalysis has not yet been maximized.

Recently, our group has synthesized pH-sensitive photocatalytic polymer nanoparticles polydiisoproylamino ethylmethacrylate-co-*N*-(4-(7-phenylbenzo[*c*][1,2,5]thiadiazol-4-yl)phenyl)methacrylate-b-benzylmethacrylate (PDPA-co-Ph_2BTMA-b-PBzMA) using reversible addition-fragmentation chain transfer polymerization induced self-assembly (RAFT-PISA), ensuring photocatalytic units are in the corona phase. At pH 4.0, the stabilizing PDPA chains containing photocatalytic centers are pronated, facilitating a stable dispersion of nanoparticles. Consequently, the photocatalytic moieties distributed in the stabilizing section are in a pseudo-homogeneous state, enabling efficient photocatalysis in water. Conversely, at pH 10.0, PDPA chains turn hydrophobic after deprotonation that leads to NP aggregations, therefore allowing an easy recycling of the materials (see Figure 1).

We have utilized these photocatalytic NPs for a variety of chemical transformations under visible light, including photo-oxidation, photo-reduction, and photo-redox reaction. As an example, at pH 4.0, positively charged PDPA chains on pH-responsive NPs not only increase the dispersibility, but also exhibit a significant accelerating effect on the reduction of negatively charged $Cr_2O_7^{2-}$ water pollutant compared to non-responsive (neutral) photocatalytic NPs, because of the charge attraction between photocatalyst and substrate. Additionally, negligible efficiency loss was observed after multiple cycles of photo-reduction of $Cr_2O_7^{2-}$, demonstrating an efficient photocatalyst for wastewater treatment. We have demonstrated that pH-responsive photocatalytic NPs are efficient photocatalysts, which can be readily recovered and recycled.

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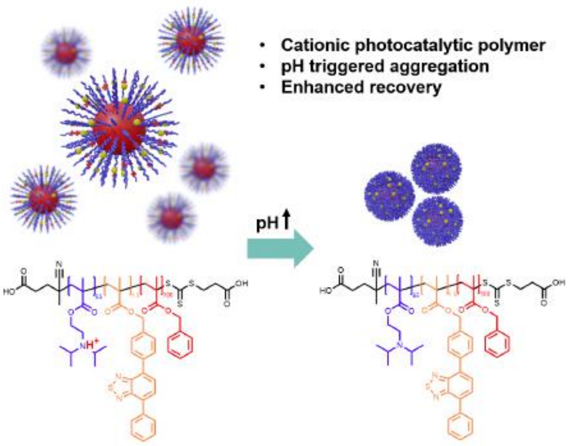


Figure 1. scheme illustration of switchable hydrophilicity and photocatalytic applications of the ph-responsive photocatalytic nanoparticles in water..png

Reprocessable and recyclable epoxy vitrimers from bio-based 2,5-furandicarboxylic acid

Monday, 24th April - 15:00: Oral Session 2-2 - Oral

Mrs. Eleonora Manarin [1], ***Prof. Stefano Turri*** [1], ***Prof. Gianmarco Griffini*** [1]

1. *Department of Chemistry, Materials and Chemical Engineering 'Giulio Natta', Politecnico di Milano, Piazza Leonardo da Vinci 32 – 20133 – Milano Italy*

Introduction

Covalent adaptable networks (CANs) have emerged as a promising alternative to conventional thermosetting polymeric systems, featuring wide interest in polymer science in the last decades. In particular, associative CANs, known as vitrimers, show reprocessing and recycling capabilities, maintaining their mechanical properties, thanks to thermally stimulated exchange reactions. In this work, we developed bio-based epoxy vitrimers combining bisphenol A diglycidyl ether (DGEBA) and bio-based 2,5-furandicarboxylic acid (FDCA) adding triazabicyclodecene (TBD) as transesterification catalyst.

Methods

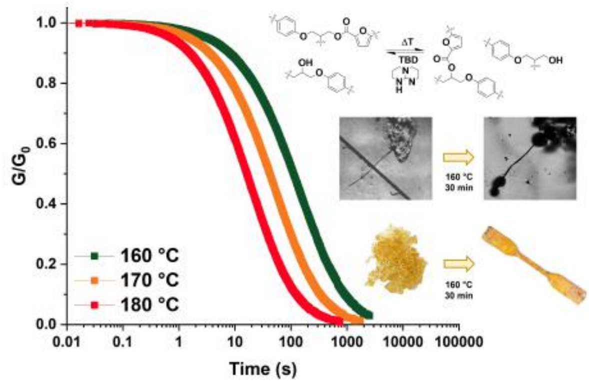
The epoxy vitrimers were prepared by heterogeneous ring opening reaction between melted DGEBA and solid dispersed FDCA. Different molar ratios were chosen to study the structure to properties relations with the variation of the bio-based content. The crosslinking reaction was studied by means of DSC, FTIR and gel content analysis, while the thermo-mechanical properties were studied by means of DMA and TGA. The vitrimeric behavior of such systems was studied by means of rheological stress relaxation tests.

Results

The activation energy of the crosslinking reaction was found to be in the order of 70 to 90 kJ mol^{-1}, depending on the composition. For all the systems, a gel fraction higher than 95% was found, confirming the formation of completely crosslinked networks with high thermal stability. DMA reported a Tg from 120 to 150 °C and a crosslinking density from 1 to 15 x 10^{-4} mol cm^{-3}, both dependent on the composition. Stress relaxation experiments showed an Arrhenius-type temperature dependence of the relaxation time. The formulation with an acid to epoxy molar ratio equal to 0.6 was optimized in terms of transesterification kinetic, with a relaxation time equal to 30 seconds at 180 °C. For such system, thermoformability, self-healing, and mechanical recyclability were demonstrated.

Discussion

We developed a series of vitrimeric systems based on transesterification exchange reactions. The stiff skeleton of the components provides high thermal stability for high-performance applicability. Moreover, the straightforward formulation process, not requiring solvents or functionalization steps, makes these materials suitable for large scale mass production. Such vitrimeric systems were demonstrated to be reprocessable, repairable, and remouldable, opening the possibility to predictive material design in the field of sustainable epoxy systems.



Fdca dgeba x apme 2023.jpg

Vitrimeric poly(ionic liquid) electrolyte for Li ion batteries

Monday, 24th April - 15:15: Oral Session 2-2 - Oral

***Mr. Zviadi Katcharava* [1], *Dr. Xiaozhuang Zhou* [1], *Dr. Rajesh Bhandary* [1], *Dr. Anja Marinow* [1], *Prof. Wolfgang H. Binder* [1]**

1. *Martin Luther Univerity Halle-Wittenberg*

Rechargeable Lithium-ion batteries (LiBs) have become crucial part of our everyday life while covering a wide range of applications. The drawbacks of current technologies (high price, low energy density, environmental and safety issues etc.) and demand for higher performance motivates the development of next generation LiBs. Currently, main safety concerns are associated with the commercially used electrolytes due to presence of flammable organic solvent-based mixtures. Polymer electrolytes (PE) are promising alternatives to overcome shortcomings and make LiBs much safer for users. Introduction of self-healing features in PE leads to prolonged life-time of LIBs, thus tackling cost and environmental issues. Among different types of polymers poly(ionic liquid)s (PILs) stand out due to their high electrochemical and thermal stability combined with comparably high ionic conductivity.

Here we present solvent free, self-healable, reprocessable, thermally stable, conductive PIL consisting of pyrrolidinium-based repeating units. In addition, PEO-functionalized styrene was used as co-monomer for improving mechanical properties and introducing pendant OH group in the polymer backbone. Addition of boric acid to a precursor polymer matrix leads to formation of dynamic boronic ester bonds, thus forming a vitrimeric material. Dynamic boronic ester linkages form non-permanent crosslinking[1] and allowing reprocessing (at 40 °C), reshaping and also the ability to self-heal the mechanical damage.

Vitrimeric PILs with different crosslinking density and content of lithium salt (LiTFSI) were synthesized and characterized. The conductivity reaches 10^{-5} S/cm at 50 °C in the optimized composition. Furthermore, electrolyte is stable up to 300 °C which is much higher than the operating temperature of batteries. Moreover, the PILs rheological properties fits the required melt flow behavior[2] (above 120 °C) for 3D printing *via* fused deposition modeling, opening the possibility to design batteries with more complex and diverse design.

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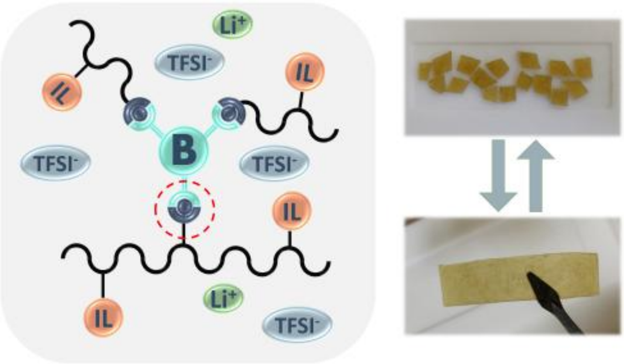

Vitrimeric-poly ionic liquid -electrolyte-for-li-ion-batteries zviadi-katcharava.png

The road to intrinsically dynamic materials: disulfide chemistry as a solution

Monday, 24th April - 15:30: Oral Session 2-2 - Oral

Dr. Qi Zhang [1]

1. Univeristy of Groningen

Disulfide bond, the bond that bridges peptides, features its dynamic covalent nature. Using disulfide bonds as reversible linkages for crosslinking covalent network has been widely investigated. Instead of crosslinking, here we propose that disulfide bonds can be used to mediate the reversible ring-opening polymerization of cyclic monomers, and the resulting polymers exhibit intrinsic dynamic functions, e.g. self-healing ability, stimuli-responsive ability, and chemical recyclability. We will focus on the poly(disulfides) derived from a natural small molecule, thioctic acid, to show the versatility of this simple and reliable dynamic chemistry in designing materials with dynamic functions [1-5]. Then I will move to our recent finding in which S−S—H−N hydrogen bonds are essential for an efficient chirality transfer in a cyclic disulfide molecule [6-7], which might open up a new avenue towards dynamic disulfide stereochemistry and chiral materials.

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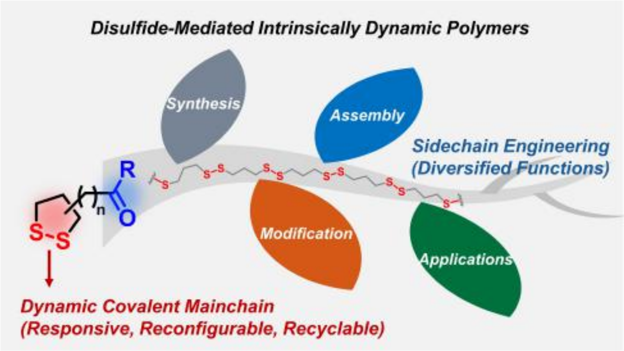
Disulfide-Mediated Intrinsically Dynamic Polymers
Synthesis
Assembly
Sidechain Engineering
(Diversified Functions)
Modification
Applications
R
O
n
S-S
Dynamic Covalent Mainchain
(Responsive, Reconfigurable, Recyclable)

Toc.jpg

Vanillin-based epoxy vitrimers : looking at cystamine hardener from a different perspective

Monday, 24th April - 15:45: Oral Session 2-2 - Oral

Ms. Solène Guggari [1]***, Dr. Fiona Magliozzi*** [2]***, Mr. Samuel Malburet*** [2]***, Dr. Alain Graillot*** [2]***, Prof. Mathias Destarac*** [1]***, Dr. Marc Guerre*** [1]

1. *Laboratoire des IMRCP, CNRS UMR 5623, Université Toulouse 3 Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France,* ***2.*** *Specific Polymers, Zac Via Domita, 150 Avenue des Cocardières, 34160 Castries, France*

Introduction:

Improving the efficiency, the sustainability and the end-of-life of polymer networks is a crucial challenge in materials science due to their important role in our society. Thus, the development of vitrimers represents a considerable interest to address the issue of recyclability while maintaining high thermomechanical performances. Epoxy vitrimers are one of the most versatile materials and candidates with potential outcome in industrial applications. This class of vitrimers encompasses many advantages compared to traditional epoxy materials such as recyclability and reprocessability.[1] These properties are quite uniquely induced by the incorporation of dynamic reversible covalent bonds.

Result and discussion:

Recently, the incorporation of aromatic disulfide bridges has expanded the development of new eco-friendly epoxy materials.[2,3] Herein, we present the bio-based aliphatic disulfide cystamine hardener with a vanillin-derived bio-sourced epoxy to prepare fully bio-based epoxy vitrimers. This work provides a comparative thermomechanical study between cystamine and an aromatic disulfide benchmark hardener (4-AFD) issued from petrol ressources. Thanks to DSC and rheological analyses, we demonstrated that the presence of this aliphatic hardener has a significant influence not only on the reactivity, but most importantly, on the resulting dynamic properties and on the recyclability of the epoxy networks. A unique and counterintuitive accelerating effect of the dynamic exchanges with the aliphatic disulfide hardener cystamine was evidenced by stress relaxation experiments. Thus, the exchange dynamics offered by cystamine could become considerably attractive as a viable alternative to the petrochemical-based counterparts. Beyond the bio-based character of cystamine, this discovery opens new perspectives as it could enable a fine tuning of the exchange dynamics by simply adjusting the ratio of cystamine in any epoxy formulation.

Aknowledgments:

This project has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement No 101023190. The JU receives support from the European Union’s Horizon 2020 research and innovation program and the Bio Based Industries Consortium.

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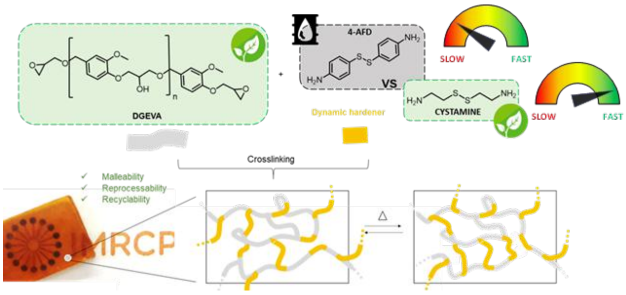

Figure. a competitive alternative for vanillin-based epoxy vitrimer synthesis guggari apme2023.png

Controlled syntheses of semiconducting polymers and their applications to synthesize organic mixed ionic/electronic conductors

Monday, 24th April - 14:00: Oral Session 2-3 - Oral

Prof. Christine Luscombe [1]

1. Okinawa Institute of Science and Technology Graduate University

Introduction

Bioelectronics focuses on the establishment of the connection between the ion-driven biosystems and readable electronic signals. Organic electrochemical transistors (OECTs) offer a viable solution for this task. Organic mixed ionic/electronic conductors (OMIECs) rest at the heart of OECTs.

Recently, polymer semiconductors have received significant amounts of attention because of their flexibility, biological compatibility and ease of fabrication. These materials, particularly thiophene-based polymers such as poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)(PEDOT:PSS) and related derivatives, have demonstrated significant enhancements in performance in a relatively short amount of time, with transconductance values of PEDOT:PSS transistors surpassing those achieved even with graphene.

Results and Discussion

In our group, we have been exploring how small changes in ethylene-glycol functionalized polythiophenes alter ion injection. Specifically, their thin film morphology, and their ionic and electronic conductivities, and comparisons against theoretical predictions have been studied. We find that very small changes in side-chain structure strongly affect the morphology and thus performance. Specifically, in the investigated polymer series showed the prototypical conflict between ionic and electronic conduction for oxygen atom content, with increasing oxygen atom content increasing ionic conductivity, but decreasing electronic conductivity; however, by increasing the oxygen atom distance from the polymer backbone, both ionic and electronic conductivity could be improved. Following these rules, we show that poly(3-(methoxyethoxybutyl)thiophene), when blended with lithium bistrifluoromethanesulfonimide (LiTFSI), matches the ionic conductivity of a comparable MIEC [poly(3-(methoxyethoxyethoxymethyl)thiophene)], while simultaneously showing higher electronic conductivity, highlighting the potential of this design strategy. We also provide strategies for tuning the MIEC performance to fit a desired application, depending on if electronic, ionic, or balanced conduction is most important. These results have implications beyond just polythiophene-based MIECs, as these strategies for balancing backbone crystallization and coordinating group interconnectivity apply for all semicrystalline conjugated polymers.

Synthetic Nanoengineered Antimicrobial Polymers (Snaps) With Antimicrobial And Antibiofilm Properties

Monday, 24th April - 14:30: Oral Session 2-3 - Oral

Prof. Sebastien Perrier [1]

1. *University of Warwick*

Antimicrobial resistance (AMR) has been declared by the World Health Organization (WHO) as one of the major public health threats facing humanity.[1] The emergence and spread of antibiotic-resistant pathogens have been predicted to cause more than 10 million deaths annually by 2050.[2] As an alternative to common antibiotics, antimicrobial peptides (AMPs) have been extensively investigated. The ability to disrupt bacterial membranes makes AMPs have a broad-spectrum activity against Gram-positive, Gram-negative, fungi and viruses. However, AMPs have limitations, such as low stability towards enzyme degradation, mammalian cytotoxicity specially against red blood cells, and a high manufacturing cost. Therefore, synthetic nanoengineered antimicrobial polymers (SNAPs) mimiking AMPs structures have gained increasing interest as a promising alternative to AMPs.[2]

We report here on the antimicrobial activity of a library of SNAPs synthetized *via* RAFT polymerization.[3,4] These copolymers show low cytotoxicity whilst they show good antimicrobial activity. The structure of SNAPs was investigated and we observed that the segregation of the hydrophobic block is crucial in the antimicrobial activity. Diblock and triblock copolymers interact strongly with the lipopolysaccharide (LPS) of the outer bacterial membrane, and can lead to membrane disruption. In order to design a therapeutic system, we combined our SNAPS with conventional antibiotics, and tested formulations against planktonic *S. aureus* and *P. aeruginosa*. The most promising pairs showing synergistic effects were tested against *S. aureus* biofilms (wound model) and *P. aeruginosa* biofilms (cystic fibrosis models). We observe that selected SNAPs/antibiotic combinations prevent biofilm formation and eradicate mature biofilms in *ex vivo* biofilm models, indicating a potent synergistic effect between the copolymer and the conventional antibiotic, thus making promising therapeutics for the fight against AMR.

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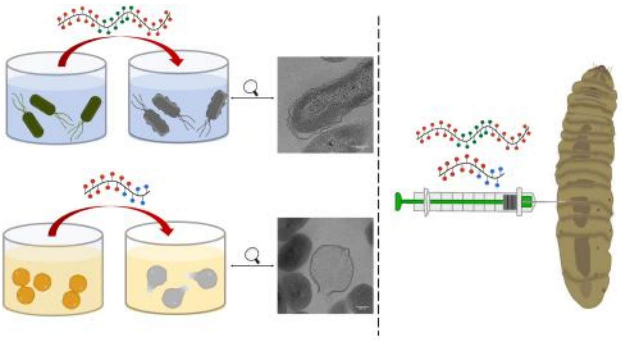

Picture 1.jpg

Synthesis and Characterization of Uniform PCL-PEG Block Copolymers

Monday, 24th April - 15:00: Oral Session 2-3 - Oral

Dr. Philipp Bohn [1], ***Prof. Micheal A. R. Meier*** [1]

1. *Karlsruhe Institute of Technology*

Inspired by the highly complex and sequence-defined structure of biomacromolecules (*e.g.* DNA, RNA or proteins), which exhibit structures of synthetically unreached complexity and thus enable complex natural processes, current research in polymer chemistry focusses on the synthesis of uniform and sequence-defined macromolecules.

Block copolymers (BCPs) are of special interest in this area. Due to their possible amphiphilic character and the ability to undergo microphase separation, these polymers are suitable for a broad range of applications in nanotechnology, medicine, or biotechnology. Particularly in the pharmaceutical sector, a uniform structure is crucial to regulate the structure-property relationship and manufacture tailor-made materials. For *in vivo* applications, biocompatibility as well as biodegradability of the respective block copolymers are crucial. Thus, poly(ethylene glycol) (PEG) and poly(ε-caprolactone) (PCL) are often studied and also utilized in this work.

For the synthesis of uniform homo-macromolecules, an iterative synthesis routes utilizing orthogonal protection groups are fundamental. In this work, the thus obtained uniform PEG and PCL macromolecular building blocks are coupled *via* Steglich esterification, varying in the length of the hydrophobic PCL block, and thus obtaining three corresponding uniform block macromolecules. Careful characterization *via* NMR, HR-MS and SEC was performed to confirm the high purity of the products.

Ring-opening polymerization of ε-caprolactone using a methoxy-PEG as initiator provided reference molecules with similar M_n and a narrow molar mass distribution ($Đ$ = 1.06). The thermal properties were investigated by differential scanning calorimetry (DSC) and the phase separation behavior of the BCPs was studied *via* small-angle X-ray scattering (SAXS). The results show a clear constitution- and dispersity-dependent structure-property relationship based on the crystallization temperature Tc and a difference in self-assembly of the smallest BCP as a function of dispersity.

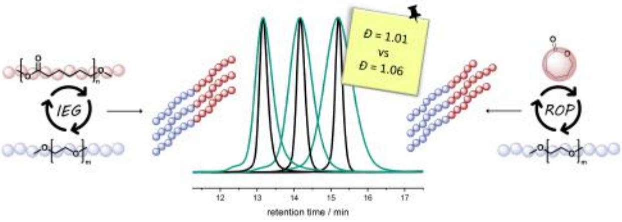

Fig. 1 synthesis of uniform and disperse peg-pcl block copolymers.png

Secondary structure studies of sequence-defined oligourethanes

Monday, 24th April - 15:15: Oral Session 2-3 - Oral

Dr. Roza Szweda [1]

1. ŁUKASIEWICZ RESEARCH NETWORK – PORT

Sequence control of abiotic polymers has been attracting considerable attention over the last few years. Similarly to natural proteins abiotic polymers can be fabricated with a defined order of monomers using multistep iterative synthesis. In other words, non-natural macromolecules can be synthesized with a controlled primary structure. However, very little is known about their folding and secondary structure which is crucial for the functionalities of biological polymers.

In this work, we evaluated various experimental techniques to develop a methodology for secondary structure characterization of sequence-defined oligourethanes. We used computational methods to reveal details about inter and intramolecular interactions of oligomers. We studied the influence of stereochemistry on conformation stability and attained conformation of oligomers.

We found that a combination of NMR, CD and IR analyses can reveal information about the structural details of attained oligourethane conformations in solution. Oligomers display secondary structures that can be tuned by the sequence of stereocenters in the backbone. For each sequence, the number of possible conformers and their distribution are different. Therefore, to correctly interpret complex experimental data sets, it is necessary to use computational methods, e.g., DFT. The conformation of oligomers is critical for their functionalities, e.g., catalytic activity and intramolecular interactions with ligands, thus stereocontrol can be used as a tool for the advanced engineering of macromolecule functions.

Acknowledgements: We are very grateful to the Polish National Science Centre (2018/31/D/ST5/01365, 2021/43/I/ST4/01294), Łukasiewicz Centre (4/Ł-PORT/CŁ/2021) and The National Centre for Research and Development (LIDER/27/0148/L-12/20/NCBR/2021) for financial support.

Sub-10 nm Nanopattern Fabrication using Silicone- and Fluorine-containing High-χ Block Copolymer

Monday, 24th April - 15:30: Oral Session 2-3 - Oral

Mr. Seungbae Jeon [1]***, Mr. Junsu Kim*** [1]***, Prof. Du Yeol Ryu*** [1]

***1.** Yonsei University*

The high-χ, low-N, low-T_g, and similar surface tensions polydimethylsiloxane-*b*-poly(2,2,3,3,3-pentafluoropropyl acrylate) (PDMS-*b*-PPeFPA) system was designed for the thin film application, with the advantage of perpendicular oriented lamellar nanopatterning with sub-10 nm feature size at room temperature without top-coat materials. The *d*-spacing was achieved from PDMS-*b*-PPeFPA which showed symmetric lamellar microdomains of 17 nm, performing nearly sub-10 nm for half-pitch feature size. Depending on the solid substrates, the orientation of lamellar structures was shifted from parallel to perpendicular as respect to native SiO_2, H-passivated Si, physisorbed layers. Irreversible physisorption of BCPs could also successfully achieved perpendicular microdomains of self-assembled BCP thin films. An effective protocol to grant surface neutrality towards symmetric BCP thin film was suggested by adsorption of the same BCP that plays a double role not only as surface modifier and but as nanopattern precursor. The compositional randomness is valid when the correlation length (ξ) of the physisorbed layers is smaller than the domain spacing of the overlying BCP. Moreover, the lateral electric fields above a threshold value induce a perfect unidirectional alignment of perpendicular oriented lamellae to relieve the local dielectric anisotropy owing to high dielectric contrast between PDMS and PPeFPA blocks.

Photo-triggered disassembly of supramolecular polymer bottlebrushes

Monday, 24th April - 15:45: Oral Session 2-3 - Oral

***Mr. Luke Harvey* [1], *Mr. Jean-Michel Guigner* [2], *Prof. Laurent Bouteiller* [3], *Dr. Erwan Nicol* [1], *Dr. Olivier Colombani* [1]**

1. *Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS Le Mans Université, France,* ***2.*** *Institut de Minéralogie et Physique des Milieux Condensés, Université Pierre et Marie Curie, Campus Boucicaut, 140 rue de Lourmel, 75015 PARIS,* ***3.*** *Sorbonne Universités, UPMC Univ Paris 06, CNRS, Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, 4 Placè Jussieu, F-75005 Paris, France*

We report the successful synthesis and light-sensitive self-assembly in aqueous medium of Azo-(U-PEO)$_2$, a polymer composed of two H-bond promoting urea groups and a photo-responsive azobenzene unit, decorated with two poly-(ethylene oxide) arms (figure 1A). The aim of this work was to form polymer bottlebrushes (nanocylinders) through the supramolecular self-assembly of this polymer in solution, and to manage to disassemble these nano-cylinders using light. While there are examples in the literature of supramolecular nano-cylinders that can be disrupted using other stimuli (temperature, pH, oxidation)[1,2], none have been reported using light. From an applicative point of view, polymer decorated nano-cylinders are known to be highly efficient in stabilizing Pickering emulsions[3], and this system could be exploited to access photo-responsive emulsions, where demulsification would occur after UV irradiation.

As long as the azobenzene is in its *trans*-configuration, self-assembly through strong cooperative hydrogen bonds is favored and the polymer can be self-assembled by first dissolving it molecularly in DMSO, followed by slowly adding water. A combination of cryo-TEM and light scattering (LS) measurements indicate that long, polydisperse nano-cylinders are formed (N_{agg}=900) in these conditions. However, upon irradiation with UV light (l=365 nm), the azobenzene unit rapidly photo-isomerizes to the *cis* configuration, which is not planar, thereby disfavoring hydrogen bonding and disassembly. Indeed, after photo-irradiation, no cylinders were observed in cryo-TEM (figure 1C) and LS showed very weak aggregation. It is worthy to note that the isomerization is fast and reversible: *cis*-azobenzene can be photo-isomerized back to the initial *trans* configuration at a second wavelength (l=450 nm) within a few minutes. However, despite *cis*-azobenzene effectively photo-isomerizing back to its *trans* isomer, nano-cylinders are not reformed; which could be explained by the fact that the self-assembled structures are kinetically frozen.

This work presents the first example of supramolecular polymer nanocylinders which can be disrupted by light irradiation.

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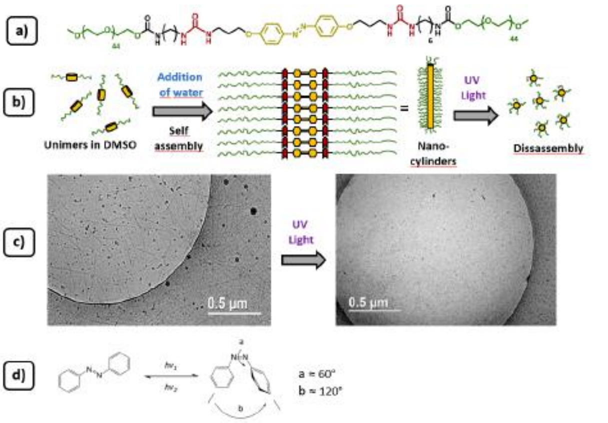


Figure 1: a) Chemical structure of Azo-(U-PEO)$_2$, **b)** Schematic principle of the supramolecular self-assembly and photo-triggered dissassembly, **c)** Cryo-TEM images of the self-assemblies before irradiation (left) and after UV irradiation (right) d) Schematic principle of azobenzene photo-isomerization

Figure 1.png

Shadows and Fog in “Grafting to” from Melt

Monday, 24th April - 14:00: Oral Session 2-4 - Oral

Prof. Michele Laus [1]

1. *DISIT Dept., Università del Piemonte Orientale “A. Avogadro”, Viale T. Michel 11, 15121 Alessandria, Italy*

The development of surfaces with well-engineered properties is a significant challenge for chemists and physicists. For example, surfaces and interfaces responsive to the surrounding environment were recently identified as essential in the design of innovative devices, from electronics to medicine.

In this perspective, *polymer brushes*, which consist of thin organic layers of polymers tethered by one end to a substrate, are an extremely versatile tool for surface engineering.

Several approaches were developed to control the surface characteristics. Among these, polymer brush technology based on the *“grafting to”* reaction has been widely applied. In the “*grafting to*” process, a functional polymer is grafted onto the substrate and good control over the brush characteristics is obtained because of the self-limiting nature of this reaction and the possibility to tune the number of chains by changing the molecular weight of the employed polymer. Furthermore, the polymeric materials suitable for the “*grafting to*” process are prepared by the quite sophisticated chemistry of controlled or living polymerizations.

However, recent investigations revealed that the “*grafting t*o” reaction is much more complex than usually believed with a shift from a diffusion-controlled to a mechanochemical driven mechanism. Moreover, partitioning by molecular weight takes place at interfaces in which the lower molecular weight species are preferably incorporated into the polymeric brush.

All these aspects will be discussed to highlight what is true, what is false and what is still not clear in this process.

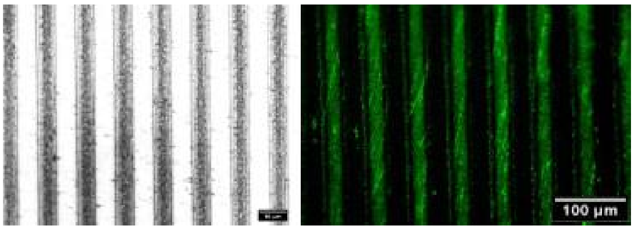
Protein patterning on microtextured polymeric nano-brush templates obtained by nanosecond fibre laser.

Monday, 24th April - 14:30: Oral Session 2-4 - Oral

Ms. Meenakshi Verma [1]

1. PhD Scholar, Department of Materials Science and Engineering, IIT Delhi

Micropatterned polymer brushes have attracted attention in several areas of biomedical science, i.e., tissue engineering, protein microarray, biosensors etc., for precise arrangement of biomolecules. Herein, we report a facile and scalable approach to create microtextured biocompatible and biofunctional polymer brushes with the ability to generate different type of protein patterns (e.g., line and circular). Nanosecond fibre laser was employed to generate around 30 micron wide patterns on the polymer brush (poly(ethylene glycol) methacrylate (polyPEGMA), a protein repellent brush) modified Ti alloy based substrate. PolyPEGMA brush of varying thickness (11-87 nm, measured by ellipsometry) was grafted on Ti alloy via surface initiated atom transfer radical polymerisation (SIATRP) using chloro functionalized ATRP initiator immobilized on Ti surface with initiator density (σ*) of 1.5 initiators/nm^2. Polymer brushes were then selectively laser ablated and their presence on non-textured area of the laser processed template was primarily confirmed by atomic force microscopy, fluorescence microscopy and X-ray Photoelectron spectroscopy. Spatial orientation of biomolecules was first achieved by non-specific protein adsorption on areas ablated by the laser, via physisorption. Further, patterned brushes of polyPEGMA were modified to activated ester that gave rise to protein conjugation specifically on non-laser ablated brush areas observed via fluorescence microscope and FESEM. Moreover, the laser ablated brush modified template forming alternate patterns was also demonstrated for generating alternate patterns of bacteria such as *E. coli* as observed via optical microscopy. This promising technique can be further extended to create interesting patterns of several biomolecules which are of great interest to biomedical research community.



Picture1.jpg

Functionalized double-decker silsesquioxanes as promising building blocks in biomaterials chemistry

Monday, 24th April - 14:45: Oral Session 2-4 - Oral

Prof. Lukasz John [1]

1. University of Wroclaw, Faculty of Chemistry

Introduction: The use of diverse biomaterials for regenerative medicine is constantly evolving. Therefore, looking for easy-to-scale-up materials in terms of preparation, less complex composition, and featuring structural and chemical stability seems justified. In this work, we report the preparation of double-decker silsesquioxane-based (DDSQ-based) composites, which, according to our best knowledge, have never been used as biomaterials.

Objective: The application of DDSQ and PVA composites as potential materials used in biomedicine.

Methods: All resulting silsesquioxanes and composites were characterized by multinuclear (^{1}H, ^{13}C, and ^{29}Si) NMR spectroscopy, FT-IR, HR-MS, and X-ray analysis. Biological studies were performed on human fibroblasts.

Results and discussion: A family of methacrylate-substituted DDSQs was obtained starting from the previously reported hydroxyalkyl double-decker silsesquioxanes. In the resulting hybrids, methacrylate groups are attached to each other's lateral silicon atoms of DDSQ in trans positions, providing an excellent geometry for forming thin layers. In contrast to pure organic methacrylates, the covalent bonding of methacrylate derivatives to inorganic silsesquioxane core improves mechanics, cell adhesion, and migration properties. Furthermore, to increase the hydrophilicity of the resulting DDSQ-based hybrids, polyvinyl alcohol (PVA) was added. The entire system forms an easy-to-obtain two-component (DDSQ-PVA) composite, which was subjected without any upgrading additives to biological tests later in the research. The resulting biomaterials fulfill the requirements for potential medical applications. Human fibroblasts growing on prepared hybrid composites are characterized by proper spindle-shaped morphology, proliferation, and activation status similar to control conditions (cells cultured on PVA), as well as increased adhesion and migration abilities.

Conclusion:

The obtained results suggest that the prepared biomaterials may be used in regenerative medicine in the future.

Acknowledgments: This work was financially supported by the National Science Centre, Poland (Grant No. 2020/39/B/ST4/00910).

Engineered Polymer Composites for High-Performance Wearable Bioelectronics

Monday, 24th April - 15:00: Oral Session 2-4 - Oral

Mr. Sang-Joon Park [1], ***Prof. Tae-Jun Ha*** [1]

1. *Kwangwoon University*

Recent progress of material design and synthesis for multi-functionality has stimulated the rapid growth of next-generation electronic applications [1]. Various materials including metal-oxides, carbon compounds, and polymers, which can be solution-processed at low temperatures, have been investigated to realize wearable bioelectronics [2]. Among them, polymer composites have been intensively investigated owing to their simple fabrication process, high flexibility, and excellent biocompatibility [3-4]. In this presentation, we will demonstrate engineered polymer composites for high-performance wearable bioelectronics directly attached on human-body. The synthesis optimization of engineered polymer composites solution-processed at low-temperatures will be discussed using various material characterization techniques. We will also demonstrate the effect of engineered polymer composites on the electrical output performances of wearable bioelectronics. The operational stability against mechanical bending stresses and environmental conditions will be discussed by investigating the corresponding mechanism. We believe that this work can open-up a prospective route to engineering polymer composites in the field of wearable bioelectronics.

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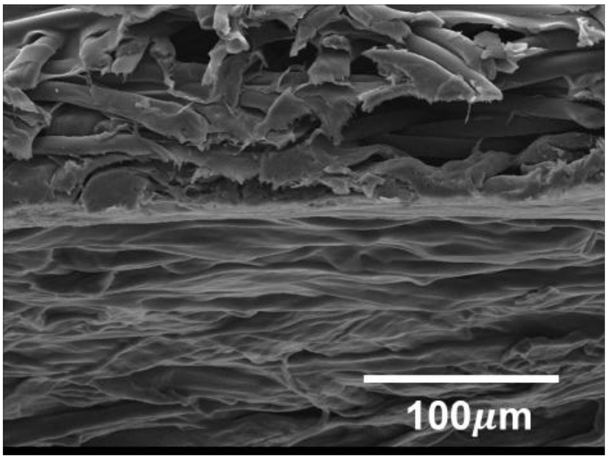
Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2021R1A2C2012855)



Sem image of engineered polymer composites.png

Iterative self-assembly of block-copolymer layers

Monday, 24th April - 15:15: Oral Session 2-4 - Oral

***Dr. Nils Demazy* [1], *Dr. Pablo Argudo* [1], *Prof. Guillaume Fleury* [1]**

***1.** Univ. Bordeaux, CNRS, Bordeaux INP, LCPO*

Nanostructured block copolymer (BCP) thin films constitute an elegant tool to generate periodic patterns with periodicities ranging from a few nanometers to hundreds of nanometers. Such well-organized nanostructures are foreseen to enable next-generation nanofabrication research with potent applications in the design of functional materials in biology, optics or microelectronics. This valuable platform is, however, limited by the geometric features attainable from diblock copolymer architectures. Therefore, strategies to control and enrich the variety of structures obtained by BCP self-assembly processes are gaining momentum [1, 2]. In particular, we have demonstrated that precise interface manipulations and iterative self-assembly of BCP layers can lead to morphological variety and advanced functional properties [3]. We have also further developed a method based on immobilized nanostructured BCP layers which yielded to the generation of non-native BCP nanostructures through “responsive layering” [1]. Accordingly, design rules have been established in order to finely control the resulting non-native BCP structures by tuning the BCP morphology, domain spacing and interfacial and topographical fields between the different layers [4]. In particular, we have investigated the complex interplay between chemical and topographical constraints for the precise control of the registration between two stacked BCP layers. We demonstrated that the change of the interfacial energy between the nanostructured BCP films, associated to the topography inherent to the immobilization of the underneath BCP layer, leads to a controlled registration of the upper BCP layer with respect to the underlying one.

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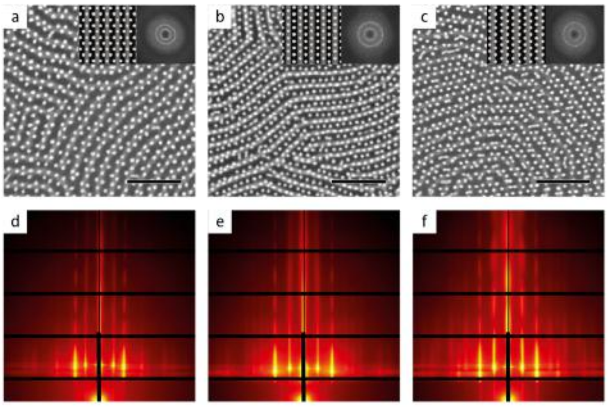


(top) SEM images and (bottom) corresponding GISAXS patterns of the stacking configurations obtained for a dot pattern on top of a line & space pattern with (a,d) a “neutral” interfacial layer , (b,e) a “PS-affine” interfacial layer and (c,f) a “PMMA-affine” interfacial layer. Top right insets are the idealized structures and FFTs. Scale bars: 250 nm.

Stacking configurations obtained for a dot pattern on top of a line space pattern.png

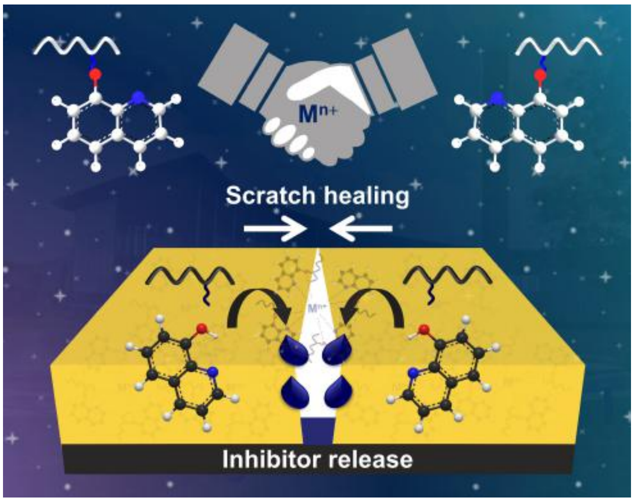
Responsive and self-healing polymers for anticorrosion application

Monday, 24th April - 15:30: Oral Session 2-4 - Oral

Mr. Krisada Auepattana-aumrung [1], *Prof. Daniel Crespy* [1]

1. Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology

Corrosion is a significant issue for metals and alloys because it critically affects their lifetimes. Coatings containing corrosion inhibitors are commonly used as barriers to protect the substrate from aggressive environments. However, the anticorrosion efficiency of the coatings is limited due to the uncontrolled leaching of inhibitors and susceptibility to mechanical damages. To overcome these issues, pH-responsive polymer containing the corrosion inhibitor 8-hydroxyquinoline (8HQ) which coordinates cerium ions is synthesized and employed as coating. The coating displays a dual function of controlling inhibitors release and repairing damages. The coating presents an excellent anticorrosion performance due to the synergistic barrier effect of the cerium compounds and the on-demand release of 8HQ during the corrosion process. Furthermore, the coating recovers ~98% of its barrier properties after mechanical damage due to its self-healing ability.



Conceptual scheme for self-healing and anticorrosion coating.jpg

Polymer Brushes by SI-PET-RAFT

Monday, 24th April - 15:45: Oral Session 2-4 - Oral

Dr. Andriy Kuzmyn [1], *Prof. Han Zuilhof* [1]
1. Wageningen University & Research, Laboratory of Organic Chemistry

Polymer brush-based coatings can provide surfaces with unique properties, including antibiofouling, antiviral, and lubrication features. To apply such coatings, a variety of controlled radical polymerization techniques have been applied. However, these methods often come at the price of complex handling and the requirement of an inert atmosphere. This stimulated the development of more robust, simpler, and milder techniques to obtain those polymer coatings. To this aim, we have adapted the photoinduced electron transfer reversible addition−fragmentation (PET-RAFT) technique for the surface-initiated synthesis of polymer brushes (SI-PET-RAFT).

SI-PET-RAFT polymerization proceeds at metal-free, oxygen-tolerant, mild conditions and is triggered by visible light [1,2]. Furthermore, using light as a trigger for this polymerization allows the creation of complex hierarchical and patterned structures [1]. Using a metal-free non-toxic catalyst such as Eosin Y (an edible dye), Rose Bengal, Erythrosin B, and Phloxine enables the application of SI-PET-RAFT to a very wide range of applications. We have explored different polymerization conditions and their effect on the control and livingness of the SI-PET-RAFT process. Moreover, we applied SI-PET-RAFT to create antibiofouling, antiviral and bioactive coatings:

- Antifouling coatings demonstrated good antifouling properties, including against undiluted human serum, as monitored by QCM-D and SPR [3].
- Coatings based on *N*-[3-(decyldimethyl)-aminopropyl] methacrylamide bromide and carboxybetaine methacrylamide-based brushes display highly promising antiviral properties, decreasing the count of viable virus particles ca. 5-6 times faster for avian flu and about 2-3 times faster for SARS-CoV-2 [4].

This approach represents a scalable, robust, oxygen-tolerant, and heavy metal-free route toward producing antifouling, antiviral and functional copolymers that opens up biosensing and tissue engineering applications.

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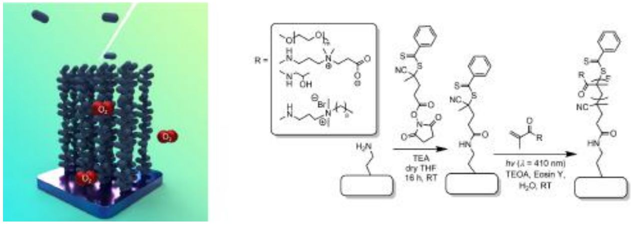

General scheme of si-pet-raft..png

Cyclic polymers: exploring their uniqueness

Monday, 24th April - 16:30: Oral Session 3-1 - Oral

Prof. Fabienne Barroso-Bujans [1]

1. *Donostia International Physics Center*

Cyclic polymers are today at the forefront of macromolecular science. This is because cyclic polymers present intriguing physical and chemical properties given only by the absence of end groups and their circular architecture. The enormous research carried out on synthetic polymers has been important to understand their property-structure relationships. This has only been possible thanks to innovative advances in organic synthesis and catalysis, creating a variety of pathways to cyclization of preformed chains through ring-closure strategies and ring-expansion polymerization of a variety of monomers. At present, cyclic polymers have found potential utility in the biomedical and pharmacological fields, surface chemistry, and plastic and electronic industry. In the long-term, versatile cyclic polymers with useful, autonomous and smart functions are expected to be produced with potential applications in broader scientific fields.

In this presentation, I will present our recent developments on the area of cyclic polymers.[1-9] This includes the design of materials, new synthetic pathways and the development of strategies for purification and detection of cyclic polymers.

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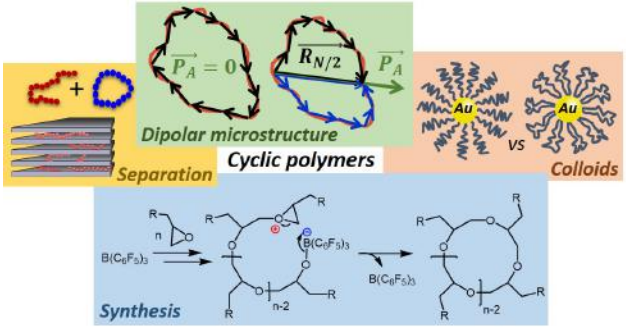

Cyclic polymers.jpg

Anionic ring-opening copolymerization of γ-thiolactones and cyclocarbonates: an alternative to the synthesis of oxidable poly(ester-alt-thioether)s

Monday, 24th April - 17:00: Oral Session 3-1 - Oral

Ms. Emma Mongkhoun [1], *Prof. Philippe Guégan* [1], *Dr. Nicolas Illy* [1]

1. *Institut Parisien de Chimie Moléculaire, Sorbonne Université, Paris*

Sulfide-containing polymers are of great interest for various industrial applications (electronics, biomedical, materials)[1]. Moreover, sulfide groups can be oxidized into sulfoxide or sulfone moieties that highly improve the thermomechanical and chemical stability of the polymer[2]. In addition to sulfur-containing moieties, the incorporation of other functional groups along the polymer backbone can bring new properties such as ester groups commonly known for their degradability. Our group has developed a new method to synthesize poly(ester-*alt*-thioether)s by alternating anionic ring-opening co-polymerization of thiolactones with epoxides[3,4]. However, due to the very high toxicity of ethylene oxide, it has not been possible to synthesize the poly(ester-*alt*-thioether) having the simplest structure without any lateral group.

Thus, we propose to copolymerize γ-thiobutyrolactone with ethylene carbonate by AROP as depicted in the mechanism on Figure 1. The γ-thiolactone is ring-opened by an alcoholate to form a thiolate that will then initiate the ring-opening of the cyclocarbonate with the concomitant decarboxylation. In a first part of this work, the polymerization conditions were optimized and poly(ester-*alt*-sulfide)s with molar masses up to 7 kg.mol^{-1} were successfully synthesized in solvent-free conditions. In a second part, the oxidation of the sulfide groups was carried out using hydrogen peroxide as the oxidant, resulting in a water-soluble material with new thermomechanical properties (semi-crystalline).

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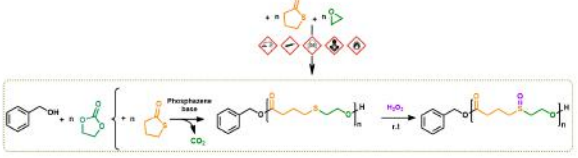

Figure 1: Poly(ester-*alt*-sulfide) synthesis by AROP of γ-thiobutyrolactone and ethylene carbonate using benzyl alcohol and a phosphazene base as the initiating system followed by its oxidation.

Figure abstract mongkhoun apme 2023bis.png

Engineering Molecular Brushes for Biomedical Applications

Monday, 24th April - 17:15: Oral Session 3-1 - Oral

Prof. Xavier Banquy [1]

1. *Universite de Montreal*

Molecular brushes are branched macromolecules whose architecture is similar to that of a bottlebrush. This class of material is ubiquitous in nature and is often found in mucinous fluids of mammals and plants where they act as lubricating agent, antifouling or trapping coatings.[1,2] During the past few years we have been investigating the behavior of molecular brushes at the solid liquid interface and more recently in biological media using a structure-property relationship approach. We have systematically compared monoblock versus multiblock molecular brushes and evaluated their lubricating and antifouling properties in a wide range of media.[3,4] Using surface sensitive techniques such as the Surface Forces Apparatus, we were able to rationalize the correlations between polymer architecture, conformation and interfacial properties.[5] Our more recent work documents the properties of these materials in living organisms, especially at the surface of cartilage and in the blood stream. Our advances in that area show that molecular brushes are excellent candidates as nanocarriers for drug delivery to the brain as well as good chondroprotective agents.[6]

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Well-defined porous biodegradable microspheres via UV photodegradation and RAFT polymerization

Monday, 24th April - 17:30: Oral Session 3-1 - Oral

Prof. Ildoo Chung [1]***, Dr. Taeyoon Kim*** [1]

1. Pusan National University

Introduction

Aliphatic polyesters such as polycaprolactone (PCL) and polylactide (PLA), endowed with semicrystallinity and degradability, has been widely used as a scaffold in tissue engineering, drug delivery systems, packaging and biomedical applications, due to its controlled biodegradability, biocompatibility, and good physical properties. Our work focuses on the successful polymerization of methyl vinyl ketone onto PCL/PLA via RAFT followed by the formation of their biodegradable microspheres that were made porous by UV irradiation.

Methods

Porous biodegradable microspheres were fabricated by successful RAFT polymerization of methyl vinyl ketone (MVK) onto PCL and PLA, which was first synthesized by ring opening polymerization of lactide followed by an oil/water emulsion-evaporation method, then finally photodegradation of PMVK blocks by UV irradiation.

Results and discussions

For photodegradation by UV light under dried condition, the molecular weight of triblock copolymer was decreased gradually with UV irradiation time, reaching close to that of macro-CTA, meaning that 90% of PMVK block was photodegraded after 24 h of UV irradiation. The morphology of microspheres was spherical with smooth surfaces before UV irradiation (Fig. 1(upper)). Microspheres fabricated only from PCL homopolymers could also retain their smooth surface after UV irradiation (Fig. 1a (bottom)). However, those from PCL-PMVK and PCL-PLA-PMVK block copolymers had rough surfaces and porous structures after UV irradiation due to the photodegradation of PMVK blocks as a porous template [Fig. 1b and c (bottom)]. The porosity and shape of the microspheres and shape of microspheres were dependent on the PMVK contents and size of microspheres.

Conclusions

Well-defined biodegradable PCL-PLA-PMVK triblock copolymers were successfully synthesized by ring-opening and RAFT polymerization. Linear increase in molecular weight and narrow polydispersities of the triblock copolymers are clear indications of a controlled polymerization mechanism. Porous microspheres were fabricated by the O/W emulsion-evaporation method followed by the photodegradation of PMVK blocks by UV irradiation. Our findings pave the way to novel methods for direct templating fabrication of porous polymers by removing template blocks by UV light.

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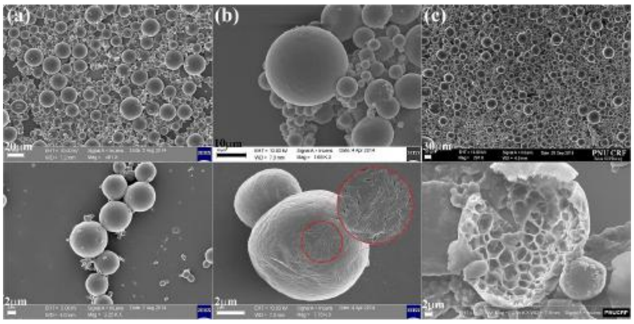

Figure 1. sem images of microspheres before upper and after bottom uv irradiation. a pcl b and c pcl-pmvk triblock copolymer pmvk contents b 16 c 45 ..jpg

Chemically-modified biopolymers for sustainable polymers and agrochemical delivery

Monday, 24th April - 16:30: Oral Session 3-2 - Oral

Prof. Frederik Wurm [1]

1. *University of Twente*

Biopolymers were the first materials that mankind used to make “plastics” - Celluloid and Cellophane are cellulose-based materials and introduced the “Polymer Age” in that we are living today, which, however, is dominated by petroleum-based polymers.

This is often due to the poor properties of biopolymers in the envisioned applications and synthetic polymers allow the broad adjustment of properties.

Also, biopolymers can be chemically modified to adjust their properties, however, biodegradation rates are often altered and mostly slowed down drastically.

We present strategies for the chemical modification of lignin and cellulose for fully biodegradable macroscopic and microscopic polymers, for packaging or agrochemical delivery.

Modification of lignin-derived compounds to bio-based polymers in environmentally friendly conditions

Monday, 24th April - 17:00: Oral Session 3-2 - Oral

Dr. Joanna Michalska-Walkowiak [1]***, Dr. Fanny Coumes*** [2]***, Prof. Jutta Rieger*** [3]***, Dr. Victorien Jeux*** [4]***, Dr. Vincent Terrasson*** [4]

1. *CNRS, UMR 8232 – IPCM – Institut Parisien de Chimie Moléculaire – Polymer Chemistry Team, Sorbonne Université, 4 Pl. Jussieu, 75005 Paris,* ***2.*** *CNRS, UMR 8232, Institut Parisien de Chimie Moléculaire (IPCM), Polymer Chemistry Team, 4 place Jussieu, 75252 Paris,* ***3.*** *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Equipe Chimie des Polymères, 75252 Paris, France,* ***4.*** *Centre de Recherche de Royallieu, Université de Technologie de Compiègne, ESCOM, Integrated Transformations of Renewable Matter (TIMR), 1 rue du Réseau Jean-Marie Buckmaster, 60203 Compiègne,*

Nowadays, the synthesis of monomers and polymers from renewable resources is intensively investigated to develop new bio-based materials that can compete with existing fossil fuel-based polymers.[1] Lignin-delivered compounds (LDCs) offer an attractive alternative for designing bio-based and cost-effective macromolecules, which exhibit interesting thermomechanical properties. By depolymerization of lignin and adequate chemical transformation, a wide variety of compounds with styrene-like structures can be obtained selectively.

In this project, we focus on designing and developing functionalized monomers from the mixture of Vanillin (V), p-Hydroxybenzaldehyde (H), and Syringaldehyde (S), which can be obtained by oxidative degradation of lignin. From this mixture we were able to synthesize in two steps, using green conditions, corresponding styrenic monomers with a wide range of functional groups. The synthesis pathway was validated either using classical conditions in solution as well as using mechanochemistry. Then, the synthesis of bio-based polymer was tested using free radical polymerization in environmentally friendly conditions (in bulk or green solvents). (Co)polymers with high monomer conversion were generally obtained at reasonable reaction times. The thermal properties of the obtained (co)polymers were comparable with thermal properties of polystyrene. We showed that they can be varied through the modification of functional groups on the aromatic unit. Overall, the developed approach demonstrates the possibility to use bio-sourced compounds instead of petroleum-based polystyrene materials.

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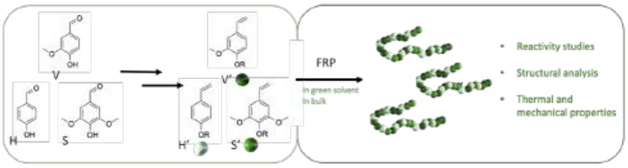

Jmw-abstract-graph.png

A glance at Avantium's furanic humins

Monday, 24th April - 17:15: Oral Session 3-2 - Oral

Dr. Sandra Constant [1], ***Mr. Tom Claessen*** [1], ***Dr. Ed de Jong*** [1], ***Prof. Pieter Bruijnincx*** [2]

1. *Avantium,* ***2.*** *Organic Chemistry and Catalysis, Institute for Sustainable and Circular Chemistry, Utrecht University*

Furanic humins are by-products obtained from carbohydrate valorization processes. Given the large amount of the carbon input that they can contain, they need to be considered as feedstock. In addition, all these product streams, when marketed at their highest value, deliver an economically viable technology for sustainable biochemicals production [1]. However, only limited valorization options are available; in fact, these materials are nowadays often simply considered as waste and mainly burnt as fuel for their heating value. Furanic humins, are formed during acid-catalyzed (hydro)thermal conversion of the carbohydrate fractions of biomass, e.g. for the production of furfural and levulinate derivatives. At Avantium, they are a side product of the YXY® process. The YXY® technology catalytically converts plant-based sugar (fructose) into FDCA, the key building block for a wide range of plant-based chemicals and plastics such as polyethylene furanoate (PEF). The furanic humins are by-products of YXY® process currently producing FDCA at the pilot plant in Geleen and larger quantities are expected from the FDCA Flagship Plant in 2024 in Delfzijl. More insight into the chemical structure and properties of these humins is essential to understand their formation, chemical-recalcitrance and to guide further development of application strategies.

In this presentation, we will provide an overview of the multitechnique characterization of Avantium's furanic humins. Size exclusion chromatography provided information on the furanic humin molar masses. Chemical structure of the humins was studied with infrared spectroscopy and extensive NMR analysis including ^{31}P NMR, ^{19}F NMR [2], HSQC 2D NMR (Figure 1). We will also give an overview of the possible applications of the furanic humins produced at Avantium.

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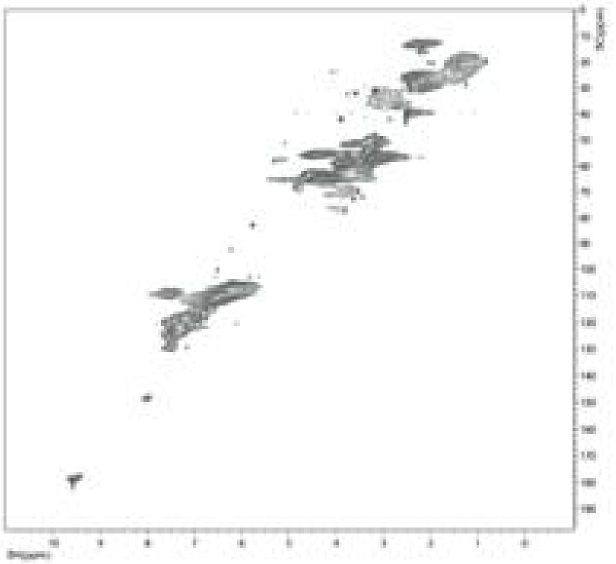

Figure 1 sconstant.png

POLYSORB®- Isosorbide as an interesting building block for Thermosetting resins

Monday, 24th April - 17:30: Oral Session 3-2 - Oral

Dr. René Saint-Loup [1]***, Dr. Jonathan Potier*** [2]***, Dr. Patrice Woisel*** [2]***, Mrs. Audrey Sahut*** [1]

__1.__ ROQUETTE, __2.__ Unité des Matériaux et Transformations, UMET, CNRS

Introduction:

Isosorbide or 1,4-3,6 dianhydrohexitol, derivated from starch and more precisely from sorbitol, is one of the chemical intermediates of interest in the field of thermoplastic materials and for curable resins application. It can be used directly as a monomer or after chemical modification.

Results:

Two type of monomers have been synthesized from isosorbide to cover different applications: epoxy derivatives and (meth)acrylics derivatives.

After developing a synthetic pathway to avoid main technical issues[1], epoxy-functionalized Isosorbide has been studied in thermosetting compositions. This evidenced improved mechanical properties (UV resistance, high toughness) and adhesion when compared to usual BPA-based epoxies, being of interest in several applications like flooring or composites[2]. On top of these applications, the specific properties of epoxies of isosorbide allowed to develop other applications like chemicals hydrogels[3] or stabilization of fibrous and porous solids[4].

In parallel to epoxy, different derivatives of (meth)acrylates of Isosorbide and their use in cross-linked[5] materials formation have been studied and evidenced interesting behaviors. The properties and the behavior of these materials will be presented and discussed.

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Showcasing research from the Polymer Systems Engineering team, laboratory UMET (University of Lille, France) in collaboration with Roquette Industry (Lestrem, France).

Isosorbide monoacrylate: a sustainable monomer for the production of fully bio-based polyacrylates and thermosets

Conventional radical polymerization of the fully bio-based isosorbide monoacrylate (IMA) has been investigated. For the first time, kinetic studies and the Mayo method allowed us to determine the transfer constant to IMA. Finally, high T_g polymers (PIMA) have been synthesized and crosslinked with bio-based succinic anhydride to obtain sustainable thermosets which show a T_g of up to 116 °C and storage modulus close to 4 GPa at room temperature.

As featured in:

See Jonathan Potier *et al.*, *Polym. Chem.*, 2020, 11, 6903.

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Apme.jpg

Bilayer-Folded Lamellae: New Order from Random Copolymer Self-Assembly

Monday, 24th April - 16:30: Oral Session 3-3 - Oral

Prof. Myungeun Seo [1], ***Prof. Dong Ki Yoon*** [1]

1. *KAIST*

We present that a periodic order can spontaneously arise from the self-assembly of random copolymers based on their collective behavior. We believe this comes from the sequence matching problem: the number of possible sequences increases exponentially with the degree of polymerization. For a long chain of AB random copolymers, it is nearly impossible to find a perfectly complementary sequence pair. Local mismatches from B-rich and B-lean segments will be inevitable. In the regime where this mismatch penalty is substantial, the ensemble seems to minimize energy by recurrent folding of the string pairs.

We investigated an amphiphilic random copolymer which contains hydrophilic and hydrophobic molecular side chains randomly fixed on the backbone. At a high concentration in water, the hydrophobic chains aggregate to form self-assembled bilayers, and further stack into a well-known multilamellar structure. At intermediate concentration, however, the bilayer repetitively folds and develops a strong lamellar order in the perpendicular direction with larger spacing. Strikingly, these “bilayer-folded lamellae” bear a resemblance to chain-folded lamellae in crystalline polymers, favored over the extended chain crystals, which are now taken for granted after the strong debate in the 1950s.

We constructed a phase diagram of amphiphilic random copolymer aqueous solutions and found that this phase is thermodynamically (meta)stable, and appears universally at different hydrophobic contents. It can unfold under high shear. But it only occurs for the random sequence, and when the degree of polymerization exceeds a critical value. We propose that the periodicity of the folding depends on the population of the single side chain-rich local sequences.

Novel columnar liquid crystalline poly(2-oxazoline)s containing side dendrons: advances in the design of biomimetic membranes

Monday, 24th April - 17:00: Oral Session 3-3 - Oral

Mr. Jordi Guardià [1], ***Dr. Xavier Montané*** [1], ***Dr. Marta Giamberini*** [2], ***Dr. José Antonio Reina*** [1]

1. *Universitat Rovira i Virgili, Department of Analytical Chemistry and Organic Chemistry, C/Marcel·lí Domingo 1, 43007 Tarragona, Spain,* ***2.*** *Universitat Rovira i Virgili, Department of Chemical Engineering, Av. Països Catalans 26, 43007 Tarragona, Spain*

Introduction

Proton transport is a natural phenomenon that occurs with high selectivity and efficiency. To mimic natural behaviour, our research group has focused during the last decades on the design of materials containing ion transport channels by self-assembling, in which the channels localize the permeation path and simultaneously protect the transport against the environment.

In the present study, we synthesized side chain liquid crystalline poly(2-oxazoline)s, poly(2-(3,4,5-tris(4-dodecyloxybenzyloxy)phenyl)-2-oxazoline) (PTOx) from its oxazoline monomer precursor, 2-(3,4,5-tris(4-docecyloxybenzyloxy)phenyl)-4,5-dihydro-1,3-oxazole) (TAPOx), by cationic ring opening polymerization (CROP) (Figure 1). Furthermore, the nature of the CROP would allow us to obtain high molecular weight side chain liquid crystalline polymers (SCLCPs), which in turn would let us prepare membranes with improved mechanical properties than the cation exchange membranes tested in polymer electrolyte fuel cells with the previously synthesized SCLCPs in our research group [1].

Methods

The mesogenic monomer, TAPOx, was synthesized as previously reported [2]. The CROP of TAPOx monomer to obtain PTOx was performed in a dried Schlenk under vacuum. Different temperatures, initiators, monomer concentrations, solvents and terminating agents were tested. The synthesized family of dendronized poly(2-oxazoline)s were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), polarized optical microscopy (POM) and size exclusion chromatography (SEC).

Results and discussion

A family of dendronized poly(2-oxazoline)s presenting degrees of polymerization between 20 and 60 kDa was synthesized. To achieve the “living” character in this CROP, the following reaction conditions were established: reaction temperature equal to 105 °C, use of methyl trifluoromethanesulfonate (MeOTf) as an initiator, chlorobenzene as a solvent, morpholine as a terminating agent, while the monomer concentration was fixed at 1.0 M. These poly(2-oxazoline)s were subsequently studied in terms of liquid crystalline behaviour, noting that the whole family exhibited liquid crystalline columnar mesophases with a clearing temperature between 71 and 81 °C. The organization of the side chain acyl-substituted poly(ethyleneimine)s columns suggests that PTOx could be promising candidates to build up membranes for proton transport applications since the presence of nitrogen atoms in the polymer main chain allows it to work as an ionic channel in the helical conformation adopted by polymer columns.

References

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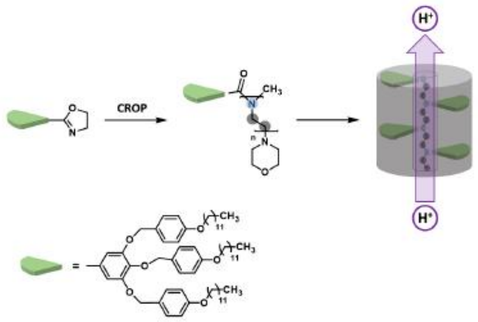


Synthesis of dendronized poly 2-oxazoline s and representation of the expected proton transport through the ion channels.png

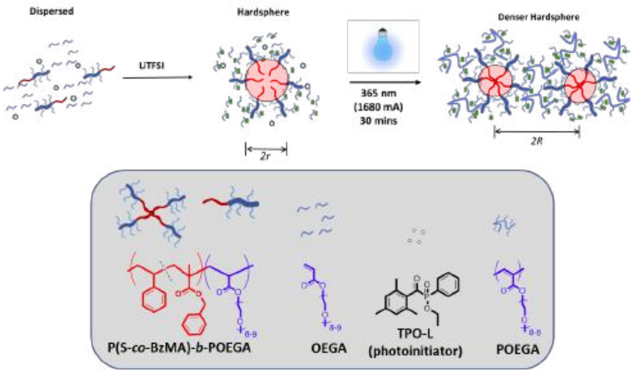
Block Copolymer Nanostructured Solid Polyelectrolyte for Lithium Batteries : From In-Equilibrium to Out-of-Equilibrium Strategies

Monday, 24th April - 17:15: Oral Session 3-3 - Oral

Mr. Kingsley Aniagbaoso [1]***, Ms. Monika Krol*** [2]***, Prof. Janne Ruokolainen*** [2]***, Prof. Antoine Bousquet*** [1]***, Dr. Maud Save*** [1]***, Dr. Laurent Rubatat*** [1]

1. *Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France,* ***2.*** *Department of Applied Physics, School of Science, Aalto University, Espoo FIN-00076, Finland*

Block copolymers (BCP) solid electrolytes are considered to replace liquid electrolytes in lithium-ion batteries for improved safety. AB type of BCP is foreseen to leverage the synergistic effect of a glassy, rigid insulating A block to prevent dendrite growth and low glass transition ion conducting B block to facilitate ion transport. However, the conductivity of BCP electrolytes is often compromised by morphology defects (e.g., dead ends at grain boundaries) which interrupt the conducting pathways thus increasing resistance to ion transport. In our work, we demonstrate how to improve the integrity of ionic pathways in BCP electrolytes by utilizing star architecture. The illustration is made possible by comparing the star BCP of poly(styrene-co-benzyl methacrylate)-b-poly(oligo(ethylene glycol) methyl ether acrylate) ((P(BzMA-co-S)-b-POEGA)) with the linear analogue. In a second step, the so-synthesized BCPs are used to modulate in-situ the formation of nanostructures simultaneously in photopolymerization of oligo (ethylene glycol) methyl ether acrylate (OEGA) via Polymerization Induced Microphase Separation (PIMS) process. Kinetically arrested hard objects in an ion conductive matrix are obtained with a variety of morphologies attributed to the lithium salt content. These synthesized solid polyelectrolytes demonstrated good mechanical properties and ionic conductivities and could be potentially introduced *in-situ* in batteries.



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Multicompartment polymeric colloids from functional precursor microgels: synthesis in continuous process

Monday, 24th April - 17:30: Oral Session 3-3 - Oral

Dr. Jacek Walkowiak [1]***, Mr. Casper van Duijnhoven*** [2]***, Ms. Pia Boeschen*** [3]***, Ms. Nadja Wolter*** [1]***, Dr. Joanna Michalska-Walkowiak*** [4]***, Dr. Martin Dulle*** [5]***, Prof. Andrij Pich*** [1]

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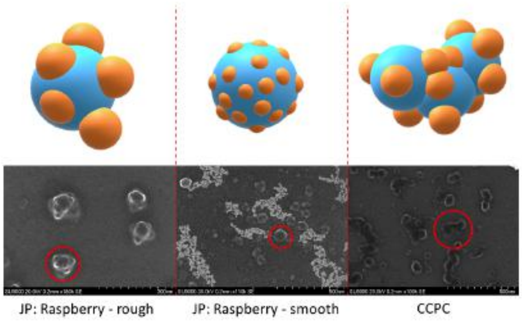
In this study we present a poly(*N*-vinylcaprolactam) (PVCL) based core-shell microgels used in seed polymerization to fabricate raspberry-like patchy particles (PPs) and complex colloidal particle clusters (CCPCs). These were obtained *via* two-, and one-step (cascade) flow process. Firstly, a surfactant-free, photo-initiated reversible addition-fragmentation transfer (RAFT) precipitation polymerization (Photo-RPP) was used to develop internally cross-linked PVCL-based microgels with narrow size distribution. Resulting microgel particles were then used to stabilize styrene seed droplets in water, producing raspberry-like PPs. In the cascade process, different hydrophobicity between microgel and PS induced the self-assembly of the first formed raspberry particles that then polymerized continuously in a Pickering emulsion to form the CCPCs. We studied the size of seed microgels, core/shell ratio and polymer packing density as a function of the retention time (Rt) within the flow reactor, proving an excellent level of control over the core/shell ratio during the polymerization process.



Graphical abstract.png

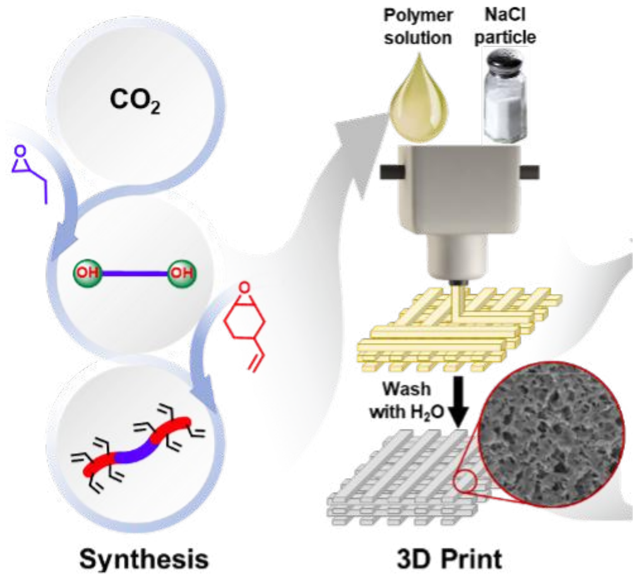
CO2-Based Triblock Copolymers as Feedstocks for Additive Manufacturing

Monday, 24th April - 16:30: Oral Session 3-4 - Oral

Dr. Perian Wei [1]***, Ms. Krista Schoonover*** [1]***, Ms. Ciera Cipriani*** [1]***, Mr. Chia-Min Hsieh*** [1]***, Prof. Don Darensbourg*** [1]***, Prof. Emily Pentzer*** [1]

1. *Texas A&M University*

As additive manufacturing techniques rapidly evolve, so must the feedstocks used to produce complex geometries on demand. A critical consideration of feedstocks is both their source and their fate after use of the printed object. Herein, we report a convenient and atom economical synthetic strategy to produce CO_2-based, chemically modifiable polycarbonates for use as feedstocks for additive manufacturing. We use the alternating copolymerization of CO_2 and epoxides to produce ABA triblock copolymers consisting of soft and hard blocks, leveraging a salenCo(III)TFA/PPNTFA binary catalyst system. The impact of chemical composition on the thermal and mechanical properties of the copolymers is reported. We then produce thixotropic inks using solutions of polymer in organic solvent and size-controlled NaCl particles. These inks were printed by direct ink write (DIW) 3D printing; after printing, the objects were washed with water to remove the solvent and NaCl, producing porous polycarbonate monoliths. Mechanical properties of the objects correlated to the ratio of hard and soft blocks. Further, we demonstrate that the structures could be dissolved in organic solvent or degraded under basic conditions. Alternatively, the tailored composition of the hard block was used for surface modification or chemical cross-linking, with the latter affording stability to organic solvent without expense to degradation via hydrolysis. This approach to ink development expands the scope of applications of this materials class for a broad range of applications



Pentzer apme polycarbonate printing.png

Polypeptoids brush layers for the deterministic doping of semiconductors

Monday, 24th April - 17:00: Oral Session 3-4 - Oral

Ms. Viviana Ospina [1]***, Dr. Riccardo Chiarcos*** [1]***, Dr. Diego Antonioli*** [1]***, Prof. Valentina Gianotti*** [1]***, Mr. Stefano Kusclan*** [2]***, Prof. Michele Laus*** [1]***, Dr. Michele Perego*** [2]

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Introduction

To move in the way of nanoelectronics, polymers can be employed for the scaling down of transistors by modulating the doping of semiconductors. Many methodologies have been explored to introduce dopant atoms inside a semiconductor precisely. Among them "monolayer doping" holds a particular position as the density of doping atoms is controlled by the steric hindrance of the dopant-containing carrier molecules. Polystyrene and polymethylmethacrylate with a terminal phosphate moiety and narrow dispersity have been used to control the dopant dose of silicon substrates by changing the molecular weight. However, it was recently demonstrated that polydispersity is still a challenge even in low molecular weight distribution once precise control of the amount of dopant atoms is required.

Therefore, monodisperse polypeptoid dopants characterized by different structures and chain lengths with phosphorus-containing moiety at one end were synthesized by solid phase sub-monomer synthesis (SPSS) and employed as a dopant source for precise control of the dopant atom amount.

Methodology

Two sets of polypeptoids were synthesized, either containing phenyl lateral chains consisting of 5, 10, 14, and 19 monomer units or containing 10 monomer units with linear lateral chains of different lengths. The polypeptoids were grafted on a silicon substrate by a hot plate at different temperatures. Finally, the phosphorus dose at the silicon surface was determined by TOF SIMS analysis.

Results and discussion

The synthesized polymers exhibited a dispersity near one as determined by MALDI TOF analysis (Figure 1). The suitable conditions for grafting to the silicon wafer by thermal annealing were determined to be 190°C for 40 s. Finally, an inverse correlation was found between the phosphorus dose determined by TOF SIMS and the polypeptoid length or lateral steric hindrance.

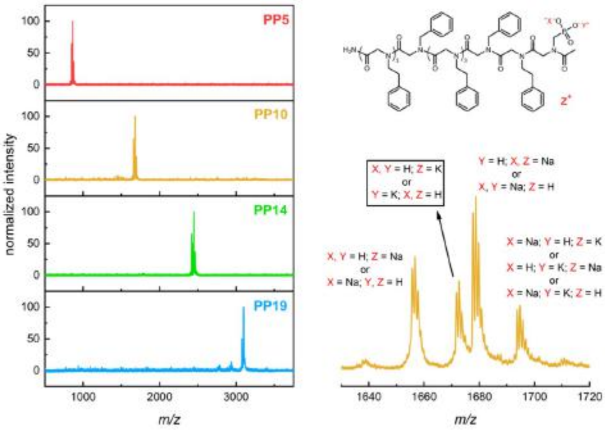


Figure 1 maldi-tof analysis of benzyl lateral chain polypeptoids peak values mz m 2na 886 1677 2309 3099 respectively . the 10 units polypeptoid structures assigned to the different signals are reported..jpg

Synthesis and Characterization of Novel Luminescent Polyurethanes for Photonic Devices

Monday, 24th April - 17:15: Oral Session 3-4 - Oral

Dr. Elisavet Tatsi [1]***, Mr. Matteo De Marzi*** [1]***, Mr. Luca Mauri*** [2]***, Prof. Alessia Colombo*** [2]***, Dr. Chiara Botta*** [3]***, Prof. Stefano Turri*** [1]***, Prof. Claudia Dragonetti*** [2]***, Prof. Gianmarco Griffini*** [1]

1. *Department of Chemistry, Materials and Chemical Engineering 'Giulio Natta', Politecnico di Milano, Piazza Leonardo da Vinci 32 – 20133 – Milano Italy,* ***2.*** *Department of Chemistry, Università degli studi di Milano, via Golgi 19, 20133 Milan,* ***3.*** *Institute of Sciences and Chemical Technologies "Giulio Natta" (SCITEC) of CNR, via Corti 12, 20133 Milano, Italy*

Introduction

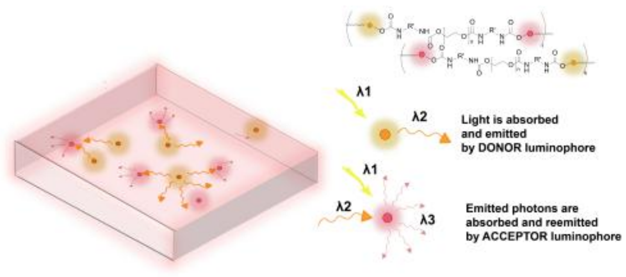
Luminescent solar concentrators (LSCs) have gained increasing attention in recent years as an attractive photovoltaic technology that offers a straightforward strategy for harvesting, spectrally converting, and optically concentrating solar photons. The main focus of research in this area has been on two major aspects: optimizing device design in search of more efficient architectures to maximize the collection, transport, and conversion of photons into usable electrical energy, and developing novel, high-emissivity luminescent species to ensure broad-light collection and efficient photon emission. Only recently attention also turned to the selection and development of suitable host matrix/waveguide materials with appropriate optical properties, sufficient chemical compatibility with the guest luminescent species, and good processability for easy device fabrication and outdoor durability.

Methods

New copolymers based on polyurethanes were synthesized from luminescent monomers and used as coatings for LSC devices. The main objective of this work was to develop a novel LSC material platform with improved performance using the mechanism of *Förster resonance energy transfer* (FRET). Specifically, two novel hydroxyl-functionalized molecules were used as donor-emitter pair for the energy transfer process within the polyurethane polymer matrix. Such polyurethanes were synthesized by a stepwise polyaddition reaction between isophorone diisocyanate and a hydroxyl-terminated oligomer, with the two fluorescent molecules and a non-luminescent diol molecule acting as chain extenders. The synthesized polyurethanes were characterized in terms of their molecular, optical, and thermal behavior prior to device fabrication.

Results and Discussion

The mechanism of energy transfer proved beneficial to the efficiency of the LSC devices, as well as the direct incorporation of the luminophores into the polymer chain compared with their random dispersion in the matrix. The device efficiencies, both photonic and photovoltaic, were in line with those reported in the literature; it was found that the devices do not distort the color of the light passing through them. Their *average visible transmittance* (AVT) values are significantly high compared to the devices reported in the literature. Moreover, the high *light utilization efficiency* (LUE) values obtained for the LSC devices fabricated with our novel fluorescent materials make them promising candidates as active host matrices for highly transparent, efficient LSCs.


λ1
λ2
Light is absorbed
and emitted
by DONOR luminophore
λ1
λ2
λ3
Emitted photons are
absorbed and reemitted
by ACCEPTOR luminophore

Toc.jpg

Self-organization and Self-alignment of Conjugated Polymers and Small Molecules on the 2D Materials

Monday, 24th April - 17:30: Oral Session 3-4 - Oral

Dr. Erol Yildirim [1]***, Ms. Tuğba Haciefendioğlu*** [1]

1. *Middle East Technical University, Department of Chemistry*

Conducting polymers (CP)-2D material nanocomposites have drawn considerable attention in recent research areas due to their enhanced physical, morphological and electrical properties which make them ideal candidates for organic electronics such as sensors, photovoltaic cells, supercapacitors and energy storage materials. However, the origin of self-organization, self-assembly and self-alignment of CPs on the 2D surface was not studied at molecular level which limit their electronic applications. To understand the general rules and parameters for self-organization and self-alignment such as the presence of any directional preference of the conducting polymers on the 2D materials such as graphene and graphene oxide; first principle methods and molecular dynamics simulation studies were performed to determine general principles for the interaction of CPs including donor-acceptor conducting copolymers and small conjugated molecules. To establish the principles of the self-organization on 2D materials, common CPs and representative molecules was selected from the experimental literature and structural optimizations were performed by using accurate first principle methods. We obtained wide range of differences for self-organization of different chains on the surfaces. We demonstrated that the origin of this difference is the ability of some CPs to position graphene carbons below their electron rich aromatic centers precisely. Due to physical template effect, 2D materials can also improve the planarity, rigidity and bond length alternation of CPs, which can lead to the enhanced optoelectronic performance. These parameters will help experimental researches to tailor CP architecture which can result in the enhanced properties such as crystalline domains with high conductivity at the material interface.

Acknowledgements: *Erol Yıldırım gratefully acknowledges support from 2232 International Fellowship for Outstanding Researchers Program of TÜBİTAK (Project No: 118C251).*

Chalcone-based oxime esters: Towards bioinspired and easily accessible visible light type I photoinitiators

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Zheng Liu [1]***, Ms. Armelle Braquemond*** [2]***, Prof. Jacques Lalevée*** [2]***, Dr. Didier Gigmes*** [3]***, Dr. Frédéric Dumur*** [3]

1. *Aix Marseille Université,* ***2.*** *Université de Haute-Alsace,* ***3.*** *Aix-Marseille Université*

During the past decades, visible light photopolymerization has been the focus of intense research efforts supported by the wide range of applications using this polymerization technique. [1] Active research activity on visible light photoinitiating systems is notably supported by the recent safety concerns raised by the use of UV light photoinitiating systems. Notably, the production of ozone during irradiation, the dangerousness of UV light that can cause eye damages and skin cancers can be cited as the main factors causing the abandoning of UV photopolymerization. Besides, photopolymerization remains an interesting polymerization technique used in research fields such as microelectronics, 3D and 4D printing adhesives, dentistry and coatings. Presently, visible light photopolymerization is facing a revolution with the development of monocomponent photoinitiating systems greatly simplifying the composition of the photocurable resins. Among unimolecular photoinitiators, oxime esters are extensively studied due to the easiness of synthesis, the versatility of the substitution pattern and the good thermal stability. Among chromophores that can be used for the design of oxime esters, chalcones that are bioinspired structures possess an intense absorption band in the visible range and have been identified as a promising scaffold for the design of oxime esters.

In this work, a series of chalcone-based oxime esters differing by the substitution pattern of the oxime ester functional group is presented. Interestingly, depending on the radicals formed, significant differences on the monomer conversions of acrylates could be demonstrated.

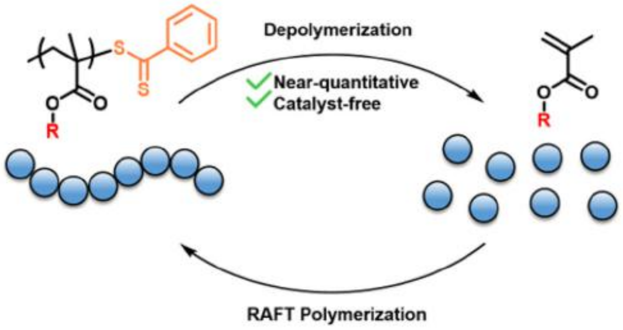
Depolymerization of RAFT-Polymethacrylates and its Applications

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Hyun Suk Wang [1], ***Dr. Nghia P. Truong*** [1], ***Mr. Zhipeng Pei*** [2], ***Dr. Glen Jones*** [1], ***Prof. Michelle L. Coote*** [2], ***Prof. Athina Anastasaki*** [1]

1. ETH Zurich, 2. Australian National University

Reversing controlled radical polymerization and regenerate the monomer would be highly beneficial for both fundamental research and applications, yet this has remained very challenging to achieve. Herein, we report a near-quantitative (up to 92%) and catalyst-free depolymerization of various linear, bulky, cross-linked, functional, and heat-sensitive polymethacrylates synthesized by reversible addition–fragmentation chain-transfer (RAFT) polymerization. Key to our approach is to exploit the high end-group fidelity of RAFT polymers to generate chain-end radicals at 120 °C. These radicals trigger a rapid unzipping of both conventional (e.g., poly(methyl methacrylate)) and bulky (e.g., poly(oligo(ethylene glycol) methyl ether methacrylate)) polymers. Importantly, the depolymerization product can be utilized to either reconstruct the linear polymer or create an entirely new insoluble gel that can also be subjected to depolymerization.



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Carbon Nitride Incorporation in Polymer Networks

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Cansu Esen [1]

***1.** Ghent University*

Incorporation of graphitic carbon nitride (g-C_3N_4) in polymeric supports endows inherent optical properties of this metal-free polymeric semiconductor with an absorption in the visible range, for photocatalytic reactions. Its facile production via thermal polymerization (around 550 °C) of nitrogen-rich precursors and resulting photophysical as well as optical properties that can be tuned via various modification (post or pre-) techniques, has drawn attention of many researchers. It has been utilized as heterogeneous photoinitiator based on the generation of photo-formed radicals under adequate light irradiation for vinyl monomers or alternatively, dispersions of g-C_3N_4 conducted into heterophase polymerization resulted in tailored hydrogels and resins. In this submission, four projects regarding the employment of g-C_3N_4 in polymer science will be presented. Firstly, fabrication of poly(styrene-co-divinylbenzene) polymer beads incorporated with g-C_3N_4 through suspension polymerization will be exhibited. In detail, it will demonstrate the effectiveness of resulting beads as recyclable photocatalysts thanks to the g-C_3N_4 photoactivity.[1] In the second example, g-C_3N_4 nanosheets embedded in a porous hydrogel network that is subsequently in-situ photomodified leading either the
'hydrophobic hydrogel' creation over an organic molecule incorporation or, formation of interlocked polymeric networks representing diverse characters of various acrylic monomers employed under light irradiation.[2] In the next project, g-C_3N_4 will be presented as a heterogeneous photoinitiator (oxidative photopolymerization) in synthesizing
non-doped processable oligo3,4-ethylenedioxythiophene (oligoEDOT) material which is prone to facile coatings and post-doping.[3] At last, g-C_3N_4 consisting thiol-ene beads synthesized via UV light irradiation will represent interfacial jamming effect over g-C_3N_4 , where it allocates itself at the interphase. Obtained high sulfur containing beads exhibiting excellent thermal stability, resulted in carbonization by retaining bead-shape in some of the cases.[4]

Acknowledgement
The authors thank the Max Planck Society for funding and providing
the infrastructure. We thank Prof. Dr. Markus Antonietti for the
continuous support and mentoring.

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2. C. Esen and B. Kumru, *Beilstein J. Org. Chem.*, **2021**, 17, 1323-1334.
3. C. Esen, M. Antonietti and B. Kumru, *ChemPhotoChem*, **2021**, 5, 857-862.
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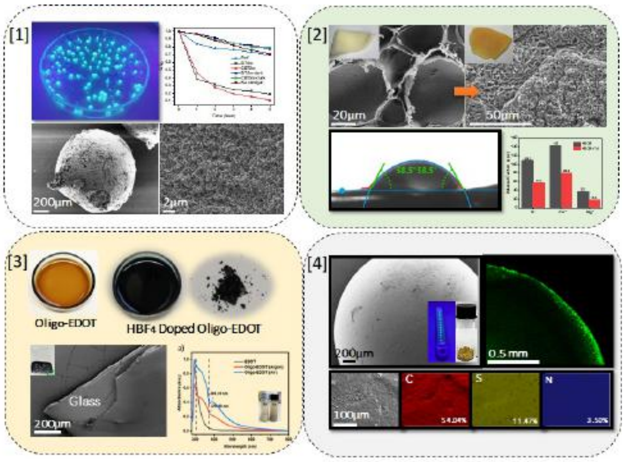


Carbon nitride incorporation in polymer networks.jpg

Synergy effect of antibacterial cationic amphiphilic copolymers with antibiotics

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mrs. Claire Caucat [1], ***Dr. Catherine Lefay*** [2], ***Dr. Yohann Guillaneuf*** [2], ***Dr. Jean-Michel Bolla*** [3], ***Dr. Marc Maresca*** [3], ***Dr. Véronique Sinou*** [4]

1. *Institut de Chimie Radicalaire - Aix-Marseille Univ., CNRS,* ***2.*** *Institut de Chimie Radicalaire - Aix Marseille Univ, CNRS,* ***3.*** *Aix Marseille Université,* ***4.*** *Aix-Marseille Université*

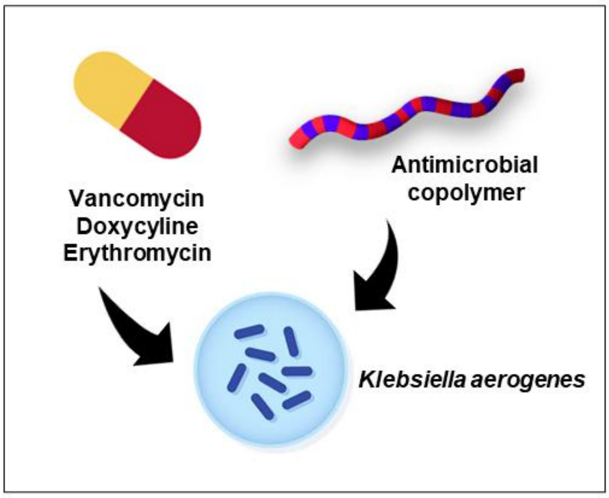
Antibiotics are the main weapon in the fight against bacterial infections.

However, the effectiveness of these treatments is decreasing because bacteria have the ability to develop protective mechanisms against antibiotics. In addition, overuse or misuse of antibiotics has resulted in some strains of bacteria becoming resistant.

To rejuvenate antibiotic therapy, one possibility is to combine them with molecules of interest (antibacterial or not).

For several years, different families of synthetic antibacterial copolymers have proven to be a possible alternative to antibiotics without inducing resistance.

In this study, we combined different antibiotics (vancomycin, erythromycin, and doxycycline) with several amphiphilic cationic antibacterial copolymers based on butyl methacrylate and *N,N*-dimethylaminoethyl methacrylate synthesized by Nitroxide-Mediated Polymerization (NMP) and studied their synergy against *K. aerogenes* that is a Gram-negative bacteria for a large number of nosocomial infections.



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New potential packaging materials based on polylactide and cellulose acetate propionate with the addition of Tween 80 and quercetin

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Prof. Ewa Olewnik-Kruszkowska [1], *Dr. Magdalena Gierszewska* [1]

1. Nicolaus Copernicus University in Toruń, Faculty of Chemistry, Chair of Physical Chemistry and Physicochemistry of Polymers, Gagarin 7 Street, 87-100 Toruń, Poland

Introduction: Initially, the role of packaging was limited to fulfilling a few basic functions, which most notably included protecting the product from mechanical damage and contamination. Currently, when designing packaging materials, it is necessary to take into account many requirements set by consumers and also enforced by legal standards. The growing ecological awareness contributes to the broader use of biodegradable materials and the search for innovative solutions in the packaging industry, ensuring the longest possible preservation of product quality. For this reason, the challenge faced in this project was to form active packaging materials by introducing a flavonoid - quercetin (Q) (from 0.5 to 4%wt.), into a biodegradable polymeric blend based on polylactide (P) and cellulose acetate propionate (C). Moreover, a surfactant - Tween 80 - was applied as a compatibilizer and plasticizer of the produced materials.

Methods: In the case of active packaging materials, the most important properties that are taken into account by the consumer and food producers are mechanical and storage properties, water vapour permeation rate, transparency, and colour changes. For this reason, corresponding analyses were performed and their results are presented in Figure 1.

Results and Discussion: With an increase in the content of the active additive, an increase in the turbidity and yellowness of the tested films is observed. The introduction of 2%wt. of quercetin into a polymeric matrix increases the elasticity as well as the tensile strength of the tested materials. Moreover, it improves their barrier properties against water vapour. It should be stressed, however, that with an increase in the content above 2%wt., a decrease in tensile strength and a simultaneous increase in water vapour permeability was observed. This is due to the increase in heterogeneity of the film's structure resulting from a higher content of the active additive.

The use of the analysed polymer films, incorporating quercetin, as packaging materials for blueberries extended the shelf life of this exemplary foodstuff. The films designed in the study impede the development of mould and preserve the firmness of the fruit during their storage.

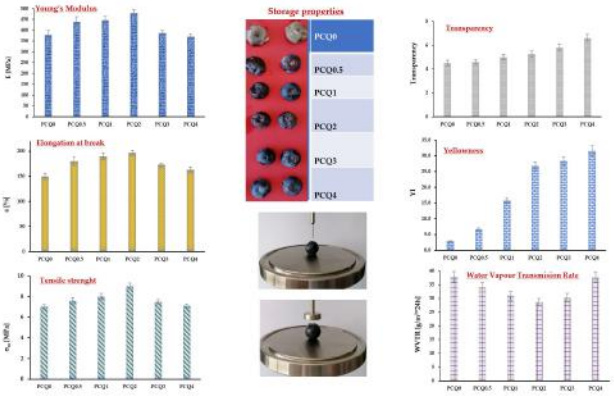


Figure 1.jpg

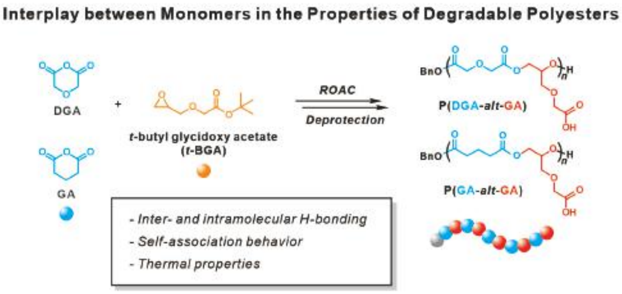
Tailoring the Interplay between Two Monomers in the Properties of Degradable Polyesters Synthesized via Ring-Opening Alternating Copolymerization

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

***Ms. Sumin Lee* [1], *Prof. Byeong-Su Kim* [1]**

***1.** Yonsei University*

Ring-opening alternating copolymerization (ROAC) of cyclic anhydrides and epoxides has emerged as a powerful strategy to produce degradable polyesters with a diverse array of structures from the combination of two distinct building blocks. In this work, we exploited the organocatalytic ROAC of cyclic anhydrides and a functional epoxide, *t*-butyl glycidoxy acetate, followed by acidic deprotection to access degradable polyesters with carboxylic acid pendants. To study the interplay between monomers, diglycolic anhydride and glutaric anhydride were used as cyclic anhydrides to prepare two polyesters. In particular, the effects of the oxygen heteroatom in the cyclic anhydrides on the properties of the carboxylic acid-containing polyesters were investigated. The introduction of the oxygen heteroatom in the cyclic anhydrides significantly influenced their thermal properties and pH-dependent self-association behavior in an aqueous solution. Furthermore, molecular dynamics simulations elucidated that the number and type of hydrogen bonds play a crucial role in the self-association behavior between the polymers both in the solution and bulk states. The findings of this study highlight the importance of the interplay between monomers in the design of functional polyesters with tunable properties.



Interplay between monomers in degradable polyesters via roac.jpg

Photo-Responsive Chiral Supramolecular Polymers Based on C3-Symmetric Triphenylene Triimides

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Namhee Kim [1] ***, Prof. Byeong-Su Kim*** [1]

1. *Yonsei University*

A new type of C_3-symmetric triphenylene triimides (TTI) bearing different oligo(ethylene glycol) side chains via imide linkages is developed in this study. By exploiting this unique TTI molecule as a building block, a supramolecular polymerization is explored on the basis of π-π stacking and hydrophilic/hydrophobic interaction depending on the type of solvents and rates of heating/cooling process. The molecular chirality of TTI monomer triggers the formation of a preferential helicity in fibrous structures. The stacking type of supramolecular polymerization is highly dependent on the presence of the point chirality of side chains, as evidenced by a collection of spectroscopic analyses including UV/vis and CD spectroscopy together with AFM, TEM, and WAXS. Interestingly, while the fibrous structure in assembled state is maintained due to the intermolecular interaction, the self-assembly does not occur in monomeric state due to the formation of radical anion of imide groups under UV irradiation. This study is anticipated to provide a new direction in the control of the supramolecular chiral assembly.

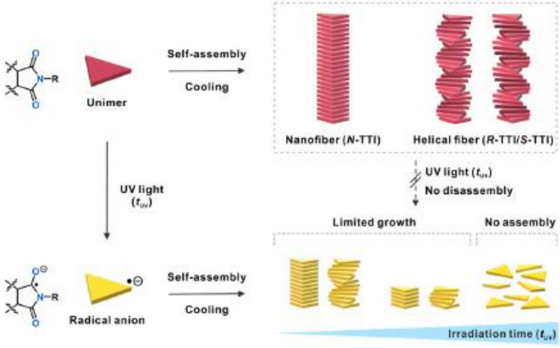


Figure.jpg

Microstructural study of cured dimethacrylates

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Prof. Giovanni Consolati [1], Prof. FRANCESCO BRIATICO VANGOSA [2], Prof. Fiorenza Quasso [3], Dr. Katharina Ehrmann [4], Ms. Katarína Cifraničová [5], Dr. Ondrej Šauša [6], Dr. Helena Švajdlenková [7]

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Dimethacrylate-based resins (poly2M) are used for a wide variety of applications such as protective and decorative coatings, dental medicine, 3D lithography. The major drawback of these materials is that the common monomers create inhomogeneous and rather brittle polymer network. Recently, it was revealed, that the photopolymerization of dimethacrylates via chain transfer agent such as thiol (poly2M-EDDT) [1] leads to the polymer with more homogeneous network architecture and pronounced increased toughness.

Recently, the real free volume characteristics of "classic" and regulated dimethacrylates were determined obtained by combining the positron annihilation lifetime spectroscopy (PALS) and dilatometry with lattice-hole theory [2]. It was established that these polymers have holes in the shape of a flattened cylinder that expand 'anisotropically' (poly2M) or 'isotropically' (poly2M-co-EDDT) (Figure) with increasing temperature (Fig. 1). The regulated dithiol-based sample (poly2M-co-EDDT) showed a high density of small free-volume holes, which lead to higher free-volume fractions than in poly2M. NIR spectra revealed that poly2M-co-EDDT exhibits stronger intermolecular H-bonds than poly2M and free NH-groups are not formed in the network. Both findings are the features of homogeneous network structure. Next, the microstructural study of poly2M samples with different thickness and amount of photoinitiator (PI) showed that an increased amount of PI and lowering the thickness lead to the appearance of the gradient in microstructural characteristics, i.e. the spatially graded free volume size, homogeneity and the concentration of voids which may influence the final material properties.

Investigation of relationships between the microstructural free volume characteristics (PALS), the intermolecular H bond interactions (NIR) can bring valuable knowledge about the key structural factors responsible for the improved material properties.

Acknowledgments

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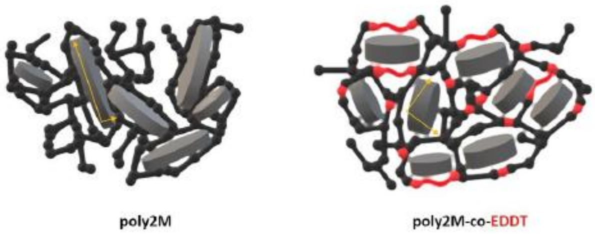


Fig. 1.jpg

Construction of Thermal Latent System in Epoxy/Imidazole Curing System by Addition of Imides and Properties of The Cured Materials

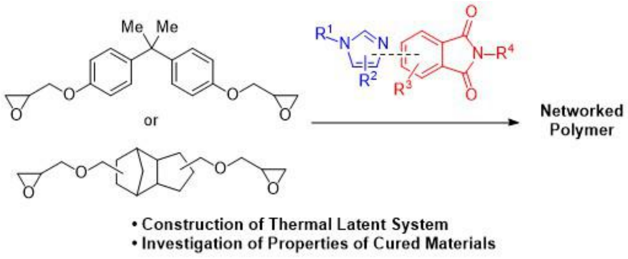
Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Yasuyuki Mori [1], ***Dr. Kenichi Tamaso*** [2], ***Mr. Junji Ueyama*** [2], ***Mr. Ippei Okano*** [2], ***Mr. Ryo Ogawa*** [2], ***Prof. Yoshio Furusho*** [1], ***Prof. Takeshi Endo*** [3]

1. Division of Chemistry, Department of Fundamental Biosciences, Shiga University of Medical Science, 2. Functional Polymers Development Laboratory, R&D Division, ADEKA Co., 3. Molecular Engineering Institute, Shiga University of Medical Science

The curing of epoxy resins has been investigated because the resulting products have good adhesiveness, chemical resistance, and thermostability. Thus, epoxy-based materials have played essential roles in sealants, adhesives, and coating materials in the chemical industry. The chemical and physical properties of cured products are affected by curing agents. Imidazoles are one of the most widely used curing agents because the curing of epoxy resins through anionic ring-opening polymerization can be performed with a catalytic amount of imidazoles, leading to good thermal and dielectric properties of the cured products. However, the curing of epoxy resins with imidazoles proceeds under mild conditions, deteriorating the storage stability in the one-liquid composition of epoxy resins and imidazoles. Therefore, the increase of the storage stability in one-liquid compositions has been a research subject.

Here, the effect of phthalimide derivatives (PIDs) on the curing behavior and storage stability of the compositions containing epoxy resins and imidazoles was examined. Besides, the thermal properties of the cured products were investigated. As a result, the curing initiation temperature in the presence of PIDs was higher than that in the absence of PIDs, and the storage stability increased by adding PIDs. The UV-Vis absorption spectrum of a mixture of PIDs and imidazoles showed a red shift of the peak compared to that of PIDs or imidazoles, suggesting the formation of the charge transfer interaction between PIDs and imidazoles, which resulted in decreasing the nucleophilicity of imidazoles. The thermal properties of the cured materials prepared from epoxy resins, imidazoles, and PIDs bearing epoxy moieties, were better than that using PIDs with no epoxy moieties.



• Construction of Thermal Latent System
• Investigation of Properties of Cured Materials

Toc-apme.jpg

Photosensitizer-based core-shell latex particles synthesized by PISA in alcoholic dispersion polymerization

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. M. Ali Aboudzadeh [1], *Mr. Guillaume Mageste* [1], *Mr. Mickael Lebechec* [1], *Prof. Thierry Pigot* [2], *Dr. Maud Save* [1]

1. Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France, 2. IPREM - Institut des sciences analytiques et de physico-chimie pour l'environnement et les materiaux

Introduction

Photosensitized $^1O_2$ production has attracted much attention to produce intermediate chemicals of interest for the fine chemicals industry. Immobilization of photosensitizers on solid substrates improves their handling, recyclability, stability and facilitates purification steps to remove photocatalyst from reactants in fine chemistry. In this context, we previously described the synthesis of photosensitizing microgels [1] or film-forming latex particles[2] by polymerization in aqueous dispersed media. Due to solubility issues, relevant photo-oxygenation reactions of biobased fine chemicals such as α-terpinene or furfural have to be performed in organic solvents, among which alcohols are the less hazardous for any application. To address these challenges, we describe here the synthesis of photosensitizing colloidal nanoparticles directly in alcoholic media by polymerization induced self-assembly (PISA) in dispersion.

Methods

The commercially available Rose Bengal (RB) was selected as photosensitizer due to its high value of singlet oxygen quantum yield in ethanol ($\Phi\Delta = 0.68–0.80$). Then to covalently anchor RB photosensitizer, we synthesized a polymerizable methacrylate monomer that can be copolymerized with poly(ethylene glycol) methyl ether methacrylate (POEGMA) to functionalize the particle shell, while benzyl methacrylate (BzMA) was then polymerized by PISA to form the core-forming alcohol-insoluble block. The macromolecular features of polymers were characterized by SEC. The resulting diblock copolymer particles were analyzed by DLS and TEM and were further assessed in terms of quantum yields of singlet oxygen production.

Result and discussion

Well-defined amphiphilic diblock copolymers P(OEGMA)-*b*-PBZMA including RB covalently-grafted were synthesized by RAFT-mediated dispersion polymerization in ethanol which resulted in stable monodisperse core–shell nanoparticles with diameters ranging from 84 to 260 nm, depending on the targeted DP of the BzMA block. Morphology transitions from spherical micelles to short worm-like micelles probably induced by sphere-sphere fusion phenomena during PISA nucleation step were observed and characterized by TEM. The synthesized photoactive colloids were efficient in producing singlet oxygen at the particle/alcohol interface under visible light irradiation, as the average quantum yield of singlet oxygen production almost reaches the level of that of free RB.

[1] L. Petrizza *et al.*, Polym. Chem., 2019, **10**, 3170

[2] C. Boussiron *et al.*, Polym. Chem., 2021, **12**, 134.

left) Structure of RB-methacrylate based monomer, right) Polymerization-induced self-assembly (PISA) in alcoholic dispersion to design shell-functionalized polymer colloids grafted by the RB organic photosensitizer.

Figure1.jpg

Sequence-defined dithiocarbamate platforms with tuneable backbone and side-chain functionalities for material and biomedical applications

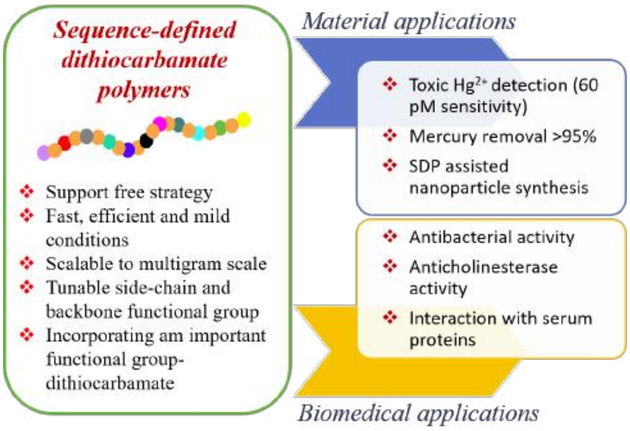
Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Anna Jose [1], *Dr. Mintu Porel* [1]

1. Department of Chemistry, Indian Institute of Technology Palakkad

Structural tunability and functional diversity attained in sequence-defined polymers (SDPs) via the sequential addition of monomers at predetermined positions leads to its varied applications. Synthetic SDPs possess a wider scope of unlimited functional groups at the side chain and in the backbone, thereby pushing the limitations of conventional polymers. This motivated us to design a support-free, protection−deprotection-free, cost-effective, and fast iterative strategy for multigram production of a novel class of SDP with dithiocarbamate (DTC) functionality. Post-synthetic modification of this platform by attaching a suitable fluorophore to study its metal interaction capacities was conducted. Sequence-defined oligomeric fluorescent probes, unlike the other fluorescent probes, offer several advantages including (i) improving the sensitivity by increasing the coordinating unit and (ii) modifying the properties by modulating the monomeric units. With this system, a selective colorimetric detection of mercuric ions (Hg^{2+}) even in competitive environments was achieved. This triggered the development of lab-on-paper-type detection which will improve the practical applicability of the probe. A very low sensitivity up to 60 picomolar was also obtained exclusively for Hg^{2+}. The same platform was also extended for removing Hg^{2+} ions from aqueous solution with a removal capacity of >95%. This system also showed excellent cellular uptake capacity and hence was utilized to probe Hg^{2+} in live cells.

A library of synthetic SDPs was designed to mimic antibacterial peptides and their interaction with bacterial lipid bilayer membranes are being studied. To facilitate the electrostatic and hydrophobic interactions of SDMs with bacterial membranes, an amphiphilic balance was preserved by judicious insertion of hydrophobic and hydrophilic groups in the sidechain. Taken together, this is a proof-of-concept for the synthesis of SDPs with tunable functionalities, to modulate their properties and to employ the best suited one from this library for any given application.



Picture1.png

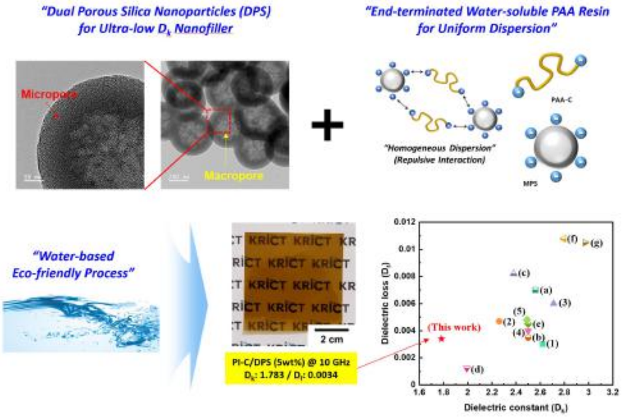
Eco-friendly and Simple Fabrication of Ultra-low Dielectric Polyimide Composites with Dual-porous Hollow Silica Particles

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Yunho Kim [1], *Dr. Jong Chan Won* [1], *Dr. Jongmin Park* [1]

1. Korea Research Institute of Chemical Tehcnology

Here, we proposed an eco-friendly synthetic method for synthesizing hybrid composites with ultra-low dielectric properties at high frequencies up to 28 GHz for true 5G communication from aqueous aromatic polyimide (PI) polymers and dual-porous silica nanoparticles (DPS). The "one-step" water-based emulsion template method was used to synthesize the macroporous silica nanoparticles (MPS). A substantially negative zeta-potential was produced along the surface of MPS by the polyvinylpyrrolidone-based chemical functionalization, enabling excellent aqueous dispersion stability. The water-soluble poly(amic acid) (PAA), as a precursor to PI, was also "one-step" polymerized in an aqueous solution. The MPS were dispersed in a water-soluble PAA matrix to create the hybrid composite films using an entirely water-based approach. The compatibility between the PAA matrix and MPS were elucidated by investigating relatively diverse end-terminated PAAs (with either amine or carboxyl group). It was also discovered that during a thermally activated imidization reaction, the MPS are in-situ converted into the DPS with macro- and microporous structure (with a surface area of 1522.4 m^2/g). The thermal, dielectric, mechanical and morphological characteristics of each composite film were examined, while the amount of DPS in the PI matrix varied from 1 to 20 wt%. With the addition of 5 wt% DPS as an optimum condition, it showed ultra-low dielectric properties, with the D_k and D_f being 1.615 and 0.003 at a frequency of 28 GHz, respectively, and compatible mechanical properties, with the tensile strength and elastic modulus being 78.2 MPa and 0.32 GPa, respectively. These results can comprehensively satisfy various physical properties required as a substrate material for 5G communication devices.



Abstract image.jpg

Bisphenol-A-free and biosourced epoxy curing using catalytic systems: towards high performance materials

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Valentine Lavaux [1]**, *Prof. Jacques Lalevée*** [2]

1. *Mulhouse Materials Science Institute,* **2.** *Université de Haute-Alsace*

Epoxides are the monomers of choice in the preparation of a large range of high performance materials with exceptional thermal and mechanical properties [1] e.g. showing excellent surface adhesion, low shrinkage and high corrosion resistance. Therefore, they cover a wide range of applications, including coatings, composites or adhesives. As epoxy curing agents (hardeners), amines and anhydrides were and are still widely used in the industry due to their good curing speeds and their excellent resulting materials performances (e.g. glass transition temperature - Tg). For high performance materials, monomers/oligomers based on the bisphenol-A scaffold are, by far, the most important category of epoxides but now suffer from high toxicity concerns. [2] The same is true for hardeners. Therefore, the development of new epoxy systems (bisphenol-A free) that can be polymerized under mild conditions (at low temperature, under air, without monomer purification) and without hardeners is a huge scientific, ecological and societal challenge. In this context, the aim of our work is to propose new bio-based epoxy systems that can be polymerized with a catalytic system based on natural compounds. The polymerizations were performed in the mildest possible conditions. Full curing can be obtained in less than 20 minutes at 70°C and high Tg were obtained for bisphenol-A-free epoxy polymers. This approach corresponds to a breakthrough in the polymerization of bio-sourced epoxides which often leads to low Tg materials. Markedly, these systems showed good stability when developed in two component (2K) cartridges.

[1] Pham, H. Q.; Marks, M. J. Epoxy Resins. In Ullmann's Encyclopedia of Industrial Chemistry, **2006**

[2] https://www.efsa.europa.eu/en/topics/topic/bisphenol

Picture lavaux.png

Recently proposed oxime-ester as blue- light-sensitive type I photoinitiators

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Fatima Hammoud [1]***, Prof. Akram Hijazi*** [2]***, Dr. Michael Schmitt*** [1]***, Dr. Frédéric Dumur*** [3]***, Prof. Jacques Lalevée*** [1]

1. *Université de Haute-Alsace,* ***2.*** *Université Libanaise,* ***3.*** *Aix-Marseille Université*

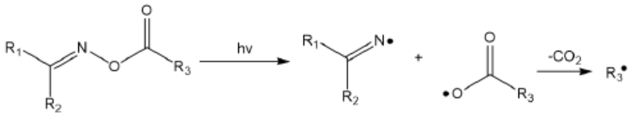
Photochemical engineering of polymers and other modern materials science and technology has led to the creation of complex but effective methods for the fabrication of innovative materials, post-functionalization of polymers and novel synthetic products. In these systems, light-activated chemical reaction pathways not only provide an excellent control over the reaction kinetics but also make it simple to carry out complex synthetic protocols. [1-3] However, the search for more ecologically friendly photoinitiating systems that can be activated with visible light is currently under progress. At present, a wide range of two- or three component photoinitiating systems with absorption spectra perfectly matching the emission of LEDs is available. Hence, in order, to create more easily free radicals directly by the cleavage of chemical bonds, one-component Type I PIs are now preferred. In this context, the high reactivities of oxime esters (OXEs) as Type I photoinitiators in free radical photopolymerization are well known. For these structures, light irradiation can lead to the homolytic cleavage of the N-O bond, generating iminyl and acyloxy radicals. [4] Several research studies have been published in recent years, with the purpose of modifying their chemical structures by introducing different chromophores or by varying the substitution pattern of the ester group, for which an interesting structure/reactivity/efficiency relationship could be achieved. In this work, an overview of the recent advances on oxime-esters based photoinitiators, as well as a comparison of the various scaffolds proposed is provided and discussed.

[1] P. Garra, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.P. Fouassier, J. Lalevée, Polymer Chemistry, 2017, 8.46, 7088-7101.

[2] J. P. Fouassier, J. Lalevée, Photoinitiators: Structures, Reactivity and Applications in Polymerization, Wiley, Weinhein, 2021.

[3] J. Xu, G. Ma, K. Wang, J. Gu, S. Jiang, J. Nie, Journal of Applied Polymer Science, 2012, 123.2, 725-731.

[4] F. Hammoud, N. Giacoletto, G. Noirbent, B. Graff, A. Hijazi, M. Nechab, D. Gigmes, F. Dumur, J. Lalevée, Materials Chemistry Frontiers, 2021.



Oxime-ester.png

Evaluation of the Efficiency of Random and Diblock Methacrylate-Based Amphiphilic Cationic Polymers against Major Bacterial Pathogens Associated with Cystic Fibrosis

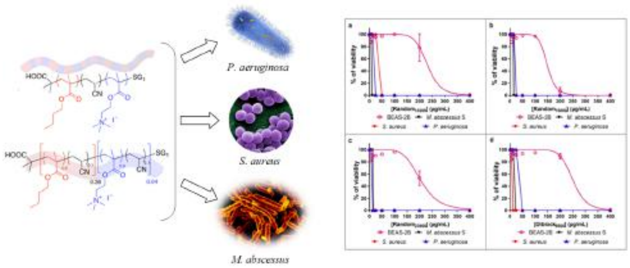
Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Baptiste Caron [1], ***Dr. Catherine Lefay*** [2], ***Dr. Yohann Guillaneuf*** [2], ***Dr. Marc Maresca*** [3]

1. *Institut de Chimie Radicalaire - Aix-Marseille Univ., CNRS,* ***2.*** *Institut de Chimie Radicalaire - Aix Marseille Univ, CNRS,* ***3.*** *Aix Marseille Université*

Over time, there is more and more bacterias which became resistant to several antibiotics. This is the case of current bacterias which leads to repeated lung infection in a context of cystic fibrosis. In function of the type of infection and the sensitivity of patient's immune system, the ineffectiveness of treatments resulting from this phenomenon can cause medical complications and deaths.

To counter this issue, there is several species that can substitute antibiotics. For example, antimicrobial peptides and active antibacterial copolymers appear like a solution that will not induce a resistance from bacterias. This work shows the efficiency of an hydrophobic and cationic methacrylate based antibacterial copolymers. Different copolymers were tested on bacterias linked to cystic fibrosis such as *P. aeruginosa*, *S. aureus* or *M. abscessus*, showing that their antibacterial mechanism are based on the rupture of bacterial membrane by interacting with anionic phospholipids. Moreover, tested methacrylates-based copolymers don't show any resistance from bacterias. Finally, tested copolymers has an antibiofilm property and aren't cytotoxic. In this respect, they represent a promising alternative to antibiotics as antibacterial agents for cystic fibrosis.



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TEMPO-Oxidized Nanofibrillated Cellulose as a potential drug carrier for sustained delivery of Triclosan

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Aiswarya T T [1]

1. *PhD Scholar, Department of Materials Science and Engineering, IIT Delhi*

There is an upsurge of interest for the development of novel techniques to combat bacterial infection, which has been intensified over decades and are gaining enormous attention. Microbial infections, are serious threats to public health, designing a suitable nanocarrier that can effectively deliver antimicrobials and render the microbial spread will help in tackling this threat. Triclosan is a broad-spectrum biocide *efficacious* against both gram-positive and gram-negative. However, its poor solubility, low entrapment efficiency and undesirable release profile limits its applicability. Moreover, it remains a challenge to develop a simple, cost-effective support for anchoring this antimicrobial drug beneficial for real field applications. In this study, we exploit a simple straight forward strategy to synthesize carboxylated Nanocellulose fibers. The effects of reaction parameters on the synthesized cellulose fibers were analysed in terms of morphology, surface charge, drug loading and drug release. Resulting oxidized NFC owes abundant carboxyl groups, better dispersibility as well higher surface/pore-volume ratio to facile the drug adsorption and release process. In addition to this, this system successfully allocates higher percentage of drug in their matrix and manifests a sustained release of drug over a period of 8 days. The drug adsorption and release mechanism were evaluated using various kinetics models and results illustrates that the drug release from the matrix involved a combination of diffusion, dissolution, and swelling mechanism. Release kinetics analysis revealed that the synergistic effect of a primary burst release stage and a secondary slow sustained release stage is crucial for the practical applicability. Assessments of antibacterial activity of the triclosan loaded system were carried out against *Escherichia coli* and *Staphylococcus;* significant sustained inhibition of bacterial growth was observed for a period of 8 days, thus making them a promising candidate for the potential applications that demands sustained antibacterial activities.

2,3-Butanediol as a Renewable Platform Monomer for the Synthesis of Bio-Based Polymers

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Anja Kirchberg **[1]** ***, Prof. Micheal A. R. Meier*** **[1]**

1. *Karlsruhe Institute of Technology*

With worldwide waste accumulation and depleting fossil resources, an increasing need to new chemical innovations based on environmentally friendlier synthesis strategies is necessary. The plastic consumption increased incredibly in the last decades, shifting the focus of academia and industry to renewable resources as alternatives to fossil-based polymers. 2,3-Butanediol (2,3-BDO), obtainable by fermentation of waste biomass, is a promising and not often used diol to prepare renewable polymer alternatives.

In this work, renewable 2,3-BDO was used as platform monomer for the synthesis of non-isocyanate polyurethanes (NIPUs) as well as for various polyesters. The NIPU was obtained *via* the cyclic carbonate of 2,3-BDO and its properties compared to other renewable diols such as propylene glycol (PG), ethylene glycol (EG) and 1,2-octanediol (Oct) revealing interesting structure-property relationships. Renewable 11-amino undecanoic acid methyl ester, the renewable monomer used for polyamide-11 production and derived from castor oil, was used to obtain carbamate monomers, being polymerized to poly(ester urethane)s. Full characterization is reported using differential scanning calorimetric (DSC), size exclusion chromatographic measurements (SEC), ^{1}H-NMR as well as IR spectroscopy. Rheological investigations of the NIPU based on 2,3-BDO suggested that produced foamed materials is possible, which will be shown as a proof-of-principle concept. Moreover, polyesters were synthesized by polycondensation of 2,3-BDO with various renewable diacids such as 2,5-furanedicarboxylic acid (FDCA), succinic acid (SA), itaconic acid (IA), adipic acid (AA) and sebacic acid (SBA). Properties were adjusted by copolymerization. Interestingly, a catalyst screening revealed a cheap and environmentally friendlier alternative to catalyse polycondensations. High molecular weights and, depending on the chosen diacid, interesting properties were observed. In summary, the potential use of 2,3-BDO for various polycondensation derived bio-based polymers is demonstrated.

Investigation of Pyrene vs. Anthracene-based oxime esters: Role of the excited states on their polymerization initiating abilities

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Hugo Bidotti [1], ***Mr. Mahmoud Rahal*** [2], ***Ms. Bernadette Graff*** [2], ***Prof. Jacques Lalevée*** [2], ***Prof. Tayssir Hamieh*** [3], ***Prof. Joumana Toufaily*** [4], ***Dr. Sylvain Duval*** [5], ***Dr. Frédéric Dumur*** [1]

1. *Aix-Marseille Université,* ***2.*** *Université de Haute-Alsace,* ***3.*** *Maastricht University,* ***4.*** *Lebanese University,* ***5.*** *Université de Lille*

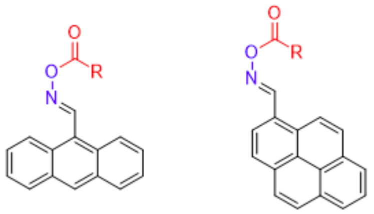
The synthesis of less energy-intensive materials, with a short preparation time, having good chemical, physical and mechanical properties currently represents a great challenge for industries wishing to manufacture more ecological materials. Hence, chemists have been interested for decades in the development of more environmentally-friendly synthetic routes by introducing light into synthetic processes. Nowadays, Free Radical Photopolymerization (FRP) is already present in different areas of our daily life, such as cosmetics, dentistry, automotive, composites and also 3D printing. To make this approach possible, very efficient photoinitiating systems capable of absorbing light must be present into the photocurable resins. Indeed, visible light is less energetic than UV light so that a higher reactivity of the photoinitiating systems has to be found in order to compensate the lower energy of photons.

In order to reduce the complexity of the formulations linked to the use of different additives (e.g. co-initiators), mono-component Type ▯ photoinitiators (PIs) are highly desired. These compounds can generate the initiating radicals through a direct homolytic cleavage of a specific bond of the molecule, the cleavage being photochemically induced by mean of the LED light. In this field, oxime esters are appealing candidates due to their easiness of synthesis, their remarkable photochemical and thermal properties. Their excited states are short-lived (vs. Type II photoinitiator) and hence less quenched by oxygen i.e. Type I PIs can be preferred for polymerization under air, these photoinitiating systems being less prone to oxygen inhibition.

In this work, the effect of the chromophore (pyrene vs. anthracene) on their photochemical properties and photoinitiating abilities will be studied (See Figure in attachment). Indeed, deexcitation from a singlet or a triplet pathway can greatly influence the efficiency of the N-O bond cleavage and thus the photoinitiating ability. The proposed PIs (An-OXEs and Py-OXEs) are characterized by good absorption properties in the near-UV and visible range. These PIs were also tested for the generation of 3D polymer patterns by 3D printing experiments.

Références :

[1] M. Rahal; H. Bidotti; S. Duval; B. Graff; T. Hamieh; J. Toufaily; F. Dumur; J. Lalevée, *Eur. Polym. J.*, 2022, **177**, 111452.



R = 18 different aliphatic and aromatic groups

Figure 1. Chemical structures of oxime esters investigated in this work.

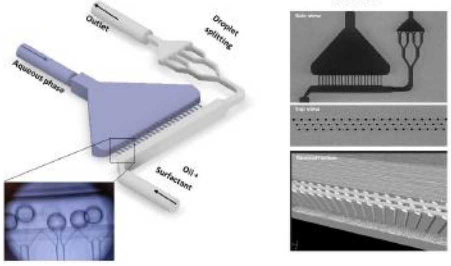
Chemical structures of oxime esters.png

High-throughput microgel production using parallelized 3D-printed microfluidics

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Michelle Vigogne [1] ***, Dr. Ricardo Bernhardt*** [1] ***, Prof. Julian Thiele*** [2]
1. *Leibniz Institute of Polymer Research Dresden,* ***2.*** *Otto von Guericke University Magdeburg*

Droplet-based microfluidics is frequently used to fabricate uniform polymer particles on a micrometer scale. Each emulsion droplet serves as reaction unit and template for polymerization of a microgel particle. High-throughput microgel production ranging from microliters per hour to microliters per minute, enables processing on a larger scale. This allows for significant saving of production time. Typically, microfluidics is performed in PDMS-based microfluidic flow cells. However, this device fabrication requires a multi-step process starting from photomask design, photo- and soft lithography. In addition, a PDMS chip is a non-monolithic flow cell that may cause detachment problems from the glass slide at high pressure. One approach to solve this problem is the use of monolithic 3D-printed microfluidic devices. In this case, the microfluidic flow cell is produced in one process step using high-resolution microstereolithography. Current work has shown that a parallelized step emulsification device leads to a significant improvement in the generation of uniform emulsion droplets. In addition, it is also known that the splitting of emulsion droplets increases the resulting number of droplets by a factor of 2^N. Parallel droplet formation and droplet splitting is currently known from PDMS-based microfluidics and we transfer these design concepts to 3D-printed microfluidic flow cells to improve and optimize the manufacturing process. Here, in a 3D-printed microfluidic device, a droplet-splitting sequence is integrated subsequent to a parallelized droplet formation. Besides increasing the microgel particle production rate based on parallelized droplet formation, the integrated droplet splitting is used for controlled stepwise adjustment of the emulsion droplet and microgel size, respectively, from 400 µm down to 200 µm. In addition to emulsion production in a high-throughput process, the polymerization of the micrometer-sized polymer particles is performed directly on- chip by a thermal crosslinking method. Establishing high-throughput microgel fabrication in parallelized 3D-printed microfluidic devices will be particularly useful for the production of particle-based bioinks, e.g., for advanced culturing platforms.



Cad design and micro-ct images of a parallelized microfluidic flow cell with integrated sequential droplet splitting element.jpg

Additive soft matter design by UV-induced polymer hydrogel inter-crosslinking

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Talika Neuendorf [1]***, Mr. Niclas Weigel*** [1]***, Ms. Michelle Vigogne*** [1]***, Prof. Julian Thiele*** [2]

1. *Leibniz Institute of Polymer Research Dresden,* ***2.*** *Otto von Guericke University Magdeburg*

Introduction

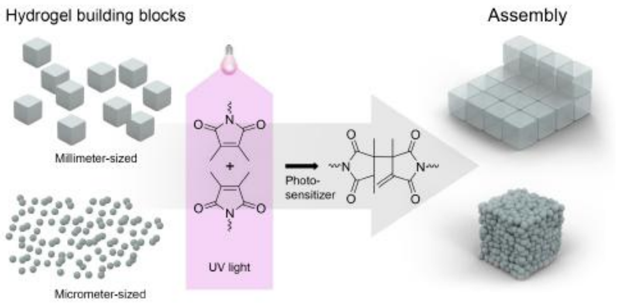
In recent years, stimuli-responsive hydrogels have gained tremendous interest in designing smart 4D materials that can change their properties on demand over time. However, at present, a hydrogel's response is often induced by merely a single stimulus, restricting its broader applicability. A design concept of soft matter that enables introducing multiple functions is based on individual hydrogel building blocks that are linked together. Thus, inter-connection stability is equally crucial as their property since it is directly associated with transferring information between the building blocks. Unfortunately, current approaches of inter-connection and assembly either lack building block inter-connection stability or controlled stacking of assemblies into 3D objects.

Methods

Macrometer-sized building blocks are fabricated *via* injection molding, and micrometer-sized hydrogel precursor particles are fabricated using PDMS-based droplet microfluidics. After photo-crosslinking, the as-formed building blocks are transferred into a mold, immersed in a photosensitizer solution, and subsequently inter-crosslinked *via* UV irradiation. Finally, the assembly's mechanical stability is quantified by mechanical agitation and swelling experiments in different solvents.

Results and Discussion

We address the challenge of inter-connection stability in hydrogel-based building block assemblies using a separate crosslinking mechanism based on UV-induced 2,3-dimethylmaleimide dimerization. We then show the controlled hierarchical assembly of various hydrogel building blocks, each with a tailored set of mechanical and physicochemical properties. To demonstrate its versatility, we first inter-connect acrylamide-based millimeter-sized cubic building blocks yielding dual-crosslinked free-standing assemblies. Second, we apply this approach to inter-connect microfluidically fabricated, acrylamide-based micrometer-sized spheric hydrogels into free-standing structures. The resulting dual-crosslinked assemblies are stable against contraction-expansion cycles in solution and shear forces during mechanical agitation. Finally, apart from only forming 2D assemblies, we build an inter-connected 3D object with the building blocks being placed at two different levels, illustrating our approach's applicability for the additive build-up of multi-materials based on individually tailored building blocks. With the studied inter-connection mechanism *via* UV-induced 2,3-dimethylmaleimide dimerization and used building blocks being scalable from micro- to millimeter size, our approach paves the way toward a novel additive manufacturing technique based on hydrogel building blocks with the capability of tuning material properties at the micrometer-scale, allowing topologically complex, multi-functional materials.



Schematic representation of the assembly fabrication.png

Long and short chain selection in “grafting to” reactions of phosphate end-capped polymers

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Riccardo Chiarcos [1]***, Ms. Viviana Ospina*** [1]***, Prof. Valentina Gianotti*** [1]***, Prof. Michele Laus*** [1]***, Mr. Stefano Kuschlan*** [1]***, Dr. Michele Perego*** [2]

1. *DISIT Dept., Università del Piemonte Orientale “A. Avogadro”, Viale T. Michel 11, 15121 Alessandria, Italy,* ***2.*** *IMM-CNR (Institute for Microelectronics and Microsystems-National Research Council of Italy)*

Introduction. Interfacial reactions between end-functionalized polymers and suitable substrates are generally defined as “grafting to” reactions and are commonly employed to cover inorganic surfaces with chemically anchored thin polymer layers.

Since the number of polymer chains included in the brush (i.e. the grafting density, Σ) is reaction-limited and proportional to $M_n^{-0.5}$, with M_n being the average molecular weight of the polymer, “grafting to” reactions were recently exploited to deliver controlled amounts of dopant atoms (typically phosphorus, P) on silicon substrates. In particular, diethylphosphate end-capped polystyrene and poly(methylmethacrylate) samples (Figure 1) with different M_n were grafted on silicon oxide substrates (SiO_2). A M_n-based control of P dose was demonstrated. However, fine tuning of the grafting density was recently demonstrated to depend on the width of the molecular weight distribution for hydroxy terminated polymers.

In this contribution, the effect of the molecular weight distribution was studied for diethylphosphate end-capped polystyrene samples using model blends consisting of samples with different M_n. These blends were grafted on SiO_2 and the brush compositions were determined by TGA-GC-MS analyses.

Methods. Binary equimolar blends of diethylphosphate end-capped polystyrene samples with different M_n were spin-coated on SiO_2 and grafted at different temperatures for different times. The two polymers were recognized in mass spectrometry by deuterium labelling. Therefore, the brush compositions were determined by TGA-GC-MS analyses.

Results. After grafting an equimolar mixture of two samples with Mn of 4800 and 24400 g/mol (Đ = 1.13 and 1.20), the composition of the brush was determined and reported in Figure 1. Preferential grafting of short chains is observed with a more pronounced effect occurring at short grafting times and low temperatures.

Discussion. The present work confirms the relevant role of polymer dispersity during “grafting to” processes. Moreover, the nature and polarity of the end-group were found to affect the evolution of the partitioning between long and short chains grafted to the substrate. In this perspective, it extremely difficult to make predictions about the actual number of the grafted polymer chains. Therefore, for precision applications it is essential to use monodisperse polymers such as for example polypeptoids.

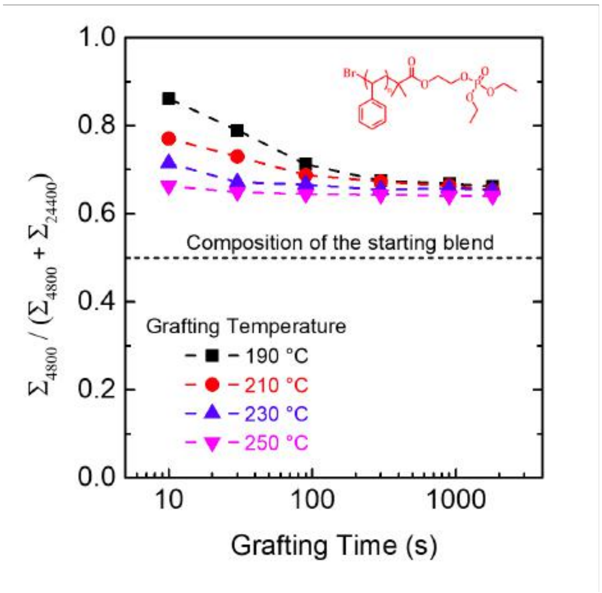

1.0
0.8
0.6
0.4
0.2
0.0
10
100
1000
Grafting Time (s)
$\Sigma_{4800} / (\Sigma_{4800} + \Sigma_{24400})$
Composition of the starting blend
Grafting Temperature
190 °C
210 °C
230 °C
250 °C
Br
O
O
O
P
O
O
O
n

Figure 1.png

Polyaddition of 5-membered cyclic carbonates and polyoxypropylenediamine catalyzed by triazabicyclodecene at room temperature.

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Ryu Tada [1]***, Prof. Yoshio Furusho*** [2]***, Prof. Takeshi Endo*** [1]

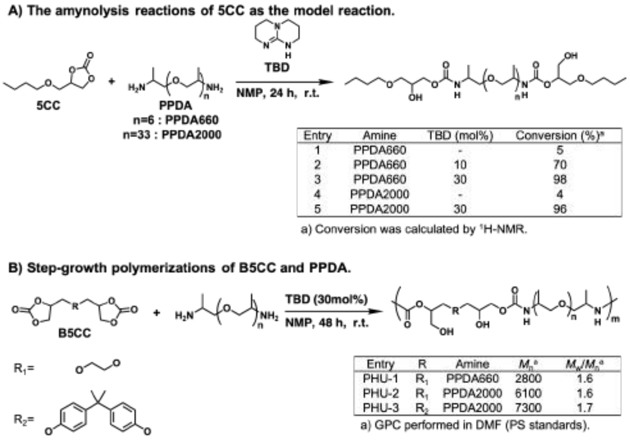
1. Molecular Engineering Institute, Shiga University of Medical Science, 2. Division of Chemistry, Department of Fundamental Biosciences, Shiga University of Medical Science

Carbon dioxide (CO_2) is contributed to global warming as a greenhouse gas, but is also a useful carbon resource from the viewpoint of organic synthesis. 5-membered cyclic carbonate (5CC) is capable of being synthesized from epoxide and CO_2, and *Bis*-functional 5CC (B5CC) reacts with diamines to form polyhydroxyurethanes (PHUs). However, the aminolysis of B5CC is strongly affected by the steric hindrance and molecular weight of the amine. The reactivity of B5CC with high molecular weight amines such as polyoxypropylenediamine (PPDA) which have a methyl group at the α-position with respect to the amino group, was extremely low. Because of this, PHUs produced from PPDA requires high temperature more than those from diamines with low molecular weight.

Recently, our group found that triazabicyclodecene (TBD) exhibits excellent catalytic efficacy in the polymerization of B5CC and amines with low molecular weight such as 1,6-diaminohexane at room temperature[1]. Thus, in order to accomplish the polymerization of B5CC and PPDA, the aminolysis of 5CC in the presence of TBD as the model reaction was adopted and the catalyst efficiency on this reaction was investigated. Moreover, the optimized reaction condition was used for the synthesis of PHUs.

The results of the model reaction showed that the aminolysis of 5CC with TBD proceeded at room temperature, while the reaction hardly proceeded at all without ones (**Figure 1A**). Furthermore, increasing the amount of catalyst could be accomplished to reach a more than 95% conversion of 5CC. Step-growth polymerizations between B5CC and PPDAs were conducted in the presence of the TBD at room temperature for 48 h, the PHUs with moderate molecular weight were obtained (**Figure 1B**).

1. Dong W, Yoshida Y, Endo T. *J. Polym. Sci.*, **2021**, *59*, 502-509.



A) The amynolysis reactions of 5CC as the model reaction.

Entry	Amine	TBD (mol%)	Conversion (%)[a]
1	PPDA660	-	5
2	PPDA660	10	70
3	PPDA660	30	98
4	PPDA2000	-	4
5	PPDA2000	30	96

a) Conversion was calculated by ^{1}H-NMR.

B) Step-growth polymerizations of B5CC and PPDA.

Entry	R	Amine	M_n[a]	M_w/M_n[a]
PHU-1	R_1	PPDA660	2800	1.6
PHU-2	R_1	PPDA2000	6100	1.6
PHU-3	R_2	PPDA2000	7300	1.7

a) GPC performed in DMF (PS standards).

R. tada apme2023 abst.png

Symmetry-Breaking of Double Gyroid Structures in Solvent-vapor-annealed Block Copolymer Films

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Seungyun Jo [1], ***Mr. Taesuk Jun*** [1], ***Dr. Sungmin Park*** [2], ***Dr. Byeongdu Lee*** [3], ***Prof. Seungwoo Lee*** [4], ***Prof. Du Yeol Ryu*** [1]

1. *Yonsei University*, ***2.*** *Korea Research Institute of Chemical Technology*, ***3.*** *Argonne National Laboratory*, ***4.*** *Korea University*

In this study, we suggest that fast deswelling upon a solvent vapor annealing process causes unique structural distortion in polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) gyroid films. The fast deswelling of the swollen PS-*b*-PMMA films immediately upon solvent vapor annealing leads to *z*-directional contraction, where the lateral dimensions remain unchanged. 2D grazing-incidence X-ray scattering (GISAXS) patterns of our non-cubic gyroid films and precise peak indexing reveal several forbidden reflections that would not be found in GISAXS pattern of a cubic gyroid structure. Considering that the forbidden reflections indicate a non-affine distortion generated during the deswelling process, we extract electron-density difference maps from GISAXS patterns and reconfigured coefficients for level-set equation to closely observe the lattice distortion. Furthermore, the forbidden reflections are identified as reflectance peaks in the UV-vis absorbance spectra and refractive index variations through material substitutions modulate the reflectance peaks.

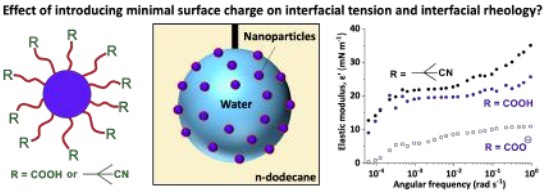
Adsorption of diblock copolymer nanoparticles at the oil–water interface: effect of charged end-groups on interfacial rheology

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Derek Chan [1]***, Prof. Steven Armes*** [1]***, Dr. Saul Hunter*** [1]***, Dr. Phil Taylor*** [2]***, Dr. Chris Lindsay*** [2]

1. University of Sheffield, 2. Syngenta

We exploit polymerization-induced self-assembly (PISA) to design a series of model organic nanoparticles for a fundamental study of the effect of surface charge on the extent of nanoparticle adsorption at the oil–water interface and the influence of such layers on the interfacial rheology. More specifically, reversible addition–fragmentation chain transfer (RAFT) polymerization is used to prepare sterically-stabilized diblock copolymer spheres of comparable size in which the steric stabilizer chain-ends comprise neutral/non-ionic, anionic or cationic groups. The RAFT aqueous emulsion polymerization of either methyl methacrylate (MMA) or benzyl methacrylate (BzMA) was conducted at 70 °C using poly(glycerol monomethacrylate) (PGMA) as a water-soluble precursor. This gave sterically-stabilized diblock copolymer nanoparticles of approximately 30 nm diameter. Carboxylic acid- or morpholine-functional RAFT agents are employed to confer anionic or cationic functionality at the ends of the PGMA stabilizer chains, with a neutral RAFT agent being used as a control. Thus the electrophoretic footprint of such minimally-charged model nanoparticles can be adjusted simply by varying the solution pH. Giant (mm-sized) aqueous droplets containing such nanoparticles are then grown within a continuous phase of *n*-dodecane and a series of interfacial rheology measurements are conducted. It was found that the interfacial tension between the aqueous phase and *n*-dodecane is strongly dependent on the charge of the terminal group on the stabilizer chains. More specifically, neutral nanoparticles produce a significantly lower interfacial tension than either cationic or anionic nanoparticles. Moreover, adsorption of neutral nanoparticles at the *n*-dodecane–water interface produces higher interfacial elastic moduli than that observed for charged nanoparticles. This is because neutral nanoparticles can adsorb at much higher surface packing densities owing to the absence of electrostatic repulsive forces in this case.



D chan interfacial rheology graphical abstract.png

Epoxide-Anhydride Co-Polymerization using Bifunctional Organocatalysts

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Max Hirschmann [1], ***Ms. Rachele Zunino*** [2], ***Dr. Sara Meninno*** [3], ***Prof. Laura Falivene*** [3], ***Prof. Tiziana Fuoco*** [1]

1. *Uppsala University, Department of Chemistry - Ångström Laboratory,* ***2.*** *Scuola Superiore Meridionale, Department of Chemical Sciences,* ***3.*** *University of Salerno, Department of Chemistry and Biology*

The strictly alternating co-polymerization of epoxides and anhydrides leads to polyesters that are in conform with the principles of a circular plastics economy[1]: renewable feedstock, high atom-economy, potential recyclability and (bio-)degradability. Despite these advantages, the requirements of (i) high chemo-selectivity (to avoid epoxide homo-polymerization that leads to ether formation) and (ii) functional group tolerance (to enable a broad monomer scope and to cope with monomer impurities likewise) in that polymerization process currently prevent its commercial use[2]. To pave the way toward commercial use, catalysts are needed that not only fulfill the already mentioned requirements, but also are non-toxic and have the potential to promote a regio- and stereo-selective ring-opening of monomers. With such a catalyst, the structure of the polyester becomes finely controllable, which leads to tunable polyester/material properties.

Many different catalyst systems were recently published that are grouped based on their *atoms* (metal catalysts *vs.* organocatalysts), their *function(s)* (acidic, basic, ionic, multi-functional) or their *number of components* (mono- *vs.* bi-component). With that in mind, we envisioned a series of *mono-component* and *bi-functional* (Lewis acid and Brønsted base) *organocatalysts*—a combination that is yet unexplored and that is easily made homo-chiral (potentially inducing stereo-selectivity)[3,4].

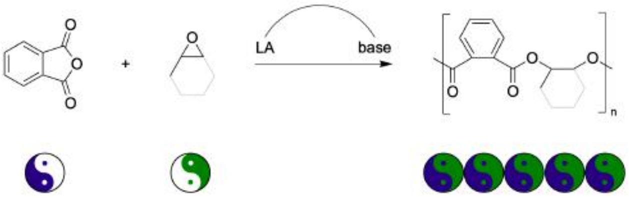
We tested these catalysts in the polymerizations of phthalic anhydride with 3 different epoxides. The interplay of the (i) Lewis acidity, (ii) Brønsted basicity, (iii) distance between both functions and (iv) overall steric demand is explored: We determined the polymerization rate and chemo-selectivity and compared these findings with DFT calculations. A strong interaction is found between the catalyst and the growing polymer chain. This strong interaction was indeed intended, as we thought it could enable chemo-, regio- and stereo-selectiveness of the polymerization process and diminish the impact of impurities that lead to low molar masses of the obtained polyesters. As the same close proximity is, however, found to decreases the polymerization rate, the strong interaction between catalyst and growing chain is critically assessed.

[1] *Acc. Chem. Res.* **2022**, *55*, 1869−1878

[2] *Chem. Rev.* **2018**, 118, 839−885

[3] *Polym. Chem.* **2021**, *12*, 2932–2946

[4] *Acc. Chem. Res.* **2020**, *53*, 2235−2247



Scheme-rocop bifunctional-organocatalyst.png

Investigating the self-lubricating properties of metal coatings induced by the incorporation of microcapsules

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Chris Zotiadis [1]***, Mr. Ilias Georgiopoulos*** [2]***, Mr. Dimitris Skaltsas*** [3]***, Dr. Dimitrios M. Korres*** [1]***, Prof. Christos I. Papadopoulos*** [3]***, Dr. Charikleia I. Sarafoglou*** [3]***, Prof. Stamatina Vouyiouka*** [1]

1. *Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece,* ***2.*** *MIRTEC S.A., Thiva Branch, 76th km of Athens-Lamia National Road, 32009, Schimatari, Greece,* ***3.*** *Shipbuilding Technology Laboratory, School of Naval Architecture and Marine Engineering, National Technical University of Athens, Zographou Campus, Athens, 157 80, Greece*

Lubrication of a mechanical system is crucial for its efficient operation. However, traditional lubrication methods are limited by working conditions, physicochemical characteristics and durability over extended periods of usage in severe environments introducing the need for periodic maintenance. Incorporating microcapsules containing lubricant into the outer surface of metal moving parts, significantly improves anti-friction properties and wear resistance. When the moving part surface is subjected to friction, the microcapsules are ruptured and the encapsulated lubricants are released onto the surface, forming a boundary lubrication film that significantly reduces friction coefficient and wear rate.

Within the current study, polysulfone microcapsules with an encapsulated commercial lubricant were produced using the emulsification-solvent evaporation technique to be used in ceramic-metal protective coatings produced *via* thermal spraying. Key parameters of the encapsulation process i.e. core to wall mass ratio, agitation type and rate were studied in respect to microcapsule characteristics. Spherical microcapsules were obtained as free-flowing colorless powder with a mean diameter from 3 to 60 μm and increased thermal stability (onset of degradation $T_{d5\%}$ > 340°C, maximum rate of thermal degradation T_d >400°C).

Styding the produced composite coatings properties it was evident that the microcapsules were able to withstand the high plasma flame temperature, were homogeneously incorporated in the matrix and finally were successfully deposited on the moving part substrate. Furthermore, the tribological properties study revealed a severe reduction (>50%) of the friction coefficient when composite (metal matrix with self-lubricating capsules) instead of respective single phased coatings were used.

This research has been co-financed by the European Regional Development Fund of the European Union and Greek national funds through the Operational Program Competitiveness, Entrepreneurship and Innovation, under the call RESEARCH – CREATE – INNOVATE (project code: T2EDK-01883)

Acknowledgement.jpg

Characterization of polymers at surfaces and interfaces on the beamline SIRIUS (SOLEIL synchrotron)

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Arnaud Hemmerle [1]***, Prof. Michel Goldmann*** [2]***, Dr. Patrick Kékicheff*** [3]***, Dr. Philippe Fontaine*** [1]

1. *Synchrotron SOLEIL, l'Orme des Merisiers, Départementale 128, 91190 Saint Aubin, France,* ***2.*** *Institut des NanoSciences de Paris,* ***3.*** *Institut Charles Sadron*

The SIRIUS beamline at the SOLEIL synchrotron is devoted to the study of surfaces and interfaces using X-ray scattering and spectroscopy in the range of tender to hard X-rays (1.1 - 13 keV). Various grazing incidence techniques are available on the beamline, such as diffraction and wide angle scattering (GIXD/GIWAXS), small angle scattering (GISAXS), fluorescence in total reflection (TRXF), as well as specular and off-specular reflectometry (XRR/GIXOS).

I will review how a growing share of SIRIUS users applies these complementary techniques to the characterization of a broad range of polymeric systems. I will describe research works relevant to the field of organic electronics, including an original approach for structural GIWAXS characterization of supramolecular nanowiring [1]. The relevance of GISAXS for measurements on thin films of functional nanomaterials will be discussed as well, with a focus on surface templating using block-copolymer self-assembly [2, 3]. Finally, I will present recent results on the *in situ* formation of nanostructured films at the air-water interface, *via* cross-linking under UV [4] and X-ray [5] photoirradiation, or *via* polymerization induced by X-ray radiolysis [6].

Figure 1 : *Supramolecular polymerization of TAA1 by an oxidation/nucleation/growth process forming nanowires connecting microelectrodes, as characterized by GIWAXS measurements on SIRIUS [1].*

[1] Galerne, M., Heinrich, B., Hemmerle, A., Fontaine, P., Giuseppone, N., Kékicheff, P., *ACS Appl. Polym. Mater.*, **3** (2021)

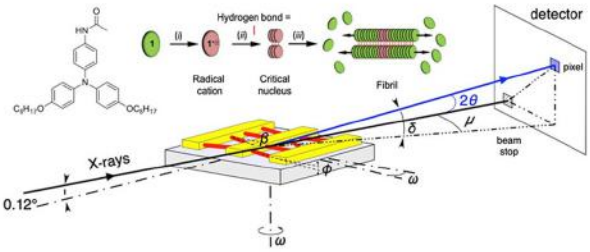
[2] Alvarez-Fernandez, A., Nallet, F., Fontaine, P., Cummins, C., Hadziioannou, G., Barois, P., Fleury, G., Ponsinet, V., *RSC Adv.*, **10** (2020)

[3] Yu, J.-Y., Landis, S., Fontaine, P., Daillant, J., Guenoun, P., *Soft Matter*, **16** (2020)

[4] Vaillard, A.-S., El Haitami, A., Fontaine, P., Cousin, F., Gutfreund, P., Goldmann, M., Cantin, S., *Langmuir*, **37** (2021)

[5] Rego, T., Spagnoli, S., Fauré, M.-C., Allain, C., Coasne, B., Malinge, J., Shen, C., Fontaine, P., Goldmann, M., *Langmuir*, **37** (2021)

[6] Bondaz, L., Fontaine, P., Muller, F., Pantoustier, N., Perrin, P., Morfin, I., Goldmann, M., Cousin, F., *Langmuir*, **36** (2020)



Giwaxs nanowires.jpg

Optimizing sensitivity of 1D and 2D NMR spectroscopy for HPLC-benchtop NMR coupling

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Marianne Marion Gaborieau [1], ***Mr. Markus Matz*** [1], ***Dr. Michael Pollard*** [1], ***Prof. Manfred Wilhelm*** [1]

1. *Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Polymeric Materials, Karlsruhe, Germany*

Combining NMR and IR spectroscopy with chromatographic separation offers a promising avenue to address the growing complexity of sample mixtures, which includes the analyte as well as contaminants and additives. This has been demonstrated through the development of affordable chromatography-spectroscopy hyphenation with the coupling of size-exclusion chromatography (SEC) with benchtop NMR spectroscopy (20-62 MHz) [1,2,3] and with infrared spectroscopy [4,5].

In this contribution this methodology has been extended to the separation of parabens by liquid adsorption chromatography (LAC) combined with their spectroscopic detection. These preservatives are commonly used in cosmetics and foods.[6] The sensitivity of one-dimensional and two-dimensional NMR spectroscopy of parabens has been optimized in preparation for the coupling HPLC-benchtop NMR (80 MHz).

[1] M Cudaj, G Guthausen, T Hofe, M Wilhelm. SEC-MR-NMR: Online coupling of size exclusion chromatography and medium resolution NMR spectroscopy, *Macromolecular Rapid Communications* 2011, 32, 665-70.

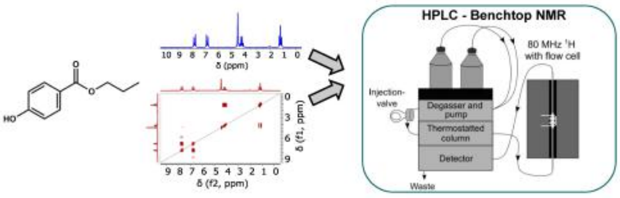
[2] C Botha, J Hoepfner, B Mayerhoefer, M Wilhelm. On-line SEC-MR-NMR hyphenation: optimization of sensitivity and selectivity on a 62 MHz benchtop NMR spectrometer, *Polymer Chemistry* 2019, 10, 2230-46.

[3] J Hoepfner, B Mayerhoefer, C Botha, D Bouillaud, J Farjon, P Giraudeau, M Wilhelm. Solvent suppression techniques for coupling of size exclusion chromatography and 1H NMR using benchtop spectrometers at 43 and 62 MHz, *Journal of Magnetic Resonance* 2021, 323, 106889.

[4] TF Beskers, T Hofe, M Wilhelm. Development of a chemically sensitive online SEC detector based on FTIR spectroscopy, *Polymer Chemistry* 2015, 6, 128-142.

[5] JM Kuebel, C Botha, A Bucka, J Hoepfner, H Zimmermann, M Godejohann, M Wilhelm. A new quantum cascade IR-Laser online detector: Chemical-sensitive size-exclusion chromatography measurement at unprecedented low levels, *Macromolecular Rapid Communications* 2019, 40, 1900228.

[5] M Matz, C Botha, M Pollard, M Wilhelm. Benchtop-NMR-Spektrometer als HPLC-Detektor. *Lebensmittelchemie* 2022, 76, 212-25.



Hplc-nmr with spectra and molecule.jpg

End of Life Assessment of Fluoropolymers: Recent Developments and Challenges

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Bruno Ameduri [1], ***Dr. Kenji Otoi*** [2], ***Dr. Atsuko Tai*** [2], ***Dr. hirofumi Mukae*** [2], ***Dr. Guido Moeller*** [2]

1. *CNRS ICGM,* ***2.*** *Daikin Industries*

Fluoropolymers (FPs) are exceptional materials with outstanding properties critical to ensure optimal performance in many applications. These specialty polymers are essential to achieving key European Union policy objectives like Green Deal, Carbon Neutrality/Decarbonization, e-Mobility and the Chemical Strategy of Sustainability. Because of their photochemical, hydrolytic, inertness and biological stability, high molar masses (several million for polytetrafluoroethylene, PTFE), they cannot cross a cell membrane, meaning they are not bioaccumulative or toxic. [1] Hence, FPs fulfill the widely accepted polymer hazard assessment criteria to be considered as Polymer of Low Concern. This poster aims at displaying a browse on the recycling, reuse, thermal decomposition (thermolysis, thermal processing, flash pyrolysis, smoldering, open burning, open air detonation, and incineration), and life cycle assessment stages of fluoropolymer creation (aka manufacturing) and disposal at the end of industrial or consumer use (aka end-of-life).[2] The recycling for virgin/unfilled FPs (e.g. PTFE) waste or scraps generated in the production has already been achieved by Daikin Company [3] in commercial scale and by Dyneon Company on a pilot scale. More recent studies on the mineralization of FPs into fluoride anions, under subcritical water, the anions reacting with Calcium to lead to CaF_2 as the starting materials on the Fluorine Chemistry. All these technologies are summarized and discussed.

Abstract apme ameduri.png

From surfactant-free latexes to vitrimer films: The key role of the hydrophilic macromolecular stabilizer

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Suren Wang [1]***, Dr. Maxime Beaugendre*** [2]***, Dr. Corinne Soulié-Ziakovic*** [2]***, Dr. Renaud Nicolaÿ*** [2]***, Dr. Franck D'Agosto*** [1]***, Dr. Muriel Lansalot*** [3]

1. *Catalysis, Polymerization, Processes and Materials (CP2M), UMR 5128 CNRS, Université Claude Bernard Lyon 1, CPE Lyon,* **2.** *Chimie Moléculaire, Macromoléculaire, Matériaux(C3M), ESPCI,* **3.** *CNRS - CP2M*

Emulsion polymerization is applied widely to produce polymer latexes stabilized by low molar mass surfactant. However, when emulsion polymers undergo film formation, these hydrophilic species could migrate and segregate at film interfaces, which negatively impacts some properties. For the past decades, it has been proved that these surfactants could be replaced by macromolecular stabilizers, including reactive hydrophilic macromolecules prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization. In this case, the hydrophilic stabilizer block is anchored to the particle surface, which ensures better stability and reduces the diffusion problems mentioned above. The properties of these films are often induced by crosslinking reactions triggered before or during their formation[1]. In 2011, Leibler et al. have discovered a new family of crosslinked polymers called vitrimers[2] that behave like thermosets at service temperature but also like thermoplastics at high temperature. The aim of our work is to investigate the design of surfactant-free latexes incorporating dynamic crosslinks and their subsequent use for the formation of surfactant-free vitrimer films based on imine-aldehyde transcarbonylation[3].

The latex synthesis starts by preparing hydrophilic poly(methacrylic acid) chains via RAFT polymerization in water. These macromolecular chain transfer agents are then extended with methyl methacrylate and *n*-butyl acrylate containing a small amount of an aldehyde-functionalized methacrylate. Dynamic imine crosslinks between polymer chains are then induced by the introduction of a diamine into the latex. The resulting mixture is dried at ambient temperature to form a film. The influence of the concentration of aldehyde functions and of the crosslink density on the film properties is studied. Other hydrophilic stabilizers, namely poly(acrylic acid) and poly(*N*-acryloylmorpholine), are also evaluated. Although used in very low amounts (□2 wt % /core monomers), the nature of the hydrophilic stabilizer chains proves to be of paramount importance to achieve dynamic exchange between the hydrophobic chains from different particles and achieve vitrimer features.

1. Lesage de la Haye, J.; Martin-Fabiani, I.; Schulz, M.; Keddie, J. L.; D'Agosto, F.; Lansalot, M., Macromolecules 2017, 50, 9315-9328.
2. Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L., Science 2011, 334, 965-968.
3. Leibler, L.; Nicolaÿ, R.; Rottger, M. WO2017029311A1, 2017

Trapping the key intermediate in nucleophile-initiated Michael reactions

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

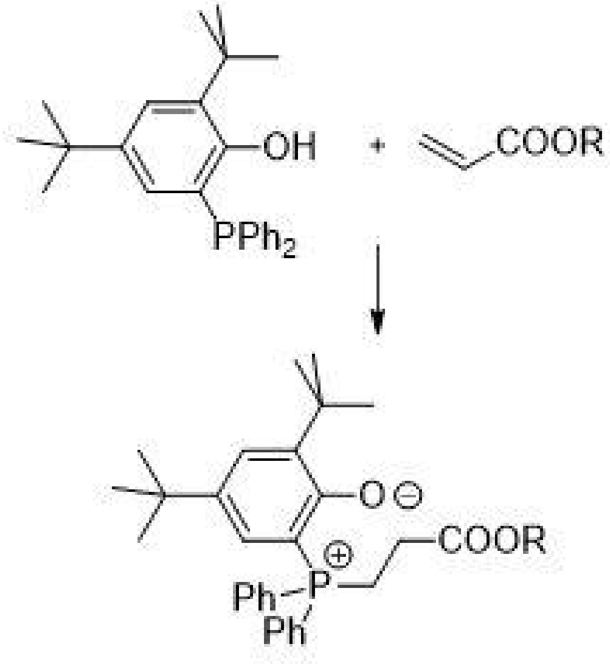
Mr. Matthias Steiner [1]***, Dr. Johann Hlina*** [2]***, Prof. Christian Slugovc*** [3]

1. Christian Doppler Laboratory for Organocatalysis in Polymerization and Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria, 2. Institute of Inorganic Chemistry, Graz University of Technology, Stremayrgasse 9, 8010 Graz, 3. Christian Doppler Laboratory for Organocatalysis in Polymerization and Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz

Phosphines are strong, versatile nucleophiles that are able to catalyze numerous reactions giving access to a wide variety of organic products. One reaction prominently catalyzed by phosphines is the oxa-Michael reaction, where alcohols react with Michael acceptors to form ethers. In our recent studies, we focused on oxa-Michael polymerization as a green alternative to aza- and thia-Michael reactions that employ toxic and environmentally unfriendly amines and thioles. The first step in catalysis is the formation of a zwitterion, generated from a nucleophile and the Michael-acceptor.

In our research, ortho hydroxy substituted phosphines are reacted with Michael acceptors generating zwitterions that are highly stabilized through the interaction of the alkoxide and the phosphonium ion. The reaction of 2,4-di-*tert*-butyl-6-diphenylphosphino-phenol (**1**) with Michael acceptors proceeds in good to near quantitative yields and the obtained zwitterions are air and moisture stable. The crystal structures of some of the zwitterions were obtained as well.

Investigations into the kinetics of zwitterion formation are carried out in order to generate further understanding of the governing factors of phosphine-based Michael reaction catalysis. Thereby, we seek to improve catalysis in polymerization and additional investigations will also be focused on zwitterionic polymers from these stabilized charged compounds.



Zwitterion formation.jpg

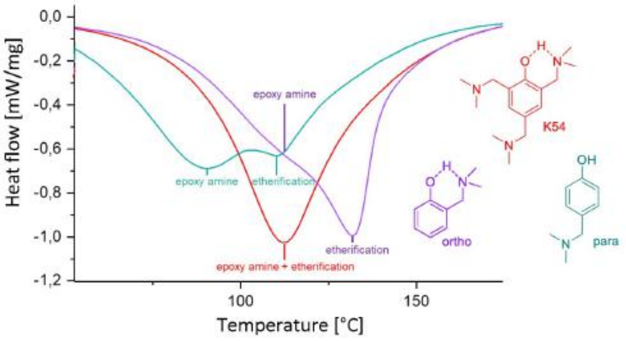
Understanding the mode of action of 2,4,6-tris(dimethylaminomethyl)phenol as curing agent in epoxy-amine formulations

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Viktor Schallert [1] ***, Prof. Christian Slugovc*** [1]

1. Christian Doppler Laboratory for Organocatalysis in Polymerization and Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz

2,4,6-Tris(dimethylaminomethyl)phenol (Ancamine K54) is a widely used curing agent in epoxy-amine chemistry. However, its mode of action is still not fully understood. To further the understanding, we herein study K54 and related model compounds in curing stoichiometric and substoichiometric epoxy-amine formulations. By a combination of dynamic DSC, NMR and IR experiments it can be shown, that the hydroxyl group of K54 interacts with one of its neighboring tertiary amines, deactivating both groups for catalysis. The residual tertiary amine-groups initiate the etherification reaction, which is particularly important for obtaining high oxirane-conversions when using formulations with substoichiometric amine content.



Abstract bild.jpg

The effects of accelerators in coreactive curing of epoxy resins

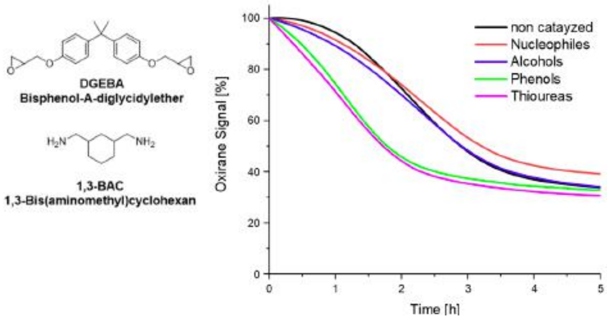
Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. David Edinger [1]***, Prof. Christian Slugovc*** [1]***, Mr. Viktor Schallert*** [2]

***1.** Christian Doppler Laboratory for Organocatalysis in Polymerization and Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz,* ***2.** Christian Doppler Laboratory for Organocatalysis in Polymerization and Institute for Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010 Graz, Austria*

Due to the huge variety of applications of epoxy resins, their curing is tuned by a plethora of accelerators to meet the different needs in industry. However, the effects of catalysis in the polyaddition of epoxides are still not fully understood. In this work, we investigated different classes of catalysts such as nucleophiles, phenols, alcohols and thioureas in epoxy amine reactions. All analysis methods namely continuous ATR-IR reaction monitoring, dynamic DSC, and oscillatory rheology show congruent results.

We could show that hydrogen bond donor catalysts are crucial for reducing induction period and accelerate curing, indicating epoxide ring activation and a facilitated proton transfer during propargation. Phenols and thioureas show hugely improved kinetics compared to nucleophiles. The results suggest, that the widely used class of tertiary amines do not accelerate the epoxy amine reaction, but rather the crosslinking due to etherification. This new insight of catalyst effects on network formation and resulting changes in the mechanical properties can advance the tailoring of existing epoxy materials.



Epoxy amine ir monitoring.png

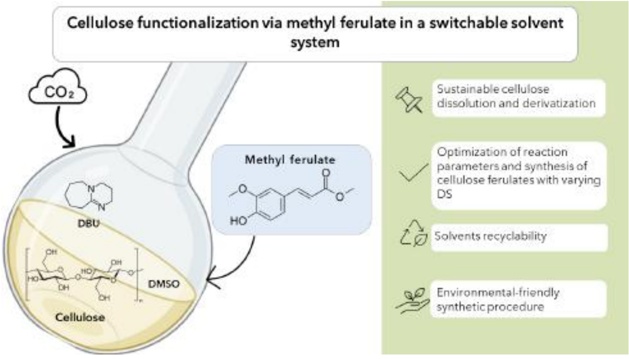
Cellulose functionalization via methyl ferulate in a switchable solvent system

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Ms. Celeste Libretti [1], ***Prof. Micheal A. R. Meier*** [1]

1. Karlsruhe Institute of Technology

Cellulose is the most abundant renewable biopolymer among the natural resources. Due to its interesting characteristics, such as biodegradability, sustainability, light weight and high thermal stability, cellulose represents a very promising material. Its peculiar molecular structure paves the way for a broad range of possible functionalizations, offering the possibility to obtain materials with tailor-made properties for specific applications. Modification of cellulose *via* homogeneous processes can lead to a higher control over the *Degree of Substitution* (DS), a smaller amount of required reactants and generally more sustainable conditions. However, the major inconvenience of this procedure is the insolubility of this biopolymer in nearly all solvents. This problem has been addressed with the advent of Ionic Liquids (ILs), solvents capable of solubilizing cellulose.
In this work, direct transesterification of cellulose was achieved in a switchable solvent system, a particular class of ionic liquids that can change its polarity from non-ionic to ionic. Therefore, cellulose was solubilized in a DBU/DMSO/CO_2 system under mild conditions, then modified with *methyl ferulate*. This derivatization agent is bioderived from lignin and has interesting antioxidant properties, besides exhibiting low toxicity. Its structure could also potentially allow further modifications of the resulting cellulose esters and enhance their thermal properties. First, optimization of the reaction parameters was conducted and the extent of the transesterification was monitored via FT-IR spectroscopy as well as ^{1}H-NMR spectroscopy. Subsequently, a series of cellulose esters with variable DS was synthesized. Modifications of the derivatizing agent were also performed, in order to evaluate the influence of functional groups on its reactivity. The thermal stability of the obtained cellulose ferulates was evaluated, as well as their antioxidant properties. Furthermore, the recyclability of the switchable solvent system was investigated.



Cellulose functionalization switchable solvent system.png

Synthesis of Imidazole-Functionalized Polymer Nanoparticles via Aqueous RAFT-Mediated Polymerization-Induced Self-Assembly

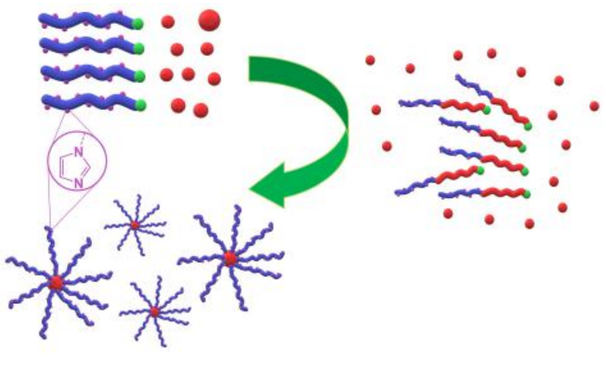
Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Gurbuz Dursun [1], ***Ms. Paula Isabel Vera Cordova*** [1], ***Prof. Guillaume Delaittre*** [1]

1. *Organic Functional (Macro)Molecules, Department of Organic Chemistry, University of Wuppertal*

Polymerization-induced self-assembly (PISA) is an alternative strategy to the conventional solution self-assembly process and enables the synthesis of diverse block copolymer nano-objects at relatively high solid contents. In a typical PISA process, the solvophilic polymer, that acts as a stabilizer for the formed latex and prevents coagulation, undergoes chain extension via reversible-deactivation polymerization (e.g., RAFT polymerization) in the presence of a core-forming monomer forming a solvophobic block. The PISA simultaneously self-assembly of the resulting amphiphilic block copolymer leads to the formation of nano-objects with various morphologies, where often no post-purification steps are required after successfully reaching complete conversion of core-forming monomers.

In this work, the aim was to obtain nanoparticles decorated with water-soluble P(NAM-co-1VI) random copolymers, which combine the properties of the individual homopolymers. Poly(*N*-acryloylmorpholine) (PNAM) are highly water-soluble polymers which makes them great candidates as hydrophilic shell of nano-objects. On the other hand, poly(1-vinylimidazole) (P1VI) as another polar compound with heterocyclic aromatic imidazole rings in side chains is of high interest for the immobilization of metal complexes/catalysts, among other applications. Therefore, P(NAM-co-1VI) macroRAFT agents with Mn of about 10 kDa, low dispersity, varying 1VI-to-NAM ratios, and high RAFT end-group fidelity were synthesized. As a second step, a series of amphiphilic block copolymers were produced via RAFT emulsion polymerization in water, with various targeted degrees of polymerization (DP = 25–750) for the hydrophobic polystyrene (PS) block and total solid contents (up to 38%). The macroRAFT composition was found to play a major role on the stability of the aggregates. Critical DP ranges of the PS block which allow formation of energetically favourable aggregations but not precipitation was determined, and reaction conditions were optimized accordingly. As a result, narrow distributions of highly stable, imidazole-containing, spherical nanoparticles ranging from 30 nm to 160 nm in diameter and with near-quantitative styrene conversion were obtained. At the time of writing this abstract, these nanoparticles were investigated as recyclable nanocatalyst precursors.



Dursun graphical abstract.jpg

Ruthenium-containing polymer colloids with red light sensitivity for anticancer phototherapy

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Yandong Ma [1]***, Dr. Min-Hui Li*** [1]***, Prof. Gilles Gasser*** [2]

1. *Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, UMR8247,* ***2.*** *Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences Laboratory for Inorganic Chemical Biology*

Polyethylene glycol (PEG) has been extensively selected as a hydrophilic shell of polymer colloids used in nanomedicine due to its stealthy property that favors the long-term systemic circulation and high enrichment in tumor sites of polymer colloids. Thus, PEGylated polymer colloids have received tremendous attention for drug delivery systems. However, PEGylation can diminish the cell uptake of polymer colloids by cancer cells and reduce anticancer efficiency. To address this issue, we develop ruthenium-containing PEGylated polymer colloids where the PEG shell ensures the stealthy property of polymer colloids, and the ruthenium (Ru) complex photosensitizer plays the role of anticancer agent whose coordination bond can be cut under red light illumination. The release of Ru complex can then be triggered by red light in tumor site out of cancer cells, followed by the easy internalization of Ru complex by cancer cells.

An amphiphilic block copolymer, PEG-b-PMeSPG (PMeSPG = poly(N-3-(methylthio)propyl glycine)), with a thioether-bearing polypeptoid PMeSPG as hydrophobic block was synthesized by ring-opening polymerization. $[Ru(tpy)(biq)(H2O)]^{2}+$ (Ru = ruthenium, tpy = 2,2′:6′,2″-terpyridine and biq = 2,2′-biquinoline) was then coordinated with the thioether of PEG-b-PMeSPG, resulting in Ru-containing polymer (PolyRu) that contained more than 30% Ru complexes. The amphiphilic PolyRu self-assemble into micelles and vesicles by nanoprecipitation depending on the co-solvent used (THF/Acetone or DMF). Red light irradiation broke the coordination bond between Ru and thioether of PMeSPG. Moreover, under irradiation the Ru complexes generated reactive oxygen species (ROS) that oxidized hydrophobic thioether to hydrophilic sulfoxides, leading to disruption of micelles and vesicles. The rupture of these self-assembles caused the effective release of the photocleaved Ru complexes from the polymer colloids and enhanced uptake of Ru complexes by tumor cells, in which chemotherapy and photodynamic therapy of Ru complexes were combined.

Yandong MIM2-IRCP-Chimie ParisTech

Ruthenium-containing polymer colloids with red light sensitivity for anticancer photodynamic therapy

PhD student: Yandong MA
PhD supervisor: Min-Hui LI

Affiliation: Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, UMR8247
e-mail address: yandong.ma@chimieparistech.psl.eu

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The abstract of yandong ma in chimieparistech.jpg

Insertion of synthetic nanopores into polymeric membranes

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Yang Yu [1], ***Prof. Philippe Guégan*** [1], ***Dr. Cecile Huin*** [1], ***Dr. Haiqin DU*** [2], ***Prof. Fernando Carlos Giacomelli*** [3]

__1.__ Institut Parisien de Chimie Moléculaire (UMR-CNRS 8232), Sorbonne Université, __2.__ State Key Laboratory of Molecular Engineering of Polymers, __3.__ Centro de Ciencias Naturais eˆHumanas, Universidade Federal do ABC

Inspired by ion channels, the generation of biomimetic nanopores and nanochannels is a delightfully scientific research field, because such biomimetic materials as a basic platform could potentially spark experimental and theoretical efforts to simulate the process of ionic transport in living organisms as well as the enhancement of the functionality of biological ion channels, and boost the development of bioinspired smart nanopore/nanochannel apparatus in the biosensors, nano-fluidic devices, and molecular filtration fields.

We would like to develop a robust system, mimicking natural cells, by inserting into polymeric membranes synthetic nanopores. Our interest to work with polymeric membranes is based on their longer stability, compared to the one shown by lipid bilayers, and the possibility to tune the thickness of the membrane, by changing the molar mass of the polymer blocks.

Our approach is to design a library of (co)polymers, able to form planar polymeric membranes and/or polymersomes, and to design synthetic nanopores based on macrocycles, allowing a pre-defined permeation structure. The synthesis part is achieved by a combination of organic chemistry and polymerization. The characterizations of the objects are performed by NMR, GPC and MS. The self-assembly of the objects in solution are evaluated by dynamic light scattering, and eventually by SAXS and cryo-TEM. The ability to insert the synthetic nanopores into polymeric membranes is assessed by electrical detection using the Black Lipid Membrane technique.

We have demonstrated that polymersomes could be obtained by cyclodextrin based star polymers having chemical structures close to the one of chemical nanopores. Permeation studies were conducted, and a translocation dependence upon the chemical nature of the analyte was observed. An extension of the seminal results is now expected, and applications to chemistry and natural science is now envisioned.

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[2] Z.S.Siwy et al. Chem. Soc. Rev. 2010, 39, 1115.
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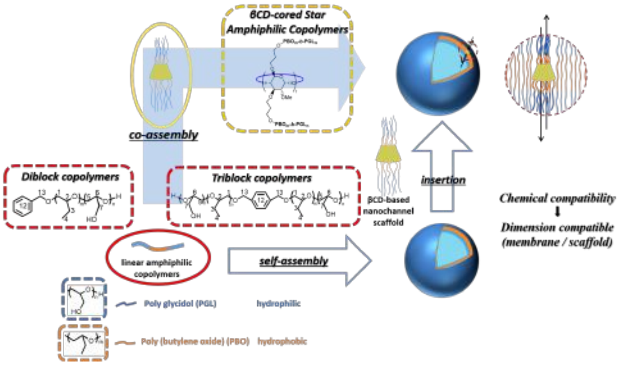


Yu yang.png

Influence of comonomer content on the cross-linkability of ethylene-octene thermoplastic elastomers

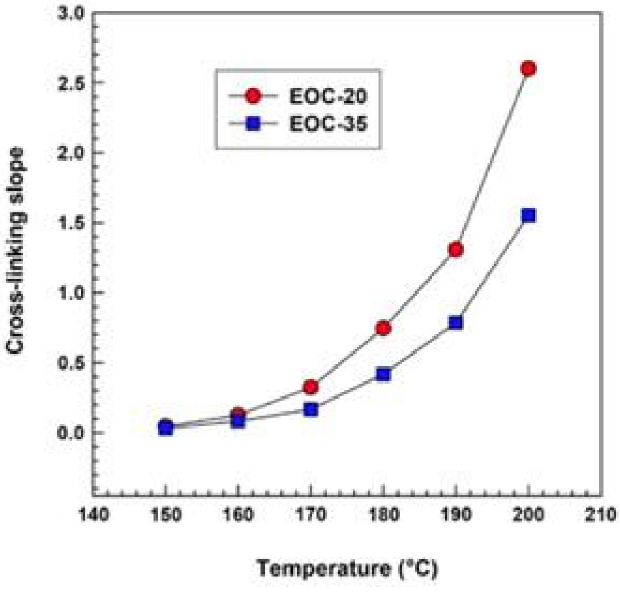
Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Dr. Rajesh Theravalappil [1], ***Prof. Petr Svoboda*** [2]

1. *Center for Refining and Advanced Chemicals, Research Institute, King Fahd University of Petroleum and Minerals, Dhahran.,*

2. *Department of Polymer Engineering, Faculty of Technology, Tomas Bata University in Zlin, Vavreckova 275, 76001, Zlin.*

Ethylene-octene copolymers (EOCs) with two different octene contents (20 and 35 wt%) and the same melt flow index (3 g/10 min) were cross-linked using various levels (0.3, 0.5 and 0.7 wt%) of dicumyl peroxide at different temperatures. Cross-linking and degradation were analyzed by rubber process analyzer (RPA) within a temperature range of 150 - 200 °C. The highest s'_{max} (maximum elastic torque) and the lowest tan(delta) which is attributed to the best elastic properties were observed for EOC-20 with low-octene content at all cross-linking temperatures. Lower peroxide efficiency was observed in the case of the high-octene copolymer. Increased degradation was observed with increasing cross-linking temperature. High-octene EOC was found to be more vulnerable to degradation. According to dynamic mechanical analysis, the storage modulus (M') and the glass transition temperature (Tg) obtained from the tan(delta) peaks were found to decrease with increasing octene content. The differential scanning calorimetry (DSC) results show that the octene content has an inverse effect on the crystallinity (X) and melting point (T_m) - due to the reduction in the average number of consecutive ethylene units. Creep testing at 150 °C confirmed the cross-linkability results obtained by RPA and the gel content analyses. Increased β-scission due to high numbers of tertiary carbon atoms present in the chain has resulted in the poorer cross-linking and inferior properties of high-octene copolymer. The cross-linking efficiency of EOCs was greatly influenced by the octene content, peroxide level, and cross-linking temperature. However, high-octene copolymer (EOC-35) was more vulnerable to degradation, which can be attributed to the increased number of tertiary carbon atoms compared with that of the low-octene EOC. Further studies can lead to invention of new commercially important products with high durability and performance.



Cross-linking slopes of two different eocs cross-linked by 0.7 wt .jpeg

Revealing the SECrets of polysaccharides using SEC/GPC with advanced detection methods

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Tamoor Babur [1]***, Mr. Subin Damodaran*** [1]***, Mr. Sebastian Rouzeau*** [1]***, Ms. farihah Haque*** [1]***, Mr. Tianyu Li*** [1]***, Mr. David Gillespie*** [1]

1. *Tosoh Bioscience*

Triple detection gel permeation chromatography (GPC) or size exclusion chromatography (SEC) is a robust method for the quantitative and qualitative characterization of macromolecules like polysaccharides, proteins and synthetic (bio) polymers. This approach utilizes both light scattering and viscometer detectors in conjunction with a refractive index (RI) detector to determine the molecular weight (MW), molecular sizes (radius of gyration (R_g) and hydrodynamic radius (R_h)) and intrinsic viscosity (IV) of polymers. With this well-established technique, one can elucidate the structure, composition as well as branching of polymers. This all can eventually lead to a comprehensive understanding of the physical and chemical properties of polymer chains in solution to develop their structure-property relationships.

The aim of our study was to demonstrate the structural, conformational and architectural characteristics of polysaccharides, mainly high molecular weight dextran and its comparison to linear pullulans using this powerful system.

On-surface synthesis of large-area 2D boroxine polymers

Monday, 24th April - 18:30: Poster Session and Cheese & Wine - Poster

Mr. Brecht Koek [1] ***, Prof. Steven De Feyter*** [1]

1. *KU Leuven*

Synthetic, crystalline two-dimensional polymers (2DPs) have received a great amount of interest over the past few years due to their modular, tailor-made structures and numerous potential applications. The on-surface synthesis of such 2DP monolayers is particularly popular, however the growth of such crystalline films is still poorly understood. Provided that the 2DPs are formed on an atomically flat conductive substrate, their structure can be characterized at (sub)molecular resolution using scanning tunneling microscopy (STM). Furthermore, for appropriate systems, the nucleation, growth and ripening of 2DPs can be monitored using STM at the liquid-solid interface providing detailed insight into the mechanism of polymerization in 2D.[1]

In this contribution, I will present initial results on the 2D polymerization of pyrene 2,7-diboronic acid (PDBA) at the solution-solid interface. The polymerization was studied at the solution/solid interface. In contrast to our previous work, where the focus was on studying the nucleation and growth processes, here we target the growth of large domains of the 2DP which could be of interest in potential applications. The 2D polymerization was studied at the octanoic acid/graphite and 1,2,4-trichlorobenzene (TCB) interface. We observe that the polymerization occurs only locally within the scanned area due to the electric field effect of the STM [2] whereas in TCB the polymer growth is found to be independent of the electric field. Large area domains spanning several thousand square nanometers were formed at the TCB/graphite interface. Interestingly, we also observed a distinct Moiré pattern in the STM images of the large domains PDBA 2DP which indicates a mismatch in the registry of 2DP with respect to the graphite lattice underneath. Such Moiré superlattices are of interest in the field of twistronics.[3]

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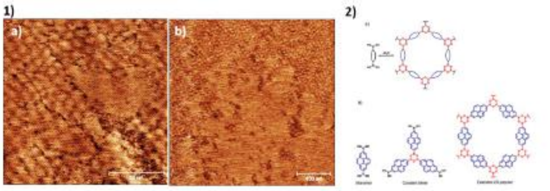
[2] N. Bilbao *et al.*, “Anatomy of On-Surface Synthesized Boroxine Two-Dimensional Polymers,” *ACS Nano*, vol. 14, no. 2, pp. 2354–2365, Feb. 2020, doi: 10.1021/acsnano.9b09520.

[3] M. Brzhezinskaya *et al.*, “Engineering of Numerous Moiré Superlattices in Twisted Multilayer Graphene for Twistronics and Straintronics Applications,” *ACS Nano*, vol. 15, no. 7, pp. 12358–12366, Jul. 2021, doi: 10.1021/acsnano.1c04286.



1) STM images of the large-area PDBA 2DP showing the moiré pattern: a) 150x150 nm, b) 500x500 nm. 2) Scheme showing: (a) General reaction scheme showing the self-condensation of aryl diboronic Acids to yield 2DP and molecular structures of the (b) PDBA monomer, covalent trimer, and the PDBA 2DP

Stm images and model of 2d boroxine polymer.jpg

Designing and translating biomaterials for advanced therapeutics and ultrasensitive biosensing

Tuesday, 25th April - 08:30: Plenary Session 2 - Oral

Prof. Molly Stevens [1]

1. *Imperial College*

TBD

Design of functional polymers based on poly(2-oxazoline)s

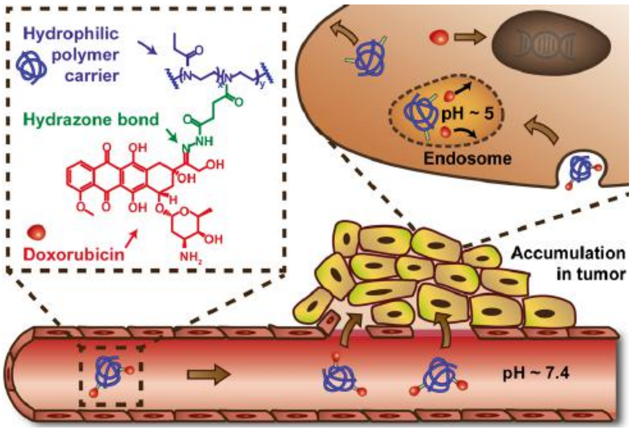
Tuesday, 25th April - 09:30: Oral Session 4-1 - Oral

Prof. Richard Hoogenboom [1]

1. *Ghent University*

Poly(2-oxazoline)s are promising as biomaterials and PAG-alternatives based on their structural variability, high hydrophilicity and anti-fouling properties.

In this lecture, our recent progress in the design of functional polymers based on poly(2-oxazoline)s will be discussed. This will include the discussion of introducing side chain ester groups and their subsequent post-polymerization modification with various amines to convert the ester into an amide. Using this general procedure a wide range of side chain functional groups has been introduced, including alkene, alkyne, amine and hydroxyl groups. In addition, the preparation of polymer-drug conjugates will be discussed and their use as polymer therapeutics as shown in the Figure. This specific example shows the coupling of doxorubicin through a pH-responsive hydrazone linker, which is stable in the blood stream but readily degrades at the lower pH in the endosomes leading to drug release upon cellular uptake. The development of super-hydrophilic poly(2-oxazoline)s with hydroxymethyl side chain will also be discussed for which it has been demonstrated that these polymers represent the most hydrophilic poly(2-oxazoline)s known to date.



Picture.png

Visible Light-Induced Cationic Polymerization of Isobutylene: Mechanistic Insight and Synthesis of End-Functional Polyisobutylene

Tuesday, 25th April - 10:00: Oral Session 4-1 - Oral

Dr. Maksim Hulnik* [1] *, Ms. Diana Trofimuk* [1] *, Ms. Tugba Celiker* [2] *, Prof. Yusuf Yagci* [2] *,
***Prof. Sergei Kostjuk* [3]**

1. *Research Institute for Physical Chemical Problems of the Belarusian State University, 220006 Minsk, Belarus,* ***2.*** *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,,* ***3.*** *Belarusian State University, Department of Chemistry, 220006 Minsk, Belarus*

The use of photocatalysis in polymer synthesis is emerging and intensively developing area of research during the last decades.[1] Although photoinduced living radical photopolymerization is in a main focus, the photocontrolled cationic polymerization is rapidly developed in last five years.[1,2] The most developed approach for conducting photocontrolled cationic polymerization consists in using suitable photoredox catalyst (PC) in conjunction with chain transfer agent (CTA).[2] Despite of great variety of PC*s* and CTA*s* reported to date, the photoinduced cationic polymerization limits to very reactive monomers such as vinyl ethers or p-methoxystyrene.[2]
Another approach toward photocontrolled cationic polymerization of vinyl ethers consisting in using benzyl bromide/$Mn_2(CO)_{10}$/diphenyl iodonium salt initiating system via radical oxidation/addition/deactivation (PROAD) mechanism has been recently reported by Yagci et al.[3]
In this work, we report for the first time the photoinitiated cationic polymerization of isobutylene (IB), the industrially relevant monomer, benzyl bromide/$Mn_2(CO)_{10}$/$Ph_2I^+PF_6^-$ initiating system. Particularly, we demonstrated that during the photoinitiated cationic polymerization of IB with above-mentioned initiating system, benzyl bromide does not initiate the polymerization, while initiation occurred via chlorine radical abstraction from solvent (CH_2Cl_2) followed by the oxidation of generated radical to corresponding cation by diphenyl iodonium salt (Scheme 1).
Scheme 1. Tentative mechanism of photoinitiated cationic polymerization of isobutylene.
The photoinitated controlled catalytic chain transfer cationic polymerization of IB proceeded with some induction period at -30 ºC in CH_2Cl_2/*n*-hexane affording *exo*-olefin-terminated polyisobutylene (*exo* content >85%) with M_n up to 3000 g mol^{-1} and relatively low polydispersity ($Đ < 1.7$). The M_n could be efficiently controlled from 2,000 to 30,000 g mol^{-1} by the concentration of diphenyl iodonium salts. The effect of diphenyl iodonium salt nature, temperature, solvent and initiator will be also discussed in details.

Acknowledgements. The authors would like to acknowledge the financial support from joint project between Belarus and Turkey BRFFR-TUBITAK (projects: X21TYB-008; 120C121).

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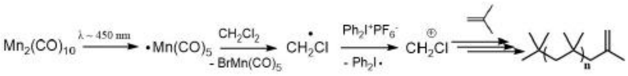
3. Ciftci, M.; Yoshikawa, Y.; Yagci, Y. *Angew. Chem. Ed.*, **2016**, *56*, 519.



Scheme 1.jpg

Cationic Reversible Addition-Fragmentation chain Transfer - Ring Opening Polymerization (CRAFT-ROP) of 2-methyl-2-oxazoline

Tuesday, 25th April - 10:15: Oral Session 4-1 - Oral

Mrs. Solène Le Roux [1], Prof. Philippe Guégan [1], Dr. Véronique Bennevault [1], Dr. Véronique Bennevault [2]

1. Institut Parisien de Chimie Moléculaire, Sorbonne Université, Paris, 2. Université d'Evry, Evry

Polyoxazolines are usually obtained through a cationic ring-opening polymerization (CROP) mechanism[1,2]. It has been shown that a cationic reversible addition–fragmentation chain transfer (RAFT) polymerization mechanism can be considered to polymerize olefins such as vinyl ethers or styrene derivatives in the presence of transfer agent[2,3]. RAFT polymerization is known to improve the control of polymerization and molar masses[3–5]. While cationic RAFT polymerization of vinylic monomers is drawing large attention, no comparable investigation has been undertaken for heterocycles and in particular 2-alkyl-2-oxazolines.

Thus, several RAFT agents were investigated to synthesize poly(2-methyl-2-oxazoline)s. RAFT agents able to react with the oxazolinium active centers were selected for further study. The amount of RAFT agent involved was studied to show its influence on the molar mass of the formed polymer and kinetic studies were performed. A CROP-RAFT mechanism could therefore be established by analogy with the radical one[4]. The polymers structures were characterized by ^{1}H, ^{13}C, COSY, HSQC and DOSY NMR and the chain ends assessments were achieved by MALDI-ToF. Finally, the molar masses were evaluated by SEC.

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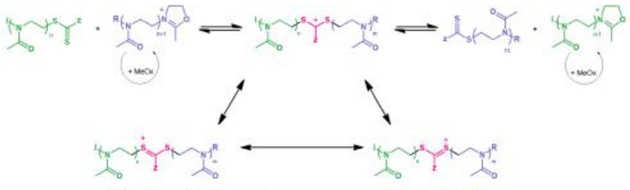

Figure 1 : Equilibrium between dormant and active species of CRAFT-ROP mechanism of 2-methyl-2-oxazoline

Equilibrium between dormant and active species of craft-rop mechanism of 2-methyl-2-oxazoline slr.png

Digital Polymer Chemistry on The Rise

Tuesday, 25th April - 09:30: Oral Session 4-2 - Oral

Prof. Tanja Junkers [1]

1. *Monash University*

Contemporary macromolecular chemistry has matured to a point where virtually any polymer structure can be synthesized via combinations of controlled polymerization approaches, post-polymerization modification and efficient ligation strategies. Still, often large hurdles have to be overcome to take the next step in research, that is being able to provide such complex materials reliably on significant scale for use in advanced applications. Digital chemistry, the fusion of classical chemistry with modern data science and computer science, opens an attractive avenue to overcome these issues. A further solution to the problem is to make use of continuous flow synthesis techniques. Flow reactors are associated with high reproducibility, intrinsically simple reaction scale-up and improved product qualities due to significant reduction of side reactions. Being an established method especially in the pharmaceutical chemistry domain, full potential with regards to macromolecular synthesis did not unfold until very recently. Among others, the benefits of using online-monitoring, reactor automation and machine-learning will be discussed and the development of fully autonomous based reactor systems presented. Machine-assisted synthesis of polymers is shown to be superior in accuracy in synthesis. Generally, the introduction of smart algorithms in synthesis control opens avenues into the digital chemistry space, and challenges and opportunities in this realm will be discussed, especially with regards to creating of ‘big data’ and handling of massive datasets in chemical research.

At the same time, machine-learning methods show their effect in polymer chemistry. The long-aimed for dream of establishing structure-property relationships with good predictability has come into reach for the first time. Some examples, for instance the prediction of propagation rate coefficients of monomers based on some physical properties of the monomers is shown and discussed.

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3D Printing of polymer foams via direct bubble writing

Tuesday, 25th April - 10:00: Oral Session 4-2 - Oral

Dr. Olivier Nguon [1], ***Ms. Prasansha Rastogi*** [1], ***Ms. Guanxing Kuang*** [1], ***Prof. Claas Willem Visser*** [1]

1. *University of Twente*

Introduction

Polymer foams are ubiquitous materials, with applications in cushioning, packaging and insulation, but also energy storage, sensing, and tissue engineering. Their properties are highly dependent on their composition, structure, and design; however, current manufacturing methods lack control over these parameters.

Direct bubble writing (DBW) is a novel platform technology enabling the 3D printing of polymer foams. With this technique, cellular solids can be constructed with well-defined and locally architected cell-size, density, and pore connectivity. Transition between open- and closed-cell structures are easily achieved, and uniform or graded foams are printed to a desired design, with a high throughput.

In this presentation, we will review DBW and disclose the most recent advances enabling the 3D printing of sustainable designer foams with applications as soft pressure sensors, and acoustic metamaterials.

Method

A tailor-made 3D printer was assembled by mounting a printhead to an automated stage (Figure 1a). The printhead was constituted of a 3D printed core-shell nozzle, and four UV LEDs. One inlet of the nozzle was connected to a gas supply and adjusted with a pressure controller. The second inlet was connected to a syringe operated with a syringe pump.

Ink formulations were prepared from aqueous solutions of poly(ethylene glycol) diacrylate (PEGDA) or non-aqueous sustainable formulations, in presence of a photoinitiator.

Results and discussion

DBW was used for the 3D printing of polymer foams based on PEGDA or sustainable macromonomers. Uniform bubble formation was obtained with the setup shown in Figure 1a. After photopolymerization, a designer foam with a uniform cell-size was obtained (Figure 1b). The cell size could be controlled by adjusting the gas pressure, and ranged from 400 to 700 µm (Figure 1c). By introducing conductive fillers, we demonstrated their application as pressure sensors. The effect of structure on the acoustic properties of the foams was also studied.

Figure 1. (a) Schematic of the direct bubble writing setup. (b) Optical image of the foam structure, scale bar: 0.5 mm. (c) Cell diameter as a function of gas pressure.

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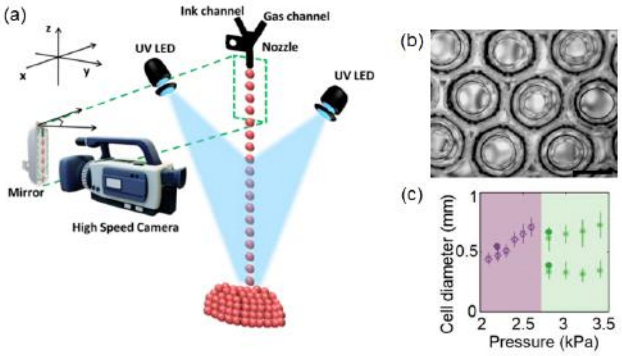


Foam 3d printing dbw.png

Photo-Polymerization Induced Microphase Separation, toward 3D Printed acrylic materials

Tuesday, 25th April - 10:15: Oral Session 4-2 - Oral

Mr. Grégoire Lahittete [1]***, Ms. Virginie Pellerin*** [1]***, Dr. Anne-Laure Brocas*** [2]***, Prof. Christophe Derail*** [1]***, Dr. Maud Save*** [1]***, Dr. Laurent Rubatat*** [1]

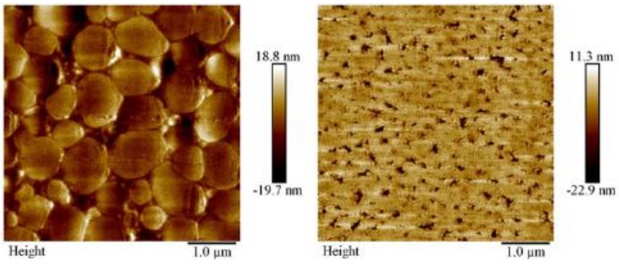
1. *Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, IPREM, Pau, France,* ***2.*** *Arkema GRL, Lacq, France*

Photo-polymerization allows synthesis of a solid polymer materials in few seconds, starting from a liquid monomer mixture. This rapid implementation process presents, thus, a significant advantage compared to thermal polymerization that can take several hours. Additionally, light curing offers a spatial control which is of interest to achieve materials with complex shapes. For those reasons photo-polymerization find an increasing interest toward many applications, with significant developments in 3D Printing.

However, the development of more complex nanostructured polymer materials generated by photo-polymerization and 3D Printing remains challenging. The aim of the present work is to control the morphology of photo-polymerized and 3D Printed materials using the photo-Polymerization Induced Microphase Separation (photo-PIMS) process, in order to obtain rubber-toughened acrylic materials. To do so, reactive first blocks are solubilized in the liquid monomer, in order to produce *in situ* block-copolymers that will phase separate during the polymerization or 3D Printing processes (i.e. macro and/or micro phase separation (*Fig. 1*)).

The influence of the reactive first block (nature of chain end, topology) on the morphology of self-assembled polymer will be discussed, as well as the influence on the mechanical properties of 3D Printed materials.

Figure 1: AFM height images of photo-polymerized samples (hard/soft phase weight ratio = 80/20 for both) showing macro (left) and microphase separation (right)



Apme23 figure abstract.jpg

Polysaccharide-based nanocarriers for biotec and medical applications

Tuesday, 25th April - 09:30: Oral Session 4-3 - Oral

Prof. Thomas Heinze [1]

1. Friedrich Schiller University Jena

Ready-to-use NPs with reactive groups are of interest that enabled direct immobilization of biomolecules. For instance, NP of a size of 200-400 nm with activated NHS ester groups could be obtained from cellulose acetate phthalate (CAP). The NHS-ester moieties are useful for an immobilization of amines. The NHS-CAP products formed spherical NP in the range of 200-400 nm.

Xylan phenyl carbonates (XPC) with different degrees of substitution were prepared under homogeneous reaction conditions applying ILs. The derivatives showed a high reactivity towards various types of functional amines leading to the formation of carbamates. The carbonate groups acted as reactive and hydrophobic groups, thus, enabling self-assembling of XPC into NP with diameters of 100-200 nm. The NP with reactive moieties (NHS-esters and aryl carbonate moieties) were stable under aqueous conditions and enabled direct immobilization of amine-functionalized dyes and enzymes under aqueous conditions with high coupling efficiencies of up to 90 %. The novel NP were demonstrated to be non-cytotoxic.

The development of bio-based NPs as drug containers is of increasing interest to circumvent common treatment disadvantages such as rapid drug metabolization, short serum half-life, and side-effects. The histone deacetylase inhibitor valproic acid (VPA) is known for its anti-inflammatory as well as anti-cancer activity. Here, recently developed VPA-loaded NPs based on cellulose- and dextran VPA esters were modified with sulfuric acid half ester moieties to improve intracellular drug release. The NPs show rapid cellular uptake, are non-toxic, highly biocompatible and are able to induce histone H3 hyperacetylation. Thus, they represent a potent drug delivery system for the application in a variety of treatment issues, such as inflammation, sepsis and defined cancer types. In addition, the flexible NP-system offers a broad range of further options of modification, e.g. for targeting strategies and multi-drug approaches.

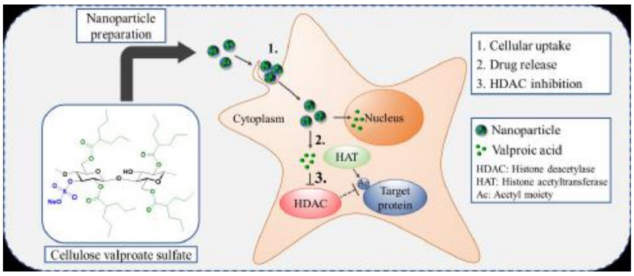


Image heinze.jpg

Valorization of Tomato Cutin as Bio-based Plasticizers for Bioplastics

Tuesday, 25th April - 10:00: Oral Session 4-3 - Oral

Dr. Raffaella Suriano [1]***, Dr. Grazia Isa Carla Righetti*** [1]***, Dr. Rita Nasti*** [2]***, Prof. Giangiacomo Beretta*** [2]***, Prof. Stefano Turri*** [1]***, Prof. Marinella Levi*** [1]

1. *Department of Chemistry, Materials and Chemical Engineering 'Giulio Natta', Politecnico di Milano, Piazza Leonardo da Vinci 32 – 20133 – Milano Italy,* ***2.*** *Department of Environmental Science and Policy, Università degli studi di Milano, via Celoria 2, 20133 Milano, Italy*

Over the last past two decades, due to the increasing environmental concern, bioplastics have gained increasing attention and a wide range of additives are used to tailor their properties for a particular application.[i] To increase bioplastic sustainability, plasticizers can be found in the agro-food sector, to substitute conventional additives that can be toxic or with high environmental impact. In light of this, tomato waste can represent a great renewable resource to find sustainable chemicals and additives. Tomato peels, which are wasted in tomato sauce industrial processing, are well known to provide a physical barrier against external agents to tomato cores thanks to the cutin, i.e. a strong polyester network. The main components of cutin are polyhydroxylated fatty acids, and in particular 10,16-dihydroxyhexadecanoic acid (10,16-diHHDA-85 % w/w), deeply exploited in literature for its easy and green extractability and its use.[ii] In this work, the application of 10,16-diHHDA as bio-based plasticizers of bioplastics was proposed and investigated for the first time. Among bioplastics, polylactic acid (PLA) represents one of the most used polymers in the market. However, due to PLA's limited flexibility, its pristine employment has always been limited, and several plasticizers have been tried to make it softer. This work aimed to improve PLA flexibility using 10,16-diHHDA extracted from tomato peel waste as renewable plasticizers, as it is or suitably derivatized to increase compatibility with PLA. The blends with PLA were obtained and characterized by differential scanning calorimetry and tensile tests. Fully bio-based PLA blends showed a clear decrease in glass transition temperatures (T_g), confirming the effectiveness of cutin monomers as plasticizers. Tensile tests also highlighted how PLA blended with one of the 10,16-diHHDA derivatives can efficiently enhance its flexibility. In light of these results, this work paves the way for the use of cutin fatty acids as bio-based plasticizers for various bioplastics.

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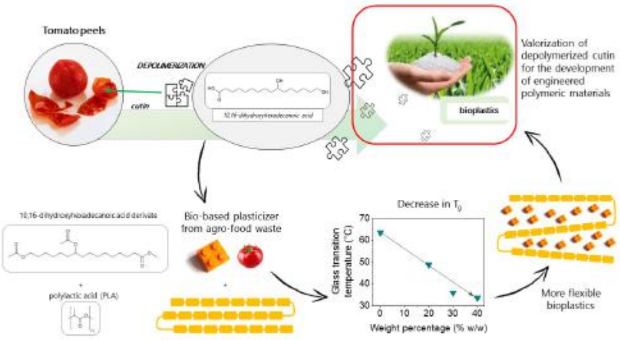
[ii] Heredia-Guerrero JA, Heredia A, Domínguez E, Cingolani R, Bayer IS, Athanassiou A, Benítez J (2017) Cutin from agro-waste as a raw material for the production of bioplastics, *Journal of Experimental Botany*, 68(19): 5401–10.



Valorization of depolymerized tomato cutin as bio-based plasticizer for the development of pla with a lower tg.jpg

Bio-based poly(hydroxy urethane)s for efficient organic high-power energy storage

Tuesday, 25th April - 10:15: Oral Session 4-3 - Oral

Dr. Étienne Grau [1]

1. Université de Bordeaux

The increasing demand in energy combined with the environmentally-motivated move away from fossil fuels has led to huge investment in more sustainable methods to produce energy, such as the exploitation of wind or solar power. However, the intermittence of these energy sources, and the increasing need for nomadic energy, has made the necessity for fast, low-cost and efficient energy storage technologies all the more critical. Dielectric-based capacitors are promising candidates, due to the high-power range that they inherently afford, resulting from their fast charge and discharge cycles.

High-power dielectric capacitors require both high permittivity (ε_r) and breakdown field, which has made vinylidene difluoride VDF-based homo- and co-polymers the standout organic candidates. However, none of these polymers can be bio-based, which will hinder their long-term use. Most other polymers have low permittivity (ε_r ~ 2-4). A new class of promising amorphous polymers have recently emerged as alternatives, referred to as dipolar glass polymers. They combine highly polar side groups such as hydroxyl or sulfonyl groups with a high-temperature glass transition (Tg), which increases their operating temperature and decreases the dielectric losses.

Due to their high concentration of hydroxyl groups and highly tuneable Tg, poly(hydroxy urethane)s (PHUs) could meet these criteria, with the added benefits of being potentially bio-based.

A series of PHUs were synthesised from reacting diglycerol dicarbonate (DGDC) or butadiene dicarbonate (BDC) with bio-based diamines (H2N-R-NH2) by reactive extrusion. The position of the Tg was manipulated through the structure of the diamine. As a result, 0°C < Tg < 100°C were obtained.

By reacting erythritol dicarbonate with bio-based diamines, fully bio-based PHUs were synthesised with Tg ~ 50 °C, εr > 8, EB > 400 MV·m-1 and low losses (tan δ < 0.03).[1] This results in energy storage performance comparable with the flagship petrochemical materials (discharge energy density, Ue > 6 J·cm-3) combined with a remarkably high discharge efficiency (η = 85%). These bio-based PHUs thus represent a highly promising route to green and sustainable energy-storage.

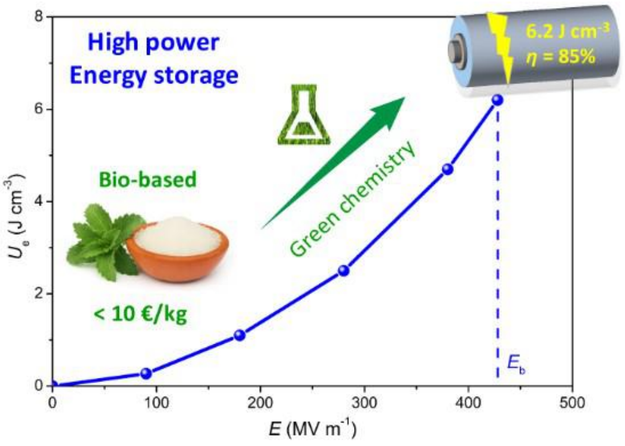


Image3.jpg

Ionic and Catalytic Photopolymerization in Hot Lithography: The bright future of 3D printing

Tuesday, 25th April - 11:00: Oral Session 5-1 - Oral

Prof. Robert Liska [1]

1. *TU Wien*

UV curing of photopolymerizable formulations has been used for more than a half century for protective and decorative coatings of paper, wood, metals or plastics. Advantages can for sure been found in the high curing speed that allows the conversion of typically (meth)acrylate-based monomers within the fraction of a second. Furthermore, a large variety of monomers is commercially available so that the mechanical properties and other polymer characteristics can be easily tuned.

In the last decade, there has been a strong demand for the curing of thicker layers or even to print arbitrarily shaped 3D cellular structures out of these materials. For the latter one, additive manufacturing technology (AMT), also called 3D printing or Rapid Prototyping, is the method of choice. Different setups are commercially available that allow the printing of photopolymerizable formulations from a simple CAD model. Laser or DLP (Digital light processing) based systems fabricate polymer parts with a feature resolution of about 10 µm. One of the major issues is that only tightly cross-linked networks are formed. These materials suffer also from an inhomogeneous polymer architecture and therefore brittle behavior. To circumvent those problems, the Hot Lithography process has been developed by Cubicure that allows processing of high molecular weight resins, leading to much tougher materials.

In contrast to radical polymerization, the kinetics of the cationic type mechanism is strongly temperature dependent. Therefore, the Hot Lithography process opens the window for entirely new classes of monomers in the field of photopolymerization in AMT. Up to now, there were no processes available for cationic photopolymerization that are used at up to 120°C. With this process, we were able to show that polyoxazolines, polyesters, polyetheresters, polycarbonates can be directly printed with this technique. Furthermore, polycondensation of pure phenolic resins is possible without bubble formation. Finally, photocatalytic cyclotrimerization of cyanatester resins gives polymers with Tg's well beyond 300°C, which has up to now been reached in light based AMT.

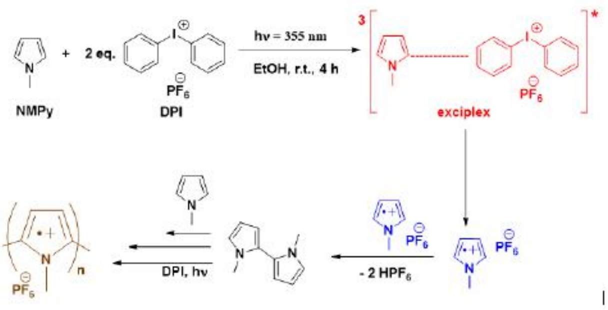
Synthesis of High Molecular Weight Poly (N-methylpyrrole) by Photoinduced Polymerization

Tuesday, 25th April - 11:30: Oral Session 5-1 - Oral

Dr. Kerem Kaya [1], ***Prof. Yusuf Yagci*** [1]

[1]. Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,

A novel and green photochemical polymerization method of *N*-methylpyrole using diphenyliodonium hexafluorophosphate photoinitiator is reported. Spectral and chromatographic characterizations revealed the formation of high molecular weight polymer (1436 kg/mol) having light absorption in the near-infrared region (~750 nm), high fluorescence emission in the visible region, high conductivity (0.062 S/cm) and good thermal stability. Powder X-ray diffractogram identified a totally amorphous polymer. According to cyclic voltammetry studies the polymer formed (PMPy) possess a relatively low electronic band gap (1.39 eV) which is very important for the (opto)electronic device applications of such materials.



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Methods of polylactide copolymer synthesis by generating tetraphenylethane inifer groups in the PLA structure.

Tuesday, 25th April - 11:45: Oral Session 5-1 - Oral

Mr. Mateusz Grabowski [1] ***, Dr. Bartłomiej Kost*** [1] ***, Dr. Melania Bednarek*** [1]

1. *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*

One of the methods of modification of polylactide (PLA), a polymer derived from renewable resources, is the introduction of other chemical structures into the PLA chain. This may be achieved (among others) by the synthesis of PLA block copolymers. Block copolymers can be synthesized by various methods. In this work, we present the synthesis of copolymers of polylactide and selected poly(vinyl monomers) (PVM) using tetraphenylethane (TPE) “inifer” groups.

TPE groups were generated in PLA-based polymer via different approaches, the starting point of which was the appropriate functionalization of 4-hydroxybenzophenone (HBP). Coupling of HBP moieties (present in low molecular weight HBP derivative or in PLA chain) under UV irradiation generated TPE groups which were able to dissociate forming radicals under moderate heating and consequently, initiate polymerization of the vinyl monomer according to Figure 1.

By applying developed by us approaches, the following PLA-based copolymers could be obtained:

1. Triblock PLA-PVM-PLA copolymer: By the initiation of lactide polymerization with HBP derivative and next UV coupling.
2. Multiblock …PLA-PVM-PLA-PVM… copolymer: By the synthesis of TPE containing diol, next coupled with PLA diol using diisocyanate.
3. PLA-based network containing reversible TPE groups with the possibility of introducing PVM sequences: By copolymerization of lactide with an epoxy compound containing HBP group and next coupling.

Acknowledgement: The study was performed within Grant NCN 2018/31/B/ST8/01969.

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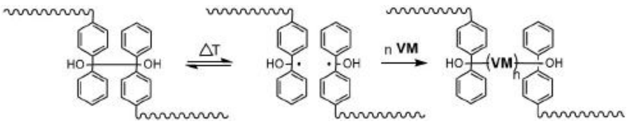

Figure 1.jpg

Buffering Volume Change in Solid-State Battery Composite Cathodes with CO2-derived Block Polycarbonate-ethers

Tuesday, 25th April - 11:00: Oral Session 5-2 - Oral

Dr. Georgina Gregory [1], ***Dr. Hui Gao*** [1], ***Prof. Charlotte Williams*** [1], ***Prof. Peter Bruce*** [1]

1. *University of Oxford*

Well-designed polymers should enable practical all-solid-state batteries.[1] Li-ion batteries based on liquid electrolytes are widely applied in consumer electronics, but greater safety and higher performance are required for widespread electric vehicle implementation.[2,3] Next-generation all-solid-state batteries meet these requirements but volume changes during charge/discharge limit real-world use.[3] Addressing this challenge by accommodating these changes, we have designed CO_2-derived polymers that are elastomeric, adhesive, ionically conductive and electrochemically stable.

Prior research has shown that incorporating elastomers such as styrenic block copolymers and rubbers into composite cathodes can improve battery capacity retention.[4] However, their low polarity results in poor adhesion to active particles limiting the effect. Polymers bearing hydrogen-bonding functionalities show stronger binding capability and further improve capacity retention but are non-conductive restricting function.[5] Here, the purpose was to incorporate poly(ethylene oxide) (PEO) as an excellent ionic conductor into ABA-type block copolymers where ‘B’ is flexible PEO and ‘A’ is rigid polycarbonate for mechanical robustness and oxidative stability. Triblock copolymers featuring various length PEO mid-segments and polycarbonate volume fractions (0.04- 0.70) were prepared by CO_2/epoxide ring-opening copolymerization. This design allowed optimization of electrochemical properties (measured by electrochemical impedance spectroscopy and voltammetry), mechanical performance (tensile testing, rheological measurements) and adhesiveness (peel tests) through phosphonic acids installed using thiol-ene chemistry.

Three lead polymer electrolytes were identified, showing good ambient ionic conductivity (> 10^{-4} S cm^{-1}), electrochemical stability (>4 V vs Li^+/Li) and elastomeric-to-plastic properties (*G*’ 0.1-67 MPa). Polymers were fabricated into full solid-state cells and showed improved capacity retention over control set-ups with elastomeric polymers, demonstrating the best performance (86% over 200 charge/discharge cycles). The block architecture was key for achieving the ‘sweet-spot’ of properties, and polymers displayed impressive chemical stability against lead inorganic solid-state electrolytes.

Figure 1. Polymer design for adhesive, ionically conductive elastomers for solid-state composite cathodes.

[1] Li *et al.*, *Adv. Energy Mater.* **2021**, 2003239.
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[3] Randau *et al.*, *Nat. Energy* **2020**, *5*, 259-270.
[4] Famprikis *et al.*, *Nat. Mater.* **2019**, *18*, 1278-1291.
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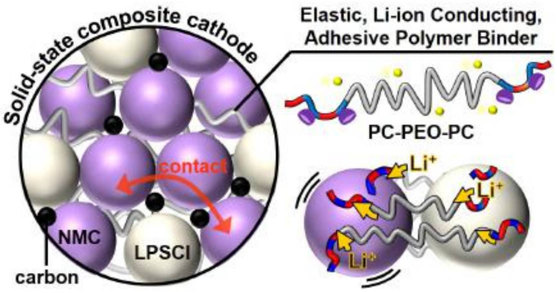

Solid-state composite cathode
Elastic, Li-ion Conducting, Adhesive Polymer Binder
PC-PEO-PC
contact
NMC
LPSCl
carbon
Li+
Li+
Li+

Figure1.jpg

Synthesis of statistical beta-amino ester copolymers and their impact on ionic conduction in solid polymer electrolytes.

Tuesday, 25th April - 11:30: Oral Session 5-2 - Oral

Prof. Tim Melander Bowden [1], ***Mrs. Orpita Majumdar*** [1]

1. Uppsala University, Department of Chemistry - Ångström Laboratory

Introduction:

Replacing the liquid electrolyte in lithium-ion batteries with polymers improves security, reduces weight, and compatibility with pure lithium anodes, thus helping to prevent dendritic growth and short circuits. Additionally, it allows for increased freedom in device design. The drawback is the poor ionic conduction, normally correlated to the segmental motion. Increasing the segmental motion (lowering the Tg) usually gives better conductivity but with the loss of mechanical properties. This presentation compares the ionic conduction in blends of homopolymers or statistical copolymers of poly(beta-amino ester) with salt (lithium-bis(trifluoromethanesulfonyl)imide) (LiTFSI).

Method:

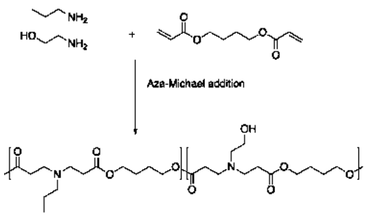
Free standing films of poly(beta-amino ester) were synthesized using the aza-michael addition of aminies (propylamine, ethanolamine or mixtures thereof) to a slight excess of a diacrylate(1,4-butanediol diacrylate), with subsequent photo-crosslinking in the presence of LiTFSI 30 wt%. Homopolymer of propyl amine and ethanol amine were produced separately. Statistical copolymers were produced by mixing the amino monomers at fixed ratios. Conductivity was evaluated using impedance spectroscopy and thermal properties studied with DSC.

Results:

All blends and preparations gave comparable free-standing films that could be further evaluated for conductivity. Impedance spectroscopy shows that the room temperature conductivity of the propyl amino ester homopolymer is 4.4E10-8 S/cm and ethanol amino ester is 1.2E-8 S/cm. Interestingly in the statistical copolymer (90% propylamine/10% ethanol amine) there is an increase in conductivinty, 5.1E-7 S/cm.

Discussion:

Solvent free production of homogenous free-standing films for use as solid polymer electrolytes were successfully produced both as homopolymers and statistical copolymers Impedance spectroscopy revealed that the homopolymer of propylamine is better than that of ethanolamine. However, it is striking that the statistical copolymers of propyl and ethanol amine e.g. 90/10 show a 12 and 42 times better room temperature conductivity than respectively homopolymer. Intuitively the homopolymers should represent upper and lower where the conductivity of statistical compositions should fall within. This positive deviation shows the potential of materials that mix functionalities as host materials in SPEs. We believe this structural effect can be understood as either a better solvation of salt or the tuning of the coordinating groups (amino and hydroxy ratio) around ions improving its mobility.



Azamichael.png

3D printing of urethane based materials by thiol-ene photopolymerization

Tuesday, 25th April - 11:45: Oral Session 5-2 - Oral

Ms. Jessica Mauriello [1]***, Dr. Jean-Louis Clément*** [1]***, Dr. Luca Pasquini*** [2]***, Dr. Yohann Guillaneuf*** [1]***, Dr. Didier Gigmes*** [2]

1. *Institut de Chimie Radicalaire - Aix Marseille Univ, CNRS,* ***2.*** *Aix-Marseille Université*

Thiol-ene photopolymerization has many advantages, including a rapid, solvent-free and high-rate polymerization. On top of that, the resulting materials are often transparent and exhibit excellent mechanical properties. In addition, its tolerance to oxygen and its applicability to a wide range of monomers make it an attractive tool for 3D printing application. Many chemistries have been studied for the backbone of these thiol-ene photopolymers including ethylene glycol, isocyanurate, or acetal.[1] However, only few works describe the use of urethane derivatives and even less involving 3D printing.[2,3] Knowing the high potential of both urethane based materials and 3D printing it is highly desirable to propose a methodology to overcome these limitations.

In this communication, the synthesis and formulation of novel allyl-urethanes for DPL 3D printing by thiol-ene photopolymerization will be presented. The thermal and mechanical properties of the printed materials will be also discussed.

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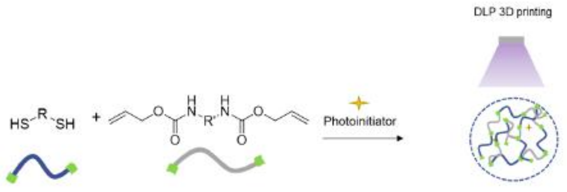
3. Warner, J. J. *et al.* 3D printable non-isocyanate polyurethanes with tunable material properties. *Polym Chem* **10**, 4665–4674 (2019).



3d printing of urethane based materials by thiol-ene photopolymerization.png

POLYMERS FROM RENEWABLE RESOURCES FOR NOWADAYS ENGINEERED MATERIALS

Tuesday, 25th April - 11:00: Oral Session 5-3 - Oral

Dr. Valeria Harabagiu [1] ***, Dr. Petrisor Samoila*** [1]

1. *"Petru Poni" Institute of Macromolecular Chemistry, Iasi*

Polymers obtained from regenerable resources are more and more reconsidered as sustained substitutes of the vanishing fossil materials. In this context, the presentation deals with cyclic oligosaccharides, polysaccharides, keratinous materials or biopolymer-inorganic (nano) particle composites engineered for bio-oriented (e.g. materials targeted for efficient drug delivery systems), high-tech (electronics, non-conventional energy production) or environment (sorbents) application. Details on the proposed preparation methods (including energy efficient processes, such as microwave and/or ultrasonic treatments) and on the structure-property relationships will be given. End-use properties and application of the prepared materials will be also discussed [1-8].

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Crosslinked polylactide-based materials containing dynamic covalent bonds

Tuesday, 25th April - 11:30: Oral Session 5-3 - Oral

Dr. Melania Bednarek [1]***, Dr. Katarina Borska*** [2]***, Prof. Andrzej Pawlak*** [1]***, Dr. Miroslav Mrlik*** [3]***, Dr. Josef Osicka*** [3]***, Ms. Danila Gorgol*** [3]

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Among the various methods of improving the properties of polylactide, a polyester obtained from renewable resources, chemical crosslinking can be found. However, permanent crosslinking limits PLA-based polymer processing. Thus, attempts are made to synthesize a crosslinked polylactide material that would contain in its structure covalent bonds capable of dissociating reversibly under appropriate stimuli (Figure 1).

The presented work includes several approaches to the preparation of crosslinked polylactide containing reversible covalent bonds. Disulfide and tetraphenylethane groups were applied as groups able to thermally dissociate. By performing thermal, mechanical, and rheological studies, it is shown that the obtained PLA-based materials are dynamic networks and can be processed. This ability was proved by repairing and 3D printing experiments.

Acknowledgment: The study was performed within Grant NCN **2018/31/B/ST8/01969.**

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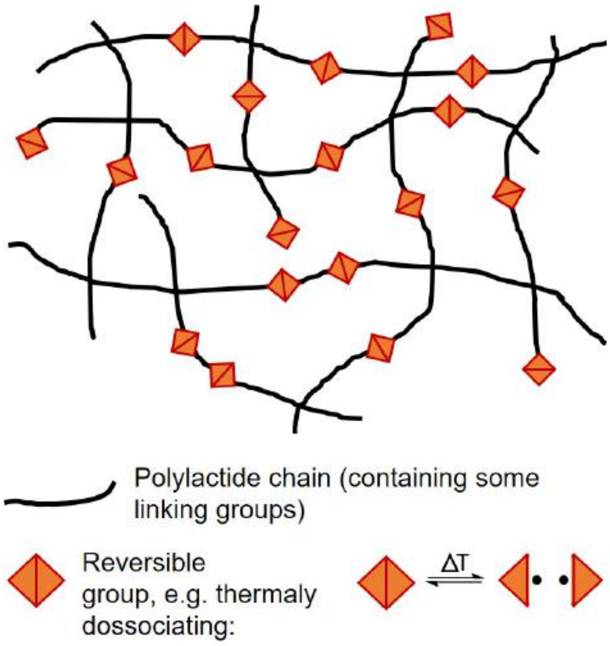
Polylactide chain (containing some linking groups)
Reversible group, e.g. thermaly dossociating:
ΔT

Figure 1.jpg

Photochemistry: Towards the Synthesis of New Innovative Biomaterials

Tuesday, 25th April - 11:45: Oral Session 5-3 - Oral

Prof. Davy-Louis Versace [1]

1. *ICMPE-CNRS*

Nosocomial infections are infections contracted in health care establishments such as hospitals and clinics and affect up to 750,000 people per year in France. The Institut National de Veille Sanitaire (InVS) estimates that in France in 2012, one out of every 20 hospitalised patients was affected. The Ministry of Health has counted more than 4,000 deaths each year in France due to these nosocomial infections. Today, the World Health Organisation does not hesitate to speak of a “global challenge for patient safety”. But beyond the health aspect, the problem is also economic. In France alone, the additional costs generated by this public health problem are estimated at more than 2 billion euros annually. A significant proportion of these diseases are caused by three main micro-organisms, including bacterial strains such as *Escherichia coli*, *Staphylococcus aureus* and *Pseudomonas aeruginosa* (source 2012 from the InVS). The treatment of choice for these infections is the use of antibiotics. Unfortunately, bacteria repeatedly subjected to these treatments develop mechanisms of resistance: mutation of genes, secretion of compounds that inactivate antibiotics. Thus, these infections are becoming increasingly difficult to eradicate and require the development of new treatments.

In this presentation, the synthesis of new antibacterial materials, among others, by photochemistry, from new monomers or photo-initiators from bio-resources, will be presented while respecting the principles of green chemistry. The different strategies for obtaining and characterizing these materials will be described in detail and concern:

- The synthesis of new photo-initiators [1, 2] from bio-resources and monitoring their reactivity by classical spectroscopic techniques such as transient absorption, electron paramagnetic resonance and infrared spectroscopy.
- The photochemical modification of polymeric substrates [3] using the “grafting-from” process under light irradiation.
- The synthesis of organic/inorganic [4] bio-based coatings (metallic or metallic oxides) under irradiation with bactericidal properties.
- The development of a new strategy to fight against bacteria: photodynamic inactivation of bacteria [5] using natural dyes that generate reactive oxygen species (ROS) under illumination.
- The development of new 3D printing and photoactive materials [5] from bio-sourced photo-initiators.

Design of phenotypic anti-inflammatory nanomedicines: synthesis of a poly(2-methacryloyloxyethyl phosphorylcholine)-poly(propylene fumarate) copolymer

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Ms. Claudia Codano [1], ***Mr. Peter Pfeifer*** [1], ***Dr. Giuseppe Battaglia*** [1]

1. *Institute for Bioengineering of Catalonia (IBEC), The Barcelona Institute of Science and Technology (BIST), 08028, Barcelona*

In recent decades, biodegradable synthetic polymers have been largely studied for many biomedical applications. Among these, poly(propylene fumarate) (PPF) has been investigated for its wide versatility of usage, from bone tissue engineering to drug delivery and regenerative medicine. PPF is a linear polyester characterised by biocompatibility and biodegradability. Upon hydrolysis of its ester linkages, the polymeric backbone releases propylene glycol and fumarate as degradation products in the cell milieu.

The challenge presented herein is to prove if such fumarate metabolites could mimic the anti-inflammatory properties of dimethyl fumarate (DMF), a drug already approved for the treatment of autoimmune disorders such as multiple sclerosis and psoriasis.

We designed a poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC)-PPF copolymer that combines the anti-inflammatory features of fumarate derivatives with the superselective targeting properties of PMPC towards macrophages and dendritic cells, the most important actors in managing inflammation[1]. The self-assembling behaviour of PMPC-PPF copolymer into a supramolecular multivalent scaffold transposes the anti-inflammatory properties of DMF to the nanoscale, making the nanoparticle the nanodrug itself and physically driving its activity through phenotypic targeting.

PPF was synthesised by step-growth polymerisation of its diester intermediate, bis(hydroxypropyl) fumarate, to accomplish this goal in a 2-step synthesis. PPF was either functionalised with 4-cyanopentanoic acid dithiobenzoate (CPADB) for reversible addition-fragmentation chain-transfer (RAFT) polymerisation or with 2-Bromoisobutyl-bromide for atom transfer radical polymerisation (ATRP) of PMPC monomer, monitoring the polymerisation to achieve the desired length of PMPC chains. Each polymer product was analysed by gel permeation chromatography (GPC) and nuclear magnetic resonance (NMR) to ensure its quality and conversion grade. After the copolymer characterisation, PMPC-PPF micelles were obtained by solvent-switch and characterised by Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM) to evaluate, respectively, their hydrodynamic diameter and morphology, aiming for a homogeneous population.

PMPC-PPF micelles were then tested on differentiated monocytes to evaluate their cytotoxicity and anti-inflammatory properties. Preliminary studies revealed a reduction in the expression of main pro-inflammatory cytokines both in pro-inflammatory and undifferentiated phenotypes, paving the way for further analysis to confirm the potentiality of this PPF-based copolymer.

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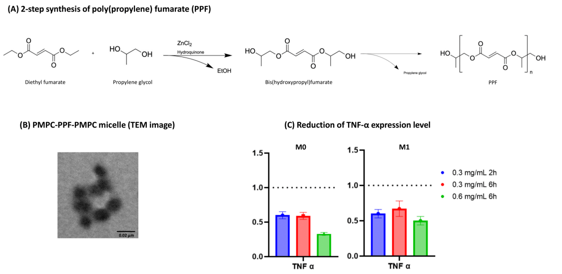

Fig.1 – **(A)** Synthesis of PPF via step-growth polymerisation of bis(hydroxypropyl)fumarate intermediate. **(B)** TEM image of PMPC-PPF-PMPC micelles, stained with phosphotungstic acid (PTA). **(C)** qPCR quantification of TNF-α expression in M0 macrophages (left-hand side) and M1 macrophages (right-hand side) treated with different concentrations of PMPC-PPF-PMPC micelles for 2h or 6h, compared to untreated cells. Data normalised to GAPDH expression, ΔΔCT method.

Pmpcppfpmpc micelles codano.png

Bacteria friendly chitosan microspheres formulation for agriculture

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Ms. Lorelei Meyer–Déru [1], ***Prof. Ghislain David*** [1], ***Dr. Remi Auvergne*** [1]
1. *CNRS ICGM*

The intensive use of synthetic fertilizers in agriculture disturbs and destroys soil microbiota determining farms sustainability [1]. An alternative to these fertilizers is possible through compounds encapsulation, and particularly bacteria. *Bradyrizhobia* are proteobacteria capable of symbiosis with *Fabaceae* plants. Throughout this symbiosis, bacteria provide plants with nitrogen in return for sugars [2]. Encapsulation of these bacteria facilitates and democratizes their transport and their use, thus optimizing agricultural yields while respecting the environment. Chitosan, a biosourced polysaccharide derived from chitin, is biocompatible and biodegradable (**A**). Its mechanical stability as well as its chemical properties allowing its functionalization make this polymer a material of choice for microorganisms encapsulation.

Post-crosslinking of emulsion-formed droplets is a simple and efficient method to obtain microspheres. This work aims to adapt this method to the encapsulation of bacteria by studying the impact of chitosan molar mass and concentration. Moreover, some parameters of the emulsion were modified such as the nature of the hydrophobic phase or the temperature of the emulsion. In the literature, chitosan crosslinking is often performed with glutaraldehyde [3]. However, this is not compatible with bacteria encapsulation because of glutaraldehyde high toxicity. Biocompatible alternative to glutaraldehyde have been developed using magnesium sulfate. The sulfate ions allow the formation of ionic bonds with chitosan protonated amines. Biosurced crosslinker synthesis derived from vanilline were also tested as potential biocompatible crosslinker.

Subsequent to best parameters selection, the encapsulation efficiency as well as release characteristics of the microspheres were studied by encapsulating patent blue (**B**).

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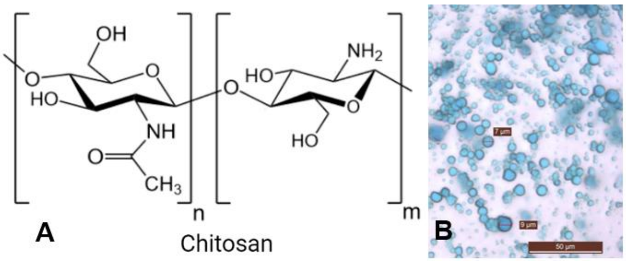


Chitosan as encapsulation material 2.png

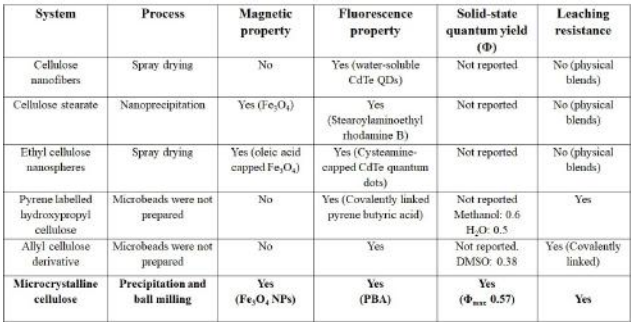
Dual responsive cellulose microspheres with high solid-state fluorescence emission

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Prashant Yadav [1]***, Dr. Kadhiravan Shanmuganathan*** [1]

1. *CSIR-National Chemical Laboratory*

Materials that respond to multiple stimuli, such as a magnetic field and light, are attractive for security and medical diagnostic applications. One of the major challenges in dual functional microspheres is that the presence of magnetic nanoparticles can quench fluorescence emission. Also, there is a probability of solid-state quenching due to the proximity of the fluorophore. We report here a facile approach to prepare cellulose microspheres with high solid-state fluorescence using 40% tetrabutylammonium hydroxide (TBAH). The fluorescence quenching effect due to the presence of Fe_3O_4 nanoparticles and solid-state quenching due to the aggregation of fluorophore was systematically investigated. Microspheres with a detectable magnetic response and fluorescence quantum yield as high as 0.57 (FMB 414) was obtained by optimizing the reaction conditions. Such a high quantum yield has not been reported before for dual stimuli-responsive fluorescent microspheres. The magnetic and fluorescent properties were found to be durable even after multiple washing cycles. These dual responsive cellulose microspheres can be added as security features to authenticate documents such as passports, degree certificates, currency notes, financial documents etc.



System	Process	Magnetic property	Fluorescence property	Solid-state quantum yield (Φ)	Leaching resistance
Cellulose nanofibers	Spray drying	No	Yes (water-soluble CdTe QDs)	Not reported	No (physical blends)
Cellulose stearate	Nanoprecipitation	Yes (Fe_3O_4)	Yes (Stearoylaminoethyl rhodamine B)	Not reported	No (physical blends)
Ethyl cellulose nanospheres	Spray drying	Yes (oleic acid capped Fe_3O_4)	Yes (Cysteamine-capped CdTe quantum dots)	Not reported	No (physical blends)
Pyrene labelled hydroxypropyl cellulose	Microbeads were not prepared	No	Yes (Covalently linked pyrene butyric acid)	Not reported Methanol: 0.6 H_2O: 0.5	Yes
Allyl cellulose derivative	Microbeads were not prepared	No	Yes	Not reported. DMSO: 0.38	Yes (Covalently linked)
Microcrystalline cellulose	**Precipitation and ball milling**	**Yes (Fe_3O_4 NPs)**	**Yes (PBA)**	**Yes (Φ_{max} 0.57)**	**Yes**

Comparison table.jpg

Eugenol-based dual-curing system with dynamic exchangeable bonds

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

***Mr. Adria Roig* [1], *Prof. Xavier Ramis* [2], *Dr. Silvia De la Flor* [3], *Prof. Angels Serra* [1]**

__1.__ Universitat Rovira i Virgili (URV), Department of Analytical Chemistry and Organic Chemistry, C/Marcel·lí Domingo 1, 43007 Tarragona, Spain, __2.__ Universitat Politècnica de Catalunya, Thermodynamics Laboratory, ETSEIB Av. Diagonal, 08028, Barcelona, __3.__ Universitat Rovira I Virgili (URV), Department of Chemical Engineering, Av. Països Catalans 26, 43007 Tarragona, Spain

Introduction

Dual-curing is a versatile methodology to prepare thermoset materials. This procedure consists of two sequential or simultaneous polymerization processes triggered by external stimuli like heat or UV light [1]. Despite the good mechanical performance of thermosets, their synthesis produces harsh environmental problems due to their impossibility to be recycled. For this reason, covalent adaptable networks (CAN's) have attracted the interest of the academic world. These materials contain dynamic covalent bonds that, through reversible chemical processes triggered by external stimuli, can change the shape of the final network enabling its reprocessability. [2]. Herein, we report the study of the curing reaction, the thermomechanical properties, and the vitrimeric behavior of a novel series of materials prepared by a dual-curing procedure using a synthesized acrylate-epoxy-eugenol (AEEU) monomer cured with different amines without the presence of a catalyst.

Methods

The characterization techniques used to study the monomer synthesized, the materials prepared and their thermomechanical behavior were ^{1}H and ^{13}C NMR spectroscopy, DSC, FTIR, and DMTA.

Results and Discussion

The starting monomer was synthesized by acrylation of eugenol and further epoxidation of the allyl group. The presence of acrylate and epoxy groups in the monomer enables the dual-curing being the first step an aza-Michael reaction and a second epoxy-amine reaction. The sequentiallity of the curing was confirmed by DSC and allowed to achieve viscous intermediate materials. The combination of two different amines (Cystamine and JeffD230) allows tailoring the characteristics of the vitrimers. All materials presented T_{tand}'s higher than room temperature and low FWHM.

The presence of disulfide groups and/or ß-aminoesters in the final material enables the stress relaxation of the network at relatively low temperatures in 10 min. The study of the relaxation at several temperatures showed an Arrhenius-type dependence of the viscosity with the temperature.

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Synthesis of cyclic oligo(t-butyl glycidyl ether): a suitable macroinitiator for cyclic-core hyperbranched polyglycidol

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Carlo Andrea Pagnacco [1] ***, Mr. Eric Gomez*** [1] ***, Prof. Fabienne Barroso-Bujans*** [1]

1. *Donostia International Physics Center*

Electrophilic zwitterionic ring expansion polymerization (eZREP) of glycidol with $B(C_6F_5)_3$ represents a direct access for the preparation of branched cyclic polyglycidol (bcPG).[1] The cationic mechanism of polymerization and the AB_2 nature of the monomer cause that the reaction proceed by activated chain end (ACEM) and activated monomer mechanism. The result is a polymer characterized by a cyclic core and branches as side chains, without control over the cyclic-core size. Herein, we propose *t*-butyl glycidyl ether (*t*-BGE) as a monomer for eZREP, where the formation of branches is hampered while cyclization is maintained. By cleavage of *t*-Bu groups, cyclic polyglycidols (cPG)s of different molecular weights can be generated. Finally, the cPG chains can be used as macroinitiators for the formation of cyclic-core hyperbranched PGs with a higher control of the topology than eZREP of glycidol.

In this study, the above-mentioned hypothesis is demonstrated. We started by evaluating the optimal experimental conditions to produce cyclic poly(*t*-BGE) with high topological purity. We observed that if cyclization of all active zwitterionic chains is not completed, the growth of non-cyclic byproducts takes place by chain propagation and termination with accidental water, as well as by transfer to monomer reactions.[2] The formation of cyclic oligo(*t*-BGE) with X_n ~ 6 was confirmed by MALDI-ToF MS. After cleaving the *t*-Bu side groups in acidic conditions, the obtained cPG was deprotonated with NaH to be used as macroinitiator for the anionic ring opening polymerization of glycidol. As a result, cyclic-core hyperbranched PGs with M_n ~ 8 kDa and degree of branching of ~ 0.6 were generated. Physical properties of these new series of structures are compared with those of star-core hyperbranched polyglycidol[3] and bcPG generated by eZREP of glycidol.[1]

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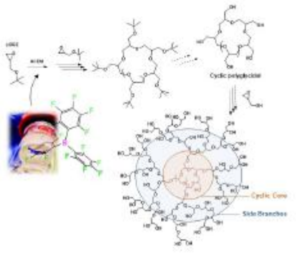

Image abstract paris2023.jpg

Evaluation of different reaction conditions for branched cyclic polyglicidol production with [B(C6F5)3].

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Eric Gomez [1]***, Mr. Carlo Andrea Pagnacco*** [1]***, Prof. Fabienne Barroso-Bujans*** [1]

1. *Donostia International Physics Center*

Our recent studies have revealed that the polymerization of glycidol (Gly) using tris-(pentafluorophenyl)borane [$B(C_6F_5)_3$] as a catalyst in bulk conditions leads to a promising result in the production of large amounts of branched cyclic polyglycidol (bcPG) structures of about 10 kDa (M_n).[1] In that work we observed an abrupt molecular weight growth at longer reaction times, which was explained by the occurrence of transfer reactions leading to molecular weight increase such as the fusion of active chains (ring fusion) and branching (reaction of a hydroxyl side group with an active chain).

In present investigation, we studied the kinetics of polymerization of Gly in solution by ^{1}H and ^{19}F NMR at different temperatures following previous study of the polymerization of Gly with $B(C_6F_5)_3$ in toluene,[2] where precipitation of bcPG occurs during reaction. We monitored a fast initial reaction step (several minutes), followed by a slower sedimentation process in the NMR tube where the polymer is phase separated from the toluene solution to form a gel-type phase. In this process, ^{1}H NMR signals of the monomer completely disappear while 30 % of the initial ^{19}F NMR signals of $B(C_6F_5)_3$ remained in solution, as expected from previous work.[2] Similar kinetics results were observed when water was delivery added to the reaction media, with the exception that larger amounts of non-cyclic structures are generated. Interestingly, the molecular characteristics of phase separated bcPG were identical as those of bcPG obtained in bulk conditions, indicating that the polymerization continues in the sediment phase and that the fast initiation occurring in solution has a minimum effect on the whole polymerization reaction. Our study can serve as a guide for the generation of bcPG in different reaction media.

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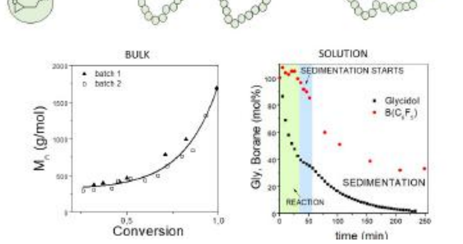

Glycidol polimerization scheme and reaction plots in bulk and solution.jpg

Covalent polymer networks with tunable properties composed of poly(2-isopropenyl-2-oxazoline) and selected aliphatic polyesters.

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Bartosz Kopka [1] ***, Dr. Bartłomiej Kost*** [1] ***, Prof. Andrzej Pawlak*** [1] ***, Dr. Agnieszka Krupa*** [2] ***, Ms. Agata Tomaszewska*** [2] ***, Dr. Marek Brzezinski*** [1] ***, Dr. Malgorzata Basko*** [1]

1. *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland,* ***2.*** *Department of Immunology and Infectious Biology, Institute of Microbiology, Biotechnology and Immunology, Faculty of Biology and Environmental Protection, University of Lodz, Banacha 12-16, Lodz 90-237*

Polymer networks, owing to their three-dimensional structure and specific properties subsequent from this architecture are an essential class of material in polymer chemistry.[1] The two-component segmented networks comprising covalently joined hydrophilic and hydrophobic segments show the unique capacity for swelling in both aqueous and organic media.[2] This feature makes networks suitable for a wide range of applications including separation techniques, pharmacy or biomedicine.[3]

To address the issue of the facile and efficient synthesis of segmented covalent networks, we studied the cross-linking process of reactive polymeric components in a system free from any catalyst and side products. To achieve the direct formation of amphiphilic networks with the structure presented in Figure 1a, an addition reaction was performed between the polyesters containing carboxyl terminal groups (HOOC-PLA-COOH or HOOC-PCL-COOH) with pendant groups distributed along poly(2-isopropenyl-2-oxazoline) (PiPOx) chains.

The obtained results demonstrated that this straightforward method enabled the synthesis of amphiphilic networks with desired composition and shape (Figure 1b-f) in simple reaction conditions (insensitive to water or oxygen) and without specialized devices. Obtained networks were characterized in terms of swelling degree in selected solvents, mechanical properties and biocompatibility.

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Acknowledgments: Financial support from the National Science Centre, Poland, Grant No. 2020/37/B/ST5/03302 is gratefully acknowledged

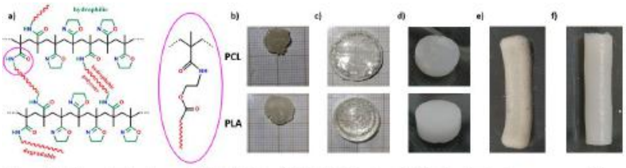


Figure 1. Schematic structure of PiPOx-*l*-PLA and PiPOx-*l*-PCL networks (a). The physical appearance of dry and swollen nonporous networks (b, c). Manipulating of the porous networks shape (d-f).

Bartosz kopka fig 1.jpg

Preparation of Functionalized Polyfarnesenes and their Physical Properties

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Dr. Taejun Yoo [1]

1. *TotalEnergies Cray Valley*

There is a growing interest in modern polymer chemistry toward the development of bio-based and biocompatible polymers as well as renewable alternatives to petrochemical-based materials. Trans-β-farnesene (farnesene, or BioFene™ from Amyris, Inc.) produced via fermentation and synthetic biology is a sustainable alternative to a broad range of petroleum-sourced feeds, and its conjugated diene structure has been shown to be a drop-in monomer for a range of polymerization chemistries, including anionic polymerization. TotalEnergies Cray Valley has developed farnesene-based anionic polymers, including mono- and di-functionalized oligomers. Due to the highly branched "bottlebrush" structure, farnesene-based polymers shows interesting rheological properties compared with linear analogs.

The anionic polymerization of trans-β-farnesene, the functionalization and modification of the oligomers, and the resulting physical properties will be discussed. Potential applications which take advantage of the new structure-property relationships will be included.

Anionic polymerization of farnesene.png

Continuous-flow block copolymer nanoparticle synthesis via telescoped RAFT solution and dispersion polymerisation

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Peter Pittaway [1], ***Mr. Ghadir Ghasemi*** [1], ***Dr. Stephen Knox*** [1], ***Dr. Olivier Cayre*** [1], ***Prof. Nikil Kapur*** [1], ***Dr. Nicholas Warren*** [1]

1. *University of Leeds*

Introduction

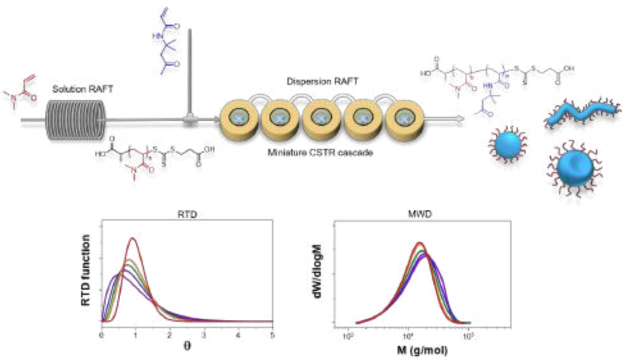
Precisely defined block copolymer nanoparticles can be prepared using reversible-deactivation radical polymerisations (RDRP) such as reversible-addition fragmentation chain transfer (RAFT) polymerisation. Lab-scale synthesis of these high-value materials can benefit from the improved economy, safety, and scalability of continuous-flow reactors. However, more traditional tubular reactors can be problematic for reactions involving multiple phases due to a lack of mixing and their susceptibility to clogging. The present work evaluates the performance of a miniaturised continuous stirred tank reactor (CSTR) cascade for the preparation of (poly)*N,N*-dimethyl acrylamide (PDMAm)-*b*-(poly)diacetone acrylamide (PDAAm) block copolymer nanoparticles.

Methods

The CSTR cascade was first characterised in the context of polymer synthesis by evaluating the mixing and heat transfer behaviour during synthesis of PDMAm homopolymers. The same synthesis was performed in configurations comprising different numbers of CSTRs to understand the importance of the characteristic residence time distribution (RTD) on polymer properties. For nanoparticle synthesis, a series of block copolymers were prepared by block extending a PDMAm macromolecular chain transfer agent (macro-CTA) with diacetone acrylamide (DAAm) both in the CSTR cascade and in an equivalent batch reaction for comparison. Finally, a telescoped tube-CSTR cascade configuration was applied to sequentially prepare the macro-CTA *via* solution RAFT polymerisation in the tube followed by block extension *via* dispersion RAFT polymerisation in the miniature CSTR cascade.

Results & Discussion

Despite changes in viscosity, the CSTR cascade offered reliable active mixing for the reactions studied, however the nature of mixed flow synthesis directly influenced the product properties. Molecular weight distributions (MWDs) were broad due to the RTD, but could be narrowed by increasing the number of CSTRs. Nanoparticles made in the CSTR cascade were found to have different macroscopic behaviour versus the batch equivalents, with different particle properties arising from the same chemistry. Applying an upstream tubular reactor enabled block copolymer nanoparticles to be prepared from their monomers in a single process, eliminating the manual handling required between stages for additional safety and convenience. These results indicate the potential of the platform for efficiently exploring the synthesis of similar products on a laboratory scale.



Telescoped-np-synthesis.png

“Super-hydrophilic” poly(2-oxazoline)

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Dr. Somdeb Jana [1], ***Mr. Milan Roels*** [1], ***Dr. Meike Leiske*** [2], ***Dr. Yann Bernhard*** [1], ***Prof. Bruno De Geest*** [1], ***Prof. Richard Hoogenboom*** [3]

1. *Ghent University,* ***2.*** *University of bayreuth,* ***3.*** *U Genth*

Avoiding non-specific interaction is one of the most important key features required by the nanoparticles (NP) for wide range of *in-vivo* applications from drug delivery to diagnostics. “Super-hydrophilic” polymers generally possess strong non-fouling characteristics and therefore, has the potential to avoid non-specific/unwanted interactions with blood proteins when applied *in vivo* for drug/gene delivery to diagnostics. Poly(2-oxazoline)s represents a special class of bio-inspired polymers with multiple applications, especially in the field of polymer therapeutics. The straightforward access to the wide verities of side chain and chain end functional poly(2-oxazoline)s via cationic ring-opening polymerization (CROP) of various 2-substituted-2-oxazoline monomers as well as post-polymerization modification strategy, in combination with their thermo-responsive, biocompatible, stealth and protein repellent properties of water soluble homologues enables the construction of highly functional poly(2-oxazoline) materials.

In this contribution, we revitalize a protected alcohol functionalized 2-oxazoline monomer, 2-acetoxymethyl-2-oxazoline, highlighted almost fifty-five years ago and explore the possibility of making “super-hydrophilic” poly(2-oxazoline) for biomedical applications. The synthesis of 2-acetoxymethyl-2-oxazoline monomer and its interesting cationic ring-opening polymerization kinetics phenomenon is demonstrated. Subsequently, controlled hydrolysis of the resulting poly(2-acetoxymethyl-2-oxazoline) (PAcOMeOx) generates alcohol (-OH) side chain functional poly(2-hydroxymethyl-2-oxazoline) (PHOMeOx) and their relative hydrophilicity were analysed and compared with previously reported most hydrophilic poly(2-oxazoline)s such as poly(2-methoxymethyl-2-oxazoline) and poly(2-methyl-2-oxazoline), revealing that PHOMeOx is the most hydrophilic poly(2-oxazoline) reported to date. Finally, cytocompatibility of the polymers with MDA-MB-231 breast cancer cells was explored where all the polymers appeared to be noncytotoxic. Most importantly, strong anti-fouling properties of intensely hydrophilic PHOMeOx against serum protein was confirmed from the cell association studies. The hydroxyl side chains provide a handle for efficient conjugation of drugs via a hydrolysable ester linker, enabling release of the drug in time. Therefore, such “super-hydrophilic” and anti-fouling PHOMeOx might lead to an interesting progress in the area of drug/nucleic acid delivery application.

Orthogonal Two Colour Switching of Single-Chain Nanoparticles

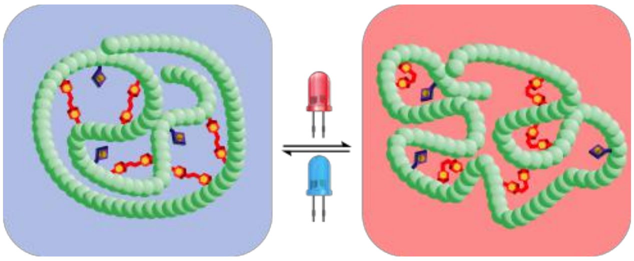
Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Aidan Izuagbe [1]***, Dr. Vinh X. Truong*** [1]***, Dr. Bryan Tuten*** [1]***, Prof. Peter Roesky*** [2]***, Prof. Christopher Barner-Kowollik*** [1]

1. *School of Chemistry and Physics, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia,* ***2.*** *Karlsruhe Institute of Technology, Institute for Inorganic Chemistry, Karlsruhe, 76131, Germany*

Linear polymer chains intramolecularly folded into discrete particles are known as single-chain nanoparticles (SCNP). Taking inspiration from enzymes which display highly selective and efficient catalysis afforded by precise polymeric intramolecular folding, SCNPs imbued with catalytic activity afford bio-inspired catalysts that display distinct catalytic properties as a result of their polymeric environment. The ability to fabricate catalytically active single-chain polymer nanoparticles, which can dynamically change their secondary and tertiary structure, is the next frontier in functional SCNP design. We introduce a single-chain nanoparticle system, whose internal structure can be dynamically adjusted by two visible orthogonal colours of light ($\lambda_{1,\ \mathrm{max}}$ = 620 and $\lambda_{2,\ \mathrm{max}}$ = 415 nm). We construct linear polymer chains via nitroxide-mediated radical polymerization based on styrene building blocks, decorated with pendant phosphine ligands complexed with catalytically active gold motifs, and collapse the chain with variable amounts of photoresponsive visible light adaptive azobenzene units (13 and 23 mol %), enabling an in-particle *cis/trans* isomerization. The initial compaction due to the intramolecular cross-linking step is highly dependent on the number of cross-linking points in the initial chain and can reduce the hydrodynamic radius of the chains by up to approximately 44% for the highest azobenzene cross-linker density. The degree of post-folding reversible light-induced compaction is dependent on the number of azo-benzene units in the chain and is associated with a distinct visible reversible change in UV absorptivity of the SCNP when switching irradiation wavelength. The reversible in-particle *cis/trans* isomerization is also well observable by ^{1}H NMR spectroscopy, indicating an in-particle light-induced polarity change. It is envisioned that the light-driven dynamically and reversibly altered particle core morphology and structure may find usage to reversibly restrict access into the SCNPs.

Izuagbe, A. E.; Truong, V. X.; Tuten, B. T.; Roesky, P. W.; Barner-Kowollik, C. Visible Light Switchable Single-Chain Nanoparticles. *Macromolecules* **2022**, *55* (20), 9242–9248. https://doi.org/10.1021/acs.macromol.2c01467.



Switchable single-chain nanoparticle.png

RAFT-mediated copolymerization of acrylic acid in aqueous dispersion

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Clément Debrie **[1], *Dr. Olivier Colombani*** **[2], *Dr. François Stoffelbach*** **[1], *Dr. Simon Harrisson*** **[3], *Prof. Jutta Rieger*** **[4]**

1. *Sorbonne University, Parisian Institute for Molecular Chemistry (IPCM), Polymer Chemistry Team, Paris,,* ***2.*** *Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS Le Mans Université, France,* ***3.*** *Laboratoire de Chimie des Polymères Organiques (LCPO), UMR 5629 CNRS Université de Bordeaux, Pessac,* ***4.*** *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Equipe Chimie des Polymères, 75252 Paris, France*

The radical (co)polymerization of acrylic acid (AA) and hydrophilic monomers has been widely studied in aqueous solution[1–3]. Because of the intrinsic lower reactivity of the acrylate ion compared to protonated AA, combined with the effects of electrostatic repulsions, the reactivity of AA generally decreases when the pH is increased. With hydrophobic monomers in aqueous dispersion, the copolymerization of AA is more challenging as the highly water-soluble AA monomers must diffuse into the hydrophobic micellar cores where the reaction takes place[4]. This could prevent the insertion of AA into hydrophobic polymer chains and favor the formation of PAA homopolymer in the aqueous phase.

In this work, we show that in typical RAFT-mediated dispersion polymerizations, the reactivity of AA is greatly reduced when the pH is increased, not only because of the intrinsic difference in reactivity between acrylate ion and protonated AA, but also due to the aggregation of the polymer chains, which creates a physical barrier to the copolymerization of ionized AA. This allows copolymers of distinct microstructures to be synthesized from the same monomer feed, simply by varying the pH of the polymerization. In particular, block-like copolymers could be obtained in one-pot by changing the pH of the reaction medium *in situ*. The thermal properties of such copolymers in water were also studied, and a strong impact of the microstructure of the chains on their thermo-responsiveness was demonstrated[5].

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A Study Of The Partial Acidic Hydrolysis Of Poly(2-alkyl-2-oxazoline)s

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

***Mr. Emiel Pattyn* [1], *Prof. Richard Hoogenboom* [2], *Dr. Maarten Mees* [3], *Dr. Valentin Victor Jerca* [4]**

1. *Ugent,* ***2.*** *U Genth,* ***3.*** *KU Leuven,* ***4.*** *Smart Organic Materials Group, “Costin D. Nenitzescu” Institute of Organic and Supramolecular Chemistry, Romanian Academy, 202B Splaiul Independentei, 060023 Bucharest*

The Partial acidic hydrolysis of poly(2-alkyl-2-oxazoline)s (PAOx) leads to the formation of PAOx-polyethylenimine (PAOx-PEI) copolymers that can be used in various applications and can serve as a reactive platform for the synthesis of functional PAOx.[1] Various studies have been reported on the synthesis and structure of these PAOx-PEI cpoolymers, but to date the exact structure of the PAOx-PEI remains unknown. In more detail, it remains uncertain whether the hydrolysis of the amide containing side chains occurs randomly along the PAOx chain or if block like regions are formed (see Figure). The latter is implied by our previous work,[2,3] but conclusive evidence has never been provided, while Perrier and coworkers recently indicated that the hydrolysis might be random. [4] Nevertheless, this question on the hydrolysis mechanism is not trivial since the distribution of the PEI units will control the distribution of the functional groups upon further reaction. Moreover, it is also not known whether the PEI distribution is of crucial importance for certain applications, such as gene delivery.

To understand this hydrolysis of PAOx, we report detailed ^{1}H and ^{13}C NMR as well as HMBC and HSQC NMR spectroscopy of a poly(2-ethyl-2-oxazoline) (PEtOx), a partially hydrolysed PEtOx-PEI copolymer and a fully hydrolysed PEI. To interpret these complicated copolymer NMR spectra, three model compounds (see Figure) have also been synthesized, which resemble different possible compositions of EtOx-EI units along the polymer chain. The same detailed ^{1}H, ^{13}C NMR, HMBC and HSQC NMR spectroscopy measurements were performed on these model oligomers enabling the full assignment and interpretation of the complex spectra of the PAOx-PEI copolymers. This in depth assignment revealed the formation of block-like PEI domains at a relatively low degree of hydrolysis of the PAOx. Hence, it is postulated that block like regions are formed through the ‘neighboring group effect’, meaning that the presence of a protonated amine facilitates the hydrolysis of a PAOx unit immediately neighboring the parent PEI units.

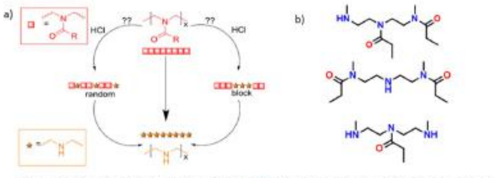


Figure 1 a) Schematic overview of the acidic hydrolysis of PAOx following a random pathway (left) or blocklike pathway (right) b)Three model compounds used in this study

Dia1.jpg

Development of Liquid Heat Resistant Resin Based on Maleimide Resin

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Dr. Shinichi Sato [1], ***Dr. Yoshiaki Yoshida*** [2], ***Prof. Takeshi Endo*** [3]

1. *Konishi Co.,Ltd.*, **2.** *Kyushu Institute of Technology*, **3.** *Molecular Engineering Institute, Shiga University of Medical Science*

Introduction:

Maleimide resins, which never make a void during a curing reaction, are well-known as raw materials to improve the heat resistance of the cured resins. However, typical maleimide resins cannot utilize as liquid adhesive and encapsulant because of the high melting point of the maleimide resins. Therefore, we have developed liquid resins at room temperature without any solvents by modification of maleimide resins with epoxy resins. In this report, we demonstrate the modification methods of maleimide resins with epoxy resins and the viscoelasticity of cured resins.

Results and Discussion:

Preparation of main agent (A): The liquid resin **(A)** was obtained by the reaction of 4,4'-bismaleimidodiphenylmethane (BMI), bisphenol-F epoxy resin (EpF), cycloaliphatic epoxy resin (CEp), and catalytic amount of hydroquinone (HQ) at 150 ºC for 3 h. This result suggested the charge transfer complex formed between BMI and HQ led to polymerization of BMI, which exhibited excellent compatibility to EpF and CEp. Furthermore, the compatibility of poly-BMI, EpF, and CEp significantly improved after reaction with 3,3'-(methylene-1,4-diphenylene)bis(3,4-dihydro-2H-1,3-benzoxadine) (P-d) at 120 ºC for 30 min.

Curing reaction: First, we tried the curing reaction of liquid resin **(A)** with diamino diethyltoluene (DADET), however, the reaction never proceeded at 120 ºC for 2 h. On the other hand, the curing reaction with DADET containing a small amount of 1,3-cyclohexanediamine (1,3-CHDA) successfully proceeded at 120 ºC for 30 min, although the curing reaction never happened with DADET containing 1,2-CHDA, 1,4-CHDA, 1,3-diaminobenzene, and various types of multifunctional amines. This result indicated that the cycloaliphatic amines having primary amino groups in α- and γ- positions were suitable hardeners for the curing reaction of the liquid resin **(A)**.

Dynamic mechanical analysis (DMA): The mixture of liquid resin **(A)** and DADET containing 1,3-CHDA at weight ratio of 5:1 was annealed at 120 ºC for 1 h as pre-curing process, and then the full-curing process of the mixture was carried out at 200 ºC for 7 h to obtain the cured product (**1**). DMA curves indicated that the cured product (**1**) was excellent heat resistance resin because the storage modulus was 1.0 x 10^8 Pa at 259 °C (Fig. 1).

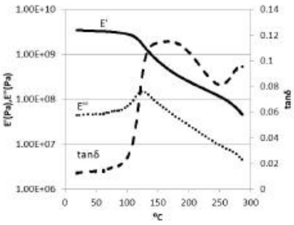


Figure 1 Dynamic mechanical properties after curing at 120 ºC for 1 h and then at 200 ºC for 7 h.

Figure1.jpg

Leakage free high thermal conductivity phase change materials

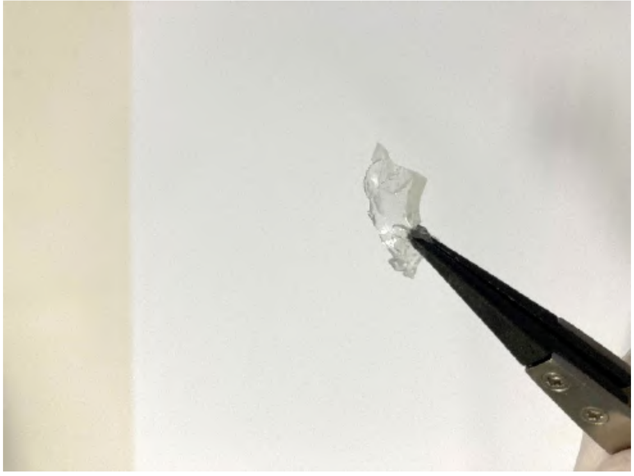
Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Dr. Gabriel Foyer [1]

1. *Thales*

Phase Change Materials (PCM) is an effective way of storing thermal energy and has the advantages of high storage density and the isothermal nature of the storage process. However, usual solid-liquid PCMs like paraffin present leakage issues and low thermal conductivities limiting their durability and their efficiency in bulky components.

The present work describes the synthesis of cross-linked acrylic polymers bearing long alkyl chains. Their semi-crystalline nature provides a phase change similar to paraffin but crosslinking durably prevents creep of the material above their melting temperature. However, crosslinking density has also an influence on the latent heat, this effect is described and a compromise between creep resistance and PCM performance is proposed. Finally, conductive nanofillers such as expanded graphite are used to increase the thermal conductivity of the polymers and obtain leakage free high thermal conductivity PCMs.



Solid-solid pcm.jpg

Tailor-made RAFT agent for the controlled synthesis of fluorescent polymers

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Sébastien Berruée [1]***, Dr. Lydia Sosa-Vargas*** [2]***, Prof. Jutta Rieger*** [3]

1. *Sorbonne Université, Institut Parisien de Chimie Moléculaire, UMR 8232, Equipe Chimie des Polymères, 75252 Paris, France,* ***2.*** *Sorbonne Université,* ***3.*** *Sorbonne Université, CNRS, Institut Parisien de Chimie Moléculaire, UMR 8232, Equipe Chimie des Polymères, 75252 Paris, France*

Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization is known as a powerful tool for preparing polymers with well-defined molar masses and low dispersities[1]. The technique is compatible with various monomers and solvents, and the synthesized polymers can exhibit high end-group fidelity. The successful (end-group) functionalization of the polymers requires the careful design of the RAFT agent used for the polymerizations[2]. New functionalities can be introduced, such as reactive functions for post-polymerization modification or stimuli-sensitive units, to name a few ones. In this work, we wish to incorporate a fluorescent dye into the polymer chains and study the emissive properties of the resulting polymers in solution.
Our approach is divided into three different steps:

- The organic synthesis of a RAFT agent bearing a fluorescent unit.
- The preparation of well-defined polymers via RAFT polymerization.
- The study of the photophysical properties of the polymers in solution.

The tailor-made RAFT agent was synthesized by a multi-step, optimized synthesis, which can be easily applied to the synthesis of other analogue RAFT agents in the future. The route was designed so that only one step needs to be changed to alter the functionalization on the fluorescent unit and then impact the resulting emissive properties. We have achieved a first set of controlled polymerizations using this RAFT agent and other monomers are currently being explored. Finally, the photophysical properties of the resulting polymers in solution are studied by UV/Visible absorption and fluorescence emission measurements.

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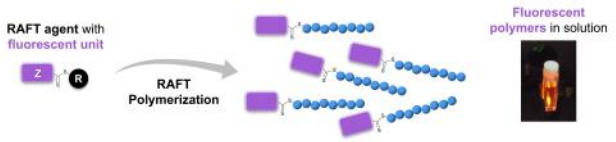

Tailor-made raft agent for the controlled synthesis of fluorescent polymers.jpg

Separation and characterisation of biobased monomers to synthesize new polymers.

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Boris Pasquiou [1]***, Dr. Kash Bhullar*** [2]***, Mr. Ludovic Dubreucq*** [1]***, Dr. Véronique Bennevault*** [3]***, Dr. Marianne Gaborieau*** [4]***, Prof. Philippe Guégan*** [5]***, Prof. Patrice Castignolles*** [5]

1. *Institut Parisien de Chimie Moléculaire, Equipe Chimie des Polymères, UMR 8232 CNRS, Sorbonne University, Paris, France,* ***2.*** *Australian Centre for Research on Separation Science, Western Sydney University, School of Science, Parramatta, Australia,* ***3.*** *Université d'Evry, Evry,* ***4.*** *Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Polymer Materials, Karlsruhe, Germany,* ***5.*** *Sorbonne Université*

Introduction

"Dimer acids" are biobased monomers sourced from renewable and natural oleic and linoleic acids extracted from various oils such as canola or most commonly tall oil, a by-product of the Kraft process. Using the renewable oil industry chain seems promising because the production and supply chain is already in place. These unsaturated fatty acids are "dimerized" on clay catalysts, leading to dimer acids [1]. The resulting dimer acids thus consist of complex mixtures including cyclic and acyclic dicarboxylic acids (diacids) along with tricarboxylic acids (triacids) and monocarboxylic acid (monoacids). The polycondensation of these dimer acids with diol or diamines lead to resins [2]. Cultivation parameters, type of clay used and reaction conditions add variability to the dimer acid structures and proportions: This study aims at understanding this extreme variability and use it to design and synthesize new macromolecular architectures with emerging properties.

Methods

Direct infusion electrospray ionization mass spectrometry (ESI)-MS and capillary electrophoresis were used in this work to separate and characterize different molecules composing different dimer acids.

Results and discussion

A large number of diacids and triacids were detected as well as monoacids and supramolecular dimers of diacids. Their m/z are consistent with molecules previously hypothesized from GC-MS, LC-MS or NMR results [1]. Each of them has a large variety of possible isomers (both positional isomers and stereoisomers). Based on molecular mechanisms, numerous new structures were proposed (see Figure). These structures are consistent with NMR spectroscopy results.

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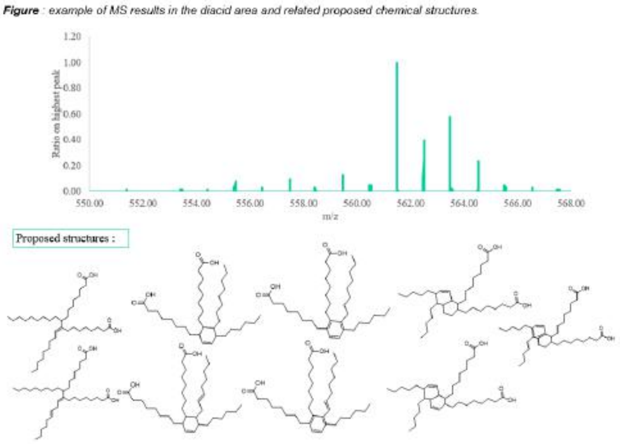

Esi-ms diacid area structures.png

Ferrocene modifications at silsesquioxane-based dendrimers

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mrs. Aleksandra Mrzygłód [1], ***Dr. Maria Pilar García-Armada*** [2], ***Prof. Beata Dudziec*** [1]

1. *Faculty of Chemistry and Centre for Advanced Technologies, Adam Mickiewicz University in Poznan,* ***2.*** *Departamento de Ingeniería Química Industrial, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid*

Dendrimers - the strictly defined, 3D, branched nano-sized structures of a wide range of functionalities and applications (e.g. supramolecular chemistry, medicine) deriving from their unique spacial construction.[1] In particular, dendrimers containing redox-active moieties have been extensively studied due to their intriguing properties and resulting usage, e.g. as electron transfer mediators, catalysts, molecular sensors.[2,3] A class of compounds used as dendrimer cores are silsesquioxanes (SQs). They are one of the specific organosilicon representatives, i.e. characterized by hybrid nature formed by an inorganic core and organic substituents attached to it. There are several types of these systems, i.a. random, ladder, cage and partial cage structures.[4] The most popular type of SQs which was used as a dendrimer core was octafunctional $T_{8.}$ Up-to-date, the reports on the formation of mono-T_8 and double-decker silsesquioxanes applied as cores of dendritic systems have been rare.[5,6,7]

The aim of this research was to obtain molecules exhibiting electrochemical potential, i.e. possessing groups amenable to oxidation/reduction, e.g. ferrocene that would be anchored to silsesquioxane cores (G2-DDSQ-Fc_{16}). The methodology for their synthesis is based on a sequence of condensation, reduction and hydrosilylation reactions. Moreover, the obtained products were tested in terms of their electrochemical properties using cyclic voltammetry.[8]

Acknowledgements: Financial support from the NCN - UMO-2021/41/B/ST5/02028 and „Excellence Initiative - Research University" 048/13/UAM/0017.

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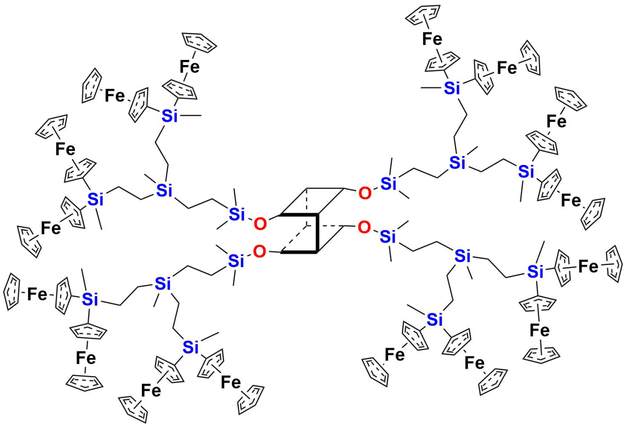

G2-DDSQ-Fc$_{16}$

Mrzyg d aleksandra.png

Bio-sourced functional liquid crystal polymers

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Yakui Deng **[1], *Mr. Gaoyu Liu*** **[1], *Dr. Patrick Keller*** **[2], *Dr. Min-Hui Li*** **[1]**

1. *Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, UMR8247,* **2.** *Institut Curie*

An analysis on the existing liquid crystal polymers reveals that the liquid crystal monomers used so far are mostly derived from fossil fuels or use them in large quantity for fabrication. Due to ecological and environmental issues, combined with the depletion of oil-based feedstocks, the shift towards greener chemical processes to produce polymer materials is a topical trend. Muconic acid is a promising renewable molecule that can be accessed from bio-fermentation of sugar, lignin or their derived compounds. Their acid groups offer a simple access to their functionalization by grafting functional moieties. Moreover, the conjugated arylate-like double bonds present in the structure make possible not only the radical polymerization but also crosslinking. In this research, we used liquid crystal molecules as functional moieties to design a series of liquid crystal (LC) muconates (LC esters of muconic acid). Their polymerization was investigated. The liquid crystal properties of these new monomers and polymers were studied. This work provides a new option to prepare liquid crystal polymers from renewable resources.

Design and physicochemical characterization of poly(butylene oxide)-stat-poly(glycidol) nanoparticles with controlled hydrophilic/hydrophobic ratios

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mrs. Hiba Khelifa [1], ***Dr. Nicolas Illy*** [2], ***Prof. Philippe Guégan*** [2], ***Prof. Kawthar Bouchemal*** [1]

***1.** Institut de Recherche de Chimie Paris (UMR-CNRS 8247), Université PSL, Paris,* ***2.** Institut Parisien de Chimie Moléculaire (UMR-CNRS 8232), Sorbonne Université, Paris*

The interaction of polymeric nanomaterials with biological media depends on several factors, including their hydrophilic/hydrophobic ratio (1,2).

We aimed to synthesize nanoparticles with well-controlled hydrophilic-to-hydrophobic ratios. First, various well-defined statistical polyglycidol/poly(butylene oxide) copolymers (PBO-stat-PG),with controlled molar masses and hydrophilic/hydrophobic ratios were synthesized by anionic ring-opening polymerization. The copolymers were carefully characterized by ^{1}H NMR, SEC and DSC. Then, spherical nanomaterials (NS) were prepared by nanoprecipitation and *in situ* polymerization of poly-cyanoacrylates. The choice of the NS preparation method is based on the polymer's solubility. TEM and SEM observations of NS were performed to characterize the morphology. Size distribution analysis was carried out on TEM images using ImageJ. NS surface potentials were characterized by zeta potential measurements.

The TEM and SEM observations revealed that spherical particles were obtained with both processes and regardless of the hydrophilic/hydrophobic ratio. The diameter varies according to the type of PBO-stat-PG copolymer and NS preparation method.

The NS with controlled hydrophilic and hydrophobic ratios designed in this study are an excellent tool to investigate further the NS *in vivo* fate depending on their hydrophilic/hydrophobic ratios.

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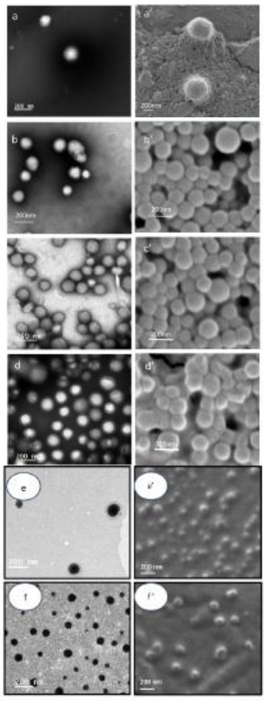


Figure: TEM (a,b,c,d,e,f) and SEM (a',b',c',d',e',f') images of NS prepared by emulsion polymerization of isobutylcyanoacrylates (a,b,c,d,a',b',c',d') and by nanoprecipiation (e,f, e',f'). (a,b,c,d) and (a',b',c',d') are images of NS prepared by emulsion polymerization of isobutylcyanoacrylates and PBO-*stat*-PG. PBO-*stat*-PG were composed of PG0/100 (a,a'), PG10/90 (b,b'), PG20/80 (c,c'), PG30/70 (c,c') and (e,f) and (e',f') are images of NS prepared by nanoprecipitation. PBO-*stat*-PG were composed of PG70/30 (a,a'), and PG85/15 (b,b').

Khelifa and al.jpg

Electroactive liquid crystal elastomers

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Gaoyu Liu [1]***, Mr. Yakui Deng*** [1]***, Dr. Tran minh giao Nguyen*** [2]***, Dr. Cédric Vancaeyzeele*** [2]***, Dr. Annie Brulet*** [3]***, Dr. Frédéric Vidal*** [2]***, Dr. Cédric Plesse*** [2]***, Dr. Min-Hui Li*** [1]

1. *Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, UMR8247,* **2.** *CY Cergy Paris Université, LPPI F95000 Cergy, France,* **3.** *Laboratoire Léon Brillouin UMR12 CEA-CNRS C.E. Saclay, Bât 563 pièce 303 91191 Gif sur Yvette Cedex FRANCE*

Liquid crystal elastomers (LCEs) are moderately crosslinked liquid crystal polymers, where LC units are oriented uniformly in the whole sample (monodomain). The key characteristic of monodomain LCEs is that they have the capability to deform unidirectionally, reversibly and largely (strains of 20 – 200%) upon stimulation of heat or light. On the other hand, an ionic electroactive polymer (EAP) is typically a tri-layer system consisting of an ionically conducting membrane sandwiched by two electronically conducting polymers as electrodes. This soft ionic EAP can convert either electrical stimulation into reversible and large bending deformations under low voltage (<2V) (actuator) or convert mechanical stimulation into electrical signal (sensor). Here, we report on a new combination of LCE and ionic EAP to get ionic electroactive LCE (eLCE), which can perform both bending and contraction/elongation deformations under direct and alternative currents of low voltage, respectively. Particularly, such an eLCE can lift a load 75 times heavier than its own weight when an electric field of ± 6V and 10 Hz is applied. These kinds of materials may find potential applications in soft robotics, electronic devices, and sensors.

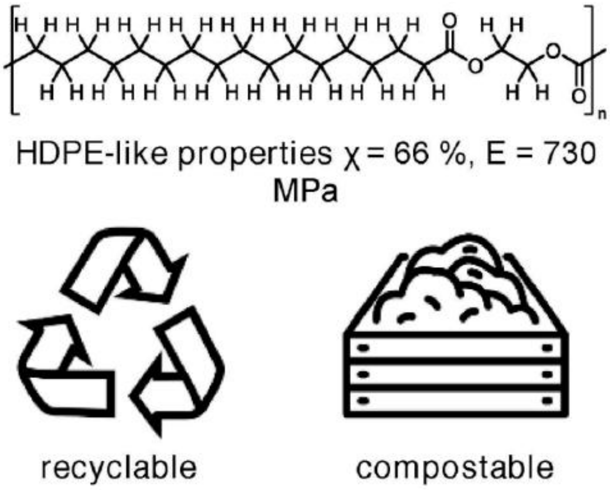
Biodegradable High-Density Polyethylene-like Material

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Simon Schwab [1] ***, Mr. Marcel Eck*** [1] ***, Prof. Stefan Mecking*** [1]

1. *Universität Konstanz*

Polyesters or polycarbonates with a low density of these functional groups in the polymer chain can possess the material properties of polyethylene (HDPE). At the same time, the in-chain functional groups allow for an efficient chemical recycling at mild conditions. The in-chain ester groups obviously offer themselves for biodegradation in principle, however, the hydrophobic and crystalline nature is expected to impede such processes.
The novel material polyester-2,18 is accessible from readily available biobased 1,18-octadecanedicarboxylic acid and ethylene glycol, and possesses a polyethylene-like solid-state structure and also tensile properties similar to HDPE.
Despite its high crystallinity and high melting point (T_m=96 °C) and similar surface free energy compared to HDPE, polyester-2,18 is subject to rapid and complete hydrolytic degradation in in vitro assays with isolated naturally occurring enzymes. Under industrial composting conditions (ISO standard 14855-1) the material is biodegraded with mineralization above 95 % within two months. Reference studies with polyester-18,18 (T_m= 99 °C) reveal a strong impact of the nature of the diol repeating unit on degradation rates, possibly related to the density of ester groups in the amorphous phase or the solubility of the diol monomer unit.
Depolymerization by methanolysis indicates suitability for closed-loop recycling.



Chemical structure and material properties of polyester-2 18.png

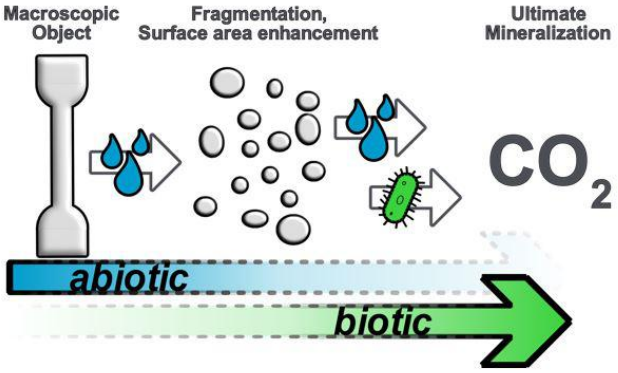
Polyethylene-like blends amenable to abiotic hydrolytic degradation

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Ms. Léa Bernabeu [1], *Mr. Marcel Eck* [1], *Prof. Stefan Mecking* [1]

1. Universität Konstanz

Plastics are essential materials for virtually any modern technology. Their environmental persistence can be problematic, however, even if a more responsible waste management were broadly implemented. The long-chain aliphatic polyester-18,18 (PE-18,18) exhibits high density polyethylene-like (HDPE) materials properties and, as opposed to the latter, can be recycled in a closed-loop *via* depolymerization to monomer under mild conditions. An approach to render PE-18,18 hydrolytically degradable is by melt-blending with long-chain aliphatic poly(H-phosphonate)s. The blends can be processed *via* common injection molding and 3D printing, and exhibit HDPE-like tensile properties, namely, a high stiffness and ductility over a wide range of blend ratios. Hydrolysis of the blend components over the bulk of the specimen was confirmed by gel permeation chromatography (GPC) measurements. Molecular weight reduction upon immersion in water resulted in embrittlement of the injection molded specimens.



Apme2023 bernabeu polyethylene-like blends amenable to abiotic hydrolytic degradation.jpg

Biodegradability and in vitro cytotoxicity study of poly(2-isopropenyl-2-oxazoline)

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

***Dr. Florica Adriana Jerca* [1], *Dr. Diana Elena Giol* [2], *Mr. Catalin Tucureanu* [2], *Dr. Iuliana Caras* [2], *Mr. Vlad Tofan* [2], *Dr. Aurora Salageanu* [2], *Mr. Emilian Ghibu* [1], *Dr. Valentin Victor Jerca* [1]**

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Functional polymers play an important role in different biomedical applications, as they can be used as drug, protein, or gene carriers. [1] Poly(2-isopropenyl-2-oxazoline) (PiPOx) is a water soluble and nontoxic polymer that attracted increasing interest recently as a reactive polymer because it can be used in the construction of functional materials, such as thermoresponsive polymers and hydrogel materials. [2-4] The synthesis of such materials is based on the post-polymerization reactions of PiPOx with (di)carboxylic acids. [3] However, these materials still retain a fraction of 2-oxazoline side units after polymer post-modification reactions, which might induce instability due to possible hydrolysis. Thus, PiPOx's aqueous behavior in simulated body fluids has been recently assessed i*n vitro*, [5] demonstrating the potential of PiPOx for developing drug delivery systems. However, the stability of polymeric materials is strongly dependent on other factors such as temperature, oxygen or oxidants, and exposure to UV light. Therefore, in the present study, the stability of PiPOx towards reactive oxidation species, the cytotoxicity, and the inflammatory response of PiPOx with different cell lines were systematically investigated. In particular, the influence of the polymer molar mass and polymer concentration was evaluated.

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Chemical modification of lignin: towards sustainable resins for stereolithography

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Evgeny Grigoryev [1]***, Mr. Henri Lila*** [1]***, Dr. Anika Kaufmann*** [1]***, Prof. Julian Thiele*** [2]

1. Leibniz Institute of Polymer Research Dresden, 2. Institute of Chemistry, Otto von Guericke University Magdeburg

Introduction

Lignin is one of the most abundant natural polymers with high aromatic content. It accumulates in large amounts during the paper production process. Despite lignin being a biodegradable and biocompatible material, its current application is limited due to its variable structure, high polydispersity and low solubility in commonly used solvents. Nevertheless, there are number of reports dedicated to chemical modification of lignin to improve its physical-chemical properties. Here, we describe the application of chemically modified lignin as a key component of resins for projection-microstereolithography (PμSL).

Methods

As starting material, we used high purity hardwood lignin from Fibenol OÜ(Estonia). Lignin was modified by (meth)acrylic anhydride to introduce photo-crosslinkable groups for PμSL. ^{1}H and ^{31}P NMR were utilized to characterize initial and target products. Commercially available acrylates were mixed with different ratios of modified lignin and a photoinitiator to test their applicability for PμSL. Ultrasonication was used to prepare homogeneously mixed resins and different process parameters were tested (e.g., ultrasonication time, amplitude, alternative mixing methods).

Results

Before modification, the exact amount of reactive hydroxy- and carboxy-groups was determined via ^{31}P NMR. The lignin used in our investigation contains 4.76 mmol g^{-1} reactive species (31 % aliphatic OH, 41 % phenolic OH, 28 % COOH). After modification, amount of functional groups decreased significantly, corresponding to successful modification of the hydroxy-groups in lignin. It was also found that the drying temperature affects the final structure and solubility of acylated lignin. Modified lignin was better soluble in the resin formulation. Since lignin also acts like a photoabsorber, the illumination time during PμSL-printing has to be raised for increasing the amount of lignin in the final resin formulation.

Discussion

Chemical modification of lignin was optimized to obtain more reactive and soluble products which are suited as resin component in PμSL. As a first goal, we particularly aimed for increasing the amount of lignin in the final resin formulations to obtain the maximum percentage of sustainable parts in the final resin. To our knowledge, the highest lignin content so far achieved in PμSL was 15 % [1].

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Green combination of bioressources and photochemistry to design performing antibacterial materials

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

***Dr. Louise Breloy* [1], *Prof. Davy-Louis Versace* [2], *Prof. Vlasta Brezova* [3], *Dr. Annalisa Chiappone* [4], *Dr. SAMIR ABBAD ANDALOUSSI* [5], *Prof. Jean-Pierre Malval* [6]**

***1.** SIMM, ESPCI, **2.** ICMPE-CNRS, **3.** STUBA, **4.** UniCa, **5.** UPEC, **6.** Université de Haute-Alsace*

The field of photopolymerization has experienced an incredible development in recent years. This technique allows to obtain materials in very short times, without solvent, using low energy. Moreover, 3D-printing processes have considerably broadened the field of applications of photopolymerization, particularly for biomedical prostheses. However, the current design of these biomaterials has certain weaknesses: risks associated with UV, major use of non-renewable compounds, or undesirable release. Furthermore, to face the double threat of nosocomial infections and bacterial resistance, it became crucial to develop strategies preventing the proliferation of bacteria on biomaterials surfaces.

In this context, innovative antibacterial materials were designed by combining photochemistry and bioresources. [1,2] Biobased monomers, such as vegetable oils or terpenes, were formulated for obtention of printable tack-free materials by free-radical photopolymerization and thiol-ene reaction. Some natural dyes, extractable from madder root, were chosen for their common backbone with a classical and performing photoinitiator, anthraquinone. These derivatives were used as photosensitizers to work exclusively under low intensity visible LEDs irradiation. The associated photochemical initiation mechanisms were studied by steady-state photolysis, fluorescence, laser flash photolysis and electron paramagnetic resonance. Polymerization kinetics were monitored in real time by infrared spectroscopy and photo-rheology. The most promising systems were selected, enabling to generate complex biobased structures by DLP 3D-printing.

The dyes were chemically modified with polymerizable acrylate groups. This change not only improved their initiating properties, but also prevented their release out of the polymer matrix. Once trapped in the network, these sensitizers could be used as photoactivable antibacterial agents: under irradiation, they generate reactive oxygen species leading to the death of bacteria at the surface of the materials, following the principle of photodynamic therapy. Natural contact-killing agents, such as certain terpenes (linalool, eugenol), can also serve as biocidal monomers. Combination of these two strategies, permanent and photo-activated, allowed to reach bacterial inhibition above 99.99% against *Staphylococcus aureus* and *Escherichia coli*, the two main bacteria responsible for nosocomial infections.

These results open promising perspectives to conciliate environmental and health considerations.

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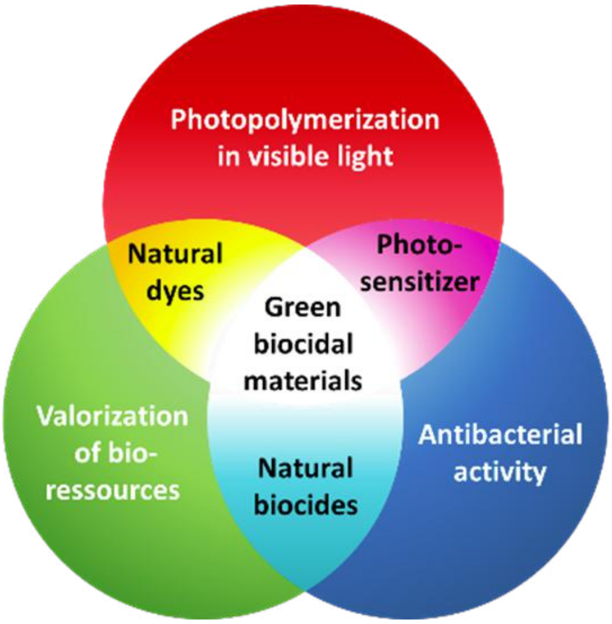
2. Breloy et al, *ACS Sustainable Chem. Eng.* **2019**



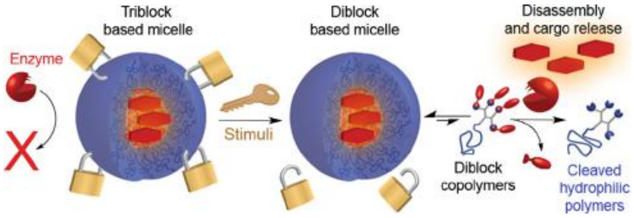
Combination of bioressources and photochemistry to design antibacterial materials.png

Stimuli-induced architectural transition as a tool for controlling the enzymatic degradability of polymeric micelles

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Ms. Shahar Tevet [1], ***Dr. Gadi Slor*** [2], ***Prof. Roey J. Amir*** [1]
1. Tel Aviv University, 2. EPFL

Enzyme-responsive polymeric micelles hold great potential as drug delivery systems due to the overexpression of disease-associated enzymes. To achieve selective and efficient delivery of their therapeutic cargo, the micelles need to be highly stable yet disassemble when encountering the activating enzyme. While high micellar stability is required in order to avoid unwanted premature off-target disassembly and cargo leakage, increasing the stability of the micelles results in a drastic decrease in their responsiveness towards enzymatically induced disassembly. The need to balance between stability and enzyme-responsiveness is one of the key challenges towards the translation of enzyme-responsive delivery platforms into therapeutic usage. In our work, we describe a general and modular method for designing highly stable enzyme-responsive polymeric micelles, which their enzyme-responsiveness can be unlocked on demand. The unlocking of the micellar responsiveness towards enzymatic degradation is triggered by exposure to external stimuli leading to the splitting of the amphiphile. This modular methodology offers a general solution to overcome the stability-responsiveness barrier in enzyme-responsive nano-assemblies, which can potentially be applied to many other self-assembled systems beyond polymeric micelles.



Stimuli-induced architectural transition as a tool for controlling the enzymatic degradability of polymeric micelles.jpeg

Polymer microgels as nucleoid mimic in synthetic biology

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Dr. Anika Kaufmann [1]***, Ms. Michelle Vigogne*** [1]***, Ms. Talika Neuendorf*** [1]***, Dr. Horacio López-Menéndez*** [2]***,***
Ms. María Reverte-López [3]***, Dr. Germán Rivas*** [4]***, Prof. Julian Thiele*** [5]

1. *Leibniz Institute of Polymer Research Dresden,* ***2.*** *Universidad Complutense Madrid,* ***3.*** *Max Planck Institute of Biochemistry, Martinsried,* ***4.*** *Centro de Investigaciones Biológicas Margarita Salas (CIB-CSIC), Madrid,* ***5.*** *Institute of Chemistry, Otto von Guericke University Magdeburg*

Introduction

Synthetic biology is a multidisciplinary research field whose significance is presented by many prominent research programs world-wide, which bring together researchers from different fields like biotechnology, molecular engineering, systems biology, biophysics, computer engineering and more. One of the major goals in the field of synthetic biology is nothing less than building a synthetic cell. For that, suitable experimental platforms are needed, which mimic the cell regarding structure and functions. Droplet microfluidics is an established method to provide such artificial cell models. Here, polymer microgels are used to investigate selected protein interactions from the complex bacterial cell division process in an artificial environment.

Methods

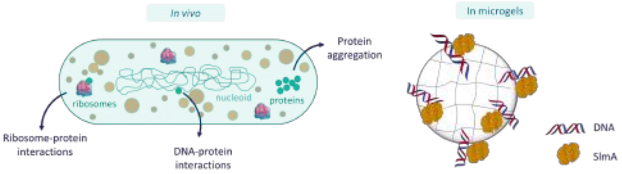
Polymer microgels were prepared by microfluidics with desired size, shape and porosity. The properties are defined by the choice of polymer precursors like hyaluronic acid (HA) or polyethylene glycol (PEG). The influence of porosity on the diffusion of different fluorescently labeled proteins was studied by confocal laser scanning microscopy. The functionalities of the polymer precursors can be used to couple short DNA sequences to investigate specific protein interactions.

Results

HA-microgels exhibited a higher protein uptake than PEG-microgels. It was shown that the short DNA sequence SBScons, which was coupled to our polymer microgels, can specifically bind to one important protein involved in bacterial cell division, namely SlmA. The specificity of the interaction was shown in comparison to a reference DNA strand. Independent of the charge of the polymer microgel, SlmA formed a corona around the microgels. The protein diffusion into HA-microgels was very fast and completed within a few minutes.

Discussion

We could show that the protein diffusion behavior in the investigated polymer microgels is in good agreement with theoretical explanations. Polymer microgels could be successfully used to mimic the DNA-rich nucleoid region of a bacterial cell by pre-coupling DNA to the functionalities of polymer precursors. With our work we aim to provide insights into single-protein interactions in a cell-like environment before moving on to more protein interactions during bacterial cell division which is an essential aspect in the self-replication of cells.



Comparison of the bacterial nucleoid region in vivo left and a microgel-based mimic right ..png

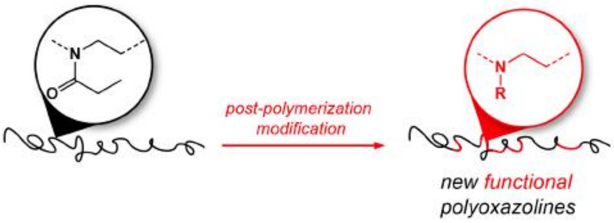
Novel functional materials by post-polymerization modification of poly(2-alkyl-2-oxazoline)

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Ms. Aikaterini Mathianaki [1], ***Mrs. Aysha Kinjo Demeler*** [1], ***Dr. Jessica Schneider*** [2], ***Prof. Guillaume Delaittre*** [1]

1. Organic Functional (Macro)Molecules, Department of Organic Chemistry, University of Wuppertal, 2. German Textile Research Institute North-West (DTNW), Krefeld

Poly(2-alkyl-2-oxazoline)s (PAOx) is a versatile class of polymers usually obtained by cationic ring-opening polymerization of 2-alkyl-2-oxazolines. Depending on the alkyl chain length and the possible presence of a cROP-stable functional group, PAOx properties can vary, for example from very hydrophilic to very hydrophobic. Poly(2-ethyl-2-oxazoline) (PEtOx) in particular, is a very attractive material due to its hydrophilicity, non-toxicity, and biocompatibility, as well as its anti-fouling properties. It is well known in the literature that PEtOx can be (partly) hydrolyzed under acidic or basic conditions and further refunctionalized with a simple alkylation or amidation affording new functionalities on the backbone. We use this methodology to produce specific materials, e.g., reactive and functional coatings for textiles. In addition, utilizing other chemical modifications which have not been applied to PAOx to date, new statistical copolymers with alternative monomeric units along the backbone give rise to derivatives with varying properties.



Mathianaki apme2023 abstract figure.png

Structure to self-healing properties relations in PDMS-based ionic supramolecular networks

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mrs. Eleonora Manarin [1] ***, Prof. Stefano Turri*** [1] ***, Prof. Gianmarco Griffini*** [1]

1. Department of Chemistry, Materials and Chemical Engineering 'Giulio Natta', Politecnico di Milano, Piazza Leonardo da Vinci 32 – 20133 – Milano Italy

Introduction

The need to develop self-healable and maintenance-free polymers that simultaneously retain their unique properties is becoming increasingly important in modern research. Within this framework, we developed here a series of intrinsically self-healable systems incorporating dynamic supramolecular ionic interactions in a polydimethylsiloxane (PDMS)-based elastomer. To improve the final thermo-mechanical properties of the materials, semi-Interpenetrated Polymer Networks (semiIPNs) were developed to connect the supramolecular network to a UV-curable network.

Methods

The ionic supramolecular character was achieved *via* an acid-base proton transfer reaction between the amino groups of the side chain of a functionalized PDMS-based elastomer and the acid groups of methacrylic acid. Additionally, the unsaturations of the acid were exploited through a UV-curing process, leading to the formation of the semiIPNs. Different formulations were developed by varying the amine protonation degree to investigate the structure-to-properties relations.

The effect of ambient moisture on the rheological, thermo-mechanical, and scratch self-healing properties of the semiIPNs was investigated systematically.

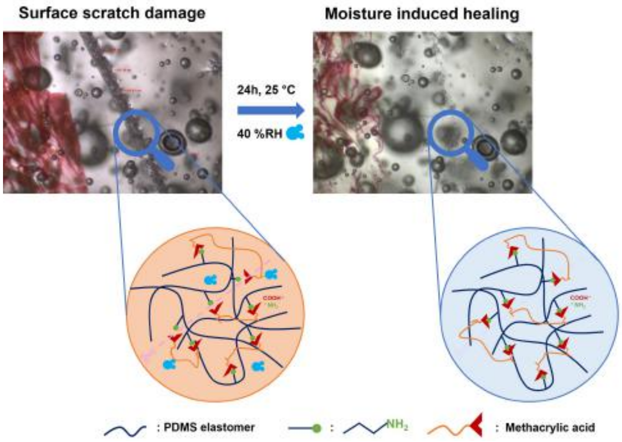
Results

Flow curve analyses confirmed the formation of efficient ionic assemblies upon blending and showed an increase in the blend viscosity with increasing ionic bond density. Moreover, FTIR spectroscopy evidenced the appearance of the peaks associated to the ammonium carboxylate ions, confirming the formation of the supramolecular networks. The degree of crosslinking was evaluated using UV-DSC analysis and gel content measurements, showing complete curing. Humidity-dependent evaluations of self-healing of scratches were performed at room temperature during 24 h, demonstrating that the water plasticization effect is fundamental for achieving complete self-healing ability.

Discussion

The correlation between ionic bond density and UV-crosslinking degree with the viscoelastic and self-healing properties was demonstrated. From a quantitative point of view, the formation of the ionic interactions was confirmed by FTIR and flow curves analyses. SemiIPNs behavior was achieved by exploiting UV-curing reactions, which resulted in an improvement of the mechanical properties of the materials.

The semiIPNs were shown to respond to stimuli, as environmental moisture was found to be essential for complete self-repairing. Additionally, the dependence of this smart behavior on both ionic density and the extent of UV-curing was highlighted.



Pdms x apme2023.jpg

Bio-based and antibacterial materials synthetized by photochemistry

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

***Ms. Christine ELIAN* [1], *Dr. SAMIR ABBAD ANDALOUSSI* [2], *Prof. Régis Moilleron* [3], *Prof. Davy-Louis Versace* [1]**

1. ICMPE-CNRS, 2. UPEC, 3. LEESU

Keywords: photochemistry, biobased material, antibacterial properties, visible light, photosensitizer, reactive oxygen species, singlet oxygen.

To get as close as possible to a “green” chemistry, photopolymerization seems to be an interesting approach because it allows fast syntheses, without solvents, and requires only low energy consumption [1–2]. In this project, we have developed a new bio-based material with antibacterial properties using photopolymerization. A natural dye from madder roots has been chemically modified to graft reactive epoxy functions and then used as a photosensitizer. Adding reactive functions to it allowed the incorporation of this molecule into the polymer network during the cationic photopolymerization. Eugenol, a natural molecule extracted from cloves and known for its antibacterial properties, was mono- and di-epoxidized to be used as a monomer. Under visible light irradiation, this new alizarin derivative photosensitizer demonstrated an excellent ability to initiate polymerization. The photoinitiator system have been fully characterized by spin-trapping EPR, laser flash photolysis and fluorescence to determinate its photophysical and photochemical properties.

Photochemistry is essential in this project because it is used both to synthesize the material and to decontaminate its surfaces. Indeed, the alizarin derivative trapped in the polymer network is able to generate reactive oxygen species, such as singlet oxygen, known to be biocide [3]. Regardless of the bacteria strain tested (*Staphylococcus aureus* and *Escherichia coli*), the irradiation of the materials allowed a decontamination of 100% of bacteria on the surfaces.

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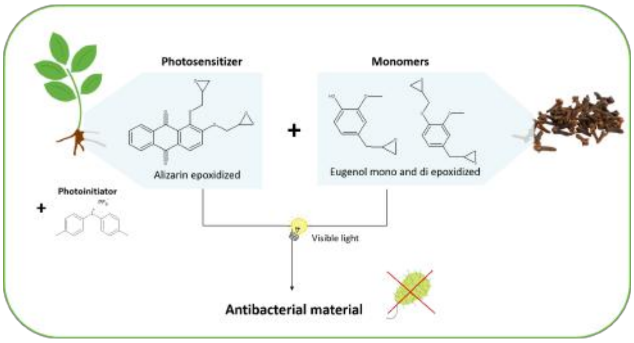

Abstract christine elian.png

SYNTHESIS OF POLYCATIONIC VECTORS FOR GENE DELIVERY

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Thibaut Nouveau [1], Dr. Tristan Montier [2], Dr. Véronique Bennevault [3], Prof. Philippe Guégan [4]

1. Sorbonne University, Parisian Institute for Molecular Chemistry (IPCM), Polymer Chemistry Team, Paris,, 2. University of Bretagne Occidental, INSERM UMR 1078, Génétique, Génomique fonctionelle et Biotechnologies, 3. Institut Parisien de Chimie Moléculaire, Sorbonne Université, Paris, 4. Sorbonne Université

Gene therapy consists in the introduction of cell function-altering genetic material, into a patient to cure a disease[1]. The use of a vector is required to protect the therapeutic nucleic acids and to facilitate the crossing of the different biological barriers inside the organism, in order for it to be transcribed inside the cell and modulate its activity. Viruses were first considered[2] but their various drawbacks (immunogene, production cost, …) opened the way to synthetic alternatives such as polymers[3]. Their main advantage is their modularity, their ease of process, their reduced toxicity and acceptable cost of production.

In this project we develop a new library of oxazoline-based amphiphilic triblock copolymers with a thermosensitive block of poly(2-ethyl-2-oxazoline) (hydrophilic at room temperature and hydrophobic at high temperature), an hydrophobic block of poly(2-*n*-propyl-2-oxazoline) and an hydrophilic block of poly(ethylenimine).

These polymers are obtained in a 2 steps procedure. A 1st step of cationic ring opening polymerization (CROP)[4] was performed to synthesize the triblock copolymer by sequential monomer addition of the 2-alkyl-2-oxazoline monomers. The 2nd step is a selective hydrolysis of MeOx units, a series of kosmotropic agent is used to facilitate the copolymer micellization[5] in acidic conditions at high temperature, thus making a core-shell system which protects the more hydrophobic blocks and exposes the hydrophilic block to hydrolysis.

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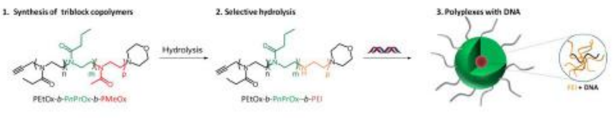


Figure 1 : How to make a synthetic vector for gene delivery

Synthesis of a polycationic vector.jpg

Chemically recyclable Supramolecular polyethylene-like Polyesters

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mrs. Melissa Birkle [1], **Prof. Holger Frauenrath** [2], **Prof. Stefan Mecking** [1]

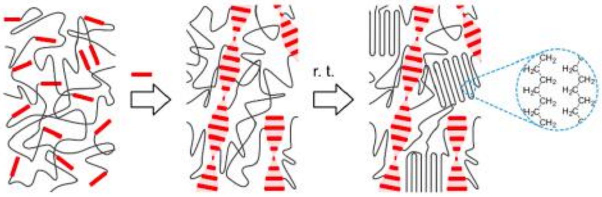
1. Universität Konstanz, 2. EPFL

Long-chain polyesters with a low density of ester groups along the polymer backbone can possess polyethylene-like material properties, while being bio-sourced and chemically recyclable. Unlike polyethylene, these semicrystalline polyesters contain functional groups in-chain and as end groups, which offers the possibility to implement advanced concepts to enhance structures and material properties.

Here, we report on the modification of such long-chain polyesters with oligopeptide end groups that are capable of forming nanofibril aggregates by the way of hydrogen bonding. In conjunction with a corresponding low-molecular weight additive that interacts with the end groups, this affords supramolecular structure formation despite the naturally small portion of end groups in high molecular weight polymers.

The resulting materials show a new rubbery plateau in dynamic shear rheology in a temperature range above the polymer melting temperature and below the melting temperature of the supramolecular structures. This rubbery plateau is tunable by the amount of additive. Moreover, processing the supramolecular polyesters into fibers leads to orientation of the material, influenced by the nanoscopic supramolecular aggregates. This results in an increased stiffness, ductility and toughness, compared to the unmodified reference material.

In addition, the long-chain aliphatic monomers can be recovered by a chemical recycling method and separated from each other.



Supramolecular polyethylene-like polyesters.png

Polymer/inorganic core-satellite nanoclusters as model systems to understand the fate of nanohybrid materials in biological media

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Ms. Olga Kuharenko **[1]*****, Dr. Christian Rossner*** **[1]*****, Dr. Annette Kraegeloh*** **[2]**

1. *Leibniz-Institut für Polymerforschung Dresden e.V.,* **2.** *Leibniz-Institut für Neue Materialien*

Introduction. Core-satellite polymer/inorganic nanohybrids represent structurally well-defined nanoarchitectures functionalities[1]. While the inorganic components contribute unique size-, shape-, and composition-dependent e.g. optical effects[2], these properties can be leveraged exploiting a soft polymeric constituent, providing structural plasticity and mediating interactions with the environment. In this regard, we report stimulus-responsive core-satellite nanostructures, with potential for diagnostics and targeted delivery applications.
Methods. Synthesized polymers were characterized using SEC and ^{1}H NMR spectroscopy. Core-satellite nancolusters were analyzed by TEM and DLS.
Results. The NIPAm-DMAm (poly(N-isopropylacrylamide-*co*-N,N-dimethylacrylamide)) random copolymers with LCST close to the normal human body temperature were synthesized via RAFT (Reversible Addition-Fragmentation chain Transfer) polymerization using difunctional pH-labile RAFT agent bearing ketal moiety. Hybrid AuNP-core–*random* copolymer-shell particles where obtained according to a “grafting-to” approach, in which the RAFT polymers bind to the gold surface with tritiocarbonate end groups. The AuNPs used for core–shell particle formation characterized by an average diameter of approximately 16 nm. Core-satellite nanostructures were formed by adding smaller AuNPs (~ 4 nm) to the precursor core-shell particles and stabilizing their surface with linear RAFT PDMAm.
Discussion. This work emphasizes versatility of RAFT polymerization technique for assembling hierarchical nanostructures adjustable decay profiles under different physiological conditions (e.g. lysosomal pH). The reported modular assembly strategy toward stimulus-responsive clusters opens up systematic investigations of structure-effect relationships, and ultimately optimized design criteria toward a new generation of nanotheranostic agents.
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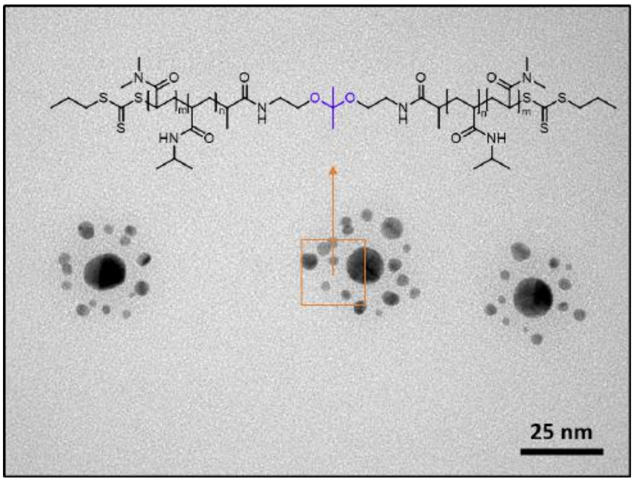

Tem image of core-satellite nanoclusters and the structure of stimuli-responsive linking polymer.png

Stereo-electronic Contributions in Yttrium-Mediated Stereoselective Ring Opening Polymerization of Functional Racemic β-Lactones

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Dr. Rama Shakaroun [1]***, Mr. Ali Ahmad DHAINI*** [1]***, Dr. Ligny Romain*** [1]***, Prof. Ali ALAAEDDINE*** [2]***, Dr. Sophie Guillaume*** [1]***, Prof. Jean-Francois Carpentier*** [1]

1. ISCR- CNRS - University of Rennes, 2. Lebanese University

Poly(hydroxyalkanoate)s (PHAs) are a family of linear aliphatic biopolyesters that gained interest in academia and industrial domains due to their eco-friendly character. PHAs, initially identified by M. Lemoigne as small granules of isotactic polyesters synthesized by bacteria, with low thermal stability which limits their industrial use.[1,2] A convenient synthetic route to enhance the properties of PHAs is the ring-opening polymerization (ROP) of four-membered β-lactones using metal-catalyzed polymerizations.[3]

The achiral yttrium complexes with diamino-bis(phenolate) ligands $\{ONXO^{R'R''}\}_2^-$ (X = NMe_2), in the presence of an initiator (isopropanol), efficiently promote the highly stereocontrolled ROP of 4-alkoxymethylene-β propiolactones (*rac*-BPL^{CH2OR}) into their corresponding poly(BPL^{CH2OR})s. Depending on the substituents onto the yttrium ancillary (R',R" = Me, Cumyl, *t*Bu, halogen), the PHAs can exhibit different microstructures. Highly syndiotactic polymers obtained when crowded substituted ligands are performing. However, the simple modification of *ortho*-substituents from crowded to dimethyl-substituted yttrium complex, gives atactic polyesters. Unexpectedly, only in the specific combination of a BPL^{FG} monomer containing two methylene hydrogens apart the central oxygen on the methylene alkoxy side-functionality along with complexes bearing halogenated ligands induces the formation of highly isotactic PHAs.

The objective of our study is to explore the contribution of the "outer" methylene group in the pendant arm of $BPL^{CH2OCH2X}$ monomers in governing isotactic PHA with the halogenated yttrium catalyst. To achieve our goal, three BPL^{CH2OR} displaying an alkoxy tertiary or quaternary carbon/silicon, namely *rac*-$BPL^{CH2OiPr}$, *rac*-$BPL^{CH2OtBu}$, and *rac*-$BPL^{CH2OTBDMS}$ deprived of an "outer" methylene within the alkoxide moiety, were explored in the yttrium-mediated ROP, and compared with BPL^{FG} containing two sets of methylene hydrogens within the side-functionality, i.e. with FG = CH_2OCH_2X with X = H, $CH{=}CH_2$, C_6H_5 as in BPL^{CH2OMe}, $BPL^{CH2OAllyl}$, BPL^{CH2OBn}, respectively. Our most recent advances in the understanding of the mechanism at play in the stereoselective ROP of BPL^{FG}will be presented.[4]

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2 S. K. Gulrez, *et al.*, Polym. Compos. **2014**, *35*, 900
3 C. G. Jaffredo, *et al.*, *Chem. Eur. J.*, **2016**, *22*, 7629
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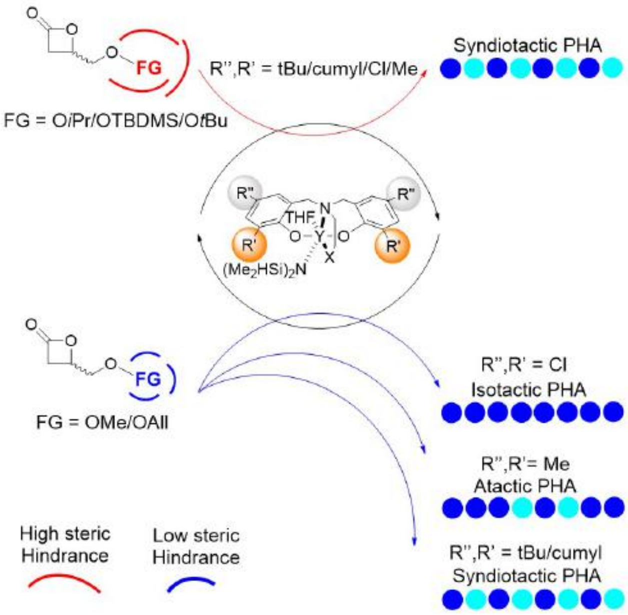


Ali dhaini apme 2023.jpg

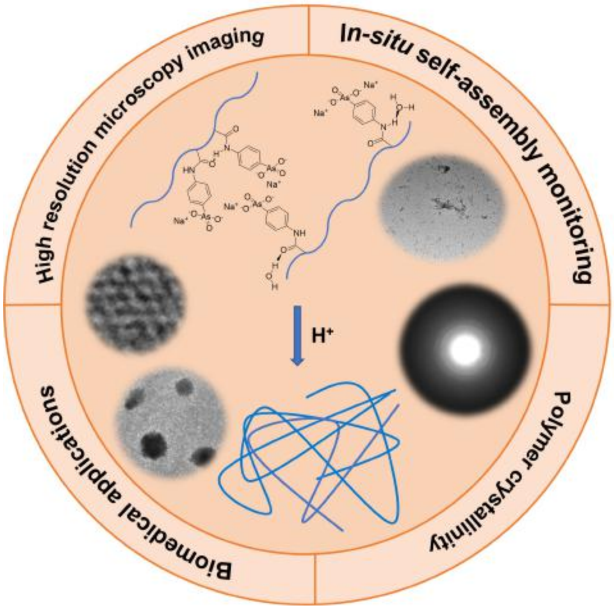
Decoding the behaviour of metalloid-containing polymers in-situ

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Alexandros Magiakos **[1]*****, Dr. Jochen Kammerer*** **[2]*****, Prof. Christopher Barner-Kowollik*** **[2]*****, Dr. Paul Wilson*** **[1]*****, Dr. Evelina Liarou*** **[1]**

1. *Department of Chemistry, University of Warwick, Gibbet Hill, Coventry CV4 7AL, UK,* **2.** *School of Chemistry and Physics, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia*

Monitoring and understanding the polymer behavior *in-situ* is fundamentally important in the field of polymers and materials. Although electron microscopy (HR-TEM, STEM) is a powerful tool, it exhibits limitations when molecular level analysis and understanding of polymer materials is desired, due to their beam-sensitive nature and the TEM substrates containing heavier atoms than the polymer sample itself. However, the presence of heavy metals and/or metalloids attached to a polymer chain (herein metalloid-containing polymers) could potentially overcome this limitation and allow for high resolution imaging of the polymer behaviour (*i.e.*, self-assembly). In particular, polymeric arsenicals are tunable, reactive, responsive and biocompatible scaffolds with distinct reactivity depending on the diverse oxidation states of As, providing an interesting platform for functional and (re)active materials in the field of polymer and (bio)materials science. Moreover, self-assembly has emerge as a significant research field in biological and non-biological applications achieving impressive morphologies due to diverse range of molecular interactions. Consequently, we have designed a platform which relies on the synthesis of metalloid-containing polyacrylamides which allow for in-depth analysis of their structural behaviour upon certain stimuli. Interestingly, the organoarsenical polymers exhibit pH-responsive aggregation behaviour, which originates synergistically from H-bonding and Van der Waals/hydrophobic interactions, as revealed by potentiometric analysis. High-resolution TEM provides information about the self-assembly, while STEM gives an important insight on single polymer chain level behaviour. Interestingly, electron diffraction revealed the highly crystalline nature of these metalloid-containing polymers, verifying the determining role of arsenic moieties on the behaviour of these materials. Finally, *in-situ* SAXS of the polymers in solution verified the diverse conformational characteristics of the organoarsenical polymers, depending on the pH environment. On one hand, the synergy of many state-of-the-art instrumentation and unconventional techniques for polymer analysis, allows for in-depth understanding of how and why polymers assemble, while on the other hand the arsenic content enables molecular level monitoring of the non-assembled polymer population.



Graphical abstract paris 2023.jpg

Preparation of Physically Cross-linked Polymer Networks via Proton Transfer

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Ms. Göknil Süsler [1]***, Ms. Ayşenur Özdemir*** [1]***, Mr. Ali Ersin Acar*** [1]

1. *Boğaziçi University*

Ionic hydrogen bonds (IHBs) have higher bond energy and are less directional compared to neutral hydrogen bonds. They form with a proton transfer (i.e., acid-base complexation) between organic anions (e.g., carboxylates, phosphates, sulfates) and cations (e.g., amines) which is well observed in biological systems like cell membranes. IHBs have recently been widely utilized to assemble supramolecular polymers due to their directionality, high stability, accessibility, and thermo-reversible nature.

Herein, we prepared a physically cross-linked network by reacting telechelic carboxylic acid functional polyesters and different amines (monomeric or polymeric). A series of non-covalent networks were prepared by simply mixing polyesters and amines in a batch reactor in the melt state. Incorporating ionic hydrogen bonds in polymer networks can considerably increase mechanical strength, flexibility, and the ability to stretch simultaneously by effectively dissipating energy during deformation. It can also impart good self-recovery properties. FTIR spectroscopy was used to analyze network formation. FTIR analysis could give insights into the formation of the amino carboxylate salt by observing the shifts in the C=O and O-H stretching peaks. Furthermore, DSC analysis can also give an understanding of the physical interactions. Eisenberg [1] discovered that groups of ion pairs come together to form multiplets, which then congregate to form larger clusters. These clusters are the physical cross-link points that restrict the mobility of polymer segments surrounding them. So, the Tg of the main polyester will be increased after physical network formation due to restricted chain mobility in the proximity of clusters which results in the formation of a hard phase. Lastly, the mechanical properties were expected to increase after network formation, which will be analyzed with rheological tests (such as temperature sweep, frequency sweep, and flow curve). The analysis of different associative pairs will be done to get an understanding about the interaction strength of the physical networks, which can be used to develop new materials in the future for different application areas.

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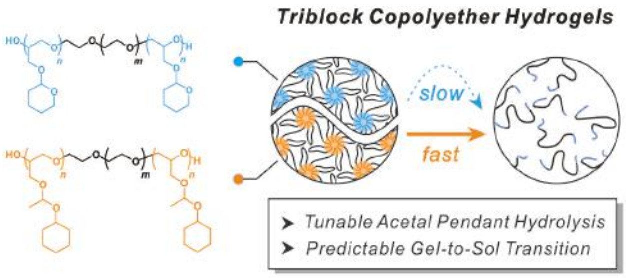
Hydrolysis-Driven Viscoelastic Transition in Triblock Copolyether Hydrogels with Acetal Pendants

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Mr. Jinsu Baek [1] ***, Prof. Byeong-Su Kim*** [1]

1. *Yonsei University*

While the hydrolytic cleavage of ester groups is widely exploited in degradable hydrogels, the scission at the midst of chain backbones can bring dramatic changes in the mechanical properties of the hydrogels. However, the predictive design of the mechanical profile of the hydrogels is a complex task, mainly due to the randomness of the location of chain scission. To overcome this challenge, we herein present degradable ABA triblock poly(ethylene oxide)-based hydrogels containing an A-block bearing acetal pendant, which provides systematically tunable mechano-temporal properties of the hydrogels. In particular, hydrophobic endocyclic tetrahydropyranyl or exocyclic 1-(cyclohexyloxy)ethyl acetal pendants are gradually cleaved by acidic hydrolysis, leading to the gel-to-sol transition at room temperature. Most importantly, a series of dynamic mechanical analyses coupled with *ex situ* NMR spectroscopy revealed that the hydrolysis rate can be orthogonally and precisely tuned by changing the chemical structure and hydrophobicity of acetal pendants. This study provides a new platform for the development of versatile degradable hydrogels in a highly controllable manner.



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Synthesis and characterization of chitosan films modified with poly(vinyl alcohol) and graphene

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

Dr. Maria Nerantzaki[1], ***Mr. Dimitrios Trikkaliotis***[2], ***Prof. George Kyzas***[2]

1. *University of Strasbourg, CNRS, ISIS, Strasbourg, France,* ***2.*** *Department of Chemistry, International Hellenic University, Kavala, Greece*

Introduction

The combination of chitosan (CS) with poly(vinyl alcohol) (PVA) holds a great potential for heavy metal removal from aqueous solutions,[1] especially when combined with a suitable third chelator, for developing highly efficient sorbents for heavy metal and organic pollutants.[2] The premise of this work is to enhance the stability and efficiency of CS-based films through modification with PVA and graphene, for possible use in heavy metal removal from water/wastewater.

Methods

PVA/CS composite films were obtained by the casting from solution technique, starting from appropriate amounts of PVA and CS, as polymer matrices, whereas graphene nanoparticles were used as reinforcing additives. Raw materials and products were characterized with several techniques, including Fourier-transform infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS), nitrogen porosimetry, Raman, spectroscopy, atomic force microscopy (AFM) and contact angle measurements.

Results and Discussion

Results obtained from the FTIR spectra and the studies on mechanical properties, revealed that interaction between CS (amino groups) and PVA (hydroxyl groups) was achieved.[3] In addition, water contact angle measurements showed an increase in the hydrophilicity of the blended films, suggesting that the blending of chitosan with PVA improved the surface wettability of the resulting films. Moreover, CS/PVA and graphene could mix with each other homogeneously and the mechanical properties of the as-prepared films were improved significantly over that of the pure CS/PVA films, especially at wet state.

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[3] W. Sun, H. Ou, Z. Chen, Nanomaterials 2022, 12, 3931.

Self-organization of the backbone of an ionomeric brush copolymer

Tuesday, 25th April - 13:00: Poster Session 2 - Poster

***Dr. Alina Mariasevskaia* [1], *Dr. Alexander I Buglakov* [1], *Dr. Denis V Anokhin* [1], *Dr. Dimitri A. Ivanov* [2], *Dr. Bruno Ameduri* [3]**

***1.** Lomonosov Moscow State University, **2.** Lomonosov Moscow State University & Institut de Sciences des Matériaux de Mulhouse-IS2M, CNRS UMR 7361, Mulhouse France, **3.** CNRS ICGM*

The work aims at designing a novel class of cost-effective PEMs, keeping the fluorinated matrix and sulfonic acids in order to maintain the required chemical stability and the proton-bearing mechanism, while integrating powerful self-organizing assembling moiety in the polymer structure in order to position the channels in an orientated way during the membrane fabrication step. The present study constitutes a preliminarily investigation of self-organization of the ionomeric moiety: $ICH_2CH_2CF_2CF_2OCF_2CF_2SO_2OH$. The Differential Scanning Calorimeter (DSC) measurements show a peak at 150°C tentatively attributed to a crystal-to-crystal transition typical of amphiphilic calamitic molecules and an intense peak at 218°C corresponding to isotropization of the sample. Temperature-resolved small- and wide-angle X-ray scattering measurements carried out at the ID02 beamline of the ESRF in Grenoble show a crystal-to-crystal transition and melting. Indexation of the WAXS pattern at room temperature shows formation of a monoclinic unit cell: a=2.72 nm, b=0.50 nm, c=0.51 nm, alfa=80°, beta=90°, gamma=90°.The high-temperature phase can be indexed to a triclinic unit cell with parameters: a=2.56 nm, b=0.51 nm, c=0.49 nm, alfa=95°, beta=97°, gamma=88°. Molecular modelling performed using the COMPASS force field allowed finding the arrangement of the ionomer in the unit cell. A **P1 cell group** with parameters $a = 0.466$ nm, $b = 2.625$ nm, $c = 0.491$ nm, $\alpha = 96.61°$, $\beta = 78.26°$, $\gamma = 100.39°$ has the lowest energy. At T = 500K, both the translational and orientation order disappears, which indicates the melting of the lattice.

Acknowledgments: The authors acknowledge Peter Boesecke from ID02 beamline of ESRF for assistance in the experiment and Ministry of Science and Higher Education of the Russian Federation (State Contract 075-15-2022-1117 from 30 June 2022) for financial support.

Photocatalytic decarboxylation to derivatize and degrade (co)polymers

Tuesday, 25th April - 14:00: Oral Session 6-1 - Oral

Prof. Brent Sumerlin [1]

1. *University of Florida*

Introduction

Post-polymerization modification strategies have advanced considerably in recent decades due to the discovery and development of highly efficient chemoselective reactions. These methods facilitate the synthesis of complex macromolecules by providing methods to transform pendent or terminal reactive groups of polymers into the desired functionality after polymerization. Post-polymerization modification often enables polymers with diverse properties to be generated from the starting material merely by using different reagents for functionalization. Ideal modifications to polymer structures are rapid, specific, efficient, and able to be performed catalytically to lead to functional polymers or copolymers that are inaccessible by direct polymerization.

Methods

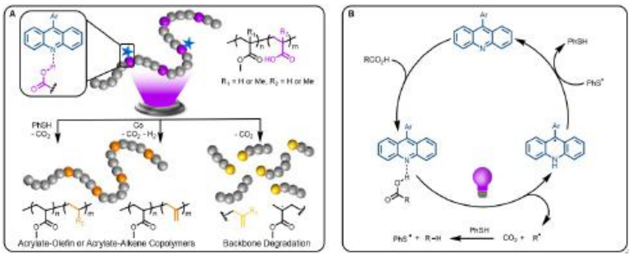
Relying solely on mild ultraviolet or visible light irradiation of thiocarbonylthio compounds, we have developed a new avenue to polymer-protein conjugates, semi-telechelic polymers, and well-defined ultrahigh molecular weight (UHMW) block polymers. Using either a photocatalyst or relying on the direct activation of photoactive functional groups, we devised a strategy to functional polymers with unprecendented molecular weights, complex architectures, and controlled microstructures.

Results

Photochemistry applied to commodity poly(meth)acrylates allowed us to (i) synthesize polymers by photoiniferter polymerization and (ii) install new functionality to these polymers to prepare copolymers of (meth)acrylates and olefins that are inaccessible by direct copolymerization. Extending these approaches to the rapidly growing field of photocatalytic decarboxylation, we were also able to prepare photodegradable polymers that have all-carbon backbones. Finally, we have demonstrated that by employing the traditional conditions of photopolymerization at elevated temperatures, we are able to achieve dramatically accelerated depolymerization to regenerate monomer, suggesting low-energy photochemistry can be leveraged to approach life-cycle circularity.

Discussion

We demonstrated that decarboxylation of copolymers possessing activated esters or carboxylic acids is a versatile method for the derivatization or degradation of polymer backbones. The process is attractive for polymer modification because it is rapid, involves mild conditions, and, in some cases, bypasses the need for preactivation, granting high atom economy. We established that the backbone radicals generated by direct decarboxylation can be converted into multiple functional groups or lead to chain cleavage, depending on the structure of the copolymer and the presence of other reagents.



Photodecarboxylation.jpg

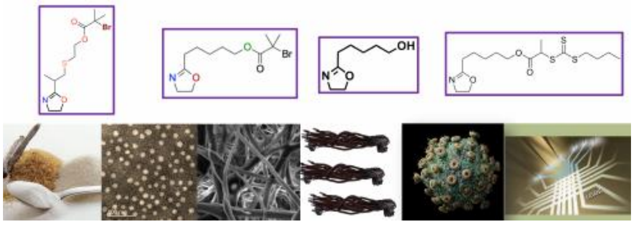
Macromolecular design strategies with poly(2-oxazoline)s

Tuesday, 25th April - 14:30: Oral Session 6-1 - Oral

Prof. Remzi Becer [1]

1. *University of Warwick*

Poly(2-oxazoline)s are a very versatile class of monomer that allows the maximum flexibility in macromolecular design. 2-Oxazoline monomers can be polymerised by cationic ring opening polymerization using initiators such as acid halides or tosylates. The living nature of the polymer chain end allows end capping of chains with high chain end fidelity. Other than the alpha/omeaga chain end functionalization it is also possible to introduce functional groups on the side chains of 2-oxazolines. In our recent studies, we have introduced radical initiators such as an alpha-isobromo butyrate or a chain transfer agent. That allows combination of catatonically polymerizable 2-oxazolines and radically polymerizable vinyl monomers. Such structures are used in a variety of applications ranging from nucleic acid delivery to engine oil additives.



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New Advances on Visible Light Induced Ambient Temperature Photodegradation and Photopolymerizations

Tuesday, 25th April - 15:00: Oral Session 6-1 - Oral

Mr. Huseyin Cem Kiliclar [1]***, Ms. Zeynep Arslan*** [1]***, Ms. Yusra Bahar Cakir*** [1]***, Mr. Ragip Talha Uzun*** [1]***,***
Prof. Yusuf Yagci [1]

1. *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,*

Visible light induced systems are at the center of attention recently as they provide spatiotemporal control over the reaction media while decreasing the energy requirements. By taking advantage of the efficient nature of light, our research group has successfully developed novel synthetic methods for several polymerizations by using visible light at ambient temperature, overcoming the negative effects of thermally induced polymerizations.[1] In this study, visible light and broadband white LED light induced systems were applied to the field of depolymerization and degradations.

Depolymerization and degradation reactions gained importance since we are moving toward a self-sustainable world. Conventional methods require high temperatures and toxic metal catalysts that decrease the overall efficiency of the method and increase operating costs. However, several research groups have developed advanced approaches to reduce the requirement for high temperatures and catalysts.[2-4] Our research group has developed novel systems to initiate the depolymerization and degradation of halogen-containing PMMA derivatives. The effect of the regional presence of halogens at the main chains on degradation yield was examined and mechanisms were proposed. Light dependence of the degradations were investigated by temporal control experiments.

Researches on this line are being developed to a variety of polymers by our research group.

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Emerging applications of poly(2-isopropenyl-2-oxazoline) materials

Tuesday, 25th April - 15:15: Oral Session 6-1 - Oral

Dr. Valentin Victor Jerca [1]***, Dr. Florica Adriana Jerca*** [1]

1. *Smart Organic Materials Group, “Costin D. Nenitzescu” Institute of Organic and Supramolecular Chemistry, Romanian Academy, 202B Splaiul Independentei, 060023 Bucharest*

Poly(2-isopropenyl-2-oxazoline) (PiPOx) has attracted an increased scientific attention as a reactive polymer for the synthesis of advanced functional materials.[1] PiPOx is a versatile polymer which is soluble in water and various organic solvents, can be prepared with well-defined characteristic, and exhibits high thermal and good hydrolytic stability.[1-3] Furthermore, PiPOx was shown to be biocompatible[4,5], rendering it suitable for medical and pharmaceutical applications. The pendent 2-oxazoline group can be transformed in an efficient, mild, and selective manner providing an extremely valuable toolbox for the synthesis of advanced materials.[1,2] The post-polymerization modification reaction with (di)carboxylic acids enabled access to a wide variety of structures with defined and controlled properties.[1] The versatility of this modification method allows the synthesis of a wide variety of functional polymers with tunable properties from soft to hard materials.[3-7]

Recent developments from our research group that illustrate the potential of PiPOx as smart (bio)materials will be discussed in this lecture, ranging from fundamental studies on ring opening addition of PiPOx with carboxylic acids to emerging applications of these polymers as biomaterials, optical data storage media and drug delivery vehicles.

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V.V.J. and F.A.J acknowledge the Romanian Ministry of Research, Innovation and Digitalization, CNCS/CCCDI – UEFISCDI, project number PN-III-P2-2.1-PED-2021-1776 within PNCDI III, for the financial support.

Molecular Photoswitching of Main-chain α-Bisimines in Solid-State Polymers

Tuesday, 25th April - 15:30: Oral Session 6-1 - Oral

Mr. Linh Duy Thai [1]***, Dr. Thiago R. Guimaraes*** [1]***, Dr. Lewis Chambers*** [1]***, Dr. Jochen Kammerer*** [1]***, Dr. Anja S. Goldmann*** [1]***, Prof. Dmitri Golberg*** [1]***, Dr. Hatice Mutlu*** [2]***, Prof. Christopher Barner-Kowollik*** [1]

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Photo-responsive polymeric materials that exhibit either reversible or irreversible behavior upon interaction with light have received growing attention recently. The unique properties of such materials are dictated by the covalently embedded photo-active elements or chromophores. The chemical transformation of those groups which occurs at the molecular level can trigger changes at the nano-/macroscopic level, namely chain folding, morphological switching, shape or color changing. Various practical applications have been found for photo-active polymers in catalysis, nanomedicine, and nanotechnology.

However, studies on photo-responsive polymers in the solid state are significantly less frequent than those in solution. Some examples are based on orientation changes of azobenzene-based block copolymer thin-film morphologies[1] or shape changes of hydrazone-derived crosslinked polymers.[2] However, there is a critical gap in the literature analyzing the impact of polymer topologies and structures on the performance of the constituting chromophores. Recently, our group has reported α-bisimine-based diblock copolymers featuring reversible isomerization of the imine-based chromophores in the backbone of one block upon UV irradiation.[3] We envisage the application of such materials in the realm of lithography, introducing the concept of 'Dynamic Block Copolymer Lithography' (DBCL).

Herein, we report a series of main-chain α-bisimine-based homopolymers synthesized from head-to-tail Acyclic Diene Metathesis (ADMET) polymerization and demonstrate that they can be photochemically switched in the solid state. We show that while there is no difference in the kinetics of the photoisomerization in solution, photoswitching kinetics of these polymers in the solid state critically depends on the polymer structures. We hypothesize that the variation in the performance of the photoswitch in the solid state is due to changes in the intermolecular stacking among the chromophores. Our investigations lay the groundwork for the future study of light-induced morphological transformation of α-bisimine-based block copolymer thin films. The macromolecular design principles established herein for efficient solid-state photoisomerization can also serve as a blueprint for enhancing the solid-state isomerization efficiency for other polymer systems.

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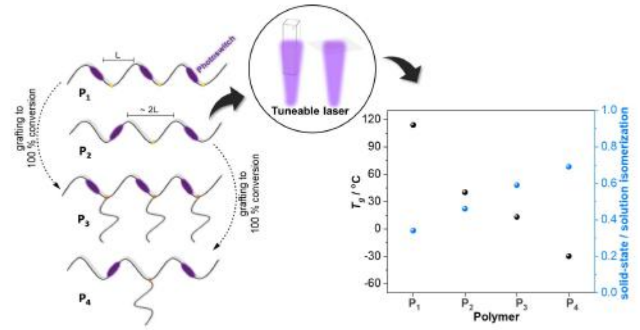

Picture4.jpg

Metal Acetylacetonate-Bidentate Ligand Interaction (MABLI) (Photo)Activated Polymerization : Toward High-Performance Amine-Free, Peroxide-Free Redox Radical (Photo)Initiating Systems

Tuesday, 25th April - 15:45: Oral Session 6-1 - Oral

<u>Mr. Nicolas Giacoletto</u> **[1]**, ***Ms. Marie Le Dot*** **[2]**, ***Dr. Fabrice Morlet-Savary*** **[2]**, ***Ms. Bernadette Graff*** **[2]**, ***Ms. Valérie Monnier*** **[1]**, ***Dr. Didier Gigmes*** **[3]**, ***Dr. Malek Nechab*** **[1]**, ***Dr. Frédéric Dumur*** **[3]**, ***Prof. Jacques Lalevée*** **[2]**

1. *Aix Marseille Université,* ***2.*** *Université de Haute-Alsace,* ***3.*** *Aix-Marseille Université*

From a circular plastic economy perspective, a new configuration of Metal Acetylacetonate Bidentate Ligand Interaction (MABLI) mechanism adapted to the chemistry of the recyclable Elium® thermoplastic resins has been developed by our group to initiate the free radical polymerization of these resins under mild conditions (under air, at room temperature, non-purified monomers, absence of hazardous chemical substances). This MABLI process involves simultaneous ligand exchange and a change of the metal oxidation degree and is associated with the efficient release of free radicals. This initiating strategy is based on the synergy between the initial MABLI couple and a phosphine oxide (Type I photoinitiator). Despite the absence of irradiation, the mere presence of the phosphine oxide significantly reduced the curing time and the final conversion obtained is nearly 100%. In order to dismantle the role of each component and to predict new high-performance MABLI redox initiating systems based on a similar configuration, a mechanistic study was carried out using mass spectroscopy, EPR measurement and theoretical calculations. It has resulted in the identification of new hybrid complexes obtained by ligand exchange between the photoinitiator and the metallic complex. On the other hand, presence of the Type I photoinitiator can level up the initiating strategy by combining MABLI and photoactivation into a dual cure approach: thereby, the photolysis yield and the polymerization efficiency of the complexed form of the phosphine oxide was studied and compared to the free form of the photoinitiator.

In this presentation, these recent developments concerning the MABLI approach will be presented.

References:

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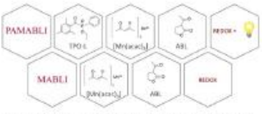

Figure 1. Compounds involved in the MABLI process and in the PAMABLI process.

Compounds involved in the pa mabli process.jpg

New strategies for storing and reading data on sequence-defined macromolecules

Tuesday, 25th April - 14:00: Oral Session 6-2 - Oral

Prof. Filip Du Prez [1]***, Dr. Nezha Badi*** [1]***, Mr. Matthieu Soete*** [1]***, Ms. Irene De Franceschi*** [1]

1. *Ghent University*

Advances made by polymer chemists in recent years have led to the preparation of highly functionalised polymer architectures with defined structure-property relationships. However, these structures do not reach the same potential as their natural counterparts such as DNA and proteins.

Thus, in the last decade, efforts have increased to achieve perfect control over the primary structure of macromolecules to create a unique correlation between properties and structure. In this context, numerous methods have been explored for the synthesis of sequence-defined macromolecules: iterative reactions on a solid or soluble support, flow reactors, small molecular machines, multicomponent reactions, etc. Such structures consist of a defined chain length (single mass), end groups, composition and topology and prove promising in application fields such as anticounterfeiting, biological mimicking and chemical data storage. Recently, lots of techniques became available to read the obtained information in efficient ways, for which an overview can be found in a very recent perspective (**Fig. 1**).[1,2]

This presentation will first shortly introduce our efforts for the synthesis and reading of sequence-defined oligomers for data storage. Our preferred chemical platform facilitated the introduction of a versatile chemical alphabet to write not only sentences but also a QR-code with the combination of computer software to enable automated reading and writing.[3] Then, the presentation will showcase the latest advancements made for the sequencing of macromolecules, both with and without MS/MS techniques.[4] Finally, our results and ambitions with regard to the upscaling of this new generation of macromolecules and the introduction in the material field will be presented.[5]

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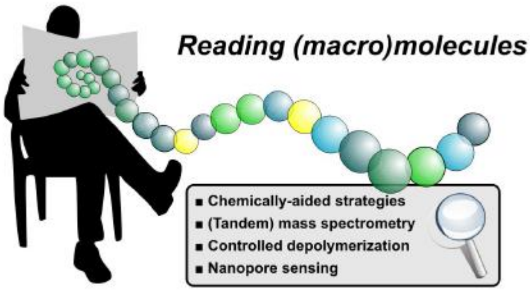

Figure abstract.jpg

Sticky stuff - precision glycopolymers to mimic and tune bioadhesion

Tuesday, 25th April - 14:30: Oral Session 6-2 - Oral

Prof. Laura Hartmann [1]

1. *Heinrich-Heine-University Duesseldorf*

In Nature, adhesion takes place on many length scales, from a mussel sticking to a rock to viruses adhering to cells in the first step of an infection. These processes are driven by biomacromolecules such as proteins and polysaccharides. In order to better understand and then address such adhesion processes e.g., to inhibit an infection or develop better glues, we can apply biomimetic polymers. Previously, we have introduced the so-called solid phase polymer synthesis that gives us straightforward access to a variety of sequence-defined peptide- and glycomimetic macromolecules. The stepwise assembly of tailor-made building blocks results in synthetic macromolecules with control over the types, number and positions of different functional moieties such as charged groups, amino acid residues or carbohydrate ligands. This lecture will present the general concept of solid phase polymer synthesis and then highlight examples where we applied our toolbox to create macromolecules that are used as model systems and modulators of bioadhesion including synthetic and biological membranes.

Concurrent control over sequence and dispersity in multiblock copolymers

Tuesday, 25th April - 15:00: Oral Session 6-2 - Oral

Ms. Maria Nefeli Antonopoulou [1]***, Prof. Athina Anastasaki*** [1]

1. *ETH Zurich*

Controlling monomer sequence in synthetic macromolecules is a major challenge in polymer science and the order of building blocks has already been demonstrated to determine macromolecular folding, self-assembly and fundamental polymer properties. Dispersity is another key parameter in material design, with both low and high dispersity polymers displaying unique properties and functions.[1] However, synthetic approaches that can simultaneously control both sequence and dispersity remain experimentally unattainable. In this talk we will present a simple, one pot, and rapid synthesis of sequence-controlled multiblocks with on demand control over dispersity while maintaining high livingness, good agreement between theoretical and experimental molecular weights and quantitative yields. Key to our approach is the regulation in chain transfer agent activity during controlled radical polymerization that enables the preparation of multiblocks with gradually ascending ($Đ$=1.16 →1.60), descending ($Đ$=1.66 →1.22), alternating low and high dispersity values ($Đ$=1.17 →1.61 →1.24 →1.70 →1.26) or any combination thereof.[2] The enormous potential of our methodology was further demonstrated through the impressive synthesis of highly ordered pentablock, octablock and decablock copolymers yielding the first generation of multiblocks with concurrent control over both sequence and dispersity.

Keywords: sequence control, multiblocks, dispersity

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AIE polymer micelles/vesicles photocatalysts combined with native enzymes for aerobic photobiocatalysis

Tuesday, 25th April - 15:15: Oral Session 6-2 - Oral

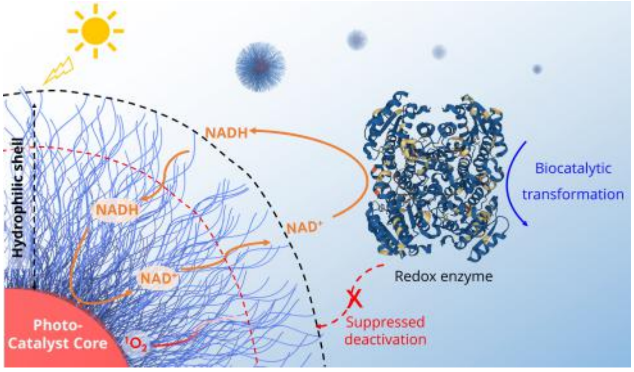
Dr. Nian Zhang [1], Dr. Sylvain Trépout [2], Dr. Hui Chen [1], Dr. Min-Hui Li [1]

***1.** Chimie ParisTech, PSL University, CNRS, Institut de Recherche de Chimie Paris, UMR8247, **2.** Institut Curie*

Biocatalytic transformation has attracted increasing attention in the green synthesis of chemicals due to the diversity of enzymes, their high catalytic activities and specificities, and environmentally benign conditions. Most of redox enzymes in nature are dependent on nicotinamide cofactors like NAD^+/NADH. The use of solar energy, especially the visible light, in the regeneration of cofactors through the combination of photocatalysis and biocatalysis provides an extraordinary opportunity to make complete green processes. However, the combination of photocatalysts and enzymes has been challenged by the rapid degradation and deactivation of the enzymatic material by photogenerated reactive oxygen species (ROS). Here, we design core-shell structured polymer micelles and vesicles with aggregation-induced emission (AIE) as visible-light-mediated photocatalysts for highly stable and recyclable photobiocatalysis under aerobic conditions. The NAD^+ from NADH can be efficiently regenerated by the photoactive hydrophobic core of polymer micelles and hydrophobic membrane of the polymer vesicles, while the enzymatic material (glucose 1-dehydrogenase) is screened from the attack of photogenerated ROS by the hydrophilic surface layer of polymer colloids. After at least 10 regeneration cycles, the enzyme keeps its active state, meanwhile polymer micelles and vesicles maintain their photocatalytic activity. These polymer colloids show the potential to be developed for the implementation of industrially relevant photobiocatalytic system.

Ref.

Zhang, N., Trépout, S., Chen, H., & Li, M. H. (2022). *J. Am. Chem. Soc.* https://doi.org/10.1021/jacs.2c09933



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Polymeric analogues of Green Fluorescent Protein with conformationally controlled fluorescence

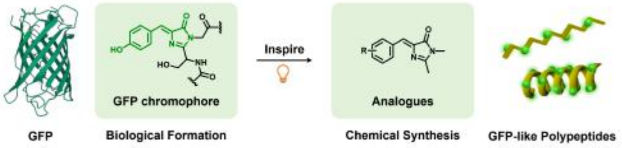
Tuesday, 25th April - 15:30: Oral Session 6-2 - Oral

Mr. Sifan Ji [1] ***, Dr. Chloé Grazon*** [1] ***, Prof. Sébastien Lecommandoux*** [1] ***, Dr. Colin Bonduelle*** [1]

1. *University of Bordeaux*

Green fluorescent protein (GFP), which is composed of a central chromophore surrounded by a protein cage, has become a unique fluorescent probe for life science awarded the 2008 Nobel Prize in Chemistry. In recent years, synthetic GFP chromophore analogues have been developed to mimic the photophysical properties of GFP. However, little attention has been paid to the influence of the polypeptide backbone environment on these chromophores to mimic the properties of natural protein.

In this context, we present the use of protein-like polymers obtained by ring-opening polymerization (ROP) of N-carboxyanhydrides (NCAs) to study the photophysical properties of several GFP chromophore analogues. Our goal is to design GFP-like polypeptides based on poly(L-glutamate) scaffolds with brightness and fluorescence efficacy in the range of GFP natural model. We observe that a precise control of the secondary structure of polypeptides confines the chromophore and restricts its rotation, thereby increasing the fluorescence. These first results show that GFP-like polypeptides obtained by ROP pave the way for applications in drug delivery, bio-imaging and bio-sensing to better control the spatial and temporal properties of light in synthetic biomaterials.



Sifan ji toc polymeric analogues of green fluorescent protein with conformationally controlled fluorescence.png

Rewritable macromolecular data storage with automated read-out

Tuesday, 25th April - 15:45: Oral Session 6-2 - Oral

Mr. Matthieu Soete [1]***, Dr. Kevin De Bruycker*** [1]***, Prof. Filip Du Prez*** [1]

1. *Ghent University*

Different reports have recently pointed out that the quantity of microchip-grade silicon will not be able to follow the increasing demand needed for storing all the data that is being created every day, hence researchers started to explore alternatives to current data storage media.[1] One of these include the storage of information on the molecular level, whereby DNA has already demonstrated to be one of the potential candidates to revolutionise routine data storage measures.[2] In addition, the use of monodisperse synthetic macromolecules, whereby information is stored on the macromolecular chains by means of their monomer order, offers a series of advantages.[3] However, the focus of this research is often directed towards the development of an archival data storage medium, whereby rarely-accessed information that has to be saved for an extended period of time, e.g. legal documents, is stored on information-containing macromolecules.[4]

Aiming to take advantage of the use of synthetic macromolecules, we reported a simple strategy for rewriting macromolecular information by introducing an editable position tag to each macromolecule.[5] By making use of this approach, which relies on the orthogonal cleavage of a thioester moiety via aminolysis, an exemplary sentence encoded on a set of macromolecules could be efficiently rewritten (**Fig.1**).

In this case, decoding the monomer order was successfully achieved by making use of tandem-MS techniques. In order to facilitate this read-out process, we also developed an algorithm that is capable of decoding large portions of macromolecular information without interference from the operator. Finally, the presence of four distinct fragmentation sets during MS/MS analysis avoided the need for error correcting schemes within the algorithm.

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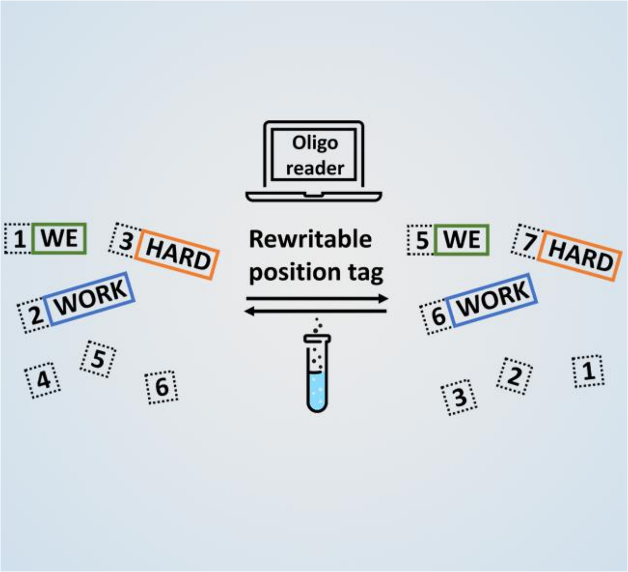

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How Does Topology Affect on the Property of Polyglycerol and Its Derivatives?

Tuesday, 25th April - 14:00: Oral Session 6-3 - Oral

Prof. Byeong-Su Kim [1]

1. *Yonsei University*

Controlling the topology of a polymer is essential in determining its physical and chemical properties. In this talk, I will discuss our recent efforts in providing a diverse array of polymeric topologies, particularly within the framework of polyglycerols (PGs). Specifically, we propose a new synthetic approach toward the controlled hyperbranched PGs using 1) conventional anionic ring-opening polymerization based on novel functional epoxide monomers, and 2) frustrated Lewis pair polymerization. The resulting hyperbranched PG and its derivatives demonstrated unique features associated with the confined three-dimensional geometry along with its rich functionality that are absent in its linear counterpart. Two specific examples including janus regulation of ice growth control and generation of reactive oxygen species will be presented with future prospectives.

Hydrophobized hyperbranched polyglycidol as a potential matrix for antifungal drug delivery

Tuesday, 25th April - 14:30: Oral Session 6-3 - Oral

Mrs. Daria Jaworska-Krych **[1]** ***, Dr. Mateusz Gosecki*** **[1]** ***, Ms. Malgorzata Urbaniak*** **[1]** ***, Dr. Monika Gosecka*** **[1]**

1. *Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*

Introduction

Nowadays most drugs used in therapies are hydrophobic, which defines their low bioavailability [1]. The improvement of the drugs solubility but also the extension of retention time of the carrier with the afflicted area is crucial. The usage of hydrogel matrices could be helpful. The utilization of micelles for the network construction may overcome the discrepancy between hydrophilic character of hydrogels and hydrophobicity of drugs. However, the disadvantage of using standard micelles is their instability at a concentration below cmc which leads to their degradation. To overcome the limitations of standard micelles unimolecular micelles (UM), which can be constructed of amphiphilic dendrimer-type, star-shaped and hyperbranched macromolecules, could be applied. Hyperbranched polyglycidol (HbPGL) has a great potential for the construction of UM. Its structure delivers many monohydroxyl groups which can be selectively modified with hydrophobic molecules to create suitable environment for water-insoluble drugs, whereas the hydrophilic corona of HbPGL assures its solubility in water [2].

Methods

The structure of obtained amphiphilic constructs was confirmed with NMR spectroscopy. Clotrimazole was applied as a model drug for experiments of the drug encapsulation. The drug release profile was determined with UPLC (photodiode array detector). The presence of diol groups in HbPGL corona enabled formation of boronic esters resulted in the dynamic hydrogels formation, which rheological properties, including self-healing and injectable behaviour were investigated.

Results

The results demonstrate the impact of the degree of hydrophobization of HbPGL on its solubilization in the aqueous medium, encapsulation of the drug, and rheological properties of formed hydrogels.

Discussion

Our studies revealed a significant influence of HbPGL core hydrophobization on the solubilization of macromolecules. Moreover, drug encapsulation efficiency depended not only on the degree of hydrophobization but also on the type of linkages with which the hydrophobic molecules were incorporated into HbPGL.

This work was supported by the NSC, Poland (UMO-2018/30/E/ST5/00576), Principal Investigator: dr hab. Monika Gosecka. This research has been completed while Daria Jaworska-Krych was the Doctoral Candidate in the IDS at the TUL, Poland.

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Imparting stress or water triggered self-folding to shape memory composite sheets

Tuesday, 25th April - 14:45: Oral Session 6-3 - Oral

Mr. Oscar Rabaux [1], *Dr. Raphaël Riva* [1], *Prof. Christine Jerome* [1]
1. University of Liège

Shape-memory polymers are a thriving class of materials able to recover their as-processed (initial) shape from another deformed fixed (temporary) shape. This functionality enables those materials to be used in a wide range of applications, especially when complex geometries are required. Among those, recently developed shape-memory composite sheets (SMCS) made of a fibrous semi-crystalline polymer filler embedded in an elastomer matrix, make easy the fabrication of self-folding sheets upon accurate stimulus by creating a gradient along the sheet thickness.

Firstly, we designed self-folding SMCS by embedding honey-comb structured electrospun poly(ε-caprolactone) (PCL) nanofiber mats in a thermally cured poly(dimethyl siloxane) (PDMS) elastomer. Structuring the electrospun mat in-plane, enabled to structure the composition of the sheet over the thickness leading to self-folding actuated by uniaxial elongation (Figure 1a). We demonstrated that the shape of the self-folded sheet is controlled by tensile-stress direction and intensity.

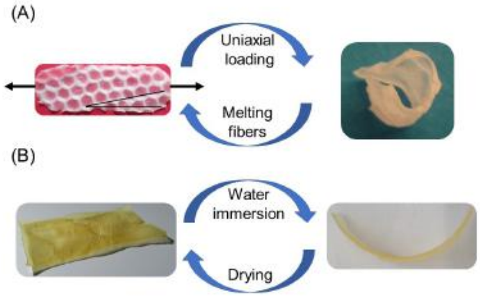
Besides, a fully degradable SMCS was designed by using a UV-cured hydrophilic poly(phosphoester) (PPE) as elastomer matrix. Different affinities between the polymers involved create a thin layer of PPE underneath the composite leading to SMCS with water triggered self-folding (Figure 1b).

For both composites, the nanofibers diameter and content were tuned to optimize the shape-memory properties of the SMCS. In both cases, fixity and recovery above 98% were achieved.

The UV curing that has the advantages to be fast over thermal curing and to occur at room temperature preserving the fibers from melting during processing was found very efficient and leads to highly homogeneous crosslinking of the PPE matrix thanks to the high scattering of the UV-A light by the fibers (diameter ≈ 600nm).

These results offer a large scope of potential biomedical applications from biostable hydrophobic sheets with biocompatible PDMS to biodegradable ones with PPE. In that case, hydrolytic degradation showed a progressive unveiling of the PCL fibers of the sheets starting after one week and being almost complete after 3 months due to the faster hydrolytic degradation of PPE than PCL.

In summary, two SMCS families were designed with controllable functionalities enlarging the scope of applications, mainly thanks to tunable degradation, stiffness and self-folding trigger.



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Processing-structure relations in individual electrospun fibers for property optimization

Tuesday, 25th April - 15:00: Oral Session 6-3 - Oral

Mr. Arnaud Laramée [1]***, Mrs. Catherine Lanthier*** [1]***, Prof. Christian Pellerin*** [1]

1. *Université de Montréal*

Electrospun fibers are nanostructures formed by the solidification of an electrified jet drawn from a viscous polymer solution. They often show an exponential increase in mechanical, electrical, and optical properties at small diameters, making them promising candidates for applications in fields such as tissue engineering, selective filtration, and energy harvesting. Grasping how polymer chains orient and change conformation during electrospinning is crucial to understand the effect of processing parameters on fiber properties. Our group has developed confocal Raman spectromicroscopy methodologies to probe orientation and structure at the individual fiber level.

This presentation highlights the impact of three major electrospinning parameters, namely the crystallinity of the polymer, the type of collector onto which fibers are deposited, and the nature of the solvent. Raman spectromicroscopy on poly(oxymethylene) (POM) and poly(ethylene oxide) (PEO) fibers of high (□60%) and very high (□75%) crystallinity, respectively, evidenced that a higher crystallinity leads to a greater molecular orientation which is maintained over a wider range of fiber diameters (500-2800 nm).[1] PEO fibers maintained this high orientation whether they are deposited on a static collector or a collector providing additional mechanical or electric stretching.[2] In contrast, low-crystallinity poly(ethylene terephthalate) (PET) fibers exhibited weaker orientation and, interestingly, the choice of collector strongly impacted the orientation-diameter curve and the development of the oriented mesophase.[3] Such variations were mainly attributed to the viscosity of the PET jet when the collector-induced stretching occurred.[3] Our current efforts aim to optimize this crucial strain-viscosity balance through the volatility and quality of the electrospinning solvent to reach higher orientations in low-crystallinity systems. With such studies, we hope to stimulate the larger-scale application of high-performance electrospun fibers of both high- and low-crystallinity polymers.

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“Super-hydrophilic” poly(2-oxazoline)

Tuesday, 25th April - 15:15: Oral Session 6-3 - Oral

***Dr. Somdeb Jana* [1], *Mr. Milan Roels* [1], *Dr. Meike Leiske* [2], *Dr. Yann Bernhard* [1], *Prof. Bruno De Geest* [1], *Prof. Richard Hoogenboom* [1]**

1. *Ghent University,* ***2.*** *University of bayreuth*

Avoiding non-specific interaction is one of the most important key features required by the nanoparticles (NP) for wide range of *in-vivo* applications from drug delivery to diagnostics. “Super-hydrophilic” polymers generally possess strong non-fouling characteristics and therefore, has the potential to avoid non-specific/unwanted interactions with blood proteins when applied *in vivo* for drug/gene delivery to diagnostics. Poly(2-oxazoline)s represents a special class of bio-inspired polymers with multiple applications, especially in the field of polymer therapeutics. The straightforward access to the wide verities of side chain and chain end functional poly(2-oxazoline)s via cationic ring-opening polymerization (CROP) of various 2-subsstituted-2-oxazoline monomers as well as post-polymerization modification strategy, in combination with their thermo-responsive, biocompatible, stealth and protein repellent properties of water soluble homologues enables the construction of highly functional poly(2-oxazoline) materials.

In this contribution, we revitalize a protected alcohol functionalized 2-oxazoline monomer, 2-acetoxymethyl-2-oxazoline, highlighted almost fifty-five years ago and explore the possibility of making “super-hydrophilic” poly(2-oxazoline) for biomedical applications. The synthesis of 2-acetoxymethyl-2-oxazoline monomer and its interesting cationic ring-opening polymerization kinetics phenomenon is demonstrated. Subsequently, controlled hydrolysis of the resulting poly(2-acetoxymethyl-2-oxazoline) (PAcOMeOx) generates alcohol (-OH) side chain functional poly(2-hydroxymethyl-2-oxazoline) (PHOMeOx) and their relative hydrophilicity were analysed and compared with previously reported most hydrophilic poly(2-oxazoline)s such as poly(2-methoxymethyl-2-oxazoline) and poly(2-methyl-2-oxazoline), revealing that PHOMeOx is the most hydrophilic poly(2-oxazoline) reported to date. Finally, cytocompatibility of the polymers with MDA-MB-231 breast cancer cells was explored where all the polymers appeared to be noncytotoxic. Most importantly, strong anti-fouling properties of intensely hydrophilic PHOMeOx against serum protein was confirmed from the cell association studies. The hydroxyl side chains provide a handle for efficient conjugation of drugs via a hydrolysable ester linker, enabling release of the drug in time. Therefore, such “super-hydrophilic” and anti-fouling PHOMeOx might lead to an interesting progress in the area of drug/nucleic acid delivery application.

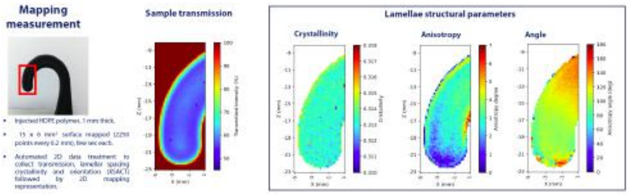
SAXS/WAXS mapping of engineered polymers: from image to nanostructure

Tuesday, 25th April - 15:30: Oral Session 6-3 - Oral

Dr. Pierre Panine [1], Dr. Alexandre Cheminal [1], Dr. Sergio Rodrigues [1]

1. Xenocs SA

The characterization of polymer materials requires most often the combination of several techniques ranging from microcopy to elemental and mechanical methods. We present in this paper the combination of imaging and nanostructure characterization that is for the first time accessible in a practical manner at the laboratory scale. Indeed, if the mapping of polymer using micron size beam is developed since 2 decades at 3rd generation synchrotron, in labs such measurement are until now limited by the flux of x-ray sources, leading to either reduced area of few mm^2 of inspection or of excessive experimental times of few days. By combining short focus optic and compact collimation, we demonstrate the capability of mapping and extracting automatically, within few seconds each, at each inspected point the nanostructural parameters of the studied polymer. In the case of a typical injected HDPE, we present the crystallinity, the lamellar spacing, its degree of and the main orientation of the lamellae in the form of maps of false colors, mapping ~ 100 mm^2 within the hour range. Further, this new capability has a large potential due to its increased x-ray flux density for broader applications such as studies of transient phenomena in organo-photovoltaic films in grazing incidence or other operando measurement such as electro-polymer embedded in renewable energy harvesting components or as in microfluidics reactors enabling high throughput self-assembly in liquido.



- Injected HDPE polymer, 1 mm thick.
- 15 x 6 mm² surface mapped (2250 points every 0.2 mm), few sec each.
- Automated 2D data treatment to collect transmission, lamellar spacing crystallinity and orientation (XSACT) followed by 2D mapping representation.

Figure abstract mapping ppanine.png

Synthesis of Polyhydroxyurethane under Near Infra Red irradiation

Tuesday, 25th April - 15:45: Oral Session 6-3 - Oral

Mr. Philibert Lenormand [1], *Dr. Didier Gigmes* [2], *Dr. Patrick Lacroix-Desmazes* [1], *Prof. Jacques Lalevée* [3], *Dr. Sylvain CAILLOL* [1], *Dr. Christine Joly-Duhamel* [1], *Dr. Julien Pinaud* [1]

1. CNRS ICGM, 2. Aix-Marseille Université, 3. Université de Haute-Alsace

Polyhydroxyurethane (PHU), obtained from the reaction of cyclocarbonates and amines, represents an eco-friendly alternative to conventionnal polyurethanes because their synthesis relies on CO_2-based precursors and does not involve toxic isocyanate compounds. However, the low reactivity of the cyclocarbonate aminolysis to form PHU represents a major drawback, particularly for industrialisation. [1] Although the kinetics of reaction can be improved in the presence of catalyst or by heating using an oven, there is still a gap of reactivity between isocyanate-alcohol and cyclocarbonate-amine additions. To overcome the lack of reactivity between cyclocarbonates and amines, we thus propose to use the photothermal effect generated by some compounds absorbing in the Near-Infra-Red (NIR) region. Indeed, photothermal effect, which consists in the production of heat at local environment by some metallic nanoparticles or organic dyes under NIR radiation, has proven very effective for increasing reaction kinetics, particularly for the synthesis of PU thermoset[2]. As NIR sensitive compound we chose the organic dye IR-813 (Figure 1) because of its commercial availability and its good solubility in organic resins. It was added to a formulation composed of trimethylolpropane tricarbonate (TMPTC) and 1,5-pentanediamine and curing of the formulation under NIR light (805 nm) was then studied. We studied various parameters such as the amount of heater or intensity of irradiation on the gel time and the maximum temperature

reached. The best system allowed reaching a temperature of 150 °C, a gel time of 3 minutes for gel contents of 94 %, using only the NIR source as external energy source. In the presence of a catalyst like DBU, even shorter gel times were observed, allowing us to envisage the use of cyclocarbonate/amine/IR-813 formulations for the production of PHU coatings and foams.

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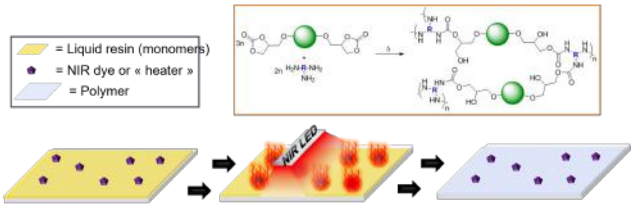

Graph abstract.png

Innovation via Polymer Assisted Encapsulation – Controlled Release Technologies

Tuesday, 25th April - 16:30: Oral Session 7-1 - Oral

Dr. Munmaya Mishra [1]

1. *ENCAPCR LLC*

Innovation is the practical implementation of ideas / technologies that result in the introduction of new products or improvement of existing products. Controlled release is a term referring to thedelivery of active ingredients in response to time or stimuli at a desired site. The control release ofactives can be achieved via encapsulation–immobilization of the same. Keeping this in mind the talk will focus on our work in the area of encapsulation – immobilization of active(s) by a variety oftechniques including controlled polymerization, coacervation, cocrystallization-complexation,emulsification, inclusion complexation, porous materials, supercritical CO2 assisted impregnation,etc. These studies will be further elaborated during this talk.

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2. M. Mishra (Ed); *Applications of Encapsulation and Controlled Release*; 2020, CRC Press (Taylor & Francis Group), Boca Raton, USA

Thermoresponsive reversible unimer micelles of amphiphilic fluorinated copolymers for encapsulation and release of hydrophobic drugs

Tuesday, 25th April - 17:00: Oral Session 7-1 - Oral

Dr. Elisa Guazzelli [1], ***Mr. Matteo Calosi*** [1], ***Prof. Marco Lessi*** [1], ***Prof. Fabio Bellina*** [1], ***Prof. Giancarlo Galli*** [1], ***Prof. Frank Uhlig*** [2], ***Prof. Elisa Martinelli*** [1]

1. Department of Chemistry and Industrial Chemistry, University of Pisa, 56124 Pisa, Italy, 2. Institute for Inorganic Chemistry, Graz University of Technology, Graz, 8010, Austria

Solvophobic interactions in amphiphilic copolymers may lead to the formation of unimer micelles in selective solvents, typically water, through single-chain folding. These unimer micelles fall in the larger category of the so-called single-chain nanoparticles (SCNPs) and feature an extremely small size range (1–20 nm). A tailored synthesis and in-depth characterization of size, shape, and conformation of these materials might drive their future exploitation in environmental chemistry, industrial catalysis, biomedicine and drug delivery.

Amphiphilic fluorinated copolymers PEGMAx-*co*-FAy were prepared by ARGET-ATRP. Combined small angle X-ray scattering (SAXS) and dynamic light scattering measurements were used to study the self-assembly behavior in water and different organic solvents. SAXS confirmed the formation of compact-globular single-chain self-folded thermoresponsive unimer micelles in water, which generally presented small hydrodynamic diameters ($D_\mathrm{h} \leq 8$ nm) as a result of the folding of the hydrophobic perfluorohexylethyl acrylate counits, and a cloud point temperature (T_cp) easily modulated by the copolymer structure in terms of composition and side-chain length of the hydrophilic component. The copolymers were also found to be able to form reverse unimer micelles in hexafluorobenzene.[1] As a proof of concept, the formation of hydrophobic nanocavities was exploited to encapsulate Combretastatin A-4 (CA-4), a very active, but poorly water-soluble, anticancer drug [2].

Results show that self-assembling amphiphilic random copolymers have the potential to be used as nanocarriers of highly hydrophobic drugs whose release rate can be tuned by varying their degree of amphiphilicity and thermoresponsive behavior.

Figure 1. Schematic representation of the single-chain folding behavior of the amphiphilic fluorinated copolymers PEGMAx-*co*-FAy and their use for the encapsulation and release of a hydrophobic drug

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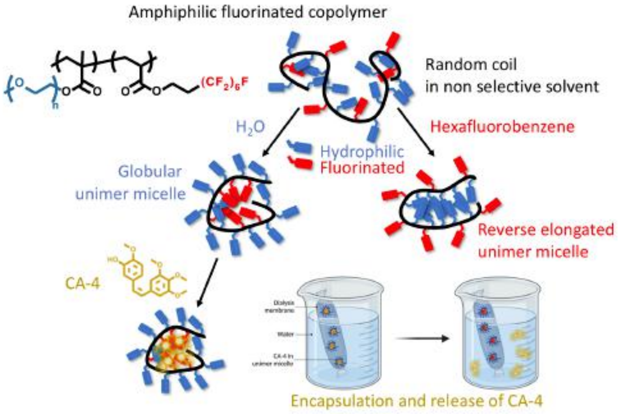

Thermoresponsive reversible unimer micelles of amphiphilic fluorinated copolymers for encapsulation and release of hydrophobic drugs.png

Fast and durable thermoresponsive hydrogel actuators – beyond template-based gelation approaches

Tuesday, 25th April - 17:15: Oral Session 7-1 - Oral

Dr. Daniel Stoebener [1], ***Prof. Richard Hoogenboom*** [1]

1. U Gent

Due to their pronounced volume phase transition, thermoresponsive hydrogels are potent materials for soft actuators. Generally, conventional isotropic hydrogels synthesized from homogeneous solution suffer from slow hydration kinetics and weak mechanical resilience. However, porous hydrogels alleviate these drawbacks by increased water diffusivity and anisotropic structural reinforcement. Introducing porosity during gelation is usually achieved via template-based techniques such as addition of pore-forming agents, emulsification, crosslinking of nanofibers and -particles or cryogelation. Here, we present a template-free approach towards supermacroporous hydrogels which exploits the cononsolvency effect. This phenomenon is based on the competitive solvation of a polymer in binary mixtures of independently good solvents which together form a nonsolvent and cause phase separation. Many thermoresponsive lower critical solution temperature (LCST)-type polymers that undergo a reversible phase transition in water, especially poly(*N*-isopropyl acrylamide) (PNIPAAm), are prone to exhibit cononsolvency in aqueous-organic solvent mixtures. Thus, we synthesized thermoresponsive PNIPAAm hydrogels via redox-initiated copolymerization with the crosslinker *N*,*N'*-methylenebis(acrylamide) (MBAAm) in suitable solvent mixtures, e.g., water-DMSO or water-DMF, to obtain fast responding hydrogel actuators. Compared to conventional hydrogels, our supermacroporous actuators exhibit excellent mechanical strength and instantaneous reversible hydration kinetics reaching equilibrium swelling in a matter of minutes. Like fast responding PNIPAAm cryogels, our hydrogels further exhibit a translucent to opaque appearance which is due to their highly interconnected pores enclosed by a much denser phase-separated and crosslinked polymer scaffold. By exploiting these unique optical properties, we further found that hydrogelation under one-directional, photo-initiated conditions leads to pronounced structural gradients along the direction of irradiation. We utilized this subsidiary effect to create PNIPAAm actuators which exhibit continuous bimetal-like bending and stretching upon temperature variation. Apart from LCST-type polymers, completely water-soluble polymers, such as poly(*N*,*N*-dimethyl acrylamide) (PDMAAm), have shown to exhibit upper critical solution temperature (UCST) cononsolvency in aqueous-organic solvent mixtures, e.g., water-dioxane, -THF or -acetone. Applying an analogous strategy, we showed that supermacroporous PDMAAm hydrogels with fast hydration rates and high mechanical resilience can be obtained. In summary, the cononsolvency approach yields new types of fast actuators and constitutes an intriguingly elegant technique for the design of novel interactive materials based on responsive, soft hydrogel materials.

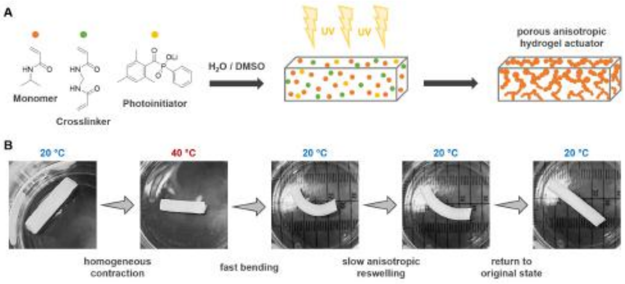

Figure. **(A)** Schematic illustration of the cononsolvency-driven, photo-initiated crosslinking of fast responding anisotropic PNIPAAm hydrogels. **(B)** Representative photographic pictures of the temperature-induced contraction, fast bending and slow reswelling of rod-like supermacroporous PNIPAAm actuators in H_2O.

Apme2023 abstract figure stoebener.jpg

Thermoresponsive Swelling of Fluorescent and Photoacoustic Single-Chain Nanoparticles

Tuesday, 25th April - 17:30: Oral Session 7-1 - Oral

Mr. Justus Friedrich Thümmler [1]***, Dr. Franz-Josef Schmitt*** [1]***, Mr. Guo Tang*** [1]***, Mrs. Samira Mahmoudi Rahmanlou*** [1]***, Prof. Jan Laufer*** [1]***, Prof. Wolfgang H. Binder*** [1]

1. *Martin Luther Univerity Halle-Wittenberg*

Modern concepts for biomedical imaging like fluorescent or (pump-probe) photoacoustic imaging need new classes of contrast agents. Solubility, matching photophysical properties, and unique contrast mechanisms are just a few of the many challenges in the development of those agents. The encapsulation of near-infrared (NIR) fluorescent dyes in single-chain nanoparticles is a promising technique to solve these challenges. Their enzyme-like, compartmentalized interior is the perfect environment to tune the properties of the fluorescent dye. [1]

Figure 1. Synthesis route to core shell structured NIR-fluorescent SCNPs with thermoresponsive swelling behaviour that is changing the photophysical properties of incorporated fluorescent dyes.

Based on our previous works [2] we have polymerized crosslinkable co-polymers *via* RAFT-polymerization reaching an M_n around 34 kDa. Hydrophilic, LCST-type PEG sidechains, as well as hydrophobic azide and alkyne crosslinking and labelling sites were incorporated for the subsequent collapse by CuAAC in water. The resulting core shell structured SCNPs were labeled with a NIR fluorescent dye that is located in the SCNPs hydrophobic core. The thermoresponsive behaviour of the SCNPs was analyzed using turbidimetry as well as DOSY-NMR measurements. Latter proved that the SCNPs are swollen with water, that gets depleted by heating the SCNPs below the macroscopic collapse temperature.

Additionally, temperature dependent fluorescence measurements and decay associated spectra revealed a rather unique photophysical behaviour of the SCNPs. The depletion of water from the SCNP's interior results in less water-caused quenching, and closer contact and hence coupling of individual fluorescent dyes. This behaviour can be used as a unique contrast mechanism for photoacoustic imaging as the heat production during the excitation leads to changes in the fluorescence behaviour increasing the contrast to the non-changing background.

[1] J. F. Thümmler, A. H. Roos, J. Kruger, D. Hinderberger, F. J. Schmitt, G. Tang, F. G. Golmohamadi, J. Laufer, W. H. Binder, *Macromol Rapid Commun* **2022**, 2200618.

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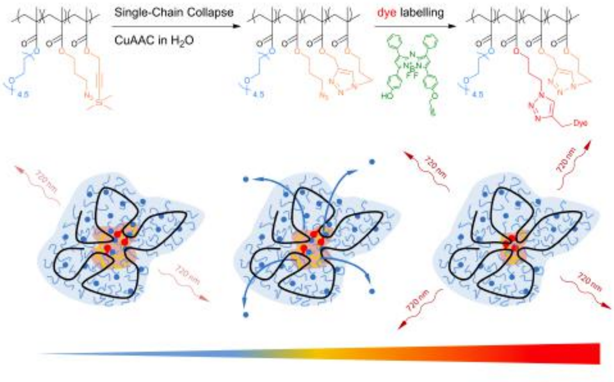

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Force-induced self-strengthening of elastomer via Bergman cyclization

Tuesday, 25th April - 17:45: Oral Session 7-1 - Oral

Ms. Yue Cai [1], ***Prof. Wolfgang H. Binder*** [1]

1. *Macromolecular Chemistry, Institute of Chemistry, Faculty of Natural Science II, Martin Luther University Halle-Wittenberg, Von-Danckelmann-Platz 4, 06120 Halle (Saale), Germany*

Since the discovery of the crucial role of enediyne (EDY) in natural antibiotics, Bergman cyclization (BC), an exclusive thermal rearrangement of enediyne, has attracted considerable attention for decades.[1] Due to the di-radical intermediate generated on site and the subsequent DNA cleavage, Bergman cyclization is widely used in pharmaceuticals, synthesis, and polymer chemistry.[2,3] As a part of the extensive research, it has been found that the critical distance between the two alkyne carbon atoms forming a new bond is one of the factors affecting the activity of BC.[4] Calculations of enediyne based on molecular structure and quantum chemistry reveals its possibility as a mechanophore.[5] To our knowledge, it has not yet been realized experimentally. In this work, several bifunctional enediynes were synthesized and embedded in polyurethane (PU) backbones, along with adaptations derived from PU lengths and diisocyanate elements, followed by characterization with nuclear magnetic resonance (NMR), gel permeation chromatography (GPC) and infrared (IR) spectroscopy. Kinetic differential scanning calorimetry (DSC) experiments were used to determine the corresponding activation energies of BC for different PUs containing EDYs and revealed a consistent sequence with the activities of the enediyne units. After heat-induced BC, an increase in toughness was observed in the tensile test. At room temperature, cyclic stretching at 300% elongation with a strain rate of 20 mm/min also resulted in increased toughness. Compared to PUs without EDY, the corresponding increased toughness could be assumed to be the result of partially activated BC. With compression of 10 t, BC-induced ΔH_{exo} decreased in DSC monitoring. In addition, a deterioration in solubility was observed, confirming the formation of BC-induced crosslinks.

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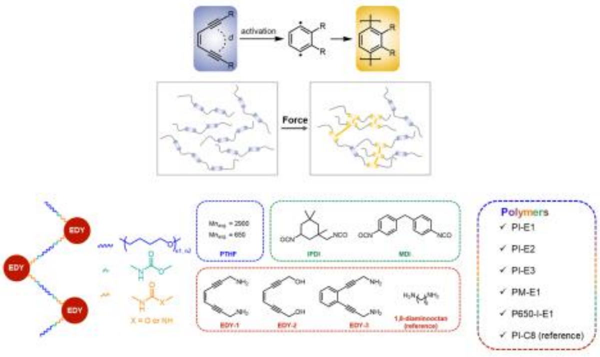

Figure force-induced self-strengthening of elastomer via bergman cyclization yue cai.jpg

When synthetic polymers start to speak

Tuesday, 25th April - 16:30: Oral Session 7-2 - Oral

Dr. Jean-François Lutz [1]

1. *University of Strasbourg, CNRS, ISIS, 8 allée Gaspard Monge, 67000 Strasbourg, France*

It has been shown in recent years that information can be stored at the molecular level in synthetic polymers. To achieve such a property, different comonomers are used as a molecular alphabet and assembled together into a defined information sequence. For instance, an alphabet based on two different monomers allows writing of binary information in a linear polymer chain. But, of course, such informational polymers cannot be synthesized using a standard chain-growth or step-growth polymerization mechanisms because these approaches lead to polydisperse samples containing pronounced sequence defects. Instead, so-called multi-step growth strategies have to be employed. For instance, solid-phase iterative chemistry allows synthesis of a wide variety of uniform sequence-defined digital polymers. This approach is not restricted to oligomers and long digital chains containing more than 100 coded residues have been prepared. Moreover, the information stored in these chains can be decoded using different sequencing techniques. In this lecture, I will highlight new directions that are currently under investigation in my laboratory for the development of such complex “coded matter”. In particular, I will describe simple strategies for the preparation of polymer materials allowing high-density information storage and anti-counterfeiting technologies. The relevance of synthetic informational polymers in the area of xenobiology will also be discussed.

Stereo- and enantiodivergent catalysis with an achiral ligand embedded into helical supramolecular polymers

Tuesday, 25th April - 17:00: Oral Session 7-2 - Oral

Dr. Matthieu Raynal [1], *Dr. Laurent Bouteiller* [1], *Mr. Ran Chen* [1], *Dr. Ahmad Hammoud* [1]

1. *Sorbonne Université*

Developing general and practical strategies for obtaining all possible stereoisomers of an organic compound with multiple stereogenic centers is of great importance,[1] especially in the drug discovery and development process. Different stereoisomers of drugs can have distinct therapeutic properties or adverse effects. Stereodivergent catalysis is the most efficient strategy to tackle this challenge but requires the use of enantiomeric catalysts to access all stereoisomers. Herein, we developed a general and predictable method for stereodivergent catalysis by means of an achiral ligand integrated in properly designed supramolecular polymer helices (***Fig.1***). Switching the enantiomeric state of a single catalyst in between sequential transformations may provide access to any stereoisomers without purification of the reaction intermediate. We demonstrate that it can be achieved by constructing supramolecular helices composed of three types of benzene-1,3,5-tricarboxamide (BTA) monomers: two ligand-free enantiopure co-monomers of opposite configurations and one phosphine-functionalized achiral monomer (for copper coordination).[2] Thanks to dynamic properties and supramolecular chiral nature of the hydrogen-bonded helices, dual stereocontrol of the asymmetric reaction is achieved in situ by addition of small amount of the enantiopure co-monomer to invert the handedness of the supramolecular helices.[3] The fast and predictable stereochemical switch play a key role in the precise stereocontrol of the catalytic reaction in real-time, which cannot be reached by conventional catalysts.[4]

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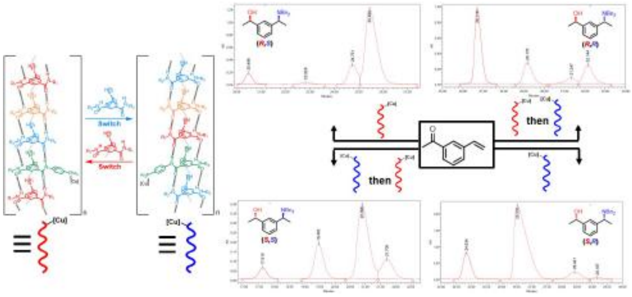
et al., *under preparation.*



Apme 2023 raynal figure.jpg

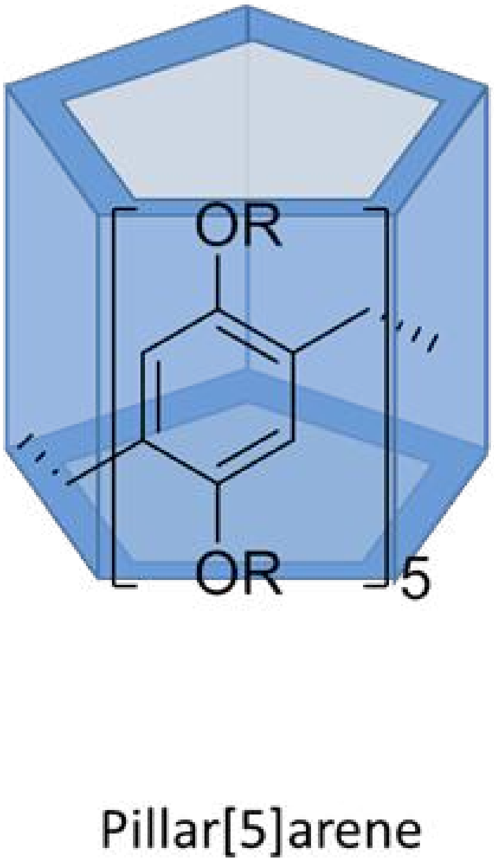
Smart and Functional Polymers Based on Pillar[5]arenes for Environment

Tuesday, 25th April - 17:15: Oral Session 7-2 - Oral

***Mrs. Solenne Ritaine* [1], *Dr. Kedafi Belkhir* [2], *Dr. Patrice Woisel* [3], *Prof. Jérôme Claverie* [4], *Dr. Jonathan Potier* [3]**

***1.** University of Lille, France & University of Sherbrooke, **2.** University of Lille, **3.** Unité des Matériaux et Transformations, UMET, CNRS, **4.** University of Sherbrooke*

Polymers are increasingly present today in many areas ranging from commodity items to nanotechnology and are produced at over 600M of tons every year. Today, society's desire to make polymers eco-friendlier is driving research into materials that are more recyclable or less toxic but still featuring sufficient mechanical and thermal properties. In this context, supramolecular chemistry is an excellent tool to create smart polymers able to respond to these constraints. Among the usual supramolecular receptors, we are particularly interested in Pillar[5]arenes, hydroquinone-based macrocycles extremely rigid and therefore perfectly suited to form materials with interesting mechanical properties. We will show that Pillararenes can be used to form physically cross-linked materials with performances close to those of usual thermosets. In this part, we will valorize hydrocarbon polymers, still little used in the field of high-performance polymers to obtain recyclable materials. Finally, Pillar[5]arenes will also be used as VOC scavengers in a new generation of plastics or as additives to induce self-healing properties.



Pillar 5 arene.png

Cucurbit[7]uril-threaded poly(3,4-ethylenedioxythiophene): - A novel processable conjugated pseudopolyrotaxane and polyrotaxane

Tuesday, 25th April - 17:30: Oral Session 7-2 - Oral

Ms. Aurica Farcas [1]*, Prof. Abdelghani Oukhaled* [2]*, Dr. ANA-MARIA RESMERITA* [3]

1. Petru Poni, 2. CY Cergy Paris Université, CNRS, LAMBE, Cergy, France, 3. "Petru Poni" Institute of Macromolecular Chemistry, Iasi

The interest in the area of conjugated polymers (CPs) has intensified during the past two decades, owing to their numerous advantages over conventional inorganic materials [1]. Among the various CPs, poly(3,4-ethylenedioxythiophene) (PEDOT) polymer is widely recognized as an interesting material whose properties are of great interest for application in various optoelectronic fields. However, several properties of the PEDOT need further improvements. The past decade has witnessed remarkable innovations and progress in polymer science and a promising approach consists in the synthesis of new classes of supramolecular materials, such as polypseudorotaxane (PS) and polyrotaxane (PR) architectures. Our efforts are being made in this direction and the cucurbit[7]uril (CB7) host molecule was used for the synthesis of PEDOT·CB7 PS and PEDOT·CB7 PR [2]. Chemical structures of the investigated PEDOT·CB7 PR, PEDOT·CB7 PS and CB7 are provided in Fig. 1.

Herein, we continue to furnish a comprehensive knowledge into the effect of CB7 encapsulation on the optical properties of the water-soluble fractions of PEDOT·CB7 PS and PEDOT·CB7 PR using transient absorption and time-resolved fluorescence spectroscopy. In addition, nanopore resistive pulse-sensing technique and computational modeling demonstrated the strong interactions of the PEDOT·CB7 PS and PEDOT·CB7 PR with a biological aerolysin nanopore [3]. With this study, we hope to provide further insights and an opportunity to accurately quantify the effect of CB7 encapsulation on the solubility, photophysical and electrical properties of these newly encapsulated PEDOT materials, which can open a wide range of opportunities in the area of organic electronics.

Acknowledgements

This work was supported by a grant from the Ministry of Research, Innovation and Digitization, CNCS – UEFISCDI, project number PN-III-P4-PCE-2021-0906, within PNCDI III.

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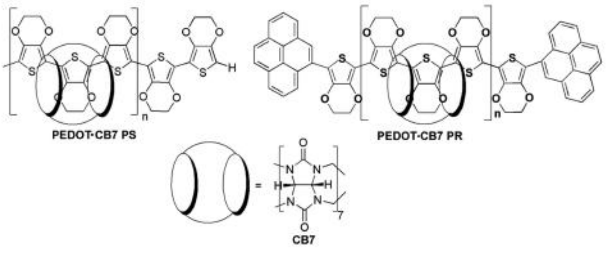

Fig. 1. chemical structures of pedot cb7 ps pedot cb7 pr and cb7..jpg

Uniform Soluble Supports for the Large-scale Synthesis of Sequence-defined Polymers and Corresponding Networks

Tuesday, 25th April - 17:45: Oral Session 7-2 - Oral

Ms. Irene De Franceschi [1] ***, Prof. Filip Du Prez*** [1] ***, Dr. Nezha Badi*** [1] ***, Dr. Chiel Mertens*** [1]

1. *Ghent University*

In contrast to biomacromolecules, synthetic polymers lack a perfectly defined monomer sequence and one of the challenges of polymer chemists is to gain more control over the primary structure of synthetic polymers. For the design of these sequence-defined oligomers, chemists mainly rely on iterative synthetic protocols.

Different strategies could be used to perform their synthesis and until now the use of solid supports proposed by Merrifield for peptides, is the main one. Nevertheless, solid-phase synthesis suffers from some limitations (*e.g.* high equivalents of reactants, non-homogeneous reactions, high cost etc.) that only allows the synthesis on milligram scale, making it difficult to upscale the product and limiting the applications. Chemists are now focusing on solution reactions that do not show constraints regarding the reaction scale.

The use of soluble supports combines the best aspects of solution- and solid-phase synthesis. These supports are soluble in the reaction medium yet provide properties that can be exploited to isolate the support-attached product from the crude medium. This work presents a strategy to upscale the synthesis of sequence-defined oligomers prepared with a thiolactone-based protocol using a monodisperse support. This support composed of three C_{18} alkyl chains has several advantages: it is affordable and easy to prepare; iterative synthesis can be performed in solution, characterisation is facilitated by monodispersity and the purification step is reduced to a precipitation in a polar solvent. As a proof of concept, an octamer with different acrylates has been synthesised and characterised. Additionally, discrete supports with cleavable linkers have been synthesised and used to build oligomers on a 10 g scale, successfully cleaved to recover the sequence-defined oligomer.[1] The scalability of sequence-defined oligomers allows their use in applications that typically require higher amounts of starting material. Therefore, my presentation will also highlight an initial investigation of a sequence-defined polymer with a new amide chemical backbone. In this context, we developed a protocol for a bidirectional growth process on the solution support, introducing relevant functionalities for network formation.

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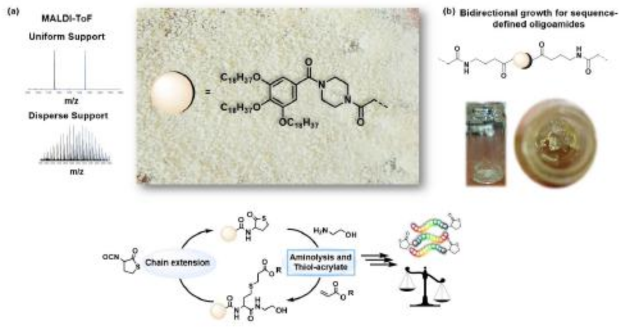

Image abstract.jpg

Material Solutions to the Problem of Plastic Pollution

Tuesday, 25th April - 16:30: Oral Session 7-3 - Oral

Prof. Seema Agarwal [1]

1. *University of Bayreuth*

New material solutions to the microplastics (MP) problem originating from different application areas are urgently needed. Among others, biodegradable polymers could be a solution to the problem originating from some, if not all application areas. From the material's point-of-view, we can hope to target this problem either by making new appropriate polymers/blends or by introducing novel degradation concepts in the known commercially available polymers. In this talk, both these strategies will be discussed. One of the fastest composting aliphatic-aromatic polyesters prepared using old chemistry of polycondensation polymerization with a good balance of mechanical and barrier properties, and their degradation behavior and mechanism will be presented. Also, enhancing the degradation of very-well known polymers by making appropriate nanocomposites will be discussed.

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3. **Stretchable and Fast Composting Polyester Films with High-Performance Oxygen Barrier.** ACS Applied Polymer Materials. (2022)DOI: https://doi.org/10.1021/acsapm.2c01040
4. **Balancing Degradability and Physical Properties of Amorphous Poly (D, L‐lactide) by Making Blends.** Macromolecular Materials and Engineering. Vol. 307 (2022) Issue 6 - No. 2100602. DOI: https://doi.org/10.1002/mame.202100602
5. 5. **Tailor-made compostable Polyurethanes.** Polymer Chemistry. Vol. 13 (2022) Issue 5. - pp. 622-630. DOI: https://doi.org/10.1039/D1PY01236C
6. 6. **Layering‐Triggered Delayering with Exfoliated High‐Aspect Ratio Layered Silicate for Enhanced Gas Barrier, Mechanical Properties, and Degradability of Biodegradable Polymers.** Global Challenges. Vol. 42 (2020) Issue 9 . - No. 2000030.
DOI: https://doi.org/10.1002/gch2.202000030

Functionalization of polyethylene glycol by bacterial degradation

Tuesday, 25th April - 17:00: Oral Session 7-3 - Oral

Dr. Anika Kaufmann [1], ***Dr. Martin Geisler*** [1], ***Mr. Jan Khan*** [2], ***Prof. Marion Ansorge-Schumacher*** [2], ***Prof. Julian Thiele*** [3]

1. *Leibniz Institute of Polymer Research Dresden,* ***2.*** *Chair of Molecular Biotechnology, Technische Universität Dresden,* ***3.*** *Institute of Chemistry, Otto von Guericke University Magdeburg*

Introduction

Synthetic polymers are key components in a multitude of functional materials ranging from pharmaceutics over colloidal building blocks to coatings. Unfortunately, further deployment of well-established polymers such as polyethylene glycol (PEG) is limited by the lack of working strategies for efficient direct and targeted functionalization. Here, enzyme-based biocatalysis has the potential to pave new ways for tailored functionalization strategies of polymers that have limited reactivity or are difficult to functionalize, while improving the sustainability of polymer material production and possibly even showing beneficial side effects in terms of (bio-)degradability.

Methods

To identify suitable enzymes for biocatalytical conversion of synthetic polymers, screening series were performed to isolate bacterial cultures from the environment (soil, wastewater, and laboratory) that grow on PEG as the sole carbon source and are therefore probably also able to modify PEG during degradation. To find chemical modifications, changes in molecular mass and its distribution, as well as the identification of new end or side groups, PEG was extracted from aliquots of the culture media after incubation with mixed and pure bacterial cultures and characterized by polymer mass spectrometry (MALDI-TOF-MS), size exclusion chromatography combined with triple detection (SEC-MALS-Visc-dRI), and NMR.

Results

We found mixed bacterial cultures from the laboratory environment that are able to grow on PEG up to 40,000 g mol^{-1} within a week. For smaller PEG with 6,000 g mol^{-1} the growth started within 2 days and degradation was faster. Pure bacterial cultures could be successfully isolated and characterized as different *Pseudomonas* species. Attempts to isolate enzymes from PEG-degrading bacteria gave a hint which enzymes may be involved in the degradation pathway.

Discussion

In this work, we address the enzymatic degradation as well as potential functionalization of the polymer backbone of PEG. Conventional chemical modification strategies have so far only targeted modifications at the end groups of the polymer. Here, we specifically aim to isolate enzymes that could introduce functional groups into the polymer backbone. In contrast to most chemical modifications, which often require harsh conditions or multi-step synthesis strategies, robust, cell-free enzymatic functionalization can be carried out under environmental-friendly, mild conditions.

From chemical end group modification to enzyme-induced backbone functionalization of peg..png

Self-healable dynamic poly(urea-urethane) gel electrolyte for lithium batteries

Tuesday, 25th April - 17:15: Oral Session 7-3 - Oral

Dr. Fermin Elizalde [1]***, Prof. Julia Amici*** [2]***, Ms. Sabrina Trano*** [2]***, Ms. Giulia Vozzolo*** [1]***, Dr. Robert Aguirresarobe*** [1]***, Dr. Daniele Versaci*** [2]***, Prof. Silvia Bodoardo*** [2]***, Prof. David Mecerreyes*** [1]***, Dr. Haritz Sardon*** [1]***, Prof. Federico Bella*** [2]

1. *POLYMAT- UNIVERSITY OF BASQUE COUNTRY UPV/EHU,* **2.** *Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Turin, Italy*

Taking into account the growing awareness on global sustainability and the increasing demand of energy storage and conversion devices, one of the greatest upcoming challenges that can be found nowadays is to develop effective, safe and recyclable electrochemical devices. Lithium-ion batteries (LIBs) have been employed in several kind of portable electronic devices, electric vehicles and implantable medical devices. However, the practicality and cycling-life of Li-ion batteries is limited by internal and external damages that can undergo over time (Figure 1A). To overcome these issues, self-healable polymer electrolytes can rapidly eliminate scratches and avoid the final shorting of the device, allowing for a longer and safer cycle (Figure 1B). Dynamic covalent networks have recently emerged as one of the best self-healable materials which allow thermosets to be reprocessed and recycled. Among all the different exchangeable bonds studied over the last few years, hindered urea bonds appear to be one of the most feasible options to create self-healable materials due to their exchange activation at low temperatures. Although this chemistry is popular in composite and coating applications, it has not been considered for designing self-healable materials for batteries. Thus, one of the remaining particular challenges is to develop suitable self-healing electrical and ionic materials to enlarge the device lifetime. In this work we synthesize a membrane containing dynamic hindered urea crosslinking points by reacting tris[2-(isopropylamino)ethyl]amine with hexamethylene diisocyanate, followed by the addition of polyethylene glycol. It is proved that this newly designed material possesses self-healable properties and higher ionic conductivity than the commercially available liquid electrolyte embedded in a porous Celgard® 2500 separator. The polyurethane gel electrolyte shows very homogeneous Li plating and stripping in Li symmetrical cells and is also compatible with Li-mediated electrochemical ammonia synthesis approaches. Most importantly, after severely mechanically damaging the gel membrane, the polymer electrolyte shows great recovery of the electrochemical properties, experiencing more than 100 charge/discharge cycles (after cutting) at C/5 rate.

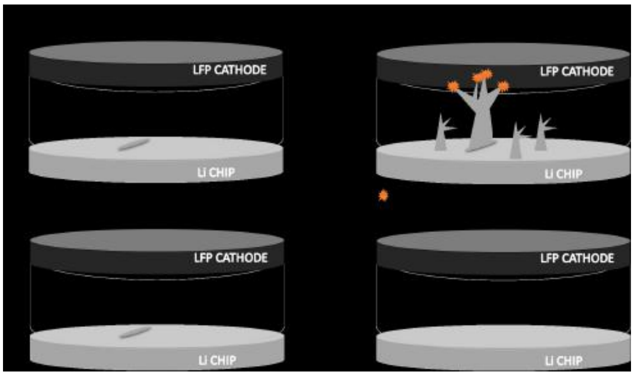

Figure1 apme 2023 fermin.jpg

Anti-corrosion and mechanical properties of bio-based epoxy thermoset resins coatings from Epoxidized Soybean Oil cured with Tannic Acid

Tuesday, 25th April - 17:30: Oral Session 7-3 - Oral

Mr. Ruben Teijido [1]***, Dr. Leire Ruiz-Rubio*** [2]***, Prof. Qi Zhang*** [1]***, Prof. Jose Luis Vilas-Vilela*** [2]***, Prof. Senentxu Lanceros-Mendez*** [1]

1. *BCMaterials, Basque Center for Materials, Applications and Nanostructures,* ***2.*** *Macromolecular Chemistry Group (LQM), Physical Chemistry Department, Faculty of Science and Technology, University of the Basque Country (UPV/EHU)*

Epoxy resins (ERs) are the most common way of protecting metallic surfaces against the effects of corrosion. Widely used industrial resins are synthetized from the reaction of Bisphenol A with Epichlorohydrin resulting in Bisphenol A Diglycidyl Ether-based resins. Environmental concerns around these resins are gaining more relevance due to this initial products provenance, derived from the petrochemistry industry. Furthermore, the potential release of toxic substances as the final resins wear off during their lifetime must also be considered, especially in applications with exposure to hazardous environmental conditions. Therefore, we present a study on the mechanical and thermal properties of fully bio-based ERs from Epoxidized Soybean Oil and Tannic Acid within a series of formulations with different epoxy:phenol molar ratios. These two bio-based resin precursors have been chosen due to their accessibility, sustainability, favourable economic conditions as products of common agricultural processes and convenient chemical functionalization.

The different epoxy:phenol molar ratios have been prepared by mixing both components in ethanol. Mixtures have been thermally cured at different temperatures, as bulk materials and coatings over carbon steel substrates, deposited by doctor blade (120±20µm) (Figure 1).

Characterization techniques performed included Fourier Transform Infrared Spectroscopy to elucidate the chemical structure of the cured resins and follow up the curing reaction. Thermo-mechanical characterization, by means of differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical thermal analysis and tensile tests, evidenced high thermal stability for the cured materials and a wide range of elastic (38.1-324.2MPa) and storage modulus (0.77-1159MPa), T_g (17-110°C), elongations and maximum stress, easy tuneable by adjusting components proportions and curing temperatures. The anticorrosion property has been studied starting by measuring coatings water contact angle (≈87°), followed by in-bulk water absorption tests (+0.7-4.2wt.%). Electrochemical impedance spectroscopy was employed to characterize these materials anticorrosion performance, evidencing high stability and insulating capabilities, due to presenting capacitive effect in the metal-polymer interphase after 14 weeks immersion.

Results obtained assessed the viability of these bio-based thermosets for a wide range of applications, regarding their specific mechanical properties, while still offering high enough thermal stability and insulating behaviour, as an alternative for developing more sustainable and economic ERs formulations.

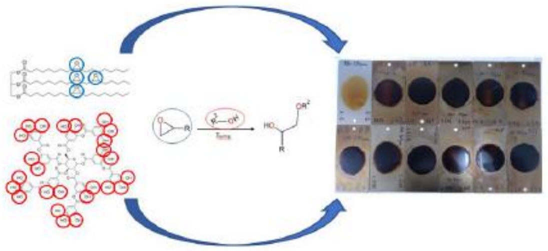

Figure 1. Chemical structure of Epoxidized Soybean Oil and Tannic Acid, curing reaction and final coated samples over carbon steel substrates.

Figure 1 apme 2023 paris conference.jpg

Polymer electrolytes: Structure and transport properties

Tuesday, 25th April - 17:45: Oral Session 7-3 - Oral

Dr. Thi Khanh Ly NGUYEN [1]

[1] *Université Grenoble Alpes & Aix-Marseille Université*

Global warming issue imposes the increase of renewable energy use in Europe by the end of 2030. However, the intermittence of renewable resources such as solar and wind requires a large scale and safer system of energy storage. Thus, one of the locks of these future systems concerns the design and development of new solid-state electrolytes[1]. Several requirements need to be fulfilled for a successful candidate of polymer-based electrolytes such as high conductivity and transport number combining with excellent mechanical properties and chemical resistance.

In this work, we discuss the advantages and inconveniences of different strategies to achieve high performance electrolytes. Blend of different electrolytes appears to be the simplest way to combine different properties. However, the compatibilization and micro-structuration of these blends must be optimized to obtain the desired combination of properties. A second route allows controllable micro-structuration of polyelectrolytes is the synthesis of single-ion conducting block polymer[2,3] but complicated and delicate chemistry and low conductivity stay as main obstacles. Finally, an alternative promising route that received much less attention is the development of bulky salts containing macroanion with negligible mobility resulting in higher transport number[4]. In all aforementioned cases, a strong relationship between structure and transport properties of polyelectrolytes was emphasized providing a handbook for polyelectrolyte design.

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Precise control of CT states in organic molecules aimed at high-performance optoelectronic devices

Wednesday, 26th April - 08:30: Plenary Session 3 - Oral

Prof. Chihaya Adachi [1]

1. *Kyushu University*

TBD

Deconstructing polymers synthesized by controlled radical polymerization

Wednesday, 26th April - 09:30: Oral session 8-1 - Oral

Prof. Athina Anastasaki [1]

1. *ETH Zurich*

In this talk, I will discuss the recent efforts of our group in reversing controlled radical polymerization. RAFT-synthesized polymers will be shown to undergo a rapid depolymerization reaction through a thermal approach to regenerate back the original polymer. The retrieved materials can then be used to either remake the initial polymer or to construct a completely new material. Notably, in the presence of visible light and Eosin Y, a much faster depolymerization can be triggered at lower temperatures and the final depolymerization conversion can also be enhanced. In the second part of the talk, I will switch to ATRP reactions and the possibility to employ Iron-catalyzed photoinduced ATRP to polymerize renewable monomers with improved control over the molar mass distributions. The possibility of these sustainable polymers to undergo rapid depolymerization will then be discussed.

Room temperature step-growth polymerization of polyesters

Wednesday, 26th April - 10:00: Oral session 8-1 - Oral

Dr. Marta Ximenis [1], ***Dr. Julien Monot*** [2], ***Dr. Elena Gabirondo*** [1], ***Ms. Janna Jeschke*** [1], ***Dr. Blanca Martín-Vaca*** [2], ***Prof. Didier Bourissou*** [2], ***Dr. Haritz Sardon*** [1]
1. POLYMAT- UNIVERSITY OF BASQUE COUNTRY UPV/EHU, 2. LHFA-CNRS

Conventional synthesis of polyesters typically implies the polycondensation between alcohols and carboxylic acids (or the corresponding derivatives). The energy demand of this process requires high reaction temperatures and the use of catalysts and sometimes the obtained molecular weights are not high enough to fulfill the application demands.[1] One of the most efficient approaches for achieving superior molecular weight control has been the use of cyclic lactones, which ring-opening behavior depends on their ring size and, consequently, the ring strain. Even though γ-Butyrolactone, a typical five-membered lactone, can polymerize by ring-opening, the reaction times are still long and it requires the use of specifically designed complex catalytic systems.[2] Herein, we have developed a reactive tethered lactone monomer (**1**) that undergoes step-growth polymerization by ring-opening towards diols, thus obtaining for the first time polyesters at room temperature.

To understand the reactivity of **1**, we first performed molecular model reactions with a representative monofunctional alcohol, and compared the reaction kinetics with typical lactones. Kinetic results show full monomer conversion for **1** in 3h while δ-valerolactone and γ-butyrolactone barely reach 5% conversion (Figure 1).

The polyester synthesis has been successful with hexanediol, triethylenglycol and benzene dimethanol at room temperature in DMF using 5% DBU as catalyst. The molecular weights obtained are between 6000 and 30000 Da. The reactivity of **1** has been also explored towards other nucleophiles, containing N- and S- obtaining a set of polyamides and polythioethers thus demonstrating the versatility of the process.

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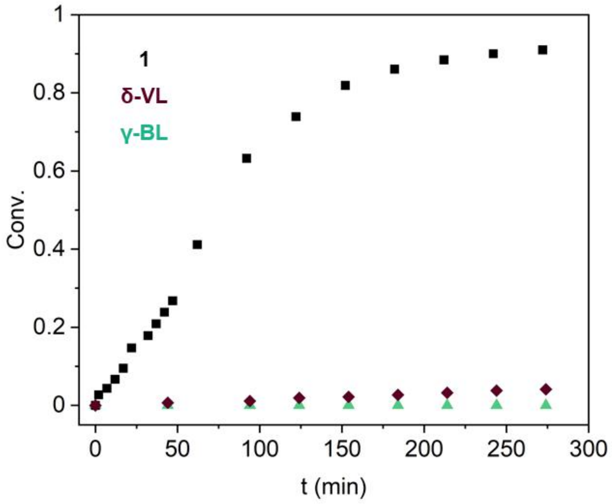


Fig1.png

New symmetrical RAFT agent for all-(meth)acrylic thermoplastic elastomers with tunable transitions

Wednesday, 26th April - 10:15: Oral session 8-1 - Oral

Mr. Maskym Odnoroh [1], ***Mr. Oleksandr Oleksandr Ivanchenko*** [1], ***Dr. Stephane Mazieres*** [1],
Dr. Marc Guerre [1], ***Prof. Mathias Destarac*** [1]

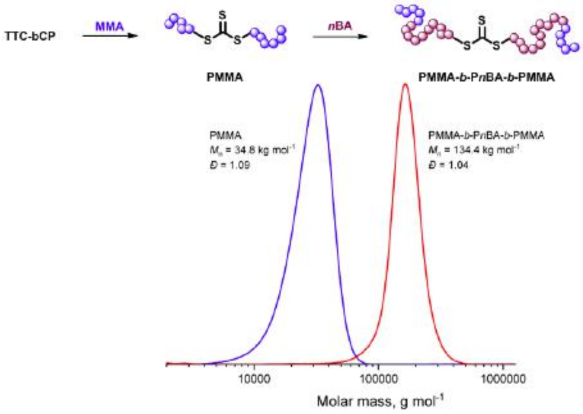
1. Laboratoire des IMRCP, CNRS UMR 5623, Université Toulouse 3 Paul Sabatier, 118 route de Narbonne, 31062 Toulouse, France

Introduction

All-(meth)acrylic TPEs present many advantages over styrenic products. Futhermore, the Tg range of (meth)acrylic monomers is very broad enabling high tunability. In the quest for all-(meth)acrylic ABA copolymers of low dispersity, RAFT polymerization suffers from a lack of symmetrical TTCs bearing suitable tertiary leaving groups for optimal control of methacrylate polymerization.[1] Therein, we report a new symmetrical trithiocarbonate (TTC-bCP)[2] with the best leaving group ever reported for RAFT polymerization.[2]

Result and discussion:

This TTC-bCP RAFT agent allowed the preparation of a high molar mass (M_n ~135 kg mol^{-1}) methyl methacrylate-n-butyl acrylate-methyl methacrylate triblock copolymer with unprecedented control (Đ = 1.04) in reversible-deactivation radical polymerization. The introduction of rigid co-monomers such as isobornyl methacrylate into the hard outer blocks endows these TPEs with tunable transition at high temperature. Furthermore, the molar masses of the hard and soft blocks can be easily varied enabling the synthesis of TPEs with tailored properties.



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From melt- to solid-stage polycondensation: how to make the polymers more sustainable

Wednesday, 26th April - 09:30: Oral Session 8-2 - Oral

Prof. Jean-Marie RAQUEZ [1]

1. *University of Mons*

Environmental and economic concerns are pushing both University and Industry efforts to the introduction of *cleaner* sustainable technologies. The highest priorities are methods avoiding the use of polluting and unsafe volatile solvents/chemicals; and allowing the facile replacement of the petrol-based monomers by biosourced monomers. With this respect, the polycondensation – a step-growth polymerization - is being attracted much attention. This process plays an important role in the synthesis of commodity and technical polyesters and polyamides - versatile classes of polymers covering large applications going from fibers to thermoplastics and elastomers. However, despite its *green* aspect, polycondensation is often complicated by its slow rate and side reactions, resulting in low molecular weight and yield of the polycondensation polymer with a lack of functionalities. Hence the lecture will highlight the benefits of using combined melt-polycondensation to other synthetic procedures as chain-coupling[1] or “click” reactions[2] in order to tailor the properties of the functional (co)polyesters in various applications[3],[4]. To extend the range of functional polymers, the solid-state modification (SSM) from batch into a continuous process by reactive extrusion (REx) will be discussed as well. As easy-to-use and solvent-free tool[5,6] , it consists by heating the starting semi-crystalline polymer together with a (co)monomer within a temperature range between the glass transition temperature and the melting temperature in an inert atmosphere and can be implemented in a (semi)continuous manner[6,7]. It results polymers of improved characteristics upon the (co)monomer used, while preserving the mechanical and thermal properties of the initial polymer. This last study encompasses the design of a new process for recycling polymeric materials and offers the possibility of making polymers more sustainable and recyclable.

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Reprocessable and self-healable networked polydithiourethanes applicable to optical materials

Wednesday, 26th April - 10:00: Oral Session 8-2 - Oral

Dr. Yoshiaki Yoshida [1]***, Mr. Ryuichi Suenaga*** [1]***, Prof. Takeshi Endo*** [2]

1. Kyushu Institute of Technology, 2. Molecular Engineering Institute, Shiga University of Medical Science

We have ever reported that polyaddition of various diisothiocyanates and dithiols is achieved with triethylamine in mild conditions to obtain the corresponding polydithiourethanes (PDTU) in higher yield and molecular weight. Particularly, PDTU containing an aliphatic moiety in the main-chain exhibited excellent optical and mechanical properties compared to that of typical polyurethanes.[1] Moreover, the cast films of aliphatic PDTUs, which were prepared from multifunctional isothiocyanate and thiols, exhibited excellent physical properties such as glass transition temperature, transparency, refractive index, and tensile strength. We also stated that the thermal decomposition of PDTUs occurred due to the cleavage of the C−S bond of the dithiocarbamate moiety in the main chain, and also that the active isothiocyanate and thiol groups were reproduced in the terminal of the decomposed polymer (**Fig. 1a**). In addition, we demonstrated that the thermal depolymerization of PDTUs at 150 °C and the repolymerization of dithiourethane oligomers at room temperature proceeded repeatedly a few times (**Fig. 1b**).[2]

Recently, we found that the networked PDTU (NPDTU) containing ether structure exhibited high flexibility and self-healing behavior (**Fig. 1c**). We hypothesize that the self-healing of NPDTU happens because of multiple hydrogen bond between not only each dithiocarbamate moieties but also the active proton of the dithiocarbamate moiety and the ether oxygen in the main-chain. The mechanical strength and thermal stability before and after self-healing process of NPDTU films are able to be strictly controlled by the structures of monomers and/or cross-linkers.

References:

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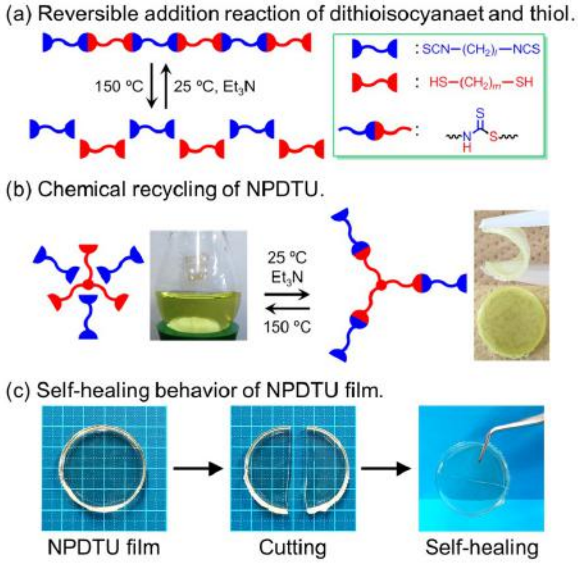

Figure 1. Chemical recycle and self-healing of PDTUs.

Figure1 chemical recycle and self-healing of pdtus.jpg

PLLA copolymer matrix composites by TP-RTM

Wednesday, 26th April - 10:15: Oral Session 8-2 - Oral

***Mr. Bernard Miranda-Campos* [1], *Dr. Gregory Stoclet* [1], *Prof. Serge Bourbigot* [1], *Prof. Gaëlle Fontaine* [1], *Prof. Fanny Bonnet* [1]**

1. Univ. Lille, CNRS, INRAE, Ecole Centrale, UMR 8207 - UMET - Unité Matériaux Et Transformations

Composite materials display many advantages over traditional materials, whether in terms of lightness or mechanical and chemical resistance. In a context of sustainable development, a growing number of works relate to the production of composites with bio-based matrices including polylactide (PLA), which has become a major actor in the market which could in the long term serve as an alternative to petroleum-based polyolefins.[1]

Among the various composites production processes, Resin Transfer Molding (RTM) is a specific process which relies on the injection, into a mold containing fibers, of a monomer and a catalyst in order to carry out the polymerization of the matrix in situ. The major advantage over conventional melt processes is the possibility of reaching a high amount of fibers while improving their wetting by the matrix. While a wide selection of thermosetting matrix resins are available on the market for RTM process, there are only a few commercial resins for thermoplastic matrices.[2]

Although work has been carried out in RTM with e-caprolactone,[2] composites with a PLA matrix via this process had never been described. Recent work carried out at UMET made it possible to obtain the first prototypes of PLLA/glass fiber composites.[3a] We present here current work aimed at strengthening the mechanical properties of the PLLA matrix by producing a novel family of composites by copolymerization of L-LA with other cyclic esters.[3b]

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PLLA / glass fibers composite

PLLA copolymer-based / glass fibers composite displays a strong rubbery character

Image2.png

Radical polymerization of dimethylaminoethyl methacrylate in aqueous solutions

Wednesday, 26th April - 09:30: Oral Session 8-3 - Oral

***Mr. Mohammad Pishnamazi* [1] *, Dr. Igor Lacik* [1]**

***1.** Polymer Institute SAS*

Introduction. Dimethylaminoethyl methacrylate, DMAEMA, belongs to the family of dialkyldimethyl methacrylates. Their polymers exhibit the pH-responsive behavior in aqueous solutions, which is of interest in different application fields. This contribution focuses on radical polymerization of DMAEMA in aqueous solutions, particularly on determination of propagation rate coefficient, k_p.

Methods. Pulsed-laser polymerization combined with size-exclusion chromatography was used to determine the k_p values. The conditions recently applied to 2-(methacryloyloxyethyl)]trimethylammonium chloride (TMAEMC) [1], the permanently charged analogue to DMAEMA, were used. The in situ ^{1}H NMR was used for measuring the monomer-to-polymer conversion and determination of $k_p/\ k_p^{0.5}$ values.

Results. Currently no data are available for the polymerization of DMAEMA in aqueous solutions. In this work, k_p values for DMAEMA were obtained for monomer concentrations 0.3 – 3 mol/L, temperatures 5 – 80 °C, pH 1 – 10, and NaCl concentrations 0.2 - 2.0 mol/L. k_p values and Arrhenius parameters for DMAEMA polymerized at acidic pH are in the range of those determined for TMAEMC, with the difference that k_p values for DMAEMA are independent of monomer concentration unlike for TMAEMC, where they increase with monomer concentration [1]. The addition of salt results in the increase in k_p values for DMAEMA, which is however less significant than for TMAEMC. This k_p behavior is also reflected in polymerization rates, $k_p/\ k_p^{0.5}$ and molar masses obtained from in situ ^{1}H NMR polymerizations. The PLP-SEC studies on non-ionized DMAEMA polymerized in aqueous solutions at basic pH reveal the behavior similar to other non-ionized monomers [2], i.e. that k_p significantly increases upon dilution of monomer by water.

Conclusion. This study provides the first kinetic description for DMAEMA polymerized in aqueous solutions, which involves the peculiarities of both ionized and non-ionized monomers polymerized in aqueous solutions. Further work needs to be devoted to polymerization of non-ionized DMAEMA and to understanding the propagation behavior of ionized DMAEMA as a function of addition of salts.

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Acknowledgement. This work was supported by the Slovak Scientific Grant Agency VEGA 2/0143/23

A versatile and straightforward process to turn plastics into antibacterial materials

Wednesday, 26th April - 10:00: Oral Session 8-3 - Oral

Dr. Catherine Lefay [1], ***Mr. Baptiste Caron*** [2]

1. Institut de Chimie Radicalaire - Aix Marseille Univ, CNRS, 2. Institut de Chimie Radicalaire - Aix-Marseille Univ., CNRS

Bacterial resistance to antibiotics is a major public health problem and there is an urgent need to find new antimicrobial materials to circumvent the development of resistant pathogens.

The objective of this work is to propose an efficient, versatile and simple method to elaborate antibacterial polymeric materials based on the simple dispersion, in different common organic matrices, of a small amount of high molecular weight (Mn > 20,000 g.mol^{-1}) cationic amphiphilic methacrylic copolymers prepared by nitroxide-mediated controlled radical polymerization.

Specifically, we demonstrated that less than 2 wt% of diblock copolymers based on butyl methacrylate (hydrophobic monomer) and quaternized *N,N*-dimethylaminoethyl methacrylate (hydrophilic monomer) dispersed by extrusion in conventional industrial polymer matrices (HDPE, LDPE, PLA and PETG) conferred antibacterial activity to these initially inactive organic materials.[1-3] This approach, which does not require the usually costly modification of the material surface and which is not based on the dispersion of small molecules (e.g. antibiotics or silver nanoparticles that can migrate out of the material), also offers the advantage of providing materials that are active against different types of Gram + (*S. aureus*), Gram $^{-}$ (e.g. *E. coli*) or multi-resistant bacteria without loss of activity with time or use (Figure 1). This method could be of great interest to develop antibacterial food packaging.

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Fig mat riaux d g - jpeg.jpg

Polymer Networks as Carrier for Organocatalysts within Continuously Driven Microfluidic Reactor Systems

Wednesday, 26th April - 10:15: Oral Session 8-3 - Oral

Dr. Naresh Killi [1]***, Mr. Amit Kumar*** [2]***, Dr. Leena Nebhani*** [2]***, Dr. Dirk Kuckling*** [1]

1. *Paderborn University, Department of Chemistry, Warburger Str. 100, 33098 Paderborn,* ***2.*** *Indian Institute of Technology, Department of Material Science and Engineering, New Delhi*

In the past two decades, amine-based catalysis has gained a significant attention in the field of organocatalysis to perform organic reactions because these the ability to form iminium ions and enamines as intermediate with carbonyl group. These intermediates can be involved in the rate determining step of the reaction and can also influence the stereo-selectivity of the reaction. Further, most of the amine based catalytic reactions were performed in homogenous catalysis. However, heterogeneous catalysis is widely used in industrial applications because of the facile separation of catalyst and lower cost.

The present work describes the combination of the concepts of Organocatalysis with continuously driven Micro Plug Flow Reactors (MPFR). Current research focused mostly on massive poly(styrene) particles as carriers for organocatalysts. These particles are typically used in packed bed reactors enabling the catalysis on the surface of the particles. However, at the same time there exists a large not usable volume within the particles. The novel approach in this proposal is the immobilization of the organocatalysts within a swellable polymer network to avoid the usage of massive particles. In contrast to published work the immobilization within a gel will increase the accessibility of the catalytically active center inside the three-dimensional structure having a positive effect on reactivity as well as selectivity.

Various catalytic monomers were synthesized and polymerized by photolithography to form polymeric gel dots with different compositions of catalyst, gelling agent and crosslinker [1]. Further, these gel dots were subjected into the microfluidic reactor and various reactions namely, asymmetric Aldol reaction, Knoevenagel reaction and Baylis-Hillman reaction were performed using different aldehydes. Conversion of the reaction was determined the at ambient conditions and the results suggested the conversion of the reaction was enhance with increase in swelling properties of the gel due to accessibility of the catalytic sites. Moreover, the conversion was influenced significantly by addition of polar solvent like water due to protonation to the carbonyl group and high swelling properties of the polymeric networks.

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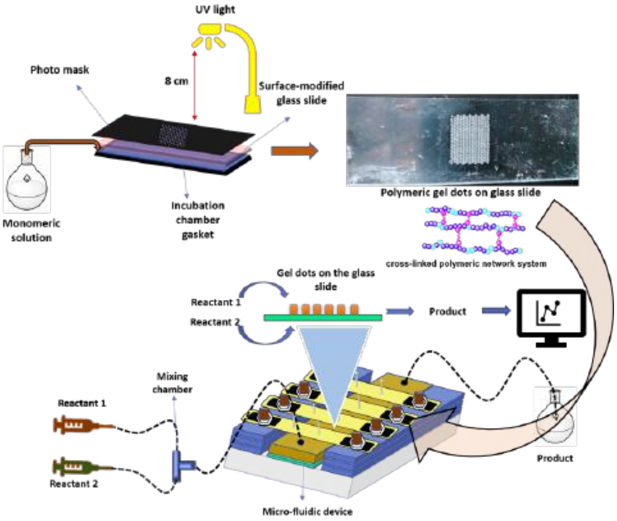
UV light
Photo mask
8 cm
Surface-modified glass slide
Monomeric solution
Incubation chamber gasket
Polymeric gel dots on glass slide
cross-linked polymeric network system
Gel dots on the glass slide
Reactant 1
Reactant 2
Product
Mixing chamber
Reactant 1
Reactant 2
Product
Micro-fluidic device

Figure 1.png

Dendritic Hyperbranched Polymers. Synthesis and Properties

Wednesday, 26th April - 11:00: Oral Session 9-1 - Oral

Prof. Shigeru Yamago [1]

1. *Kyoto University*

Highly branched polymers have attracted much attention due to their unique physical properties compared to linear polymers. However, the development of materials science based on highly branched polymers lags far behind that of linear polymers. This is because the structural control and the practicality are the trade-offs in the conventional highly branched polymer synthesis; dendrimers and dendrons having completely controlled ranched structure and molecular weights are synthesized by the stepwise condensation reactions, and hyperbranched polymers (HBPs) are synthesized in one step but with low control of their structure. [1] Here, we report on the new one-step synthetic method of structurally controlled HBPs in terms of molecular weight, dispersity, number of branching points, branching density, and number of chain-end groups by radical polymerization.[2] The control was achieved by designing a new branching monomer with a potential activating group. While the group in the monomer is inert for radical generation, it can be activated and initiate polymerization once the monomer has been incorporated into the polymer chain. Copolymerization of this new monomer with a conventional monomer, such as acrylate and styrene, under organotellurium-mediated radical polymerization (TERP).[3] As the branching number can be rigorously controlled and the (pseudo) generation can be defined, we believe that this type of HBPs can be named dendritic HBPs.

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Autonomous RAFT polymerisation using multi-objective algorithms in closed-loop optimisation

Wednesday, 26th April - 11:30: Oral Session 9-1 - Oral

Dr. Stephen Knox[1], *Dr. Sam Parkinson*[1], *Ms. Clarissa Wilding*[1], *Prof. Richard Bourne*[1], *Dr. Nicholas Warren*[1]

1. University of Leeds

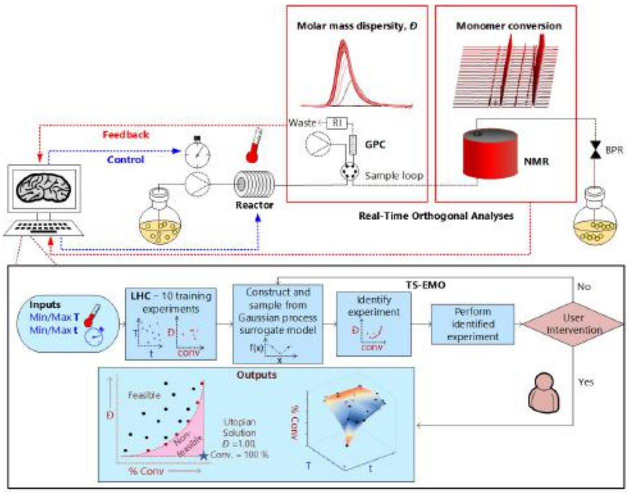
Application of automation and machine learning algorithms to polymer science represents an exciting opportunity for exploration and optimisation of polymerisations. Our work shows the development and application of a platform capable of autonomous multi-objective optimisation of a range of polymerisations. Inline automated analyses (NMR, GPC) which generate real-time data are complemented by a self-optimising algorithm which use that data to identify and perform experiments of interest. This can be used to investigate a range of chemical systems, varying the chemistry of the reaction mixture and reaction conditions, with a heavily reduced workload for the user.

Methods

A computer-controlled reactor platform was developed, comprising (briefly); pumps, a custom-built tubular flow reactor (heated by a temperature controller and cartridge heaters) a benchtop NMR instrument and a custom-built GPC setup, all controlled by MATLAB software. RAFT solution polymerisations were performed using the platform by preparing standard reaction solutions (comprising monomer, RAFT agent and initiator in solvent) and connecting them to the flow platform.

Results and discussion

A range of polymerisations were optimised using the platform, exploring the trade-off between two key objectives for polymer synthesis; molar mass dispersity and monomer conversion. Typically, it is desirable to minimise the former and maximise the latter, but at high conversions, these objectives compete. Optimisations were performed for the polymerisation of tert-butyl acrylamide in the presence of a range of RAFT agents, enabling a comprehensive comparison of the achievable optima for each system. The development of medium resolution benchtop NMR methodology as a tool to probe more complex copolymer systems was also explored and shown to be applicable even where resolution limits are exceeded for conventional applications.



Auto polymer synth platform.jpg

Supramolecular Engineering of Microgels

Wednesday, 26th April - 11:45: Oral Session 9-1 - Oral

Dr. Nicolas sanson [1]

1. *Sorbonne Université*

Microgels are soft colloidal particles which exhibit a network made of crosslinked polymer chains swollen by the solvent in which they are suspended (1). The microgels engineering have become a tremendous field in past few years due to their highly tunable structure (2). One can take advantage from both their extensive chemical versatility of polymers and their colloidal behavior to elaborate functional materials. Our original work aims at developing inter-tunable crosslinks between microgels by introducing metallo-supramolecular chemical units within the microgel's network. The combination of supramolecular chemistry and soft colloids as microgels represents an ambitious way to develop multi-versatile colloidal assemblies.

Terpyridine-functionalized poly(N-isopropylacrylamide) (PNiPAM) microgel building blocks are shown to undergo an assemble–freeze–disassemble process. The microgel assemblies, which are controlled by monitoring the attractive and repulsive potentials between the soft colloidal particles, are then frozen by forming inter-particle metal–terpyridine bis-complexes upon addition of metallic cation. By oxidation of the metal–terpyridine bis-complex links, the aggregates open up, which is due to the complex dissociation releasing the connected particles in the form of single microgels. We extended our work to the development of 1D filaments and 2D membranes materials made of soft particles connected via supramolecular chemistry (3).

Finally, formed supramolecular microgels are proposed as a 3D printable ink that is cured post-printing by iron (II) cations for long-term stabilization. The supramolecular bonds are sufficiently strong and long-lived to maintain scaffold integrity during manual handling or immersion in liquid medium for over two months. The thermosensitivity of the micro-gels endows the printed construct with reversible and cyclable temperature-induced resolution enhancement, while the supramolecular cross-linking provides an asset of disintegration on-demand (4).

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High Performance PhotoPolymerization Systems

Wednesday, 26th April - 11:00: Oral Session 9-2 - Oral

Prof. Jacques Lalevée [1]

1. *Université de Haute-Alsace*

Photopolymerization technology has been developing steadily benefiting from the characteristics of spatial and temporal controllability, environmental protection, and efficient processes. Light-emitting diodes (LEDs) have been used as irradiation sources in photopolymerization increasingly due to their higher safety, lower energy consumption and longer emission wavelength than the conventional mercury lamps. Nowadays, LEDs are almost the primary choice to carry out photopolymerization experiments. In this work, new photoinitiating systems for radical, cationic or hybrid polymerization will be presented for different spectral ranges: near UV, visible, Near Infrared. This work will be extended to photopolyaddition processes. Some applications for coatings, 3D printing and photocomposites will be provided. The mechanical properties of the generated polymers/composites will be also investigated

Designing of Photo-responsive Polymers from Renewable Resources

Wednesday, 26th April - 11:30: Oral Session 9-2 - Oral

Ms. Pallabi Sinha Roy [1], Prof. Gil Garnier [2], Prof. Florent Allais [3], Prof. Antonio Patti [1], Prof. Kei Saito [4]

1. School of Chemistry, Monash University, Clayton, VIC 3800, Australia, 2. Department of Chemical Engineering, Bioresources Processing Research Institute of Australia (BioPRIA),Monash University, Clayton, VIC 3800, Australia, 3. URD Agro-Biotechnologies Industrielles (ABI), CEBB, AgroParisTech, 51110 Pomacle,France, 4. Graduate School of Advanced Integrated Studies in Human Survivability, Kyoto University, Higashi-Ichijo-Kan, Yoshida-nakaadachicho 1, Sakyo-ku, Kyoto, 606-8306, Japan

Introduction:

Lignin is an abundant natural resource that has the potential to replace fossil-based chemicals because of its aromatic-rich structure.[1] The paper-pulp and the bioethanol industry produce a substantial amount of lignin as a byproduct, most of which is used as a source of energy, and a very insignificant portion is further utilized to manufacture value-added chemicals.[2, 3] On the other hand, glycerol is another bio-resource generated as a byproduct in the biodiesel industry.[4] Lignin has a specific structural advantage to be used as a photo-responsive material, i.e., the occurrence of α,β-unsaturated ester bonds in the lignin-derived *p*-hydrocinnamic acids. When exposed to UV light, these bonds can undergo [2+2] cycloaddition reaction, which is photo-reversible.[5] However, specific design aspects were required to be considered in order to utilize this natural feature to synthesize high-value polymers.

Methods:

Lignin-derived aldehydes were used in this research along with glycerol and other linkers to design multi-functional monomers with α,β-unsaturated ester moiety *via* Knoevenagel–Doebner condensation reaction.[5] These monomers were further functionalized with longer alkyl chains by Williamson etherification. The multi-functional monomers thus formed can be crosslinked by applying UV light to synthesize photo-responsive polymers with reversible properties.

Result and discussion:

The main target properties of the multi-functional monomers, such as the crosslinking percentage, extent of decrosslinking and glass transition temperature at polymeric and oligomeric states, were optimized by targeted structural modifications. A structure-activity relationship (SAR) analysis was conducted to meet these property requirements for the self-healing application and later utilized as switchable polymer adhesives.[6] This research shows a pathway to utilize renewable resources and waste materials to design products for specialty application areas.

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A Fully Wavelength Orthogonal Photoresist

Wednesday, 26th April - 11:45: Oral Session 9-2 - Oral

Dr. Tugce Nur Eren Mert [1], ***Dr. Katharina Ehrmann*** [2], ***Dr. Florian Feist*** [1], ***Prof. Christopher Barner-Kowollik*** [2]

__1.__ Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), __2.__ School of Chemistry and Physics, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia

One of the most important challenges in synthetic chemistry is to control chemical reactions. Light is a key stimulus for this purpose, not only because of its advantages; spatiotemporal control and its innocuous nature, but also due to its potential to adress specific chemical reactions in a selective manner. By the judicous choice of wavelength and intensity, λ-orthogonal reactions can be performed.[1] Herein, we introduce a sequence-independent λ-orthogonal system to form a cooperative network only upon exposure to two colours of light. A heterotelechelic dilinker based on poly(ethylene glycol) (PEG) was synthesized by the substitution of fully λ-orthogonal chromophores, i.e. *N,N*-(dimethylamino)pyrene aryl tetrazole (APAT) at one end and o-methyl benzaldehyde (*o*-MBA) at the other end. A polymer bearing maleimide units is used as a reaction partner. The APAT terminus of the dilinker can undergo a NITEC reaction in the visible light regime (450 nm) with maleimides, where the *o*-MBA remains unaltered. Conversely, UV light (325 nm) activates *o*-MBA to perform an *o*-quinodimethane-driven Diels-Alder reaction with maleimides, while APAT remains inactive. One color irradiation leads to polymer post-modification through functionalization with respective chromophores. Upon exposure of two light sources either in a sequence-independent sequential or simultaneous fashion, the heterotelechelic linker functions as a crosslinker and takes part in polymer network formation.The functionalized polymers formed after each separate irradiation with one color of light was characterized using NMR spectroscopy. The changes in the topology of the maleimide polymer after each irradiation step were monitored by size exclusion chromatography. Upon irradiation with one colour of light, the increase in the molecular weight of maleimide polymer was observed while its molecular weight distribution remains similar. Subsequent irradiation with the other wavelength of light or simultaneous irradiation results in the formation of a graft polymer by interconnection of the prepolymer chains in a cumulative fashion, indicating the onset of crosslinking. To the best of our knowledge, the current photoresist system is the first to employ a fully λ-orthogonal crosslinker.

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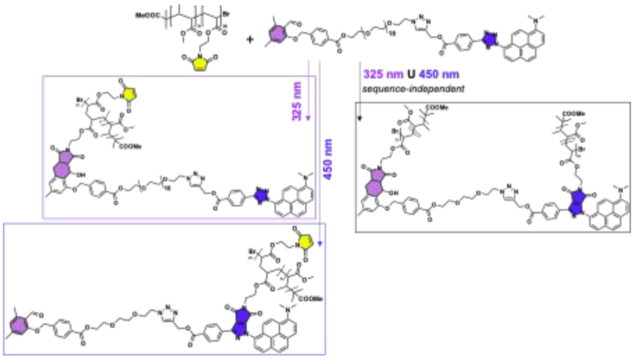

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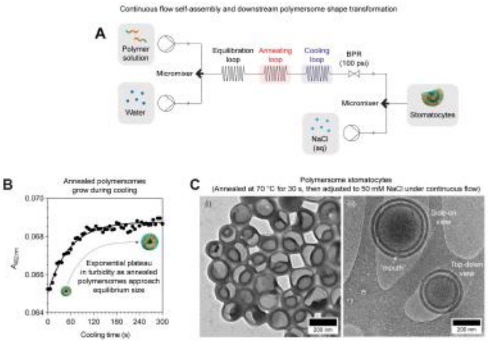
Dynamic Metastable Polymersomes: Towards Continuous Flow Manufacturing

Wednesday, 26th April - 11:00: Oral Session 9-3 - Oral

***Dr. Chin Ken Wong* [1], *Ms. Rebecca Lai* [1], *Prof. Martina Stenzel* [1]**

1. *University of New South Wales*

Polymersomes are polymeric analogues of liposomes with exceptional physical and chemical properties. Despite being dubbed as next-generation vesicles since their inception nearly three decades ago, polymersomes have yet to experience translation into the clinical or industrial settings. This is due to a lack of reliable methods to upscale production without compromising control over polymersome properties.[CKW1] [MS2] Herein we report a continuous flow methodology capable of producing near-monodisperse polymersomes at scale (≥3 g/h) with the unprecedented option of performing downstream manipulation. Unlike conventional polymersomes, our polymersomes exhibit metastability under ambient conditions, persisting for a lifetime of ca. 7 days, during which polymersome growth occurs until a dynamic equilibrium state is reached. We demonstrate how this metastable state is key to the implementation of downstream processes to e.g., manipulate polymersome size and/or shape in the same continuous stream. The methodology operates in a plug-and-play fashion and is applicable to various block copolymers.



Flow picture.jpg

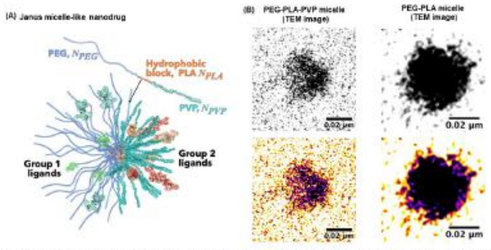
Design and characterisation of bifunctional hydrophilic Janus micelles for the development of novel nanodrugs

Wednesday, 26th April - 11:30: Oral Session 9-3 - Oral

Mr. Jose Muñoz-López [1]***, Dr. Lorena Ruiz-Pérez*** [1]***, Dr. Giuseppe Battaglia*** [1]

1. *Institute for Bioengineering of Catalonia (IBEC)*

Janus micelles are featured by their biphasic geometry of heterogeneous composition and distinctive properties in the core and corona. Such anisotropic design has attracted much attention from the scientific community due to the versatility of chemistries employed for generating Janus' morphologies and their potential applications. In this work, we present a novel ABC amphiphilic triblock copolymer system with the ability to form Janus micelles. The micelles are generated by solution-mediated self-assembly of the A and C hydrophilic, and B hydrophobic blocks. Subsequently, the hydrophilic blocks in the proposed triblock system will be functionalized with different and specific bioactive ligands to enable the constitution of multifunctional supramolecular scaffolds. The final aim of the project herein presented is to develop nanodrugs with well-defined dissimilar phenotypical domains, in the same fashion as the asymmetric functionalisation of antibodies that already exist in nature, to perform alike. To this end, poly(ethylene glycol)-polylactide-poly(*N*-vinylpyrrolidone) PEG-PLA-PVP triblock copolymer was synthesised in two steps: first, poly(ethylene glycol)-polylactide-2-bromo-2-methylpropanoate (PEG-PLA-Br) diblock macroinitiator was synthesized by the ring-opening polymerization of DL-lactide with commercial poly(ethylene glycol) and quenched with 2-bromo-isobutiryl-bromide. After that triblock copolymer was synthesized by the atom transfer radical polymerization (ATRP) of *N*-vinylpyrrolidone monomer (NVP) initiated by the PEG-PLA-Br diblock produced in the former synthetic step. The characterization of the produced diblock and triblock copolymers were carried out by nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC). Such techniques enabled us to verify the controlled radical polymerization of NVP and the complete conversion of PEG-PLA-Br diblock to the proposed PEG-PLA-PVP triblock. The morphologies adopted by PEG-PLA-Br and PEG-PLA-PVP in solution were investigated by transmission electron microscopy (TEM), confirming the formation of micelles for both block copolymers. TEM images showed differences in the negative stained micelles generated in the diblock and triblock copolymers systems. Such differences indicate the asymmetric distribution of both hydrophilic blocks, PEG and PVP, in the self-assembling of the PEG-PLA-PVP triblock system. Further structure characterizations will include atomic force microscopy (AFM), cryo-TEM, electron energy loss spectroscopy (EELS), and ultimately the functionalization of both coronas with different targeting ligands.



(A) Schematic model of Janus-like nano drug formed by the self-assembling of difunctionalized PEG-PLA-PVP triblock copolymer, showing the different lengths and densities of the PLA and PEG regions of the corona. Group 1 and 2 proposed ligands located in the PEG and PLA regions respectively are also displayed in the model. (B) TEM images of PEG-PLA-PVP (left-hand side) and PEG-PLA (right-hand side) micelles stained with phosphotungstic acid PTA. Images of the triblock (left-hand side) indicate an asymmetric distribution of the dark and bright areas suggesting phase separation within the micellar structure.

Graph abs apme2023.jpg

Thiomaleimides photodimerisation: new opportunities for covalently crosslinked polymer networks?

Wednesday, 26th April - 11:45: Oral Session 9-3 - Oral

Dr. Hannes Houck [1]***, Mr. Mohammed Aljuaid*** [1]***, Dr. Paul Wilson*** [1]***, Prof. David Haddleton*** [1]

1. *University of Warwick*

Maleimides are highly enabling scaffolds in (bio)conjugation and polymer chemistry. In particular, maleimide reactions with thiols and furans have received wide attention because of the reversible covalent bond-forming nature of the resulting thiol-Michael and Diels-Alder addition products. Hence, a multitude of maleimide-based dynamic polymer networks have been designed, enabling reshaping, healing and reprocessing of covalently crosslinked materials. Furthermore, maleimide compounds have been demonstrated to undergo [2+2] homo-dimerization and even cross-cycloadditions in the presence of alkenes upon UV irradiation, thereby providing swift access to valuable substituted cyclobutane motifs both for small molecule synthesis and polymer modification.

In contrast to conventional maleimides, mono-thiomaleimide analogues have been seldomly explored. Indeed, only recently, thiomaleimides were observed to undergo a UV-induced [2+2] cycloaddition. Thus far, this thiomaleimide photodimerisation has only been applied to three (bio)conjugation studies,[1-3] despite showing interesting advantages over the traditional [2+2] maleimide cycloaddition, including faster kinetics and milder irradiation conditions. Here, we highlighted this efficient [2+2] dimerisation for the first time in polymer crosslinking by photo-curing a polyacrylamide hydrogel via thiomaleimide side chains.

Powder Coating Formulation with Improved Storage Stability

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Ayşenur Özdemir [1], ***Ms. Göknil Süsler*** [1], ***Mr. Ali Ersin Acar*** [1]

1. *Boğaziçi University*

Powder coatings are the most environmentally friendly system for the coating industry. The system does not include any volatile organic compound (VOC-free). Additionally, it does not include water in formulations. Therefore this system is more environmentally friendly than liquid coatings. Powder coating formulations basically consist of a resin, a crosslinker, and a catalyst that can be curable with the heat on a substrate. Other components like pigments, fillers, and flow modifiers are added to the formulations based on the application areas. Powder coatings are used in automotive, architecture, and other metal industries. For these areas, the curing temperature range varies between 140°C and 200°C. Due to high curing temperatures, powder coatings could not be used for heat-sensitive substrates such as wood, MDF, and plastics until recent years. Nowadays, there is an interest in decreasing curing temperatures of powder coating systems (120°C-140°C) so that they can be used in the wood industry. Starting from this point, the resins with low molecular weights and low viscosities for low curing temperature powder coating systems have become commercial. However, there are some disadvantages of newly commercial resins. The most severe and essential problem is powder coatings' poor storage stability, including low curing resins. In this study, a new resin has been developed by chain extension of a commercial low curing resin in the extruder. New powder coating formulations have been studied with chain extended resin. During chain extension and powder coating studies, a single screw extruder was used. Newly synthesized resins were analyzed by FTIR and GPC. Powder coatings were analyzed by FTIR, rheometer, inclined plate flow test, impact test, and gloss determination. Additionally, powder coatings were kept in an oven to observe storage stability. At the end of the study, satisfactory results were obtained.

Polymer nanocapsules based on amphiphilic polyelectrolytes

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

***Ms. Aneta Medaj* [1], *Ms. Klaudia Minor* [1], *Prof. Szczepan Zapotoczny* [1]**

1. *Faculty of Chemistry, Jagiellonian University*

Amphiphilic polyelectrolytes with comb-like graft architecture efficiently stabilize the nanocapsules by self-assembly process without any surfactants. Polymeric nanocapsules are efficient containers of hydrophobic and lipophilic substrates.

In this work different polyelectrolytes based on poly(allylamine hydrochloride) were obtained and characterized in order to optimize properties of nanocapsules towards enhancing the ability for encapsulation of hydrophobic compounds. Dynamic light scattering and zeta potential measurements were used to determine physicochemical properties. Morphology of capsules was determined by scanning and transmission electron microscopy. The ability of encapsulation of hydrophobic compounds was examined by confocal microscopy.

Performed studies confirmed that applied amphiphilic polyelectrolytes provide long-term stabilization of oil-in-water emulsion.

Micro-compartments of UCST hydrogels for microfluidic biotechnologies

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Léa Milenkovic [1], ***Mrs. Yvette Tran*** [1], ***Mrs. Nadège Pantoustier*** [1]

1. Soft Matter Sciences and Engineering, ESPCI Paris, PSL University, Sorbonne University, CNRS, Paris, France

Thermo-sensitive polymers are of growing interest in many biomedical applications. The general idea of my PhD thesis is to design hydrogel micro-compartments with UCST (Upper Critical Solution Temperature) polymers for microfluidic biotechnologies. Hydrogels can be actuated by temperature change to close/open micro-compartments or micro-cages to trap single cells for analysis [1]. Thethermo-actuable hydrogel is patterned and grafted on the bottom substrate of a microfluidic chip to form tens of thousands of micro-cages using photolithography. In the collapsed state, the micro-cages are opened, and in the swollen state, the hydrogel contacts the top substrate of the chip to close the micro-cages. Actuator technology based on UCST hydrogel micro-cages closed at 37°C, allows most of molecular biology operations under physiological conditions.

The challenge is thus to modify UCST polymers to form a hydrogel matrix based on thiol-ene click reaction, that can be micro-fabricated by Cross-Linking And Grafting (CLAG) [2], without leading sacrificing the thermo-sensitivity (Figure 1). As for the biological applications the polymers selected must not be very sensitive to saline solutions, the affinity of the polymer with water has to be governed by hydrogen bond interactions which can be finely tuned with temperature (T < UCST: aggregation of polymers, T > UCST: solubility of polymers).

We focus on acrylamide-based copolymers which can keep their UCST behavior in salt conditions. We synthesize the monomers and polymers that are used as elementary bricks for UCST hydrogels and study their thermo-responsive properties in aqueous and physiological solutions, such as poly(N-acryloylglycinamide)- or poly(N-methacryloylglycinamide)-based copolymers [3].

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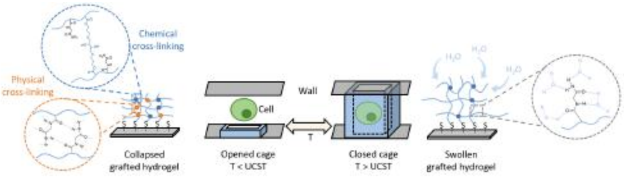


Micro-cage cell encapsulation process.png

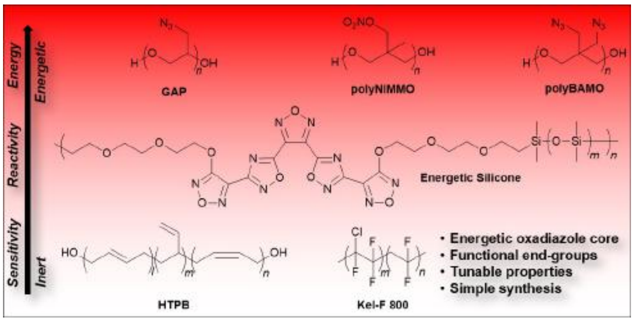
Energetic silicones: synthesis and characterization of pentaoxadiazole-PDMS copolymers

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Trevor Shear [1]

1. Lawrence Livermore National Labratory

Standing at the forefront of energetic research is the exploration of new energetic binders. Traditionally, these binders are functionalized with azide, nitro, or nitrate ester explosophores resulting in high energy density but poor safety, mechanical, and thermal properties. Utilization of heterocyclic scaffolds in these endeavors provides a path toward materials with high density that exhibit robust safety performance while maintaining tunable mechanical and thermal properties. In this effort, we have developed the first energetic silicone polymers based on the hydrosilylation of a penta-oxadiazole based molecule and PDMS without using sensitive explosophores, resulting in properties that lie between, or exceeded, the thermal and mechanical properties of inert and commonly used energetic binders.



Energetic silicone.jpg

Alginate/PVA hydrogels crosslinked with boronate esters: study of viscoelasticity and metoclopramide release through shear forces

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Prof. Bruno Urbano [1]***, Ms. Yessenia Oyarzun*** [1]***, Dr. Jose Ulloa*** [1]

1. *Universidad de Concepción*

The development of new smart biomaterials has been of great interest due to their attractive applicability in different areas of biomedical sciences. In particular, the elaboration of hydrogels with boronic acids can form dynamic covalent bonds with cis 1,2- and 1,3-diols to form boronate esters, which can be reversible and sensitive to pH, conferring properties such as self-healing, stimuli-sensitivity, injectability, and dynamism in the connectivity of the polymeric network, among others. These characteristics help study and develop of controlled drug delivery systems.

In this research, the modification of sodium alginate with 4-aminophenyl boronic acid (AlgBA) and the formation of hydrogels with poly(vinyl alcohol) (PVA) of variable molar mass (60 and 145 kDa) are proposed. These systems allow the encapsulation and subsequent release of the drug metoclopramide. Furthermore, we hypothesized that the molar mass of PVA and pH (6.0, 7.4, and 9.0) would modify the degree of connectivity of the hydrogel network and, thus, the drug release performance. In addition, we studied the release of metoclopramide through the induction of shear forces to compare the release with classical diffusion-based experiments and followed through UV-Vis at 309 nm.

Characterization of the hydrogels through rheometry showed that increasing the molar mass of PVA and pH increases viscosity and storage modulus (Figure 1a). Also, an increment of pH increases the hydrogel's relaxation time which is associated with the crosslinking dissociation rate constant. These results reveal that the molar mass of PVA increases the degree of crosslinking while increasing the pH alters the boronic acid structure allowing the formation of more stable boronate esters.

On the other hand, release studies showed that increasing pH decreases the amount of drug released and slightly slows down the release of metoclopramide, attributed to a more crosslinked network. However, shear force-induced release revealed a more significant diminish in metoclopramide's release rate (Figure 1b).

Acknowledgements: The authors thanks to Fondecyt Regular 1211450.

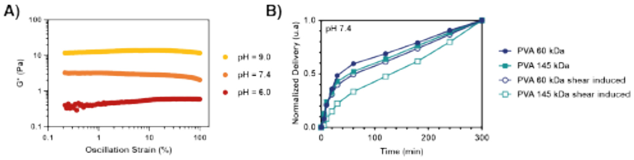


Figure 1. A) Complex modulus as a function of pH for AlgBA/PVA 145 kDa, B) Metoclopramide release studies.

Figure 1.png

Synthesis of Conjugated Microporous Polymer Network by Atom Transfer Radical Cross-coupling Reactions

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Busra Nakipoglu [1], ***Dr. Cansu Aydogan*** [1], ***Prof. Yusuf Yagci*** [1]
1. *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,*

Since the discovery of the first examples of conjugated microporous polymers (CMPs) in 2007, these materials have been extensively synthesized and researched due to their exceptional properties, particularly the π-conjugation present throughout the extended network.[1] These properties make them useful for optoelectronics, such as photoredox catalysis, light emission, and energy storage. In addition, CMPs possess alkyne struts and have adjustable linker length. These segments contribute to their low-density porous network and offer potential applications for molecular separation and gas storage.[2]
Atom transfer radical polymerization (ATRP) is a versatile polymerization technique that enables the controlled synthesis of well-defined polymers by initiating radical polymerization through a transition-metal complex, allowing the use of a wide range of monomer types.[3] Atom transfer radical coupling processes proceed through forming a covalent bond of thermally or photochemically formed different radicals. The reactions generally favor high radical concentrations.[4] The combination of ATRP with atom transfer radical coupling (ATRC) reactions was performed by our group in the past to obtain polyesters.[5] Herein, we report a novel and versatile method for the synthesis of conjugated microporous polymers by cross-coupling bifunctional monomers under ATRP conditions with CuBr as catalyst, PMDETA as ligand, Cu(0) as reducing agent, and toluene as solvent. The structures will be characterized by spectroscopic (FT-IR, ^{1}H - ^{13}C CP/MAS solid-state NMR, UV-vis, solid-state UV-vis DRS, fluorescence), thermal (DSC, TGA), electrochemical (CV, DPV), microscopic (SEM) and BET surface area analyzes.

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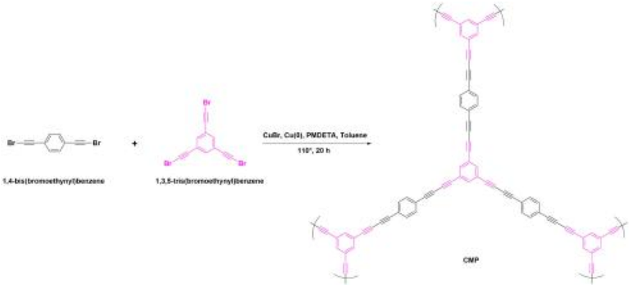


Nakipoglu.jpeg

Grafting anhydride derivatives on chitosan oligomers: synthesis, characterization and quantification method

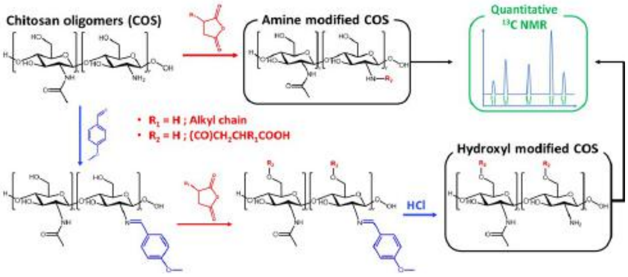
Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Paul Morandi [1]***, Mr. Aurelien Lebrun*** [2]***, Ms. Karine Parra*** [2]***, Mr. Steve Berthalon*** [1]***, Dr. Claire Negrell*** [1]***, Prof. Ghislain David*** [1]

1. *CNRS ICGM,* ***2.*** *CNRS IBMM*

Since their discovery, the production of polymers materials has always been growing exponentially, despite the use of petroleum derivatives and the negative ecological. While scientists were used to develop materials with the least possible constraints and without taking in consideration the ecological impact, the ecological transition makes us think different and look for any possible application using eco-friendly materials, despite the related constraints. Therefore, being both bio-based and biodegradable, chitosan is one of the most interesting eco-friendly polymers. Also, the hydroxyl and amine groups can be used to modify chitosan, using the great reactivity of anhydride groups. Several studies report the grafting of anhydride derivatives on chitosan, but there is a lack of characterization and none of them describe the
grafting quantification.

The point of this work is to propose a simple method for grafting cyclic anhydrides onto specific sites of chitosan oligomers and with a targeted substitution degree. Anhydrides, being able to react on both amine and primary alcohol of chitosan, a protection/deprotection method is needed in order to graft them on specific sites. In the first place, model reactions have been developed using glucosamine (representing repeating units of chitosan): the amine group was protected with *p*-anisaldehyde in order to graft anhydride derivatives on the hydroxyl groups. On the other side, the hydroxyls were protected with acetate groups to let anhydrides derivatives react only with the amine. The final products of the model reactions were then analyzed by NMR spectroscopy (^{1}H, ^{13}C, HSQC and HMBC analysis), providing useful information needed for the analysis of modified chitosan coming after the model reactions. The same method was then applied on chitosan oligomers, leading to a precise grafting of cyclic anhydrides. The primary amines of chitosan being way more nucleophilic than the hydroxyls, the grafting of anhydrides onto amines can be done without protecting the hydroxyls. On the other hand, grafting anhydrides on hydroxyls was possible after the protection of the amines using *p*-anisaldehyde, which can be easily removed. At the end, the modified chitosan samples were characterized by quantitative ^{13}C NMR spectroscopy, in order to determine precisely the substitution degree.



Chitosan oligomers functionalization using cyclic anhydrides derivatives.jpg

Polybutadiene - a versatile platform for the synthesis of unique organofunctional polymers

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Rafal Januszewski [1]***, Dr. Michal Dutkiewicz*** [2]***, Dr. Bartosz Orwat*** [3]***, Dr. Ireneusz Kownacki*** [1]

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Polymeric materials have become indispensable elements of our everyday life thanks to the possibility of precise adjustment of their properties for tailored applications. One of the most important groups of synthetic polymers are polyolefins. However, polyolefins as a consequence of their hydrophobicity caused by the lack of functional groups, exhibit poor compatibility to nitrogen- or oxygen-containing compounds, and inorganic materials, which makes them unsuitable for applications that require good surface adhesion properties, toughness, solvent resistance, or miscibility with the polar group-containing polymers. These inconveniences can be overcome by the incorporation of even small amounts of functional groups into the hydrocarbon backbones, which may significantly extend the number of potential applications, making these new materials more versatile and valuable. As the most common polyolefins such as polyethylene or polypropylene contain only carbon-carbon and carbon-hydrogen bonds, any functionalization must involve the cleavage of these units which remains challenging due to high dissociation bond energies. Considering the above, in this work, we present a completely different approach, which relies on the application of polybutadiene as a starting material in the preparation of two novel polymeric precursors containing side hydrosilyl and ethynyl groups and their subsequent transformations through transition metal-catalyzed reactions. The developed synthetic strategy enables the incorporation of a wide variety of functional units into the polymer chains, which cannot be introduced through conventional polymerization protocols [1-5].

The authors wish to thank the National Science Centre, Poland, for their financial support under project UMO-2019/32/C/ST4/00178

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Characterization of supramolecular polymers based on bridged β-cyclodextrins

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

***Dr. Gaëlle Pembouong* [1], *Dr. Wenting Hu* [1], *Dr. Julien Rossignol* [1], *Dr. Pierre Evenou* [1], *Dr. Mickaël Ménand* [1], *Prof. Matthieu Sollogoub* [1], *Dr. Laurent Bouteiller* [1]**

1. *Sorbonne Université, Institut Parisien de Chimie Moléculaire, Paris, France*

The development of supramolecular anisotropic assemblies is a challenge of great interest. Indeed, these morphologies are involved in numerous applications as mechanical reinforcement or as templates for porous materials. Moreover, the use of supramolecular interactions can provide versatile properties to these assemblies. To tackle this challenge, we chose cyclodextrins as molecular block because of their water solubilty and their biocompatibility. Then AB-type β-CD monomers selectively functionalized with an adamantyl guest have been synthesized and characterized. Previous work have shown that the addition of an aliphatic bridge on the primary rim of the CD suppresses self-inclusion of the adamantyl group of a monomer in its own cavity and thus favors polymerization [1].

To continue this work, a second bridged AB-type β-CD monomers was designed with a less constrained bridge and a central adamantyl group. NMR studies have shown that at high concentration and in acidic media this monomer is indeed not self-included [2]. The capacity of this acidic monomer to form a supramolecular polymer was assessed via viscosimetry, ITC and SANS analyses. Viscosimetry analysis evidenced the formation of supramolecular assemblies. ITC measurements enabled to determine an association constant of 9000 M^{-1}, similar to the one of the first bridged monomer. Finally, SANS analysis confirmed the formation of anisotropic structures.

To conclude, this study led us to develop 2 water-soluble tunable supramolecular polymers based on functionalized β-CDs with a relatively high DP. The different architecture of these monomers and their charged nature will enable us to use them as a platform to access higher level of architectures via secondary interactions. This will in turn, provide some insight into supramolecular assembling processes.

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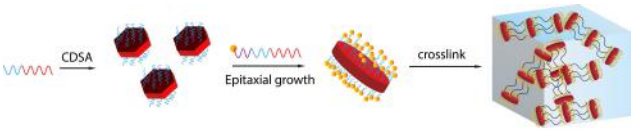
‘Living’ crystallisation-driven self-assembly of functional lactone-based polymers

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

***Dr. Bo Li* [1], *Prof. Andreas Heise* [1]**

1. *Royal College of Surgeons in Ireland*

Bio-compatible nanomaterials are of great interest in various fields such as drug delivery and tissue engineering. The advent of crystallisation-driven self-assembly (CDSA) has simplified access to a wide range of precisely size-controlled nanomaterials. Among the studies of crystallisation-driven self-assembly, polyester has drawn increasing attention due to its biocompatibility and degradability. However, the scope of polyesters in CDSA has narrowed between polycaprolactone and polylactide. Herein, we reported the CDSA of polyambrettolide copolymer with a semi-crystalline polymacrolactone as core-forming block for the first time, while the double bond of polyambrettolide has enabled potential functionalisation. Aiming at a transition from two-dimension nanomaterial to three-dimension crosslink hydrogel, a third block has been introduced for post-functionalisation of polyambrettolide copolymer. A series of 2D nanosheets with modified surfaces were then prepared from epitaxial growth of polyambrettolide triblock polymer. Gelation was triggered by crosslinking the chain end on the surface of nanosheets. Tunable mechanical properties of crosslinked hydrogel could be achieved by changing the size of applied nanosheets. This method has offered a new pathway for CDSA to various applications beyond the current scope.



Poster apme.jpg

Redox-triggered Self-immolative Polymers as Drug Delivery Systems

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Katharina Völlmecke [1]***, Dr. Dirk Kuckling*** [1]***, Dr. Klaus Langer*** [2]

1. Paderborn University, Department of Chemistry, Warburger Str. 100, 33098 Paderborn, 2. Institut für Pharmazeutische Technologie und Biopharmazie Correnssstr. 48 D - 48149 Münster

According to the WHO cancer is accountable for one in six deaths worldwide, with breast cancer being the most prevalent of all cancer types. While some breast cancer types can be effectively targeted via antibodies, this treatment is expensive and not possible for all forms, such as HER2-negative types. To overcome this issue, polymeric nanoparticles can take advantage of the enhanced permeation and retention effect to passively target tumor cells and release drugs upon an exogenous or endogenous trigger e.g. light irradiation[1] or the presence of reducing agents e.g. glutathione (GSH).[2] In previous works self-immolative polydisulfides have been known to show a fast and complete degradation upon the addition reducing agents and therefore are interesting candidates for this application.[3]

In a well reproducible fashion, dithiothreitol (DTT) was polymerized using 2,2'-dipyridyl disulfide (DPD) as an oxidant that at the same time serves as the end-cap. The isolated polymer was characterized using ^{1}H-NMR spectroscopy, GPC and DSC. Further, the degradability was shown via ^{1}H-NMR spectroscopy by addition of reducing agents DTT and GSH. Nanoparticles were prepared by the nano-precipitation method yielding particles with a z-average diameter of ca. 160 nm and a PdI of 0.2. To show the applicability as degradable nanoparticles in biomedical applications, particle stability was tested at 37 °C in PBS buffer with added reductants DTT and GSH at biologically relevant concentrations (10-0.1 mM). The particles showed a decrease in countrate upon the trigger, which relates to a degradation of the particle. To test the ability to incorporate hydrophobic drugs Nile red was used as a dummy substance and was added to the polymer solution in advance. Further, exogenous triggers can be included via light cleavable end-groups. The irradiation of a particle solution with UV-light (200 mW/cm^2; 120 s) showed a significant drop in countrate as well.

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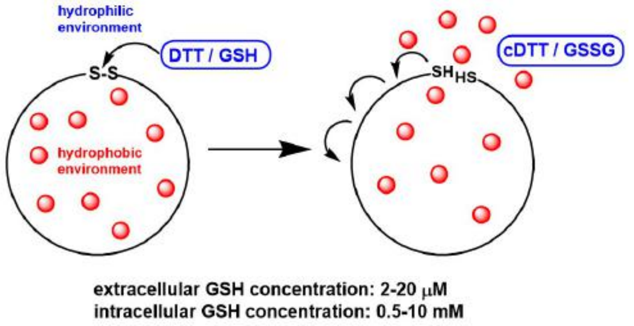

Reductant induced particle disruption and drug release.jpg

Intermolecular hydrogen bonding between single chain polymer nanoparticles

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

***Ms. Alisa Bouketov* [1], Prof. Maya Davidovich-Pinhas [2], Prof. Charles E. Diesendruck [3]**

***1.** Schulich Faculty of Chemistry, Technion – Israel Institute of Technology, Haifa 3200003, Israel, **2.** Faculty of Biotech. & Food Eng., Technion – Israel Institute of Technology, Haifa 3200003, Israel, **3.** Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 3200003, Israel*

Single-chain polymer nanoparticle (SCPN) is an interesting polymer architecture in which the chains are chemically folded into well-defined shape and size, similar to proteins, which are typically collapsed into tertiary structures. We have shown that this chain folding reduces the entanglement density of the polymer in bulk, reducing chain-chain interaction and therefore changing the mechanical properties of the material.[1] As the intermolecular interactions in our previous studies were mostly limited to London dispersion, many interesting aspects seen in biomaterials can still be introduced to bulk polymers made of SCNPs. Strong complementary hydrogen bonding units on the surface of each SCPN will affect the energy of interaction between individually folded chains, further affecting organization and properties in bulk polymers as well as polymer solutions, perhaps replacing the absence of chain entanglements. The main goal of this research is to understand the impact of surface-to-surface hydrogen bonding interactions between SCPNs by looking at the rheology behavior of SCPN systems in solution.

In order to assess the influence of intermolecular hydrogen bonds, two sets of linear copolymers were prepared, one with adenine side groups and the other with thymines. SCPNs were prepared using each of these copolymers and the rheology of each of the linear and the SCNPs in solution was measured. Next, solutions of complementary linear and complementary SCPN blends were prepared, and their rheology behavior was tested.

Our results show that the viscosity measured for the SCPN blend yielded higher values compared to each of the copolymer solutions separately. These results imply the formation of complementary hydrogen bonding interactions between the folded polymer chains. On the other hand, such trend was not seen for the linear blend, in which the blend has indistinguishable viscosity from the individual sets. Importantly, the individual copolymers can still make weak hydrogen bonds amongst themselves, but not on the energy level of having complementary groups. Our results indicate that while polymer folding increases the critical interaction concentration,[1] the folded morphology enhances the non-covalent interactions between particles.

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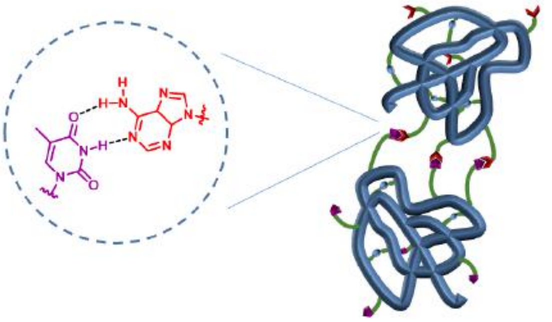

Intermolecular hydrogen bonding between single chain polymer nanoparticles.png

CO2-Derived Block Polycarbonate-Ethers for Accommodating the Volume Change in Solid-State Battery Composite Cathodes

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Hui Gao [1], ***Dr. Georgina Gregory*** [1], ***Prof. Peter Bruce*** [1], ***Prof. Charlotte Williams*** [1]

1. *University of Oxford*

All-solid-state batteries have gained increasing attention because of their high energy density and safety. Several inorganic solid electrolytes achieved the requirement of lithium-ion conductivity for all-solid-state batteries. However, the rigid and brittle nature of inorganics prevents good interfacial contact with electrodes. The active materials are subjected to volume change upon charging/discharging. This leads to contact loss between active materials and electrolytes in the composite cathode (including the active material, inorganic solid electrolyte and carbon), resulting in poor cycling stability of the cells. To overcome the contact loss, the polymers can be introduced into cathode composites to improve the interfaces, cohesion and mechanical properties. Herein, we prepare the cathode composite of solid-state batteries by adding purpose-designed triblock polymers, poly(4-vinyl cyclohexene oxide carbonate)-*b*-poly(ethylene oxide)-b-poly(4-vinyl cyclohexene oxide carbonate) (PC-*b*-PEO-*b*-PC). Triblock polymers are synthesised by hydroxyl telechelic PEO as a macroinitiator for CO_2/epoxide ring-opening copolymerization and a well-controlled Mg(II)Co(II) catalyst at 1 bar CO_2. The correlation of ion conductivity and mechanical properties with the block polymer composition is investigated. Three lead polymers are identified. These block polymers show high ionic conductivity (10^{-4} S cm^{-1}) at room temperature, lithium-ion transport (t_{Li+} 0.3-0.62), good electrochemical oxidative stability (> 4 V vs Li^+/Li) and elastomeric or plastomer properties (G’ 0.1 -67 MPa). The solid-state batteries with the block polymer in the $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ cathode composite demonstrate greater capacity retention than equivalent cells featuring PEO homopolymer or without any polymer.

Polypyrrole-gelatin cryogels as precursors for supercapacitor electrodes

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Konstantin Milakin [1]***, Dr. Sonal Gupta*** [1]***, Dr. Ognen Pop-Georgievski*** [1]***, Dr. Zuzana Morávková*** [1]***,***
Mr. Udit Acharya [1]***, Dr. Patrycja Bober*** [1]

1. *Institute of Macromolecular Chemistry, Czech Academy of Sciences, 162 00 Prague 6, Czech Republic*

Polypyrrole-gelatin cryogels are novel composite materials, which have macroporous structure and high electronic conductivity together with good handling properties [1]. Their developed surface and the presence of nitrogen-containing components in their structure makes them promising precursors for conversion to carbon-based electrode materials for energy storage applications. The present work [2] is focused on studying the influence of the cryogel carbonization temperature on structure, physicochemical properties and electrochemical performance of resulting carbonaceous materials.

Polypyrrole-gelatin cryogels were synthesized by oxidative cryopolymerization of pyrrole in the frozen aqueous solution of gelatin. The prepared cryogels were carbonized at various temperatures (100-700 °C) in inert atmosphere to obtain carbogels. The materials were characterized by scanning electron microscopy, thermogravimetric analysis, Raman and X-ray photoelectron spectroscopy, conductivity measurements, specific surface area and total pore volume measurements, cyclic voltammetry and galvanostatic charge-discharge.

The prepared polypyrrole-gelatin cryogels had macroporous structure (pore size 10–50 μm) and conductivity in the range 2–5 S cm^{-1}. After the carbonization at all temperatures the materials maintained their mechanical integrity and porous morphology. Increasing the carbonization temperature resulted in gradual increase of carbonization degree and enhancement of the carbogel structural order. The fully carbonized material reached conductivity 2×10^{-5} S cm^{-1} (700 °C), and its specific surface area and pore volume (441.7 m^2 g^{-1} and 0.21 cm^3 g^{-1} at 600 °C, respectively) were one order of magnitude higher than for the precursor. The highest gravimetric capacitance (273 F g^{-1}) was achieved for the carbogel, prepared at 700 °C. The material was stable for at least 1000 cycles.

The authors wish to thank the Technology Agency of the Czech Republic under the EPSILON Programme (TH80020001) within the M-ERA.NET 3 Cofund Call (project BATMAN) for the financial support.

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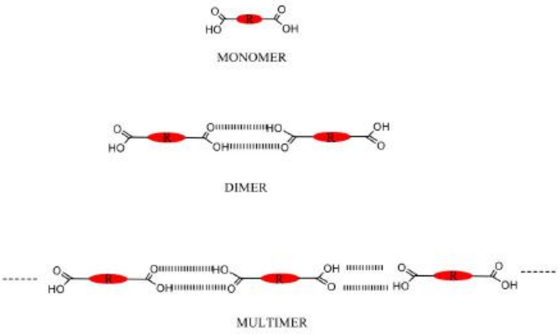
Self-association of dicarboxylic acids in the presence of common diols

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Mrs. Halenur Karakaya Kabasakal [1], ***Ms. Vehibe Nazlı Can Çiçek*** [1], ***Mr. Ali Ersin Acar*** [1], ***Mr. Eray Şenli*** [2]

1. *Boğaziçi University,* ***2.*** *SASA Polyester Sanayi A.Ş.*

FT-IR spectroscopy has been utilized to investigate the H-bonding interactions in terephthalic acid (TPA) and isophthalic acid (IPA), which are extensively used in industry. In general, self-association of dicarboxylic acids through H-bonding was studied in their solid-states or in the presence of solvents (ie. DMSO, $CHCl_3$, CHEX, CCl_4). However, TPA and/or IPA undergo melt polymerization with diols such as ethylene glycol (EG), 1,4-butanediol (1,4-BDO), and 1,3-propanediol (1,3-PDO) as a common industrial practice. Therefore, any change in inter-molecular H-bonding of TPA and IPA within these diols may provide a different insight on these monomers. In this study, the self-association of TPA and IPA with respect to a variety of diols, concentration and temperature was investigated. The extent of H-bonding was probed *via* FT-IR by comparing the intensity and wavenumber of -OH and C=O bands.



Abstract..jpeg

Aminated ePTFE for grafting of antibacterial molecules, cytotoxicity, and antibacterial assessment.

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Yaëlle Roina [1]***, Prof. Guillaume HERLEM*** [1]***, Dr. Gwenael Rolin*** [2]***, Prof. Didier Hocquet*** [3]***, Dr. Marlene Sauget*** [3]***, Prof. Frédéric Auber*** [1]

1. *Nanomedicine lab EA 4662, UFR Sciences & Techniques, Besançon, France,* ***2.*** *Centre d'investigation clinique Inserm 1431, CHU de Besançon – Inserm UMR 1098 RIGHT, France,* ***3.*** *Laboratoire Chrono-Environnement UMR 6249 CNRS, Besançon, France*

Introduction

Widely used in the medical field as surgical materials, fluoropolymers can benefit from enhancement of anti-bacterial properties. The rise of multi-resistant bacteria evolves rapidly worldwide, which is why there is an important need for alternative solutions to antibiotics. ePTFE is a widely used material for implants. We previously developed a method with the action of lithium alkylamidure, resulting from the reaction between Lithium and ethylenediamine (LiEDA) or diethylenetriamine (LiDETA), to obtained defluorinated and aminated ePTFE. We present here the functionalization with chitosan (CHI), polyethylenimine (PEI) and polyvinylpyrrolidone iodine (PVP) of the aminated ePTFE obtained in solution with lithium alkylamides.

Methods

Functionalization with PEI and CHI is obtained via the grafting with glutaraldehyde and PVP after immersion, as showed in the attached figure. The grafting success was evaluated using IR-ATR spectroscopy. MTT first assays of cytotoxicity and proliferation assays on murine fibroblasts were carried out. Anti-bacterial properties were evaluated on six bacterial species usually causing nosocomial infections : *Staphylococcus epidermidis, Staphylococcus aureus, Klebsiella pneumoniae, Escherichia coli, Enterococcus faecalis and Pseudomonas aeruginosa.* This test consists in counting the bacteria attached to the material and calculating the antibacterial activity.

Results

IR-ATR spectroscopy revealed the presence of imine bonds on the functionalized materials. MTT indirect tests show a satisfactory rate of living fibroblasts for the LiEDA and LiDETA method alone and for the functionalization with PEI, CHI and PVP. Antibacterial activity of the treated samples is evaluated on the 6 bacteria. The most efficient surface modification that is effective on all the bacteria tested is the combination of LiDETA and PEI.

Discussion

These first results would benefit from more tests, as these are preliminary results of an innovative method. The surprising opposed tendencies observed between MTT and proliferation assays would benefit from direct MTT tests on the material. The effects of the procedure for antibacterial tests were not evaluated on the chemical composition on the surface of the samples.

High concentration synthesis of single-chain polymer nanoparticles via acyloin condensation

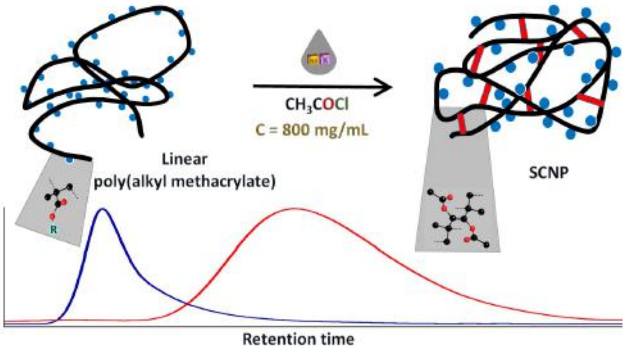
Wednesday, 26th April - 13:00: Poster Session 3 - Poster

***Dr. Sinai Aharonovich* [1], *Prof. Charles E. Diesendruck* [1]**

***1.** Schulich Faculty of Chemistry, Technion - Israel Institute of Technology, Haifa 3200003, Israel*

Single chain polymer nanoparticles (SCNPs) are soft nanoparticles built from a single polymer chain, folded onto itself by intramolecular cross-linkages. The unique properties of SCNPs, such as molecular recognition, catalysis, controlled release of encapsulated molecules, and shear-resiliency have stimulated recently increasing interest in their applications across various nanoscience disciplines. To avoid thermoset formation, the intramolecular cross-linkages that form SCNPs normally requires high dilution of the linear polymer precursor, typically <1 mg per mL. However, when multi-kilogram or higher amounts of SCNP are considered, the copious amounts of solvents involved become increasingly prohibitive. Hence, methods for selective high concentration syntheses are pivotal for any scaling up or commercialization of SCNP-based technologies.

Herein, we present a new, one pot, post-polymerization approach for the preparation of SCNPs that does not require catalysts or costly chemicals and produces SCNPs at very high polymer concentrations (up to 800 mg/mL), without any thermoset formation and in high yields. The acyloin condensation-based chain folding utilizes ester groups that are already present in poly(alkyl methacrylates) as the coupling sites, and thus enables these readily available polymers to be used as linear precursors without the need to introduce any other cross-linkable groups to the chain. Thus, three poly(alkyl methacrylates) (alkyl = methyl, cetyl/stearyl) linear precursors were reacted with potassium or potassium-sodium (NaK) alloy and the resulted enediolate-bearing SCNP were quenched by an electrophile (acetyl chloride or chlorotrimethylsilane). The produced SCNPs were characterized by I.R and 1- and 2-D NMR spectroscopy, which supported the presence of the enediolyl ether/ester functional groups, and by SEC, which showed the formation of SCNPs via the increase of their retention times and decrease of the hydrodynamic volumes as compared to the linear polymers. Control experiments showed that the SCNPs produced by the alkali metals are nearly free of carboxylates, and that they can regain hydrodynamic volume when some of their acyloin groups are oxidatively cleaved back to esters. Finally, we also demonstrated how the cross-linkage degree can be easily controlled by stepwise addition of NaK/electrophile, allowing the preparation of organic nanoparticles with varying sizes.



Scnps via acyloin condensation at high concentration.jpg

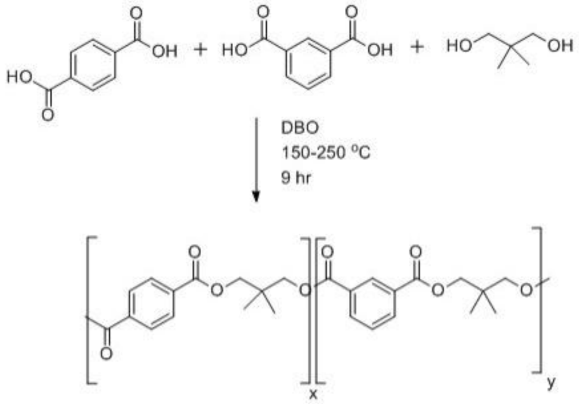
Sequence analysis of Poly(neopentyl-terephthalate-co-isophthalate) copolymers by 13C-NMR

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Mrs. Halenur Karakaya Kabasakal [1], ***Ms. Göknil Süsler*** [1], ***Mr. Ali Ersin Acar*** [1]

1. *Boğaziçi University*

The microstructure of copolymers provides a better understanding of molecular mobility related properties. ^{13}C-NMR spectroscopy is an useful tool for the sequence analysis of copolyesters because the ipso (quaternary) carbons are more sensitive to sequence effects than any other aromatic carbons in the aryl diesters. Neopentyl glycol, terephthalic acid and isophthalic acid based polymers are commonly used in powder coating due high hydrolytic and UV stability, weatherability, and good balance between flexibility and hardness. In this study, ^{13}C-NMR of Poly(neopentyl-terephthalate-co-isophthalate) (PNIT) copolymers with different monomer ratios were studied. The distribution of dyads and triads was estimated and the randomness of polymer chains was determined through using the relative integral values of quaternary carbons.



Resim1.jpg

White LED Light Induced Degradation of Polyacrylates as a Green Alternative for Polymer Recycling

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Yusra Bahar Cakir [1]***, Mr. Huseyin Cem Kiliclar*** [1]***, Prof. Yusuf Yagci*** [1]

1. *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,*

Developing efficient recycling methods for widely used polymers has always been an immensely important topic as we are moving towards a greener and more sustainable world while daily life is becoming increasingly dependent on commodity plastics. Poly(methyl methacrylate) (PMMA) combines high-impact strength and optical clarity with lightweight nature that constitutes an important branch of mentioned materials. High consumption amounts caused by the wide range of applications of PMMA produce excessive waste that highlights the necessity of recycling. Since PMMA does not have a hydrolysable main chain, depolymerization or degradation requires advanced recycling methods, mainly involving elevated temperatures and toxic metal catalysts. This work uses broadband white LED light (450 nm-800 nm) and 400 nm blue led in combination with dyes namely, eosin y, erythrosin b, and 10-phenylphenothiazine in the novel photodegradation system to overcome the requirement of heat and metal catalysts. To obtain polymers that can be degraded by visible light in ambient conditions and also shares similar physical properties with PMMA, two copolymers consisting of methyl methacrylate (MMA), methyl α-chloroacrylate (MCA), and ethyl cis-3 bromoacrylate (EBA) were synthesized by conventional reversible addition-fragmentation chain-transfer polymerization. Synthesized copolymers were degraded to extraordinarily low molecular weights by white light and organo photocatalysts. Physical properties and the kinetics were investigated by DSC, TGA, H-NMR, and GPC analyses. Degradation up to 80% was observed at ambient temperature.

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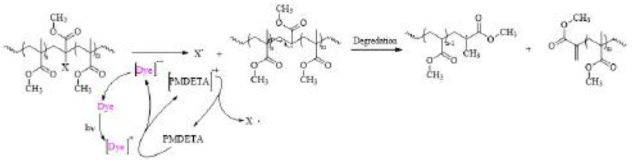

Mechanism of degradation.jpg

Synthesis of Quinoline-Based Polybenzoxazines as Corrosion Inhibitors in Epoxy Coating

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Zeynep Deliballi [1]***, Prof. Baris Kiskan*** [1]***, Dr. Didem Balun Kayan*** [2]***, Prof. Yusuf Yagci*** [1]

1. *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,,* ***2.*** *Department of Chemistry, Faculty of Science and Arts, Aksaray University*

Metallic corrosion has a negative impact on the environment and the global economy, causing direct or indirect costs to human and material resources that are projected to account for a sizeable portion of the gross domestic product (3–4%) in industrialized nations. As a result, over the past ten years, many strategies have been created to prevent or reduce losses caused by corrosion. One of the most promising methods for providing adequate corrosion protection for metals is the application of protective coatings made of polymers.[1] Due to their unique advantages, such as flexibility in molecular design, low water absorption, low flammability, low surface free energy, zero volume shrinkage upon curing, low dielectric constant, and higher glass transition temperature, polybenzoxazines have recently attracted much interest in anti-corrosion coatings. [2, 3] The anti-corrosive properties of quinoline and its derivatives have been the subject of numerous reports. Generally, quinoline derivatives have better corrosion resistance than quinoline itself. [4] In this work, new type of quinoline-based benzoxazines were synthesized (Scheme 1) and analyzed by spectral and thermal methods. The steel plates were coated with blends that were made using different mole ratios of benzoxazine/epoxy resin and cured at high temperatures. The results show that the addition of quinoline-based polybenzoxazines in epoxy coating has a positive effect on corrosion resistance.

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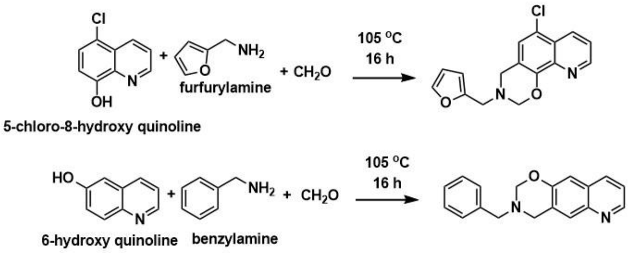

Synthesis of quinoline-based benzoxazine monomers - sheme 1 .jpg

Bismuthene as a Photo-Catalyst for CuAAC Click Chemistry

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Zehra Gul Coban [1], ***Dr. Zafer Eroglu*** [2], ***Dr. Azra Kocaarslan*** [3], ***Dr. Onder Metin*** [2], ***Prof. Yusuf Yagci*** [1]

1. *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,,* ***2.*** *Koç University,* ***3.*** *Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Polymeric Materials, Karlsruhe, Germany*

In the last few years, two-dimensional materials (2D) have attracted great attention in material science due to their physical and chemical properties. Because of their semiconductor features these materials have found a place for potential usage areas in electronics, energy conversion, storage and even in organic synthesis. As heterogeneous photocatalysts, significant efforts have been made in the development of semiconductor materials. However, most of the traditional semiconductors have a wide bandgap, which means UV light irradiation is needed to activate their photocatalytic activities. During the last decades, most of the studies have focused on designing novel photocatalysts that can harvest a broad range of solar light, especially in near-infrared (NIR) region. In this regard, bismuthene has great advantages compared to other 2D materials due to its low toxicity, cost-effectiveness, high stability properties, and activation at relatively longer wavelength. Moreover, bismuthene has semiconducting characteristics with a variable band gap of 0.3-1.0 eV, making it a potentially efficient photocatalytic material [1].

Copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction has found enormous importance in polymer science as a direct result of click polymerization and click post-functionalization for a variety of chemical substrates. 2D materials are very useful tools for CuAAC chemistry. These materials are able to produce electron-hole pairs under suitable light irradiation. The resulting electron interacts with the responsible molecules and initiates the photo-redox reaction. Depending on the 2D material, it is well known that the semiconductors are able to reduce the copper (II) species to copper (I) under light irradiation which is the responsible species for the click reaction [2].

In this study, we demonstrated a new strategy for photoinduced CuAAC click reaction using exfoliated 2D few-layer bismuthene as the semiconductor photocatalysts. Several click reactions were performed between the different azide and alkyne compounds containing various functional groups under NIR light irradiation.

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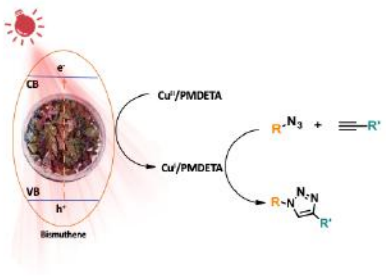

Bismuthene as a photoctalyst for cuaac click chemistry.png

Photo-copolymerization of EDOT and ε-Caprolactone Using Single Component Photoinitiator

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Mr. Tugberk Tabak [1]***, Dr. Kerem Kaya*** [1]***, Prof. Yusuf Yagci*** [1]

1. *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,*

Light weight conducting polymers (CPs) are gaining increasing interest from the scientific community due to their adaptable opto-electronic and thermal feautures making them promising materials for the use in wearable electronic devices[1]. Poly(3,4-ethylene dioxythiophene) (PEDOT) is one of the most important CPs in the field of electronics because of its intrinsic properties such as high conductivity, thermal stability, and biocompatibility[2]. One of the major problems related with PEDOT is its poor solubility making its processability difficult. In order to overcome the solubility problem, polymer scientists have recently synthesized copolymers of EDOT with a variety of monomers including styrene sulfonate[3], lactide[4] and ε-caprolactone[5,6]. All these copolymerizations were previously performed using chemical oxidative polymerization methods. Herein, we report the first time photo-copolymerization of EDOT and ε-caprolactone (CL) using a single-component photoinitiator namely, phenacyl bromide (PAB) under near-UV and visible light. In light of our previous studies concerning the synthesis of CPs using PAB[7.8], we aimed to use the HBr released in the cationic polymerization of CL. UV-vis, fluorescence and GPC measurements revealed the presence of high molecular weight PEDOT-*co*-PCL.

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Curing of benzoxazines by elemental sulfur at low temperatures using catalysts or UV light

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Cansin Birsen BULDUM [1]***, Mr. Tugberk Tabak*** [1]***, Prof. Baris Kiskan*** [1]***, Prof. Yusuf Yagci*** [1]

1. *Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469,*

Polybenzoxazines (PBzs) emerged as an alternative to phenol-formaldehyde (PF) resins, particularly to Novolac. PBzs are thermally stable and have high flame resistance. Moreover, PBzs can endure against corrosive chemicals. [1] In addition to these features, polybenzoxazines exhibit better dimensional stability and the glass transition temperatures. Moreover, the mechanical properties of PBzs are comparable to phenol-formaldehyde resins. The ease of derivatization and improved processability of polybenzoxazines are crucial additional characteristics. On the other hand, the polymerization temperatures are high to produce benzoxazine polybenzoxazine. The ring opening polymerization temperatures of benzoxazines are between 200–260 °C depending on their monomer structures. [2] These temperatures limit the application of polybenzoxazines in many technological areas. [3] Therefore, curing temperatures should be reduced to temperatures below 150-160 °C for large-scale applications. This study suggests the use of catalysts to reduce the curing temperatures. Sulfur is used as a catalyst to lower the ring-opening polymerization (ROP) temperature of simple 1,3-benzoxazines. However, the amount of sulfur used is around 50-60% by mass. [4] The problem here is that the material used in a 1:1 ratio by mass is not good enough to be termed as a catalyst. In this study, it will be tried to reduce the curing temperature by using less sulfur. For this purpose, the use of vulcanization catalysts is suggested here. In addition to the catalytic approach, benzoxazines could be cured with sulfur at room temperature by light. With this method, sulfur is expected to convert to thiol derivatives at lower temperatures and open the benzoxazine ring.

References

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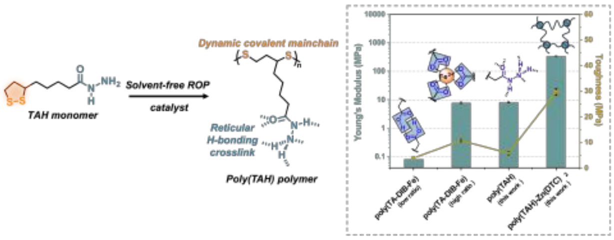
Reticular hydrogen bonds enable robust, tough and dynamic supramolecular materials

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Yuanxin Deng [1], ***Dr. Qi Zhang*** [2], ***Ms. Chenyu Shi*** [3], ***Dr. Ryjun Toyoda*** [1], ***Prof. Da_hui Qu*** [3], ***Prof. He Tian*** [3], ***Prof. Ben Feringa*** [1]

1. University of Groningen, 2. Univeristy of Groningen, 3. East China University of Science and Technology

Supramolecular materials are widely recognized among the most promising candidates for future generations of sustainable plastics because of their dynamic functions. However, the weak noncovalent crosslinks that endow dynamic properties usually trade off materials' mechanical robustness. Here, learning from ice, we present the discovery of a simple and robust supramolecular crosslinking strategy based on acylhydrazine units, which can hierarchically crosslink the solvent-free network of poly(disulfides) by forming unique reticular hydrogen bonds, enabling the conversion of soft into stiff dynamic material. The resulting supramolecular materials exhibit increase in stiffness exceeding two to three orders of magnitude compared to those based on the hydrogen-bonding network of analogous carboxylic acids, simultaneously preserving the repairability, malleability, and recyclability of the materials. The materials also show strong adhesion strength on various surfaces while allowing multiple surface attachment cycles without fatigue, illustrating a viable approach how robustness and dynamics can be merged in future material design.



Reticular hydrogen bonds enable robust tough and dynamic supramolecular materials.png

Development of new compatibilizers with controlled structure for incorporation on polyethylene/polypropylene recycled blends

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Mónica A. F. F. Reis [1], ***Dr. Graça Brotas*** [2], ***Dr. Tiago Filipe*** [2], ***Prof. Arménio C. Serra*** [1], ***Prof. Jorge F. J. Coelho*** [1], ***Prof. Ana C. Fonseca*** [1]

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Directive (EU) 2019/904 of the European Parliament and of the Council provides for the effective collection of 90% of plastic waste generated by 2029 and its reprocessing in applications similar to virgin material in its origins. This is a major challenge since recycled materials usually do not have the mechanical properties of the virgin materials, which affects their applications.

Polyolefins, particularly polyethylene (PE) and polypropylene (PP), are among the most widely used plastics in the packaging industry and are therefore some of the most commonly recycled. Usually, the recycling streams of polyolefins contain both PE and PP, since they are very difficult to separate due to their chemical similarity. PE itself loses properties during processing and recycling. Contamination with PP, even in very small amounts, further affects the performance of thin films made with such material. This happens because PE and PP are immiscible polymers. This induces a phase separation in the molten state, where the PP aggregates in the PE matrix creating "islands" which end up being weak spots in the extruded film. One possible strategy to improve the mechanical properties of such recyclates is the addition of compatibilizers.

In this work, novel block copolymers based on olefinic monomers were prepared by reversible deactivation radical polymerization (RDRP) and used as compatibilizers in PE /PP recyclate blends. The compatibilizers were characterized in terms of their chemical structure and thermal properties. The blends were characterized in terms of their internal morphology and mechanical properties. Overall, the results indicate that the copolymers in the above mentioned blends can act as compatibilizers.

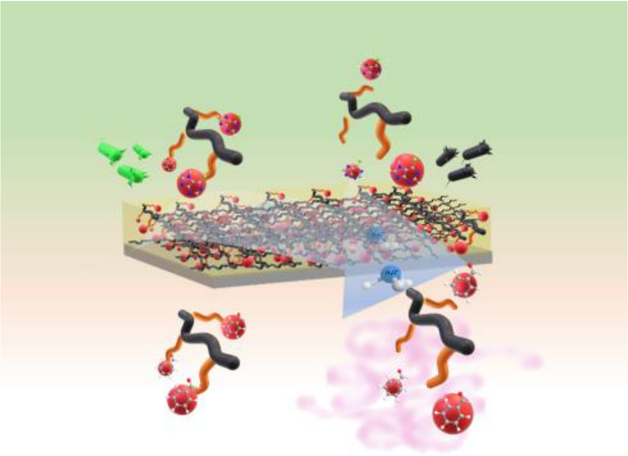
Controlling the release of active molecules from pH-responsive coatings

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Piangtawan Phoungtawee [1], ***Prof. Daniel Crespy*** [1]

1. Vidyasirimedhi Institute of Science and Technology, Rayong 21210, Thailand

Active compounds such as antibacterial agents or fragrances in coatings suffer from the fact that they are usually quickly released, hereby limiting the active lifetime of the coatings. To overcome this issue, we conjugated antibacterial agents or fragrances to monomers via pH-responsive linkages such as hydrazone and hemiaminal ether bonds. The functional monomers were then copolymerized with a urethane acrylate by photopolymerization to yield thin polymer coatings. The release of the active compounds from the coatings was sustained due to the slow kinetics of the hydrolysis of the selected pH-responsive linkage. Moreover, an excellent antibacterial performance was achieved against *S. aureus* and *E. coli* bacteria. The fragrance could be released upon contact with artificial sweat.



Piangtawan figure.jpg

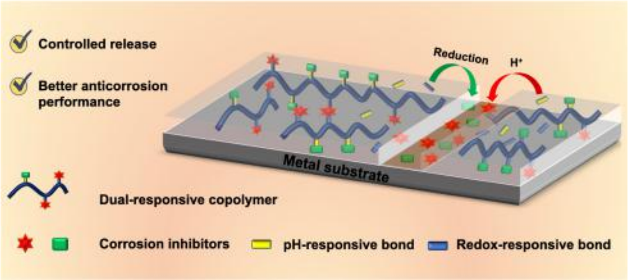
Dual-responsive polymers for anticorrosion application

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Pichapak Srikamut *[1]*, ***Prof. Daniel Crespy*** *[2]*

1. *Vidyasirimedhi Institute of Science and Technology (VISTEC), Rayong 21210, Thailand,* ***2.*** *Department of Materials Science and Engineering, School of Molecular Science and Engineering, Vidyasirimedhi Institute of Science and Technology*

Abstract: Corrosion is an electrochemical process leading to metals deterioration. Because the corrosion process involves a change of local pH value and electrochemical potential, designing coatings which can be activated by these two stimuli is an interesting option for decreasing the corrosion rate of metals.[1] We designed copolymers with pH and redox sensitivity for protecting metals against corrosion.[2] A pH-responsive monomer and a redox-responsive monomer were conjugated to two different corrosion inhibitors via acetal and disulfide linkage, respectively. After radical polymerization, the copolymers were applied as coatings on steel substrates. We demonstrated that the dual-responsivity led to a better anticorrosion performance compared with single-responsive or non-responsive coatings.



Pichapak srikamut figure.jpg

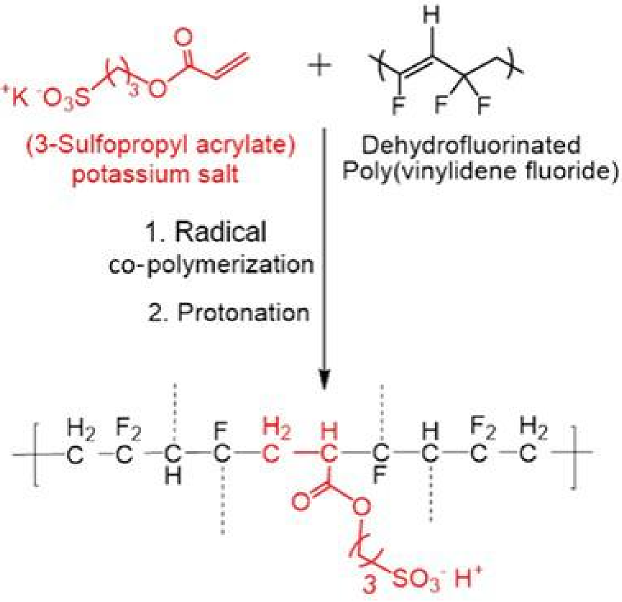
Synthesis and characterization of poly(vinylidene fluoride) grafted 3-Sulfopropyl acrylate based polyelectrolyte membrane for electrochemical energy applications

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Mr. Jeet Sharma [1]***, Dr. Vaibhav Kulshrestha*** [1]***, Dr. Bruno Ameduri*** [2]

__1.__ 1 Council of Scientific and Industrial Research - Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), Membrane Science and Separation Technology Division, Bhavnagar, India-364002., __2.__ CNRS ICGM

A graft co-polymer of 3-Sulfopropyl acrylate potassium salt (3SAPS) onto the dehydrofluorinated poly(vinylidene fluoride) (PVDF) is designed **(Figure 1.)** and comprehensively characterized using ^{1}H and ^{19}F NMR spectroscopy. First, a simple dehydrofluorination of PVDF occurred in using isopropyl alcohol/sodium hydroxide mixture. Then, the free radical graft copolymerization of the resulting unsaturated PVDF with 3SAPS, initiated by Azobisisobutyronitrile, led to various PVDFs bearing sulfonate side function. The influence of variable 3SAPS grafting proportions on surface wettability and electrochemical properties were corroborated based on dynamic contact angle measurements and electrochemical impedance spectroscopy. With 15.0wt% 3SAPS grafting, the membrane offered contact angle of 71° ± 2° and proton conductivity of □9.5 mS cm^{-1} at 25 °C. Furthermore, the hydrolytic and oxidative stability, monitored for 360 h in acidic solution (3.0M H_2SO_4) and with Fenton's reagent showed that the membranes sustained mechanically with >90.0% ± 2.0% residual proton conductivity. In vanadium redox flow battery (VRFB) application, the membrane showed voltage efficiency and energy efficiency values from 80.20%, 70.15%, 59.86% and 74.08%, 65.95%, 58.04% at 50 mA cm^{-2}, 100 mA cm^{-2} and 150 mA cm^{-2} current density operations, respectively. The coulombic efficiency is found ≥95.00%. These results suggest the suitability of such materials in electrochemical energy storage devices, especially, vanadium redox flow battery (VRFB).



Abstract.jpg

Depolymerization of post-consumer PET under mild conditions by Lewis/Brønsted acidic deep eutectic solvents

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Mr. Marco Rollo [1], ***Ms. Francesca Raffi*** [1], ***Ms. Elisa Rossi*** [1], ***Dr. Matteo Tiecco*** [2], ***Prof. Elisa Martinelli*** [1], ***Prof. Gianluca Ciancaleoni*** [1]

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The number of plastics in circulation is projected to increase from 236 to 417 million ton per year by 2030. New recycling techniques are desperately needed in modern society to deal with the impressive amount of plastic items that are annually discarded. Chemical recycling is gaining interest, as complementary to traditional recycling methods, especially when it is a selective process capable of returning the polymer to its monomeric feedstocks.[1] Deep Eutectic Solvents (DESs) have shown interesting results in the depolymerization of polyethylene terephthalate (PET)[2], but most of the procedures still need harsh conditions of temperature and pressure. In the present study, we propose a bifunctional Lewis/Brønsted acidic DES composed of $FeCl_3$□$6H_2O$, cheap and barely toxic, in combination with a variety of acids, including some of natural origin (citric and acetic acid) (Figure 1). We have showed that the LBDES formed with methanesulfonic acid and paratoluenesulfonic acid are capable of quantitatively depolymerizing PET under mild conditions, with a temperature of 100 °C and a reaction time of 1 h, affording high purity terephthalic acid in high yield.[3] Different strategies to optimize the PET/LBDES ratio has been successfully tested, as the consecutive addition of multiple aliquots of PET or the filtration and reuse of the solvent. The best solvent has been characterized through the comparison of theoretical and experimental eutectic phase diagram, confirming its nature of DES.

Figure 1: Reaction performance of different Lewis/Brønsted mixtures (0.3 g of PET, 4.0 g of LBDES, T = 100 °C, reaction time = 30 min)

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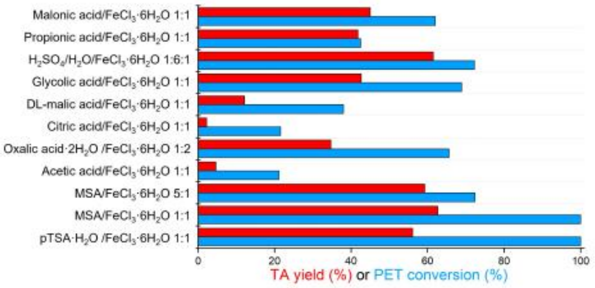

Pet depolymerization rollo apme 2023.jpg

Developments in the recycling of PE/PA multilayer films

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Andreia Romeiro [1], ***Dr. Henrique Costa*** [2], ***Dr. Jorge Coelho*** [1], ***Dr. Arménio Serra*** [1]

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Recycling plastic packaging is becoming increasingly important to preserve limited resources and protect the environment from plastic waste. Until now, multilayer packaging has mostly been incinerated or landfilled.[1] The current EU-strategy states that by 2030 all plastic packaging placed on market in the EU should be reusable or economically (mechanically) recyclable.

Multilayer films are typically used for plastic food packaging to maintain integrity and protect against degradation processes. The different materials in multilayer films have different functions. For example, low-density polyethylene (PE) or ethylene vinyl acetate is commonly used on the inside of the food packaging to provide low-temperature heat seal ability, polyethylene terephthalate on the outside to improve printability and abrasion resistance and polyamide 6 (PA) or ethylene vinyl alcohol in the middle as a gas barrier layer [2].

Mechanical recycling of multilayer films is challenging because the plastic layers are not compatible with each other. Consequently, recycling multilayer films by blending results in an immiscible polymer blend with a coarse phase morphology and poor adhesion between phases.

The resulting material generally has very poor mechanical properties far below those of components [1,3].

Therefore, for a good recycling process it is necessary to separate the different components of the multilayer films or melt processing where compatibility of the polymers should be promoted[2]. Compatibility is typically promoted by the addition of graft or block copolymer known as compatibilizer to the blend, which reduces the interfacial tension between the phases, improves their dispersion and promotes adhesion [1,4,5].

In this work we developed and use a compatibilizer produced by Inventive Matl to the recycling process of a multilayer film of PE/PA converted into monolayer PE/PA film. Different amounts of compatibilizer were used to evaluate the mechanical properties, elongation stress and tensile stress. The barrier effect of O2 and water vapor, was also evaluated, and the results were promising considering the monolayer structure of the film.

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Integrated functional MXene/cellulose cloth (if-Cloth) for personal heating and steam generation

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Mr. Jian Chang [1]***, Prof. Jiayin Yuan*** [1]

1. *Stockholm University*

Given the vast abundance of solar irradiation on the entire planet, advanced cloth coupled with sufficient photothermal effect can contribute to personal thermal management and clean water production in a decentralized and energy-saving manner. Herein, a biodegradable cellulose-based cloth incorporated with MXene nanosheets is fabricated *via* electrospinning method. This composite cloth is well equipped with desirable mechanical/chemical stability, mechanical performance, structural flexibility, wettability and photothermal conversion capability. Endowed by the photothermal performance of MXene, a 0.1-mm-thick composite cloth produces a 5.6 °C enhancement on human body in comparison to that of a commercial cotton cloth of 5 times thicker under sunlight at ambient temperature of 11.2°C. Remarkably, the composite cloth can in a wet state capture solar energy more efficiently with a photothermal conversion efficiency of 87.7% than that in a dry state. Correspondingly, such cloth working in a wet environment as a steam generator, possesses a superior water evaporation rate of 1.34 kg m^{-2} h^{-1} under one sun irradiation (1000 W m^{-2}), and remains its performance fitting into simulated solar desalination. This cloth integrates considerable merits of excellent mechanical performance, wearability, and fast steam generation rate, and thus enriches its diverse outdoor applications in solar-driven water evaporation and personal heating.

Figure 1.fw.png

A Self-Healable and Injectable Metallohydrogel for Drug Encapsulations and Drug Release

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Ms. Mita Dutta [1]***, Prof. Manish Bhattacharjee*** [1]

1. *Indian Institute of Technology, Kharagpur, 721302, India*

Hydrogel-based drug delivery holds great promise in the treatment of cancer. The metallohydrogel with a low molecular weight (LMW) gelator and a biogenic metal centre, with control mixing of drugs and solvent, leads to a robust biomaterial mimicking nanofibrous tissue topography that are also injectable to enable minimally invasive delivery. In this work, we have prepared fibrous supramolecular-assembled metallohydrogel composed of $Mn(CH_3COO)_2$ and LMW Na_2HL gelator that exhibit rapid self-healing, shear thinning, pH sensitivity and cytocompatibility. The obtained Mn based metallohydrogel (**MOG**) was characterized by several spectroscopic and microscopic techniques. Non-steroidal anti-inflammatory drug (NSAID) Indomethacin (IND) and anti-cancer drug gemcitabine (GEM) were encapsulated into the bulk metallohydrogel. The drug-loaded gels (MOG_IND and MOG_GEM) showed that they were viscoelastic in nature and had great mechanical strength when tested with a rheometer. The stability and high mechanical strength of the MOG_GEM, making it useful as anti-tumour drug delivery vehicle. To established the drug delivery application, successive release of the drug from MOG_GEM was performed in pH 5.8 and pH 7.4 for the duration of 48 h of incubation at 37 ° C. The study indicates the plausible use of the MOG a DDS. Furthermore, the cancer treatment effect of MOG_GEM was demonstrated through in-vitro cell culture MTT assay, live dead assay and cell migration assay. These efforts portend promising results with the potential of MOG_GEM to be use as chemotherapeutic agent in cancer treatment.

Donnor-Acceptor Polymers for High-Performances Organic Solid-State Lasers

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Mr. Robin Troiville-Cazilhac [1]

[1] *Sorbonne Université*

Interest in organic electronics has been increasing during the last decades, leading to the production of several devices based on organic semiconductors such as organic light-emitting diodes (OLEDs).[1] In parallel to OLEDs, the development of efficient organic lasers is still a challenge. Such devices are very interesting because they can generate a monochromatic and coherent light. Their structure is composed of a gain material that is responsible for the stimulated emission, coupled with a resonator and an energy source.

It's been years that organic lasers exist from gain materials in solution.[2] Now, the development of new solid-state gain materials gives access to organic laser diodes (OLDs), which are based on the direct conversion of an electric current into laser light. The first evidence of an OLD was recently shown by the group of Prof. Adachi, using an amorphous material based on a pi-conjugated blue-emitting molecule as gain material.[3] However, this result was obtained with only one example of dye so far, and showed several limitations such as a very short device lifetime. In this context, the development of new efficient gain materials is highly necessary.

In this context, we were interested in designing new lasing materials that will be compatible with both optical and electrical pumping. To this end, we proposed to develop novel light-emitting polymers based on electron donor and electron acceptor moieties to be used as gain media. In such systems, it is possible to tune the intermolecular packing in playing with the chemical structure of the core, seeking for chemical modulation and processability. Thus, the photophysical and amplified spontaneous emission (ASE) properties of these materials will be presented, as well as their lasing performances.

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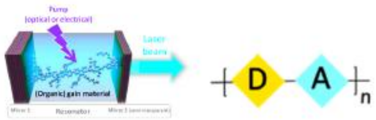

Figure 1: (Left) Laser structure (right) Generic structure of gain materials based on D-A copolymers

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Unique method for facile post-synthetic modification of non-isocyanate polyurethanes

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

***Dr. Sergei Zubkevich* [1], *Prof. Alexander Shaplov* [1], *Prof. Daniel Schmidt* [1]**

1. Luxembourg Institute of Science and Technology

Polyurethanes (PUs) are produced industrially on a large scale since they have a broad scope of applications (foams, coatings, varnishes etc.) defined by the versatility of their properties. This versatility is a result of a vast variety of monomers – isocyanates and polyols, available for the synthesis of PUs. However, isocyanates are toxic compounds and present respiratory and dermal hazards leading to chronic illnesses and even death upon overexposure. Non-isocyanate polyurethanes (NIPUs) and especially their sub-class – polyhydroxyurethanes (PHUs), are broadly investigated as a potential “green” substitution of conventional PUs [1]. However, PHUs currently suffer from excessive hydrophilicity that results from the presence of OH groups in their backbone. That fact significantly limits their potential practical application due to the decreased mechanical properties in humid atmosphere and the possibility of hydrolysis during processing.

In this study we present a novel and simple approach to solve this issue by using “click” reaction of aldehydes with appropriately spaced hydroxyl groups in PHU backbone to obtain materials with increased hydrophobicity and thus improved performance profile at different humidities.

This “click” reaction was conducted in homogeneous medium with the use of acidic catalyst, such as p-toluenesulfonic acid, resulting in high degrees of PHU modification (up to 84%) and moderate to high yields (50-80%). The appropriate choice of aldehyde allowed to reduce moisture uptake up to 3 times for modified polymers compared to unmodified ones and allowed to retain the mechanical behavior of modified PHUs for humidities up to 85%. Moreover, the modified PHUs exhibited elastic behavior similar to unmodified PHU in the range of storage moduli from 1250 to 1650 MPa as measured by DMTA at 20 o C. More important is that the developed method can be used to provide any task specific properties to PHUs depending on the nature of the applied aldehyde.

This work was supported by European Commission’s project 101066839 (SPRUT) under
HORIZON-TMA-MSCA-PF-EF action.

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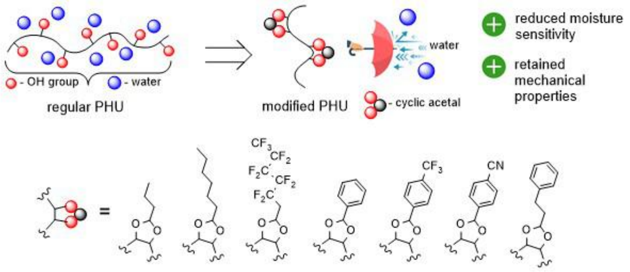

Impact of facile post-synthetic modification on phu properties..jpg

Physicochemical analysis of chitosan matrices with the use of vibrational spectroscopy

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Maryna Khalavka [1]***, Dr. Barbara Gieroba*** [1]***, Dr. Grzegorz Kalisz*** [1]***, Dr. Liudmyla Nosach*** [2]***, Dr. Paulina Kazimierczak*** [2]***, Dr. Vladyslav Vivcharenko*** [2]***, Prof. Agata Przekora*** [2]***, Dr. Anna Sroka–Bartnicka*** [1]

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The linear polysaccharide chitosan, which is the derivative of the natural biopolymer chitin, has recently attracted much attention of researchers. Chitosan offers many potential applications in a number of fields, ranging from tissue regeneration, scaffolds, biocompatible coatings, cosmetics and many others.

Unique properties of chitosan make possible to use it, for example, as a polymer matrix for systems with controlled and sustained release of drugs.

Chitosan has some limitations for use in a biological system, including its poor solubility under physiological conditions, which can cause difficulties in the development of chitosan-based drugs. To overcome these limitations, researchers focused on the derivatisation of chitosan by chemical modifications and partially enzymatic hydrolyzed chitosan containing various reactive functional groups.

In this work the characterization of the physico-chemical and structural changes of 2% chitosan (high) matrices with and without ibuprofen, before and after drug release carried out in PBS solution was performed.

Infrared spectra were collected with the application of an FT-IR Nicolet 6700 (Thermo Scientific, Waltham, MA, USA) spectrometer in the attenuated total reflection (ATR) mode. Spectra's were recorded with the use of Omnic 8 software from Thermo Fisher Scientific (Madison, WI, USA)

Vibrational spectroscopy includes several methods of identifying and classifying compounds based on the vibrations of their bonds that are used to determine the molecular structure of a substances. FTIR is one of the method allowing for characterization of chitosan based on different bands corresponding to the $-NH_2$ group, which can be allocated to the symmetrical COO^- gather extending vibration.

The attenuated total reflection (ATR) mode of FTIR sampling has been applied frequently in biomaterials studies. Results of this study will help to optimize manufacturing process of the matrices and allow to obtain appropriate physico-chemical properties for effective ibuprofen release.

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Comprehensive use of physicochemical methods for the development and investigation of new polymeric materials

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Olena Mozgova [1]***, Dr. Vladyslav Vivcharenko*** [2]***, Prof. Agata Przekora*** [3]***, Dr. Anna Sroka–Bartnicka*** [4]***, Prof. Robert Nowakowski*** [5]***, Dr. Izabela S. Pieta*** [5]

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Introduction. Polymers are giant molecules with a high molecular weight called macromolecules, mainly formed by joining a large number of tiny molecules called monomers. Their high molecular mass relative to low molecular compounds produces unique physical properties. The description of polymers has been mainly centred on surface analysis methods and traditional characterisation techniques developed to determine the topography of surfaces, composition, morphology, crystallinity, shape, and size. Those physico-chemical characterization techniques can be successively applied for polymer precise characterization instead *in-vivo* testing. Herein the following methods were used in developing and producing polymers:

Methods: X-ray photoelectron spectroscopy, Atomic Force Microscopy, X-ray diffraction.

Results and Discussion. The level of surface contamination and the surface composition was determined by X-ray photoelectron spectroscopy (XPS). XPS is a good option for surface analysis since XPS detects and can provide information regarding atomic composition of the material's ultra-thin and thin surface layers, usually 1-10 nm in-depth. The XPS method measures the kinetic energy of the emitted electrons due to the exciting sample surface with X-rays. Thus, the energy spectrum is characteristic of the elemental composition and binding state of atoms at the sample surface, allowing for given thin-film surface elemental composition specification.

For high-resolution surface morphology and topography investigations, Atomic Force Microscopy (AFM) technique is used. As opposed to optical or electron microscopes, AFM does not use glass or magnetic lenses for producing an image of the sample but a sharp tip probe. The interaction between the probe and the surface is measured. AFM reproduces the 3D surface topography at a sub-angstrom height and nanometer lateral resolution for various materials, from incredibly soft biological samples to hard metals in air, fluid, or vacuum.

X-ray diffraction (XRD) is a non-destructive and versatile technique that gives information on the crystal structure, microstructure, chemical composition, lattice constants, and particle size of a given material. The XRD method is based on measuring the intensity and scattering angles of X-rays, leaving the material with the same energy as the incident radiation. In the biopolymers science it allows for any structural changes observation during material tuning to given functionality.

Conclusions. Each of the surface analysis techniques supplies various information from different sampling depths. Hence, obtaining a detailed interpretation of a polymer's surface chemistry and structure requires investigation with multiple techniques.

The authors would like to provide acknowledgement for financial support to Foundation for Polish Science within Reintegration grant POIR.04.04.00-00-4398/17-00 (REINTEGRATION/2017-4/14).

Temperature Cross linked polymers - Spectroscopic and microscopic study of hybrid chitosan/1,3-β-D-glucan matrices

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Nadiia Kovalska [1], ***Dr. Barbara Gieroba*** [1], ***Dr. Paulina Kazimierczak*** [2], ***Dr. Grzegorz Kalisz*** [1], ***Dr. Liudmyla Nosach*** [3], ***Dr. Vladyslav Vivcharenko*** [2], ***Dr. Agnieszka Szebeszczyk*** [4], ***Prof. Agata Przekora*** [2], ***Dr. Anna Sroka–Bartnicka*** [1]

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Chitosan- and 1,3-β-D-glucan (curdlan)-based polysaccharide matrices are widely used in biomedicine, including tissue engineering, as a base for various biomaterials production, including bone scaffolds. Different spectroscopic approaches were applied to detect the structural changes in hybrid chitosan/1,3-β-D-glucan polymeric matrices cross-linked at two various temperatures: 70 °C and 80 °C. Attenuated Total Reflection Fourier transform infrared (ATR FT-IR) and Raman spectroscopy are complementary techniques which enabled insightful characterization of molecular organization of designed polymers. The physicochemical properties and the morphology of the surface were investigated using ATR FTIR amd Raman spectroscopy

Stronger interactions and more dense package were detected at higher studied gellation temperature (80 °C), where also the α-helices content decreases and deprotonation occurs, which suggest different chain folding in this cross-linking temperature compared with 70 °C. Temperature-dependent differences in chemical interactions between 1,3-β-D-glucan units and N-glucosamine in chitosan resulting in surface polarity changes were found.The presence of different active groups on the surface may promote specific protein adsorption, affecting cell recruitment, proliferation and differentiation on the samples surface.

Within this study it was demonstrated that spectroscopic methods could be applied as an efficient and non-destructive tools to study the molecular composition, and develop the manufacturing process of polymeric matrices designed for potential biomedical applications to achieve optimal physical/biochemical characteristics.

Keywords: biopolymers, chitosan, Raman, ATR-FTIR.

The authors would like to provide acknowledgment for financial support to Foundation for Polish Science within Reintegration grant POIR.04.04.00-00-4398/17-00 (REINTEGRATION/2017-4/14).

Molecularly-defined DNA-polymer bioconjugates: Synthesis, characterization and potential applications

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Maria Nerantzaki [1], ***Prof. Laurence Charles*** [2], ***Dr. Jean-François Lutz*** [3]

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Introduction

The combination of synthetic polymers with nucleic acids opens up interesting perspectives for the development of new types of smart materials, but the precise synthesis of such bio-hybrid macromolecules remains challenging. Here, we describe and evaluate phosphoramidite polymer chemistry (PPC) as a novel straightforward approach to prepare functional DNA-polymer bioconjugates with high degree of molecular control.

Methods

Bio-hybrid poly(phosphodiester)s (PPDE) with different compositions and block lengths were synthesized by automated phosphoramidite chemistry, using biological monomers (i.e. nucleoside phosphoramidites) and synthetic phosphoramidite monomers. The resulting bio-hybrid polymers were characterized by various techniques, including electrospray mass spectrometry (ESI-MS) and ion-exchange HPLC.

Results and Discussion

As evidenced by the results molecularly-defined macromolecules with controlled chain-length and monomer sequences were obtained. These DNA-polymer bioconjugates were also evaluated for the preparation of various types of materials. For instance, DNA hybridization was used for the preparation of linear and nonlinear self-assembled superstructures.[1] Due to the versatility of PPC, it is relatively easy to synthesize uniform DNA-polymer conjugates and to assemble them into precise linear or nonlinear constructs. In all cases, the self-assembled topologies were characterized by a combination of gel electrophoresis, UV spectroscopy, and atomic force microscopy. It was found that the quality of the assembly depends on the starting number of macromolecular precursors. Although well-controlled assembly was observed with four bio-hybrid components, a higher amount of defects was detected when 10 components were used. PPC was also evaluated for the preparation of bioconjugates containing synthetic polymer segments associated to DNA aptamers.[2] This new class of molecularly-defined polymer-aptamer conjugates could be interesting for applications in nanomedicine and biotechnologies.

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Microstructural analysis of regulated methacrylate networks

Wednesday, 26th April - 13:00: Poster Session 3 - Poster

Dr. Helena Švajdlenková [1]***, Dr. Christian Gorsche*** [2]***, Prof. Robert Liska*** [2]

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Photopolymerization has found widespread usage not only in classical coatings, but also in more advanced fields like biomedicine or 3D printing due to their appealing tuneable material properties. The polymerization of commonly used di(meth)acrylates gives inhomogeneous crosslinking with high shrinkage stress leading to the brittle character of such polymers. Here a promising approach is the change of the polymerization process by the use of chain transfer agents such as thiols [1] or addition fragmentation-based chain transfer reagents,[2] which form more homogeneous network architectures with reduced shrinkage stress and an significantly increased toughness.

Deeper view into the microstructure of cured materials but also the crosslinking process itself can contribute to the better understanding and tuning of the material properties.

The free volume investigation of cured pure and regulated dimethacrylate-based resins yield to the real microstructure arrangement below and above glass transition.[3,4] The combined macro and micro expansion behaviour showed the others important key microstructural factors, i.e., free volume void size, free volume number density per unit mass N', and free volume fraction f, specifically for photopolymers with tailored network architectures.

For the first time, the in situ investigation of microstructure during photopolymerization by the combination of PALS and NIR-photorheology were carried out.[5] Photopolymerization associated with the evolution of microstructural free-volume shrinkage was evaluated via free volume distributions reflecting the homogeneity during network formation. PALS is a promising tool for better understanding of crosslinking process from the view of free volume aspects and dynamics.

Acknowledgments

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Atom Transfer Radical Polymerization As Universal Tool For Macromolecular Engineering

Wednesday, 26th April - 14:00: Oral Session 10-1 - Oral

Prof. Krzysztof Matyjaszewski [1]

***1.** Carnegie Mellon*

Various advanced functional materials were designed and prepared by controlled/ living radical polymerization. Copper-based ATRP (atom transfer radical polymerization) catalytic systems with polydentate nitrogen ligands are among the most efficient controlled/living radical polymerization systems. Recently, by applying new initiating/catalytic systems, Cu level in ATRP was reduced to a few ppm. ATRP of acrylates, methacrylates, styrenes, acrylamides, acrylonitrile and other vinyl monomers was controlled by various external stimuli, including electrical current, light, mechanical forces and ultrasound, also in open air. ATRP was employed for synthesis of polymers with precisely controlled molecular architecture with designed shape, composition and functionality. Block, graft, star, hyperbranched, gradient and periodic copolymers, molecular brushes and various hybrid materials and bioconjugates were prepared with high precision. These hybrids provide access to new materials for application related to biomedicine, environment, energy and catalysis using ATRP as an universal tool for macromolecular engineering.

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Radical ring-opening copolymerization in aqueous emulsion: synthesis of degradable vinyl polymer particles

Wednesday, 26th April - 14:30: Oral Session 10-1 - Oral

Dr. Muriel Lansalot [1]***, Dr. Paul Galanopoulo*** [1]***, Dr. Noémie Gil*** [2]***, Dr. Maëlle Lages*** [3]***, Dr. Julien Nicolas*** [3]***, Dr. Didier Gigmes*** [2]***, Dr. Catherine Lefay*** [2]***, Dr. Yohann Guillaneuf*** [2]***, Dr. Franck D'Agosto*** [4]

1. *Catalysis, Polymerization, Processes and Materials (CP2M) - CNRS, Université Claude Bernard Lyon 1, CPE Lyon,* ***2.*** *Institut de Chimie Radicalaire - Aix Marseille Univ, CNRS,* ***3.*** *Institut Galien Paris-Saclay - Université Paris-Saclay, CNRS,* ***4.*** *Catalysis, Polymerization, Processes and Materials (CP2M), CNRS, Université Claude Bernard Lyon 1, CPE Lyon*

Introduction. The backbone of vinyl polymers cannot be easily degraded, which is a valuable property for most applications. However, it also limits their use in some fields where (bio)degradability is sought, notably in biomedical applications. In addition, considering the current quest for more environmentally friendly polymer products, including possible recycling, the synthesis of (bio)degradable vinyl polymers is a real challenge. Cyclic ketene acetals (CKAs) can lead to ester-containing vinyl polymers through radical ring-opening polymerization (rROP).[i] The obtained copolymers can be degraded into oligomers by cleavage of in-chain ester functions. However, CKAs show low reactivity toward traditional vinyl monomers and are quickly hydrolyzed in water, a major drawback for aqueous emulsion polymerization.

Methods. Thionolactones have recently appeared as an interesting alternative to CKAs. In particular, the groups of Roth[ii] and Gutekunst[iii] proposed the rROP of dibenzo[c,e]oxepane-5-thione (DOT), which can afford in-chain thioester functions. DOT shows high stability against hydrolysis, a valuable asset for polymerizations in aqueous dispersed media. Besides its fundamental interest, the success of such transposition would put forward an original way of introducing degradability into latex technology and related applications. It could additionally give access to original degradable particles complementary to their well-known polyester counterparts, yet obtained by nanoprecipitation of preformed chains, leading to low solids content dispersions.

Results and discussion. In our work, we studied the aqueous emulsion copolymerization of DOT with *n*-butyl acrylate and styrene. Stable latexes were obtained under very conventional conditions. These latexes are not only composed of degradable chains but also feature a broad range of Tg.[iv] In addition, surfactant-free degradable latexes can also be obtained using reactive polymer chains as stabilizer following a RAFT-mediated polymerization-induced self-assembly (PISA) approach.

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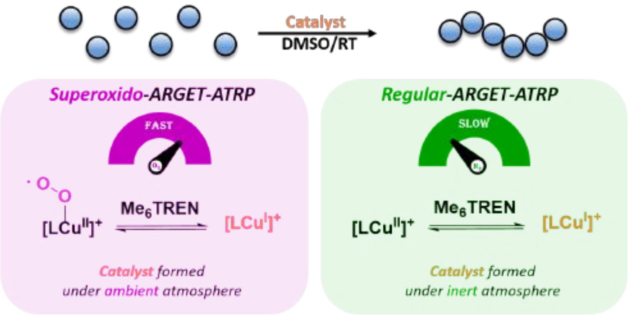
Oxygen-Enhanced Atom Transfer Radical Polymerization through the Formation of a Copper Superoxido Complex

Wednesday, 26th April - 15:00: Oral Session 10-1 - Oral

Mr. Kostas Parkatzidis [1], ***Dr. Nghia P. Truong*** [1], ***Dr. Richard Whifield*** [1], ***Ms. Chiara Campi*** [2], ***Dr. Benjamin Grimm-Lebsanft*** [3], ***Mr. Sören Buchenau*** [3], ***Prof. Michael Rübhausen*** [3], ***Dr. Simon Harrisson*** [4], ***Prof. Dominik Konkolewicz*** [5], ***Prof. Siegfried Schindler*** [2], ***Prof. Athina Anastasaki*** [1]

__1.__ ETH Zurich, __2.__ University of Gießen, __3.__ University of Hamburg, __4.__ University of Bordeaux, __5.__ Miami University

In controlled radical polymerization, oxygen is typically regarded as an undesirable component resulting in terminated polymer chains, deactivated catalysts, and subsequent cessation of the polymerization. Here, we report an unusual atom transfer radical polymerization whereby oxygen favors the polymerization by triggering the in-situ transformation of CuBr/L to reactive superoxido species at room temperature. Through a superoxido ARGET ATRP mechanism, an order of magnitude faster polymerization rate and a rapid and complete initiator consumption can be achieved as opposed to when unoxidized CuBr/L was instead employed. Very high end-group fidelity has been demonstrated by mass-spectrometry and the one-pot synthesis of block and multiblock copolymers, while pushing the reactions to reach near-quantitative conversions in all steps. A high molecular weight polymer could also be targeted (DP_n=6,400) without compromising the control over the molar mass distributions ($Đ$ < 1.20), even at an extremely low copper concentration (4.5 ppm). The versatility of the technique was demonstrated by the polymerization of various monomers in a controlled fashion. Notably, the efficiency of our methodology is unaffected by the purity of the starting CuBr, and even a brown highly-oxidized 15-year-old CuBr reagent enabled a rapid and controlled polymerization with a final dispersity of 1.07, thus not only reducing associated costs but also omitting the need for rigorous catalyst purification prior to polymerization.



Oxygen-enhanced atrp.png

Tailoring the properties and responsiveness of elastomeric supports by grafting polymer brushes

Wednesday, 26th April - 15:15: Oral Session 10-1 - Oral

Dr. Francesca Lorandi [1]***, Mr. Matheus Saccardo*** [2]***, Prof. Carlos Scuracchio*** [3]***, Prof. Edmondo M. Benetti*** [1]

1. *Laboratory for Macromolecular and Organic Chemistry (MOC), Department of Chemical Sciences, University of Padova, Padova, Italy.,* ***2.*** *Universidade Federal de São Carlos (UFSCar), and Laboratory for Macromolecular and Organic Chemistry (MOC), Department of Chemical Sciences, University of Padova, Padova, Italy.,* ***3.*** *Universidade Federal de São Carlos (UFSCar)*

Poly(high internal phase emulsion)s (polyHIPEs) are porous emulsion-templated polymers that can serve as scaffolds for a variety of materials.[1] Herein, we prepared elastomeric poly(HIPE)s embedding atom transfer radical polymerization (ATRP) initiating sites, by introducing an ATRP inimer (i.e. initiator-monomer) in the HIPE formulations. These initiating sites were exploited to grow polymer brushes via surface-initiated ATRP (SI-ATRP), using Cu(0) as reducing agent and supplemental activator.[2] The versatility of polyHIPE synthesis enabled to prepare supports of different geometries and porosity, while the spatial control over brush growth provided by SI-ATRP offered wide tunability of the morphology and properties of these 3D materials. In particular, three-dimensional brush gradients,[3] ion-conducting brushes, and thermoresponsive brushes were grafted from poly(HIPE)s. The morphology and properties of resulting materials were characterized. Poly(HIPE)s functionalized with ion-conducting polymer brushes could be employed as ion conducting membranes for composite actuators.

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ACS Macro Lett. 2021, 10, 1099–1106.

Embedding peptides into synthetic polymers

Wednesday, 26th April - 15:30: Oral Session 10-1 - Oral

Ms. federica sbordone [1]***, Dr. Hendrik Frisch*** [1]

1. School of Chemistry and Physics, Queensland University of Technology (QUT), Brisbane, QLD 4000, Australia

Biopolymers such as proteins and nucleic acids are the key building blocks of life. Synthetic polymers have nevertheless revolutionized our everyday life through their robust synthetic accessibility. Combining the unmatched functionality of biopolymers with the robustness of tailorable synthetic polymers holds the promise to create materials that can be designed ad hoc for a wide array of applications, including catalysis[1] and degradation.[2] Radical polymerization is the most widely applied polymerization technique in both fundamental science and industrial polymer production. While this polymerization technique is robust and well controlled, it currently yields exclusively unfunctional all-carbon backbones. Combinations of natural polymers such as peptides, with synthetic polymers, are thus limited to tethering peptides onto the side chains or chain ends of the latter. This synthetic limitation is a critical restraint, considering that the function of biopolymers is programmed into the sequence of their main chain (i.e. primary structure). We report the radical copolymerization of peptides and synthetic comonomers yielding synthetic polymers with defined peptide sequences embedded into their main chain.[3] We developed a solid phase chemistry approach to synthesize peptide conjugates containing allylic sulfides that, following peptide cyclisation, can be readily copolymerized with *N*,*N*-dimethylacrylamide (DMA) – controlled by Reversible Addition−Fragmentation chain-Transfer (RAFT).

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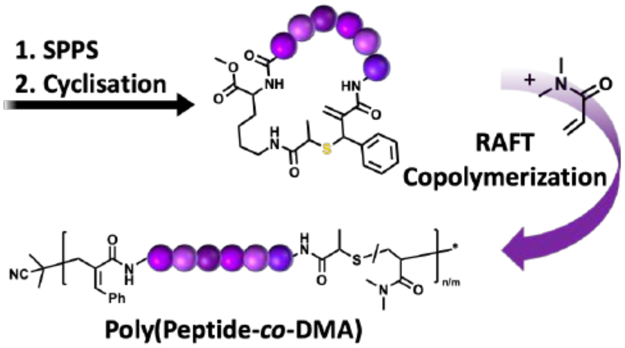

Toc.png

A versatile methodology for the synthesis of organofunctional polyolefins through a post-polymerization approach

Wednesday, 26th April - 15:45: Oral Session 10-1 - Oral

Dr. Rafal Januszewski [1], ***Dr. Bartosz Orwat*** [2], ***Dr. Michal Dutkiewicz*** [3], ***Dr. Ireneusz Kownacki*** [1]

1. *Faculty of Chemistry and Centre for Advanced Technologies, Adam Mickiewicz University in Poznan,* ***2.*** *Department of Molecular Physics, Lodz University of Technology,* ***3.*** *Poznan Science and Technology Park, Adam Mickiewicz University Foundation*

Nowadays, over 150 million tons of polyolefins are produced annually worldwide, mainly in catalytic reactions. High chemical resistance, biological inertness, and attractive mechanical properties are the factors that have made organic polymers permanent and indispensable elements of everyday life[1]. The common organic polyolefins (polyethylene, polypropylene), as a consequence of their low polarity and lack of functional groups, exhibit poor compatibility to nitrogen- or oxygen-containing compounds, polar pigments, and low adhesion to inorganic surfaces. Thus, the introduction of polar functionalities into nonpolar polymers is highly desirable since it would increase the number of potential applications and render these materials even more versatile. The several strategies leading to functional polymers have been developed and the chemical transformation of existing polymers (post-polymerization) has recently emerged as a topic of increasing importance in macromolecular chemistry [2-4]. Among the large group of known organic polymers, polybutadiene is a versatile and convenient starting material for further functionalization, due to the high content of readily accessible double bonds revealing reactivity in a wide range of stoichiometric and catalytic transformations and also thanks to the possibility of controlling the microstructure and molecular weight during anionic polymerization. Therefore, butadiene-based polymers seem to be excellent precursors for the synthesis of organofunctional polymers[5].
In this contribution, an efficient methodology for the synthesis of new organofunctional polyolefins is proposed. It includes the transformation of polybutadiene through catalytic reactions, which simply leads to the unique functional polyolefins. The developed synthetic strategy enables the incorporation of a wide variety of organic and organometallic groups into the polymer chains, which cannot be or are technically difficult to be carried out with conventional polymerization protocols.

The authors wish to thank the National Science Centre, Poland, for their financial support UMO-2019/32/C/ST4/00178

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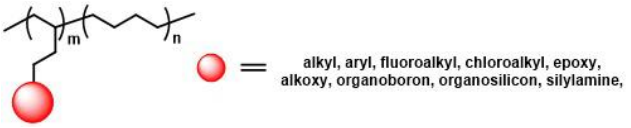


Figure 1.jpg

Stereocontrolled ROP of β-lactones: a catalytic handle to tune the properties of functional poly(hydroxyalkanoate)s (PHAs)

Wednesday, 26th April - 14:00: Oral Session 10-2 - Oral

Prof. Sophie GUILLAUME [1]

1. ISCR- CNRS - University of Rennes

Poly(hydroxyalkanoate)s (PHAs) are a class of natural or synthetic aliphatic polyesters which feature the same three-carbon backbone structure, only differing by their substituent (R) in b-position. PHAs have attracted considerable interest as “green” engineering plastics. These biodegradable and biocompatible polymers represent a targeted choice for in particular single-use plastics, packaging, and biomedical applications in tissue engineering and as drug delivery systems.

Recent highlights of research at Rennes University in the field of 1) tunable organic or organometallic catalytic systems for the ring-opening (co)polymerization (ROP) of functional b-lactones, namely b-butyrolactone (BPL^{Me}), b-malolactonates (BPL^{CO2R}s; R = CH_2Ph (Bn), $(CH_2)_2$=CH_2 (All)), 4-alkoxymethylene-β-propiolactones (BPL^{CH2OR}s; R = Me, Ph, Allyl, Bn, *i*Pr, *t*Bu, Si(*t*BuMe$_2$)), or 3-thiobutyrate (TBL) into their corresponding poly(thio)ester, that is (poly(3-hydroxybutyrate) (PHB), poly(alkyl b-malolactonate)s ($PBPL^{CO2R}$s), poly(alkoxymethylene-β-propiolactone)s ($PBPL^{CH20R}$s), or poly(3-thiobutyrate) (PTBL), respectively, 2) original sequence controlled PHAs featuring a high degree of control over molecular, microstructural and topological (linear, circular) characteristics, and 3) PHA copolymers as promising drug delivery systems, will be presented. Our most significant achievements in this endeavor include the development of strategies that enable the synthesis of stereoregular and alternated PHA-based (co)polymers, and evidences of the relationship between the catalytic system, the functional group onto the monomers, the topology, composition and tacticity of the corresponding PHAs.

Radical Ring-Opening Polymerization as a Powerful Tool to Prepare Degradable Materials

Wednesday, 26th April - 14:30: Oral Session 10-2 - Oral

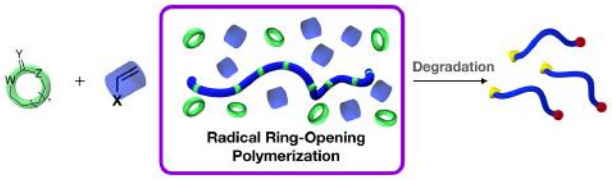
Dr. Yohann Guillaneuf[1]

1. Institut de Chimie Radicalaire - Aix Marseille Univ, CNRS

A simple and useful method of incorporating weak bonds randomly onto the C−C polymer backbone is by radical copolymerization of vinyl monomers with cyclic monomers via radical ring-opening polymerization (rROP). This method combines both the advantages of ring-opening polymerization and radical polymerization, that is the production of polymers having heteroatoms and/or functional groups in the main chain together with the robustness, the ease of use and the mild polymerization conditions of a radical process. The polymerization occurs via the addition of radicals onto cyclic monomers bearing an exo-methylene function or equivalent groups followed by a fragmentation of the intermediate cyclic radical to afford a new radical and the incorporation of heteroatoms into the C-C backbone.

Our approach consists in understanding the impact of the structure of the cyclic monomer on the degradability of the copolymer obtained via a theoretical/experimental approach. These studies have made possible to highlight key parameters to obtain degradation products with low molar masses and thus to conclude on the impact of the structure of the cyclic monomer on the copolymerization.

In this presentation we will focus on the preparation on both the synthesis of new thionolactones and also to the preparation of degradable poly(methyl methacrylate)



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A Novel Class of Dithiocarbamate-based Organic Polymer: Design, Synthesis, and Environmental Remediation Applications

Wednesday, 26th April - 15:00: Oral Session 10-2 - Oral

Mrs. Liya Thurakkal [1], *Dr. Mintu Porel* [1]

1. Department of Chemistry, Indian Institute of Technology Palakkad

Organic polymers are on the cutting edge of research due to their structural stability, scalability, and also tuneability. Functionally tuneable materials are the ones whose properties can be tuned by changing their functional groups, chain size, and other structural moieties. This tuneability can be exploited to customize the properties by tailoring the structure of the material as per the requirement for desirable application. One prime challenge in various class of materials is to balance between the activity and the expense. In this work, a new class of functionally tuneable organic polymer with dithiocarbamates appended in the backbone were synthesized in a simple, mild, two-step reaction condition within a short time of total 90 minutes in a scalable manner using inexpensive starting materials. The diversity in the structure attained by incorporating different functional groups and chain size resulted in different physical, thermal, morphological, and porous properties.

The synthesized dithiocarbamate-based organic polymer (DTC-OP) was rich in aromatic rings, and many heteroatoms like nitrogen, oxygen, and sulphur; and were insoluble in water and also in many organic solvents. Thus, were applied for detoxification of water from contaminants like toxic heavy metals including mercury, organic dyes, radioactive contaminant like iodine, diclofenac, volatile organic compounds, and hazardous permanganate ions. Along with the high uptake capacity, the material showed exceptionally fast kinetics with each contaminant by complete removal in a few seconds when compared to the state-of-the art materials for similar purposes. The material also showed good antibacterial property as well. This DTC-OP is a promising multifunctional material which can be used for diverse applications in environmental remediation by stabilizing economy and performance.

Multifunctional aspect of dtc-op.png

Towards more sustainable amphiphilic polymers

Wednesday, 26th April - 15:15: Oral Session 10-2 - Oral

Prof. Patrizio Raffa [1]

1. Univeristy of Groningen

Amphiphilic copolymers (or polymeric surfactants) have received increasing attention in the past decades, due to their interesting properties and self-assembly in water. [1] They find application as rheology modifiers, encapsulating agents and/or emulsifiers, and are found in many commercial products, such as detergents, cosmetics, pharmaceuticals, coatings and paints.

As such, they constitute a serious concern for the environment, as currently most amphiphilic polymers are fossil-based and non-biodegradable. In the current society, where sustainability has become one of the milestones of chemical industry, this is not acceptable anymore.

A first step towards more sustainable amphiphilic polymers can be done by replacing fossil-based monomers with analogous biobased ones. This is typicall more challenging than for traditional polymers, as amphiphilicity is required.

In this contribution, I will show some examples of biobased alternatives to amphiphilic polymers from recent literature and from research performed in our lab, where we used controlled radical polymerization to produce amphiphilic copolymers with interesting properties. [2,3,4]

Keywords: amphiphilic polymers, controlled radical polymerization, bio-based building blocks; sustainable polymers

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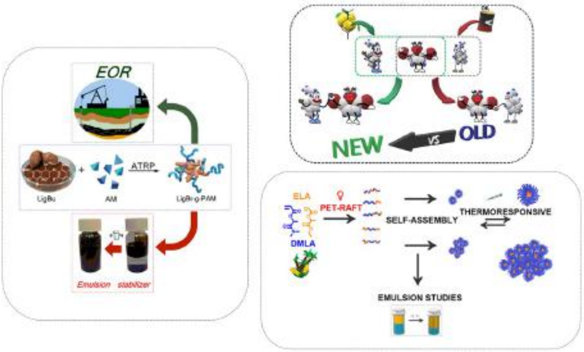


Amphi bio.jpg

RAFT polymerization of pH responsive methacrylates to investigate the mechanism of microalgae flocculation

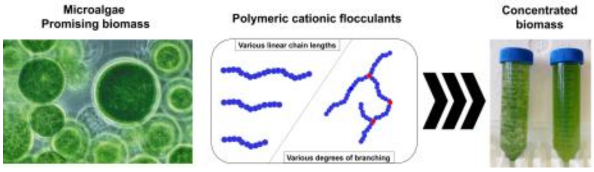
Wednesday, 26th April - 15:30: Oral Session 10-2 - Oral

Dr. Valentin Beyer [1], Dr. Jonas Blockx [1], Ms. Ayessa Pires Maciel [1], Ms. Sakshi Tyagi [1], Dr. Irem Demir-Yilmaz [2], Dr. Cécile Formosa-Dague [2], Prof. Koenraad Muylaert [1], Prof. Wim Thielemans [1]

***1.** KU Leuven, **2.** University of Tolouse*

Microalgae are a promising CO_2-fixing feedstock which is gaining growing attention for the production of biofuel, the extraction of valuable fatty acids, and other high value chemicals. Despite the great potential of microalgae, their production and especially the isolation of the biomass remains economically unsustainable due to the high energy cost for harvesting. Since microalgae carry an overall negative surface charge, sedimentation can be induced by addition of cationic flocculants, which is a common harvesting technique. The presented work will investigate the structural impact of polymeric flocculants by assessing different macromolecular architectures, namely linear, branched, and core-crosslinked polymers. RAFT copolymerisation of commercially available 2-(dimethylamino)ethyl methacrylate (DMAEMA) and a dimethacrylate crosslinker is demonstrated to be a suitable technique for the synthesis of all three target architectures with different compositions. Additionally, the synthesis of 2-(dialkylamino)etyhl methacrylates with different alkyl groups is demonstrated in order to assess the impact of bulky susbstituents around the cationic charge on flocculation behaviour. The polymer library is thoroughly analysed in order to confirm their absolute structure, molecular weight and solution properties. Furthermore, the results of flocculation tests on fresh water algae under various conditions are presented and a relationship between polymer architecture and flocculation efficiency is assessed. The findings are complemented with titration, surface charge measurements, and atomic force microscopy to give mechanistic insights in the flocculation behaviour of the synthesised polymers.

Keywords: Cationic polymers, RAFT polymerisation, pH responsive, thermoresponsive, core-crosslinking, microalgae harvesting, atomic force microscopy



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Closing the loop of Polyurethanes: from biobased and non-isocyanate polyurethanes to vitrimers and upcycling materials

Wednesday, 26th April - 15:45: Oral Session 10-2 - Oral

Dr. Sylvain CAILLOL [1]

[1] *CNRS ICGM*

Recent years have witnessed an increasing demand for environmentally friendly materials, particularly for polyurethanes (PU)s, which correspond to 6^{th} polymer in the world with an annual production close to 20Mt. We have synthesized the first fully biobased PU from commercial biobased isocyanates. Furthemore, in order to reduce the environmental impact, we have also developed a platform approach for the synthesis of non-isocyanates PUs, particularly with the aminolysis of cyclic carbonates. We have thoroughly investigated the reactivity, the interest and limits of this reaction leading to polyhydroxyurethanes (PHU)s, and particularly to hybrid PHUs. Hence, we have demonstrated the high reactivity of the biobased β-hydroxy amines that we have synthesized from biobased resources. We have designed the first self-healing non-isocyanate PUs. Most of PU are used as foams. Hence, we have also designed biobased and non-isocyanates PU foams (PUF). To consider the full life cycle of such materials, these PUFs were upcycled and reshaped to bulk polyurethanes (PUs) by transcarbamoylation reaction up to 5 cycles. Moreover, a unique material (mixPU) composed of the four PUFs was prepared and reshaped, by compression molding at 160 °C for 30 min, thus demonstrating the potential of this recycling pathway for PUFs from different origins. Finally, stress-relaxation experiments were carried out to evaluate the dynamic properties of the mixPU material, which was shown to behave as a covalent adaptable network vitrimer.

Figure 1. Recycling of biobased PU foams

Caillol.jpg

From natural proteins to polymer synthesis by aqueous ring-opening polymerization

Wednesday, 26th April - 14:00: Oral Session 10-3 - Oral

Dr. Colin Bonduelle [1]

1. University of Bordeaux

Proteins are natural building blocks that have many features still unrivaled by their synthetic counterparts, including chemical diversity, hierarchical structure, specific chemical modification, programmed system dynamics, etc. Combined with their possible metabolism in living systems (biodegradation, etc.), these properties make peptidic backbones very interesting for designing the polymers of tomorrow. In this stimulating context, the most economical and efficient route to polypeptides is the ring-opening polymerization (ROP) of amino acid N-carboxyanhydride (NCA) monomers.[1] Those polypeptides combine advantageous features of other synthetic polymers (solubility, process, rubber elasticity, etc.) with those of natural proteins (secondary structure, functionality, biocompatibility, etc.).[2] NCA polymerization still suffers from significant limitations including tedious monomer purification steps, significant sensitivity to moisture, and processing in toxic solvents. Recent progresses have been impressive: efforts have focused on promoting the polymerization without the use of a catalyst, exploring more reactive initiators, and using heterogeneous processes including emulsion polymerization.[3] In this context, this talk will illustrate 1) how aqueous ROP of NCA monomers can be extended to a PISA process,[4] and 2) how polymerization of NCA can afford simplified analogues of thermoresponsive or antimicrobial proteins.[5]

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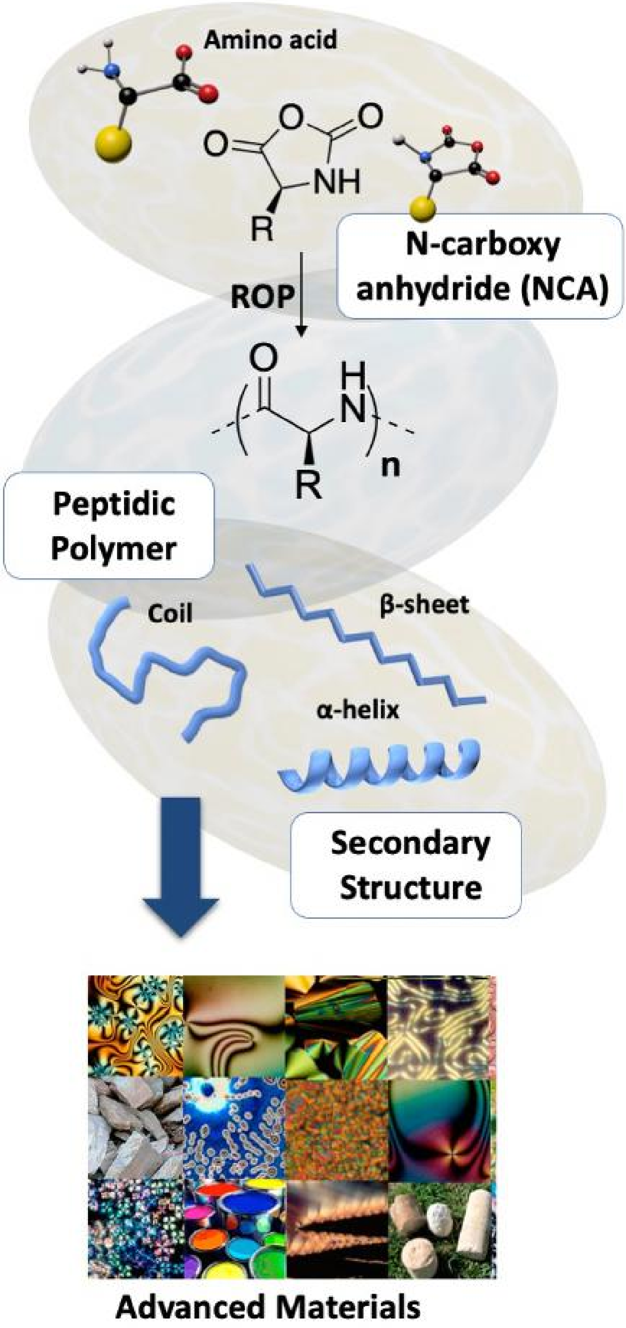
5. C. Bonduelle et al., a) *Patent application* **2021** EP21305198.0. b) *Biomacromolecules* **2021**, *22*, 57. c) *J. Am. Chem. Soc.* **2021**, *143*, 3697. d) *Polym. Chem.* **2022**, *13*, 600. e) *Patent application* **2022** EP22306210.0. f) *Angew. Chem. Int. Ed.* **2022**, just accepted (https://doi.org/10.1002/ange.202209530)



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Polymer assemblies with life-like behavior

Wednesday, 26th April - 14:30: Oral Session 10-3 - Oral

Prof. Jan van Hest [1]

1. *Eindhoven University of Technology*

Compartmentalization is generally regarded as one of the key prerequisites for life. In living cells, not only the cell itself is a compartment, with its properties controlled by the semipermeable cell membrane, but also the organelles play a crucial role in protecting and controlling biological processes. To better understand the role of compartmentalization, there is a clear need for model systems that can be adapted in a highly controlled fashion, and in which life-like properties can be installed. Polymer-based compartments are robust and chemically versatile, and as such are a useful platform for the development of life-like compartments. In this lecture both nanomotors and artificial cell systems will be discussed. The nanomotors are composed of biodegradable amphiphilic block copolymers that self-assemble into vesicular structures. By introducing asymmetry in the structure and by functionalizing them with propelling units they can be converted into nanomotors. For example, via a shape change process a bowl-shaped structure is obtained out of a spherical vesicle. Within the cavity of the bowl enzymes are loaded which provide the nanostructure with motility upon conversion of chemical energy into kinetic energy. These nanomotors are explored for biomedical applications, in particular photodynamic therapy

The synthetic cell platform is composed of a complex polymer coacervate, stabilized by a biodegradable block copolymer which creates a semi-permeable membrane. The coacervate structures resemble better the crowded environment observed in the cytoplasm than vesicular structures normally do. Cargo can be effectively loaded in the coacervates, based on complementary charge and affinity, e.g. by using Ni-NTA-His tag interactions. This allows protocell communication with this robust synthetic platform. Via this system we have been able to show that we can bring enzymes involved in cascade reactions closer to each other, facilitating the outcome of the process. We can controllably release proteins from the artificial cell, mimicking natural secretion, and we can incorporate multiple artificial organelles in the interior, thereby mimicking the architecture of a eukaryotic cell. Finally, we are able to incorporate life-like features such as motility in these structures, making this class of artificial cells a very versatile platform to study and mimic biological processes.

Reversible pH-responsive polyelectrolyte/protein complexes for targeted delivery

Wednesday, 26th April - 15:00: Oral Session 10-3 - Oral

Dr. Anastasiia Murmiliuk [1], ***Dr. Hiroki Iwase*** [2], ***Dr. Jia-Jhen Kang*** [1], ***Dr. Martin Dulle*** [1], ***Dr. Thomas Gensch*** [1], ***Dr. Kathleen Wood*** [3], ***Dr. Kuno Schwärzer*** [1], ***Dr. Jürgen Allgaier*** [1], ***Dr. Beate Förster*** [1], ***Dr. Marie-Sousai Appavou*** [1], ***Dr. Aurel Radulescu*** [1]

__1.__ Forschungszentrum Jülich GmbH, __2.__ Comprehensive Research Organization for Science and Society, __3.__ Australian Nuclear Science and Technology Organisation

Co-assembly of proteins with oppositely charged polyelectrolytes is a well-studied approach for designing complexes with tunable properties thanks to their responsiveness to pH and ionic strength. [1,2] Combining these features with morphology diversity of the formed complexes (Fig.1) allows us to create nanocarriers for targeted delivery with controlled encapsulation and release of a cargo. However, the complexity of protein structure limits the ability to predict and tune properties of the formed nanoparticles. The ultimate goal of our research is to reveal the main triggers for the morphological transition of protein/polyelectrolyte complexes, their encapsulation efficacy and particles stability by systematic study of complexes formed by block copolymers with proteins and ionic drugs. Using scattering and microscopy techniques, we showed that block copolymers consisting of a weak polyelectrolyte block and a neutral hydrophilic block co-assemble with proteins at pH close to protein isoelectric point and the morphology of the formed particles can be tuned by varying pH and nature of proteins. Moreover, we observed that formed protein/polyelectrolyte complexes with an excess of a charge can be used for encapsulation of an oppositely charged drug thus allowing us to use one carrier for both protein and drug delivery, and to design nanocapsules with such tunable properties as charge, stability and size.

Acknowledgments:

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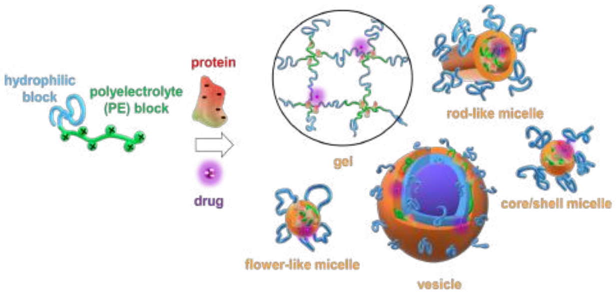

Fig.1 polyelectrolyte-protein complexes.png

Polymers as Broad Spectrum Antivirals

Wednesday, 26th April - 15:15: Oral Session 10-3 - Oral

Dr. Jungyeon Kim [1], *Dr. Samuel Jones* [1]
1. University of Manchester

Polymers that can inhibit the viral replication process have been investigated for many decades, a prime example being the sulfonated polysaccharide, heparin. The many repeating units of a polymer and the high molecular weight nature leads to properties that differ vastly from small molecule antivirals. In addition, polymeric antivirals tend to be broad spectrum, allowing them to target multiple viruses as well as being effective against mutations.

However, some antiviral polymers have shown to have a reversible interaction with the virus; whilst the anionic charge on the polymers initially surround the virus inhibiting its viral activity, *in vivo* experiments have shown that due to the dissolution effect, the binding become reversible making the virus active again. These have been termed as being “virustatic” as the viral inhibition process is reversible.

In this work, we present highly sulfonated polymers of branched architecture showing irreversible interacting with viruses, which are termed “virucidal”. Comparing linear polymers of the same composition to its branched analogue, the antiviral activity switches from virustatic to virucidal, showing that architecture plays a key role.

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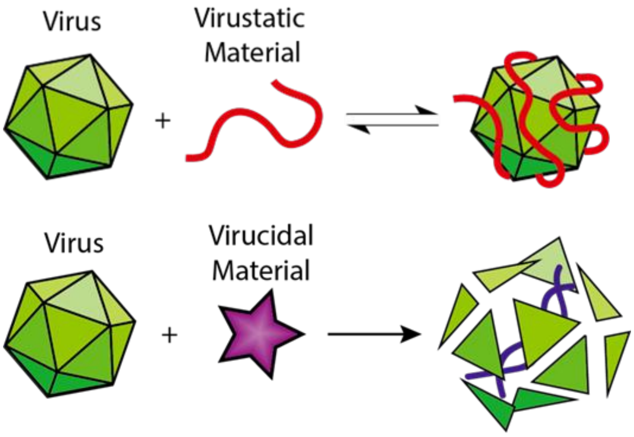

Apme23 abstract.png

Spatial control over peptide presentation in polymeric TRAIL mimics

Wednesday, 26th April - 15:30: Oral Session 10-3 - Oral

Mr. Zifei Han [1]***, Dr. Zihao Li*** [1]***, Prof. Martina Stenzel*** [1]***, Dr. Robert Chapman*** [2]

1. *University of New South Wales,* ***2.*** *University of Newcastle*

The tumor necrosis factor (TNF-α) related apoptosis inducing ligand (TRAIL) has attracted much interest for its ability to specifically trimerize death receptor proteins (DR4 and DR5) on the surface of cancer cells, triggering apoptosis (**Figure 1A**). This protein holds great therapeutic promise because of its high potency and specificity, but no variants of native TRAIL have yet made it through clinical trials.[1] We are interested in designing synthetic polymer scaffolds that present multiple DR5 binding epitopes for i) mimicking the natural protein, providing new therapeutic leads without the pharmacokinetics and immunogenic concerns that have hampered TRAIL, and ii) for studying the mechanism of TRAIL signaling. The spatial organization of cell-surface receptors plays a pivotal role in controlling many cellular signaling cascades, and we expect that successful synthetic TRAIL mimics could be deployed in regulating a wide array of cell signaling process.

In any synthetic protein mimic, directing the conformational structure to precisely present multiple DR5 binding ligands with the desired spacing and orientation is a major challenge. We have used high throughput screening to develop scaffolds that do this through the folding of star-shaped peptide-polymer conjugates (**Figure 1B**), [2,3] and by the self-assembly of polymer micelles in aqueous solution (**Figure 1C**). The ability of these constructs to trigger DR5 clustering is confirmed by caspase 8 production, and results in toxicities approaching native TRAIL in colon cancer cell lines.[4]

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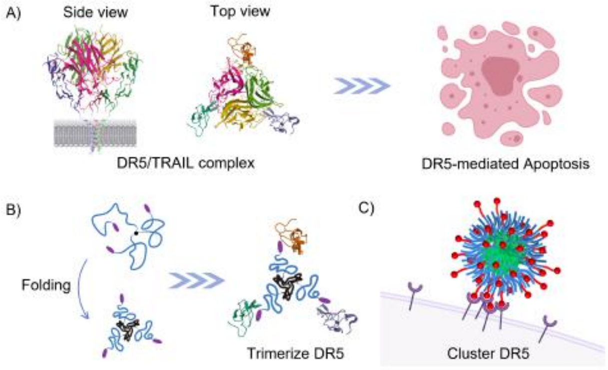


Figure 1. schematic showing **A)** binding mode of how TRAIL protein trimerizes DR5 and kill tumor cells. (Crystal structures taken from RCSB 6NHY, 1DU3). Ligand presentation manipulation of polymeric TRAIL mimics through **B)** polymer folding, and **C)** micelle surface modification.

Figure1 spatial control over peptide presentation in polymeric trail mimics.png

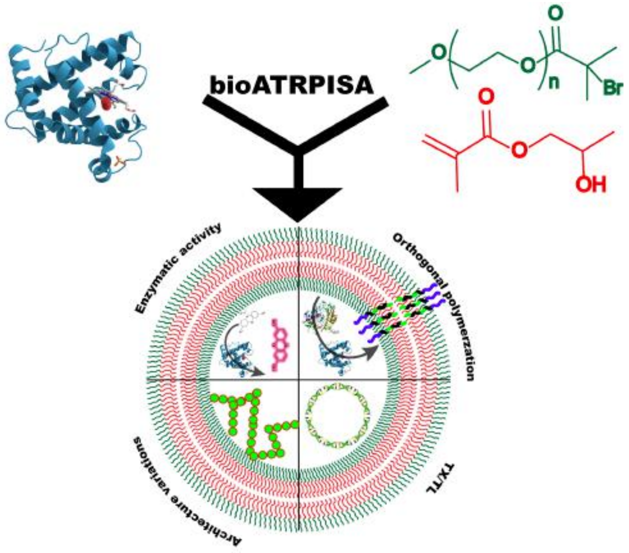
Ghost in the cell: artificial cells via enzyme-mediated polymer synthesis and self-assembly

Wednesday, 26th April - 15:45: Oral Session 10-3 - Oral

Dr. Andrea Belluati [1], *Dr. Sètuhn Jimaja* [2], *Mr. Christopher Glynn* [1], *Prof. Nico Bruns* [1]

1. *Technische Universität Darmstadt,* ***2.*** *Adolphe Merkle Institute*

Polymersomes are sought-after structures for artificial cells, thanks to their liposome-like structure, improved stability, and chemical versatility. However, the use of amphiphilic bloc copolymers is currently limited by the need to produce the building blocks beforehand, via classical organic synthesis methods. We developed a myoglobin-mediated atom transfer radical polymerization (bioATRP) of 2-hydroxypropyl methacrylate (HPMA) with a monomethyl poly(ethylene glycol) macroinitiator, yielding a mPEG-*b*-PHPMA block copolymer that self-assembles in vesicles as the PHPMA chain is elongated, in a bio-inspired ATR polymerization-induced self-assembly (bioATRPISA). Myoglobin could self-encapsulate into cell-sized vesicles, which effectively harboured a plethora of cargoes, from small molecules to nanoparticles, and several enzymes as well, becoming multi-functional microreactors, capable of becoming luminescent, fluorescent and use a second step of internal enzymatic polymerization to change their shape and size. Moreover, they could encapsulate bacterial lysate and plasmids as well, becoming able to express proteins on demand: an actin-based cytoskeleton and alkaline phosphatase, which was ultimately able to entrap these artificial cells within a biosimilar mineral matrix.



Toc.png

Macromolecules with complex architecture - synthesis, properties and applications

Wednesday, 26th April - 16:30: Oral Session 11-1 - Oral

Dr. Joanna Pietrasik [1]

1. *Lodz University of Technology*

Reversible-deactivation radical polymerizations, including, among others, atom transfer radical polymerization (ATRP) or addition-fragmentation chain transfer radical polymerization (RAFT), are excellent tools for the synthesis of well-defined polymers. It is possible to obtain polymers with a strictly defined molecular weight and its distribution, the assumed chemical composition of a single chain, its functionality, as well as topology. As a result, both the ATRP and RAFT methods drove new perspectives in the synthesis of advanced materials and their applications. For example, macromolecules in the form of stars, molecular brushes, gradient copolymers or multi-block copolymers should be mentioned here. These mechanisms also make it possible to conduct polymerization reactions from the surface of solids or various biomolecules. Precise synthesis and processing of polymers enable one not only to achieve the required properties but also to transfer them into a wide range of their applications.

This presentation will present examples of materials obtained using the ATRP and RAFT polymerization methods, in which the properties are determined primarily by the specific topology of macromolecules and the ordering of polymer chains. In particular, modifications of the surface of graphene oxide and its application in polymer blends will be presented. Examples of molecular brushes with lubricating properties will also be shown. In addition, examples of hydrogels with potential applications in dressing materials will be demonstrated.

Financial support: National Science Centre, Poland, Opus-Lap (Grant UMO-2020/39/I/ST5/02108), Opus (UMO-2018/29/B/ST5/02412).

Kinetic and microstructural investigations of high-temperature acrylate polymerizations

Wednesday, 26th April - 17:00: Oral Session 11-1 - Oral

Mr. Jonas Mätzig [1]***, Dr. Marco Drache*** [1]***, Prof. Sabine Beuermann*** [1]

1. *Clausthal University of Technology*

The design of polymer products and technical processes requires detailed mechanistic understanding and knowledge of kinetic data of all elemental reactions occurring during polymerizations. This is particularly true for radical polymerizations of acrylates since the polymer microstructure as well as the rate of polymerization are significantly influenced by intramolecular backbiting reactions leading to less reactive tertiary midchain radicals. Especially at high temperatures, these radicals may undergo β-scission leading to secondary chain end radicals and macromonomers with a reactive double bond. Moreover, polyacrylates are significantly branched as a consequence of intra- and intermolecular transfer to polymer.

In order to obtain more detailed insights into the reaction mechanism and to derive kinetic coefficients for individual elemental reactions experimental and modeling efforts are combined. To provide a sound base for kinetic Monte Carlo simulations and parameter estimation, pulsed laser initiated polymerizations and high-temperature polymerizations with in-line FT-NIR monitoring of monomer conversion are carried out. Polymer analysis by triple detector SEC provides access to the degree of branching as a function of polymerization temperature, type and concentration of solvent. More detailed information, e.g., type of branching and number of branches per polymer, or the ratio of midchain to endchain radicals is obtained from Monte Carlo simulations. The contribution focusses on butyl acrylate and is accompanied by investigations into polymerizations of acrylates with, e.g., branched alkyl ester as well as cyclic and sterically demanding ester groups. Further, the impact of solvent on the thermal self-initiation of butyl acrylate polymerizations is discussed. In particular knowledge gained on the branching behavior allows for better control of the microstructure of polyacrylates in polymerization processes.

New developments synthesizing poly(vinyldene fluoride) aerogels

Wednesday, 26th April - 17:15: Oral Session 11-1 - Oral

Prof. Barbara Milow [1] , ***Prof. Sabine Beuermann*** [2]

1. *Deutsches Zentrum für Luft- und Raumfahrt, (German Aerospace Center),* **2.** *Clausthal University of Technology*

Aerogels are nanostructured open-pored solids with an unexpected combination of properties. Due to their structural properties, they exhibit enormously high porosity, low densities, low thermal conductivity and good acoustic damping properties.

While conventional aerogels are synthesized via the sol-gel process, starting from monomeric precursors, and subsequent drying of the wet gel, the synthesis of poly(vinyldene fluoride) (PVDF)-based aerogels needs to be newly developed. In this regard, steam-induced phase separation appears to be promising.

In our development work, different precursors and synthesis conditions are investigated and the obtained PVDF materials are characterized.

In our presentation, suitable synthesis conditions and investigations into the morphology and properties of PVDF aerogel will be discussed.

Synthesis of fluorinated polyacrylamides as highly sensitive 19F MRI tracers

Wednesday, 26th April - 17:30: Oral Session 11-1 - Oral

Prof. Ondrej Sedlacek [1]

1. *Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Prague 128 40, Czech Republic*

^{19}F magnetic resonance imaging (MRI) using fluoropolymer tracers has recently emerged as a promising, non-invasive diagnostic tool in modern medicine.[1] In this contribution, we report our recent achievements in the field of ^{19}F MRI tracers based on fluorinated polyacrylamides. In the first part, we will focus on hydrophilic fluorinated polymers.[2] To obtain a strong ^{19}F MR signal, a relatively high content of chemically equivalent fluorine atoms is usually necessary. Unfortunately, the increasing fluorine content generally leads to the decreasing water solubility of the polymer. We synthesized a library of new water-soluble fluorinated (co)polymers with fine-tuned structures for maximal ^{19}F MRI performance and good solubility in water. The most promising polymers show excellent MRI signal that enables tracer visualization at unprecedented low concentrations.

In the second part, we present a straightforward synthetic route to highly fluorinated ^{19}F MRI nanotracers via aqueous dispersion polymerization-induced self-assembly (PISA) of a water-soluble fluorinated monomer.[3] A polyethylene glycol-based macromolecular chain-transfer agent was extended by RAFT-mediated *N*-(2,2,2-trifluoroethyl)acrylamide polymerization in water, providing fluorine-rich self-assembled nanoparticles in a single step. After optimizing their structure to maximize the magnetic relaxation of the fluorinated core, we obtained a strong ^{19}F MR signal in water. Their non-toxicity was confirmed on primary human dermal fibroblasts. Moreover, we visualized the nanoparticles by ^{19}F MRI, both in vitro and in vivo (after subcutaneous injection in mice), thus confirming their biomedical potential.

Acknowledgments

Financial support from the Ministry of Health of the Czech Republic (grant NU22-08-00286) and Charles University Prague (grant PRIMUS/21/SCI/007) is gratefully acknowledged.

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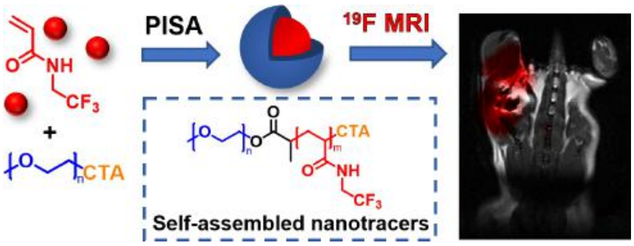

Fluorinated mri tracers.jpg

Engineering carbohydrates towards more sustainable polymers and advanced functional materials

Wednesday, 26th April - 16:30: Oral Session 11-2 - Oral

Prof. Antoine Buchard [1]

1. *University of Bath*

Introduction

The intensive use of polymers has brought challenges associated with their overwhelming reliance on fossil-fuel resources, limited end-of-life options and environmental persistence. Towards a circular economy, our vision for sustainable polymers involves creating materials derived from renewable feedstocks and with multiple closed-loop life cycles. However, one major challenge is to obtain materials with adequate properties.

Method

Towards this goal, our team has been investigating the incorporation of monosaccharide units into synthetic polymer backbones. Our hypothesis is that because sugars are natural, abundant, non-toxic, biodegradable, biocompatible, and highly functionalisable, renewable materials with desirable attributes could be made.

Results

Various classes of monosaccharide-based, oxygenated polymers (including ethers, esters, carbonates) can be made using polymerisation techniques such as acyclic metathesis polymerisation (ADMET) [1-2], thiol-ene polymerisation, and ring-opening (co)-polymerisation (ROP and ROCOP) [3-5]. Sugar-based monomers can be combined with other renewable feedstocks such as fatty acids derivatives, renewable cyclic anhydrides or CO_2, to produce polymers with up to 100% renewable content.

Discussion

Throughout our studies, we have refined our understanding of the structure/properties relationship of those sugar-based polymers, changing the nature of the monosaccharide or comonomer used, replacing oxygen atoms for sulfur in the polymer backbone [5-6], exploiting the sugar's stereochemistry to tune crystallinity, and assessing the overall recyclability and degradability (in particular to UV light) of the materials made.

The resulting sugar-based polymers form a promising, tuneable, bio-derived and degradable material platform. Their use in commodity and specialty applications will be presented (*e.g.*, polyethylene-like films for packaging, solid and gel polymer electrolytes for battery applications [7-8]).

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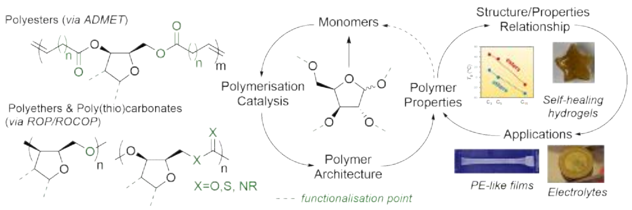


Xylose-based polymer platform and applications.png

Polypeptide based ionogels – new and biodegradable polyelectrolites from renewable materials

Wednesday, 26th April - 17:00: Oral Session 11-2 - Oral

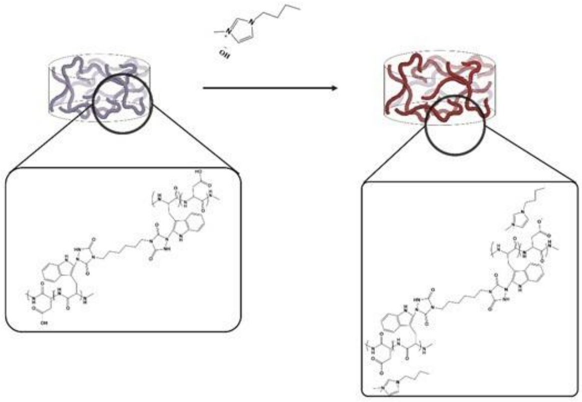
Dr. Rafal Bielas [1], ***Prof. Andreas Heise*** [1]

1. *Royal College of Surgeons in Ireland*

Glutamic acid and aspartic acid are common amino acids that, when converted to their respective N-carboxyanhydrides, can be subjected to ring-opening polymerization. As a result, polyacids can be obtained, which can then be modified by introducing appropriate cations. This is a particularly attractive path for the production of biodegradable poly(ionic liquid)s.

By using the previously developed technique of cross-linking polypeptides with bistriazolinediones (bisTAD), chemically cross-linked polypeptide organogels can be obtained. These, in turn, after functionalization with ionic liquids, can be an alternative to currently used polyelectrolytes derived from non-renewable sources.

In the presented work, the synthesis of polypeptide gels, their modification with ionic liquids and the characteristics of their properties will be discussed. The introduction of imidazolium cations to the polypeptide network triggers changes in the mechanical properties making the gels much softer as confirmed by rheology. Additionally the thermal properties of the obtained materials will be shown by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The tested ionogels will be compared with the starting gels based on poly(glutamic acid) and poly(aspartic acid), and their potential as solid polyelectrolytes will be investigated, as well as the possibility of their use in new batteries.



Preparation of polypeptide based ionogels.jpg

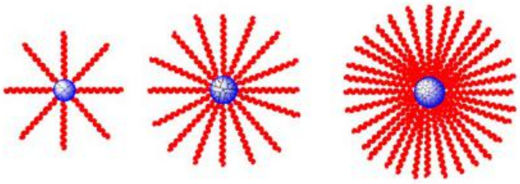
Star polypeptide vectors with degradable core for gene delivery applications

Wednesday, 26th April - 17:15: Oral Session 11-2 - Oral

Mrs. Smiljana Stefanovic [1], ***Ms. Katie McCormick*** [2], ***Dr. Sarinj Fattah*** [2], ***Prof. Ruairi Brannigan*** [3], ***Prof. Sally-Ann Cryan*** [2], ***Prof. Andreas Heise*** [1]

1. *Department of Chemistry, RCSI University of Medicine and Health Sciences, Dublin 2, Ireland.,* ***2.*** *School of Pharmacy and Biomolecular Sciences RCSI University of Medicine and Health Sciences.,* ***3.*** *School of Chemical Sciences, Dublin City University, Collins Avenue, Whitehall, Dublin 9, Ireland.*

Cationic star-shaped poly(L-Lysine) are efficient nanovectors for the delivery of nucleic acids (gene delivery). They are commonly obtained by the ring-opening polymerisation (ROP) of L-Lysine N-carboxyanhydrides (NCA) from multifuctional amine initiator such as dendrimers. To date commonly reported dendritic precursors are non-degradable which can cause dose dependant cytotoxicity *in vivo*. Herein, we present a new synthetic approach for the preparation of fully degradable star-shaped polypeptides. The polymerisation of ε-carbobenzyloxy-L-lysine (ZLL) NCA has been studied in the presence of three generations of ammonium terminated 2,2-*bis*-(hydroxymethyl)propionic acid (*bis*-MPA) dendrimers. Star polypeptides with different numbers of arms and amino acid units per arm, were synthesised by varying the dendrimer generation and adjusting the monomer feed ratio of ZLL NCA. The presence terminal primary amino salts, in comparison to primary amines, prevent deprotonation of ZLL NCA monomer avoiding initiation *via* the activated monomer mechanism and thus the formation of ill-defined polymers. Hence, the obtained polymers were exceptionally well-defined and exhibited a low dispersities ($Đ_M$<1.05). Molecular weights obtained by NMR spectroscopy showed good correspondence with the theoretical values. The ability of efficient dendrimer core degradation was confirmed under physiological and basic conditions. The polymers were successfully evaluated as potential plasmid DNA (pDNA) carriers. This new class of fully degradable and biocompatible gene vectors has demonstrated very promising *in vitro* performance.



Schematic representation of three generations of bis-mpa-poly l-lysine s with 8 16 and 32 l-lysine arms..jpg

Energy-Autonomous Seawater Desalination by Thermo-Responsive Hydrogels

Wednesday, 26th April - 17:30: Oral Session 11-2 - Oral

Prof. Sebastian Seiffert [1]**,** ***Dr. Amir Jangizehi*** [1]

1. *Johannes Gutenberg University Mainz*

Water scarcity is one of the most serious global challenges of our time. One of the main solutions to address this challenge is water desalination. In this respect, forward osmosis (FO) has gained significant attention. For this purpose, thermo-responsive hydrogels containing ionic groups are a class of materials that can be potentially utilized as draw agent. The ionic groups induce the water flow in the process, and they also serve to block and thereby seperate salt. By increase of temperature above the volume phase transition temperature (VPTT) of the hydrogels, the hydrogels shrink, whereby the absorbed, purified water is recovered. Considering this effect, the idea of a membrane-free FO desalination process by ionic hydrogels has been introduced, in which hydrogels serve as both separation and draw agents. However, the use of thermo-responsive hydrogels in that approach is faced with different challenges such as (i) the significant detrimental effect of charged groups on the water recovery efficiency of hydrogels, and (ii) the need for designing FO agents with high salt rejection and water flow performance as well as with low fouling effect. Considering these challenges, we study the influence of the chemical composition, morphology, microstructure, and molecular architecture of charged, thermoresponsive hydrogels based on N-isopropyl acrylamide (NIPAAm) and sodium acrylate (SA) on the efficiency of FO seawater desalination in terms of salt rejection and water recovery. Based on these achievements, we design a simple, efficient, and relatively non-expensive desalination process with a production capacity targeted to serve the demands of small villages via a FO process.

Understanding and steering morphological transitions in PISA

Wednesday, 26th April - 16:30: Oral Session 11-3 - Oral

Dr. Jutta Rieger [1]

1. Sorbonne Université & CNRS, Institut Parisien de Chimie Moléculaire, Paris, FRANCE

Polymerization-induced self-assembly (PISA) has proved to be a powerful and efficient process to produce block copolymer nanoparticles of various morphologies (spheres, worms, vesicles etc.).[1,2] PISA relies on the chain extension of a first, soluble block with a monomer whose corresponding homopolymer is insoluble in the solvent of polymerization (water in majority of cases). As the second block grows above a certain degree of polymerization, it becomes insoluble, which drives the assembly of the amphiphilic chains into core-shell nano-objects. Their morphology is principally determined by the polymer concentration, the solvent and the block lengths, which in turn affect the packing parameter. As the hydrophobic block length increases progressively during PISA, in many cases, spheres are initially formed that further transform to worms and then to vesicles, provided that the final block is sufficiently long.

In contrast to spheres and vesicles, the pure worm phase is generally obtained in a very small experimental window. Therefore, recent works aimed at devising robust methods to favour the formation of the worm morphology in PISA.[3,4] For some copolymers/solvents systems however, only spherical particles have been observed, and the reasons why the formation of higher-order morphologies is possible or inhibited in PISA are still not fully understood.[5]

In this communication, we will discuss two strategies that we explored recently to control and favour the formation of higher-order particle morphologies in PISA.

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Functional and Biocompatible Nanoobjects Synthesized by Polymerization-Induced Self-Assembly

Wednesday, 26th April - 17:00: Oral Session 11-3 - Oral

Prof. Guillaume Delaittre [1]

1. *Organic Functional (Macro)Molecules, Department of Organic Chemistry, University of Wuppertal*

The field of polymerization-induced has tremendously expanded since the pioneering works of Hawkett, Charleux, Pan, and Armes.[1] The initial quest for molar mass control in an emulsion or dispersion radical polymerization process first made way to investigations dedicated to shape control. Indeed, besides classic spherical nanoparticles, a host of morphologically distinct nanoobjects could be obtained and their formation could be monitored postmortem or even live.[1,2] PISA entered a new era, where applications are targeted. In this context, not only the shape but also the functionality and the reactivity of the nanoobjects are pivotal.[3]

In this presentation, our contribution to the field will be showcased. Notably, we use various polymerization mechanisms (nitroxide-mediated polymerization, RAFT polymerization, ring-opening cationic or metathesis polymerization) to produce part of or entire nanoobjects. In most cases, the corresponding nanoparticles are found to be biocompatible (*in vitro* and *in vivo*). Surface or core functionality can simply be introduced through a specifically designed controlling agent or by copolymerization with specifically designed monomers.

Examples of nanoobjects for protein immobilization, catalysis, therapy, and biomaterial design will be presented.

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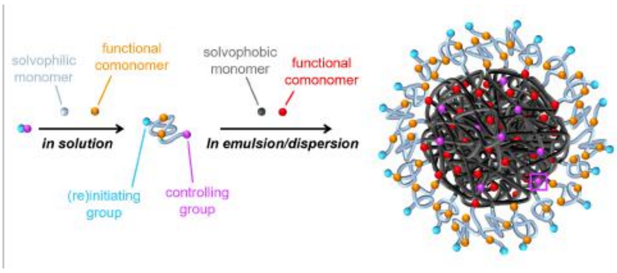


Delaittre figure.png

Exploring one-step living anionic polmerisation induced self-assembly (LAPISA) of butadiene-styrene statistical copolymers

Wednesday, 26th April - 17:30: Oral Session 11-3 - Oral

Mr. Toby Read [1], ***Dr. Nicholas Warren*** [1], ***Dr. Lian Hutchings*** [2]

1. *University of Leeds,* **2.** *Durham University*

Polymerization induced self-assembly (PISA) is a methodology where block copolymers undergo self-assembly, in a selective solvent, during the polymerisation. This reduces synthetic steps as the polymer does not need to be redissolved. The resulting nanoobjects could find application in gels, elastomers, coatings, or as rheological modifiers.

PISA has been explored extensively with methacrylate monomers and RAFT polymerization by groups like Armes *et al.* Morphologies identified by transmission electron microscopy (TEM) include spheres, worms, and vesicles.

However, PISA using living anionic polymerization (LAP) has remained relatively unexplored, despite advantages of LAP over RAFT polymerization including greater control over molar mass and dispersity, ease of polymerization of dienes and pre-existing use in industry. Zhou *et al*[HLR1] . reported PISA using LAP with the synthesis of block copolymers of isoprene and styrenic monomers by the convention “sequential addition of monomers” approach.

However, we report (for the first time) a more facile approach using LAP: a statistical copolymerisation taking advantage of the inherent copolymerisation kinetics to produce a tapered (diene/styrene) block copolymer in a single step. This will be demonstrated as a proof-of-concept using styrene and butadiene in heptane, a solvent in which r_{Bd} = 7.0 and r_{Sty} = 0.1 and a selective solvent for polybutadiene[HLR2] . (Figure 1) This concept could be applied to other diene monomers including isoprene and myrcene. In our methodology, dry styrene, dry heptane and dry butadiene were distilled into a trap-to-trap distillation equipment under vacuum, with styrene:butadiene ratios of 2:1, 1:1 and 1:2 for samples 1, 2 and 3 respectively; then initiated with sec-BuLi; reacted for 5 days and terminated with minimum quantities of methanol. Solutions turned from colourless to orange at ~44 hours. Samples had varying physical properties with 1 as a blue iridescent liquid, 2 as a cloudy white gel, and 3 as a milky white liquid. Samples were analysed by Nuclear magnetic resonance (NMR), Gel permeation chromatography (GPC), dynamic light scattering (DLS) and TEM. DLS revealed spherical nanomorphologies for samples 1 and 3 but non-spherical morphologies for sample 2. However, TEM revealed spherical morphologies for all samples.

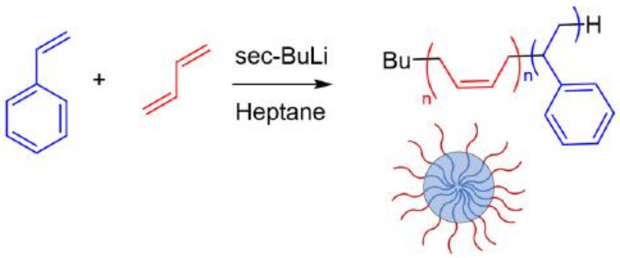


Image of reaction.png

Multiresponsive graft and double-crosslinked hydrogels as smart materials for actuator and sensor functions in microfluidic applications

Thursday, 27th April - 08:30: Plenary Session 4 - Oral

Prof. Brigitte Voit [1]

1. *Institute of Macromolecular Chemistry*

Responsive polymeric materials are becoming a highly studied field especially with regard to their use in technical applications, e.g. as sensors and actuators in microsystems and microfluidic applications, since they are able as volume gels to carry out mechanical work reacting on an e.g. chemical stimulus. In addition, compartimentalization becomes an issue for being able to localize specific actions and reactions e.g. by patterning specific hydrogel compartments. We will report on the preparation and integration of responsive and biocompatible hydrogel dots and hydrogel dot arrays of high flow and shear stability in microfluidic channel and chamber reactors. For that, multiresponsive hydrogels are developed making use of interpenetrating network approach and the concept of graft copolymer networks for retaining responsivity for up to four different stimuli in one hydrogel. The hydrogels have been adapted for integration into microfluidic devices as volume-changing gels, adjusting degree of swelling as well as mechanical stability and allowing their use as effective sensors and actuators as needed for a chemical valve function. First examples of their use as chemical transistors and the development of logical modules for achieving basic logic gate functions through a microfluidic setup are shown. Further optimization has been achieved by combining in double-crosslinked systems permanent and dynamic and reversible crosslinking points introducing redox functions and host-guest interactions. The dynamic responsive behavior could be translated into micrometer hydrogel dots in microsystems combining actuator function with specific bioresponse. First results are presented to use reversible redox bonding in hydrogels for triggered peptides capturing and release, and to adapt hydrogel dots as enzyme carriers in multi-chamber microreactors for complex cascade enzymatic reactions.

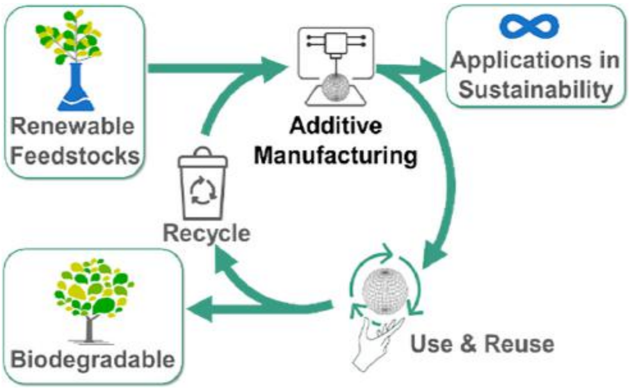
Sustainability Aspects in Additive Manufacturing: From biomass utilization to recyclability

Thursday, 27th April - 09:30: Oral Session 12-1 - Oral

Mr. Xabier Lopez de Pariza [1]***, Dr. Haritz Sardon*** [1]

1. POLYMAT- UNIVERSITY OF BASQUE COUNTRY UPV/EHU

Initially developed for rapid prototyping, additive manufacturing (AM) (colloquially 3D printing) is now scaling up its capacity to foster Industry 4.0 and operate a paradigm shift in the way products are manufactured. In addition to enabling new design capabilities, AM holds promises for increased social, economic, and environmental sustainability. Among AM methods vat photopolymerization(VP) techniques are desired owing to their improved efficiency and printing resolution. Nevertheless, the major portion of resins available for VP are based on systems coming from petroleum and/or with limited or negligible recyclability. In this lecture we will show how we can exploit the use of biomass as alternative interesting source for the production of 3D objects with enhanced properties and how we can implement new chemistries that differ from conventional ligh mediated non-recyclable free radical or cationic photopolymerization of (meth)acrylate or epoxide monomers to produce resins with circularity built into their perfomance.



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Following the biodegradation of aliphatic polyesters with varying chain lengths using 13C-labelling

Thursday, 27th April - 10:00: Oral Session 12-1 - Oral

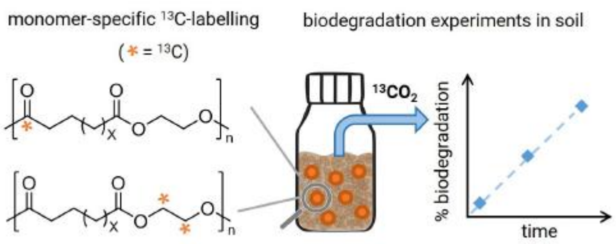
Dr. Taylor Nelson [1], ***Mr. Felix Schoder*** [1], ***Mr. Simon Schwab*** [1], ***Prof. Stefan Mecking*** [1]

1. Universität Konstanz

Due to the recalcitrance of conventional plastic materials such as high-density polyethylene (HDPE), their high production and application volumes results in environmental plastic pollution. Therefore, polymers with comparable mechanical and thermal properties, but which are non-persistent in the environment, are desirable. Recently, we produced a polyester derived from the polycondensation of ethylene glycol (C_2-diol) with 1,18-dimethyl octadecanedioate (C_{18}-dimethyl ester) (i.e., polyester-2,18 or PE-2,18) with HDPE-like mechanical properties and a high melting temperature (T_m = 96 °C), which was also readily compostable.

Following this approach to produce biodegradable, HDPE-like materials, we herein investigated the environmental biodegradation of PE-2,18 under milder conditions, along with that of additional polyesters of the structure PE-2,X to elucidate the effect of the diacid chain length on the properties and degradability of these materials. To this end, we prepared ^{13}C-labelled PE-2,X polymers via incorporation of $^{13}C_2$-ethylene glycol, or via ^{13}C-labelling of the C_1 position of the diacid monomer units. These ^{13}C-labelled polymers allowed for conducting incubations in an agricultural soil, coupled to isotope-sensitive analysis of the soil efflux gas to quantify mineralization rates and extents of the polyester carbon. In addition, to further investigate the effect of diacid chain length of the biodegradability of the polyesters, we measured rates of their enzymatic hydrolysis (understood to be the rate-limiting step of polymer biodegradation) by isolated microbial estereases.

Enabled by the ^{13}C-labelling approach, we were able to accurately quantify mineralization rates and extents of the different polyesters of the form PE-2,X to CO_2 by native soil microorganisms at 25 °C, as well as close mass balances on the added polyester-^{13}C. We found that mineralization rates increased for polyesters with shorter chain lengths, and these results were also supported by faster enzymatic hydrolysis rates for polyesters with shorter diacids. Further characterization of polymer physicochemical properties (e.g., crystallinity, melting temperature) were measured to understand the relationship between polyester chemical structure and their susceptibility to enzymatic hydrolysis. These results provide evidence for the potential of sustainable plastic materials to act as alternatives to conventional polyolefins by exhibiting similar desired properties, while being non-persistent in the environment.



Soil 13c incubations a.jpg

Moving from isocyanate hydrolysis to cyclic carbonate decarboxylation: development of sustainable self-foaming isocyanate-free polyurethane formulations

Thursday, 27th April - 10:15: Oral Session 12-1 - Oral

Mr. Florent Monie [1]***, Dr. Bruno Grignard*** [2]***, Dr. Thomas Vidil*** [3]***, Dr. Etienne Grau*** [3]***, Prof. Henri Cramail*** [3]***, Dr. Christophe Detrembleur*** [2]

1. *University of Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, Pessac, France - Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liège, Department of Chemistry, Liège, Belgium,* ***2.*** *Center for Education and Research on Macromolecules (CERM), CESAM Research Unit, University of Liège, Department of Chemistry, Liège, Belgium,* ***3.*** *University of Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, Pessac, France*

Since their discovery, polyurethanes (PU) have been increasingly present in our daily life, particularly under the form of expanded low density materials, *i.e.* PU foams (PUF).[1] For decades, poly-isocyanates have been the key precursors to prepare PUF. They react concomitantly with polyols to form the PU matrix and with water, to generate CO_2 as a blowing agent. However, the growing ecological awareness of our societies comes with restrictive worldwide regulations towards the use of isocyanates, which are toxic and carcinogenic. This context led to the development of non-isocyanate polyurethane (NIPU), *i.e.* PU obtained through isocyanate-free synthesis pathways. In particular, polyhydroxyurethanes (PHUs), resulting from the aminolysis of 5-membered cyclic carbonate (5CC), are among the most promising PU alternatives.[2] In the absence of isocyanate, PHU foams (PHUF) were first obtained by using physical and chemical blowing agents, including undesirable ozone-depleting substances or flammable dihydrogen gas.[3] Very recently, our group in Liège marked a turning point in PHUF synthesis by developing a simple and safe methodology for the self-blowing of 5CC-based formulations in a way that mimics the historical isocyanate hydrolysis.[4] In this presentation, we will explain how soft-nucleophile thiol species are used to promote the poly-5CC decarboxylation concomitantly with their aminolysis. The in-situ generated CO_2 was successfully used as a blowing agent. We will further demonstrate that thiolactone can be used as an innocuous and latent form of thiol.[5] Eventually, we will illustrate how the vitrimeric properties of the PHUF can be used to repurpose the as-prepared foams into structural composites, showing the first example of recyclable NIPU foams.

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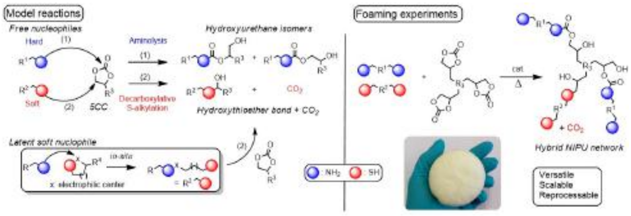

Self foaming nipu.jpg

Synthesis optimization of non-isocyanate thermoplastic polyurethanes via reactive extrusion

Thursday, 27th April - 10:30: Oral Session 12-1 - Oral

Mr. Nichollas Guimarães Jaques [1]***, Dr. Audrey Llevot*** [2]***, Dr. Étienne Grau*** [3]***, Dr. Thomas Vidil*** [2]***, Prof. Michael Meier*** [4]***, Prof. Henri Cramail*** [2]

1. *University of Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, Pessac, France Institute of Organic Chemistry & Institute of Biological and Chemical Systems – Functional Molecular Systems, KIT, 76131 Karlsruhe (Germany).,* ***2.*** *University of Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, Pessac, France,* ***3.*** *Université de Bordeaux,* ***4.*** *Institute of Organic Chemistry & Institute of Biological and Chemical Systems – Functional Molecular Systems (IBCS-FMS), Karlsruhe Institute of Technology, 76131 Karlsruhe (Germany).*

Polyurethanes (PUs) are versatile polymers thanks to the variety of possible chemical structures used in their synthesis. PUs are commonly produced in the industry via the polyaddition of isocyanates with polyols. However, isocyanates are harmful to the environment and human health.[1,2] As a greener route, non-isocyanate polyurethanes (NIPU) are an interesting alternative to substitute such conventional PUs.[1,2] Among the different synthesis routes towards thermoplastic NIPUs, one of the most promising is the polycondensation of biscarbamates with diols.[1,2] Classically, biscarbamates are obtained through the oxycarbonylation of amines using biscarbonates.[1,2] Advantageously, the melt transurethanization of biscarbamates with diols provides NIPUs with the same chemical structure as isocyanate-based PU, contrary to polyhydroxyurethanes NIPUs obtained from polyaddition of diamines on biscyclic carbonates.[1,3] However, this polymerization requires the use of catalysts and high temperatures to achieve polymers with suitable conversions and molar masses.[3] Thus, the improvement of melt transurethanization remains a challenge. To overcome this obstacle, we propose the use of reactive extrusion to improve the efficiency of melt transurethanization. This same strategy was previously applied to other NIPU syntheses with success, including the aminolysis of cyclic carbonates to form polyhydroxyurethanes.[4] In this work, several biscarbamates were synthesized by the oxycarbonylation approach. The latter were polymerized through melt transurethanization with different diols (low molecular weight diols and hydroxyl-terminated telechelic oligomers). Melt transurethanization was optimized through a catalyst screening and by comparing different mixing methods with a special emphasis on reactive extrusion, since this technique is a solvent-less and more efficient approach to achieve higher molar masses of polymers when used in conjunction with other techniques. The NIPUs produced by these procedures exhibited similar thermal properties and chemical structure to isocyanate-based PUs.

Keywords: NIPU, transurethanization, reactive extrusion, thermoplastic polyurethanes.

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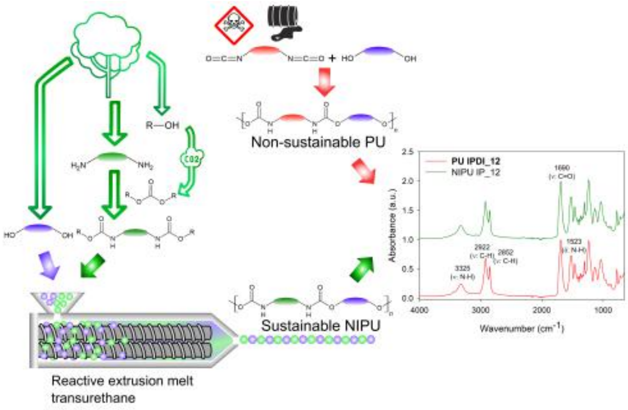


Graphical abstract apem.png

Molecular Design of Thermal Latent Initiator (Catalyst) for Novel Functional Network Polymers

Thursday, 27th April - 09:30: Oral Session 12-2 - Oral

Prof. Atsushi Sudo [1], ***Prof. Takeshi Endo*** [2]

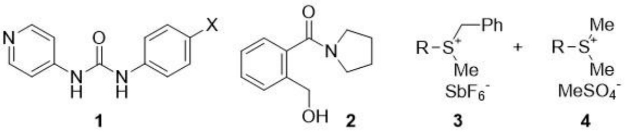
1. Kindai University, 2. Molecular Engineering Institute, Shiga University of Medical Science

Thermal latency of initiators and catalysts is an important property required for practical applications such as coating and adhesion. An ideal thermal latent initiator is inactive in its mixtures with monomers at ambient temperature, and the corresponding one-component formulations can be stored as long as they are not heated. When the formulations are heated above the threshold temperature, the thermal initiator contained in the formulations dissociates thermally to provide the active species for initiating polymerization.

Even now, the development of thermal latent initiators that can achieve both storage stability and high sensitivity to thermal stimuli continues. Here we report our recent molecular designs of latent initiators. The examples can be categorized into two: those that initiate anionic polymerization and those that initiate cationic polymerization.

The former involves 4-aminopyridine derivatives **1**. Their thermal dissociation gives 4-aminopyridine, which initiates ring-opening polymerization of epoxide efficiently. Another example is utilization of appropriately designed hydroxy amides **2**, of which cyclization accompanies dissociation of amine-type initiators.

The latter involves a dual sulfonium system consisting of **3** and **4** with two different counter anions. Compared to the conventional single sulfonium system, the newly developed system allows significant improvement of stability of epoxy formulations during storage at ambient temperature without sacrificing their curability at elevated temperatures.



Abstract endo .jpg

Weathering effects on microplastic chemical characterization

Thursday, 27th April - 10:00: Oral Session 12-2 - Oral

Dr. Samantha Phan [1]**, *Prof. Christine Luscombe*** [1]

1. *Okinawa Institute of Science and Technology Graduate University*

Microplastics are composed of different polymers, dyes, additives, and plasticizers that complicate their chemical identification. Furthermore, when plastics enter the environment, they are modified through various processes such as fragmentation, photodegradation, or biofouling and ultimately forming microplastics. Spectroscopic techniques such as IR and Raman spectroscopy help identify microplastics, but there is limited Raman spectroscopic information on weathered microplastics. Laboratory investigations of single simulation factors do not reflect actual weathering processes and it is useful to study multiple weathering conditions to close the gap between environmental and laboratory microplastic weathering. This work systematically investigates the influence of artificial weathering in four different weathering conditions (air, DI water, artificial seawater, and Puget Sound seawater) for 26 weeks on the chemical identification of some common plastics (polyethylene, polypropylene, polystyrene, polyethylene terephthalate, polyamide (nylon), and polyvinyl chloride). The results show that different weathering conditions have unique influences on the weathering of plastic. In particular, Raman data indicated variations in the crystallinity and amorphous domains in the weathered plastics. IR data revealed different functional group formation in the weathered plastics depending on the weathering conditions. Additional weathering information on microplastics with spectroscopic techniques will help researchers more easily identify microplastics and elucidate the nuances of microplastic weathering.

Thermoresponsive functional polymers for lithium recovery

Thursday, 27th April - 10:15: Oral Session 12-2 - Oral

Ms. Ariella Liberati [1], ***Dr. Benedicte Prelot*** [1], ***Dr. Jean-Pierre Mericq*** [2], ***Prof. Catherine Faur*** [2], ***Prof. Sophie Monge*** [1]

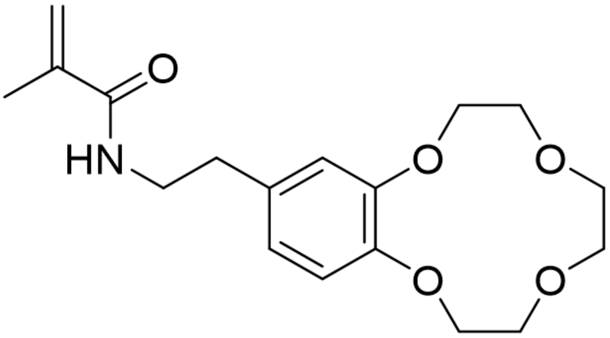
1. *ICGM,* ***2.*** *Institut Européen des Membranes Montpellier*

The recent development of the electric car industry has led to an over-consumption of non-renewable resources such as lithium. Furthermore, it was estimated that 200 to 500 million tons of spent lithium-ion battery (LIB) waste were annually generated by 2020. The current industrial battery recycling processes are mainly pyrometallurgy and hydrometallurgy, which are rather polluting, energy-consuming and onerous. Lithium-selective inorganic materials are available but limited to laboratory-scale studies at the moment due to their synthesis and processability drawbacks. Organic molecules that are capable of selectively and efficiently interacting and bonding with lithium ions have been abundantly reported in the literature. In particular, crown-ethers (CEs) provide lithium-ion selectivity over plenty of other alkali metal ions, mild-condition synthesis, great adaptability and easy processing.

In this context, in the present contribution, we report the synthesis of an original functional polymer, with the objective of designing a CE-based material capable of reversibly and selectively complexing lithium ions. Grafted onto a polymeric support, CEs could serve as an efficient and selective tool for the recovery of lithium from LIB leachates (aqueous solutions that are produced during recycling steps of wasted LIBs).

An original monomer functionalized with a crown-ether moiety was developed, namely the 2-(benzo-12-crown-4-ether)ethyl methacrylamide (BCEEM). It was successfully prepared using two different reactional pathways and fully characterized, notably by 1D and 2D NMR, and LC-MS. Then, free radical polymerizations of BCEEM and BCEEM/N-isopropylacrylamide (NiPAAm) mixtures were carried out, leading to P(BCEEM) and P(BCEEM-*st*-NiPAAm) polymers, respectively. PNiPAAm moieties induced thermoresponsive properties to the final materials. Lower Critical Solubility Temperatures were found to be around room temperature and will be exploited for an improved processability of the material.

Preliminary sorption experiments were carried out using Isothermal Titration Calorimetry (ITC) and Ionic Chromatography (IC) in order to determine the complexation capacity of the synthesized polymers. First results proved that lithium ions were sorbed onto the developed materials.



Chemical structure of 2- benzo-12-crown-4-ether ethyl methacrylamide bceem monomer.png

Designing biobased polyamide adhesives: Predicting functional properties with solid-state NMR spectroscopy

Thursday, 27th April - 10:30: Oral Session 12-2 - Oral

Dr. Kash Bhullar* [1]*, Dr. Richard Wuhrer* [2]*, Prof. Patrice Castignolles* [3]*,
***Dr. Marianne Marion Gaborieau* [4]**

***1.** Australian Centre for Research on Separation Science, Western Sydney University, School of Science, Parramatta, Australia, **2.** Advanced Materials Characterisation Facility, Western Sydney University, Parramatta, Australia, **3.** Sorbonne University, Parisian Institute for Molecular Chemistry (IPCM), Polymer Chemistry Team, Paris, France, **4.** Karlsruhe Institute of Technology (KIT), Institute for Chemical Technology and Polymer Chemistry, Polymeric Materials, Karlsruhe, Germany*

Solid-state NMR is invaluable for the molecular characterisation of polymeric materials. It is commonly used to elucidate chemical composition, and can also reveal other important molecular attributes, as shown on acrylic pressure-sensitive adhesives [1,2].

Hot-melt adhesives are a repair tool of choice for damaged conveyor belts on mining sites, a demanding application in terms of adhesive and mechanical properties [3]. To aid the development of new generations of biobased adhesives, quantitative ^{13}C NMR at high-temperature allowed quantification of the composition, while 2D WIdeline Separation (WISE) allowed probing for heterogeneity [4]. The relationships between T_2 relaxation and the mechanical (Young modulus) or adhesive (peel strength) properties were investigated [4]. Further work is in progress to monitor the synthesis of these biobased polyamide adhesives, as well as to assess their chemical resistance and degradation mechanisms.

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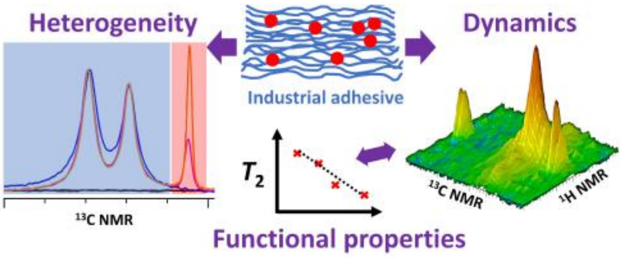
Invited article for themed collection: Polymer Chemistry Pioneering Investigators 2021



Solid state nmr to understand function.jpg

Direct defluorinative amination of fluoropolymers by lithium alkylamides

Thursday, 27th April - 10:45: Oral Session 12-2 - Oral

Prof. Guillaume HERLEM [1]***, Dr. Yaëlle Roina*** [2]***, Prof. Fabien Picaud*** [1]***, Prof. Hélène Cattey*** [3]***, Dr. Mathieu Frégnaux*** [4]***, Prof. Anne-Marie Gonçalves*** [4]***, Prof. Frédéric Auber*** [1]

1. *Nanomedicine lab EA 4662, UFR Sciences & Techniques, Besançon, France,* ***2.*** *Nanomedicine,* ***3.*** *Institut de Chimie Moléculaire de l'Université de Bourgogne (ICMUB), UMR 6302, Université de Bourgogne, Dijon, France,* ***4.*** *Institut Lavoisier de Versailles, UVSQ, UMR CNRS 8180, Versailles France*

Introduction

Fluoropolymers (F-polymers) are widely used in many industrial applications. Their functionalization allows keeping their remarkable bulk properties (chemical, thermal and mechanical stability, mainly) by modifying only their surface. But it is challenging due to their chemical inertness. Here, we demonstrate that lithium alkylamides can reduce very stable C-F bonds and substitute fluorine by the organic moiety of the lithium alkylamide salt by a one-pot experimental process. This generalization of the Benkeser-like reaction is applied to polytetrafluoroethylene (PTFE), poly(vinylidene fluoride) (PVDF) and Nafion as a proof of feasibility.

Methods

Lithium alkylamides are formed (with hydrogen evolution) by the reaction between lithium and an aliphatic di- or triamine such as ethylenediamine(EDA), diethylenetriamine (DETA) and 1,3-diaminopropane (DAP) to form LiEDA, LiDETA and LiDAP, respectively.

The chemical modifications of F-polymers by lithium alkylamides were carried out in a glovebox under argon stream (O_2 and H_2O concentration less than 1 ppm). For each material, the identical following one-pot experimental process is applied as following. The reaction consists of immersing the material in the amine and adding the lithium. When lithium is below the stoichiometric proportions with the amine, the lithium alkylamide is formed extemporaneously and reacts with the F-polymer immediately. The solvent is not entirely consumed, which ensures a good liquid-solid contact. The surfaces of PTFE, PVDF or Nafion quickly change irreversibly and takes on a blackish colour.

Results

Defluorinated and aminated surfaces of PTFE, PVDF and Nafion were examined by several techniques such as contact angle, XPS, IR-ATR on Ge crystal, SEM. All these techniques shows the elimination of fluorine and the presence of amino groups on the surfaces. The reaction between LiEDA and PTFE or Nafion were modelized by AIMD calculations in order to clarify the reaction mechanism.

Discussion

Direct defluorinative amination of F-polymers is achieved quickly in one-pot synthesis in mild condition (20°C, 1 bar) under argon atmosphere by a lithium alkylamide salt in a di- or triamine (Figure). Defluorination and amination steps do not occur simultaneously, and the whole reaction follows a nucleophilic substitution S_N1.

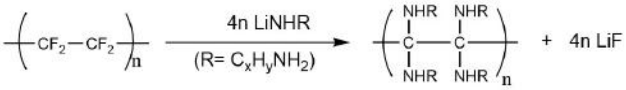


Figure.jpg

Synthesis of diblock and triblock polymers via miniemulsion ROMP

Thursday, 27th April - 09:30: Oral Session 12-3 - Oral

Prof. Michael Cunningham [1], ***Dr. Olga Lidia Torres Rocha*** [1], ***Prof. Cathleen Crudden*** [1]

1. *Queen's University*

Introduction Ruthenium-based metathesis catalysts are employed extensively in ring opening metathesis polymerization (ROMP) due to their remarkable tolerance to air, moisture, and functional groups. These features have propelled ROMP-based polymers into many fields such as biomaterials, liquid crystalline polymers, self-healing materials, degradable plastics, and nanocomposites. However, comparatively little attention has been given to conduct ROMP in aqueous dispersions, despite the numerous advantages they offer.

Methods Ring opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene (COD) and norbornene (NB) in miniemulsion was conducted utilizing a water soluble TEGylated ruthenium alkylidene catalyst that was designed to undergo phase transfer from the aqueous phase to the monomer droplets or polymer particles following activation (**Figure 1**). This new catalyst design enabled the synthesis of both COD and NB latexes via miniemulsion polymerization, yielding highly stable latexes. By sequential monomer addition, we were also able to make diblock and triblock copolymers, and even to extend the process to polymerization-induced self-assembly (PISA).

Results Ring opening metathesis polymerization (ROMP) of COD and NB in miniemulsion was conducted utilizing a water soluble TEGylated ruthenium alkylidene catalyst that was designed to undergo phase transfer from the aqueous phase to the monomer droplets or polymer particles following activation. Our new TEGylated ruthenium alkylidene catalyst yielded colloidally stable latexes of both poly(COD) and poly(NB) with ~100% conversion, often in less than one hour. Kinetic studies revealed first-order kinetics with good livingness. Depending on the surfactants used, the particle sizes ranged from 100 to 300 nm with monomodal distributions. Different block copolymers were also synthesized yielding PCOD-*b*-PNB, PNB-*b*-PCOD and PCOD-*b*-PNB-*b*-PCOD. Polymerization–induced self-assembly (PISA) involves the synthesis of amphiphilic block copolymers: a hydrophilic block is first polymerized homogeneously in water followed by polymerization of a second hydrophobic block, resulting in a diblock copolymer that self-assembles into nanoparticles. A water-soluble modified-norbornene monomer was polymerized in water, then 1,5-cyclooctadiene (COD) was added to produce amphiphilic block polyolefins.

Discussion Our results demonstrate that is possible to obtain nanoparticle latexes from ROMP-based monomers with block copolymer architectures, creating the opportunity to copolymerize olefins bearing different functional groups for the synthesis of new materials.

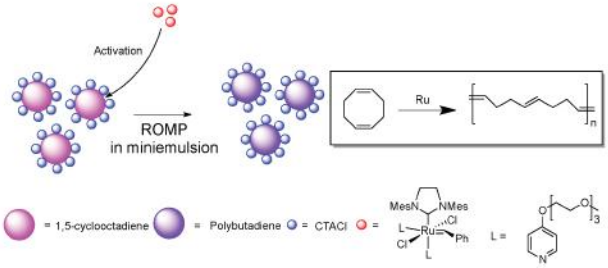

Activation
ROMP
in miniemulsion
Ru
n
= 1,5-cyclooctadiene
= Polybutadiene
= CTACl
=
MesN
NMes
Cl
L
Ru
Ph
Cl
L
L =
O
O
3
N

Figure 1.png

Polymer synthesis and functionalisation using electrochemistry

Thursday, 27th April - 10:00: Oral Session 12-3 - Oral

Dr. Paul Wilson [1]

1. *University of Warwick*

Electrochemical intervention in synthesis and catalysis has received renewed interest over the last 5 – 10 years. It can confer spatiotemporal control over electron transfer processes that have been exploited to drive chemical reactions, thus enabling the synthesis of small and macromolecular organic molecules/polymers, amongst others. From a synthetic point of view, the direct use of electrons can enhance selectivity of chemical transformations, whilst from a process point of view, the use of electrons derived from sustainably generated power (solar, wind, water, etc), also significantly improves sustainability and reduces the carbon footprint of analogous chemically-driven processes/reactions. Thus, we have been exploring the use of electrochemistry to synthesise and functionalise polymer scaffolds. Here, our investigations into electrochemical ATRP will be described. Furthermore, an electrochemical Hoffmann reaction (eHoffmann), whereby primary amides are employed as surrogates for isocyanates, to functionalise acrylamide (co) polymers with nucleophilic reagents (e.g. alcohols and amines) will be introduced. Successful functionalisation of these scaffolds has led to the preparation and characterisation of a library of novel polyvinyl carbamate (co)polymers, the properties of which have been previously unexplored.

A Design-Led Synthesis of Conjugated, Polyelectrolyte and Hybrid Porous Polymers by Concentrated Emulsions

Thursday, 27th April - 10:15: Oral Session 12-3 - Oral

Prof. Sebastijan Kovačič [1] ***, Mr. Tomaž Kotnik*** [1] ***, Dr. Sarah Jurjevec*** [1]

1. *National Institute of Chemistry*

Emulsion-templating is gaining increasing attention as a technique for producing porous polymers. Among the most interesting emulsion templates are highly concentrated or high-internal-phase-emulsions (HIPEs), which after polymerization usually form monolithic polymer foams referred to as polyHIPE (PH). The main advantage of PHs, is the tunability of their porous properties, i.e., pore volume, size, and interconnectivity, simply by manipulating the emulsion system with changes in phase volume ratio, surfactant, or polymerization chemistry.(1)
In the virtue of the design possibilities offered by emulsion-templating, we would like to discuss various PHs, i.e., π-conjugate, polyelectrolyte, and hybrid systems. The π-conjugated and polyelectrolyte PHs are based on poly(arylene-ethynylene), poly(arylene-cyano-vinylene), poly(imine), or linear aliphatic poly(azine) networks and were synthesised by Sonogashira-Hagihara,(2) Knoevenagel,(3) or Schiff base(4) condensation reactions in the continuous phase of oil-in-oil HIPEs. On the other hand, hybrid PHs were prepared by the hydrosol-in-oil HIPEs as structural templates, in which the polymerization of monomers in the external phase and the hydrolytic condensation of tetramethyl orthosilicate in the internal phase take place simultaneously, resulting in a highly porous PH structure homogeneously filled with silica aerogel.(5)
These results clearly demonstrate that emulsion-templating is indeed a versatile platform for exploring new polymerization chemistries for PH synthesis or developing novel (hierarchically) porous architectures.

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(5) S. Kovačič et al., Chem. Eng. J., 2022, 450, 138251.

Novel Conjugated Polymers with High Porosity: Eco-Friendly Synthesis Methods

Thursday, 27th April - 10:30: Oral Session 12-3 - Oral

Mr. Tomaž Kotnik [1], ***Prof. Sebastijan Kovačič*** [1]

1. National Institute of Chemistry

In recent years, there has been a growing interest in the development of highly-porous conjugated polymers due to their unique properties and potential applications in fields such as energy storage, catalysis, and organic electronics.[1] However, the synthesis of conjugated polymers, usually by Suzuki, Sonogashira, or Yamamoto cross-couplings, requires the use of transition metal catalysts such as Pd, Rh, or Ni and large quantities of high-boiling solvents such as N,N-dimethylacetamide (DMAc), toluene, or dimethylformamide (DMF). These factors drive costs, affect sustainability, and limit large-scale production.[2]

With the growing consumption and production of energy devices, where CPPs have emerged as a new class of materials, it is important to consider environmentally friendly routes for their synthesis. In this discussion, we will present metal-free and water-based reactions for the preparation of CPPs through emulsion-templating. These sustainable synthesis routes involve Knoevenagel[3] or Schiff-base[4] condensations as metal-free reactions and, e.g., vegetable oil-in-water high internal phase emulsions (HIPEs) as structural templates.

The versatility of this synthetic pathway is demonstrated, and three different classes of conjugated scaffolds, including aerogels, polyHIPEs, and carbonized polyHIPES (referred to as carboHIPE), were prepared. Finally, by taking advantage of the light-harvesting ability of our conjugated systems, we have tested various photocatalytic reactions, such as the degradation of organic pollutants in water and the synthesis of valuable compounds, which we will also be discussed.

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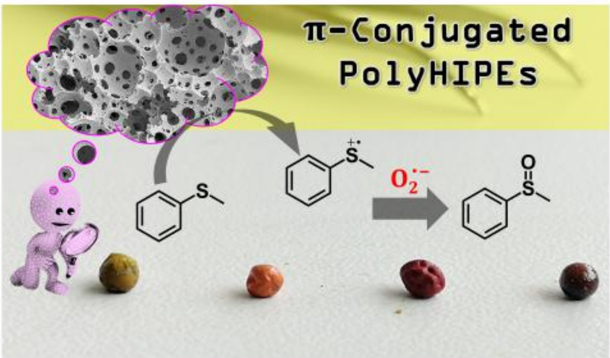

Conjugated polyhipe beads as heterogeneous photocatalysts.jpg

Electrochemical properties of redox-active polymer nanogels on the base of TEMPO-modified PNIPAM

Thursday, 27th April - 10:45: Oral Session 12-3 - Oral

Dr. Elena Kozhunova [1], ***Dr. Elena N. Govorun*** [2], ***Ms. Alina Inozemtseva*** [3], ***Mr. Mikhail Nazarov*** [3], ***Mr. Anatoly Nikolenko*** [1], ***Dr. Daniil Itkis*** [3], ***Dr. Alexander Chertovich*** [3]

1. *Lomonosov Moscow State University,* ***2.*** *Lomonosov Moscow State University, Russia & ESPCI Paris,* ***3.*** *Semenov Research Center of Chemical Physics*

Currently, flow batteries are one of the promising devices for use in large stationary energy storage systems, due to their scalability and relatively low cost. There is a trend of transition from traditional inorganic redox systems (for example, based on vanadium or zinc) to improved organic systems [1]. Replacing redox systems based on expensive and often toxic inorganic metal compounds with redox-active organic compounds can contribute to the creation of cheaper, environmentally friendly, and safe flow batteries.

The use of high-molecular-weight (polymeric) systems with “attached” redox-active groups can significantly reduce the requirements for membrane materials, up to the use of dialysis membranes with submicron or even micropores [2].

In this work, we propose an approach that involves the use of weakly cross-linked submicron-sized polymer networks (so-called microgels and nanogels) as redox-active systems [3]. Such systems have a low viscosity characteristic of micellar or colloidal solutions, while the concentrations of redox active groups can be as high as for linear polymer systems. Another advantage is the use of aqueous medium as a solvent.

We synthesized microgels based on poly-N-isopropylacrylamide (PNIPAM) modified with redox-active groups of (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) derivatives and studied its electrochemical properties in aqueous solution. According to the light scattering data, these microgels have a rather narrow size distribution, with an average diameter of 80 nm. The electrochemical properties were investigated in a three-electrode electrochemical cell on a glassy carbon working electrode. It was shown that such polymeric microparticles have electrochemical activity and are capable of being reversibly charged and discharged. Using the methods of cyclic voltammetry, the effective diffusion coefficient of microgel particles and the effective concentration of redox centers involved in the electrochemical reaction were determined.

This work was supported by the Russian Science Foundation (project no. 22-13-00115).

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