

# 48<sup>th</sup> International Colloquium of GFP

Polymers and light  
Polymer interfaces and (nano) composites  
Macromolecular and supramolecular engineering  
Polymers and sustainable development  
Polymer materials : from structure to properties

Monday - Friday  
25-29 november  
2019

Mulhouse, KinePolis Conferences Center

EAU LOURDE, Claire Morel - Amandine Sacquin © photographie Catherine Kohler

Email : [gfp2019.is2m@uha.fr](mailto:gfp2019.is2m@uha.fr)  
<https://gfp2019.sciencesconf.org>

 UNIVERSITÉ  
HAUTE-ALSACE





# Welcome

---

On behalf of the Board of Directors of the French Polymer Society (GFP), we warmly welcome you in Mulhouse to attend the 48<sup>th</sup> International Colloquium of GFP from 25 to 29 November 2019.

Located in the South of Alsace, Mulhouse is the second largest city in the Alsace region. The largest protestant building in France, the most prestigious car collection in the world, a unique collection of museums, the only Michelin-starred Italian restaurant in France, protected animals living in an exceptional Botanical garden, rehabilitated industrial zones, the largest market in eastern France, artisan boutiques, charming timber villages... these are only a few of the special attractions that make Mulhouse and the surrounding region an Alsatian destination that is unique, dynamic and surprising, attracting 2.5 million visitors per year.

Thanks to the privileged location of Mulhouse, at the border with Germany and Switzerland, this year, we wish to give a more international dimension to this meeting. Both highly renowned scientists and young scientists from academia and industry will present their most recent results in fields related to polymers (synthesis, characterization, processing, properties, applications).

Welcome to the 48<sup>th</sup> International Colloquium of GFP.

Have a fruitful and a pleasant stay in Mulhouse.

With warm regards,

For the local organizing committee.



Vincent Roucoules, Chair



# The colloquium

---

Colloquium schedule running from Monday, November 25<sup>th</sup> to Friday, November 29<sup>th</sup>. Each day will start with a Plenary Session and will continue with sessions with a total of 11 invited speakers, and 42 oral presentations. Five major topics will be addressed:

*Polymers and light*

*Polymer interfaces and (nano)composites*

*Macromolecular and supramolecular engineering*

*Polymers and sustainable development*

*Polymer materials: from structure to properties*

Following in the footsteps of the 2018 GFP edition, there will be four *3-min poster pitches sessions* for graduate students (Mon, Tues, Wed and Thu), *regular poster sessions* during lunch time will follow and an additional poster session is scheduled on Wednesday morning. The program also includes *two round tables* with recognized experts in their fields. The first round table will deal with “*open access publications*” and the second round table with the question of plastics “*the plastics: truths and untruths*”.

The GFP Prize, *the Grand Prix du GFP*, will be awarded to Professor Bernadette Charleux (Saint-Gobain). Professor Bernadette Charleux will give a lecture entitled “*From years dedicated to controlled free-radical polymerization in water to sustainable construction products at Saint-Gobain*” on Thursday, November 28<sup>th</sup>.

The conference booklet contains the detailed program, the list of oral and poster contributions, the list of awards and the list of our generous sponsors. The proceedings of all contributions are available on the GFP2019 website at [gfp2019.sciencesconf.org](http://gfp2019.sciencesconf.org). We thank all the colleagues involved in the organization of this colloquium, and all of you for contributing to exciting new developments and discoveries. Enjoy GFP2019, enjoy Mulhouse and France.



# The scientific international committee

---

Dr Jorg Baschnagel (Strasbourg, France)  
Dr Michel Bouquey (Strasbourg, France)  
Pr. Maurice Brogly (Mulhouse, France)  
Pr. Christophe Chassenieux (Le Mans, France)  
Pr. Jean-François Gérard (Lyon, France)  
Pr. Yves Grohens (Lorient, France)  
Dr Sophie Guillaume (Rennes, France)  
Dr Vincent Ladmiral (Montpellier, France)  
Pr. Jörg Lahann (Karlsruhe, Germany)  
Pr. François Lequeux (Paris, France)  
Pr. Rolf Mülhaupt (Freiburg, Germany)  
Dr Bastian Rapp (Freiburg, Germany)  
Pr. Günter Reiter (Freiburg, Germany)  
Pr. Vincent Roucoules (Mulhouse, France)  
Dr Julien Thuilliez (Clermont-Ferrand, France)  
Pr. Christop Weder (Fribourg, Switzerland)  
Pr. Manfred Wilhelm (Karlsruhe, Germany)  
Pr. Dominik Wöll (Aachen, Germany)

# The local organizing committee

---

Dr Stéphane Mery (IPCMS, Strasbourg)  
Dr Julien Poly (IS2M, Mulhouse)  
Dr Philippe Mesini (ICS, Strasbourg)  
Dr Eric Pollet (ICPEES, Strasbourg)  
Pr. Xavier Coqueret (ICMR, Reims)  
Dr Christelle Kowandy (ICMR, Reims)  
Dr Lavinia Balan (IS2M, Mulhouse)  
Dr Dimitri Ivanov (IS2M, Mulhouse)  
Dr Olivier Soppera (IS2M, Mulhouse)  
Dr Florence Bally-Le Gall (IS2M, Mulhouse)  
Dr Arnaud Spangenberg (IS2M, Mulhouse)  
Dr Abraham Chemtob (IS2M, Mulhouse)  
Dr Khalid Ferji (LCPM, Nancy)  
Philippe Kunemann (IS2M, Mulhouse)  
Dr David Ruch (LIST, Luxembourg)  
Pr. Boris Lakard (UTINAM, Besançon)  
Pr. Cécile Nouvel (LRGP, Nancy)  
Pr. Jacques Lalevee (IS2M, Mulhouse)  
Pr. Vincent Roucoules (IS2M, Mulhouse)  
Christelle Portier (IS2M, Mulhouse)  
Dr Fabrice Morlet-Savary (IS2M, Mulhouse)  
Dr Laurent Vonna (IS2M, Mulhouse)  
Isabelle Lefevre (SUAC UHA, Mulhouse)  
Viviane Breyer (SUAC UHA, Mulhouse)  
Nathalie Castelein (IS2M, Mulhouse)

## Student Staff committee

Vitalii Tkachenko  
Syrine Jebali  
Chloé Simet  
Alexandre Mau  
Jamerson Oliveira  
Florian Ponzio  
Emma Geisler  
Ching-fu Lin  
Quentin Kirscher  
Laurent Noël  
Mariem Ghali  
Chaima Brahmi  
Xingyu Wu  
Farid Kameche  
Rana Mhanna  
Nghia Le  
Mehdi Belqat  
Berengère Aubry  
Jihane Mzoughi





# Oral contributions



## Monday, November 25<sup>th</sup>

13.45 Opening Ceremony

### Macromolecular and supramolecular engineering - Session 1 -

*Chairs: Patrick Theato & Abraham Chemtob*

14.00 **Jean-François Lutz**

Digital Polymers: Emergence of a new class of macromolecules

14.40 **Stephen Schrettl**

Tunable and Responsive Supramolecular Polymer Materials

15.00 **Jean Raynaud**

Dynamic boron-based polymers & Networks for hydrogen storage

15.20 **Cecile Nouvel**

Submicronic emulsions produced by phase inversion temperature with polymeric surfactants

15.40 **Mirella Wawrzych**

Artificial Extracellular Matrix Design

16.00 3 min Poster Pitches - Session 1 -

16.25 Sponsor Pitch: Bruker

16.30 Coffee break

### Macromolecular and supramolecular engineering - Session 2 -

*Chairs: Jean-François Lutz & Abraham Chemtob*

16.50 **Patrick Théato**

New synthetic routes towards sulfur containing functional polymers

17.30 **Mathias Destarac**

Organotin raft agents: A range apart

17.50 **Vincent Monteil**

New trends in free radical polymerization of ethylene under moderate pressure conditions

18.10 **Vincent Ladmira**

Synthesis and self-assembly of PVDF-based block copolymers

18.30 **Delphine Chan-Seng**

Unexpected UCST behavior of cationic comb homopolymers in water

18.50 End of the day



# Digital Polymers: Emergence of a New Class of Macromolecules

Jean-François Lutz\*

a Université de Strasbourg, CNRS, Institut Charles Sadron UPR22, 23 rue du Loess, 67034 Strasbourg Cedex 2, France.

\* E-mail : [jflutz@unistra.fr](mailto:jflutz@unistra.fr)

## Abstract:

It has been shown in recent years that information can be stored at the molecular level in synthetic polymers.<sup>1, 2</sup> 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.<sup>3</sup> But of course such digital 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.<sup>4</sup> For instance, solid-phase iterative chemistry allows synthesis of a wide variety of uniform sequence-defined digital polymers.<sup>3, 4</sup> This approach is not restricted to oligomers and long digital chains containing more than 100 coded residues have been prepared.<sup>5</sup> Moreover, the information stored in these chains can be easily decoded by tandem mass spectrometry. As shown very recently, not only short but also long digital sequences can be deciphered using this analytical technique.<sup>6</sup> Furthermore, the information stored in the polymer chains can be edited using physical triggers such as temperature or light.<sup>7</sup>

Since multi-byte digital encryption and decryption of a synthetic polymer chain has now been clearly demonstrated, the next important challenge in this emerging field of research will be the application of such digital polymers in technological areas; for example for the development of molecular memories. However, such applications are quite demanding and imply to move from simple proofs-of-concept at the single-chain level to complex multi-chain libraries allowing storage and manipulation of larger amounts of information. 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. Specific emphasis will be put on the development of planar digital micro-arrays as well as on the three-dimensional organization of digital polymers.<sup>8</sup>

## References :

- [1] : Lutz, J.-F.; Ouchi, M.; Liu, D. R.; Sawamoto, M. *Science*, 341, 1238149 (2013)
- [2] : Colquhoun, H.; Lutz, J.-F. *Nat. Chem.*, 6, 455-456 (2014)
- [3] : Roy, R. K.; Meszynska, A.; Laure, C.; Charles, L.; Verchin, C.; Lutz, J.-F. *Nat. Commun.*, 6, 7237 (2015)
- [4] : Lutz, J.-F.; Lehn, J.-M.; Meijer, E. W.; Matyjaszewski, K. *Nat. Rev. Mater.*, 1, 16024 (2016)
- [5] : Al Ouahabi, A.; Kotera, M.; Charles, L.; Lutz, J.-F. *ACS Macro Lett.*, 4, 1077-1080 (2015)
- [6] : Al Ouahabi, A.; Amalian, J.-A.; Charles, L.; Lutz, J.-F. *Nat. Commun.*, 8, 967 (2017)
- [7] : König, N. F.; Al Ouahabi, A.; Oswald, L.; Szweda, R.; Charles, L.; Lutz, J.-F. *Nat. Commun.*, 10, 3774 (2019)
- [8] : Szweda, R.; Tschopp, M.; Felix, O.; Decher, G.; Lutz, J.-F. *Angew. Chem., Int. Ed.*, 57, 15817-15821 (2018)

# Tunable and Responsive Supramolecular Polymer Materials

Stephen Schrettl<sup>\*a</sup>

<sup>a</sup> *Adolphe Merkle Institute, University of Fribourg – Switzerland*

\* Email address

## Abstract:

The assembly of monomeric units equipped with binding motifs that form directional, non-covalent interactions such as hydrogen bonds or metal-ligand coordination complexes furnishes supramolecular polymers.[1] Stimuli such as heat, light, mechanical force, or certain chemicals disrupt the reversible and dynamic linkage, leading to a (temporary) disassembly into the monomers and pronounced changes of the materials properties.[2] This renders supramolecular polymers uniquely suited for the development of materials with useful functions such as healing, chromism, changes in shape, or reversible adhesion.[3,4] However, on account of the low glass transition temperature ( $T_g$ ) of the typically employed building blocks, most supramolecular polymers display mechanical properties comparable to elastomers.

In this presentation, we report how metallosupramolecular polymers with mechanical properties comparable to those of commodity plastics can be obtained by blending a semicrystalline component with a rubbery one.[5] Both components feature the same metal-ligand complexes, which leads to a co-assembly into uniform blends. The mechanical properties of these materials are readily adjusted by varying the ratio of the two constituents. Some of the blends display a strength, toughness, or failure strain that substantially exceeds the one observed for either metallosupramolecular polymer alone, thereby granting access to mechanical properties that so far remained difficult to access with supramolecular materials. Moreover, to gain a deeper understanding of how metallosupramolecular polymers rearrange during healing processes, bulk investigations of healed samples were combined with an analysis of the network relaxation and the reshuffling at the interface.[6] The diffusion processes and growth of a mixed interphase was correlated with the healing efficiency, which establishes a first step toward a better understanding of such dynamic processes

## References :

- [1] : L. Yang; X. Tan; Z. Wang; X. Zhang, *Chem. Rev.* 2015, **115**, 7196–7239.
- [2] : M. A. C. Stuart; et al., *Nat. Mater.*, 2010, **9**, 101–113.
- [3] : K. M. Herbert; S. Schrettl; S. J. Rowan; C. Weder, *Macromolecules* 2017, **50**, 8845– 8870.
- [4] : C. Calvino; L. Neumann; C. Weder; S. Schrettl, *J. Polym. Sci. Part A* 2017, **55**, 640–652.
- [5] : J. Sautaux; I. Gunkel; F. Marx; C. Weder; S. Schrettl, Submitted.

# DYNAMIC BORON-BASED POLYMERS & NETWORKS FOR HYDROGEN STORAGE

Juliette Brunet, Audrey Ledoux, Matthieu Humbert, Lionel Perrin, Fabrice Brunel, Damien Montarnal, Emmanuel Lacôte, Jean Raynaud\*

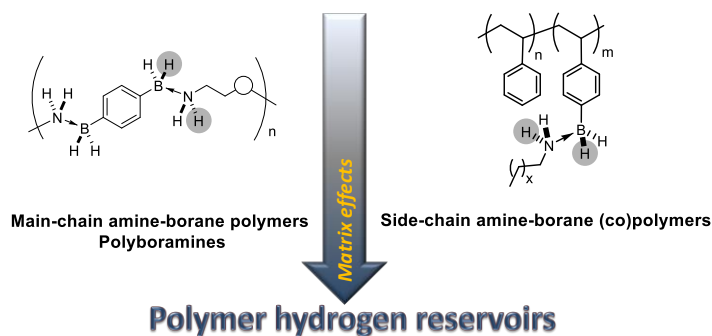
Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2) and ICMBS, LHCEP / Villeurbanne, France

\* jean.raynaud@univ-lyon1.fr

**Key-Words:** amine-boranes, dehydrogenation, Lewis pairs, dynamic networks, organoboron polymers.

## Abstract:

The inclusion of hydrogen-bearing Lewis pairs, i.e. amine-borane moieties ( $R-NH_2 \rightarrow BH_2-R'$ ) in polymeric scaffolds has been investigated as a template for promising hydrogen-storage material that temperature of hydrogen release could be adjusted depending on chosen parameters such as degree of functionalization, architecture and/or nature of the amine-borane moieties and usage in a blend with ammonia/borane. Dihydrogen storage and controlled release has become an essential area of research aspiring to answer the ever-growing energetic demand. If ammonia-borane ( $NH_3-BH_3$ ) was early on identified as a premium candidate to constitute a  $H_2$  reservoir, due to its maximum storage capacity (19.6 wt.%  $H_2$ ), [1] researchers have then identified its shortcomings such as uneasy trigger of smooth/controlled dehydrogenation without catalyst, poor processability and troublesome material recycling. [1] We have proposed to address these issues through the synthesis of new polymers containing the amine-borane motif inserted in a polymer scaffold, harnessing improvements brought by the polymer backbone on the reactivity and material properties. Polymers comprising boronate groups are excellent precursors to install the amine-borane motif and have been the focus of intensive research due to their unique properties associated with the electron deficiency of boron conferring reactivity harnessed *via* post-polymerisation through simple nucleophilic coordination at the boron vacancy. [2-6] We aimed at an ease of preparation, an enhanced processability but also an access to recyclable materials via simple re-hydrogenation techniques. We have synthesized these polymers from available organic building blocks, difunctional boronates [4] or copolymerization of boronate-functionalized styrene, [5,6] followed by one-pot treatment of either difunctional or monofunctional ammonium and corresponding boronates with  $LiAlH_4$  (see scheme). [4,5] We showed that the polymer-matrix dynamics have a drastic effect on kinetic and thermodynamic parameters of the dehydrogenation process, and in particular on the temperature of dehydrogenation. [4-6] We investigated the role of structural parameters on the reactivity and finally were able to design hybrid materials using borazane and amine-borane-containing polymer scaffolds with  $H_2$  loadings close to 8 wt.%.



**Aknowledgements:** ANR (Agence Nationale de la Recherche) is acknowledged for financial support (projects ANR-17-CE07-0006 and ANR-15-CE06-0001).

## References :

- [1] A. Staubitz, A. P. M. Robertson & I. Manners *Chem. Rev.* **2010**, *110*, 7
- [2] F. Jäkle *Chem. Rev.* **2010**, *110*, 3985
- [3] W. L. A. Brooks & B. S. Sumerlin *Chem. Rev.* **2016**, *116*, 1375
- [4] A. Ledoux, P. Larini, C. Boisson, V. Monteil, J. Raynaud\* & E. Lacôte *Angew. Chem. Int. Ed.* **2015**, *54*, 15744
- [5] A. Ledoux, J. Brunet, J. Raynaud\* & E. Lacôte *Angew. Chem Int. Ed.* **2019**; DOI: 10.1002/ange.201904898
- [6] J. Brunet, F. Collas, M. Humbert, L. Perrin, F. Brunel, E. Lacôte, D. Montarnal & J. Raynaud\* *Angew. Chem Int. Ed.* **2019**, *58*, 12216

# Submicronic emulsions produced by phase inversion temperature with polymeric surfactants

Martin Meulders<sup>a</sup>, André Barrizzelli Murino<sup>a</sup>, Véronique Sadtler<sup>a</sup>, [Cécile Nouvel](mailto:Cecile.Nouvel@univ-lorraine.fr)<sup>a,\*</sup>

<sup>a</sup> LRGP Laboratoire Réactions et Génie des Procédés, UMR CNRS-Université de Lorraine 7274, Nancy F-54000, France

\* cecile.nouvel@univ-lorraine.fr

**Key-Words:** Low-energy emulsification, Interfaces, Formulation, ATRP, Thermosensitive

## Abstract:

Nanoemulsions are remarkable for their high specific area and kinetic stability among others. They have many pharmaceutical or cosmetic applications for their high performances in drug delivery [1] and are often required as an intermediate for the formulation of nanocapsules [2]. Nevertheless, their making requires high mechanical energy input through traditional emulsification methods also called “high energy methods” [3]. Therefore, low-energy methods such as Phase Inversion Temperature (PIT) can be cost-effective alternatives for the production of nanoemulsions [4]. The principle of the PIT relies on the ability of a temperature-sensitive surfactant to shift its overall affinity from the aqueous phase of the emulsion [5] to the hydrophobic one with increasing temperature. Examples of PIT are reported with small commercially available surfactants but almost never for polymeric surfactants [6].

In this work, we have studied the PIT process on a dodecane/water system using various polystyrene-*b*-poly(oligo(ethylene glycol) methyl ether methacrylate) (PS-*b*-POEGMA) as surfactants. A two-step synthetic pathway using the Atom Transfer Radical Polymerisation was adapted from the literature [6, 7] to synthesize the copolymers with various molecular weights and POEGMA/PS weight ratios. To monitor PIT process, emulsification was carried out under a constant temperature rise and under gentle stirring in a rheometer with a helical ribbon, equipped with conductivity and temperature probes (figure 1 a) as set up before in our laboratory [8]. The potential of such surfactants in PIT process and to produce nanoemulsions was investigated and compared to a model small surfactant (Brij30). The design of the copolymer (molecular weight, hydrophilic/hydrophobic ratio) and the number of cycles have shown to be crucial to control the performances of the PIT process.

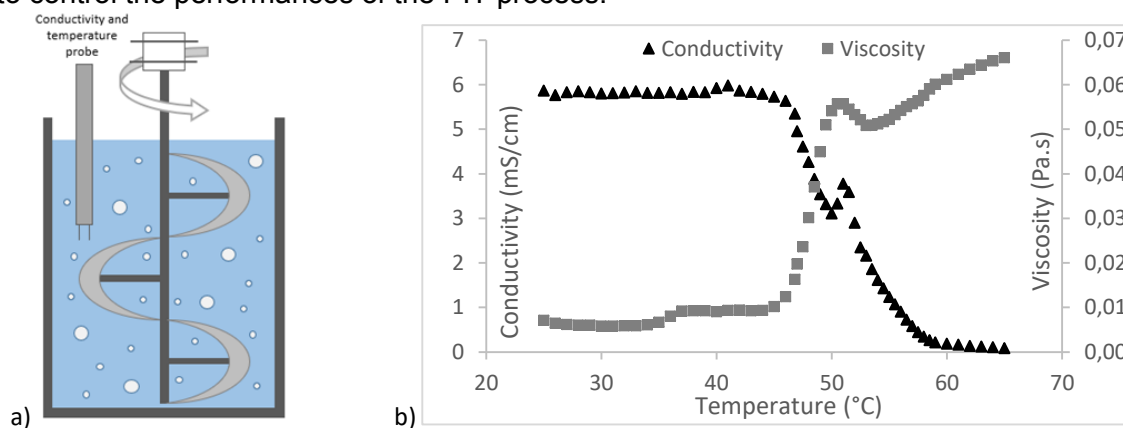


Figure 1. Conductivity and viscosity monitoring of the PIT a) Experimental setup b) Example of results with dodecane/water system using one PS-*b*-POEGMA surfactant ( $M_w = 17\,500$  g/mol,  $D=1.4$ ).

## References :

- [1] : S. Yuvraj, G.M. Jaya, R. Kavita, A.K. Farooq, C. Mohini, K.J. Nitin, C. Manish, *J. Control Release*, 2017 **252**, 28-49
- [2] : L.M. Forero, J. Babin, A. Durand, J-L Six, C. Nouvel, *Colloids and Surfaces A*, 486 (2015) 60–68; N. Anton, J.P. Benoit, P. Saulnier. *J. Control Release*, 2008, **128**, 185-199
- [3] :M. Jaiswal, R. Dudhe, P.K. Sharma, *Biotech.*, 2015, **5**, 1273-1277
- [4] : M.I. Guerra-Rosas, J. Morales-Castro, L.A. Ochoa-Martinez, L. Salvia-Trujillo L, O. Martin-Belloso, *Food Hydrocoll.*, 2016, **52**; 438– 446
- [5] :C. Solans, I. Solé, *Curr. Opin. Colloid Interface Sci.*, 2012, **17**, 246–254.
- [6] :Y. Sasaki, N. Konishi, M. Kasuya, M. Kohri, T. Taniguchi, K. Kishikawa, *Colloids Surf. Physicochem. Eng. Asp.*, 2015, **482**, 68–78
- [7] :W. Jakubowski, K. Min, K. Matyjaszewski, *Macromolecules*, 2006, **39**,39-45
- [8] :J. Allouche, E. Tyrode, V. Sadtler, L. Choplin, J.L Salager, *Langmuir*, 2004, **20**, 2134-2140



# Artificial Extracellular Matrix Design

Mirella Wawryszyn <sup>a</sup>, Dylan Neale <sup>b</sup>, Joerg Lahann <sup>\*c</sup>

<sup>a</sup> Soft Matter Synthesis Laboratory, Institute for Biological Interfaces 3 (IBG-3), Karlsruhe Institute of Technology (KIT), Campus North, Hermann-von-Helmholz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

<sup>b</sup> University of Michigan, 2800 Plymouth Road, Ann Arbor, MI 48109, USA

<sup>c</sup> Director of the Biointerfaces Institute, Professor of Chemical Engineering, Materials Science and Engineering, Biomedical Engineering, and Macromolecular Science Engineering

University of Michigan, 2800 Plymouth Road, Ann Arbor, MI 48109, USA

Head of the Soft Matter Synthesis Laboratory, Institute for Biological Interfaces 3 (IBG-3)

Karlsruhe Institute of Technology (KIT), Campus North, Hermann-von-Helmholz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

\* lahann@umich.edu

**Key-Words:** Extracellular matrix, biomacromolecular networks, fibrillar fibronectin, hyaluronic acid, bioconjugation

## Abstract:

The extracellular matrix (ECM) is a non-cellular biomaterial composed of water, proteins, and polysaccharides where specific tissue niches are characterized by an ECM with unique composition, topology, as well as mechanical properties.[1] Efforts in mimicking the ECM by engineering bio-macromolecular networks were made since decades and is still a worthwhile goal for translatable in vitro cell studies and biomedical applications such as cell biology or tissue engraftment.[2] However, engineering analogs remains challenging due to the tremendous variation of topological features, heterogeneity as well as chemical compositions and physical properties. A crucial factor in ECM design is determined by currently available engineering technologies, providing an elastic, insoluble, still bioactive and fibrillar framework of proteins – and a polyanionic polysaccharide hydrogel at the same time.

By mimicking natural fibrillogenesis on supported polymer scaffolds utilizing a shear-induced process we developed an artificial ECM 3-D fibrillar framework by applying fibronectin (Fn) as an ECM protein.[3] Moreover, we extended our 3-D platform into a two-component system by incorporating chemically modified hyaluronic acid (HA) as an ECM polysaccharide, essential for the matrices' hydrogel formation, withstanding compressive forces and being involved in essential biological functions and cell processes. Both biomaterials were covalently bonded via disulfide bridges undergoing a thiol-disulfide interchange reaction and therefore specifically addressing the Fn's free-thiol cysteine moieties. The insertion of the pyridyl disulfide moiety at the glycopolymer was performed through a triazine-activated amidation reaction with adjustable substitution degree. Topographical features were analyzed through high resolution scanning electron micrographs as well as laser scanning confocal micrographs (LSCM) confirming the presence of homogeneously distributed HA on Fn fibrils (see Figure 1).

Our ECM frameworks showcase a next-generation 3D cell culture platform tunable towards more complexity incorporating distinct ECM proteins such as collagen, elastin as well as glycosaminoglycans whereby ensuring high precision and reproducibility, adaptable on multiscale and high throughput techniques.

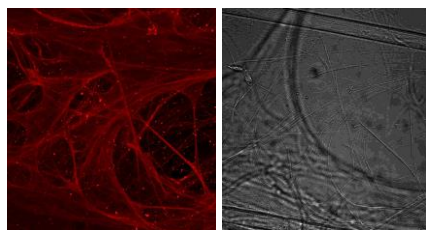


Figure 1: 3-D fibrillar framework of conjugated HA-Fn biomaterial; (left) LSCM visualization via fluorescent hyaluronic acid binding protein staining; (right) HA-Fn network under brightfield.

## References:

- [1] V. M. Weaver, *Journal of Cell Science*, 2010, **123**, 4195-4200.  
 [2] R. A. Clark, *Tissue Engineering*, 2006, **12(3)**, 601-613.  
 [3] J. Lahann, *Advanced Materials*, 2019, in press.

# New Synthetic Routes towards Sulfur Containing Functional Polymers

[Patrick Theato](#),<sup>\*a,b</sup> Hatice Mutlu,<sup>b</sup>

<sup>a</sup>*Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Engesserstraße 18, 76128 Karlsruhe, Germany*

<sup>b</sup>*Soft Matter Synthesis Laboratory, Institute for Biological Interfaces III, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

\* E-mail : [patrick.theato@kit.edu](mailto:patrick.theato@kit.edu)

**Key Words:** thioacetals; thiosulfonates; polymers; sulfur copolymers

## Abstract :

Functional polymers are based on certain chemical functional groups. As such, the inspiration from organic chemistry has always been fruitful to the development of new synthetic routes to functional polymers. In this regard, sulfur and particular its functional groups have been major players in this area of exciting research, and further have been utilized for the design and preparation of polymeric materials that lead to a plethora of applications.[1] Herein, we present our recent developments on the synthesis of polymers that derive their functionality from sulfur in the form of oligosulfides, thioacetals, [2] thiosulfonates, [3] as well as thiocarbonates.

Respectively, to realize this aim, we have developed new and efficient synthetic protocols that allow the preparation of polymers utilizing new synthetic routes towards thioacetals and thiosulfonates. Synthetic advantages as well as limitations will be discussed. Last but not least, the grand aim to underpin the importance of sulfur in modern polymer chemistry and materials science will be presented by selected first investigations towards applications.

## References :

[1] : Mutlu, H.; Ceper, E. B.; Li, X.; Yang, J.; Dong, W.; Ozmen, M. M.; Theato, P. Sulfur Chemistry in Polymer and Materials Science. *Macromol. Rapid Commun.* **2019**, *40*: 1800650.

[2] : Mutlu, H.; Theato, P. Synthesis of polythioacetals. *to be submitted*.

[3] : Sehn, T.; Mutlu, H.; Theato, P. Polythiosulfonates: A new synthesis route. *to be submitted*.

# ORGANOTIN RAFT AGENTS : A RANGE APART

I. KULAI <sup>1 a,b</sup>, Z. VOITENKO <sup>b</sup>, S. MAZIERES <sup>\*a</sup>, M. DESTARAC <sup>\*a</sup>

<sup>a</sup> IMRCP, UMR 5623, Université de Toulouse, 118, route de Narbonne F-31062 Toulouse, Cedex 9, France

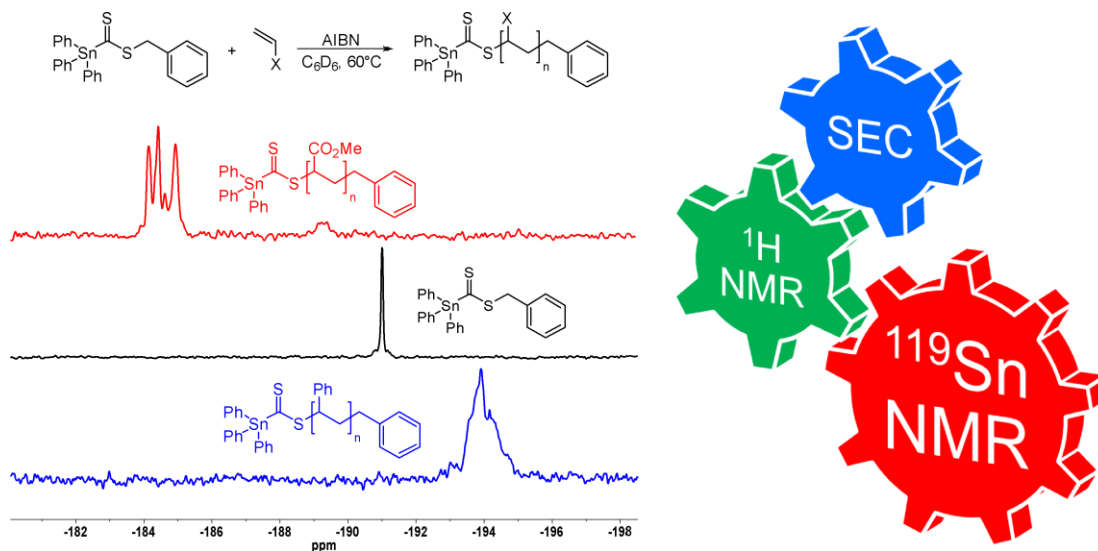
<sup>b</sup> Taras Shevchenko National University of Kyiv, Department of Chemistry, 64/13, Volodymyrska Street, Kyiv, Ukraine 01601

\* [mazieres@chimie.ups-tlse.fr](mailto:mazieres@chimie.ups-tlse.fr); [destarac@chimie.ups-tlse.fr](mailto:destarac@chimie.ups-tlse.fr)

**Key-Words:** organotin, RAFT, polymer, NMR

## Abstract:

A range of triaryltin-based reversible addition-fragmentation chain-transfer (RAFT) agents [1,2] is described and evaluated for the polymerization of acrylamides, acrylates and styrene. These organometallic compounds are highly reactive reversible transfer agents which allow an efficient control of the polymerization of substituted acrylamide monomers, whereas RAFT control for methyl acrylate and styrene polymerization is contaminated by side reactions. The Sn-RAFT chain end appears to be thermally unstable, and degrades over prolonged reaction times. The kinetics and mechanism of degradation is studied with model reactions by simply heating the starting Sn-RAFT agents at different T between 60°C and 110°C. This study helped us to define low temperature conditions (T=30°C) for which the control of the polymerization was greatly improved. <sup>119</sup>Sn NMR is showed to be an informative instrument for the monitoring of Sn-RAFT-mediated model reactions and polymerizations. Sn-RAFT polymerization is one of the few examples of a reversible-deactivation radical polymerization process where heteronuclear NMR allows observation of an initialization step, determination of chain transfer constants and the revelation and identification of RAFT agent decomposition products.



*Sn-RAFT polymerization*

## References :

- [1] :I. Kulai, O. Brusylovets, Z. Voitenko, S. Harrisson, S. Mazières, M. Destarac, *ACS Macro Lett*, 2015, **4**, 809-813.  
 [2] :I. Kulai, N. Saffon-Merceron, Z. Voitenko, S. Mazières, M. Destarac, *Chem. Eur. J.* 2017, **23**, 16066-16077.

# NEW TRENDS IN FREE RADICAL POLYMERIZATION OF ETHYLENE UNDER MODERATE PRESSURE CONDITIONS

Vincent Monteil,\* Guilhem Billuart, Etienne Grau, Arne Wolpers, Cédric Bergerbit, Florian Baffie, Franck D'Agosto, Muriel Lansalot, Elodie Bourgeat-Lami, Fabrice Brunel

Université de Lyon, Univ. Lyon 1, CPE Lyon, CNRS, Laboratoire de Chimie Catalyse Polymères et Procédés (C2P2) / Villeurbanne, France

\* Vincent.Monteil@univ-lyon1.fr

**Key-Words:** Polyethylene, Controlled Radical Polymerization (CRP), Block Copolymers, Emulsion, Nanoparticles.

## Abstract:

Polyethylenes (PEs) are the most industrially produced polymers. Low density polyethylene (~20 % PE) is produced by free radical polymerization under severe conditions ( $P > 1000$  bars and  $T > 200^\circ\text{C}$ ). In 2010 we reported that it is still possible to innovate in free radical polymerization of ethylene.[1]

By an appropriate choice of polymerization organic solvent (in particular the use of polar solvent such as THF or carbonates) we demonstrated the feasibility of the polymerization of ethylene under slurry conditions at moderate pressure (50-250 bar) and low temperature ( $< 80^\circ\text{C}$ ). Polymerization medium is multiphasic because of low critical point of ethylene.[2] An organization of ethylene molecules due to the presence of polar solvents was found to explain rather high activities at moderate pressures as recently evidenced by theoretical calculations.

Benefiting from this work the first examples of controlled radical polymerization of ethylene (CRPE) were also reported using reversible addition fragmentation (RAFT), tellerium-mediated (TERP) or Iodine transfer (ITP) polymerization techniques allowing more recently the synthesis of original polar-apolar olefins block copolymers.[3]

Alternatively free radical polymerization was also implemented in aqueous dispersed media.[4] This original emulsion process gives access to stable dispersions of PE nanoparticles exhibiting non-spherical morphologies. Unusual crystallization phenomena of PE located in the confined environment of nanoparticles were evidenced from DSC, DLS and synchrotron-SAXS/WAXS analyses.[4c] Various applications of these PE nanoparticles are thus envisaged such as phase change materials. They are also well suited as realistic models for studying degradation of PE waste accumulated in oceans.

**Acknowledgements :** ANR (Agence Nationale de la Recherche) is acknowledged for financial support (projects FRaPE; ANR-11- JS08 008 01 and Polar OBC: ANR-15-CE07-0015).

## References :

- [1] : a) Grau, E.; Broyer, J. P.; Boisson, C.; Spitz, R.; V. Monteil V. *Macromolecules* 2009, 42, 7279. b) Grau, E.; Broyer, J. P.; Boisson, C.; Spitz, R.; V. Monteil V. *Polym. Chem.* 2011, 2, 2328.  
 [2] : Grau, E.; Broyer, J. P.; Boisson, C.; Spitz, R.; V. Monteil V. *Phys. Chem. Chem. Phys.* 2010, 12, 11665.  
 [3] : a) Dommanget, C.; D'Agosto, F.; Monteil V. *Angew. Chem. Int. Ed.* 2014, 53, 6683. b) Nakamura, Y.; Ebeling, B.; Wolpers, A.; Monteil, V.; D'Agosto, F.; Yamago S. *Angew. Chem. Int. Ed.* 2018, 57, 305. c) Wolpers, A.; Bergerbit, C.; D'Agosto, F.; Monteil, V. *Angew. Chem. Int. Ed.* 2019 Early View, DOI 10.1002/anie.201905629.  
 [4] : a) Grau, E.; Dugas, P.Y.; Broyer, J.P.; Boisson, C.; Spitz, R.; Monteil V. *Angew. Chem. Int. Ed.* 2010, 49, 6810. b) Billuart, G.; Bourgeat-Lami, E.; Lansalot, M.; Monteil V. *Macromolecules* 2014, 47, 6591. c) Brunel, F.; Dugas, P.Y.; Billuart, G.; Bourgeat-Lami, E.; Lansalot, M.; Monteil V. *Macromolecules* 2017, 50, 9742.

# Synthesis and self-assembly of PVDF-based block copolymers

Enrique Folgado<sup>a, b</sup>, Mona Semsarilar<sup>a\*</sup>, [Vincent Ladmiral](mailto:Vincent.Ladmiral@enscm.fr)<sup>b\*</sup>

<sup>a</sup> IEM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

<sup>b</sup> ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

\* [Mona.semsarilar@umontpellier.fr](mailto:Mona.semsarilar@umontpellier.fr), [Vincent.Ladmiral@enscm.fr](mailto:Vincent.Ladmiral@enscm.fr)

**Key-Words:** Block copolymer, Self-assembly, PVDF

## Abstract:

Polyfluoroolefins such as polyvinylidene fluoride (PVDF) and its copolymers are an important class of semi-crystalline high added-value polymers, owing to their uncommon properties of chemical and ageing resistance as well as their superior electroactivity.<sup>1</sup> The preparation of well-defined polyfluoroolefin-based architectures such as block copolymers is not easy due to the peculiar reactivity of the fluorinated monomers. Recent studies of the RAFT polymerization of VDF showed how this chemistry could be harnessed to synthesize a large range of original block copolymers (BCP).<sup>2,3</sup> However, amphiphilic PVDF-based block copolymers are still very rare.<sup>4</sup> This communication will present recent advances in the macromolecular engineering of VDF-based materials allowing the preparation of amphiphilic di- and triblock copolymers. It will also show how these semicrystalline BCP can self-assemble in solution to form unprecedented higher-order morphologies via crystallization-driven self-assembly (Figure 1).

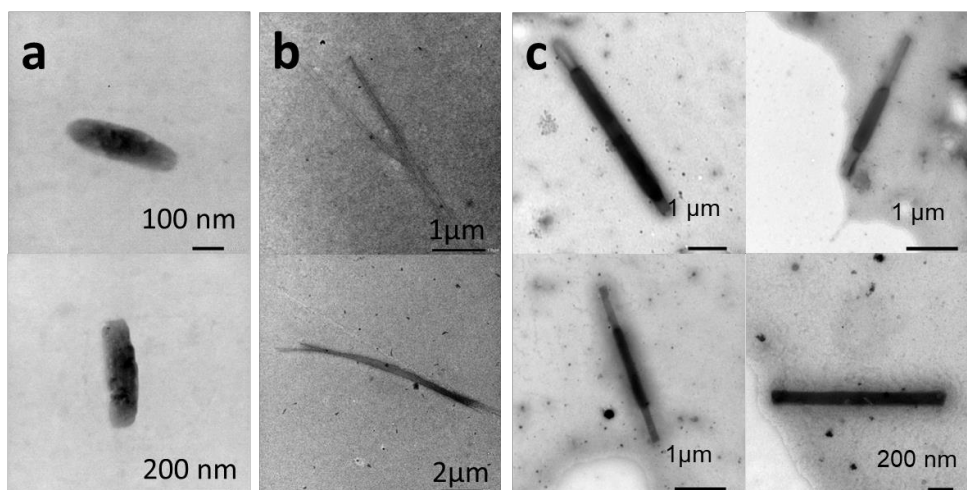


Figure 1. TEM images of the  $P(\text{VDF-co-HFP})\text{-}b\text{-PEG-}b\text{-P}(\text{VDF-co-HFP})$  triblock copolymer self-assembled structures in DMF (a and b) and in acetone (c)

## References :

- [1] : T. Soulestin; V. Ladmiral; F. Domingues Dos Santos; B. Améduri, *Progress in Polymer Science* 2017, **72**, 16-60.  
 [2] : M. Guerre; S.M. W. Rahaman; B. Améduri; R. Poli; V. Ladmiral, *Polymer Chemistry*, 2016, **7**, 6918-6933.  
 [3] : M. Guerre; M. Uchiyama; E. Folgado; M. Semsarilar; B. Améduri; K. Satoh; M. Kamigaito; V. Ladmiral *ACS Macro Letters* 2017, **6**, 393-398  
 [4] : M. Guerre; J. Schmidt; Y. Talmon; B. Amédurii ; V. Ladmiral, *Polymer Chemistry*, 2017, **8**, 1125-1128.

# Unexpected UCST behavior of cationic comb homopolymers in water

Nicolas Zydziak <sup>a</sup>, Muhammad Haseeb Iqbal <sup>a</sup>, Emeric Wasielewski <sup>b</sup>, Philippe Lavallo <sup>c</sup>,  
Fouzia Boulmedais <sup>a</sup>, Delphine Chan-Seng <sup>\*a</sup>

<sup>a</sup> Université de Strasbourg, CNRS, Institut Charles Sadron, F-67000 Strasbourg, France

<sup>b</sup> Université de Strasbourg, Université de Haute-Alsace, CNRS, Laboratoire d'innovation moléculaire et applications, F-67000 Strasbourg, France

<sup>c</sup> Université de Strasbourg, INSERM, Biomaterials and bioengineering, F-67000 Strasbourg, France

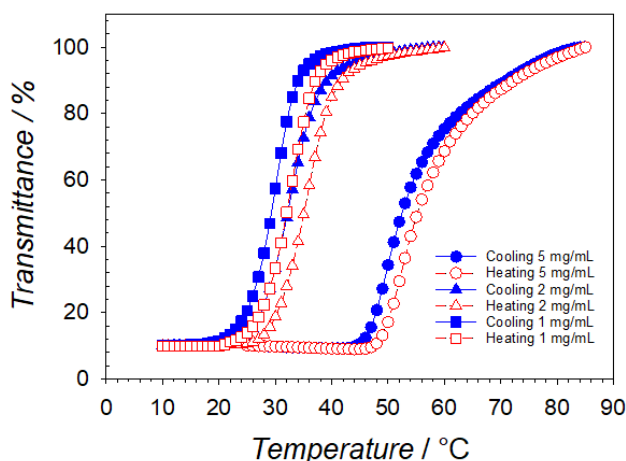
\* delphine.chan-seng@ics-cnrs.unistra.fr

**Keywords:** Thermoresponsive polymer, arginine, upper critical solution temperature

## Abstract:

Advances in the field of polymer chemistry have permitted to prepare polymers with controlled topologies, functionalities and microstructures using various strategies to access complex architectures (*e.g.* star, comb and hyperbranched polymers) with a variety of functional groups positioned at well-defined localizations on the polymer chain.[1] This ability to control the architecture and microstructure of polymers along with their functionalities are an asset to adjust the properties of polymers and tune their performances according to the targeted application.[2-3] The strategy chosen aims at combining natural and synthetic building blocks on macromolecules to tune their architectures and composition.[4] The approach discussed in this communication focuses on associating solid-phase peptide synthesis to prepare peptide-based macromonomers with traditional polymerization techniques such as reversible addition-fragmentation chain transfer (RAFT) polymerization for applications in the biomedical field (drug and gene delivery systems, antimicrobial materials, etc.).

This presentation will be illustrated by the synthesis of cationic comb polymers depicting an unexpected thermoresponsiveness (*i.e.* upper critical solution temperature, UCST). UCST phase transition is usually driven by hydrogen bond or Coulomb interactions.[5] In the case of Coulomb interactions, this behavior is observed for zwitterionic polymers or polyelectrolyte with specific salts (*e.g.* hydrophobic and multivalent counterions), which does not correspond to our system. This unexpected behavior of fully cationic polymers in water without any added salts will be discussed.



UCST behavior of comb polymer based on arginine by turbidimetry

## References :

- [1] : K. Matyjaszewski, *Prog. Polym. Sci.* 2005, **30**, 858-875  
 [2] : C. Zhu; C. Ninh; C. J. Bettinger, *Biomacromolecules* 2014, **15**, 3474-3494  
 [3] : N. Gangloff; J. Ulbricht; T. Lorson; H. Schlaad; R. Luxenhofer, *Chem. Rev.* 2016, **116**, 1753-1802  
 [4] : a) Parelkar S.S., Chan-Seng D., Emrick T. *Biomaterials* 2011, **32**, 2432; b) Chan-Seng, D.; Lutz, J.-F. *ACS Macro Lett.* 2014, **3**, 291-294  
 [5] : a) Seuring J., Agarwal S. *ACS Macro Lett.* 2013, **2**, 597-600; b) Niskanen J., Tenhu H. *Polym. Chem.* 2017, **8**, 220-232

## Tuesday, November 26<sup>th</sup>

### Polymer materials: From structure to properties - Session 1 -

*Chairs: Guillaume Fleury & Olivier Soppera*

- 8.30 **Sabine Ludwigs**  
Bioinspired multifunctional polymer films for polymer electronics applications
- 9.10 **Sébastien Clément**  
Cationic conjugated polythiophene for optoelectronic applications: Influence of counteranions
- 9.30 **Ernst Meyer**  
Preparation of molecular wires using on-surface chemistry
- 9.50 **Housseem Chabane**  
Fire behavior and morphology of epoxy-amine matrix designed by polyhedral oligomeric silsesquioxane-supported imidazolium ionic liquid (IL-g-POSSPh)
- 10.10 Coffee break

### Polymer materials: From structure to properties - Session 2 -

*Chairs: Sabine Ludwigs & Arnaud Spangenberg*

- 10.30 **Guillaume Fleury**  
Nanostructured thin films from block copolymer self-assembly: exquisite symmetries from macromolecular design
- 11.10 **Marianne Benoit**  
Self-oscillating polymer interfaces to design life-like pulsatile membranes
- 11.30 **Julien Crozzolo**  
Synthesis and study of associative water-soluble copolymers for enhanced oil recovery
- 11.50 **Antoine Hinaut**  
Electrospray deposition of molecules in ultra-high vacuum: building large molecular assemblies
- 12.10 **Farzad Ramezani**  
Entropy in stock in non-equilibrated polymer melts: translating molecular relaxation into lifting macroscopic weights
- 12.30 Lunch – POSTER SESSION

### Polymer materials: From structure to properties - Session 3 -

*Chairs: Ernst Meyer & David Ruch*

- 14.00 **Guillaume Sudre**  
Polysaccharide-based highly stretchable physical hydrogels obtained by interpolymer complexation
- 14.20 **Yvette Tran**  
Responsive hydrogel films for novel functionalities
- 14.40 **Dominik Wöll**  
Nanosopic imaging of functional, responsive microgels

15.00 **Benyahia Lazhar**

Study of thermos-induced behavior and rheological properties of hydrogels based on mixing bis-hydrophilic block copolymers with metallic ions

**Polymers and sustainable development - Session 1 -**

*Chair: Eric Pollet*

15.20 **Michael Meier**

Renewability is not enough: Sustainable approaches to monomers and polymers from renewable resources?

16.00 3 min Poster Pitches - Session 2 -

16.25 Sponsor Pitch: Xenocs

16.30 Pitch: Plastipolis

16.35 Coffee break

17.30 **Round Table - Plastics: Truths or untruths**

*Moderator: Dominique Siedlaczek*

Jacques Reis / Fabienne Lagarde / Thierry Yoh-Recham / Marie-France Vallat

*Campus La Fonderie (Amphi 1)*

19.30 End of the day



# Bioinspired Multifunctional Polymer Films for Electrochemical Devices

Sabine Ludwigs\*<sup>a</sup>

<sup>a</sup> *IPOC-Functional Polymers, Institute of Polymer Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart*

\* [sabine.ludwigs@ipoc.uni-stuttgart.de](mailto:sabine.ludwigs@ipoc.uni-stuttgart.de)

## Abstract:

The beauty and multifunctionality of nature have been a constant inspiration for chemists to mimic functionalities and hierarchical structures in man-made materials. Both, color and motion in plants are examples which can be - to some extent - replicated by stimuli-responsive functional polymers and materials thereof.

The field of expertise of my group are conducting polymer films which are optimized for organic field effect transistors and organic solar cells but also applicable in electrochemical devices. In the latter electronic and ionic charge transport are intimately linked with each other because counterions are needed to maintain electroneutrality when conducting polymers are doped.[1,2,3]

Going beyond neutral thiophene-containing polymers, we study their combination with polyelectrolytes both in blends, such as in poly(ethylenedioxythiophene) / poly(styrenesulfonate) (PEDOT/PSS), and in conjugated polyelectrolytes namely in poly(thiophen-hexane-1-sulfonate)-sodium (PTS-Na). These systems are multifunctional: 1) the electronic conductivity can be varied by the degree of doping and 2) humidity can be used to swell the polyelectrolyte phase which is accompanied by huge variations of the ionic conductivity.[4,5] As methods AC-impedance and dc measurements in combination with quartz crystal microbalance measurements are applied to decouple electronic and ionic conductivity as function of water uptake. First experiments towards actuating stimuli-responsive devices will be discussed as applications.

## References :

- [1] : P. Reinold, K. Bruchlos, S. Ludwigs, *Simultaneous Doping and Crosslinking of Polythiophene Films*, Polymer Chemistry 2017, **8**, 7351.
- [2] : Y. M. Gross, D. Trefz, C. Dingler, D. Bauer, V. Vijayakumar, V. Untilova, L. Biniek, M. Brinkmann, and S. Ludwigs, *From Isotropic to Anisotropic Conductivities in P(NDI2OD-T2) by (Electro-)Chemical Doping Strategies*, Chemistry of Materials, 2019, **31**, 3542.
- [3] : J. Heinze, B. Frontana-Uribe, S. Ludwigs, *The Electrochemistry of Conducting Polymers. Persistent Models, New Concepts*, Chemical Reviews 2010, **110**, 4724
- [4] : R. Merkle, P. Gutbrod, P. Reinold, M. Katzmaier, R. Tkachov, J. Maier, S. Ludwigs, *Mixed Conductivity of Polythiophene-based Ionic Polymers under Controlled Conditions*, Polymer 2017, **134**, 216.
- [5] : M. Wieland, C. Dingler, R. Merkle, J. Maier, S. Ludwigs, *Humidity-controlled water uptake and conductivities in ion and electron mixed conducting polymer films*, submitted.

# CATIONIC CONJUGATED POLYTHIOPHENE FOR OPTOELECTRONIC APPLICATIONS: INFLUENCE OF COUNTERANIONS

Michèle Chevrier<sup>a,b</sup>, Jurgen Kesters,<sup>c</sup> Judith E. Houston,<sup>d</sup> Sébastien Richeter,<sup>a</sup> Ahmad Mehdi,<sup>a</sup> Rachel C. Evans,<sup>e</sup> Wouter Maes,<sup>c</sup> Philippe Dubois,<sup>c</sup> Sébastien Clément<sup>\*a</sup>

<sup>a</sup> Institut Charles Gerhardt, University of Montpellier, 34095 Montpellier, France

<sup>b</sup> Laboratory for Polymeric and Composites Materials, Center for Innovation in Materials and Polymers, Research Institute for Science and Engineering of Materials, University of Mons – UMONS, 23 Place du Parc, B-7000 Mons, Belgium.

<sup>c</sup> Institute for Materials Research (IMO), Design & Synthesis of Organic Semiconductors (DSOS), Hasselt University, Agoralaan 1-Building D, B-3590 Diepenbeek, Belgium.

<sup>d</sup> European Spallation Source ERIC, Box 176, SE-221 00 Lund, Sweden

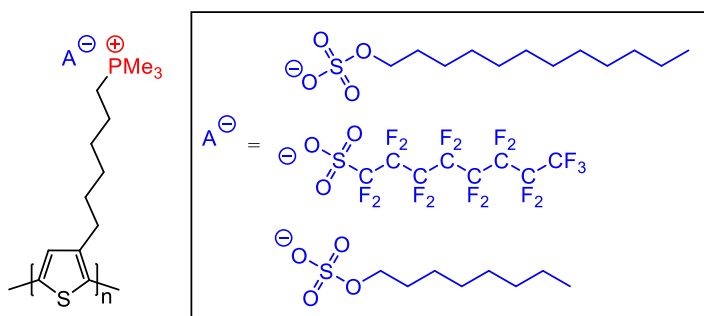
<sup>e</sup> Department of Materials Science & Metallurgy, University of Cambridge, 27 Charles Babbage Road, Cambridge, CB3 0FS, UK.

\*sebastien.clement1@umontpellier.fr

**Key-Words:** conjugated polyelectrolytes, counteranion, interfacial layers, solar cells

## Abstract:

Conjugated polyelectrolytes (CPEs) are defined as polymers with an extended  $\pi$ -conjugated backbone and ionic pendant groups, which combine the organic semiconductor properties and charge-mediated characteristics of polyelectrolytes in a single functional material.[1] Their unique optical and electronic properties have been successfully exploited in a wide range of polymer optoelectronic devices including organic photovoltaics or light emitting diodes.[2] Many structural components of CPEs, including the conjugated backbone, counterion, and appended ionic group have been found to influence their optoelectronic properties, their self-assembly in solution or their nanoscale morphology.[2,3] However, the relationship between their structure and their properties is still not well understood and necessitates further investigation. Herein, we describe the preparation of phosphonium-based conjugated polyelectrolytes with different counteranions (perfluorooctylsulfonate (PFOS), octylsulfate (OS) and dodecylsulfate (DS)) (Scheme 1) aiming at studying the influence of the nature of the counterions on their self-assembly in solution but also, their nanoscale morphology into thin films.[4-6] The correlation between the counteranion species of these CPEs and their photovoltaic properties will also be presented.[6]



Structure of phosphonium-based conjugated polythiophene with different counterions

## References :

- [1] : *Conjugated polyelectrolytes. Fundamentals and Applications* (Eds. B. Liu and G. C. Bazan), Wiley-VCH, Weinheim, 2013.
- [2]: W. Lee, J. H. Seo, H. Y. Woo, *Polymer* 2013, **54**, 5104-5121.
- [3]: J. E. Houston, S. Richeter, S. Clément, R. C. Evans, *Polym. Int.* 2017, **66**, 1333-1348.
- [4]: M. Chevrier, J. E. Houston, J. Kesters, N. Van den Brande, A. E. Terry, S. Richeter, A. Mehdi, O. Coulembier, P. Dubois, R. Lazzaroni, B. Van Mele, W. Maes,\* R. C. Evans, S. Clément, *J. Mater. Chem. A* 2015, **3**, 23905-23916.
- [5]: J. E. Houston,\* M. Chevrier, M.-S. Appavou, S. M. King, S. Clément, Rachel C. Evans, *Nanoscale* 2017, **9**, 17481-17493.
- [6]: Under preparation

## Preparation of molecular wires using on-surface chemistry

Ernst Meyer<sup>a</sup>, Remy Pawlak<sup>a</sup>, Philipp D'Astolfo<sup>a</sup>, Carl Drechsel<sup>a</sup>, Guilherme Vilhena<sup>a</sup>, Antoine Hinaut<sup>a</sup> and Thilo Glatzel<sup>a</sup>

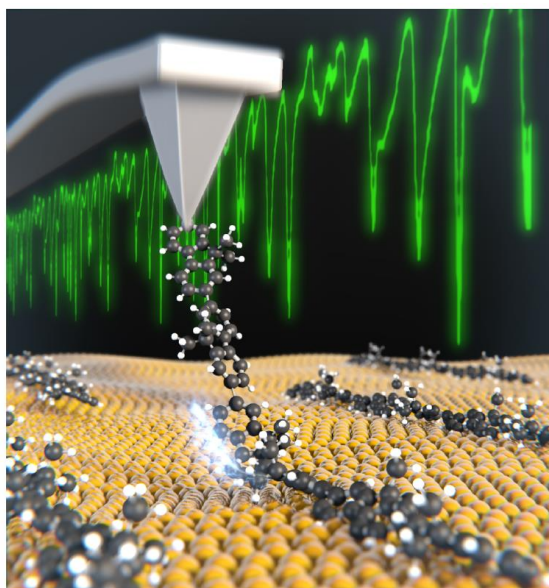
<sup>a</sup> Department of Physics and Swiss Nanoscience Institute, Klingelbergstr. 82, CH-4056 Basel

\* Ernst.meyer@unibas.ch

**Key-Words:** polymeric wires, nanoribbons, on-surface chemistry

### Abstract:

Single molecules on surfaces are prepared by on-surface chemistry, where the polymers are formed by Ullmann coupling. Then, the probing tip of the atomic force microscope is used for high resolution to observe the molecular structure on the surface. In a second step, the probing tip is used as an active tool to pull the polymer across the surface or to detach it from the surface. The force measurements give quantitative information about the interactions of the molecules with the surface as well as the mechanism of friction and adhesion [1]. A similar experimental setup can be used to study the motion of graphene nanoribbons on metallic surfaces. We do observe ultralow friction, also called superlubricity, which corresponds to ultralow frictional forces due to the incommensurability of the contacting surfaces [2]. A third example will be pyrenylene chains, where conformational changes due to twisting and bending of the subunits are observed by mechanical means.



A polymeric chain is pulled by a force microscope to determine adhesion of the subunits as well as friction forces.

### References :

[1] S. Kawai, M. Koch, E. Gnecco, A. Sadeghi, R. Pawlak, Th. Glatzel, J. Schwarz, S. Goedecker, S. Hecht, A. Baratoff, L. Grill, and E. Meyer, Quantifying the atomic-level mechanics of single long physisorbed molecular chains, Proc. Natl. Acad. Sci. USA, 2014, 111, (11), 3968.

[2] S. Kawai, A. Benassi, E. Gnecco, H. Söde, R. Pawlak, X. Feng, K. Müllen, D. Passerone, C. A. Pignedoli, P. Ruffieux, R. Fasel, E. Meyer, Superlubricity of graphene nanoribbons on gold surfaces, Science, 2016, 351, (6276), 957.

# Fire behavior and morphology of epoxy-amine matrix designed by polyhedral oligomeric silsesquioxane-supported imidazolium ionic liquid (IL-g-POSSPh)

Houssém Chabane<sup>a</sup>, Sebastien Livi<sup>a</sup>, Rodolphe Sonnier<sup>b</sup>, Loïc Dumazert<sup>b</sup>, Jannick Duchet-Rumeau<sup>a</sup>, and Jean-François Gérard<sup>a</sup>

<sup>a</sup>IMP Ingénierie des Matériaux Polymères – Université de Lyon - INSA Lyon, UMR CNRS 5223 – France

<sup>b</sup>Centre des Matériaux (C2MA) – Ecole des Mines d'Alès – France

**Key-Words:** Ionic liquid, Polyhedral oligomeric silsesquioxane (POSS), Epoxy-amine, Hybrid organic-inorganic nanomaterials, Flame-retardancy.

## Abstract:

The design of new nanostructured and high performance polymer materials is a major challenge for industrial applications (1). Here, two novel polyhedral oligomeric silsesquioxane-supported imidazolium ionic liquids having chloride (Cl<sup>-</sup>) and bis(trifluoromethane)sulfonimide (NTf<sub>2</sub><sup>-</sup>) counter anions have been synthesized and used as nano-objects of epoxy networks prepared from copolymerization of diglycidyl ether of bisphenol A (DGEBA) and isophorone diamine (IPD). 5 wt % of hybrid organic-inorganic nanomaterials have been introduced into epoxy prepolymer leading to a homogeneous and uniform dispersion of these nano-objects into networks (10 - 100 nm) (2). The flame retardancy of these networks was studied using pyrolysis-combustion flow calorimetry (PCFC) and cone calorimetry. Finally, the use of low amount of these polyhedral oligomeric silsesquioxane-supported imidazolium ionic liquids led to a significant decrease of the peak of heat release rate (between -53 and -56 %) with a substantial and effective intumescent-like behavior compared to the neat epoxy-amine and the epoxy hybrid containing POSSPh-triol (Fig.1).

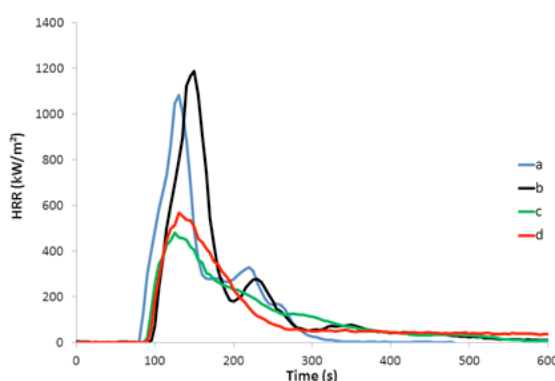


Fig. 1. Cone calorimeter HRR curves of the neat epoxy-amine (a) and the epoxy hybrid O/I networks containing POSSPh-triol (b), IL.Cl-g-POSSPh (c) and IL.NTf<sub>2</sub>-g-POSSPh (d).

## References :

- [1] : K. CARL C, Nanostructured materials: Processing, Properties and Applications, second edition : Materials science and Process technology series, in: Norwich, Gary-McGuire, 2006.
- [2] : H. Chabane; S. Livi; H. Benes; C. Ladavière; P. Ecorchard; J. Duchet-Rumeau; J.F.Gérard, Eur. Polym. J. Polyhedral oligomeric silsesquioxane-supported ionic liquid for designing nanostructured hybrid organic-inorganic networks, 2019, **114**, 332-337.

# Nanostructured thin films from block copolymer self-assembly: exquisite symmetries from macromolecular design

Guillaume Fleury<sup>a\*</sup>, Karim Aissou<sup>a</sup>, Eric Cloutet<sup>a</sup>, Cyril Brochon<sup>a</sup>, Georges Hadziioannou<sup>a</sup>, Virginie Ponsinet<sup>b</sup>, Giuseppe Portale<sup>c</sup>

<sup>a</sup> Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France

<sup>b</sup> Univ. Bordeaux, CNRS, Centre de Recherche Paul Pascal (CRPP), UMR 5031, 33600 Pessac, France

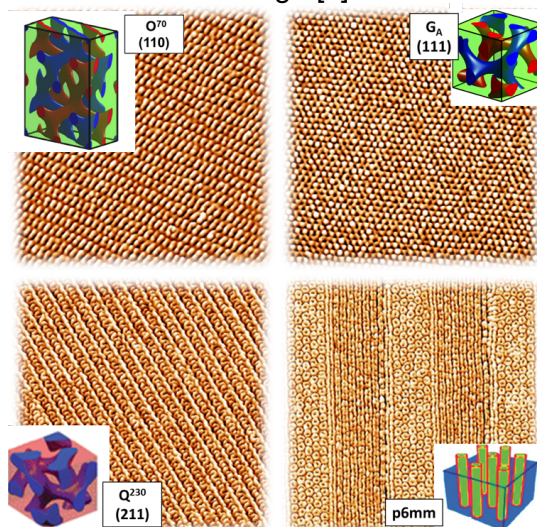
<sup>c</sup> Zernike Institute for Advanced Materials, Nijenborgh 4, NL-9747 AG Groningen, the Netherlands

\* gfleury@enscbp.fr

**Key-Words:** block copolymer, self-assembly, nanostructured thin films

## Abstract:

Block copolymers are a unique class of materials which self-assemble into periodic structures at the nanometer scale with a range of controllable morphologies, including lamellae, cylinders, spheres and unique network morphologies. Their self-assembly into nanostructured thin films offers a promising route to provide a significant advancement in technological applications such as lithography, non-linear optics or ultrafiltration. Over the last years we have developed a first generation of lithographic materials based on the directed self-assembly of PMMA-*b*-PS and highlights on the use of Grazing Small X-ray Scattering to probe their self-assembly kinetics and the resulting mesostructures will be presented.[1] Following this study, we have designed new block copolymer systems characterized by higher segregation strengths and more complex architectures which allow the definition of sub-20 nm features with exquisite symmetries.[2,3] A few anecdotes related to their thin film self-assembly and their segregation behavior as regards to the processing parameters will be presented.[4,5] In particular, we will show that precise macromolecular engineering allow the formation of complex patterns which can be hybridized to form interesting metallic structures for metasurfaces design.[6]



Examples of complex block copolymer structures stabilized in thin film configuration.

## References:

- [1] M. Maret, R. Tiron, X. Chevalier, P. Gergaud, A. Gharbi, C. Lapeyre, J. Pradelles, V. Jousseau, G. Fleury, G. Hadziioannou, N. Boudet, C. Navarro, *Macromolecules* 2014, **47**, 7221.
- [2] K. Aissou, M. Mumtaz, G. Fleury, G. Portale, C. Navarro, E. Cloutet, C. Brochon, C. A. Ross, G. Hadziioannou, *Adv. Mater.* 2015, **27**, 261.
- [3] Y. Rho, K. Aissou, M. Mumtaz, W. Kwon, G. Pécastaings, C. Mocuta, S. Stanecu, E. Cloutet, C. Brochon, G. Fleury, G. Hadziioannou, *Small* 2015, **11**, 6377.
- [4] K. Aissou, W. Kwon, M. Mumtaz, S. Antoine, M. Maret, G. Portale, G. Fleury, G. Hadziioannou, *ACS Nano* 2016, **10**, 4055.
- [5] K. Aissou, M. Mumtaz, P. Marcasuzaa, C. Brochon, E. Cloutet, G. Fleury, G. Hadziioannou, *Small* 2017, **13**, 1603184.
- [6] A. Alvarez-Fernandez, K. Aissou, G. Pécastaings, G. Hadziioannou, G. Fleury, V. Ponsinet, *Nanoscale* 2019, **1**, 849.

# Self-oscillating polymer interfaces to design life-like pulsatile membranes

Marianne Benoit<sup>a</sup>, Joël Lyskawa<sup>b</sup>, David Fournier<sup>b</sup>, Patrice Woisel<sup>b</sup>, Claire Antonelli<sup>\*a</sup>,  
Damien Quémener<sup>\*a</sup>

<sup>a</sup> Institut Européen des Membranes (IEM UMR 5635), Université de Montpellier, CC047-2 pl. E. Bataillon 34095, Montpellier Cedex 05, France

<sup>b</sup> Unité Matériaux et Transformations, Université de Lille, 59655 Villeneuve d'Ascq

\* damien.quemener@umontpellier.fr and claire.antonelli@umontpellier.fr

**Key-Words:** pH-responsive membrane, self-oscillating, pH-oscillator, PMAA

## Abstract:

Soft matter materials research has considerably evolved the last decades mainly by promoting responsive polymer systems. Up to now, the dynamic behavior, although bringing new functions, was always reached by the action of an outside trigger (pH, light, T°C...). In this work, it is envisioned to prepare autonomous oscillatory polymer interfaces synchronized by chemical reaction networks (pH-oscillators). The self-regulating pH waves will be read in time by synthesized polymer interfaces to undergo autonomous macroscopic motions. The objectives are the preparation of autonomous dynamic soft interfaces characterized by their constantly evolving surface properties, and the design of new integrated membranes showing a chemically-powered autonomous pulsatile flow. The self-oscillatory system is obtained from the combination of a pH-responsive polymer and an oscillating chemical reaction. In this work, functionalized poly(methacrylic acid) (PMAA) was prepared by RAFT polymerization and grafted at the interface of a commercial alumina membrane. Then mounted in a filtration setup, the PMAA-functionalized membrane was synchronized to a pH oscillator (Bromate-Sulfite-Ferrocyanide: BSF) (Figure 1). When the flow through the membrane reaches the pH oscillation domain, a pulsatile flow with impressive permeability cycles was observed. BSF pH-oscillator leads to a cyclic change of the pH between 3.5 and 6.5 in the filtration cell. Since PMAA has a pKa around 4.8, a cyclic extension-contraction of the polymer chains is obtained which leads to a synchronized change in the pore size. Therefore, a direct consequence is an oscillatory modulation of the membrane permeability.

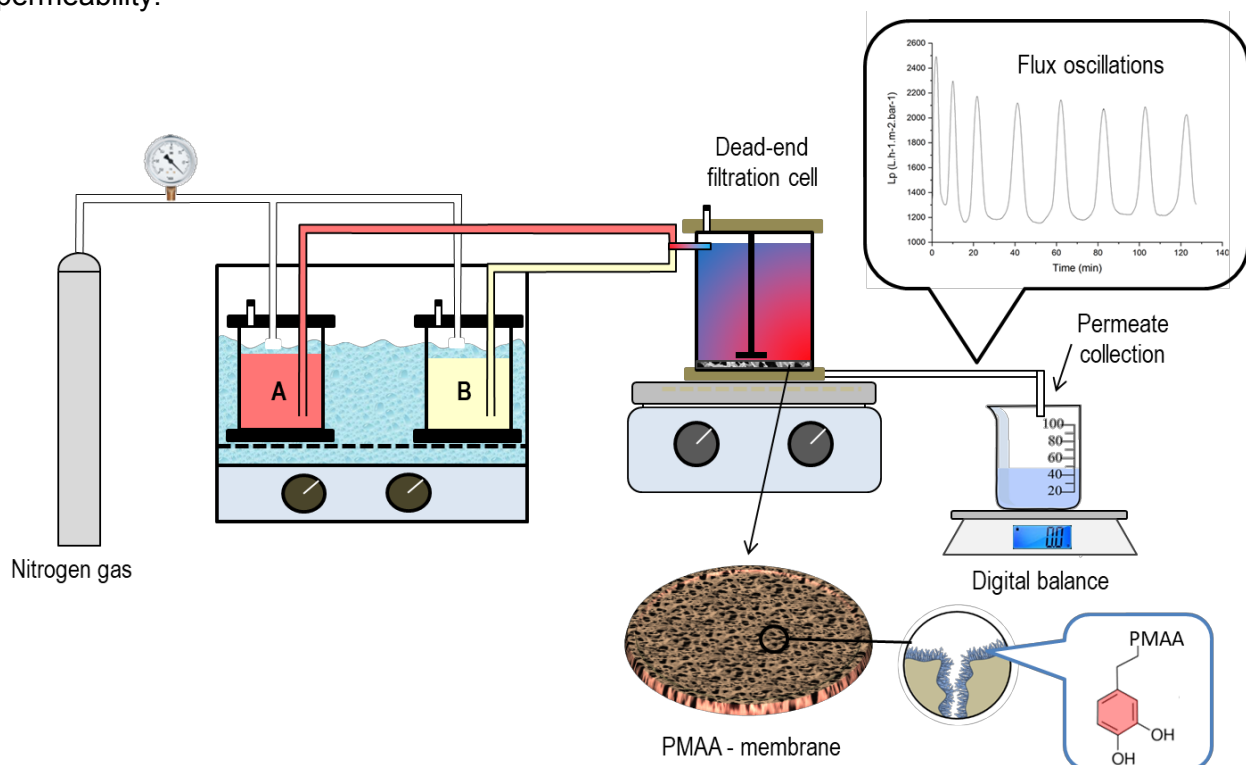


Figure 1: Filtration setup of self-oscillating membrane

# Synthesis and Study of Associative Water-Soluble Copolymers for Enhanced Oil Recovery

Julien Crozzolo<sup>a,b</sup>, Stéphane Jouenne<sup>b</sup>, Renaud Nicolay<sup>\*a</sup>

<sup>a</sup> Molecular, Macromolecular Chemistry and Materials, ESPCI Paris, CNRS, PSL University, 10 Rue Vauquelin, 75005 Paris, France

<sup>b</sup> Total PERL – Pôle d'Etudes et de Recherche de Lacq – 64170 Lacq

\* renaud.nicolay@espci.psl.eu

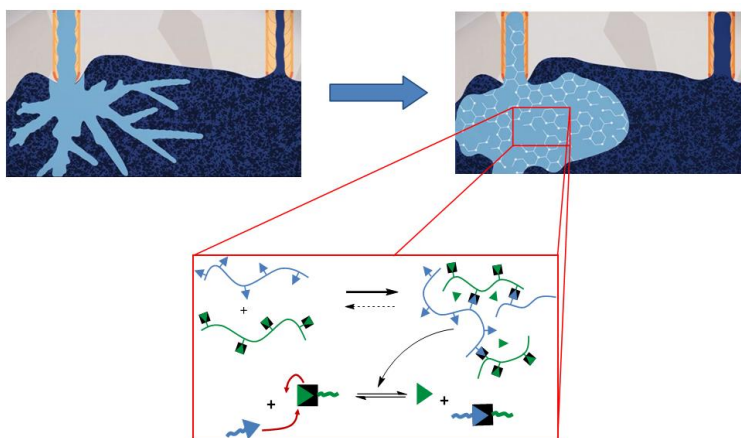
**Key-Words:** Enhanced Oil Recovery, Dynamic Covalent Chemistry, Rheology

## Abstract:

Enhanced Oil Recovery is an important challenge for petroleum industry due to the decrease of the easily recoverable oil stocks, but also because conventional methods do not allow recovering in full the oil present in the reservoirs. One of the solutions is the use of aqueous formulations of polymers in order to improve the rheological properties of the extraction fluid [1]. Actually, very long polymer chains are already used but this technique is limited by the fact that when the polymer solutions are injected, they are submitted to very high shear rates that irreversibly break the polymer chains, which leads to a loss of the viscosifying properties of the fluid.

To address this problem, we aim at developing a system that can support the shear rate induced by the injection [2]. Based on reversible covalent chemistry this system uses the association of two polyacrylamides bearing complementary moieties, amine and benzaldehyde respectively, which can associate to form dynamic and reversible imine bonds. The mixing of these two polymer solutions provides viscous solutions as well as visco-elastic gels at low polymer concentrations.

The association reaction, responsible for the increase of viscosity of the formulations was studied by <sup>1</sup>H-NMR using both model small molecules and polymers with different compositions and degree of functionality. The rheological properties of formulations containing the complementary copolymers were also studied by rheometry in different concentration regimes. The impact, on the association constant and rheological behavior, of various parameters of interest for Enhanced Oil Recovery, such as pH, salinity or temperature, was also investigated.



*Schematic representation of the use of a system based on DCC for Enhanced Oil Recovery*

## References:

[1] : D.A.Z. Wevera, F. Picchionia, A.A. Broekhuis, *Prog. Polym. Sci*, **2011**, *36*, 1558.

[2] : S. Jouenne, U. Naessens, L. Leibler, I. Iliopoulos. "Associative water-soluble polymers and their use for enhanced hydrocarbon recovery" Application FR1363529

# Electrospray deposition of molecules in ultra high vacuum : building large molecular assemblies.

Antoine Hinaut <sup>\*a</sup>, Sebastian Scherb <sup>a</sup>, Remy Pawlak <sup>a</sup>, Guilherme Vilhena <sup>a</sup>, Klaus Müllen <sup>b</sup>, Thilo Glatzel <sup>a</sup>, Akimitsu Narita <sup>b</sup>, Ernst Meyer <sup>a</sup>

[speaker must be underlined]

<sup>a</sup> Department of Physics, University of Basel, 4056 Basel, Switzerland

<sup>b</sup> Max Planck Institute for Polymer Research, 55128 Mainz, Germany

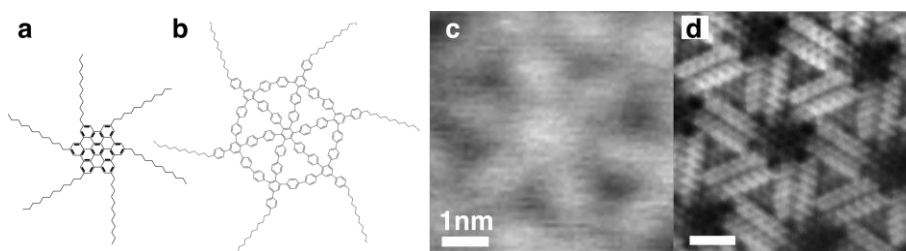
\* antoine.hinaut@gunibas.ch

**Key-Words:** electrospray, ncAFM, molecular assemblies, thermal expansion

## Abstract:

Supramolecular chemistry allows new avenues in understanding how single molecules, when assembled together can give rise to collective phenomena not present on single molecular level. Possible uses range from sensors to molecular electronics and even to pharmaceutical sciences. Such assemblies are built up by self-assembly mechanisms due to molecular recognition and result in non-covalent bonded networks. For two-dimensional supramolecular chemistry not only molecule-molecule recognition, but also interactions at interfaces must be considered for the creation and tuning of the material properties. Thermal expansion is an important aspect in the study of applicable materials, especially for mechanical uses. Fundamental studies are useful for material knowledge allowing the reduction of material aging and the elaboration of materials with thermomechanical behavior.

Here we present the study of electrospray deposited [1,2] large organic molecules that self-assemble on surface in UHV conditions. A large hexa-benzo-coronene derivative [3] (Figure a,c,d) as well as a shape-persistent polyphenylene spoked wheel [4] (Figure b) are deposited on Au(111). The molecules are based on aromatic core and equipped with long alkyl chain to promote molecular assemblies stabilization. The assemblies are characterized by high resolution room temperature AFM and low temperature AFM/STM (Fig c,d). At both low and room temperature, assemblies are observed, directed by alkyl-alkyl interaction and also influenced by the measurement temperature. Complimenting with state-of-the-art, micro-second long all atom molecular dynamics simulations of the spoked wheel formed molecular assemblies, we find that alkyl chain functionalizing molecular cores promotes large thermal expansion of the molecular network when heated as a result of entropic effects enhanced by large fluctuations experienced by the alkyl chains.



**Figure** a),b) molecular schemes of two deposited molecules. Room temperature ncAFM topography c) and low temperature CO functionalized tip AFM topography d) of of molecule in a) on Au(111).

## References :

- [1] A. Hinaut et al., *Beilstein J. Nanotechnology* **6**, 1927–1934. (2015).
- [2] A. Hinaut et al., *Nanoscale* **10**, 1337–1344. (2018).
- [4] Samori et al., *Langmuir* **18**, 4183–4185. (2002).
- [5] Liu et al., *J. Am. Chem. Soc.* **138**, 15539–15542. (2016).



# ENTROPY IN STOCK IN NON-EQUILIBRATED POLYMER MELTS: TRANSLATING MOLECULAR RELAXATION INTO LIFTING MACROSCOPIC WEIGHTS

Farzad Ramezani<sup>a</sup>, Jörg Baschnagel<sup>b</sup>, Günter Reiter<sup>\*a</sup>

<sup>a</sup> Institute of Physics, University of Freiburg, Herman-Herder-Str. 3, 79104 Freiburg, Germany

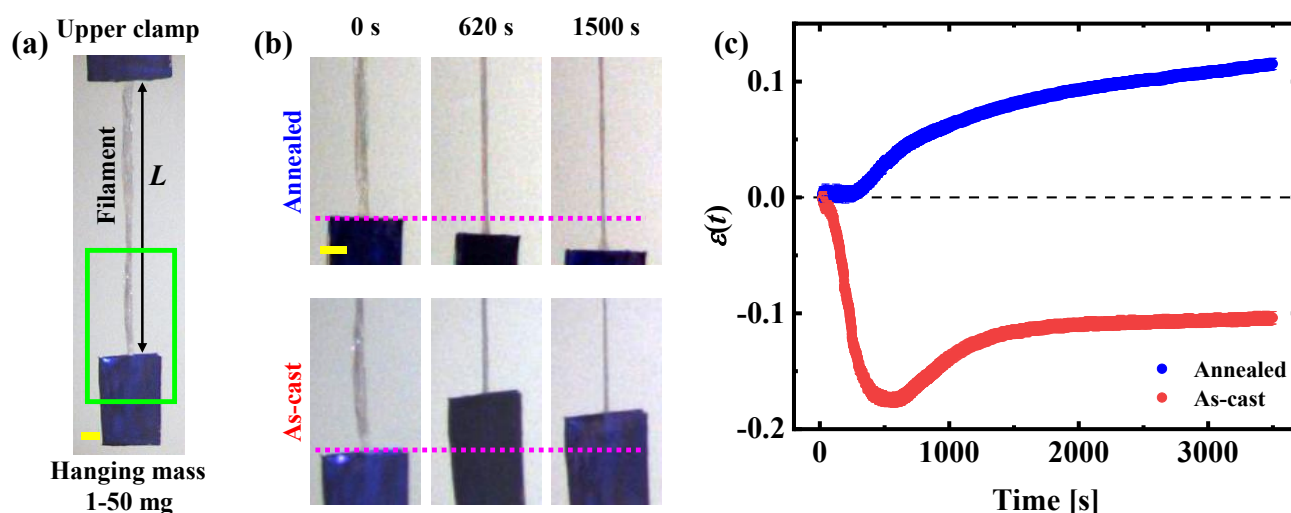
<sup>b</sup> Institut Charles Sadron, University of Strasbourg & CNRS, 23 rue du Loess, 67034 Strasbourg Cedex, France

\* guenter.reiter@physik.uni-freiburg.de

**Key-Words:** Polymer, Thin film, Non-equilibrium, Creep, Contraction

## Abstract:

Many properties of long chain-like polymers are controlled by their large conformational entropy, representing the huge number of chain configurations, i.e., the number of possibilities of arranging the sub-units (monomers) of a polymer chain in space. A typical example is rubber elasticity, where the force required to deform an initially equilibrated rubber relates to the corresponding reduction in entropy. Here, we quantify the deviations from equilibrium conformations in a polymer melt, introduced in a controlled way by sample preparation, by determining the force, which brings the melt back to the equilibrium state. To this end, we performed creep experiments under various applied loads on molten filament-like samples derived from spin-coated polymer films. We verified that filaments made from annealed films reproduced the expected behavior of an equilibrated polymer melt, a time-dependent monotonic elongation. However, filaments made from as-cast (non-equilibrated) films behaved like a stretched rubber after the release of an applied force. They contracted, allowing lifting loads up to a thousand times the weight of the filament over a distance of almost up to 40% its initial length. The corresponding energy gain per polymer chain was about  $20 k_B T$ . By generalizing our observations, we argue that novel materials properties can be tailored by preparation conditions.



Creep tests exhibiting opposite responses for filaments made from an annealed and an as-cast (spin coated) film: (a) A representative photograph of the experimental set-up used for the creep test in the present study, consisting of a filament made from a spin coated film, attached to a non-movable clamp on top. At the bottom, various weights can be attached. (b) Photographs corresponding to the green region in (a) taken at different times, as noted in the figure, during a creep experiment performed at 130 °C with an applied load (weight acting on the cross-sectional area of the filament) of  $41 \pm 4$  kPa. Both filaments were obtained from spin coated films of atactic polystyrene ( $M_W = 524$  kg/mol) having the same dimensions ( $15 \pm 1$  mm width and  $100 \pm 10$  nm thickness), one was annealed (“Annealed”) and the other one was used as prepared (“As-cast”). The dotted pink lines represent the position of the lower edge of filaments at  $t = 0$ . (c) As further quantification, we plot the time evolution of the Hencky strain corresponding to both filaments. The scale bars in (a) and (b) represent the length of 1 mm.

# POLYSACCHARIDE-BASED HIGHLY STRETCHABLE PHYSICAL HYDROGELS OBTAINED BY INTERPOLYMER COMPLEXATION

Gautier Lalevée<sup>a,b</sup>, Laurent David<sup>a</sup>, Alexandra Montembault<sup>a</sup>, Agnès Crépet<sup>a</sup>,  
Sébastien Malaise<sup>b</sup>, John Meadows<sup>b</sup>, Thierry Delair<sup>a</sup>, Guillaume Sudre<sup>\*a</sup>

<sup>a</sup> IMP, CNRS UMR 5223, Univ Claude Bernard Lyon 1, Univ Lyon, 15 bd Latarjet, 69622 Villeurbanne, France  
<sup>b</sup> Laboratoire ObvieLine - Sinclair IS Pharma, France

\* guillaume.sudre@univ-lyon1.fr

**Key-Words:** Hydrogel, Polysaccharides, Complexation, Stretchable

## Abstract:

Hyaluronic acid (HA) is an anionic polysaccharide naturally present in the human body and chitosan (CS) is the only naturally occurring cationic polysaccharide obtained from the partial deacetylation of chitin. These two polysaccharides are known for their biocompatibility, bioactivity, and biodegradability. The controlled interpolymer complexation of oppositely charged HA ( $M_w \sim 800\text{--}1000 \text{ kg mol}^{-1}$ ) and CS ( $M_w \sim 160 \text{ kg mol}^{-1}$ , degree of acetylation = 15%) led to hydrogel biomaterials with controllable properties in terms of elasticity and strength.

In this work, we were able to form interpolymer complexes by controlled self-assembly via desalting of a high ionic strength soluble mixture of the two natural polyelectrolytes thanks to a dialysis process. [1,2] Depending on the experimental conditions during the dialysis process, and in particular the pH, we obtained hydrogels with very different mechanical behaviors.

First, for pHs from 5.5 to 7.5, weak interpolymer complexes could be formed due to low CS protonation and poor polyelectrolyte associations. Then, for pHs from 3.0 to 5.5, strong interpolymer complexation and syneresis led to free-standing and easy to handle hydrogels. Finally, for pHs from 2.0 to 3.0 (close to the pKa of HA), we observed the unusual stretchability of the obtained hydrogels (Fig. 1 – Left) that could arise from the pre-folding of HA chains while physical crosslinking was achieved by HA/CS polyelectrolyte complexation. These differences were investigated by SAXS and SANS (Fig. 1 – Right) and a first comprehension of these systems will be reported. [3]

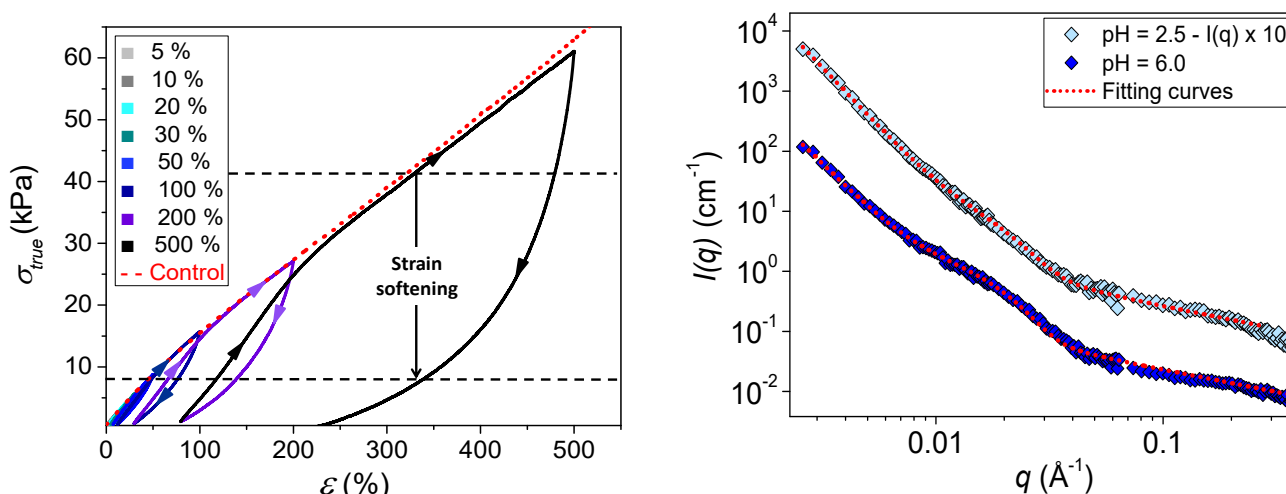


Figure 1. (Left) Dynamic tensile test (5 cycles of loading and unloading at increasing maximum stress) at 10 mm/min of HA/CS hydrogel dialyzed at pH = 2.5. (Right) Small Angle Neutron Scattering diagrams of HA/CS hydrogels dialyzed at pH 2.5 and 6.0.

## References:

- [1] : M. Costalat; L. David; and T. Delair, *Carbohydrate Polymers*, 2014, **102**, 717-726.
- [2] : G. Lalevée, G. Sudre, A. Montembault, J. Meadows, S. Malaise, A. Crépet, L. David, T. Delair, *Carbohydrate Polymers*, 2016, **154**, 86-95.
- [3] : G. Lalevée, L. David, A. Montembault, K. Blanchard, J. Meadows, S. Malaise, A. Crépet, I. Grillo, I. Morfin, T. Delair, G. Sudre, *Soft Matter*, 2017, **13**, 6594-6605.

# Responsive hydrogel films for novel functionalities

Yvette Tran

Sciences et Ingénierie de la Matière Molle (SIMM)  
ESPCI Paris - Université PSL - Sorbonne Université - CNRS, 75005 Paris, France

yvette.tran@espci.fr

**Key-Words:** Hydrogel, Thin layers, Responsive, Grafting, Micro-actuators

## Abstract:

Smart or switchable materials by means of synthetic **stimuli-responsive polymers** have gained much attention owing to their potential applications from sensors to actuators. Surface-attached hydrogel films are actual novel alternative to brushes and layer-by-layer assemblies as polymer coatings. They are multifunctional and multiscale materials with thickness widely ranging from **a few nanometers to several micrometers**. Despite their high potential, responsive hydrogel films are scarcely investigated probably due to a lack of common strategy for reproducible and well-controlled synthesis. We have developed a simple and versatile approach to fabricate reliable and reproducible surface-attached hydrogel films on plane solid substrates. Our strategy provides the facile tailoring of chemical properties (such as response to temperature) and physical properties (size and architecture) of hydrogel films.

Surface-attached hydrogel films show remarkable responsive properties. (i) Hydrogel films reversibly modify their thickness with temperature by absorbing/expulsing water with high amplitude change (the change is four-fold or more). (ii) The transition is sharp and rapid, within a few degrees around the transition temperature and below one second. (iii) Hydrogels with adjustable internal architectures can be built: multilayer hydrogel films, nanocomposite hydrogel films, patterns of hydrogels with micrometric resolution.

The tailoring of surface-attached hydrogels with well-controlled chemistry enables us to address new challenges in various and divergent domains. This new approach of polymer thin layers makes possible fundamental studies such as a fine characterization of mechanical properties of hydrogel films in water: **wetting, underwater friction and adhesion**. We also showed that temperature-responsive hydrogels have excellent performances as micro-actuators. Responsive hydrogels embedded inside **microfluidic devices** operate as functional gates or valves which are reversibly open/close for fluid flows, allowing the development of cheap and handy lab-on-a-chip. The caging functionality for encapsulation is very promising for biotechnological applications. Responsive hydrogel films are also suitable for the development of **modulable optics**.

## References:

- [1] Li, M.; Bresson, B.; Fretigny, C.; Cousin, F.; Tran, Y. Submicrometric films of surface-attached polymer networks: temperature-responsive properties. *Langmuir* **2015**, *31*, 11516-11524.
- [2] Chollet, B.; Li, M.; Martwong, E.; Bresson, B.; Fretigny, C.; Tabeling, P.; Tran, Y. Multiscale surface-attached hydrogel thin films with tailored architecture. *ACS Appl. Mat. Interfaces* **2016**, *8*, 11729-11738 (front cover).
- [3] D'Eramo, L.; Chollet, B.; Leman, M.; Martwong, E.; Li, M.; Geisler, H.; Dupire, J.; Kerdraon, M.; Vergne, C.; Monti, F.; Tran, Y.; Tabeling, P. Microfluidic actuators based on thermo-responsive hydrogels. *Nature Micro Nano* **2018**, *4*, 17069.
- [4] Delavoipière, J.; Tran, Y.; Verneuil, E.; Heurtefeu, B.; Hui, C. Y.; Chateauminois, A. Friction of poroelastic contacts with thin hydrogel films. *Langmuir* **2018**, *34*, 9617-9626.
- [5] Dompé, M.; Cedano Serrano, F. J.; Heckert O.; Tran, Y.; Hourdet, D.; Van den Heuvel, N.; Van der Gucht, J.; Creton, C.; Kamperman, M. Thermoresponsive complex coacervate-based underwater adhesive. *Adv. Mater.* **2019**, *31*, 1808179.

# Nanoscopic imaging of functional, responsive microgels

Dominik Wöll

*RWTH Aachen University - Germany*

## Abstract:

Super-resolution fluorescence imaging has been frequently used for biological and biomedical applications.[1] Applying these methods to material science, and in particular to polymer systems, bears high potential to unravel details on the nanoscopic scale and to learn about local environments in polymers. In my talk, I will present our work on the nanoscopic imaging of functional PNIPAM (poly(Nisopropylacrylamide)) microgels that can swell and collapse in response to stimuli such as changes in temperature, ionic strength or pH. We could show that compartmentalized microgels can be specifically labelled in the core or in the shell and, this way, visualize these compartments via localization-based super-resolution fluorescence imaging methods.[2] Applying switchable fluorescent diarylethene cross-linkers during the synthesis of microgels by precipitation polymerization, we could determine the positions of single cross-linkers within the microgels.[3] Cross-linking has direct influence on the mechanical properties of microgels and determines their deformation at solid-liquid and liquid-liquid interfaces. Also, these deformations can be readily visualized with super-resolved fluorescence imaging. Finally, it is of paramount importance to understand which local environment molecules "feel" in microgels. This question can be addressed by a super-resolution method call PAINT (Point Accumulation In Nanoscale Topography) with the solvatochromic dye Nile Red. We found the existence of surprisingly apolar environments in PNIPAM microgels.[4]

## References :

- [1] : S. W. Hell, Nature Methods 2009, **6**, 24.
- [2] : A. Gelissen, A. Oppermann, T. Caumanns, P. Hebbeker, S. Turnho\_, R. Tiwari, S. Eisold, U. Simon, Y. Lu, J. Mayer, W. Richtering, A. Walther, D. Wöll, Nano Lett. 2016, **16**, 7295.
- [3] : E. Siemes, O. Nevskiy, D. Sysoiev, S. K. Turnho\_, A. Oppermann, T. Huhn, W. Richtering, D. Wöll, Angew. Chem. Int. Ed. 2018, **57**, 12280.
- [4] : A. Purohit, S. P. Centeno, S. K. Wypysek, W. Richtering, D. Wöll, Chem. Sci. 2019, accepted.

# STUDY OF THERMO-INDUCED BEHAVIOR AND RHEOLOGICAL PROPERTIES OF HYDROGELS BASED ON MIXING BIS-HYDROPHILIC BLOCK COPOLYMERS WITH METALLIC IONS

Angélique Gutierrez <sup>a</sup>, Maël Le Bohec <sup>a</sup>, Manon Banère <sup>a</sup>, Sagrario Pascual <sup>a</sup>, Laurent Fontaine <sup>a</sup>, Sandie Piogé <sup>a\*</sup>, [Lazhar Benyahia](#) <sup>a\*</sup>

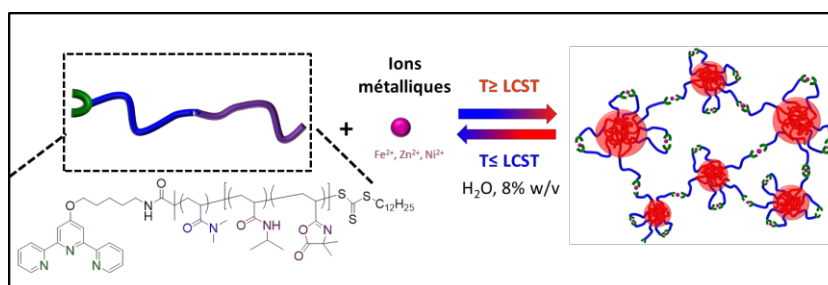
<sup>a</sup>Institut des Molécules et Matériaux du Mans, UMR 6283 CNRS - Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans cedex 9 - FRANCE

\* sandie.pioge@univ-lemans.fr; lazhar.benyahia@univ-lemans.fr

**Key-Words:** Metallo-supramolecular Hydrogel, Metal Ion Mixture, Thermorheological Behavior

## Abstract:

Smart metallo-supramolecular hydrogels offer the ability to combine the physical-chemical and rheological properties of hydrogels with the self-assembly features of metal-ligand interactions. In this study we develop a new strategy to elaborate smart hydrogels thanks to a thermo-induced micellar aggregation of metal-bis(terpyridine) complexes linked to poly(*N,N*-dimethylacrylamide)-*b*-poly(*N*-isopropylacrylamide) (PDMA-*b*-PNIPAM). Thermosensitive metal complexes  $[M(\text{Tpy-PDMA-}b\text{-PNIPAM})_2]^{2+}$  were obtained by dissolving hydrophilic block copolymers PDMA-*b*-PNIPAM in water at room temperature in the presence of metal ions  $M^{2+}$  ( $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ). Rheological measurements showed a thermo-reversible sol-gel transition indicating the formation of a percolated three-dimensional network provided by the aggregation of PNIPAM blocks at temperatures above the LCST (Lower Critical Solution Temperature).<sup>1</sup> At temperatures below the LCST, the rheological study showed that thermosensitive complexes self-assemble into living micelles with a finite lifetime that is independent of the molar concentration of metal ions. In addition, the newtonian viscosity and the elastic modulus of the solutions increase sharply with the molar concentration of metal ions compared to that of terpyridine units. The viscoelastic behavior of the sticky reptation type has been confirmed by UV spectroscopy and depends on the number of bridges that increases proportionally with the number of  $[M(\text{Tpy-PDMA-}b\text{-PNIPAM})_2]^{2+}$  complexes. With regard to the mixing of metal ions ( $\text{Fe}^{2+}/\text{Zn}^{2+}$ ), the study showed that the total amount of metal ions prevails over the nature of the metal ions. At temperatures above the LCST, only the  $\text{Fe}^{2+}$  and  $\text{Ni}^{2+}$  metal ions lead to gelling networks where the moduli are proportional to the amount of  $[M(\text{Tpy-PDMA-}b\text{-PNIPAM})_2]^{2+}$  complexes. The study of metal ion mixtures showed that it was possible to adjust the elastic moduli by modifying the composition into metal ions.<sup>2</sup>



*Elaboration of smart hydrogels via thermo-induced micellar aggregation metal-bis(terpyridine) complexes linked to poly(*N,N*-dimethylacrylamide)-*b*-poly(*N*-isopropylacrylamide).*

## References :

- [1] : M. Le Bohec, M. Banere, S. Piogé, S. Pascual, L. Benyahia, L. Fontaine, *Polym. Chem.*, 2016, **7**, 6834  
 [2] : M A. Gutierrez, S. Pascual, L. Fontaine, S. Piogé, L. Benyahia, *Polym. Chem.*, 2018, **9**, 2494

# Renewability is not Enough: Sustainable Synthesis of Biomass-derived Monomers and Polymers

Michael A. R. Meier\*

<sup>a</sup> Karlsruhe Institute of Technology (KIT), Institute of Organic Chemistry (IOC), Materialwissenschaftliches Zentrum MZE, Straße am Forum 7, 76131 Karlsruhe, Germany.

\* m.a.r.meier@kit.edu

## Abstract:

In ages of depleting fossil reserves and an increasing emission of greenhouse gases, it is obvious that the utilization of renewable feedstocks is one necessary step towards a sustainable development of our future. In order to develop truly 'green' approaches, using renewable resources is insufficient.[1] The available feedstocks rather have to be used in a sustainable fashion by combining as many of the principles of green chemistry as possible and by accessing and comparing the sustainability of chemical transformations. Within this contribution, new approaches for the synthesis of monomers as well as polymers from plant oils,[2,3] lignin[4] and carbohydrates will be discussed, thereby highlighting developed sustainable (catalytic) modification strategies. The focus of this presentation will be on novel approaches towards the sustainable functionalization of cellulose[5] and lignin, including new solubilisation and catalysis concepts as well as the use of multicomponent reactions.

For instance, a switchable ionic liquid, first introduced by Jerome[6] as well as Xie[7] for cellulose solubilisation, was studied and optimized[8] and later on applied for cellulose aerogel preparation.[9] The use and the advantages of this switchable solvent system for the preparation of various cellulose derivatives, for instance fatty acid cellulose esters (FACEs)[10] or cellulose succinylation with subsequent grafting via multicomponent reactions,[11] will be discussed in detail.

## Références :

[1] A. Llevot, P.-K. Dannecker, M. von Czapiewski, L. C. Over, Z. Söyler, M. A. R. Meier, *Chem. Eur. J.* **2016**, *22*, 11510-11521. [2] M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 1788-1802. [3] L. Montero de Espinosa, M. A. R. Meier, *Eur. Polym. J.* **2011**, *47*, 837-852. [4] L. C. Over, M. A. R. Meier, *Green Chem.* **2016**, *18*, 197-207. [5] K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2019**, *7*, 1826-1840. [6] Q- Zhang, N. S. Oztekin, J. Barrault, K. de Oliveira Vigier, F. Jérôme, *ChemSusChem* **2013**, *6*, 593-596. [7] H. Xie, X. Yu, Y. Yang, Z. K. Zhao, *Green Chem.* **2014**, *16*, 2422-2427. [8] K. N. Onwukamike, T. Tassaing, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2018**, *6*, 1496-1503. [9] K. N. Onwukamike, L. Lapuyade, L. Maillé, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2019**, *7*, 3329-3338. [10] K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *ACS Sustainable Chem. Eng.* **2018**, *6*, 8826-8835. [11] Z. Söyler, K. N. Onwukamike, S. Grelier, E. Grau, H. Cramail, M. A. R. Meier, *Green Chem.* **2018**, *20*, 214-224.

## Wednesday, November 27<sup>th</sup>

### Polymers and sustainable development - Session 2 –

*Chairs: Cécile Nouvel & Jacques Lalevee*

- 8.30 **Stéphanie Baumberger**  
Combining chemical tools and biological transformation for a cascade valorization of lignin
- 9.10 **Frédéric Ruch**  
Upcycling for thermoplastic composites: How to recycle with added value with ThermoPRIME<sup>®</sup> & ThermoSaic<sup>®</sup> technologies
- 9.30 **Rama Shakaroun**  
Organocatalyzed ring-opening polymerization (ROP) of functional  $\hat{\text{I}}^2$ -lactones: New insights into the ROP mechanism and poly(hydroxyalkanoate)s (PHAs) macromolecular structure
- 9.50 **Fanny Coumes**  
Design of biobased nanoparticles through polymerization induced self-assembly of biosourced monomers

10.10 Coffee break

**10.30 General Assembly of GFP for adherents**    **10.30 Poster Session**

12.30 Lunch – POSTER SESSION

### Polymers and Light - Session 1 -

*Chairs: Yohann Guillaneuf & Xavier Coqueret*

- 14.00 **Kurt Dietliker**  
Photobase technology: A versatile tool for the preparation of new materials
- 14.40 **Christine Joly-Duhamel**  
Maleimide monomers: an alternative to the UV formulation based on a radical photoinitiator
- 15.00 **Remi Canterel**  
Photopolymerization in dispersed media under visible light
- 15.20 **Frédéric Dumur**  
Mechanosynthesis: Green chemistry applied to the design of copper-based photoinitiators
- 15.40 **Laurent Heux**  
Biomimetic photonic cellulose films

16.00 3 min Poster Pitches - Session 3 -

16.25 Sponsor Pitch: Phoseon

16.30 Coffee break offered by THERMOFISHER

## Polymers and Light - Session 2 -

*Chairs: Kurt Dietliker & Fabrice Morlet-Savary*

16.50 **Yohann Guillaneuf**

Preparation of micro-patterned surfaces by the use of light-sensitive alkoxyamines

17.30 **Eirini Skoufa**

Low energy miniemulsification device

17.50 **Miriam Unger**

Latest advances in nanoscale IR spectroscopy and imaging

18.10 **Andreas Reisch**

Bright and small fluorescent polymer nanoparticles for intracellular imaging

18.30 End of the day / Free: Christmas market



# Combining chemical tools and biological transformation for a cascade valorization of lignin

Stéphanie Baumberger \*

*Institut Jean-Pierre Bourgin  
UMR1318 INRA-AgroParisTech-ERL3559 CNRS  
INRA Centre de Versailles-Grignon  
Route de St-Cyr (RD10)  
78026 Versailles Cedex France*

\* stephanie.baumberger@inra.fr

**Key-Words:** Biomass valorization, lignin, green chemistry, biotechnologies.

## **Abstract:**

Lignins are versatile phenolic polymers occurring naturally in the cell-wall of vascular plants supporting tissues. Their multifunctionality, together with the necessity to valorize their industrial derivatives in order to improve biorefineries sustainability, currently stimulates intensive research and innovation at international level. Whereas using industrial lignins as renewable fuel is the main route exploited nowadays, new strategies have been implemented this last decade to convert lignins into higher-value products.

One of this strategy consists in combining chemical tools and biological transformation to produce a set of products fitting with industry requirements in terms of homogeneity, purity and functionalities. The case of the Zelcor European project (“Zero-waste Ligno-cellulosic Bio-refineries”, H2020 BBI-JU project) is used here to illustrate the possibility to recover standardised antioxidant extracts of interest for plastics and cosmetics along with carbohydrate-rich substrates suitable for bioconversions or composites production.

Efforts to limit as far as possible the environmental impact of the process are presented and discussed, including the use of ionic liquids as alternative solvents and/or reagents for lignin depolymerisation.

# Upcycling for thermoplastic composites: How to recycle with added value with ThermoPRIME ® & Thermosaic ® technologies

Frédéric Ruch\*<sup>1</sup>, Clément Callens<sup>1</sup>, and Séverine Thellier<sup>1</sup>

<sup>1</sup>*Cetim Grand Est - Cetim grand est - France*

## Abstract:

Cetim Grand Est developed an original and innovative recycling line for both thermoplastic injected parts and thermoplastic composite materials, which is unique in Europe. Indeed, the technology is based on an "upcycling" approach and starting from waste, allows the production of large-scale panels with optimized mechanical performances. This semi-continuous line is based on a thermomechanical and "step by step" process and is a practical cost-effective recycling technology which provides a way to reuse the generated waste or end-of-life components by producing new materials with a competitive cost/performance ratio. Two ways of production are possible with the same line and with the common objective of adding value to the recycled product:

- Thermosaic ® technology: recovery of thermoplastic composite production scraps and/or end-of-life waste, sorted and crushed beforehand, then shredded. The shreds are bounded together by thermocompression into the shape of structural panels with a continuous production. The breakdown approach is to keep the intrinsic value of the composite (no separation of the fibre and the matrix) during the recycling process.

- ThermoPRIME ® (Thermo Plastic Recycling for Innovative and Ecodesign) technology: recycled plastic materials are preliminary associated with continuous or long fiber reinforcements, to produce laminated recycled composite panels with a higher technical and economic value.

Easy to use and cost-effective, the technology is based on usual industrial equipment, with initial investment and operating cost lower than a continuous production line (double belt press). The exhibility of the line is also an advantage for the industry: it allows the process of thermoplastic matrices of different types (PP, PA, PET, PPS, etc.), with different kinds or mixed reinforcements (fiberglass, carbon, linen... - in the form of mats or fabrics).

ThermoPRIME ® & Thermosaic ® technologies will contribute:

- to promote the use of recycled raw materials in particular in countries like France where their reincorporation rate represents only about 7% of total plastic production
- to give new opportunities for the waste management of industrials, with an "upcycling" way for more added value in recycled products, instead of "downcycling" ways usually proposed on the market.

# Organocatalyzed ring-opening polymerization (ROP) of functional $\beta$ -lactones: New insights into the ROP mechanism and poly(hydroxyalkanoate)s (PHAs) macromolecular structure

Rama Shakaroun\*<sup>1</sup>, Sophie Guillaume<sup>2</sup>, Ali Alaaeddine<sup>3</sup>, and Jean-Francois Carpentier<sup>4</sup>

<sup>1</sup>*Institut des Sciences Chimiques de Rennes - Université de Rennes 1 : UMR6226 - France*

<sup>2</sup>*Institut des Sciences Chimiques de Rennes ; UMR 6226 CNRS ; Université de Rennes 1, Campus de Beaulieu, 263 Avenue du Général Leclerc, F-35042 Rennes Cedex, France - CNRS : UMR6226 - France*

<sup>3</sup>*Faculty of Science I, Lebanese University, Lebanon - Lebanon*

<sup>4</sup>*Organometallics: Materials and Catalysis, Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS Université de Rennes 1 - Organometallics: Materials and Catalysis, Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS Université de Rennes 1 - France*

**Key-Words:** Ring-opening polymerization (ROP), Poly(hydroxyalkanoates) PHAs, Organocatalysis,  $\beta$ -Lactones, MALDI-TOF mass spectrometry

## Abstract:

To date, polyesters, both natural and synthetic, constitute the most fully developed class of (bio)degradable polymers. Within the general contexts of environmentally friendly "green" chemistry and of polyesters designed for the biomedical and microelectronic industry, organocatalysis has become valuable due to its metal-free approach. Organocatalysis is currently of topical interest for its low toxicity, high chemical stability, low cost, easy accessibility and high performances in polymerization reactions. The organocatalyzed ring-opening polymerization (ROP) of 4-alkoxymethylene-  $\beta$ -propiolactones "BPLOs" towards the formation of the corresponding poly(hydroxyalkanoate)s (PHAs) "PBPLORs" is investigated using basic organocatalysts of the guanidine (1,5,7-triazabicyclo[4.4.0]dec-5-ene, TBD), amidine (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU), and phosphazene (2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2diazaphosphorine, BEMP) type. In-sights into the polymerization mechanism is gained through detailed 1D/2D NMR spectroscopy and MALDI-TOF/ESI MS analyses of the resulting "PBPLORs" and in particular of the end-capping groups.

# Design of biobased nanoparticles through polymerization induced self-assembly of biosourced monomers

Fanny Coumes<sup>\*a</sup>, Jutta Rieger<sup>a</sup>, François Stoffelbach<sup>a</sup>

<sup>a</sup> Polymer Chemistry team, Institut parisien de Chimie Moléculaire (IPCM)  
Sorbonne University, Campus Pierre et Marie Curie  
4, Place Jussieu, 75005 PARIS

\* [fanny.coumes@sorbonne-universite.fr](mailto:fanny.coumes@sorbonne-universite.fr)

**Keywords:** biobased monomers, PISA, RAFT, nanoparticles

## Abstract:

From a global point of view, the development of greener processes and the use of “greener” building blocks are one of the main challenges that synthetic chemists must address to solve current environmental and economic issues. Polymers represent an important class of materials widely used in industrial applications. Nevertheless, apart from natural polymers, synthetic polymers are essentially based on petrosourced monomers. To achieve sustainable chemistry, several teams are currently investigating the synthesis of biosourced polymers.<sup>1–3</sup> In our group, we decided to combine the use of the polymerization induced-self-assembly (PISA) technique and reversible-deactivation radical polymerization (RDRP) in green solvents (ultimately in water) to engineer nanoparticles (NPs) based on new **biobased amphiphilic copolymers**. While the RDRP -such as the radical addition-fragmentation transfer (RAFT) polymerization - allows the preparation of defined polymers in a controlled fashion<sup>4</sup>, the PISA approach, proceeding in heterogeneous potentially “green” conditions, relying on the use of a hydrophilic macromolecular control agent to promote the polymerization of hydrophobic monomers, leads to the formation of amphiphilic block copolymers that self-assemble into self-stabilized nanoparticles (NPs), avoiding the use of any free surfactant in the medium.<sup>5,6</sup>

In this work, hydrophobic and hydrophilic biobased radically polymerizable monomers were either purchased or designed from **biosourced precursors**. Then, a hydrophilic biobased reactive block, namely a macro-RAFT agent, was used in the PISA approach to generate completely biosourced NPs. The polymerization conditions were varied (concentration of the hydrophobic monomer, DP targeted) in order to achieve the *in situ* formation of various morphologies. Kinetic studies were performed to assess the control of the polymerization using <sup>1</sup>H NMR and size-exclusion chromatography (SEC). Then, the shape and size of the NPs were assessed by means of dynamic light scattering (DLS) and cryo-transmission electronic microscopy (cryo-TEM) as illustrated on Figure 1.

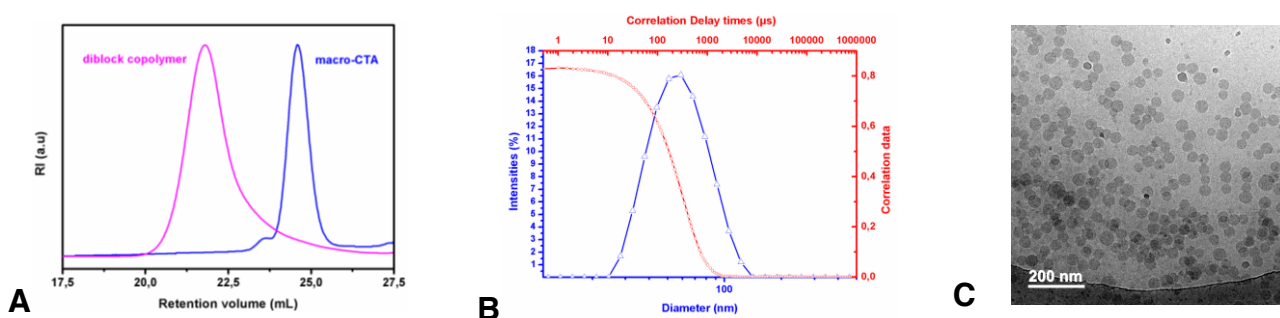


Figure 1: (A) Size-exclusion chromatography profiles (in THF), (B) DLS profile in water; (C) Cryo-TEM image of NPs in water

Since various potential applications of PISA NPs have already been described in the literature, ranging from biomedical applications to reinforcement agents for materials<sup>7</sup>, physico-chemical studies of our biobased NPs will be done shortly.

## References :

- [1] Molina-Gutierrez, S.; Ladmiral, V.; Bongiovanni, R. M.; Caillol, S.; Lacroix-Desmazes, P. *Green Chem.* 2019, **21**, 36–53. [2] Thomsett, M. R.; Moore, J. C.; Buchard, A.; Stockman, R. A.; Howdle, S. M. *Green Chem.* 2019, **21** (1), 149–156. [3] Li, W. S. J.; Negrell, C.; Ladmiral, V.; Lai-Kee-Him, J.; Bron, P.; Lacroix-Desmazes, P.; Joly-Duhamel, C.; Caillol, S. *Polym. Chem.* 2018, **9** (18), 2468–2477. [4] Semsarilar, M.; Perrier, S. *Nat. Chem.* 2010, **2** (10), 811–820. [5] Rieger, J. *Macromol. Rapid Commun.* 2015, **36** (16), 1458–1471. [6] Lansalot, M.; Rieger, J. *Macromol. Rapid Commun.* 2019, **40** (2), 1–3. [7] Albigès, R.; Klein, P.; Roi, S.; Stoffelbach, F.; Creton, C.; Bouteiller, L.; Rieger, J. *Polym. Chem.* 2017, **8** (34), 4992–4995.

# PHOTOBASE TECHNOLOGY: A VERSATILE TOOL FOR THE PREPARATION OF NEW MATERIALS

Kurt Dietliker

Swiss Federal Institute of Technology Zurich (ETH-Z)  
Department of Chemistry and Applied Biosciences  
Vladimir-Prelog-Weg 1  
CH-8093 Zurich, Switzerland  
e-mail: [kdietliker@ethz.ch](mailto:kdietliker@ethz.ch)

and

SCD GmbH  
Rheinfelderstrasse 27  
D-79395 Neuenburg am Rhein  
Germany  
e-mail: [kurt.dietliker@sommerchem.com](mailto:kurt.dietliker@sommerchem.com)

## Abstract:

Radiation curing is a well-established technology, providing numerous advantages to the end user. Besides economic benefits and an advantageous ecological footprint, outstanding technical properties, such as control of polymerization both in time and space, fast processes, and a consistently high product quality allow industrially attractive processes, spanning from conventional applications such as coatings, printing inks, adhesives to recent developments such as additive manufacturing. While in the meantime many materials used in this technology became commodities, new technologies, novel applications and an increasingly stringent legislation require continuous development of new compounds.

While most commercial applications are based on radical photopolymerization on to a lesser extent on photoacid catalyzed processes, photolatent bases (PLB) are a relatively new development that allows triggering of effects other than simple curing. This can open interesting possibilities in the design of smart coatings, which provide additional value on top of simple protective and decorative effects. An interesting field is organic-inorganic hybrid materials, which combine properties of an organic network with an inorganic material. The use of photobases to trigger the concomitant crosslinking of organic and inorganic materials allows formation of well-defined inorganic nanoparticles in an organic matrix in a bottom-up approach. By appropriate selection of organic and inorganic precursors, cured materials with outstanding properties are obtained. Thus, the introduction of photolatent bases expanded photocuring to the vast field of materials cross-linkable under base catalysis.

Recently it was shown that the same PLB can also induce the *in-situ* reduction of graphene oxide in parallel to the crosslinking of a Michael-type formulation, resulting in a significant decrease in electrical resistance and a concomitant increase in thermal conductivity of the cured material in electrical resistance and a concomitant increase in thermal conductivity of the cured material. The finding that photolatent bases can catalyze different processes in addition to crosslinking opens interesting avenues for the design of materials with outstanding properties

# Maleimide monomers: an alternative to the UV formulation based on a radical photoinitiator

Céline Bonneaud<sup>1</sup>, Roberta Bongiovanni<sup>2</sup>, Chadron Friesen<sup>3</sup>, [Christine Joly-duhamel](#)<sup>1</sup>

<sup>1</sup> Institut Charles Gerhardt, UMR CNRS 5253, Ingénierie et Architectures Macromoléculaires, Ecole Nationale Supérieure de Chimie de Montpellier, 8, rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France

<sup>2</sup> Department of Chemistry, Trinity Western University, Langley, British Columbia V2Y 1Y1, Canada

<sup>3</sup> Department of Applied Science and Technology, Politecnico di Torino, 10128 Torino, Italy

## Abstract:

Photopolymerization has become a well-established industrial process used in a large variety of industrial applications such as coatings, paints, adhesives, inks, dental materials, microelectronics, composite materials, photolithography, etc. This technique combines many advantages: higher productivity (due to the high reactivity of the formulations), low energy consumption, solvent-free formulation, ambient temperature conditions, spatial resolution, etc. (1-3) The major photocurable formulations used in industrial applications are based on acrylate or methacrylate monomers and oligomers. These free radical systems are dependent upon UV irradiation on the presence of a photoinitiator to allow the polymerization to process. However, the presence of a photoinitiator can be detrimental to the aging resistance of materials. Indeed, the consumption of a photoinitiator may be incomplete during the photopolymerization process and the remaining residues are generally toxic and may lead to undesired coloration of the materials.

The use of maleimide monomer could be an alternative to the use of (meth)acrylate formulations. Maleimide monomers are known to be photosensitive and could homopolymerize without any addition of photoinitiator under UV irradiation. The addition of a comonomer with a function as vinyl ether to the maleimide monomer is able to increase the rate of the photopolymerization due to a charge transfer complex based on the photocopolymerization of electron donor/acceptor monomers (AD). (4-6) In addition, this alternative system is more environmentally-friendly than the usual photoinitiator-containing formulations. They are also known to be less sensitive to dioxygen in comparison to usual radical photopolymerization (meth(acrylate)). But, only few oligomers are commercially available, so their synthesis is necessary to access to new oligomers.(7) An update of their use will be done following the different aspects as: synthesis, homopolymerization, copolymerization, and their applications and prospect of application (biphotonic stereolithography).

## References :

[1] : J. P. Fouassier, X. Allonas and Editors *Basics And Applications Of Photopolymerization Reactions*, **2010**, Vol. 1, 284.

[2] : J. P. Fouassier, X. Allonas and Editors *Basics And Applications Of Photopolymerization Reactions*, **2010**, Vol. 2, 257.

[3] : J. P. Fouassier, X. Allonas and Editors *Basics And Applications Of Photopolymerization Reactions*, **2010**, Vol. 3, 220

[4] : E. S. Jonsson, P. E. Sundell, M. Shimose, J. Owens and C. E. Hoyle, *Proceedings of the American Chemical Society Division of Polymeric Materials: Science & Engineering*, **1995**, 72, 3.

[5] : C-P. Vazquez, C. Joly-Duhamel, B. Boutevin, *Macromolecular Chemistry and Physics*, **2013**, 214 (14), 1621-1628.

[6] : C. Bonneaud, J.M. Burgess, R. Bongiovanni, C. Joly-Duhamel, C.M. Friesen, *J. Polym. Sci. Part A Polym. Chem.* **2019**, 57, 699-707

[7] : E. Dolci, V. Froidevaux, C. Joly-Duhamel, R. Auvergne, B. Boutevin, S. Caillol, *Polymer reviews*, **2016**, 56 (3), 512-556.

A part of this work is in the frame of the Project RISE-Horizon 2020 –Project ID: 690917 PhotoFluo

# Photopolymerization in dispersed media under visible light

Rémi Canterel\*<sup>1</sup>, Daniel Subervie<sup>1</sup>, Elodie Bourgeat-Lami<sup>1</sup>, Emmanuel Lacôte<sup>2</sup>, Jacques Lalevée<sup>3</sup>, and Muriel Lansalot<sup>1</sup>

<sup>1</sup>Laboratoire de Chimie, Catalyse, Polymères et Procédés, R 5265 - Université Claude Bernard Lyon 1, Ecole supérieure de Chimie Physique Electronique de Lyon, Centre National de la Recherche Scientifique : UMR5265 - France

<sup>2</sup>Laboratoire Hydrazines et Composites Énergétiques Polyazotés - Université Claude Bernard Lyon 1, Centre National d'Études Spatiales [Toulouse], Centre National de la Recherche Scientifique : UMR5278, Centre National d'Études Spatiales [Toulouse] - France

<sup>3</sup>Institut de Science des Matériaux de Mulhouse - Université de Haute-Alsace (UHA) Mulhouse - Colmar, Centre National de la Recherche Scientifique : UMR7361, université de Strasbourg, Université de Haute-Alsace (UHA) Mulhouse - Colmar : FR3627, Institut National de la Santé et de la Recherche Médicale, Centre National de la Recherche Scientifique, Université de Haute-Alsace (UHA) Mulhouse - Colmar: FR3678 - France

## Abstract:

Photo-induced polymerization in dispersed media has been reported for the first time in the 1980s, while polymerization in dispersed media has wide industrial applications for the production of polymer colloids for more than a century. Indeed, synthetic latexes are used in numerous fields such as coatings, paints and adhesives. Since the 1980s, the studies on photo-induced polymerization in dispersed media remain rare, and only few monomers such as methyl methacrylate and styrene have been investigated. [1] However, photo-polymerizations are attractive, since there are triggered by light, and as such subject to external temporal and spatial control. [2] Efficient strategies must thus be developed to combine the advantages of photo-polymerization with those of polymerization in dispersed media.

We have recently reported a new water-soluble photo-initiating system (PIS) absorbing visible light at room temperature, which consists of a dye, a disulfide compound and a N-heterocyclic carbene borane. [3] The use of LEDs as visible-light source compared to UV light produce photons with longer wavelengths, allowing the transposition of this system to dispersed media. [4] Indeed, the photons in the visible range are less subject to the scattering effects induced by the presence of the particles, thus allowing a better light penetration. Our PIS is indeed capable of initiating the emulsion photo-polymerization of styrene and acrylic monomers, and the obtained final latexes are highly stable, with particle sizes ranging from 50 to 300 nm and solids content up to 30%. The different species of the PIS can however partition between the different phases of the system (water, monomer droplets and particles), resulting in broad particle size distributions.

In this work, we will discuss new options that can lead not only to monodisperse but also bigger particles. The synthesis of both polymer particles and hybrid latex particles is investigated in dispersion photo-polymerization, where the mixture is initially totally homogeneous.

## References :

- [1] : F. Jasinski, P. B. Zetterlund, A. M. Braun, A. Chemtob Progress in Polymer Science 2018, 84 , 47-88
- [2] : J. P. Fouassier, J. Lalevée, Photoinitiators for Polymer Synthesis , Wiley-VCH, Weinheim 2012
- [3] : M. Tehfe, J. Monot, L. Fensterbank, J. P. Fouassier, D. P. Curran, E. Lacôte, J. Lalevée ACS Macro Lett. 2012, 1, 92-95
- [4] : F. Le Qu\_ém\_ener, D. Subervie, F. Morlet-Savary, J. Lalevée, M. Lansalot, E. Bourdeat-Lami, E. Lacôte Angew. Chemie - Int. Ed. 2018, 57, 957-961

# Mechanosynthesis: Green Chemistry applied to the design of copper-based photoinitiators

F. Dumur,<sup>a</sup> M. Bouzratti-Zerelli,<sup>b,c</sup> G. Noirbent,<sup>a</sup> P. Garra,<sup>b,c</sup> H. Mokbel,<sup>b,c</sup> J. Lalevée,<sup>b,c</sup> D. Gigmes,<sup>a</sup>

<sup>a</sup> Aix Marseille Univ, CNRS, ICR UMR 7273, F-13397 Marseille, France.

<sup>b</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse.

<sup>c</sup> Université de Strasbourg, France

\* frederic.dumur@univ-amu.fr

**Key-Words:** Photopolymerization, Green Chemistry, Mechanosynthesis

## Abstract:

Photoinitiated polymerization plays a more and more important role in industry as reflected by the continuously growing number of applications of this technique in conventional areas such as coatings, inks, and adhesives but also in high-tech domains, like optoelectronics, laser imaging, stereolithography and nanotechnology. Indeed, photopolymerization presents several advantages such as very short reaction time even at room temperature and the absence of solvents avoiding the formation of volatile organic compounds (VOC). Moreover, the possibility to irradiate with high precision specific zones allows the spatial-control of the polymerization.[1] Since 2011, photoinitiating systems able to initiate polymerization under soft light irradiation sources have been the subject of intense efforts to minimize the risks and the costs related to the conventional UV irradiation. However, even if some results are promising, so far the reported systems still present low to moderate reactivity and can hardly compete with actual UV systems.

In the search for new photoinitiating systems, copper (II) complexes have been identified as promising candidates for the development of photoinitiating systems usable in industrial processes for coating applications and the production of thick epoxy/glass fiber composites. Parallel to high photoinitiating efficiencies, the mechanosynthesis of copper complexes has been identified as a promising approach for the design of photoinitiators.

In this presentation, a comparison of copper complexes with reference photoinitiating systems is also provided. The development of photoredox catalysts based on copper complexes provides a means for creating photoinitiating systems with unprecedented reactivity. Currently, no photoredox catalysts exist on the market and the design of photoinitiators by mechanosynthesis is not under use in industry yet.

## References :

[1] H. Mokbel, D. Anderson, R. Plenderleith, C. Dietlin, F. Morlet-Savary, F. Dumur, D. Gigmes, J.-P. Fouassier, J. Lalevée, *Polym. Chem.* **2017**, *8*, 5580–5592.



## Biomimetic photonic cellulose films

Axel Fouques<sup>a,b</sup>, Bruno Frka-Petesic<sup>b</sup>, Laurent Heux<sup>a\*</sup> and Silvia Vignolini<sup>b\*</sup>

<sup>a</sup> CERMAV, Univ. Grenoble Alpes - CNRS UPR 5301, F-38000 Grenoble, France

<sup>b</sup> University of Cambridge - Melville Laboratory for Polymer Synthesis, Department of Chemistry Lensfield Road  
CB2 1EW Cambridge - UK

\* Email contact : laurent.heux@cermav.cnrs.fr ; sv319@cam.ac.uk

**Key-Words:** nanocellulose, photonics, nanocomposites, biomimetic materials

### Abstract:

Cellulose nanocrystals (CNCs) are an excellent example of biosourced nanomaterials with a unique combination of mechanical and optical properties that can be used to design biomimetic materials. These nanorods form stable suspensions in aqueous media and self-assemble into cholesteric liquid crystalline phases above a critical concentration. Such behavior can be preserved in dry films, leading to color effects through the strong reflection of left circular polarization of light at a specific wavelength in the visible, reminiscent of natural structures<sup>1</sup> (Figure 1a). Nevertheless, the films produced so far usually display a polydomain structure, whereby the orientation of the helix  $h$  is not controlled and leads to a pixelated and polychromatic aspect.



Figure 1: a) Pixelated rainbow-like aspect of *Pollia Condensata*<sup>1</sup>. b) « Fingerprint pattern » of cholesteric cellulose nanocrystals in polarized optical microscopy. c) Cholesteric helices observed in scanning electron microscopy.

Although chemical and physical methods have both been used to control cellulose nanocrystals' optical response, the use of external fields, e.g., electric and magnetic, has been limited to only a few examples. Recently, our two groups (Vignolini and Heux) have demonstrated the possibility of using magnetic and electric fields to control the optical response of photonic cellulose-based structures<sup>2</sup>. Moreover, we have shown that the electric and magnetic field alignment could be further transferred into polymer nanocomposites, leading to materials with novel optical properties.

During this communication, we will discuss how electric and magnetic fields can be engineered to generate various degrees of orientation of the cholesteric domains and how it can be used to shape a dynamic optical response of CNC suspensions/films. Finally, we will show how the resulting optical properties can be transferred into a polymer nanocomposite.

### References :

- [1] S. Vignolini et al, *PNAS* 2012, **109**(39), 15712-15715  
[2] B. Frka-Petesic et al, *Adv. Mater.* 2017, **29**, 1606208

# Preparation of micro-patterned surfaces by the use of light-sensitive alkoxyamines

Yohann Guillauneuf

<sup>a</sup> Aix-Marseille-Univ, CNRS, Institut de Chimie Radicalaire, UMR 7273, F-13397 Marseille, France.

\* [yohann.guillauneuf@univ-amu.fr](mailto:yohann.guillauneuf@univ-amu.fr)

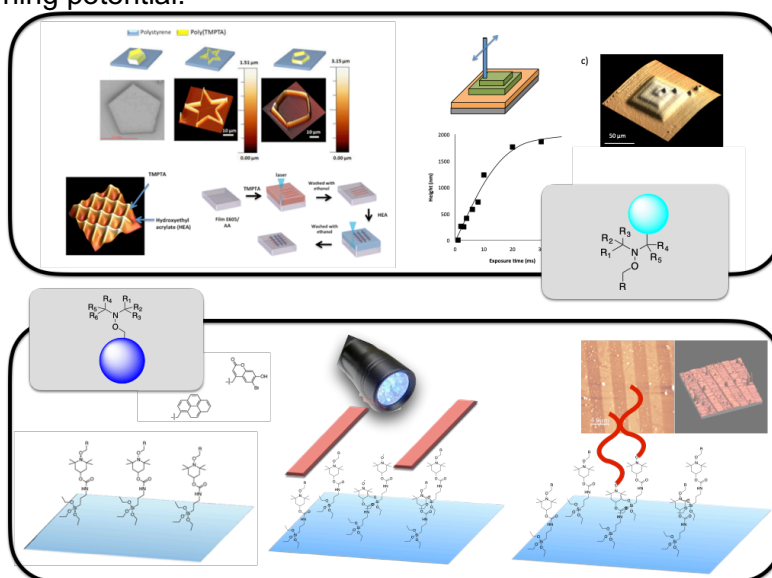
**Key-Words:** Nitroxide Mediated Photo-polymerization, Surface patterning, alkoxyamine, photo-protection of nitroxide

## Abstract:

The spatially controlled functionalization of surface is currently widely investigated for several applications. Two techniques could be used to prepare such micropatterns. The first one is a photopolymerization from the surface whereas it is also possible to couple polymers onto surfaces by efficient ligation methods.

Since ten years, we are working on the development of light-sensitive alkoxyamines as a efficient method to generate alkyl and nitroxide radicals with both temporal and spatial control. The position of the chromophore is a key parameter for its use. If located on the nitroxide moiety, it will allow to perform Nitroxide Mediated Photopolymerization (NMP2). Using both mask and direct laser writing, we showed that reinitiation of a polymerization from a surface prepared using a first monomer could occur and that patterns with another monomer having different properties could be obtained. It is also possible to tune the height of the pattern with the irradiation time (microstructure thickness from tens of nanometers to micrometers). The influence of the nitroxide design will be highlighted in this presentation.

Secondly several methods for the light induced formation of reactive groups on surfaces have been developed recently which avoid the loss of spatial resolution through diffusion of the photoactive component. Functional groups can be utilized for the efficient ligation of an appropriate reaction partner but require specific end-group for both partners. As the combination of alkyl radicals and nitroxides could be seen as a clean “click” reaction, we thus prepare light-sensitive alkoxyamines but with the chromophore on the alkyl moiety to selectively trigger the release of the nitroxide. Using an alkoxyamine covalently bound on surface, it is thus possible to generate patterns of nitroxides that could be coupled with a variety of alkyl radicals to prepare interesting micropatterns. The two approaches will be discussed in term of micropatterning potential.



## References :

- [1] Telitel, S.; Telitel, S.; Bosson, J.; Spangenberg, A.; Lalevée, J.; Morlet-Savary, F.; Clement, J.-L.; Guillauneuf, Y.; Gignes, D.; Soppera, O. *Adv. Mater. Interfaces* **2014**, 1 (5), 140067–5.  
 [2] Baron, M.; Morris, J. C.; Telitel, S.; Clement, J.-L.; Lalevée, J.; Morlet-Savary, F.; Spangenberg, A.; Malval, J.-P.; Soppera, O.; Gignes, D.; Guillauneuf, Y. *J. Am. Chem. Soc.* **2018**, 140 (9), 3339–3344.

## Low Energy Miniemulsification Device

Eirini Skoufa\*, Madeline Vauthier, Michel Bouquey, and Christophe A Serra

<sup>1</sup>*Institut Charles Sadron - Université de Strasbourg, CNRS - France*

### Abstract:

Miniemulsions are specially formulated heterophase systems in which stable nanodroplets of one phase are dispersed in a second, continuous phase. The size of the droplets is ranging between 50 and 500 nm [1]. In this project a low energy emulsification device, operating at pressures lower than 6 bars, was developed to produce monomodal thiol-ene miniemulsions. The process comprises an elongational flow mixer (pRMX) which accommodated a mixing element of four drilled holes of 1mm ID x 1cm L each [2]. A coarse emulsion was prepared. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP) - Diallyl phthalate (DAP) with hexadecane (HD) as hydrophobe, 2,5-Di-tert-butylhydroquinone (DBHQ) as radical inhibitor and Diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide (DTPO) as photoinitiator constitute the dispersed phase. While distilled water was used for the preparation of the continuous phase of the miniemulsion containing the surfactant, sodium dodecyl sulfate (SDS). This macroemulsion was initially charged in a chamber and pushed through the mixing element at a given flow rate by a pneumatic activated piston to fill in a downstream chamber (Figure1a). Then the flow was reversed and the whole operation counted for one cycle. Typical experiments accounted for 100 to 400 number of cycles. Upon recovery, the miniemulsion polymerization was triggered by UV-irradiations in a continuous-flow photoreactor to give rise to monomodal poly(thiol-ene) minisuspensions (Figure 1b). The wavelength of the UV lamp was  $\lambda = 365$  nm, which was corresponding to the minimum absorbance of the photoinitiator added into the dispersed thiol-ene phase. Typical residence time of the miniemulsion under the UV light was calculated to be 7 min [3].

This thiol-ene system was investigated in terms of increasing the number of cycles, inhibitor addition, surfactant and monomer concentration. The aforementioned factors were adequately controlled to get different particle sizes. Specifically, the diameter of the droplets was estimated using Dynamic Light Scattering (DLS) while at the same time Transmission Electron Microscopy (TEM) images of the samples were also taken. The droplet size range received from pRMX experiments was 100-250 nm. In more details, the addition of the inhibitor in the thiol-ene miniemulsion led to slightly bigger droplet diameter compared to the one without DBHQ. Also, the increase of the surfactant concentration resulted in even bigger sizes, while the biggest of all the diameters were obtained by increasing the solid content up to 40%. Nanodroplets and nanoparticles were also characterized by Proton Nuclear Magnetic Resonance (1H NMR) and Fourier-Transformed Infrared Spectroscopy (FTIR).

Conventional emulsification devices were also used for preparation of thiol-ene miniemulsions [4]. In more details, rotor-stator mixer (Ultra-Turrax) and sonicator [5] were employed and the obtained results were compared with those of pRMX. The resulting aqueous polymer minisuspensions obtained with the pRMX allowed getting systematically smaller sizes than those produced with the other two conventional emulsification devices. Regarding the literature, it is expected that the droplet size is strongly affected by the choice of the homogenizer [6]. In this case, pRMX dissipates the energy in much shorter time causing the power density to be higher, which leads to smaller droplet size.

### References :

- [1] : K. Landfester; N. Bechthold; S. Förster; and M. Antonietti, *Macromol. Rapid Commun.*, 1999, 20, 81-84
- [2] : I. Souilem; R. Muller; Y. Holl; M. Bouquey; C.-A. Serra; T. Vandamme; N. Anton, *Chemical Engineering Technology*, 2012, 35, 1-8
- [3] : W. Yu; C.-A. Serra; I.-U. Khan; M. Er-Rafik; M. Schmutz; I. Kraus; S. Ding; L. Zhang; M. Bouquey; R. Muller, *Macromolecular Reaction Engineering*, 2017, 11, 1600025
- [4] : C.-E. Hoyle; T.-Y. Lee; T. Roper, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2004, 42, 5301-5338
- [5] : F. Jasinski; A. Rannée; J. Schweitzer; D. Fischer; E. Lobry; C. Croutxé-Barghorn; M. Schmutz; D.-L. Nouen; A. Criqui; A. Chemtob, *Macromolecules*, 2016, 49, 1143-1153
- [6] : J.-M. Asua, *Progress in Polymer Science*, 2002, 27, 1283-1346

# LATEST ADVANCES IN NANOSCALE IR SPECTROSCOPY AND IMAGING

[Miriam Unger](#) <sup>\*a</sup>, Anirban Roy <sup>b</sup>, Qichi Hu <sup>b</sup>

<sup>a</sup> Bruker Nano Surfaces, 76187 Karlsruhe, Germany

<sup>b</sup> Bruker Nano Surfaces, Santa Barbara, CA 93117, USA

\* miriam.unger@bruker.com

**Key-Words:** nanoscale IR Spectroscopy, Photothermal AFM-IR, IR s-SNOM, nanoscale analysis

## Abstract:

For the last few decades the rapid growth in the field of nanoscience and technology has led to the development of new characterization tools for nanoscale materials. Traditional IR and Raman spectroscopy and imaging offers excellent chemical insights; however, the spatial resolution is limited by the optical diffraction limit ( $\sim\lambda/2$ ). Although, recent Super-resolution microscopy techniques offer superior spatial resolution, they are primarily implemented in fluorescence imaging, hence needs external fluorophore tag for detection. Alternatively, nanoscale IR spectroscopy/imaging offers a “tag free” spectral detection with high spatial resolution beyond optical diffraction limit (2-5  $\mu\text{m}$ ) by exploiting an AFM probe [1] to detect either photothermal expansion force (PTIR) or near field scattered IR light (sSNOM).

Recent developments in PTIR and sSNOM technology have significantly augmented the speed and spatial resolution for chemical analysis. One of the new developments (Tapping AFM-IR) allows acquisition of IR images at a specific absorption band simultaneously with sample topography and nano-mechanical properties, providing a complete set of topographical, chemical and mechanical insights with <10 nm spatial resolution. These high-resolution measurements are currently accompanied by high speed tunable laser enabling fast point spectral acquisition (1-2 ms/spectrum) leading to hyperspectral data cube for rigorous statistical analysis like Chemometrics applications.

In this presentation, we will highlight the technical background and applications to study polymeric nanostructures, ranging from the identification of polymeric defects, nano-phase separation in polymer blends and nano-composites.

## References :

[1] : A. Dazzi and C.B. Prater, *Chem. Rev.*, 2016, **117**, 5146-5173

# Bright and Small Fluorescent Polymer Nanoparticles for Intracellular Imaging

Andreas Reisch <sup>\*a</sup>, Anne Runser <sup>a</sup>, Vitalii Rosiuk <sup>a</sup>, Yuliia Koval <sup>a</sup>, Pascal Didier <sup>a</sup>, Denis Dujardin <sup>a</sup>, Andrey Klymchenko <sup>a</sup>

<sup>a</sup> Laboratoire de Bioimagerie et Pathologies, UMR CNRS 7021, University of Strasbourg, 74 route du Rhin, 67401 Illkirch; France

\* reisch@unistra.fr

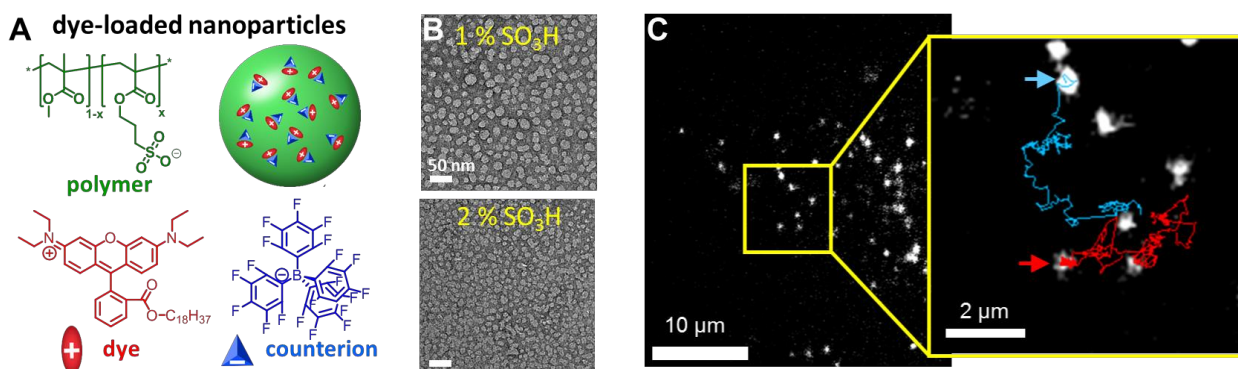
**Key-Words:** fluorescent nanoparticles, polymer nanoparticles, bioimaging

## Abstract:

Fluorescent polymer nanoparticles encapsulating large quantities of dyes, so-called dye-loaded polymer nanoparticles (NPs), have emerged over the last years as an attractive alternative to inorganic fluorescent NPs, notably quantum dots (Fig. A).<sup>[1]</sup> These new nanomaterials can combine biodegradability and low toxicity with superior brightness, which can drastically improve speed, resolution and sensitivity in fluorescence bioimaging.

Here, we show how simple polymer chemistry can be used to control key properties of these NPs in view of their use as bright labels for intracellular imaging: Variation of the fraction and type of charged groups on the polymers enabled preparation of polymer NPs with controlled sizes from 50 down to 7 nm through nanoprecipitation (Fig. B).<sup>[2,3]</sup> Tracking these NPs at the single particle level inside living cells showed that a particle size of less than 23 nm is needed for free particle diffusion in the cytosol (Fig. C).

Adjusting the composition and hydrophobicity of the polymers used for NP assembly, and encapsulating charged fluorophores with bulky hydrophobic counterions, allowed to optimize the fluorescence quantum yield and thus the brightness of the NPs, and to obtain fluorescent NPs 100 times brighter than quantum dots.<sup>[4,5]</sup> At the same time the dye-organization inside the polymer matrix could be influenced: This allowed tuning the collective behavior of the encapsulated dyes and creating blinking and non-blinking particles, optimized for single molecule imaging.<sup>[6]</sup>



(A) Schematic view of dye-loaded polymer nanoparticles and the used dyes, counterions and polymers; (B) transmission electron micrographs of particles made from polymers bearing different amounts of charged groups; (C) fluorescence microscopy images of nanoparticles microinjected into living cells.

## Acknowledgements:

This work was supported by the Agence National de Recherche JC/JC grant ANR-16-CE09-0007 and by the European Research Council ERC Consolidator grant BrightSens 648528.

## References :

- [1] A. Reisch, A. S. Klymchenko, *Small* **2016**, *12*, 1968.
- [2] A. Reisch, A. Runser, Y. Arntz, Y. Mély, A. S. Klymchenko, *ACS Nano* **2015**, *9*, 5104.
- [3] A. Reisch, D. Heimburger, P. Ernst, A. Runser, P. Didier, D. Dujardin, A. S. Klymchenko, *Adv. Funct. Mater.* **2018**, *28*, 1805157.
- [4] A. Reisch, P. Didier, L. Richert, S. Oncul, Y. Arntz, Y. Mély, A. S. Klymchenko, *Nat. Commun.* **2014**, *5*, 4089.
- [5] V. Rosiuk, A. Runser, A. Klymchenko, A. Reisch, *Langmuir* **2019**, *35*, 7009.
- [6] A. Reisch, K. Trofymchuk, A. Runser, G. Fleith, M. Rawiso, A. S. Klymchenko, *ACS Appl. Mater. Interfaces* **2017**, *9*, 43030.

## Thursday, November 28<sup>th</sup>

### Polymer interfaces and (nano)composites - Session 1 -

*Chairs: Alexandre Beigbeder & Dimitri Ivanov*

8.30 **Adrian Dinu & Wolfgang Meier**  
Amphiphilic Block Copolymers: From Synthetic Pathways Towards Functional Biomimetic Membranes

9.10 **Pascal Carrière**  
Graphene oxide as in-situ hydrolytic aging sensor using Raman spectroscopy for thermosets matrix

9.30 **Virginie Goetz**  
Reduction of the sensitivity of a metal-oxide energetic composition by adding a conducting polymer

9.50 **Benjamin Le Droumaguet**  
Hypercrosslinking approach toward high surface area functional polyHIPes: Towards efficient supports for heterogeneous supported catalysis

10.10 Coffee break

10.30 **Michel Fontanille**  
*Prix d'honneur* of the French Polymer Society

10.45 **Round Table: Open Access Publication**  
*Moderator: Abraham Chemtob*  
Adeline Rege / Jehanne Ducros-Delaigue / Sylvain Ribault / Frédéric Hélein

12.30 Lunch – POSTER SESSION

### Polymer interfaces and (nano)composites - Session 2 –

*Chairs: Adrian Dinu & Florence Bally- Le Gall*

14.00 **Alexandre Beigbeder**  
Adding value to composites through in situ functionalisation : use of printed electronic and nanofillers

14.40 **Olivier Felix**  
Engineering the properties of self-assembled bio-inspired nanocomposite materials

15.00 **Patrick Masson**  
PMMA brushes: Routes toward Ti/PMMA/Ti sandwich for biomedical implant

15.20 **Meike Koenig**  
Functional poly-p-xylylene coatings via chemical vapor deposition polymerization

15.40 **Fouzia Boulmedais**  
Electrotriggered self-construction of polymeric films: new concept and application

16.00 3 min Poster Pitches - Session 4 -

16.25 Coffee break

16.50 **Alexandre Legris / Yves Grohens / Jannick Rumeau**  
*Action Convergence* CNRS

17.10 **Jessica Delavoipiere**  
*Prix de thèse* of the French Polymer Society

17.20 **Marvin Langlais**  
*Prix de thèse* of the French Polymer Society

17.30 **Bernadette Charleux**  
*Grand Prix* of the French Polymer Society  
From years dedicated to controlled free-radical polymerization in water to sustainable construction products at Saint-Gobain.

18.00 Gala Dinner

# Amphiphilic Block Copolymers: From Synthetic Pathways Towards Functional Biomimetic Membranes

Ionel Adrian Dinu and Wolfgang Meier\*

Department of Chemistry, University of Basel, Mattenstrasse 24a,  
BPR 1096, 4058 Basel, Switzerland

\*wolfgang.meier@unibas.ch

**Key-Words:** amphiphilic polymers, block copolymers, self-assembly, polymersomes.

## Abstract:

Amphiphilic block copolymers possess several interesting properties similar to surfactants or lipids including the capability to self-assemble in aqueous media into micelles, membrane-like structures or other supramolecular architectures. The morphology and stability of these self-assembled superstructures can be controlled via the selection of suitable monomers, the precise adjustment of molecular weight and the rigorous choice of hydrophilic-to-hydrophobic block length ratios [1-3]. The large variety of available monomers gives the possibility to synthesize a broad range of block copolymers, whose physical and chemical properties can be tailored by introducing simultaneously various functionalities into one single macromolecule. In this manner, we synthesized and characterized a lengthy series of amphiphilic block copolymers, which were able to form artificial membranes that can structurally resemble the cell membranes. When compared to those prepared from low molar mass molecules (e.g. lipids), the membranes based on macromolecular self-assembly have not only a superior stability and toughness, but offer the appropriate synthetic environment to host a plethora of active compounds, including catalysts or biomolecules [1,3].

Such systems can also provide the possibility to control the release of some encapsulated drugs as a response to an external trigger. In addition, well-defined functions can be introduced by combining the artificial polymer architectures with biologically relevant functional units, e.g. membrane proteins [1,4]. Thus, the block copolymer membranes allow for the reconstitution of many transmembrane proteins. Interestingly, a guided insertion of integral proteins was observed when there is a preferential interaction between the intra-/extracellular domains of the protein and the inner/outer surfaces of an asymmetric polymer membrane. Depending on the membrane composition, the predominant orientation of the inserted protein enables a directed transport of the substrates across the membrane [5-7]. This promising concept can be used in synthetic biology, particularly to obtain various drug-delivery systems, nanoreactors as mimics of natural organelles or to develop more complex cell-inspired responsive systems.

## References :

- [1] : S. Y. Avsar; M. Kyropoulou; S. Di Leone; C.-A. Schoenenberger; W. P. Meier; and C. G. Palivan, *Frontiers in Chemistry*, 2019, **6**, 645
- [2] : V. Chimisso; V. Maffei; D. Hürliemann; C. G. Palivan; and W. Meier, *Macromolecular Bioscience*, 2019, 1900257, DOI: 10.1002/mabi.201900257
- [3] : M. Gami; R. Wehr; S. Y. Avsar; C. John; C. Palivan; and W. Meier, *European Polymer Journal*, 2019, **112**, 346–364
- [4] : S. Tamboo; A. Najer; A. Belluati; C. von Planta; D. Wu; I. Craciun; W. Meier; and C. G. Palivan, *Advanced Functional Materials*, 2019, **29**, 1904267
- [5] : E. V. Konishcheva; U. E. Zhurav; and W. P. Meier, *Macromolecules*, 2017, **50**, 1512–1520
- [6] : E. V. Konishcheva; D. Daubian; S. Rigo; and W. P. Meier, *Chemical Communications*, 2019, **55**, 1148–1151.
- [7] : J. Gaitzsch; S. Hirschi; S. Freimann; D. Fotiadis; and W. Meier, *Nano Letters*, 2019, **19**, 2503–2508.



# GRAPHENE OXIDE AS AN *IN-SITU* HYDROLYTIC AGING SENSOR USING RAMAN SPECTROSCOPY FOR THERMOSETS MATRIX

Hamza Bekkali <sup>a,b</sup>, Alexandre Merlen <sup>b</sup>, [Pascal Carriere](mailto:pascal.carriere@univ-tln.fr)<sup>\*a</sup>

<sup>a</sup> Université de Toulon, Laboratoire MAPIEM, CS 60 584 – 83041 TOULON CEDEX 9 FRANCE

<sup>b</sup> Université de Toulon, Aix Marseille Univ. IN2MP, CS 60 584 – 83041 TOULON CEDEX 9 FRANCE

\* pascal.carriere@univ-tln.fr

**Key-Words:** Raman spectroscopy, graphene oxide, interface aging in composites

## Abstract:

Glass fibers epoxy composites are used in engineering structures such as aircraft, space structure, wind turbine or piping in offshore environments. Due to the inaccessibility of these structure in operation and their exposure to aggressive environment, the need to remotely monitor the material behavior is more and more important to prevent any fatal failure and improve the maintenance structures plan. Different real-time, in situ, and nondestructive technique had been developed to sense the fibers' strain condition. Using Raman spectroscopy to monitor the deformation behavior is only possible when well-defined Raman spectra can be obtained from fibers which is not the case for glass fiber. Therefore, incorporation of Raman sensitive materials is needed [1]. Graphene oxide is a good candidate because of its resonantly enhanced Raman bands. Moreover, graphene's strain inducing different peak shifts are well-described [2] and recently applied to composite materials [3]. In addition to the mechanical stresses of composite materials, there are also the effects of environmental aging such as hydrolytic aging, which strongly modify the interphase between the fiber and the resin [4]. The main consequences of hydrolytic aging are: matrix plasticization, microcracks density that increase with water sorption-desorption cycles and internal stresses increase over time. The mechanical properties are thus usually reduced by these plasticization effect and hydrolysis reactions [5], but also counterbalanced by a reinforcing effect induced by the hydrogen bonds that water molecules can generate with the network resulting in physical crosslinking [6] or even post-crosslinking the matrix network.

In this study, we demonstrated the possibility of using graphene oxide combined with Raman spectrometry to finely monitor the complex hydrolytic aging mechanisms involved in epoxy matrix. Indeed, in one hand, we had chosen different amine hardeners (aliphatic and aromatic ones) in order to tune the strain surrounding graphene oxide, and in the other hand we had controlled the hydrolysis reactions during hydrolytic aging. The strain sensitivities of different epoxy matrix was determined by Raman spectroscopy during aging and compared to thermomechanical properties achieved by Dynamic Mechanical Analysis and network chemical degradation by Infra-Red spectroscopy. First, we show that peak shift observed by Raman spectroscopy can be not only correlated to internal strain as expected but also to graphene oxide reduction induced by chemical reaction with absorbed water at graphene oxide interface with epoxy. Second, resin network degradation by oxidation process yield fluorescence which can be sensed by Raman spectroscopy. These different informations obtained by Raman spectroscopy from graphene oxide as a relevant sensor for monitoring resin aging will be discussed in detail.

## References :

- [1] A. Barber, Q.Zhao, H. Wagner;C. Baillie, *Compos. Sci. Technol.*, 2004, **64**,1915
- [2] T.M.G. Mohiuddin, A. Lombardo, R.R.Nair, A. Bonetti, G. Savini, R. Jalil, N. Bonini, D.M. Basko, C. Galiotis, N. Marzari, K.S. Novoselov, A.K. Geim, A.C. Ferrari, *Phys. Rev. B: Condens. Matter Mater. Phys.*2009, **79**, 205433
- [3] D.G. Papageorgiou, I.A. Kinloch, R.J. Young, *Prog. Mater. Sci.*, 2017, **90**,75,
- [4] S. Sethi, B.C. Ray, *Advances in Colloid and Interface Science* 2015, **217**, 43
- [5] M.C. Lee, N.S. Peppas, *Prog. Polym. Sci.* 1993, **18**, 947
- [6] J.M. Zhou, J.P. Lucas, *Polymer* 1999, **40**, 5505.

# Reduction of the sensitivity of a metal-oxide energetic composition by adding a conducting polymer

Virginie Goetz <sup>\*a</sup>, Pierre Gibot <sup>a</sup>

<sup>a</sup> Laboratoire Nanomatériaux pour les Systèmes Sous Sollicitations Extrêmes (NS3E) UMR 3208 ISL/CNRS/UNISTRA, Institut franco-allemand de recherches de Saint-Louis (ISL), 5 rue du Général Cassagnou, 68301 Saint-Louis cedex - France

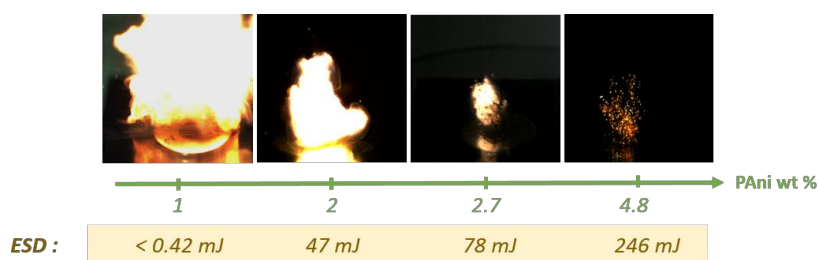
\* virginie.goetz@isl.eu

**Key-Words:** Thermite energetic materials, Polyaniline polymer, Nanocomposite, Electrostatic discharge desensitization

## Abstract:

Nanothermites are mixtures made of metal (fuel) and metal oxide (oxidizer) nanoparticles that react according to an exothermic reaction by releasing high amounts of heat ( $3.5 - 27 \text{ kJ/cm}^3$ ) at high temperatures (2000 - 3000 K) [1]. With such properties, nanothermites are good candidates for being pyrotechnic igniters. But these compositions exhibit an extreme sensitivity to the electrostatic discharge (ESD) making their handling and transport hazardous. The desensitization of the nanothermites to the ESD can be performed by adding a third component such as carbon (nanofibres/nanotubes [2,3]) or polymers [4,5]. The idea is to create a conducting network within the nanothermite which will be able to rapidly dissipate the electrostatic charges in order to avoid high energy density on the surface of particles. This would prevent any thermal heating and also accidental ignition of energetic materials. However, large amounts of additive ( $\geq 4 - 5 \text{ wt. } \%$ ) are needed to mitigate the sensitivity which lead to an important degradation of the reactivity (combustion velocity).

Herein, an intrinsic conducting polymer such as polyaniline (PAni) was selected and introduced in an Al/SnO<sub>2</sub> energetic composition by means of synthesis of a SnO<sub>2</sub>/PAni hybrid matrix [6]. First results reveal an interesting gradual desensitization to the ESD, as a function of polyaniline amount. For instance, with only 2 wt. % of PAni, the ESD sensitivity threshold of the Al/SnO<sub>2</sub>-PAni thermite is much higher (47 mJ) than the thermite without polymer (0.42 mJ). This is really interesting because this value is also higher than what a human body can dissipate (8.33 - 20 mJ) [7,8]. More, as illustrated on the figure below, the reactivity of the Al/SnO<sub>2</sub>-PAni is acceptable for future applications. Through this approach, moderate sensitive and reactive nanothermite could be obtained with a low rate of additive.



Combustion images of the Al/SnO<sub>2</sub>-PAni nanothermite depending of the PAni amount. The corresponding ESD threshold values are given.

Funding from the French-German Research Institute of Saint Louis (ISL) and the Agency Defence Innovation (AID)

## References:

- [1] : H. Goldschmidt, Method of Producing Metals & Alloys, 1897, 578-868.
- [2] : B. Siegert, M. Comet, O. Muller, G. Pourroy, D. Spitzer, *J. Phys. Chem. C*, 2010, **114**, 19562-19568.
- [3] : K.H. Poper, E.S. Collins, M.L. Pantoya, M.A. Daniels, *J. Electrostat.*, 2014, **72**, 428-432.
- [4] : P. Gibot, A. Bach, L. Vidal, F. Schnell, R. Gadiou, D. Spitzer, *J. Ener. Mater.*, 2017, **35:2**, 135-147.
- [5] : S. Apperson, S. Bhattacharya, Y. Gao, S. Subramanian, S. Hasan, M. Hossain, R.V. Shende, P. Redner, D. Kapoor, S. Nicolich, K. Gangopadhyay, S. Gangopadhyay, *Mater. Res. Soc. Symp. Proc.*, 2006, **896** (6p).
- [6] : B. Zhang, Y. Du, P. Zhang, H. Zhao, L. Kang, X. Han, P. Xu, *J. Appli. Polym. Sci.*, 2013, **130**, 1909-1916.
- [7] : W.D. Greason, *J. Electrostat.*, 2003, **59**, 285-300.
- [8] : M.B. Talawar, A.P. Agrawal, M. Anniyappan, D.S. Wani, M.K. Bansode, G.M. Gore, *J. Hazard Mater.*, 2006, **137:2**, 1074-1078.



# HYPERCROSSLINKING APPROACH TOWARD HIGH SURFACE AREA FUNCTIONAL POLYHYPES: TOWARDS EFFICIENT SUPPORTS FOR HETEROGENEOUS SUPPORTED CATALYSIS

Benjamin Le Droumaguet,<sup>a,\*</sup> Sarra Mezhoud,<sup>a</sup> Muzafer Paljevac,<sup>b</sup> Amadeja Koler,<sup>b</sup> Daniel Grande,<sup>a</sup> Peter Krajnc<sup>b</sup>

<sup>a</sup> Université Paris-Est, Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182 CNRS-UPEC, 2 rue Henri Dunant, 94320 Thiais, France

<sup>b</sup> University of Maribor, Faculty of Chemistry and Chemical Engineering, PolyOrgLab, Smetanova 17, 20000 Maribor, Slovenia

\* ledroumaguet@icmpe.cnrs.fr

**Key-Words:** porous materials, hypercrosslinking, metallic nanoparticles, supported heterogeneous catalysis

## Abstract:

Porous polymeric materials have known a tremendous interest from the research community in the last decade, notably regarding their potential use as frameworks meant for heterogeneous supported catalysis, after suitable immobilization of metallic nanoparticles at their pore surface. [1-3] In this purpose, highly porous poly(2-hydroxyethyl methacrylate-co-*N,N'*-methylenebisacrylamide) frameworks were prepared from oil-in-water high internal phase emulsions (HIPes). Upon subsequent functionalization through a two-step synthetic pathway involving activation of the hydroxyl functions exposed at the pore surface and subsequent functionalization with allylamine or propargylamine, two distinct functionalized porous polymers were obtained. A final step relying on radical thiol-ene/yne “click” additions with di- or tetrathiols was further investigated so as to hypercrosslink the resulting porous materials and eventually decorate the pore surface with thiol functions. They were further characterized in terms of porosity and chemical composition through mercury intrusion porosimetry, nitrogen adsorption-desorption porosimetry, and Raman spectroscopy, respectively. Unprecedented very high specific surface area values, as determined by nitrogen sorption porosimetry, were found, namely up to 1500 m<sup>2</sup>.g<sup>-1</sup> for HEMA-based material functionalized with allylamine after hypercrosslinking with pentaerythritol. [4] *In-situ* generated gold nanoparticles were immobilized at the pore surface, and one such strategy allowed for the preparation of hybrid materials that were successfully applied for the supported heterogeneous catalytic reduction of a nitroaromatic compound, *i.e.* *p*-nitrophenol, and of a pollutant dye used in textile industry, *i.e.* Eosin Y, as depicted in Fig. 1.

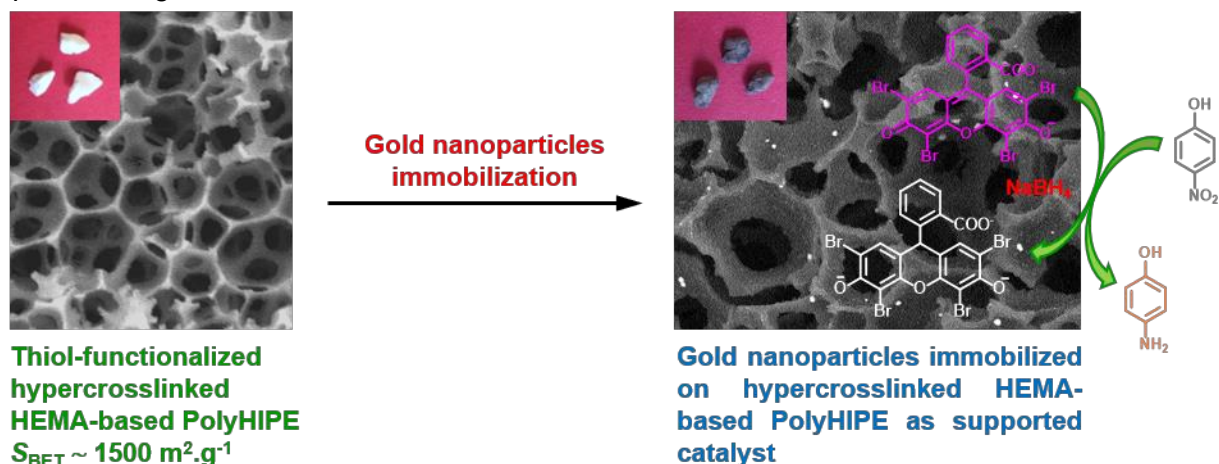


Fig. 1: Schematic representation of the immobilization of *in situ* generated gold nanoparticles at the pore surface of hypercrosslinked thiol-decorated PHEMA-based porous frameworks.

## References :

- [1] : R. Poupart, B. Le Droumaguet, M. Guerrouache, D. Grande, B. Carbonnier, *Polymer*, 2017, **126**, 455-462  
 [2] : R. Poupart, A. Benlahoues, B. Le Droumaguet, D. Grande, *ACS Appl. Mater. Interfaces*, 2017, **9**, 31279-31290  
 [3] : B. Le Droumaguet, R. Poupart, D. Grande, *Polym. Chem.*, 2015, **6**, 8105-8111

[4] : S. Mezhoud, M. Paljevac, A. Koler, B. Le Droumaguet, D. Grande and P. Krajnc, *React. Funct. Polym.*, 2018, **132**, 51-59

# Adding value to composites through in situ functionalisation : use of printed electronic and nanofillers

[Alexandre BEIGBEDER](#)<sup>a\*</sup>, Lionel TENCHINE<sup>a</sup>, Patrick DEWAILLY<sup>a</sup>, Pascal FRANCESCATO<sup>a</sup>, Alexandre PEREIRA<sup>b</sup>

\* [alexandre.beigbeder@ct-ipc.com](mailto:alexandre.beigbeder@ct-ipc.com)

<sup>a</sup>IPC – Centre Technique Industriel de la Plasturgie et des Composites

<sup>b</sup>Commissariat à l'énergie atomique et aux énergies alternatives, CEA, LITEN

**Key-Words:** Smart Composites, printed electronics, nanofillers

## Abstract:

With increasing demand related to environmental impact reduction of transportation means, composites are appraised for their high specific resistance and design freedom allowing for 15 to 40% mass reduction against metal parts. However, in spite of the introduction of new materials and processes, composite solutions still lack competitiveness against standard metal parts in various applications. Adding new functions with in-process integration in composites is therefore a way to improve their overall economic balance and open new opportunities. Thus, for example, the heterogeneous structure of composites offers new possibilities for functions.

In this presentation, we will present the integration of printed electronics inside a composite part and the investigation of its influence on the overall performances of the device, with two main focuses: the modification of the composite mechanical properties, and the potential damaging of the electronics functionality related to process conditions.

Mechanical properties modifications induced by the integration of printed electronics in the composite part architecture is studied by means of fatigue tests under specific loads. Various combination of printed electronics substrates (PET, PI, paper, ...), are tested and characterized. In addition, Double Cantilever Beam test is performed using dedicated test samples, in order to analyse Mode I rupture toughness evolution due to printed electronics embedding in the composite structure. This analysis will be supported by modelling and simulation, enabling a deeper understanding of the failure mechanisms in smart composites, in particular in relation with delamination and fracture propagation.

We will also present some recent works on the development on numerical approaches of the properties of nanocomposites materials. Self-responsive studied properties are based on piezo resistivity and joule effect

The reported study is illustrated with various functional demonstrators recently developed by IPC.

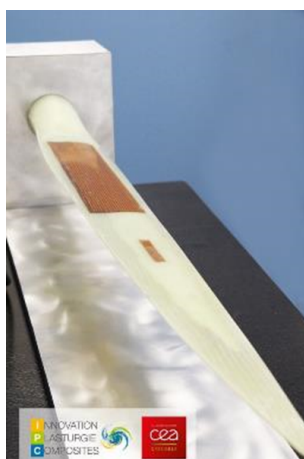


Figure 1: Wind turbine blade demonstrator. thanks to the use of a functional film, ten individual components were added in a single step (see figure 10): six strain gages, three temperature sensors (one not shown on figure) and a heating element.

# Engineering the properties of self-assembled bio-inspired nanocomposite materials

Olivier Félix<sup>a,\*</sup>, Rémi Merindol<sup>a,b</sup>, Rebecca Blell<sup>a,b</sup>, Xiaofeng Lin<sup>a,b</sup>, Matthias Pauly<sup>a,b</sup>, Thierry Roland<sup>a,c</sup>, Christian Gauthier<sup>a,b</sup>, Gero Decher<sup>a,b</sup>

<sup>a</sup> Institut Charles Sadron UPR22-CNRS, 23 rue du Loess, 67034 Strasbourg Cedex 2, France;

<sup>b</sup> Université de Strasbourg, 1 rue Blaise Pascal, 67008 Strasbourg, France

<sup>c</sup> Institut National des Sciences Appliquées de Strasbourg, 24 Bd de la Victoire, 67084 Strasbourg, France

\* olivier.felix@ics-cnrs.unistra.fr

**Key-Words:** LbL assembly, grazing incidence spraying, nanocomposite materials, anisotropic properties, bio-inspired complex superstructures

## Abstract:

Through evolution, nature has developed composite materials (e.g. bone, wood, nacre or crustacean exoskeleton) with complex and hierarchical organization from the nano- to the macro-scale via molecular assembly. Such materials possess fascinating combinations of properties such as lightweight, strength or shock resistance by assembling hard and soft elements. The remarkable mechanical performance of such natural hybrid materials has prompted the fabrication of bio-inspired composites.

The development of nanocomposite materials of high compositional and structural complexity is generally thought to be very important but not much explored due to the lack of appropriate methods for their preparation. With respect to the preparation of multimaterial thin films with a high level of control over the spatial positioning of their constituents, Layer-by-Layer (LbL) assembly [1,2] has gained its merits as a simple and highly versatile nanofabrication method. While the sequence of components in layered multimaterial films can be very well controlled by LbL-assembly, tuning of the in-plane anisotropy has not yet been achieved. Recently, we have introduced a novel method called "Grazing Incidence Spraying" for the in-plane alignment of anisotropic nanoparticles (cellulose nanofibrils, metallic nanowires and nanorods, ...) on large areas [3,5]. Its combination with the LbL-approach permits to extend it toward the preparation of complex (e.g. helical) multilayer films in which the composition and orientation can be controlled independently in each layer.

The talk will illustrate some of our recent results on the design of bio-inspired nanostructured materials combining hard anisotropic elements like nanofibrillated cellulose and silver nanowires with soft polymer building blocks. The preparation of such thin films will be presented and their optical and mechanical properties as function of the film composition and geometry will be discussed.

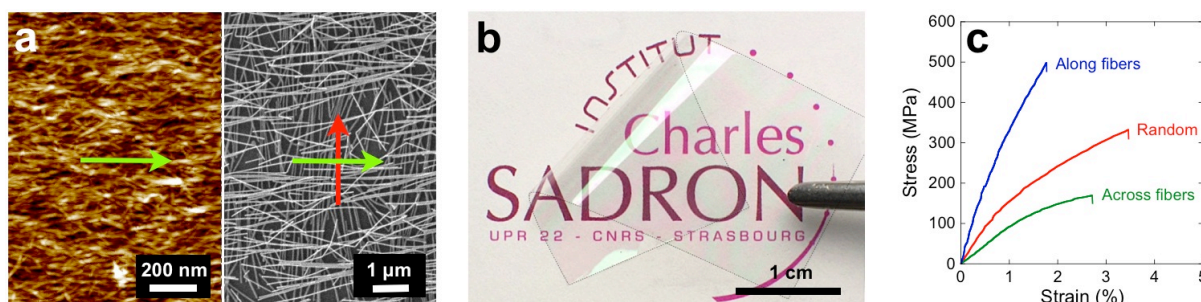


Fig. 1: (a) In-plane alignment of anisotropic nano-objects (1D (left) and crisscross (right)). (b) Optical photograph of a cellulose based-LbL film. (c) Tensile properties of random (red) and oriented nano-composites (along (blue) and across (red) the direction of orientation).

## References :

- [1] : G. Decher, *Science*, 1997, **277**, 1232-1237
- [2] : Multilayer Thin Films: Sequential Assembly of Nanocomposite Materials, 2nd Edition (Eds: Decher, G. and Schlenoff, J. B.), Wiley-VCH: Weinheim, 2012
- [3] : S. Sekar, V. Lemaire, H. Hu, G. Decher, M. Pauly, *Faraday Discuss.*, 2016, **191**, 373-389
- [4] : H. Hu, M. Pauly, O. Felix, G. Decher, *Nanoscale*, 2017, **9**, 1307-1314
- [5] : R. Blell, X. Lin, T. Lindström, M. Ankerfors, M. Pauly, O. Felix, G. Decher, *ACS Nano*, 2017, **11**, 84-94

# PMMA Brushes: Routes toward Ti/PMMA/Ti Sandwich for Biomedical Implant

Melania Reggente<sup>a,b,#</sup>, Wenjia He<sup>a</sup>, Tiphaine Schott<sup>c</sup>, Martial Morin<sup>a,d</sup>, Françoise Liautaud<sup>c</sup>, Véronique Migonney<sup>d</sup>, Patrick Masson<sup>a\*</sup>, Geneviève Pourroy<sup>a</sup>, Heinz Palkowski<sup>b</sup>, Adele Carradò<sup>a</sup>

<sup>a</sup> Université de Strasbourg – CNRS, UMR 7504, IPCMS, 23 rue du Loess, 67034 Strasbourg, France

<sup>b</sup> Clausthal University of Technology, Institute of Metallurgy, Robert Koch Strasse 42, 38678 Clausthal-Zellerfeld, Germany

<sup>c</sup> CETIM Grand EST, 21 rue de Chemnitz 68068 Mulhouse, France

<sup>d</sup> UMR CNRS 7244 Institut Galilée Université Paris 13, 99 avenue Clément, 93430 Villetaneuse, France

\* patrick.masson@ipcms.unistra.fr

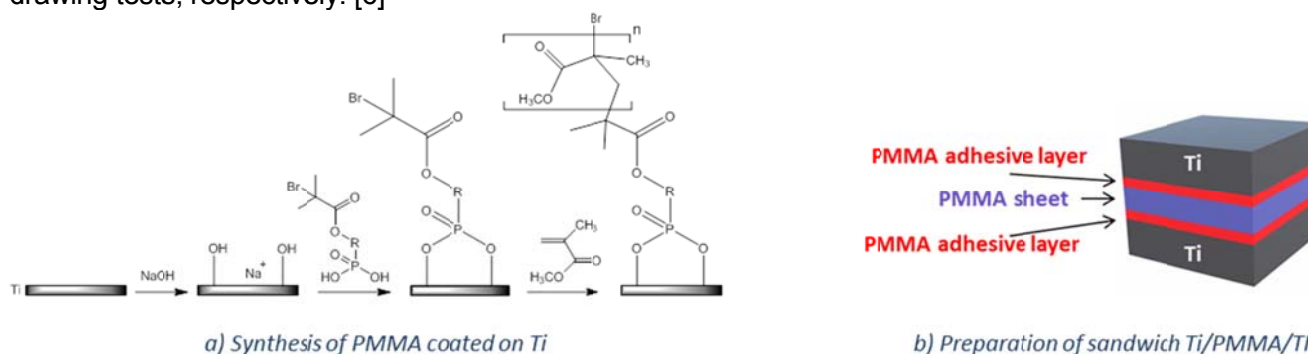
**Key-Words:** biomedical, hybrid material, sandwich structure, formability

## Abstract:

Due to its biocompatibility, Titanium (Ti) is an extensively used material in biomedical applications. Nevertheless, the differences of mechanical properties between Ti and surrounding tissues lead to stress shielding, one cause to implants failures. To overcome this effect, sandwich Ti/polymer/Ti structures were developed. For non-biological applications, bonding between metal and polymer is normally achieved using a (cytotoxic) epoxy resin. In our investigations, we designed innovative epoxy resin-free sandwich materials based on Ti and poly(methylmethacrylate) (PMMA). [1]

The elaboration of three-layered biocompatible sandwich structures composed of Ti and polymer sheets (Ti/PMMA/Ti) with a resin-free interlayer for bonding via “Grafting from” method was successfully carried out. Indeed, to create a strong interface, the two materials are attached through covalent bonds. To achieve this, Ti surface undergoes a structuring alkaline treatment prior to the reaction of a phosphonic acid-containing ATRP polymerization initiator. The PMMA brushes were then grown from the modified Ti surface via controlled radical polymerization. [2]

We present the multi-technique characterization of the Ti/PMMA construct. We show - that the preparation conditions of the interface [3] strongly influence the thickness, morphology and porosity of the PMMA brush - must be controlled to achieve specific properties. [4] Moreover, the durability of this system was evaluated by studying its corrosion resistance in biological medium. [5] Ti/PMMA/Ti sandwiches were obtained by hot-pressing, exploiting the interpenetration between the grafted PMMA chains and those of an adhering PMMA foil used as core material. Ti/PMMA/Ti bonding strength, mechanical properties and forming behavior were evaluated performing pull-off tests, standard tensile, bending, Erichsen and deep-drawing tests, respectively. [6]



## References:

- [1] M. Reggente, P. Masson, C. Dollinger, H. Palkowski, S. Zafeiratos, L. Jacomine, D. Passeri, M. Rossi, N. Vrana, G. Pourroy, A. Carradò, *ACS Appl. Mater. Interfaces*, 2018, **10**, 5967-5977.
- [2] V. Vergnat, G. Pourroy, P. Masson, *Polymer International*, 2013, **62**, 878-893.
- [3] M. Reggente, S. Kriegel, P. Masson, G. Pourroy, F. Mura, J. Faerber, D. Passeri, M. Rossi, H. Palkowski, A. Carradò, *Pure Appl. Chem.*, 2019, doi.org/10.1515/pac-2019-0223.
- [4] M. Reggente, M. Natali, D. Passeri, M. Lucci, I. Davoli, G. Pourroy, P. Masson, H. Palkowski, U. Hangen, A. Carradò, M. Rossi *Colloids and Surfaces A*, 2017, **532**, 244-251
- [5] T. Schott, F. Liautaud, S. Kriegel, J. Faerber, W. He, P. Masson, G. Pourroy, A. Carradò, *Pure Appl. Chem.*, 2019, doi.org/10.1515/pac-2018-1218.
- [6] M. Reggente, M. Harhash, S. Kriegel, P. Masson, J. Faerber, G. Pourroy, A. Carradò, H. Palkowski, *Composite Structures*, 2019, **218**, 107-119.

# Present address: Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland

# Functional Poly-p-xylylene Coatings via Chemical Vapor Deposition Polymerization

Meike Koenig <sup>\*a</sup>, Joerg Lahann <sup>a,b</sup>

<sup>a</sup> Karlsruhe Institute of Technology, Institute of Functional Interfaces, Department of Advanced Polymers and Biomaterials, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

<sup>b</sup> University of Michigan, Biointerfaces Institute, 2800 Plymouth Rd, Ann Arbor, MI 48109, USA

\*meike.koenig@kit.edu

**Key-Words:** chemical vapor deposition, vapor-deposited polymers, functional coatings, responsive coatings

## Abstract:

For many years, coatings from unsubstituted, as well as mono and dichlorated poly(p-xylylene) (PPX) fabricated via Chemical Vapor Deposition (CVD) polymerization have already been widely applied, for instance in the semiconductor industry and in biomedical areas. [1,2] The main advantages of this coating technique are that the polymer film is applied from the gas phase in a vacuum setup without the use of any solvent, catalyzer or liquid phase leading to defect-free coatings without impurities. Since the polymerization only happens on the cooled substrate, PPX can be coated uniformly and conformally even on structured substrates. Using a great variety of otherwise functionalized [2.2] paracyclophane-derivatives as a precursor material, we are able to produce diverse homopolymer, copolymer or copolymer gradient coatings for the subsequent immobilization of active moieties, such as proteins or signal molecules. [3,4]

The chemical functionality and morphology of the coatings is investigated comprehensively utilizing various characterization techniques including infrared spectroscopy, X-ray photoelectron spectroscopy or atomic force microscopy. A special focus lies on the characterization of the films using ellipsometry. Besides being a standard tool for quality control of the thickness and optical properties of the deposited films, spectroscopic and imaging ellipsometry can be utilized to assess property changes of the polymer layer, for instance upon thermal treatment or ageing both in the dry state and in situ. [5,6]

Current research focuses on the usage of the functionalized coatings for various applications, such as sensor systems, membrane functionalization or cell culturing. [7]

## References :

- [1] : W.F. Gorham, *J. Polym. Sci., Part A: Polym. Chem.*, 1966, **4**, 3027
- [2] : M. E. Alf. et al., *Adv. Mater.* 2010, **22**, 1993
- [3] : J. Lahann, *Polym. Int.* 2006, **55**, 1361
- [4] : A. Ross, et al., *Langmuir*, 2015, **18**, 5123
- [5] : J.J. Senkevich, S.B. Desu, V. Simkovic, *Polymer*, 2000, **41**, 2379
- [6] : M. Koenig et al., *Macromol. Chem. Phys.*, 2017, **218** (9), 1600521
- [7] : A.-L. Winkler, M. Koenig et al., *Biomacromolecules*, 2017, **18** (10), 3089



# Electrotriggered self-construction of polymeric films : new concept and application

Gauthier Rydzek<sup>a</sup>, Alexandre Dochter<sup>a</sup>, Clément Maerten<sup>a</sup>, Janwa El Maiss<sup>a</sup>, Pierre Schaaf<sup>b</sup>,  
Loïc Jierry<sup>a</sup>, Fouzia Boulmedais<sup>a,\*</sup>

<sup>a</sup> Institut Charles Sadron, Université de Strasbourg, CNRS  
<sup>b</sup> Biomateriaux et Bioingénierie, INSERM UMR 1121

\* boulmedais@unistra.fr

**Key-Words:** Click-chemistry, self-assembly, polyelectrolytes, catechol, coordination bonds

## Abstract:

Surface functionalization allows controlling the interaction of materials with their surrounding environment. During the last decades, progress in surface science allowed modifying and tuning material's surface properties in a highly controlled way by the development of new coating methods. Among them, the use of an external stimulus, such as an electric signal or light, appears as a convenient way of inducing a film buildup in a one pot manner. In 2011, we introduced a new type of electro-construction of polymeric film induced by an electro-generated gradient of morphogens. In biology, morphogens are specific molecules to which cells respond in a concentration-dependent manner. We extended this definition to film buildup on a surface where morphogens are molecules or ions that induce a chemical reaction or interaction in a confined space near a surface (Figure). The obtained films are based on the formation of covalent bonds [1, 2], host-guest interactions [3], electrostatic interactions [4], or coordination bonds [5] between (macro)molecules.

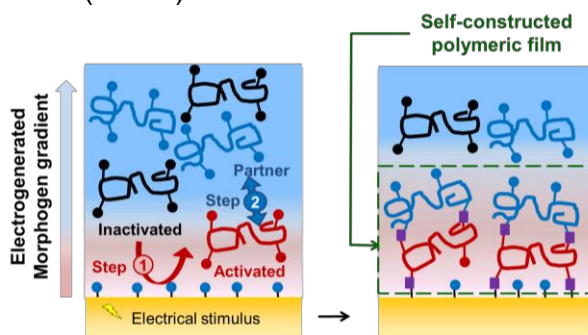


Figure : Schematic representation of electrotriggered self-construction of films based on a morphogen gradient

In a first study, Huisgens – Sharpless click reaction was used to induce a reticulation between two polymers by electro-oxidation of  $\text{Cu}^{2+}$  into  $\text{Cu}^+$  [1, 2]. Merging the fields of polyelectrolyte multilayers and morphogen-driven film buildup, we developed a strategy which allows the self-assembly of oppositely charged macromolecules on a surface [4]. Inspired by the catechol numerous properties, a mussel protein derived molecule, we designed a catechol based electrochemically triggered construction of films based on an organic morphogen: a synthesized ethylene glycol spacer bearing catechol groups on both sides, named bis-catechol [2] and on tannic acid and iron(III) [5]. Recently, a glucose biosensor was successfully developed based on the electrocrosslinking of enzymes by biscatechol molecule [6]. The electrotriggered self-construction of films is well suited for the functionalization of micro-electrodes by enzymes opening the route towards miniaturized biosensors or biofuelcells.

## References :

- [1] G. Rydzek, L. Jierry, A. Parat, J.S Thomann, J. C. Voegel, B. Senger, J. Hemmerle, A. Ponche, B. Frisch, P. Schaaf, F. Boulmedais, *Angew. Chem. Int. Ed.* 2011, **50**, 4374.
- [2] C. Maerten, T. Garnier, P. Lupattelli, N.T.T. Chau, P. Schaaf, L. Jierry and F. Boulmedais *Langmuir* 2015, **31**, 13385
- [3] G. Rydzek, A. Parat, P. Polavarapu, C. Baehr, J. C Voegel, J. Hemmerle, B. Senger, B. Frisch, P. Schaaf, L. Jierry, F. Boulmedais *Soft Matter* 2012, **8**, 446.
- [4] A. Dochter T. Garnier, E. Pardieu, N.T.T Chau, C. Maerten, B. Senger, P. Schaaf, L. Jierry and F. Boulmedais *Langmuir* 2015, **31**, 10208.
- [5] C. Maerten, L. Lopez, P. Lupattelli, G. Rydzek, S. Pronkin, P. Schaaf, L. jierry and F. Boulmedais *Chem. Mater.* 2017 **29**, 9668.
- [6] J. El Maiss, M. Cucarrese, C. Maerten, P. Lupattelli, C. Chiummiento, M. Funicello, P. Schaaf, L. Jierry and F. Boulmedais *ACS Appl. Mater. Interfaces* 2018, **10**, 18574.

**Friday, November 29<sup>th</sup>**

**Polymer interfaces and (nano)composites - Session 3 -**

*Chairs: Philippe Mésini & Lavinia Balan*

- 8.30 **Véronique Michaud**  
Capillary effects in composite materials processing by liquid composite moulding
- 9.10 **Xiang Yan**  
Fabrication of PP microfiber fabrics with potential surface functionality from melt-spun PP-PVA fibers
- 9.30 **Jannick Duchet-Rumeau**  
Fibre/Matrix interface: a still key component in new SMC composites
- 9.50 **Madeline Vauthier**  
Nanoemulsions for biomedical applications: Comparison of various emulsification Devices
- 10.10 **Maurice Brogly**  
Looking for perfect adhesion: turning the holy grail into reality

10.30 Coffee break

**Polymers and sustainable development - Session 3 -**

*Chairs: Véronique Michaud & Maurice Brogly*

- 10.50 **Fanny Bonnet**  
Recent advances in the synthesis of poly(lactic acid) by reactive extrusion process
- 11.10 **Sophie Wendels**  
Synthesis and properties of biodegradable and biobased macromolecular architectures from bacterial polyesters for biomedical applications.
- 11.30 **Hanène Salmi**  
An eco-friendly process to develop antibacterial poly(ethylene terephthalate) surfaces grafted with bio sourced polymer incorporating silver nanoparticles

11.50 Closing Ceremony



# Capillary effects in composite materials processing by Liquid Composite Moulding

Véronique Michaud

*Head of Laboratory for Processing of Advanced Composites (LPAC)*

*MXH145, Station 12*

*Ecole Polytechnique Fédérale de Lausanne (EPFL)*

*CH 1015 Lausanne, Switzerland*

*Tel: (41) 21 693 49 23*

*Web: <http://lpac.epfl.ch>*

## **Abstract:**

During composite processing by Liquid Composite Molding (LCM), a fluid precursor of the matrix phase (an uncured thermoset resin, a thermoplastic polymer or a pre-polymer) is made to infiltrate the open pore space within a reinforcement preform. Understanding the flow kinetics governing the part production cycle time, and the final part quality in terms of void content and reinforcement homogeneity has been a main area of research over the past 20 years, enabling these processes to reach many industrial applications, in particular for medium volume applications. As most reinforcements are based on textile fabrics, the pore size distribution in the textile tend to show a binary profile, with small intra-tow spaces and larger inter-tow areas; the inner geometry of the textile fabric is thus a crucial parameter, that will influence not only the overall flow kinetics, through its permeability tensor, but also the flow front morphology, driven by the interplay between capillary and hydrodynamic effects. This last point is of course also highly related to the matrix material properties, i.e. surface tension and viscosity, and the textile surface properties. The presentation will review through several recent examples of research in our laboratory, on the processing of thermoplastic and thermoset matrix composites by Liquid Composite Modling, the effect of capillary effects on the flow front kinetics and saturation, and the resulting guidelines for an optimised composite quality.

# Fabrication of PP microfiber fabrics with potential surface functionality from melt-spun PP-PVA fibers

Xiang Yan <sup>a,\*</sup>, Aurélie Cayla <sup>a</sup>, Eric Devaux <sup>a</sup>, Fabien Salaün <sup>a</sup>

<sup>a</sup> ENSAIT, GEMTEX – Laboratoire de Génie et Matériaux Textiles, F-59000 Lille, France

\* xiang.yan@ensait.fr

**Key-Words:** melt spinning, microfiber, biphasic polymers

## Abstract:

A series in-depth investigations have been carried out about the melt spinning of the biphasic polymers with different functionalities. As a branch of the research, efforts were made to melt-spin the immiscible polymer blends, of which one is water-soluble. The subsequent strategy is to remove one of the phases to manufacture the porous fibers, and meanwhile endow them with nanoparticles, including spherical silica as well as patchy kaolinite particles with Janus properties [1][2][3][4]. The raw materials were selected as polypropylene (PP) and poly(vinyl alcohol) (PVA) (70 wt.%/30 wt.%), as PVA is a water-soluble and even reusable polymeric materials. The feasibility has been proved to localize the fillers at the interface of the two polymers, and the fillers can be exposed after the removal of PVA. With the further research goes on, it has been found that the reversion of the polymer ratios can give more possibilities for manufacturing high-specific-area materials. For instance, 30 wt.% of PP and 70 wt.% of PVA are supposed to be an ideal formula for producing PP microfibers. The biphasic blends are melt-spun, twisted and knitted. Afterwards, the knitted fabrics were selectively extracted in hot water. The SEM images of the knitted fibers before/after selective extraction are displayed in Figure 1. The extraction process does not damage the fabric structure significantly, also reflected in the high retention rate of mechanical properties (more than 50% in maximum stress). As the magnification increases, it can be distinguished that there are tremendous PP microfibers after the removal of PVA. In addition, it has been also demonstrated that PVA matrix can be completely removed. Accompanied with the thermodynamical control of the fillers at the interface of the biphasic fibers, it is of great potential to fabricate the surface-tailored PP microfiber fabrics after the selective extraction. It is expected to be applied in many fields, including microfluid, antibacterial, and so on. In addition, the melt spinning technology has a huge output compared with electrospinning, therefore, it has a bright future for producing the microfiber fabrics in industrial scale.

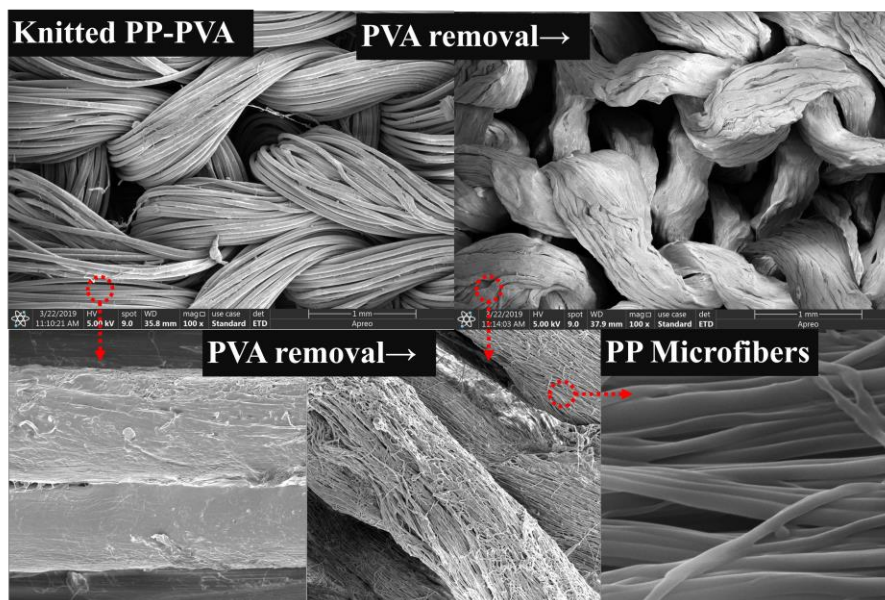


Figure 1. The SEM images of knitted PP<sub>30</sub>-PVA<sub>70</sub> fibers before/after selective extraction (the red arrow represents an increase in magnification)

## References :

- [1] : Yan X\*, Cayla A, Devaux E, Otazaghine B, Salaün F. Industrial & Engineering Chemistry Research. 2019, **58(25)**:10931–40.
- [2] : Yan X\*, Cayla A, Salaün F, Devaux E, Liu P, Huang T. Textile Research Journal. 2019.
- [3] : Yan X\*, Cayla A, Salaün F, Devaux E, Liu P, Mao J, Huang T. Journal of Applied Polymer Science. 2019.
- [4] : Yan X\*, Cayla A, Devaux E, Salaün F. Polymers. 2018, **10(9)**:1031.

# **FIBRE/MATRIX INTERFACE : A STILL KEY COMPONENT IN NEW SMC COMPOSITES**

Thibaut Bénéthuil<sup>a, b</sup>, Jean-François Gérard<sup>a</sup>, Elise Dubost<sup>b</sup>, Christophe Peyre<sup>b</sup>,

Jannick Duchet-Rumeau<sup>a</sup>

<sup>a</sup>Ingénierie des Matériaux Polymères (IMP) UMR CNRS 5223, INSA Lyon – Université de Lyon  
F- 69621 Villeurbanne, France

<sup>b</sup>Plastic Omnium Auto Exterior – Sigmatech.  
F-01150 Sainte Julie, France

\* E-mail [jannick.duchet@insa-lyon.fr](mailto:jannick.duchet@insa-lyon.fr)

**Key-Words:** Interface, Wettability, Interfacial Shear Stress, Multiscale Characterization

## **Abstract:**

The fibre/matrix interfaces into the composites are essential components for the long term durability of these materials since the damages happening all along the composite life take place preferentially at the interface. These damages (or defects) occur particularly during high energy impact or fatigue tests and after the composite aging in presence of moisture and temperature.

In this talk, a multi-scale methodology will be proposed for controlling and characterizing the interface : **i) at the molecular scale**, *i.e.* where interactions and interfacial bonds take place involving sizing and phase separation phenomena with the matrix able to generate a composition gradient since the fiber surface up to the bulk, **ii) at the fiber scale** by analyzing the surface chemistry and the topography in order to assess the wettability of the fiber by the matrix and to determine the interfacial shear strength by the pull out test and **iii) at the composite scale** to characterize the interlaminar shear strength on unidirectional composites.

This approach will be illustrated on sheet moulding compounds (SMC). These materials are thermoset-based composite materials consisting of vinyl ester (VE) diluted either in styrene or butanediol dimethacrylate (BDDMA) and thickened with magnesium oxide, reinforced with glass or carbon fiber and calcium carbonate fillers. During the processing of composite, different interphases based on VE -styrene /glass or carbon fiber or styrene free VE/glass fiber are generated depending on the chemical nature of sizing which can be **reactive or not** towards the thermosetting system and which can be **partially or totally miscible** within the matrix.

The interfacial mechanical properties are determined first on model systems involving one single fiber embedded into the matrix by using the pull out test. The micromechanical analysis of interfaces will be correlated at the macroscale onto unidirectional SMC composites. The impregnation of fibers by the matrix will be evidenced by tomography and short beam shear and off-axis tensile tests allow to determine the interlaminar shear strength. The long term behavior of interfaces after aging will be also discussed since the aging is very sensitive to the quality of the interface. All the analyses show the need of developing compatible sizing for glass or carbon fiber in SMC composites in order to generate an intimately built and robust interface.

## **References :**

- (1) K. Liao, CR. Schultheisz, DL Hunston, DL, LC Brinson, Journal of Advanced Materials, 1998, **30(4)**, 3-40

## Nanoemulsions for Biomedical Applications: Comparison of Various Emulsification Devices

Madeline Vauthier,<sup>a\*</sup> Ane Larrea,<sup>b</sup> Victor Sebastian,<sup>b</sup> Christophe A. Serra <sup>a</sup>

<sup>a</sup> Institut Charles Sadron (ICS) – UPR 22 CNRS, 23 rue du Loess, F-67034 Strasbourg, France

<sup>b</sup> Aragon Institute of Nanoscience (INA) – University of Zaragoza, Department of Chemical Engineering, S-50018 Zaragoza, Spain

\* vauthier@unistra.fr

**Key-Words:** elongational-flow reactor and mixer, nanoparticles, PLGA, dye delivery

### Abstract:

Nowadays, producing smaller and smaller nanoparticles becomes a trend, in order to diversify the application fields, such as sensors or biomedical applications dealing with drug delivery. In this context, we studied the possible formation of poly(lactic-co-glycolic acid) PLGA biodegradable[1] nanoparticles by various processes: rotor-stator mixing (forming nanodroplets by shearing forces), sonication (promoting nanodroplets' implosion) and elongational-flow micromixing.

Since PLGA isn't soluble in water, oil-in-water o/w nanoemulsions were realized with the three previously mentioned processes. Cryo-TEM images and DLS measurement were realized in order to investigate the nanoparticles sizes, there stability and the size polydispersity. This study lead to the determination of optimal mixing parameters and optimal emulsification time for the three devices and the formation of PLGA nanoparticles of various, controlled diameters (always lower that 200 nm). These particles sizes compete well with other studies that mainly obtain bigger particles.[1-3] Moreover, we noted that the best results were obtained with elongational-flow micromixer, probably because of the quite high viscosity of the polymer solution. Our team also successfully encapsulated a dye inside the nanoparticles and released it in aqueous medium.

As a conclusion, we highlighted very encouraging results to further develop biomedical-related sytems: the possibility to obtain monodispersed biodegradable, biocompatible polymer nanoparticles in which (bio)molecules can be encapsulated.

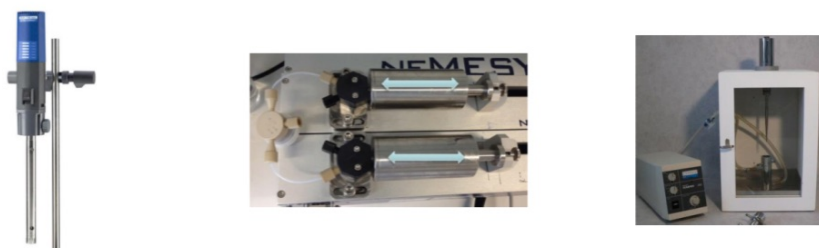


Figure 1. (From left to right) Rotor-stator mixer, elongational-flow micromixer and sonicator.

### References :

- [1]: J. M. Anderson; M. Shive, *Advanced drug delivery reviews*, 2012, **64**, 72-82  
 [2]: W. Yu; C. A. Serra; I. U. Khan; M. Er-Rafik; M. Schmutz; I. Kraus; S. Ding; L. Zhang; M. Bouquey; R. Muller, *Macromolecular Reaction Engineering*, 2017, **11**, 1600025  
 [3]: V. Andreu; A. Larrea; P. Rodriguez-Fernandez; S. Alfaro; B. Gracia; A. Lucia; L. Usón; A. C. Gomez; G. Mendoza; A. Lacoma; J. Dominguez; C. Prat; V. Sebastian; J. A. Ainsa; M. Arruebo, *Nanomedicine*, 2019, **14**, 30938

# Looking for perfect polymer adhesion ?

## Turning the holy grail into reality

Maurice Brogly<sup>a</sup>,

<sup>a</sup> UHA – LPIM, Mulhouse, France

\* Maurice.brogly@uha.fr

**Key-Words:** Adhesion, surface, interface, nanoscale

### Abstract:

What is adhesion? How to measure it? How to control it? What are the differences between adhesion and non-adhesion, adhesion and adhesive strength? What is the role of mechanical interlocking, intermolecular forces, actual contact area between adherents? What are the dissipative and rupture mechanisms activated during the separation of an interface or an interphase? The glass, tires, wood, metal, ceramics, paints, coatings, cosmetics and medical devices industries are concerned by these simple even complex questions. The science of adhesion is a multidisciplinary science, bringing together knowledges in chemistry and physics of polymers, materials, surfaces and interfaces. Moreover, the understanding of adhesion mechanisms often involves the implementation of advanced spectroscopic or analytical methods. As a result the global understanding of an adhesion phenomenon, and its control, may be only multi-disciplinary and multi-scales. It is the recent advances in chemistry, physics, mechanics, and surface and interface spectroscopy that helps understanding adhesion mechanisms. This science has progressed considerably over the past ten years and this presentation aims to deliver, on the basis of practical examples, a current panorama of the concepts and experiences to master in order to control adhesion

### References :

- [1] Influence of specific thermal treatment on Young's modulus changes in a natural rubber-based compound: study by AFM nanoindentation, T. Linck, R. Mruk, B. Zielinski, S. Bistac, M. Brogly  
*Rubber Chemistry and Technology* 2015, **88**, 234-247
- [2] Adsorption of alkanethiols on gold surfaces : PM-IRRAS study of the influence of terminal functionality on alkyl chain orientation, T. Elzein, A. Fahs, M. Brogly, A. Elhiri, B. Lepoittevin, P. Roger, V. Planchot  
*The Journal of Adhesion*, 2013, **89**, 416-432
- [3] Elastic recovery and creep properties of waterborne two-component polyurethanes investigated by micro-indentation, L. Chagnon, G. Arnold, S. Giljean, M. Brogly  
*Progress in Organic Coatings*, 2013, **76**, 1337-1345
- [4] Assesment of Nanoadhesion and Nanofriction Properties of Formulated Cellulose-Based Biopolymers by AFM, M. Brogly, A. Fahs, S. Bistac  
In *Nanoscience and Technology, Scanning Probe Microscopy in Nanoscience and Nanotechnology*, B. Bhushan Ed., Springer Berlin Heidelberg, Chap. 16, pp 473-504 (2011)
- [5] Hydroxypropyl methylcellulose (HPMC) formulated films : Relevance to adhesion and friction surface properties, A. Fahs, M. Brogly, S. Bistac, M. Schmitt  
*Carbohydrate Polymers*, 2010, **80**, 105-114
- [6] Contact Atomic Force Microscopy : a Powerful Tool in Adhesion Science, M. Brogly, H. Awada, O. Noel  
In *Nanoscience and Technology, Applied Scanning Probe Methods XI*, B. Bhushan & H. Fuchs Eds., Springer Berlin Heidelberg, pp 73-93 (2009)



# RECENT ADVANCES IN THE SYNTHESIS OF POLY(LACTIC ACID) BY REACTIVE EXTRUSION PROCESS

Elodie Louisy <sup>a</sup>, Gaëlle Fontaine <sup>a</sup>, Serge Bourbigot <sup>a</sup>, Laurence Rozes <sup>b</sup>, Fanny Bonnet <sup>\*a</sup>

<sup>a</sup> Univ. Lille, CNRS, INRA, ENSCL, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille, France.

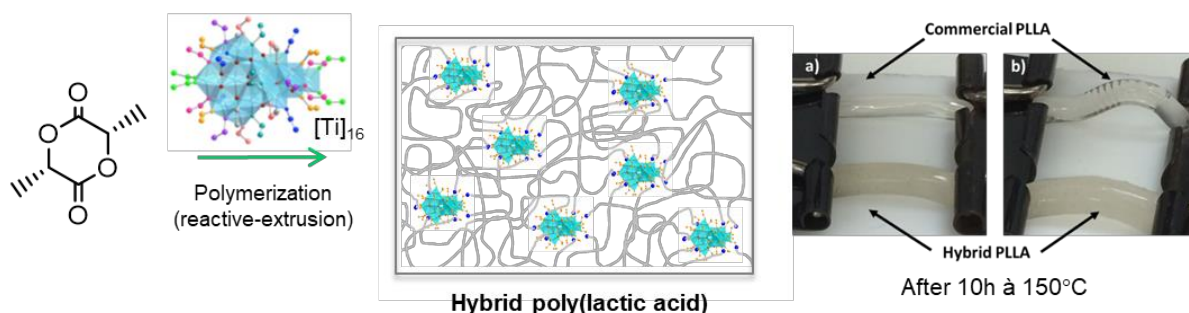
<sup>b</sup> Sorbonne Université, CNRS, LCMCP, Laboratoire Chimie de la Matière Condensée de Paris, F-75005 Paris, France.

\* fanny.bonnet@ensc-lille.fr

**Key-Words:** Poly(lactic acid), reactive extrusion, macrocyclic PLLA, titanium oxo-cluster

## Abstract:

Among the different biobased materials available on the market, poly(lactic acid) (PLA) is becoming more and more competitive and accounts for about a quarter of biodegradable bioplastic production. This biodegradable and biocompatible polyester is synthesized either by direct polycondensation of lactic acid, resulting from the fermentation of agroresources, or by Ring Opening Polymerization (ROP) of lactide, a cyclic ester derived from oligomerization-cyclization of lactic acid. Although the second synthetic route requires an additional step, it allows the formation of poly(lactic acid) of higher molar masses and is most commonly employed in industry [1]. Among ROP methods, coordination-insertion polymerization monitored by metal-based catalysts is a powerful and versatile technique, allowing access to well-defined high molar mass polymers. One of the most efficient metal-based catalyst is tin octoate which is used for the industrial production of PLA. The latter has also been shown to be highly active for the polymerization of L-lactide by reactive extrusion, a green process allowing the continuous polymerization of a monomer without solvent [2]. With the aim of developing catalysts involving low-toxicity metals which could be used in reactive extrusion process, we have demonstrated that lanthanide trisborohydrides were efficient catalysts which were able to form macrocyclic poly(lactic acid) in a continuous way [3]. More recently, we reported the production of novel hybrid poly(lactic acid) by use of a titanium oxo-cluster, acting both as a catalyst and crosslinking agent of the polymer matrix [4].  $Ti_{16}O_{16}(OEt)_{32}$  ( $[Ti]_{16}$ ) [5] was found to be highly active for the bulk polymerization of L-lactide under reactive extrusion conditions, affording hybrid-PLLA materials with high  $M_n$  values. It was further shown that the hybrid PLLA containing  $[Ti]_{16}$  display superior dimensional stability under heat than commercial PLLA of same molar mass.



## References :

- [1] (a) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* 2004, 104, 6147-6176. (b) C. Jérôme, P. Lecomte, *Adv. Drug Delivery Rev.* 2008, **60**,1056-1076.
- [2] S. Jacobsen, H.G. Fritz, Ph. Degée, P. Dubois, R. Jérôme. *Polymer* 2000, 41, 3395-3403.
- [3] F. Bonnet, F. Stoffelbach, G. Fontaine, S. Bourbigot. *RSC Adv.* 2015, **5**, 31303-31310.
- [4] E. Louisy, S. Bellayer, G. Fontaine, L. Rozes, F. Bonnet. *Eur. Polym. J.* 2019, doi.org/10.1016/j.eurpolymj.2019.109238.
- [5] G. Fornasieri, L. Rozes, S. Le Calve, B. Alonso, D. Massiot, M. N Rager, M. Evain, K. Boubekeur, C. Sanchez, *C. J. Am. Chem. Soc.* 2005, 127, 4869-4878.

# Synthesis and properties of biodegradable and biobased macromolecular architectures from bacterial polyesters for biomedical applications.

[Sophie Wendels](#)<sup>a</sup>, Luc Avérous<sup>\*a</sup>

<sup>a</sup> BioTeam/ICPEES-ECPM, Université de Strasbourg, 25 rue Becquerel, Strasbourg, France 67087

Email: [luc.averous@unistra.fr](mailto:luc.averous@unistra.fr)

**Key-Words:** Biobased, Biodegradable, Polyurethane, Polyhydroxybutyrate, Biomedical

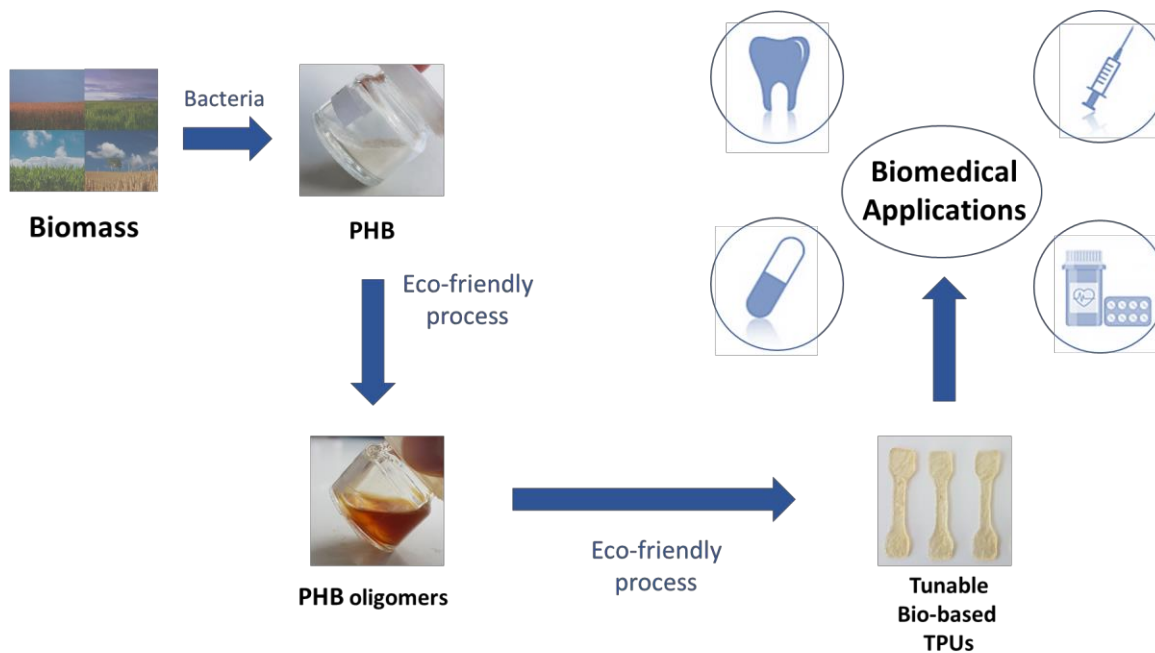
## Abstract:

Conventional plastics are generally fossil-based polymers having a wide range of applications in our daily lives from packaging, coatings to the medical field [1]. However, a major concern of these polymers is their end-of-life management. Only 9% of plastics are recycled, while 4 to 12 million metric tons end up in the oceans with the generation of microplastics [2]. In reaction to this, research has been focused for over two decades in the development of new sustainable macromolecular architectures derived from renewable resources with a controlled end of life. Their higher cost is still a limiting factor for their increased production at the industrial level [3]. To surmount this, research intends to develop bio-based polymers with new architectures and enhanced properties compared to fossil-based polymers.

One particular family of bacterial biopolymers, the Polyhydroxyalkanoates (PHAs), has grown in considerable interest over the last years. PHAs are biopolyesters synthesized as intracellular carbon and energy storage by several types of microorganisms [4]. According to their chemical structures, PHAs show competitive and variable properties such as biodegradability, non-toxicity, thermal and mechanical properties, low water vapor permeability and piezoelectricity [5]. However, some PHAs present limited applications due to their high degrees of crystallinity, leading to brittleness and therefore poor deformation at break, and low thermal stability. Some of the main PHAs, such as the polyhydroxybutyrate (PHB) presents some strong drawbacks linked to a low processability with a fast degradation with the formation of crotonic groups and shorter chains above the melting temperature, which limits their industrial applications. One of the best ways to overcome this weakness and to increase their uses is to modify PHB into valuable building blocks, PHB oligomers, to produce a new generation of bio-based materials with controlled architectures [6].

BioTeam activity at University of Strasbourg (France) is focused on the development of new bio-based and biodegradable macromolecular architectures for environmental and biomedical applications. This presentation will discuss our current works in developing new bio-based polymers derived from PHB for medical applications [7, 8].

New controlled chemical modifications of PHB chains to obtain short PHB oligomers with controlled molar mass (up to 300 g.mol<sup>-1</sup>) were performed. The dependence of the reaction parameters on the obtained chains structure and length was particularly studied. In a two-step process, these short PHB oligomers were then used as starting material of fully bio-based thermoplastic polyurethanes (TPUs), following several principles for a green chemistry (catalyst and solvent-free synthesis). Main properties such as physicochemical, thermal and mechanical behaviors of the synthesized TPUs, were analyzed and will be discussed in the presentation. These new tunable bio-based TPUs are developed for several biomedical applications [7, 9]. Cytotoxicity and the main properties in connection with these usages are carefully tested and evaluated.



*From Biomass to biobased TPUs for biomedical applications*

## References:

- [1] PlasticsEurope, 2018  
from [https://www.plasticseurope.org/application/files/6315/4510/9658/Plastics\\_the\\_facts\\_2018\\_AF\\_web.pdf](https://www.plasticseurope.org/application/files/6315/4510/9658/Plastics_the_facts_2018_AF_web.pdf)
- [2] G. Jambeck, Wilcox, Siegler, Perryman, Andrady, Narayan, *Science*, 2015.
- [3] Nova-Institute, European Bioplastics, Bioplastics market data, 2018.
- [4] Z.A. Raza, S. Abid, I.M. Banat, *International Biodeterioration & Biodegradation*, 2018, **126**, 45-56.
- [5] E. Pollet, L. Averous, Production, chemistry and properties of polyhydroxyalkanoates, *John Wiley & Sons Ltd.*, 2011, p. 65-86.
- [6] T. Debuissy, E. Pollet, L. Avérous, *Journal of Polymer Science Part A: Polymer Chemistry*, 2017, **55**, 1949-1961.
- [7] J. Zhang, E.I. Shishatskaya, T.G. Volova, L.F. da Silva, G.Q. Chen, *Mater Sci Eng C Mater Biol Appl*, 2018, **86**, 144-150.
- [8] G.Q. Chen, J. Zhang, *Artif Cells Nanomed Biotechnol*, 2018, **46**, 1-18.
- [9] A.P. Reyes, A. Martinez Torres, P. Carreon Castro M.del, J.R. Rodriguez Talavera, S.V. Munoz, V.M. Aguilar, M.G. Torres, *Sci Rep*, 2016, **6**, 31140.

# An eco-friendly process to develop antibacterial poly(ethylene terephthalate) surfaces grafted with bio sourced polymer incorporating silver nanoparticles

Hanène Salmi-Mani<sup>1</sup>, Grégory Balthazar<sup>1</sup>, Aymes-Chodur Caroline<sup>1</sup>, Gabriel Terreros<sup>2</sup>, Nadine Barocca-Aubry<sup>1</sup>, Christophe Regeard<sup>2</sup>, and Philippe Roger<sup>1</sup>

<sup>1</sup>ICMMO - Université Paris Sud - Paris XI - France

<sup>2</sup>I2BC - Université Paris Sud - Paris XI - France

## Abstract:

Poly(ethylene terephthalate) (PET) material is one of the most commonly used polyester polymer for industrial applications[1]. Due to its remarkable mechanical and physicochemical properties[1], PET is widely used in food packaging[2], separation membranes[3], textile industry[4], automotive industry[5], medical devices[6], etc. Considering food industry and/or medical applications, improving antibacterial properties of PET is necessary to prevent food alterations, infections or contaminations. For instance, in hospital environment, contaminated surfaces are an important source for transmission of many health care-associated pathogens which constitutes a major public health problem. The use of natural antimicrobial compounds such as low-molecular weight phenolic compounds like vanillin, eugenol, guaiacol, thymol or other natural capsaicin species have received considerable attention from scientific communities due to their important antibacterial activity associated to their high availability [7].

In this study, we report the development of new vanillin derived monomer. Afterwards, biobased monomer is grafted on a PET surface by a two-steps strategy. First, an aminolysis treatment to ensure the immobilization of tertiary amino groups acting as highly reactive type II photoinitiator species onto the PET surface is performed [8]. Then a link of the bio-based monomer through a "photografting from" process is achieved. Photopolymerization reaction allows depositing on the PET surface a covalently attached anti-microbial bio-based polymer layer [9]. To improve the antibacterial properties of the new PET surface, silver nanoparticles, well known for their biocide activities, were directly produced in the polymer network according to a AgNO<sub>3</sub> photoreduction process. Those grafted PET surfaces are characterized by XPS and UV/visible spectroscopies and water contact angle. Finally, antibacterial activity of those elaborated materials against gram-positive (*Rhodococcus wratislaviensis* and *Staphylococcus aureus*) and gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) bacteria is investigated through biotests.

## References :

- [1] : P.M. Visakh, M. Liang, Poly(Ethylene Terephthalate) Based Blends, Composites and Nanocomposites, William Andrew, 2015.
- [2] : S. Clark, S. Jung, B. Lamsal, Food processing: principles and applications, JohnWiley & Sons, 2014.
- [3] : S.P. Nunes, K.-V. Peinemann (Eds.), Frontmatter and Index, Wiley-VCH VerlagGmbH, Weinheim, FRG, 2001.
- [4] : T. Denton, Automobile electrical and electronic systems, Routledge, 2004.
- [5] : D.F. Williams, R. Roaf, D.O. Maisels, Implants in Surgery, Saunders, London, 1973.
- [6] : J.G. Cook, Handbook of textile fibres: man-made fibres, Elsevier, 1984.
- [7] : Y.K. Vaghasiya, R. Nair, M. Soni, S. Baluja, S. Shanda, Synthesis, structural determination and antibacterial activity of compounds derived from vanillin and 4-aminoantipyrine, J. Serbian Chem. Soc. 69 (2004) 991-998
- [8] : D. He, M. Ulbricht, Synergist immobilization method for photo-grafting: factors affecting surface selectivity, Macromol. Chem. Phys. 208 (2007) 1582-1591.
- [9] : H. Salmi-Mani, G. Terreros, N. Barocca-Aubry, C. Aymes-Chodur, C. Regeard, P. Roger Poly(Ethylene Terephthalate) Films Modified by UV-Induced Surface Graft Polymerization of Vanillin Derived Monomer for Antibacterial Activity. Eur. Polym. J., 103 (2018) 51-58.

# Poster contributions



# Poster contributions

---

## Macromolecular and supramolecular engineering

- P-1** PROGRAMMED DRUG RELEASE VIA ROLLED-UP BIOPOLYMER  
*Riccardo Pedron, Thierry Vandamme, Valery Luchnikov*
- P-2** FULLY ISOTACTIC POLY(P-METHYLSTYRENE) : PRECISE SYNTHESIS VIA CATALYTIC POLYMERIZATION AND CRYSTALLIZATION STUDIES  
*Pierre J Lutz, Luis Valencia, Thomas Pfohl, Barbara Heck, Günter Reiter, Mühlaupt Rolf*
- P-3** CHARACTERISATION OF SUPRAMOLECULAR ASSEMBLIES BY SCANNING PROBE NEAR-FIELD MICROSCOPY: OPTICAL AND ELECTRONIC PROPERTIES  
*Jean-Luc Bubendorff, Sven Renkert, Sajede Motamen, Dominique Aubel, François Vonau, Marion Cranney, Günter Reiter, Laurent Simon*
- P-4** PREPARATION OF MULTI-ALLYLIC DENDRONIZED POLYMERS VIA ATOM-TRANSFER RADICAL POLYMERIZATION  
*Stephane Mery, Pierre-Olivier Schwartz, Firmin Moingeon, Jérôme Roeser, Patrick Masson*
- P-5** FUNCTIONAL NANOFIBERS FROM SUPRAMOLECULAR INTERACTIONS  
*Guy Schlatter, Anne Hébraud*





# Programmed drug release via rolled-up biopolymer

Riccardo Pedron<sup>a,b</sup>, Thierry Vandamme Thierry<sup>a</sup>, Valeriy Luchnikov<sup>b</sup>

<sup>a</sup> Université de Strasbourg, Faculté de Pharmacie-CNRS UMR 7199, Ilkirch-Graffenstaden, France

<sup>b</sup> Université de Haute-Alsace, IS2M-CNRS UMR 7361, F-68100 Mulhouse, France

\* [rpedron@unistra.fr](mailto:rpedron@unistra.fr), [vandamme@unistra.fr](mailto:vandamme@unistra.fr), [valeriy.luchnikov@uha.fr](mailto:valeriy.luchnikov@uha.fr)

**Key-Words:** modified drug release, temporal drug delivery, inkjet printing, reservoir devices.

## Abstract:

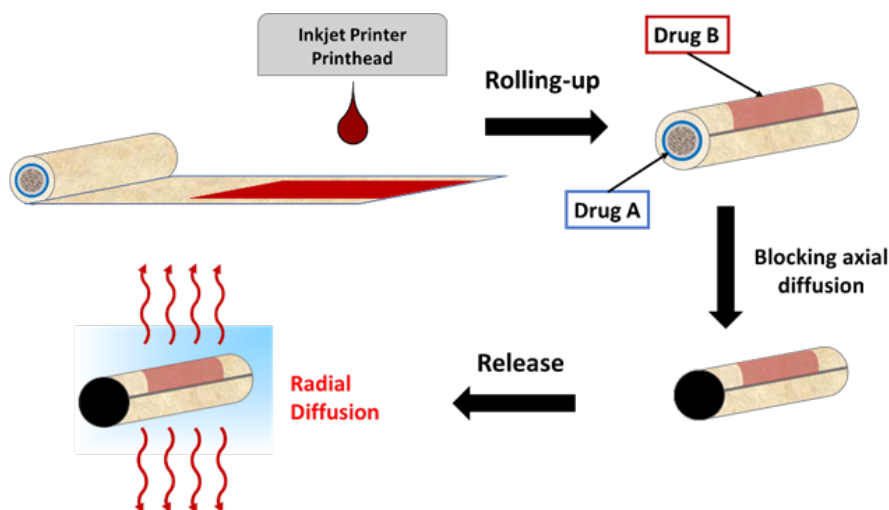
From the recent advances of chronobiology, it is clear that a precise scheduling of the dosing time of medication (chronotherapy) produces an actual advantage to optimize outcomes and minimize adverse effects [1]. The success of this approach is consequently bound to the adherence of the patient to the therapy which often would require non-permissive administration times [2].

Several drug delivery devices have been developed to fit the proper timing of release without reducing patient's compliance [2]. By following the promising results obtained previously from our group [3], herein it is presented a versatile method for the realization of a novel drug delivery device that by leveraging inkjet printing technologies, allows to shape the release by simply changing some manufacturing parameters.

The proposed system it is composed by a chitosan acetate film on which surface it is deposited via inkjet printing one or more model drugs with a specific pattern, prior to rolling it up.

By allowing only the radial diffusion and changing the printed model drug(s)'s patterns or the length of the film in front of the printed area, it has been possible to obtain sustained releases after a precise lag time or after a burst release of one or more drug's models.

These results confirm the possibility to realize several Chronopharmaceutical drug delivery systems (ChrDDS) with this technology.



*Preparation scheme of a multi-drug release drug delivery system.*

## Références :

- [1] R. Dallmann, S.A. Brown, F. Gachon, *Annual review of pharmacology and toxicology*, 2014, **54**, 339–361;  
 [2] A.S. Mandal, N. Biswas, K M Karim, A. Guha, S. Chatterjee, M. Behera, K. Kuotsu *Journal of Controlled Release*, 2010, **147**, 314–325;  
 [3] A.I. Egunov, A. Inaba, S. Gree, J.-P. Malval, K. Tamura, Y. Saito, V. A. Luchnikov, *Journal of Controlled Release*, 2016, **233**, 39-47;

## Acknowledgement:

Generous financial support from Agence Nationale de la Recherche (ANR 17-CE18-0021-01).

# FULLY ISOTACTIC POLY(*p*-METHYLSTYRENE) : PRECISE SYNTHESIS VIA CATALYTIC POLYMERIZATION AND CRYSTALLIZATION STUDIES

Tianyu Wu <sup>a</sup>, Luis Valencia <sup>b1</sup>, Thomas Pfohl <sup>a</sup>, Barbara Heck <sup>a</sup>,  
Günter Reiter <sup>a</sup>, Pierre J. Lutz <sup>\*c</sup>, Rolf Mülhaupt <sup>d</sup>

<sup>a</sup> University of Freiburg, Physikalisches Institut, Freiburg, Germany  
Hermann-Herder-Str.03, Freiburg 79104, Germany

<sup>b</sup> University of Freiburg, Institut für Makromolekulare Chemie, Freiburg, Germany

<sup>c</sup> University of Strasbourg, Institute Charles Sadron, CNRS UPR 22,  
23, rue du Loess, F-67034 Strasbourg, France

<sup>d</sup>University of Freiburg, Freiburg Materials Research Center FMF,  
Stefan-Meier-Str. 21, D-79104 Freiburg, Germany

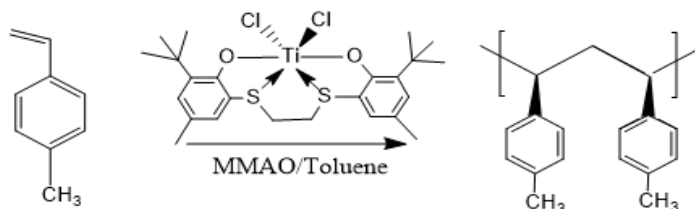
<sup>b1</sup> Present address: Division of Materials and Environmental Chemistry,  
University of Stockholm, Frescativägen 8, Stockholm 10691, Sweden.

\* Email address : [pierre.lutz@ics-cnrs.unistra.fr](mailto:pierre.lutz@ics-cnrs.unistra.fr)

**Key-Words:** isotactic polymers, coordination polymerization, slow evaporation, dendritic crystal

## Abstract:

The versatility of functionalization of poly(*p*-methylstyrene) (PpMS), together with its lower density, higher  $T_g$  and lower melt viscosity in comparison to conventional polystyrene have attracted the attention of research effort during the last decades. On the other hand the isospecific polymerization of *p*-MS, early reported by Natta and coworkers [1], has been widely studied by means of different polymerization techniques [2], however a poor stereocontrol (only 40% of isotactic pentads) was in most cases reported (pre-fractionation value). Therefore the interesting features and capabilities of iPpMS have never been fully explored. In this work, we systematically study the isospecific polymerization *p*MS in the presence of the catalyst dichloro[1,4-dithiabutanediyl-2,20-bis(4,6-ditert-butyl-phenoxy)]titanium, activated by MMAO, introduced by Capacchione *et al.* [3]. The resulting polymers were highly isotactic (iPpMS), with more than 95% isotactic pentad fraction and narrow dispersities. The kinetics of the formation of iPpMS and their structural and molecular parameters including their microstructure, thermal behavior and crystallinity were investigated in details [4].



**Scheme** : Isospecific polymerization of *p*-methylstyrene

## Acknowledgement

The authors thank specially the DFG (IRTG Soft Matter Science 1642) for financial support

## References :

- [1] : G. Natta; P. Pino, *J. Am. Chem. Soc.*, 1955, **77**, 1708-1710.  
 [2] : B. Li; Y. Wu. *Polymer*, 2012, **53** (17), 3726-3734.  
 [3] : F. De Carlo; C. J. Capacchione. *Polym. Sci., Part A*, 2006. **44**, 1486-1491.  
 [4] : T. Wu; L. Valencia; T. Pfohl; B. Heck; G. Reiter; P. Lutz; R. Mülhaupt, *Macromolecules*, 2019, **52**, 4839-4846.

# Characterisation of supramolecular assemblies by Scanning Probe Near-field Microscopy: optical and electronic properties

Jean-Luc Bubendorff<sup>1\*</sup>, Sven Renkert<sup>1,2</sup>, Sajedah Motamen<sup>2</sup>, Dominique Aubel<sup>1</sup>, François Vonau<sup>1</sup>, Marion Cranney<sup>1</sup>, Günter Reiter<sup>2</sup>, Laurent Simon<sup>1</sup>

<sup>1</sup>Institut de Science des Matériaux de Mulhouse (IS2M-UMR 7361 CNRS), Université de Strasbourg-Université de Haute Alsace, 3b rue Alfred Werner, 68093 Mulhouse Cedex, France.  
<sup>2</sup>Physikalisches Institut, Albert-Ludwigs-Universität Freiburg i.Br., Hermann-Herderstraße 3, 79104 Freiburg, Germany.

\* jean-luc.bubendorff@uha.fr

**Key-Words:** supramolecular self assembling, Conductive Atomic Force Microscopy, organic electronic, OFET.

## Abstract:

The use of thin layers of semiconductor organic molecules for applications in microelectronic devices such as solar cells, light-emitting diodes or transistors is an increasingly important area of research grouped under the generic name 'organic electronics'. To realize an organic field-effect transistor type structure (OFET), it is possible to produce an almost "all organic" device. Thus, the channel consists of an assembly of  $\pi$ -conjugated molecules. Most of the transport properties depending on the interface between the channel and the rest of the device (typically single layers), it appears that the electrical characteristics, their reproducibility (mobility of charge carriers, on/off ratio) and all other characteristics of this type of structure are highly dependent on the organization of the molecules.

We study how the conformation of a molecule can have an effect on the structure of a supramolecular assembly at the mesoscopic scale and therefore on the optical [1] and electronic [2] properties in order to optimize and create new types of organic solar cells [3]. We will present the results obtained for two types of conjugated molecules, namely poly (3-hexylthiophene) or P3HT and a new family of thienylene-dialkoxybenzene-based oligomers (3 TBT or 5TBT).

For nTBT-type molecules, we have shown, by LT-STM and STS, an unprecedented self-assembly effect consisting on the rotation of thiophene groups at the end of the molecular chain which makes it possible to create a  $\pi$ - $\pi$  stacking coupling and the formation of 1D supramolecular line with a charge delocalization along the line [4]. Since a very long distance spatial coherence along these wires is obtained, we used this result to create 2D supramolecular assemblies and 3D monocrystals perfectly organized over scales of millimeters. We studied the photoluminescence properties [1], the organization of molecules by AFM and the conductivity of these objects by C-AFM and into a FET structure.

On P3HT crystals, we show by C-AFM a very strong link between charge transport and crystallographic directions in supramolecular crystals. We can thus consider the use of these new supramolecular materials in new types of organic solar cells.

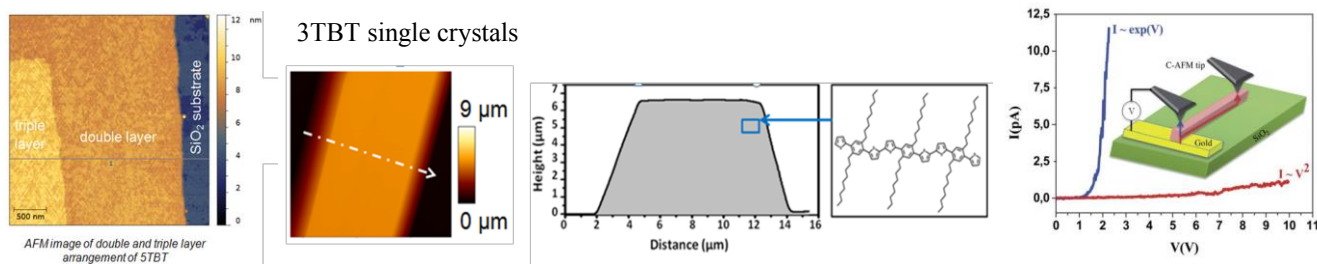


Figure 1: From the left to the right side : 5 TBT 2D supramolecular layers and 3TBT single crystals by AFM; principle of measurements and results on P3HT single crystals by C-AFM.

## References :

- [1] Motamen, S. et al *American Chemical Society Photonics*, 2016, 3, 2315.
- [2] Hourani, W. et al *Nanoscale*, 2014, 6, 4774.
- [3] Würfel, U. et al. *Advanced Energy Material*, 2016, 6, 1600594.
- [4] Shokri, R. et al. *Journal of the American Chemical Society*, 2013, 135, 5693.

# Preparation of multi-allylic dendronized polymers via atom-transfer radical polymerization

Pierre-Olivier Schwartz, Firmin Moingeon, Jérôme Roeser, Patrick Masson & Stéphane Méry\*

IPCMS, Université de Strasbourg, CNRS, UMR 7504, 23 rue du Loess, 67034 Strasbourg France

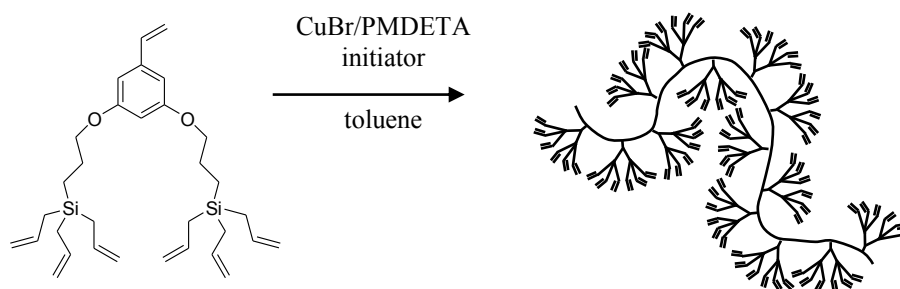
\* [mery@ipcms.unistra.fr](mailto:mery@ipcms.unistra.fr)

**Key-Words:** Dendronized polymer, functional macromonomer, alkene branches, ATRP, steric congestion

## Abstract:

Atom-transfer radical polymerization (ATRP) was investigated to polymerize a styrene macromonomer carrying carbosilane dendrons with 6 terminal allyl branches. Polymers with a monomodal molar mass distribution and low polydispersity have been produced, while by comparison the free-radical polymerization technique led to chain transfer early in the polymerization. Steric effect brought by the dendrons result in a slow polymerization rate, leading to an apparent saturation of the degree of polymerization. By pushing up the polymerization conditions (eg. increase of temperature or concentration), interchain couplings started to take place, most likely from reactions at the allyl branches.[1] These results are very similar to the ones previously reported for the anionic polymerization of this same multi-allylic dendronized monomer.[2,3]

To the best of our knowledge, these polymers constitute the first example of polymers carrying multiple alkene pendants, prepared by a “controlled” radical polymerization technique. These results then pave the way to the preparation of well-defined polymers with multiple reactive alkene groups, as well as to the controlled-radical polymerization of sterically demanding macromonomers.



*Polymerization of allyl-branched dendritic monomer under ATRP*

## References :

- [1] : P.O. Schwartz, F. Moingeon, J. Roeser, E. Couzigné, E. Voirin, P. Masson, S. Méry, *Eur. Pol. J.* 2019, **118**, 358  
 [2] : F. Moingeon, P. Masson, S. Méry, *Macromolecules* 2007, **40**, 55  
 [3] : a) F. Moingeon, J. Roeser, P. Masson, F. Arnaud, S. Méry, *Chem. Commun.* 2008, **11**, 1341 ; b) J. Roeser, F. Moingeon, B. Heinrich, P. Masson, F. Arnaud-Neu, M. Rawiso, S. Méry, *Macromolecules*, 2011, **44**, 8925 ; c) J. Roeser, B. Heinrich, C. Bourgoigne, M. Rawiso, S. Michel, V. Hubscher-Bruder, F. Arnaud-Neu, S. Méry, *Macromolecules*, 2013, **46**, 7075.

# Functional nanofibers from supramolecular interactions

Guy Schlatter, Anne Hébraud

Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé (ICPEES), UMR 7515 CNRS-University of Strasbourg, ECPM, Strasbourg, France

\* [guy.schlatter@unistra.fr](mailto:guy.schlatter@unistra.fr), [anne.hebraud@unistra.fr](mailto:anne.hebraud@unistra.fr)

**Key-Words:** electrospinning, nanofibers, cyclodextrin, tannic acid, supramolecules

## Abstract:

Electrospinning is a versatile process allowing the elaboration of nanofibrous materials under the action of an intense electric field. In the light of several examples, we will show that the use of supramolecular interactions between the processed molecules can be a solution of choice for the elaboration of novel kinds of functional nanofibers and the processing in water avoiding the use of toxic solvents.

Polycaprolactone (PCL) electrospun fibers are widely developed for biomedical applications. However, their hydrophobicity and passivity towards cell growth is an important limitation. In a first example, we will demonstrate that star pseudopolyrotaxanes (star-pPRs) obtained from the inclusion complexation of  $\alpha$ -cyclodextrin (CD) and four-branched star poly( $\epsilon$ -caprolactone) (star-PCL) organize into nanoplatelets in dimethyl sulfoxide at 35 °C. This peculiar property allows the electrospinning of star-pPRs while preserving their supramolecular assembly. Thus, original PCL:star-pPR nanofibrous materials were obtained allowing further functionalization with any bioactive molecules.<sup>[1,2]</sup> More recently, we have shown that hydroxypropyl- $\beta$ -cyclodextrin (HP $\beta$ CD) can also be advantageously used to electrospin hyaluronic acid (HA) in water thanks to favorable supramolecular interactions. Furthermore, the beneficial presence of HP $\beta$ CD allowed the encapsulation of drugs enabling the development of safe functional nanofibrous wound dressings.<sup>[3]</sup>

Electrospinning is known as a process allowing the preparation of nanofibrous materials from a solution usually based on a high molar mass polymer. Indeed, the polymer chains bring entanglements avoiding any breaking or Rayleigh instability of the electrospun jet resulting thus in the deposition of a continuous solid nanofibre. In the last example, it will be shown that tannic acid can be electrospun in water without using a carrier polymer thanks to favorable supramolecular interactions. The resulting materials are mechanically stable and can be handled and wrapped. Furthermore, the nanofibers can be cross-linked in water with Fe(III) by a combination of oxidative reaction and the formation of coordination complexes. The proposed electrospinning and cross-linking strategy is easy, of low cost, and scalable and uses nontoxic solvents as well as biocompatible and biofunctional molecules. Furthermore, thanks to the chelation capacity of tannic acid having the ability to coordinate with a wide variety of metals, hybrid smart nanowebs can be envisaged for diverse applications such as biomedical, catalysis as well as environment. Finally, low molar mass polymers could also be processed in combination with TA.<sup>[4]</sup>

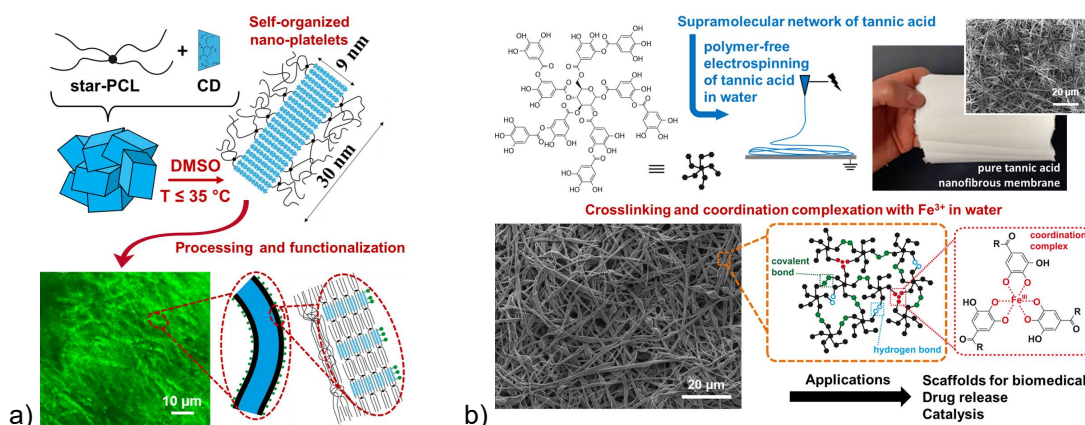


Figure: a) Electrospinning and functionalization of self-organized star-pPR nano-platelets. b) Polymer-free electrospinning of tannic acid and the cross-linking of the fibers with Fe(III).

## References :

- [1] M. Oster et al., *Macromolecular Rapid Communications*, 2015, **36**, 292–297.
- [2] M. Oster et al., *Journal of Materials Chemistry B*, 2017, **5**, 2181–2189.
- [3] M. Séon-Lutz et al., *Carbohydrate Polymers*, 2019, **207**, 276–287.
- [4] M. Allais et al., *Nanoscale*, 2018, **10**, 9164–9173.

# Poster contributions

## Polymer materials: From structure to properties

- P-6** SEMICONDUCTING POLYMERS WITH SILOXANE SIDE-CHAINS FOR ORGANIC ELECTRONICS  
*Stephane Mery, Olzhas Ibraikulov, Pablo Durant, Benoît Heinrich, Kamatham Narayanaswamy, Thomas Heiser, Patrick Lévêque, Nicolas Leclerc*
- P-7** POLYELECTROLYTE COMPLEX COACERVATES AS SOFT UNDERWATER ADHESIVES  
*Mehdi Vahdati, Francisco Cedano, Costantino Creton, Dominique Hourdet*
- P-8** ON THE BRITTLE-TO-DUCTILE TRANSITION OF PLA : INFLUENCE OF MACROMOLECULAR ORIENTATION  
*Shanshan Xu, Jean-Francois Tahon, Isabelle De Waele, Gregory Stoclet, Valérie Gaucher*
- P-9** CONTROLLING THE SURFACE CRYSTALLIZATION AND ORIENTATION OF BIOPOLYMERS.  
*Marion Brosset, Thierry Falher, Gilles Dennler, Bertrand Fillon, Martin Brinkmann*
- P-10** CHARACTERIZATION OF BOVINE GELATIN FILMS REINFORCED BY DHT CROSSLINKING FOR DRUG RELEASE: PRELIMINARY STUDY  
*Jihane Mzoughi*
- P-11** BRANCHED SILICONE POLYMERS FOR RELEASE COATING APPLICATION  
*Aurélie Boulegue Mondière*
- P-12** SYNTHESIS AND CHARACTERIZATION OF SEMI-CONDUCTING POLYMERS BASED ON ANILINE AND/OR O-ANISIDINE: OPTICAL AND ELECTRICAL PROPERTIES  
*Kenane Abdelbassat, Ahmed Yahiaoui, Aïcha Hachemaoui, Ali Mustapha Benquider, Oana Rasoga, Aurelian Catalin Galca, Anca Stanculescu*
- P-13** DESIGN, SYNTHESIS, CHARACTERIZATION AND TRANSPORT PROPERTIES INVESTIGATIONS OF POLYMERIC BIPOROUS MATERIALS  
*Benjamin Le Droumaguet, Sarra Mezhoud, Patrick Aïmedieu, Vincent Monchiet, Michel Bornert, Daniel Grande*
- P-14** ON THE IMPACT OF MACROMOLECULES SIZE ON THE RIGID AMORPHOUS FRACTION OF COLD CRYSTALLIZED PLA  
*Yoga Sugama Salim, Estève Ernault, Nicolas Delpouve, Benoit Vieille, Laurent Delbreilh, Sophie Eve, Eric Dargent, Antonella Esposito, Loïc Le Pluart*

- P-15** SELF-OSCILLATING POLYMER INTERFACES TO DESIGN LIFE-LIKE PULSATILE MEMBRANES  
*Marianne Benoit, Joël Lyskawa, David Fournier, Patrice Woisel, Claire Antonelli, Damien Quémener*
- P-16** FROM A NEW GENERATION OF IONIC LIQUID MONOMERS TOWARDS THERMOSETTING EPOXY POLYMERS  
*Sébastien Livi, Charline Chardin, Luanda. C. Lins, Jérôme Baudoux, Jean-François Gérard, Jannick Duchet-Rumeau*
- P-17** INVESTIGATION OF THE NANOMECHANICAL PROPERTIES OF 3D PRINTED MICROSTRUCTURES  
*Mehdi Belqat, Arnaud Spangenberg, Jean-Pierre Malval, Karine Mougin*
- P-18** A SIMPLE WAY TO GRAFT BIOACTIVE POLYMERS ON SILICONE IMPLANTS TO IMPROVE THE BIOLOGICAL RESPONSE  
*Mylan LAM, Vivien Moris, Vincent Humblot, Veronique Migonney, Céline Falentin-Daudre*
- P-19** POLYETHYLENE AEROGELS COMBINING PHYSICAL AND CHEMICAL CROSSLINKING FOR IMPROVED MECHANICAL RESILIENCE.  
*Douriya Khedaoui, Franck D'Agosto, Christophe Boisson, Damien Montarnal*
- P-20** MICRO & NANOSTRUCTURED CONDUCTING POLYMERS PLATFORM TO INTERFACE WITH ELECTROACTIVE CELLS  
*Mohammed El Mahmoudy, Rodney O'Connor, George Malliaras, Sébastien Sanaur*
- P-21** RELATIONSHIP BETWEEN SILICONE ACRYLATE STRUCTURE AND RELEASE COATING PROPERTIES  
*Emilie Vialle Désormière*
- P-22** SYNTHESIS OF IONIC LIQUID CORE/SILICA SHELL MICROCAPSULES AS FUNCTIONAL AGENTS OF EPOXY NETWORKS  
*Ting Shi, Sébastien Livi, Jannick Duchet-Rumeau, Jean-François Gérard*

# Semiconducting Polymers with Siloxane Side-Chains for Organic Electronics

K. Narayanaswamy<sup>a</sup>, O. Ibraikulov<sup>b</sup>, P. Durant<sup>c</sup>, B. Heinrich<sup>a</sup>, T. Heiser<sup>b</sup>, P. Lévêque<sup>b</sup>, N. Leclerc<sup>c</sup>, S. Méry<sup>a\*</sup>

<sup>a</sup> Institut de Physique et de Chimie des Matériaux de Strasbourg (IPCMS), CNRS, Université de Strasbourg, UMR 7504, 23 rue du Loess, 67034, Strasbourg, France

<sup>b</sup> Laboratoire ICube, CNRS, Université de Strasbourg, UMR 7357, 23 rue du Loess, 67037, Strasbourg, France

<sup>c</sup> Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé (ICPEES), CNRS, Université de Strasbourg, ECPM, UMR 7515, 25 rue Becquerel, 67087, Strasbourg, France

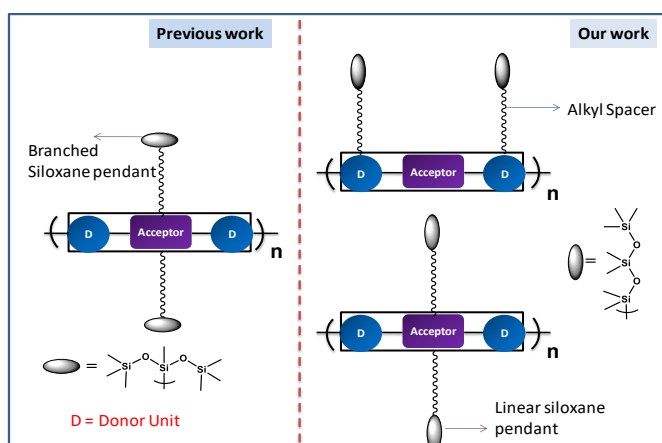
\* [mery@ipcms.unistra.fr](mailto:mery@ipcms.unistra.fr)

**Key-Words:** semiconducting polymers, charge transport, organic photovoltaic, siloxane functionalization

## Abstract:

In the state-of-the art polymer designs, side chain engineering can significantly affect molecular ordering and thin-film morphology in addition to its conventional role as a solubilizer.[1] Linear and branched alkyl side chains have been widely utilized for a long time.[2] Recently, a number of studies have demonstrated the substantial impact of siloxane-terminated side chain (far-branched pendant through alkyl spacer) in conjugated semiconducting polymers on the performance of organic field effect transistors (OFETs) and organic solar cells (OSCs).[3] Relative to the great endeavors and encouraging success of conjugated polymers with branched siloxane-terminated side chain in OFETs, research reports for their photovoltaic properties are extremely scarce and importantly, linear siloxane-terminated side chains have not been explored so far in organic electronics.

For the first time, we have designed and synthesized different types of D-A conjugated polymers with linear siloxane-terminated side chain for OFETs and OSCs applications (see figure). These polymers exhibit good solubility in common organic solvents and display broad absorption from 300 to 700 nm. The siloxane-functionalized polymers display one order of magnitude higher hole mobilities in OFETs as well as in SCLC devices, as compared to polymers containing classical alkyl chains. Among different polymers, a polymer donor gave promising PCE > 8% with PC70BM as an acceptor. In this communication, we will provide guidelines for the molecular design of new semiconducting polymers with linear hybrid side chains.



*Schematic representation of the novel D-A polymers functionalized with linear siloxane side-chains, as compared to the ones functionalized by branched siloxane chains*

## References :

- [1] J.Y. Back, H. Yu, I. Song, I. Kang, H. Ahn, T. J. Shin, S.-K. Kwon, J.H. Oh, Y.-H. Kim, Chem. Mater. 27(5), 1732-1739. (2015).
- [2] T. Kumari, S.M. Lee, K.C. Lee, Y. Cho, C. Yang, Adv. Energy Mater. 8, 1800616. (2018).
- [3] A.-R. Han, J. Lee, H.R. Lee, J. Lee, S.-H. Kang, H. Ahn, T.J. Shin, J.H. Oh, C. Yang, Macromolecules, 49, 3739-3748. (2016).



# Polyelectrolyte Complex Coacervates as Soft Underwater Adhesives

**Mehdi Vahdati, Francisco Cedano, Costantino Creton, Dominique Hourdet**

Soft Matter Sciences and Engineering (SIMM), ESPCI Paris, PSL University,  
Sorbonne University, CNRS, F-75005 Paris, France  
Mehdi.vahdati@espci.fr

Associative, liquid-liquid phase-separation of oppositely-charged polyelectrolytes, leading to a polymer-rich coacervate and a polymer-lean supernatant, is called “polyelectrolyte complex coacervation”. This phenomenon is ubiquitous in biological systems. For instance, the underwater adhesive of a marine organism called sandcastle worm is based on coacervates.

Inspired by this organism, we have developed viscoelastic complex coacervates from synthetic polyelectrolytes as model systems for underwater adhesion. Due to the electrostatic nature of the ionic bonds between the charged polyelectrolytes, the mechanical properties of these systems are highly sensitive to the ionic strength of the medium. The dynamic properties of the materials are studied over a large range of time scales owing to the application of Time-Salt Superposition principle. The adhesive properties of the coacervates are studied using a custom-built *underwater* probe tack test upon a “salt switch”, i.e. after immersing the coacervates prepared at high salt concentrations in a low salt medium. While this method is a promising way of hardening injectable underwater adhesives, the highest adhesion energies on the order of  $15 \text{ J}\cdot\text{m}^{-2}$  were measured with the coacervate closest the sol-gel transition without a major salt switch. The highly rate-dependent behavior of this coacervate is reminiscent of generic Pressure-Sensitive Adhesives (PSAs). With performance under physiological conditions and the possibility to be directly applied under water, these materials hold great promise as spontaneous biomedical adhesives without relying on chemical reactions.

# ON THE BRITTLE-TO-DUCTILE TRANSITION OF PLA : INFLUENCE OF MACROMOLECULAR ORIENTATION

S. Xu<sup>a</sup>, J.-F. Tahon<sup>a</sup>, I. De-Waele<sup>b</sup>, G. Stoclet<sup>a</sup>, V. Gaucher <sup>\*a</sup>

<sup>a</sup> Univ. Lille, CNRS, INRA, ENSCL, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000 Lille.

<sup>b</sup> Univ. Lille, CNRS, UMR 8516- LASIR- Laboratoire de Spectrochimie Infrarouge et Raman, F-59000 Lille.

\* Email address: valerie.gaucher@univ-lille.fr

**Key-Words:** polylactide, structure, biorientation, mechanical behavior

## Abstract:

This work deals with the influence of molecular orientation on the mechanical behavior of amorphous Polylactide (PLA) films. Macromolecular orientation has been induced under biaxial tension at temperature just above the glass transition. Then, the uniaxial tensile behavior of undrawn and biaxially stretched films has been investigated at room temperature. While undrawn PLA sample exhibited a brittle behavior, a remarkable enhancement of strain at break was observed for biaxially stretched PLA films (Fig.1). In order to better understand the origin of this brittle to ductile transition, structural characterizations by X-ray diffraction and FTIR spectroscopy have been performed. In particular, trichroic FTIR analysis has been used to quantify the molecular orientation as a function of the biaxial drawing parameters. This study shows for the first time that a critical chain orientation of amorphous phase is necessary to induce a ductile behavior. In-situ Small Angle X-ray Scattering experiments and post-mortem microscopic observations have revealed that the origin of the brittle to ductile transition is due to a change of the elementary plastic deformation mechanism.

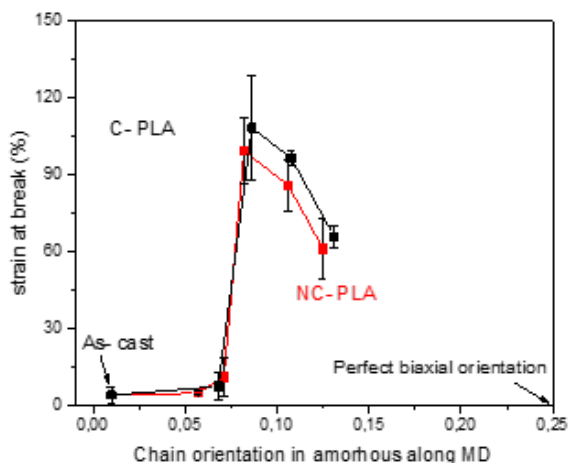


Fig. 1. Strain at break as a function of chain orientation in amorphous phase for crystallizable and non crystallizable PLA (C- PLA and NC-PLA).

# CONTROLLING THE SURFACE CRYSTALLIZATION AND ORIENTATION OF BIOPOLYMERS.

Brosset Marion<sup>1</sup>, Falher Thierry<sup>2</sup>, Dennler Gilles<sup>2</sup>, Fillon Bertrand<sup>2</sup>, Brinkmann Martin<sup>1</sup>

<sup>1</sup> Institut Charles Sadron, CNRS – Université de Strasbourg, 23 rue du Loess, Strasbourg, 67034, France

<sup>2</sup> Centre Technique Industriel de la Plasturgie et des Composites, Oyonnax, 01100, France

\* Email address : marion.brosset@ics-cnrs.unistra.fr

**Key-Words:** bio-sourced polymers, crystallization, processing, electron microscopy.

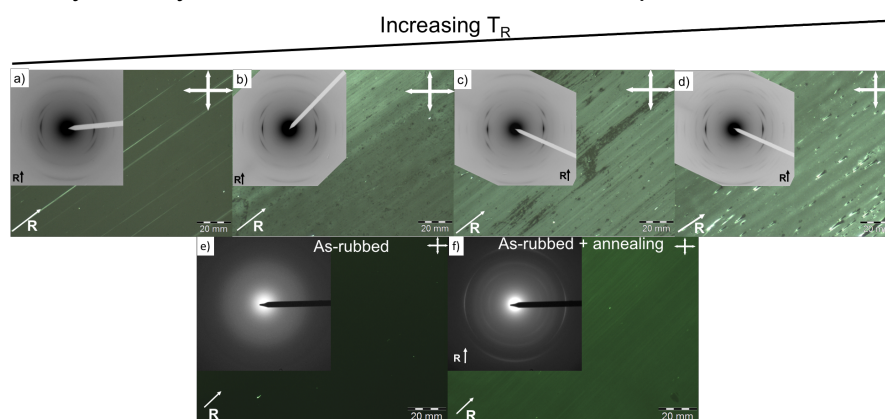
## Abstract:

Until now, petrochemical-based plastics such as polyethylene terephthalate (PET) and polyethylene (PE) have been increasingly used in the form of films, sheets, bottles, etc.. because of their relatively low cost, their good mechanical performance and their good oxygen and water vapor barrier property [1]. However, these synthetic polymers are not fully recyclable and not biodegradable, leading to serious ecological problems. With the growing awareness of sustainability in recent years, developing new biodegradable materials from renewable resources to replace conventional petroleum-based polymers has become a primary objective. Natural compounds, like cellulose and starch are hydrophilic polymers, water wettable or swellable and consequently biodegradable but they are not technologically relevant for packaging. Therefore, hydro-biodegradable aliphatic polyesters such as polylactic acid (PLA) and poly(hydroxyacid) (PHA) show great potential as environmentally friendly alternative polymers due to their transparency, easy processability and good mechanical strength.

Many properties of semi-crystalline polymers depend on their crystallinity. Currently, one of the ways to improve their crystallization is the incorporation of nucleating agents [2]. A second approach consists to align polymer chains during the crystallization process. In the case of a thin film, the crystallization can be induced by a method such as high temperature rubbing [3]. Rubbing has been widely used to prepare polyimide alignment layers. We show that this fast orientation method can be successfully applied to orient et crystallize different biopolymers.

The influence of two keys parameters (rubbing temperature and annealing temperature and time) on the orientation and crystallization of thin films of one biopolymer (POLY1) has been studied by DSC, POM and TEM.

By controlling the rubbing temperature, we can control precisely the film crystallinity between 29% and 54%. The higher the rubbing temperature, the more crystalline, oriented and birefringent the polymer films are. However, for high rubbing temperatures, the films show scratches and tend to rupture. This is why, annealing experiments have been performed for films rubbed at low temperature. Such films display high orientation and crystallinity without substantial scratches and pinholes.



Figures : POM images under crossed polarizers and Electron diffraction patterns of thin films of POLY1 showing the increasing orientation/crystallinity for increasing rubbing temperature (a to d) or after thermal annealing of films rubbed at low temperature (e and f).

## References :

[1] : V. Siracusa, et al, *Trends in Food Science & Technology*, 2008, **19**, 634.

[2] : H. Nakajima, et al, *Macromolecular Materials and Engineering*, 2010, **295**, 460.

[3] : L. Biniek, et al, *Macromolecules*, 2014, **47**, 387.

# Design of rolled-up capsules with non-trivial spatial drug distributions for drug release application

## Characterization of bovine gelatine films reinforced by DHT crosslinking

\*Jihane Mzoughi <sup>a, b</sup>, Luc Delmotte <sup>a</sup>, Cyril Vaultot <sup>a</sup>, Simon Gree <sup>a</sup>, Valeriy Luchnikov <sup>a</sup>

<sup>a</sup> Institut De Science des Matériaux de Mulhouse

<sup>b</sup> Faculté de Pharmacie de Strasbourg

\* jihane.mzoughi@uha.fr

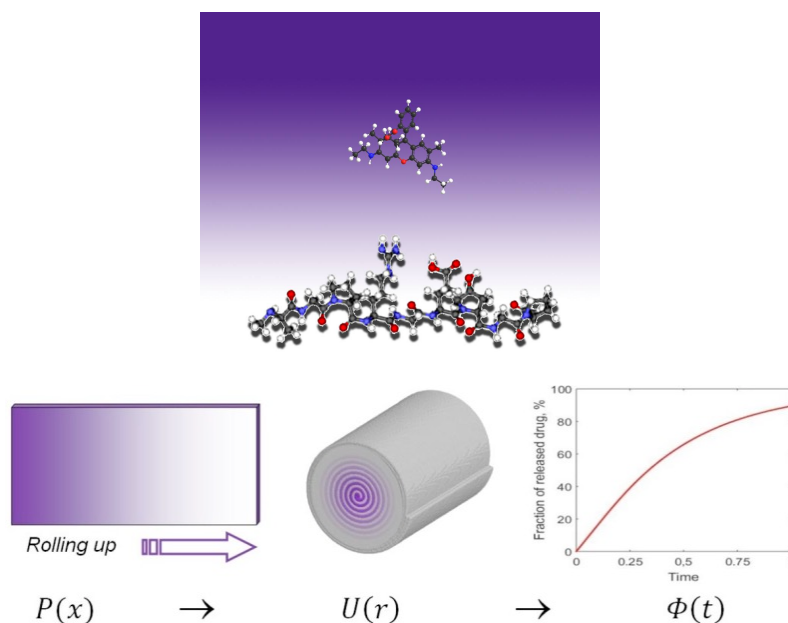
**Key Words:** Gelatine, Rh6G, DHT, TGase, Drug release

### Abstract:

To develop a material with a potential drug delivery application, Dehydrothermal treatment (DHT) was applied on crude gelatin films obtained by casting. This physical treatment is an interesting alternative for chemical and enzymatical crosslinking since it diminish undesirable side effects of chemicals. Interestingly, only 4 hours of DHT treatment at 150 °C are sufficient and efficient to obtain enhanced structural, thermal and mechanical properties suitable for the intended purpose.

Firstly, TGA, DSC, AFM, tensile testing, contact angle, swelling and mass loss measurements were performed in order to compare the untreated films to the treated ones. Findings suggest that the obtained films, which are flexible and stable in physiological conditions, showed a more hydrophobic surface and a better mechanical resistance with a limited swelling percentage and a low mass loss. Furthermore, FTIR highlighted the esterification induced by DHT.

On the other hand, the formulation based on Rhodamine 6G has been optimized. The capsules have been stabilized against unrolling with TGase. The radial diffusion profile was explored by fluorescent imaging of the cross sections of the capsules. Dissolution tests are under study.



**Fig1.** A drug distribution over a biopolymer stripe,  $P(x)$ , is transformed by rolling into radial distribution in the cylindrical capsule,  $U(r)$ , which determines the kinetics of the drug release,  $\Phi(t)$ .

# Branched silicone polymers for release coating application

Aurélie Boulegue Mondière<sup>a\*</sup>, Fabien Dupin<sup>a</sup>, Delphine Blancs<sup>a</sup>,

Frédéric Magd<sup>a</sup>, Yassine Maadadi<sup>a</sup>, Agnes Jolly<sup>a</sup>

<sup>a</sup> Elkem Silicones France

\* aurelie.boulegue-mondiere@elkem.com

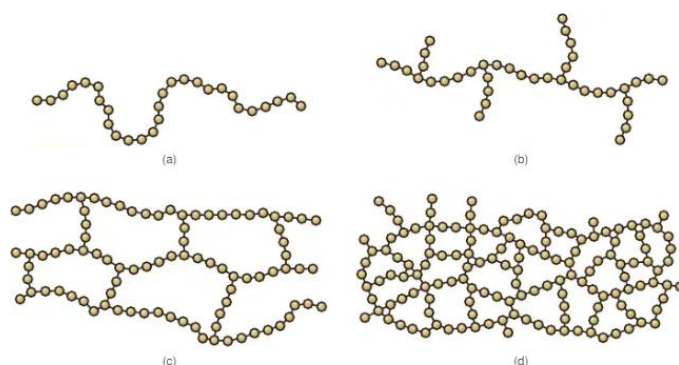
**Key-Words:** silicone, branched, polymers, release coating

## Abstract:

During last three decades, dendritic polymers have become one of the fastest growing areas of interest in polymer science. Branched polymers as dendritic polymer has an architecture-specific property there are not found in any traditional linear or crosslinked compounds. Branches were able to have lower viscosities than the corresponding linear polymers even with same higher molecular weight. <sup>[1]</sup>

For the silicone scientist, branched polymers have been very attractive for silicone formulation composition. They have been showed very good performances for release coating application. The curable based branched silicone compositions could give fast curing with platinum content reduced.

we are presenting simultaneously the synthesis of branched silicones used for paper release coating composition and some of application results.



*Various structures of polymer molecules: (a) linear, characteristic of thermoplastics; (b) branched; (c) loosely cross-linked as in an elastomer; and (d) tightly cross-linked or networked structure<sup>[2]</sup>*

## References:

[1]: E. M. Valles, C. W. Macosko, *Macromolecules*, 1979, **12**(3), 521-562

[2]: *Fundamentals of Modern Manufacturing: Materials, Processes and Systems*, 7th Edition. Mikell P. Groover. ISBN: 978-1-119-47521-7. Sep 2018.

# SYNTHESIS AND CHARACTERIZATION OF SEMI-CONDUCTING POLYMERS BASED ON ANILINE AND/OR O-ANISIDINE: OPTICAL AND ELECTRICAL PROPERTIES

Abdelbassat Kenane \* <sup>a, b</sup>, Ahmed Yahiaoui <sup>a</sup>, Aicha Hachemaoui <sup>a</sup>, Ali Mustapha Benquider <sup>a</sup>, Oana Rasoga <sup>b</sup>, Aurelian Catalin Galca <sup>b</sup>, Anca Stanculescu <sup>b</sup>.

<sup>a</sup> *Laboratoire de Chimie Organique Macromoléculaire et des Matériaux. (LCOMM), University of Mascara, Algeria.*

<sup>b</sup> *National Institute of Material Physics, 405A Atomistilor, 077125 Magurele, Romania.*

\* Email address: a.kenane@univ-mascara.dz

**Key-Words:** polymers, chemical oxidation, semi-conductive polymer, energy storage devices, optical gap

## Abstract:

The growing interest in nanostructured conducting polymers is caused by expanding the area of their practical application. In the last decade, an increased interest in PANI and derivatives have been observed, a conductive or semi-conductive polymer have been used in a wide range of application specially in rechargeable batteries, energy storage devices, electronic and optical devices due to its high stability and unique complex of properties [1-2]. For the use of commercial products, it is necessary for PAN being mixed with other polymers or inorganic materials.

This work is a study on several polymers like polyaniline (Pani), poly (ortho-anisidine) (p(o-ANIS)) and (poly(ortho-anisidine-co-aniline)). The polymers are synthesized by oxidation chemical polymerization method of aniline and/or o-anisidine in 1M of Hydrochloric acid solution using ammonium persulfate (APS) as oxidizing agent, these polymers have been characterized by Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy to study the chemical structure of polymers. The cyclic voltammetry (C V) is used to discuss the electrical effect.

The results obtained are promising and the characteristic of the prepared polymers by chemical oxidative polymerization show that these materials can be further used in the elaboration of photovoltaic devices.

## References:

- [1]: Baker, C.O., Huang, X., Nelson, W., Kaner, R.B., Chem. Soc. Rev 2017 46, 1510–1525  
[2]: Huang, J., Pure Appl. Chem 2006. 78, 15–27

# DESIGN, SYNTHESIS, CHARACTERIZATION AND TRANSPORT PROPERTIES INVESTIGATIONS OF POLYMERIC BIPOROUS MATERIALS

Benjamin Le Droumaguet,<sup>a, \*</sup> Sarra Mezhoud,<sup>a,b,c</sup> Patrick Aïmedieu,<sup>b</sup> Vincent Monchiet,<sup>c</sup> Michel Bornert,<sup>b</sup> Daniel Grande<sup>a</sup>

<sup>a</sup> Université Paris-Est, Institut de Chimie et des Matériaux Paris-Est (ICMPE), UMR 7182 CNRS-UPEC, 2 rue Henri Dunant, 94320 Thiais, France

<sup>b</sup> Laboratoire Navier, CNRS-IFSTTAR-ENPC, France

<sup>c</sup> Laboratoire de Modélisation et Simulation Multi-Echelle, Université Paris-Est Marne-la-Vallée, Marne-la-Vallée, France

\* ledroumaguet@icmpe.cnrs.fr

**Key-Words:** biporous polymers, microstructure, microtomography, transport properties, computed simulation

## Abstract:

Biporous polymeric materials possess a number of potential applications in diverse area, among which civil engineering and soil mechanics. The role of each porosity level on transport properties of such polymeric frameworks still remains a fundamental issue. In this context, a scientific approach combining the design, synthesis and physico-chemical characterization of polymeric materials presenting two porosity levels has been developed. Model biporous networks based on poly(2-hydroxyethyl methacrylate) have thus been prepared by using two types of distinct porogens: sieved NaCl particles as macroporogens in conjunction with solvents (alcohols) used as nanoporogens [1]. NaCl particles presenting different sizes have been preliminary sintered by Spark Plasma Sintering technique so as to obtain 3-D templates. A structural and morphological characterization has been achieved by scanning electron microscopy (SEM), as shown on Fig. 1, and mercury intrusion porosimetry (MIP). A nanoporous network presenting pore sizes in the 10 nm to 10  $\mu\text{m}$  range as well as 100  $\mu\text{m}$ -sized macropores have been observed. In order to describe more finely the microstructure, notably to get a precise shape of the pores and a better idea of the interconnectivity of the two porosity levels, X-ray microtomography analyses have been implemented. The effect of the size and interconnectivity of macroporogenic agents on the porosity of as-obtained materials has been investigated. Finally, permeability measurements to water have been achieved so as to study the transport properties of these complex polymeric structures in relationship with their porous morphology.

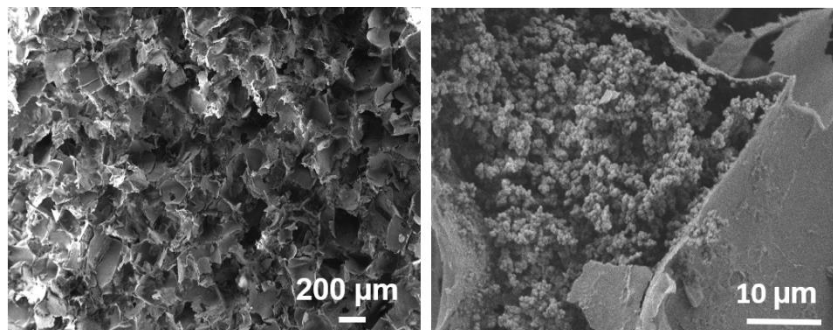


Fig. 1: SEM micrographs of poly(2-hydroxyethyl methacrylate)-based biporous materials prepared in this study.

## References :

[1] : H. B. Ly, B. Le Droumaguet, V. Monchiet, D. Grande, *Polymer*, 2015, **78**, 13-21

# On the impact of macromolecules size on the rigid amorphous fraction of cold crystallized PLA

Yoga Sugama Salim<sup>a</sup>, Estève Ernault<sup>b</sup>, Nicolas Delpouve<sup>b</sup>, Benoît Vieille<sup>b</sup>, Laurent Delbreilh<sup>b</sup>, Sophie Eve<sup>c</sup>, Eric Dargent<sup>b</sup>, Antonella Esposito<sup>b</sup>, Loïc Le Pluart<sup>\*a</sup>

<sup>a</sup> Normandie Univ, ENSICAEN, UNICAEN, CNRS, LCMT, 14000 Caen, France

<sup>b</sup> Normandie Univ, UNIROUEN Normandie, INSA Rouen, CNRS, Group de Physique des Matériaux, 76000, Rouen, France

<sup>c</sup> Normandie Univ, ENSICAEN, UNICAEN, CNRS, CRISMAT, 14000 Caen, France

\* loic.le\_pluart@ensicaen.fr

**Key-Words:** PLA, average molar mass, rigid amorphous fraction, cold crystallization, MT-DSC

## Abstract:

A three-phase microstructure involving crystalline, rigid and mobile amorphous regions has been successfully used to describe the macromolecular arrangements in poly(lactic acid) (PLA) [1, 2]. The Rigid Amorphous Fraction (RAF) is known to depend on the crystallinity degree as well as on the crystallization temperature, but how does it change for different lengths of the polymer chains? To investigate this, a commercial grade of polylactic acid (PLA) was hydrolyzed by extrusion in controlled conditions of time, temperature and water content. Seven fractions encompassing the range of ( $M_n$ ) 5,000 to 90,000  $\text{g}\cdot\text{mol}^{-1}$  were obtained. Their microstructure was characterized by Modulated Temperature Differential Scanning Calorimetry (MT-DSC) on amorphous and cold-crystallized PLA. In amorphous PLA,  $\Delta C_p$  is the highest for the lowest  $M_n$  and vice versa. Characterizations by X-Ray Diffraction (XRD) showed changes in the shape of the amorphous halo, which were tentatively related to the stiffness of the glassy materials by nanoindentation modulus measurements. Above the  $T_g$  of cold-crystallized samples, the PLA sample with the highest  $M_n$  exhibits single melting peak ( $T_m$ ), whereas two  $T_m$  can be observed in the PLA samples with lower  $M_n$ . The existence of these peaks is attributed to the ability of short chains in  $\alpha'$ -crystals to reorganize and form more perfect  $\alpha$ -crystals. The enthalpy of melting was logically found to increase linearly with the reduction of  $M_n$ . By using the three-phase model for the microstructural characterization of the cold-crystallized samples, it is shown that less RAF is formed in PLA with lower  $M_n$  but that the relative amount of RAF in the amorphous region is unchanged.

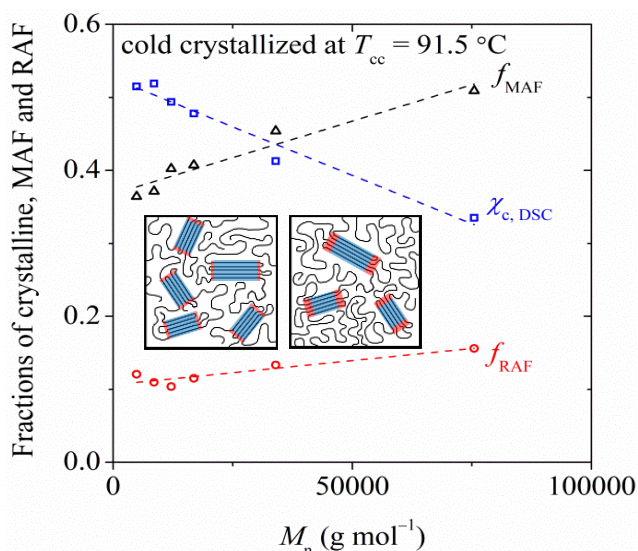


Figure 1. Values of  $X_c$ ,  $f_{MAF}$  and  $f_{RAF}$  in PLA samples isothermally crystallized at 91.5 °C after melt quenching, obtained upon heating from the glassy state by MT-DSC ( $q^* = 2$  °C  $\text{min}^{-1}$ , period 60 s, amplitude  $\pm 0.318$  °C  $\text{min}^{-1}$ ). The insets show a representation of cold-crystallized PLA without taking into consideration lamellae thickness and chain folding.

## References :

- [1] : N. Delpouve; L. Delbreilh; G. Stoclet; A. Saiter; E. Dargent, *Macromolecules*, 2014, **47**, 5186  
 [2] : M.C. Righetti; E. Tombari, *Thermochim. Acta*, 2011, **522**, 118



# Self-oscillating polymer interfaces to design life-like pulsatile membranes

Marianne Benoit<sup>a</sup>, Joël Lyskawa<sup>b</sup>, David Fournier<sup>b</sup>, Patrice Woisel<sup>b</sup>, Claire Antonelli<sup>\*a</sup>, Damien Quémener<sup>\*a</sup>

<sup>a</sup> Institut Européen des Membranes (IEM UMR 5635), Université de Montpellier, CC047-2 pl. E. Bataillon 34095, Montpellier Cedex 05, France

<sup>b</sup> Unité Matériaux et Transformations, Université de Lille, 59655 Villeneuve d'Ascq

\* damien.quemener@umontpellier.fr and claire.antonelli@umontpellier.fr

**Key-Words:** pH-responsive membrane, self-oscillating, pH-oscillator, PMAA

## Abstract:

Soft matter materials research has considerably evolved the last decades mainly by promoting responsive polymer systems. Up to now, the dynamic behavior, although bringing new functions, was always reached by the action of an outside trigger (pH, light, T°C...). In this work, it is envisioned to prepare autonomous oscillatory polymer interfaces synchronized by chemical reaction networks (pH-oscillators). The self-regulating pH waves will be read in time by synthesized polymer interfaces to undergo autonomous macroscopic motions. The objectives are the preparation of autonomous dynamic soft interfaces characterized by their constantly evolving surface properties, and the design of new integrated membranes showing a chemically-powered autonomous pulsatile flow. The self-oscillatory system is obtained from the combination of a pH-responsive polymer and an oscillating chemical reaction. In this work, functionalized poly(methacrylic acid) (PMAA) was prepared by RAFT polymerization and grafted at the interface of a commercial alumina membrane. Then mounted in a filtration setup, the PMAA-functionalized membrane was synchronized to a pH oscillator (Bromate-Sulfite-Ferrocyanide: BSF) (Figure 1). When the flow through the membrane reaches the pH oscillation domain, a pulsatile flow with impressive permeability cycles was observed. BSF pH-oscillator leads to a cyclic change of the pH between 3.5 and 6.5 in the filtration cell. Since PMAA has a pKa around 4.8, a cyclic extension-contraction of the polymer chains is obtained which leads to a synchronized change in the pore size. Therefore, a direct consequence is an oscillatory modulation of the membrane permeability.

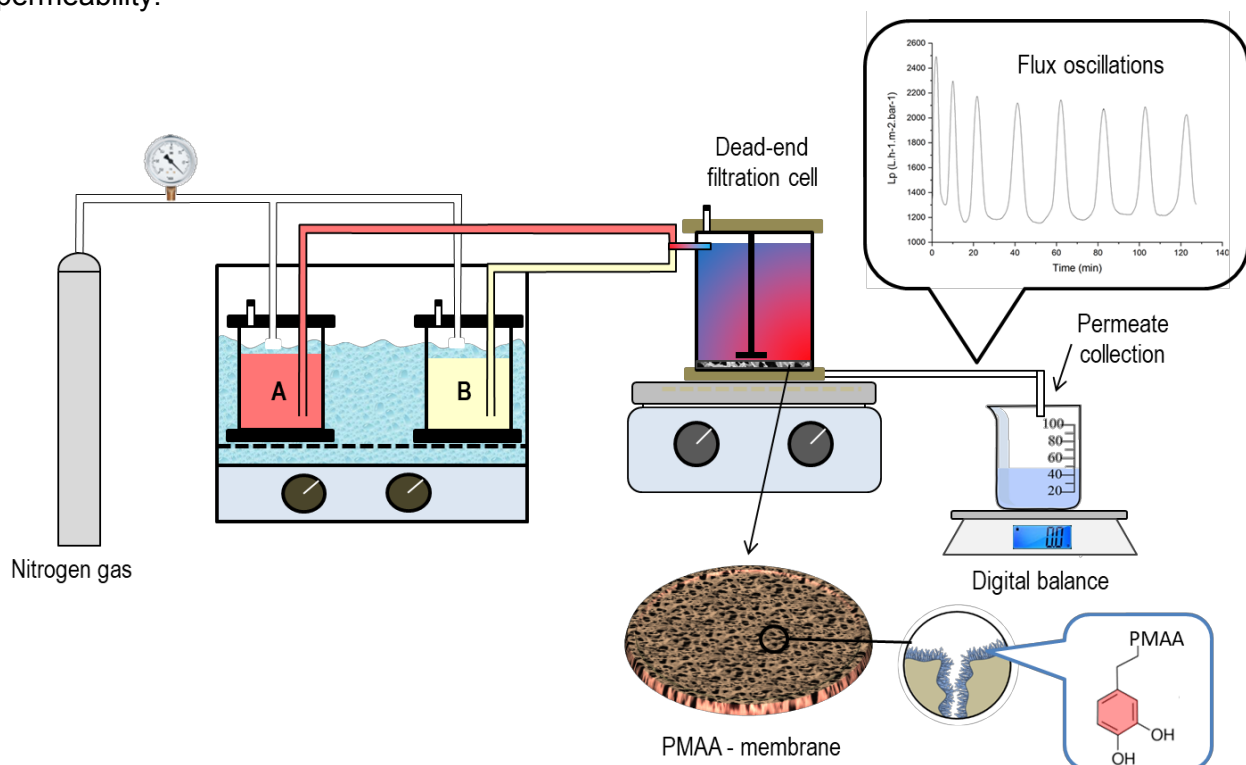


Figure 1: Filtration setup of self-oscillating membrane

# FROM A NEW GENERATION OF IONIC LIQUID MONOMERS TOWARDS THERMOSETTING EPOXY POLYMERS

Sébastien Livi<sup>\*a</sup>, Charline Chardin<sup>b</sup>, Luanda. C. Lins<sup>c</sup> Jérôme Baudoux<sup>b</sup>, Jean- François Gerard<sup>a</sup>, Jannick Duchet-Rumeau<sup>a</sup>

<sup>a</sup> Université de Lyon, F-69003, Lyon, France; INSA Lyon, F-69621, Villeurbanne, France CNRS, UMR 5223, Ingénierie des Matériaux Polymères.

<sup>b</sup> Laboratoire de Chimie Moléculaire et Thio-organique, ENSICAEN, Université de Normandie, CNRS, 6 boulevard du Maréchal Juin, 14050 Caen, France.

<sup>c</sup> Instituto de Quimica (IQ), Universidade Estadual de Campinas (UNICAMP), CEP 13083–970, Caixa Postal 6154, Campinas, SP, Brazil.

\* sebastien.livi@insa-lyon.fr

**Key-Words:** Ionic liquids, Epoxy networks, Polymerization reaction mechanisms, Mechanical properties

## Abstract:

In this work, new highly effective (multi)functional-dedicated polymer materials were designed and processed from the co-polymerization between novel imidazolium ionic liquid monomers (ILMs) having a similar structure of conventional Bisphenol A diglycidyl ether epoxy prepolymer (DGEBA) and conventional polyetheramine denoted Jeffamine D230 [1-2]. First, the main mechanisms of epoxy opening leading to polymerization with different kinetics were modeled through the reaction between monofunctional epoxy and aliphatic mono- and diamines by using “in situ” NMR spectroscopy [3]. Then, the ultimate role of the monomers architecture on the epoxy conversion as well as on the reactivity of the epoxy-functionalized imidazolium ionic liquid monomers with an aliphatic amine (D-230) was investigated while the average molecular weight between crosslinks ( $M_c$ ) and the relaxation temperature of the resulting networks were determined. Thus, new epoxy thermosets with an excellent thermal stability, high hydrophobic behavior and good storage modulus at room temperature were produced. In addition, antimicrobial tests against *E. coli* were performed for the first time on these new cross-linked epoxy networks leading to a very strong inhibition of *E. coli* biofilm formation (- 95%) [4].

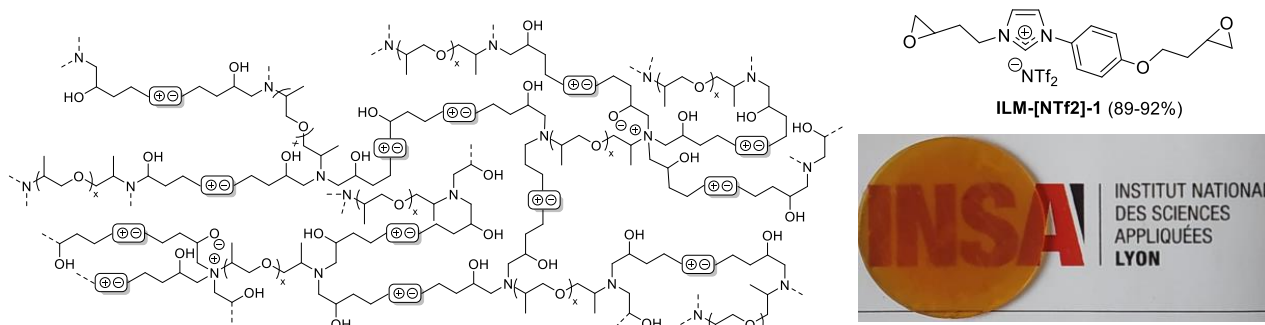


Fig. 1: Epoxy networks containing imidazolium and ammonium species

## References :

- [1] : C. Chardin, J.H. Rouden, S. Livi\*, J. Baudoux, Green Chem., 2017, 19, 5054-5059.
- [2] : C. Chardin, J.H. Rouden, S. Livi\*, J. Baudoux, Molbank, 2018, M974; DOI:10.3390/M974.
- [3] : S. Livi\*, C. Chardin, L.C. Lins, N. Halawani, S. Pruvost, J. Duchet-Rumeau, J-F. Gerard, J. Baudoux, ACS Sustainable Chem. Eng., 2019, 7, 3, 3602-3613.
- [4] : S Livi\*, L.C Lins, L. B. Capeletti, C Chardin, N Halawani, J. Baudoux, M.B. Cardoso, European Polymer Journal, 2019, 116, 56-64.



# Investigation of the nanomechanical properties of 3D printed microstructures

Mehdi Belqat, Arnaud Spangenberg, Karine Mougín, Jean-Pierre Malval

Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse

Mehdi.belqat@uha.fr

**Key-Words:** Two photon polymerization, 3D microstructures, AFM, Young's modulus

## Abstract:

Direct laser writing (DLW) based on two photon polymerization (2PP) represents a powerful technique for the fabrication of 3D micro- and nano-structures, which have a number of promising applications in areas including biology and cell cultures up to microsensors<sup>1-4</sup>. New applications often entail the contact and movement of nanoscale areas, therefore understanding of the mechanical properties involved in such systems is necessary for creating reliable micro&nanoscale applications<sup>5</sup>. Failure of nanoscale applications can be caused by a mechanical defect in the surface or in the material bulk. Therefore, knowledge about nanomechanics of 3D printed structures and its dependence on its geometry and contact size remains essential. Furthermore, the influence of the fabrication parameters have not been yet intensively investigated and detailed in the literature, leaving many unanswered questions about nanoscale contact.

As a result, this study deals with the investigation of the nanomechanical properties of 3D printed microstructures by Atomic Force Microscopy. Using the QNM PeakForce mode of Bruker's AFM, it was possible to determine the influence of the laser power and the monomer on the micromechanical properties, in particular the Young's modulus. The fabricated structures are 2D structures, consisting of successive lines, separated by 300 nm, forming a square. Two different resins have been used: PEGDA (Poly(ethyleneglycol)diacrylate) and PETA (Pentaerythritol triacrylate). The Young modulus of these raw material have been determined and are of the order of 1 to 5.5 MPa for PEGDA, and 800 to 3000 MPa for PETA. The results obtained show that the increase in Laser power increases the Young's modulus, since it induces a higher crosslinking density. A mixture of resin has also been realized and Young's modulus increases with the amount of PETA. This major result is particularly interesting in cell cultures, to tune both chemical and mechanical properties of 3D scaffold.

## Références :

1. E.D. Lemma, S. Sergio, B. Spagnolo, et al. *Microelectron. Eng.* **2018**, 190, 11–18.
2. E.D. Lemma, B. Spagnolo, F. Rizzi, et al. *Adv. Healthc. Mater.* **2017**, 6 (22), 1–10.
3. S.Y. Yu, G. Schrodj, K. Mougín, et al. *Adv. Mater.* **2018**, 1805093, 1–8.
4. L.P.C. Gomez, A. Spangenberg, X.A. Ton, et al. *Adv. Mater.* **2016**, 5931–5937.
5. S. Oras, S. Vlassov, M. Berholts, R. Löhmus, K. Mougín. *Beilstein J. Nanotechnol.* **2018**, 9 (1), 660–670.

# A simple Way to graft bioactive polymers on silicone implants to improve the biological response

Mylan Lam<sup>a\*</sup>, Vivien Moris<sup>a</sup>, Vincent Humblot<sup>b</sup>, Véronique Migonney<sup>a</sup>, Céline Falentin-Daudre<sup>a</sup>

<sup>a</sup> LBPS/CSPBAT, UMR CNRS 7244, Institut Galilée, Université Paris 13 Sorbonne Paris Cité, 99 avenue JB Clément 93430- Villetaneuse

<sup>b</sup> Laboratoire de Réactivité de Surface (LRS)- CNRS : UMR7197, Université Paris VI - Pierre et Marie Curie-3 rue Galilée 94200 Ivry-sur-Seine, France

\* mylan.lam208@gmail.com

**Key-Words:** Silicone, bioactive polymer, biocompatibility, grafting

## Abstract:

Poly(dimethylsiloxane) (PDMS) more commonly known as silicone is an elastomer widely used in the medical field for various surgery applications. As an example, silicone-based breast implants are used since the 1970's for reconstructive or plastic surgery. Nevertheless, after long term implantations, several issues appeared such as ruptures and fibroses leading to discuss and re-consider the PDMS non-invasive aspect and biocompatibility. Indeed, in the past years many cases of large cell anaplastic lymphoma have been reported <sup>[1]</sup> on women with breast implants after 8-10 years post-surgery. A deformation around the outer shell is visible, which may be due to an inflammatory response. This non controlled host response results in the generation of a fibrous envelope around the implant which in the long term leads to complications such as the calcification of the breast implant - that is responsible for pains and skin deformations. The main hypothesis to explain such deformation is the bacterial contamination located at implant's surface. Indeed, the hydrophobic surface of the silicone tends to promote the adsorption of plasmatic proteins leading to the adhesion and proliferation of bacteria *in fine*. LBPS team has developed functionalization methods of bioactive polymers on metallic surfaces (titanium and its alloys <sup>[2][3]</sup>), polymers surfaces (PET<sup>[4]</sup> + PCL<sup>[5][6]</sup>) and ceramics. These polymers exhibit specific functional groups allowing the modulation of the biological response and in particular the conformation of the proteins adsorbed on the surface, and thus may prevent bacterial adhesion. It has been shown that a silicone based quarterpolymer <sup>[7][8]</sup> carrying bioactive functions reduces the bacterial adhesion of 80% *in vitro* (*S. Aureus* & *S. Epidermidis*). In addition, *In vivo*, a decrease of 1.5 to 2log was observed <sup>[9]</sup>. Such polymers can reduce significantly the risk of infection while improving the biocompatibility.

In order to improve the biological response of silicone material, we developed a strategy (Figure1) to graft bioactive polymers bearing sulfonate groups on silicone surfaces. Different characterization methods are used to follow the experiment: Fourier-transform infrared spectroscopy (FTIR), colorimetry, scanning electron microscope (SEM), water contact measurements and X-ray photoelectron spectroscopy (XPS).

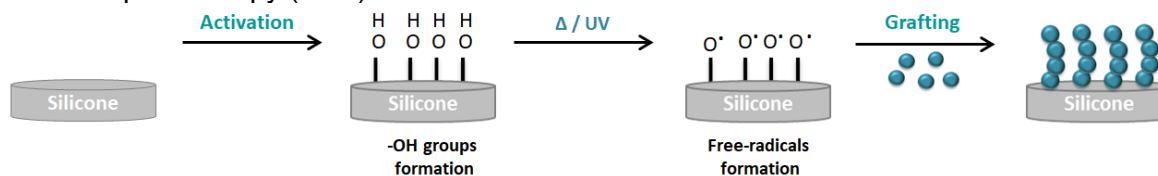


Figure 1: Mechanism of grafting

## Références :

- [1] <https://www.e-cancer.fr> (accessed Sep 11, 2019).
- [2] H. Chouirfa; V. Migonney; C. Falentin-Daudré, *RSC Advances*, 2016, **6**, 13766-13771
- [3] C. Falentin-Daudré; V. Migonney; H. Chouirfa; J.S. Baumann, "Procédé de greffage de polymères bioactifs sur des matériaux métalliques". Patent B248515D34589, 2015.
- [4] G. Pavon-Djavid; L. Gamble; M. Ciobanu; V. Gueguen; D. Castner; V. Migonney. *Biomacromolecules* 2007, **8** 3317-3325.
- [5] A. Leroux; C. Egles; V. Migonney; *PLoS ONE*, 2018, 13.
- [6] G. Amokrane; C. Falentin-Daudré; S. Ramtani; V. Migonney, *IRBM* 2018, **39**, 268-278.
- [7] F. El Khadali; G. Hélay; G. Pavon-Djavid; V. Migonney, *Biomacromolecules*, 2002, **3**, 51-56.
- [8] P. Yammine; G. Pavon-Djavid; G. Hélay; V. Migonney, *Biomacromolecules*, 2005, **6**, 2630-2637.
- [9] A.C. Cremieux; G. Pavon-Djavid; A. Saleh Mghir; G. Hélay; V. Migonney, *J Appl Biomater Biomech*, 2003 **1(3)**:178-85.

# POLYETHYLENE AEROGELS COMBINING PHYSICAL AND CHEMICAL CROSSLINKING FOR IMPROVED MECHANICAL RESILIENCE

Douriya Khedaioui<sup>a</sup>, Christophe Boisson<sup>a</sup>, Franck D'Agosto<sup>a</sup>, Damien Montarnal<sup>\*a</sup>

<sup>a</sup> Univ Lyon. Université Claude Bernard Lyon 1, CPE Lyon, CNRS, UMR 5265, Chemistry, Catalysis, Polymers and Processes, 43 Bvd du 11 Novembre 1918, F-69616 Villeurbanne, France

\* damien.montarnal@univ-lyon1.fr

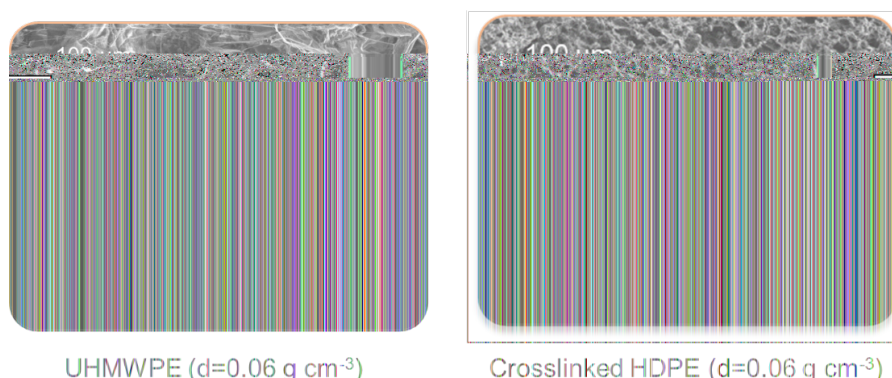
**Key-Words:** functional polyethylene, crystallization, crosslinking, aerogels

## Abstract:

Organic aerogels formed from highly crosslinked polymers have received a lot of attention in the last decades as tougher replacements of silica aerogels. Aerogels from semicrystalline and hydrophobic thermoplastics are however much more recent, and control over the crystallization of the polymer has opened vast opportunities to tune the pores morphology and the physical properties of these materials. In this context, syndiotactic-polystyrene, poly(vinylidene fluoride) or poly(4-methyl-pentene) have been exploited to obtain mesoporous aerogels. High density linear polyethylene (HDPE) displays numerous advantages in this scope: it is widely available, inexpensive, intrinsically hydrophobic, has an excellent chemical resistance, high crystallinity and melting temperatures above 100°C compatible with many insulation requirements. Yet, previous attempts to obtain polyethylene aerogels have resulted in materials with very poor mechanical resilience and an absence of nano- and mesoporous structure.<sup>[1]</sup>

In the present work, we combined physical gelation (obtained by crystallization of HDPE) with chemical crosslinking in highly dilute polymer solutions. Our approach benefits from well-defined, telechelic polyethylenes synthesized by Catalyzed Chain Growth (CCG) polymerization developed in the laboratory C2P2. CCG leads to highly functional (functionalization above 90%), linear HDPE with low dispersity ( $D = 1.1 - 1.2$ ), and a range of molar mass between 500 and 3000 g mol<sup>-1</sup>.<sup>[2]</sup>

We will show that careful optimization of the crosslinking reaction of HDPE segments enables to obtain aerogels with compression moduli up to 5 times higher than those obtained for the benchmark ultra-high molecular weight polyethylene-based aerogels. Additionally, our aerogels showed complete recovery of dimensions after several compression cycles (about 50% compression) and contain pores with sizes lower than 100 nm.<sup>[3]</sup>



*SEM micrographs of aerogels obtained from UHMWPE and Crosslinked HDPE*

## Références :

- [1] C. Daniel; S. Longo; G. Guerra, *Polyolefins Journal*, 2015, **1**, 49–55  
 [2] I. German; W. Kelhifi; S. Norsic; C. Boisson; F. D'Agosto, *Angew. Chem. Int. Ed.*, 2013, **12**, 3438–3441  
 [3] D. Khedaioui; C. Boisson; F. D'Agosto; D. Montarnal, *Angew. Chem. Int. Ed.*, 2019, **58**, 2–9

# Micro & nanostructured conducting polymers platform to interface with electroactive cells

Mohammed ElMahmoudy<sup>a</sup>, R. O'Connor<sup>a</sup>, George M. Malliaras<sup>b</sup>, Sébastien Sanaur<sup>c,\*</sup>

<sup>a</sup> IMT Mines Saint-Etienne, Provence Microelectronics Center, Department of Bioelectronics, Gardanne (France)

<sup>b</sup> Electrical Engineering Division, Department of Engineering, University of Cambridge (UK)

<sup>c</sup> IMT Mines Saint-Etienne, Provence Microelectronics Center, Department of Flexible Electronics, Gardanne (France)

\* sanaur@emse.fr

**Key-Words:** Capillary Force Lithography, Conducting Polymers, Organic Bioelectronics, nanotechnologies

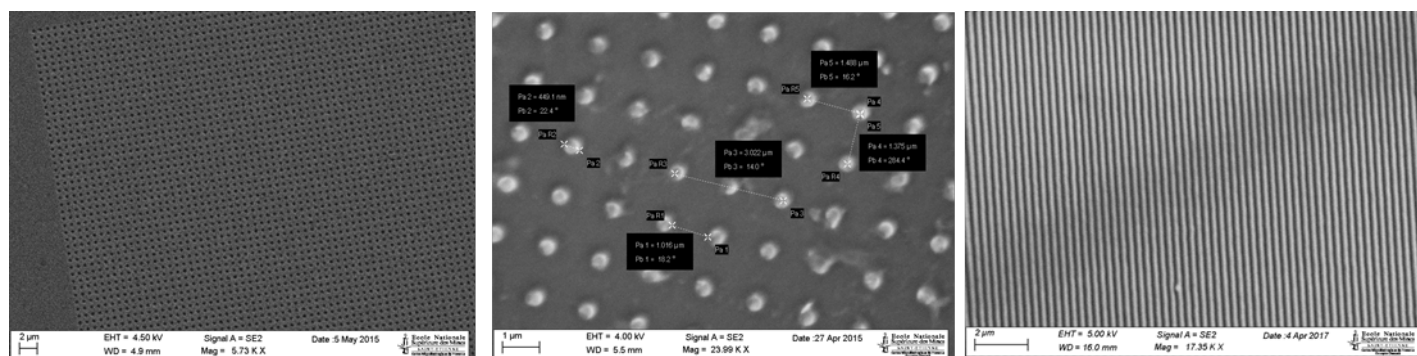
## Abstract:

Surgeons and physicians need more and more efficient medical tools. In particular the need for electrodes, for both *in vivo* and *in vitro*, for recording and/or stimulation of high quality electronic signal is indispensable [1]. Much of these devices are planar biocompatible substrates and do not provide close contact with cells, resulting in higher electrical impedance at those interfaces.

This talk will present about a new, facile top-down method for a 3D micro and nanopatterning of conducting polymers. Its benefit over others methods such as nanoimprint lithography (NIL) and capillary force lithography (CFL) will be here presented and discussed.

That method is using an epoxy supporting layer to facilitate the transfer of nanopatterns from a polydimethylsiloxane (PDMS) mold to rigid or flexible substrates (Figure 1). A supporting layer, as such UV-curable epoxy, advantageously allows i) a dry release of the patterned polymer layer and/or gold layer and ii) the sticking of a such stack to a substrate.

Finally, Electrochemical Impedance Spectroscopy (EIS) measurements show how such micro/nanostructures are a benefit to lower their impedance, as instance for electrophysiological applications, where the reduction in size of the electrodes is required [2].



**Figure 1** – SEM pictures of conducting polymer micro/ nano holes (a), pillars (b) and grooves (c)

## Références :

- [1] M.E. Spira, A. Hai, Multi-electrode array technologies for neuroscience and cardiology, *Nat. Nanotech.*, 2013, **8**, 83-94.
- [2] M. ElMahmoudy, A.M. Charrier, G.G. Malliaras, and S. Sanaur, *Adv. Mater. Technol.*, 2018, **3**(5), 1700344.

# Relationship between silicone acrylate structure and release coating properties

Emilie Vialle Désormière<sup>\*a</sup>, Laura Tuccio<sup>a</sup>, Delphine Blanc<sup>a</sup>, Stéphanie Benitou<sup>a</sup>, Perrine Theil<sup>a</sup>, Tania Ireland<sup>a</sup>

<sup>a</sup> ELKEM Silicones France

\* emilie.vialle-desormiere@elkem.com

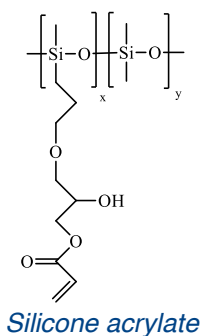
**Key-Words:** Silicone acrylate, release coating, relationship structure/activity

## Abstract:

Silicone materials present a great interest in many applications, especially for release coating. Ultra-violet (UV) curing of functionalized silicone polymer to coat thin films is a well-known and increasing technology in order to set up release coating over thermally sensitive substrates with a high throughput. The chemical structure of the silicone polymers has a major influence on the release forces.

Elkem Silicone has a strong know-how concerning the design of silicone acrylates<sup>1</sup> dedicated to UV-curing and pursue to increase it.

The poster will deal with an innovative synthesis route of acrylated silicones and the relationship of the structure of the polymer (functionality type and position, chain length, ...) on the properties of the cured material in UV release coating application.



## References:

[1]: EP127625.

# Synthesis of Ionic Liquid Core/Silica Shell Microcapsules as Functional Agents of Epoxy Networks

Ting SHI \*<sup>a</sup>, Sébastien LIVI<sup>a</sup>, Jannick DUCHET-RUMEAU<sup>a</sup>, Jean-François GERARD<sup>a</sup>

<sup>a</sup> Université de Lyon, INSA Lyon, IMP UMR CNRS 5223, F-69621 Villeurbanne, France

\* ting.shi@insa-lyon.fr

**Key-Words:** ionic liquids, microcapsules, epoxy networks

## Abstract:

Ionic liquids were found to be efficient additives of epoxy networks even at very low content. In fact, they could bring large improvement of fire resistance as well as shape-memory effects and are expected to be efficient as self-healing agents<sup>[1]</sup>. In this work, we propose a new way to introduce ionic liquids in polymer networks as microcapsules in which ionic liquid is trapped and deliverable under heat or fracture. Phosphonium type IL, i.e.(tetradecyl(trihexyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate), was successfully encapsulated in silica shell microcapsules (SiO<sub>2</sub>@ILs) in from IL-emulsion in water in the presence of ionic surfactants followed by a sol-gel process using tetraethoxysilane (TEOS). Mixtures of sodium dodecyl sulfate (SDS) and hexadecyltrimethylammonium bromide (CTAB) were considered to prepare the IL emulsions. The morphology of microcapsules was characterized by TEM and Dynamic Light Scattering (DLS), which indicates their spherical shape and their hollow structure as well as the size distributions. Different characterization methods of the SiO<sub>2</sub>@IL microcapsules were carried out using EDX in order to prove the ionic liquid entrapment inside the capsules, FT-IR spectroscopy, and Thermogravimetric Analysis (TGA). In a second step, the SiO<sub>2</sub>@ILs were introduced in a reactive mixture of comonomers based on diglycidylether of bisphenol A and 4,4'-methylene-bis(cyclohexylamine) which was reacted to lead to SiO<sub>2</sub>@IL-filled epoxy networks. Work is in progress to characterize the ability of the IL after fracture of these microcomposites to get self-healing properties.

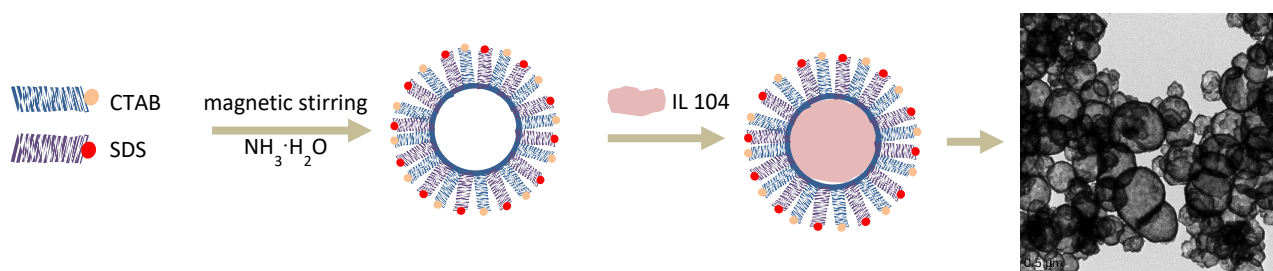


Fig.1 Schematical synthetic procedure of silica shell ionic liquids core microcapsules

## References :

[1] : N Saurin; J Sanes ; M D Bermúdez, *Tribology Letters*, 2015, **58(1)**: 4



## Poster contributions

### Polymers and sustainable development

- P-23** STUDY OF THE MECHANICAL PROPERTIES OF AGAVE / PVC COMPOSITES  
*Ahmed Benaboura, Lynda Chelali*
- P-24** SPATIO-TEMPORAL STUDY OF POLY(MALEIC ANHYDRIDE) PLASMA DEPOSITION USING A MACROSCOPIC DESCRIPTION  
*Syrine Jebali, Aissam Airoudj, Isabelle Ferreira, Vincent Roucoules, Florence Bally-Le Gall*
- P-25** STUDYING THE MORPHOGENESIS OF NANOSTRUCTURES IN MALEIC ANHYDRIDE PLASMA POLYMER FILMS FORMED ON CHEMICALLY DIFFERENT SURFACES  
*Nghia Huu Le, Magali Bonne, Aissam Airoudj, Florence Bally-Le Gall, Bénédicte Lebeau, Vincent Roucoules*
- P-26** STABILIZATION OF MAGNETITE AQUEOUS DISPERSION BY PS-PEO COPOLYMER AND ITS USE AS ADSORBENT FOR REMEDIATION OF METAL IONS IN POLLUTED WATER  
*Amane Jada, Ikram Hachilif*
- P-27** CONTRIBUTION TO VALORISATION AND RECYCLING OF WEEE DERIVED-PLASTICS CONTAINING BROMINATED FLAME RETARDANTS  
*Layla Gripon, Imane Belyamani, Eric Lafranche, Laurent Cauret*
- P-28** CORE-SHELL ARCHITECTURE BASED ON BIO-SOURCED POROUS CARBON: SHAPE FORMATION MECHANISM AT THE SOLID/LIQUID INTERFACE LAYER  
*Amane Jada, Zakaria Anfar, Abdellah Ait El Fakir, Nouredine El Alem*



# study of the mechanical properties of agave / pvc composites

Lynda Chelali, [Ahmed Benaboura](#)

<sup>a</sup> *Universite des Sciences et de la Technologie Houari Boumediene*  
*Faculte de chimie*  
*Laboratoire de Synthèse Macromoléculaire et Thio organique Macromoléculaire*  
*B.P. 32 El Alia Bab ezzouar 16111 Alger ALGERIE*

[\\*abenaboura@usthb.dz](mailto:*abenaboura@usthb.dz)

[benaboura@hotmail.com](mailto:benaboura@hotmail.com)

**Key-Words:** Agave, PVC, mechanical properties;

## **Abstract:**

This work consists in reinforcing a thermoplastic recovered after a plasturgic process by a plant fiber. The thermoplastic considered is the polyvinyl chloride (PVC) that was used as a matrix to prepare a new composite material with a plant fiber extracted from the agave americana, a plant that grows easily in a Mediterranean climate as in North Africa. However, after the fiber extraction, a prior chemical treatment of this fiber is necessary to improve its surface state in order to optimize the adhesion between this fiber and the PVC recovered. It consists of an alkaline treatment followed by a modification reaction of the fiber with acetic anhydride. Composites formed from PVC / fiber blends of various compositions ranging from 5% to 30% were prepared by mechanical mixing followed by extrusion. The effects of incorporation of raw agave and treated fibers into the composites on the mechanical properties (Young modulus - breaking strength - elongation at break) of the prepared composites were examined for each material on the one hand the fiber rate in the composite and on the other hand the treatment that the fiber has undergone

# Spatio-temporal study of poly(maleic anhydride) plasma deposition using a macroscopic description

Syrine Jebali<sup>a,b</sup>, Aissam Airoudj<sup>a</sup>, Isabelle Ferreira<sup>b</sup>, Vincent Roucoules<sup>a</sup>, Florence Bally-Le Gall<sup>\*a</sup>

<sup>a</sup> Université de Haute-Alsace, IS2M-CNRS UMR 7361, F-68100 Mulhouse, France

<sup>b</sup> Institut Français du Textile et de l'Habillement (IFTH), F-68100 Mulhouse, France

\* florence.bally-le-gall@uha.fr

**Key-Words:** Plasma polymerization, Maleic Anhydride, Deposition rate, Macroscopic approach, Activation energy

## Abstract:

Plasma polymerization is a vapor-based surface functionalization process consisting of the synthesis and deposition of functional polymer coatings. A macroscopic approach can be chosen to describe plasma polymerization and to control film growth, which relies on the concept of chemical quasi-equilibrium. In fact, for radical-dominated plasma polymerization, the film deposition rate solely depends on the energy provided per particle of the gas mixture flowing through the plasma phase. Taking into account geometrical parameters of the reactor, this macroscopic approach enables the correlation of the polymer thin film deposition rate with an apparent activation energy associated to a specific state of the precursor [1].

Our group works on the engineering of functional polymer films by plasma polymerization which includes investigations on plasma deposition kinetics and mechanisms [2] in order to achieve better control of surface properties. The temporal control of plasma species generated during (pulsed) plasma polymerization of maleic anhydride has already been investigated by tuning operating parameters such as the on and off times used for pulsed plasma polymerization [3]. In this project, we have decided to investigate additionally the spatial control of plasma species during plasma polymerization of maleic anhydride by building a new low pressure plasma reactor, being 1m long and enabling the deposition of polymer within or outside the glow discharge. Hence the evaluation of the poly(maleic anhydride) deposition rate was performed in three different regions of the plasma reactor: pre-discharge, discharge and post-discharge zones for various operating parameters (power, duty cycle in pulsed mode). The plasma discharge has been particularly characterized using the optical emission spectroscopy (OES) while the resulting plasma polymer films have been analyzed by several physico-chemical surface characterization techniques such as infrared and X-ray photoelectron spectroscopies. This fundamental study has enabled the identification of different growth regimes during the deposition of the plasma polymer as well as the calculation of the corresponding apparent activation energies, which can be correlated to the plasma chemical reactions involved in plasma polymerization.

This spatio-temporal study of poly(maleic anhydride) plasma deposition thus allowed us to control more precisely plasma polymerization mechanism of this precursor in order to get functional polymer coatings with more diverse surface properties.

## References:

- [1] : D. Hegemann; M. Mokbul Hossain; and E. Enrico Koerner ; *Surf. Plasma Process Polym*, 2007, **4**, 229.  
[2] : a) D. M. Veillet; L. Ploux; A. Airoudj; Y. Gourbeyre; E. Gaudichet-Maurin; and V. Roucoules, *Plasma Process. Polym*, 2017, **14**, e1600215. b) F. Bally-Le Gall; A. Mokhter; S. Lakard; S. Wolak; P. Kunemann; P. Fioux; A. Airoudj; S. El Yakhlifi; C. Mgnet; B. Lazard; and V. Roucoules; C. Oehr, *Plasma Process Polym*, 2019, **16**, e1800134.  
[3] : F. Siffer; A. Ponche; P. Fioux; J. Schultz; and V. Roucoules, *Analytica Chimica Acta*. 2005, **539**, 289.

# STUDYING THE MORPHOGENESIS OF NANOSTRUCTURES IN MALEIC ANHYDRIDE PLASMA POLYMER FILMS FORMED ON CHEMICALLY DIFFERENT SURFACES

Nghia Huu Le <sup>a,b,\*</sup>, Magali Bonne <sup>a,b</sup>, Aissam Airoudj <sup>a,b</sup>, Florence Bally-Le Gall <sup>a,b</sup>, Bénédicte Lebeau <sup>a,b</sup>, Vincent Roucoules <sup>a,b</sup>

<sup>a</sup> Université de Haute Alsace (UHA), CNRS, IS2M, UMR 7361, 68100 Mulhouse, France

<sup>b</sup> Université de Strasbourg, CNRS, 67000 Strasbourg, France

\* Email address: huu-nghia.le@uha.fr

**Key-Words:** maleic anhydride, nanostructures, plasma polymerization, morphogenesis, surface functionalization

## Abstract:

In recent times, surface functionalization by thin film deposition, has attracted the scientific and industrial interests due to the possibility of obtaining materials with a great variety of mechanical and chemical surface properties.<sup>1</sup> Plasma polymerization has been proven to be a distinguished process for the surface modification consisting in the deposition of polymer thin films from almost any organic vapor on any substrate. In this respect, maleic anhydride (MA) – a typical monomer with dual functionality composed of carbon double bond and a reactive anhydride group – is considered as a good candidate for plasma polymerization. The interest of maleic anhydride plasma polymer (MAPP) films deposition lays on the high degree of retention of anhydride groups associated to the global chemistry of the films, the numerous structures formed (beads, needle-like, branched or rod-shaped structures) and the growth kinetic which can be finely controlled by playing with various experimental plasma parameters (monomer flow rate, input energy, modulated pulse time). The presence of MAPP films makes possible the surface functionalization of materials for controlled nanopatterning, adhesion improvement, biocompatibility and biomedical applications.

Most studies involving plasma polymer morphology have revealed that plasma polymerization induces heterogeneous growth into distinct nanostructures. Nanostructured films have indeed been obtained by using monomers such as hydrocarbons, fluorocarbons and MA similarly. The possibility to tailor the nanostructured plasma polymer films has further been observed by varying the experimental plasma parameters and particularly by performing pulsed plasma polymerization.<sup>2</sup> In this study, we have decided to investigate also the influence of surface chemistry of substrate on the obtained polymer nanostructures. For this purpose, three different kinds of substrate surfaces were studied: native silicon oxide, hydroxyl-rich silicon oxide layer and alkyl-terminated monolayer. It is worth noting that an original heterogeneous morphology of MAPP films has been obtained on the alkyl-terminated monolayer, while homogeneous films have been formed on the two other surfaces even at the early stage of plasma process (Figure 1). The rod-shaped structure on silicon wafer covered by an alkyl-terminated monolayer continuously grew up as a function of time when radicals, generated in the plasma phase, have enough time to migrate on the surface and further combine with nucleation sites.

As proposed by other authors, the formation of the nanostructured films was ascribed to the decoupling and competition between rate of deposition and diffusion of active plasma species. Beyond the prevailing process conditions, such as gas pressure, surface temperature, plasma specific parameters, our study has additionally given an important attention on the remarkable effect of the interface energy on the morphology of the MAPP films. This work has brought a complementary information in the understanding of the structure morphogenesis induced by plasma polymerization.

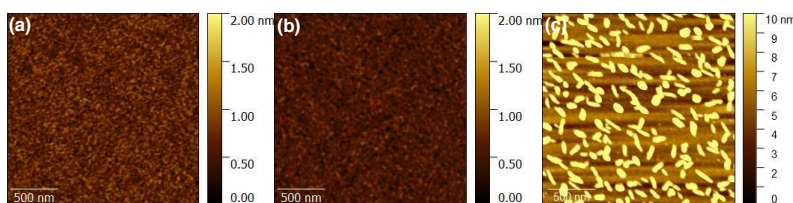


Figure 1. Height AFM images of the MAPP films on (a) native silicon oxide, (b) hydroxyl-rich silicon oxide layer, (c) alkyl-terminated monolayer

## References:

[1] J. Friedrich, *Plasma Process. Polym.*, 2011, **8**, 783

[2] M. Brioude; M-P. Laborie; A. Airoudj; H. Haidara; V. Roucoules, *Plasma Process. Polym.*, 2014, **11**, 943

# Stabilization of magnetite aqueous dispersion by PS-PEO copolymer and its use as adsorbent for remediation of metal ions in polluted water

Hachilif Ikram<sup>a,b</sup>, Jada Amane<sup>a,b,\*</sup>

<sup>a</sup> Mulhouse Materials Science Institute – CNRS (IS2M), University Haute Alsace, F-68100, Mulhouse, France

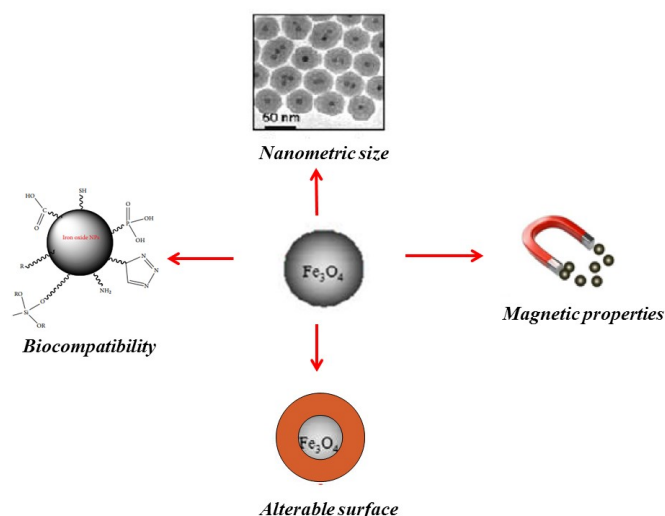
<sup>b</sup> University of Strasbourg, Strasbourg, F-67081, France

\* amane.jada@uha.fr

**Key-Words:** Non-ionic copolymer; Solid/liquid; Interface; Heavy metals; Iron oxide; Textile effluent; Streaming Induced Potential; Particle size

## Abstract:

Pollution of water by organic and inorganic substances has become very worrying today. Heavy metals such as chrome, copper, lead and zinc, contribute to this pollution since they are non-biodegradable and toxic species. In fact, these metals are continually discharged into the aquatic ecosystems, as resulting from various human activities, and their accumulation in the environment has negative effects on the human health. It is therefore essential to develop efficient adsorbents allowing the removal of these heavy metals from polluted water. Various methods such as chemical oxidation, reverse osmosis, coagulation–flocculation, filtration, adsorption, and photo degradation have all been applied to effluent treatment, yet vary in their effectiveness, cost, and environmental impact. Overall, adsorption has been the most competitive of these methods because of its simplicity, high efficiency, and availability. Many materials have been made available for this process, with adsorbents containing natural biopolymers such as chitosan drawing particular interest recently. However, these adsorbent materials can accumulate in the discharge, resulting in secondary pollutants. Therefore, developing magnetic adsorbents which will be more easily separable would significantly improve the process. During last decades, the application of iron oxides nanoparticles has grown radically, in several relevant fields such as medicine, electronics, and mainly in environmental remediation. However, in the environmental field, the main problem occurring with the use of pure iron oxide nanoparticles, as an adsorbent of pollutants in water remediation, is their low stability and/or their flocculation and sedimentation in the aqueous media. To overcome these limitations, the surface of the nanosized magnetite particles should be modified with organic or inorganic moieties in order to stabilize them in aqueous suspensions. The aim of the present work is to investigate the effect of non-ionic copolymer such as polystyrene–poly (ethylene oxide) diblock copolymer (PS-PEO), on the particle size and the surface charge of iron oxide nanoparticles. Subsequently, the modified magnetite particles ( $\text{Fe}_3\text{O}_4$ -PS-PEO), are expected to have controlled sizes and surface charges, and will suitable as adsorbent for the remediation of metal ions such as Cu(II), Zn(II), Mg(II), Ca(II) and Ba(II), present in contaminated water.



Main features of the iron oxide particles

# Contribution to valorisation and recycling of WEEE derived-plastics containing brominated flame retardants

Layla Gripon<sup>a,b</sup>, Imane Belyamani<sup>b\*</sup>, Eric Lafranche<sup>a</sup>, Laurent Cauret<sup>b\*</sup>

<sup>a</sup> Department of Polymer and Composites Technology and Mechanical Engineering, IMT Lille Douai, 941 Rue Charles Bourseul, 59500 Douai (France)

<sup>b</sup> Institut Supérieur de Plasturgie d'Alençon (ISPA), Pôle Universitaire d'Alençon, 61250 Damigny (France)

\* imanebelyamani@ispa.asso.fr, laurentcauret@ispa.asso.fr

**Key-Words:** WEEE, recycling, brominated flame retardants, ABS

## Abstract:

Fast technological innovations in the field of electrical and electronic equipment (EEE) and their shorter lifespan lead to an increase of post-consumer waste electrical and electronic equipment (WEEE) stream. In 2016, 44.7 million tons of WEEE were generated in the world<sup>[1]</sup> and only 20% was properly collected and recycled.<sup>[2]</sup> To limit the pollution and the consumption of non-renewable resources, the European Directive on WEEE decrees valorisation and recycling objectives.<sup>[3]</sup> Considering the higher and optimistic targets set by the European Commission, the recovery of polymer materials through re-use and recycling becomes very important. Most polymer materials used in WEEE contain flame retardant additives such as brominated flame retardants (BFR) to comply with safety flammability standards. The Stockholm convention and the European Directive on hazardous substances (RoHS) aim to phase out or limit the use of some BFR molecules recognized as POP.<sup>[4,5]</sup> Consequently, physico-chemical treatment, incineration, and the use as a fuel or other means to generate energy are the only allowed operations for the end-of-life of BFR containing plastics. Nevertheless, if the restricted BFR contents are below the concentration limits, the plastic waste is considered as a non-hazardous material and can, therefore, be recycled mechanically.<sup>[4]</sup>

The objective of the present work is to present the composition of a BFR containing ABS derived from WEEE. The impurities that it contains, and the properties of the polymer were determined before recycling it. First, a sampling method was used to obtain representative samples from a 600 kg big bag which were then analysed using physico-chemical, thermal, rheological and mechanical techniques. Flakes of the material were analysed by FTIR-ATR to determine the composition of the batch. The results show that the batch is mainly constituted of ABS but contains also organic impurities (i.e. polypropylene, PA-6,6) and inorganic impurities (CaCO<sub>3</sub>). The presence of PP was confirmed by DSC measurements. The BFR contained in the batch were identified and quantified by GC-MS and compared with the concentration limits decreed. The regulated BFR content in the sample was around four times higher than the regulatory limits<sup>[4]</sup> so physico-chemical treatments must be undertaken before recycling it. TGA measurement show two decomposition steps due to the presence of BFR and Sb<sub>2</sub>O<sub>3</sub>, a synergic agent detected in the sample by X-ray fluorescence spectrometry. Finally, mechanical properties of the polymer were determined by tensile and Charpy test. As expected, mechanical properties of the polymer are inferior to virgin ABS because of aging and inhomogeneity. Following this study, different physico-chemical treatments to remove BFR from the polymer matrix, such as supercritical CO<sub>2</sub> extraction, have been studied in order to comply with regulatory limits.

## References:

- [1] R. Horta Arduin *et al.*, *Waste Management* **2019**, *84*, 256, DOI: 10.1016/j.wasman.2018.12.002.
- [2] C. P. Baldé *et al.*, 'The Global E-waste Monitor - 2017, United Nations University (UNU), International Telecommunication Union (ITU) & International Solid Waste Association (ISWA), Bonn/Geneva/Vienna.', **2017**.
- [3] Directive 2012/19/UE of the European Parliament and of the Council on waste electrical and electronic equipment (WEEE)
- [4] Regulation (EC) NO 850/2004 of the European Parliament and of the Council on persistent organic pollutants
- [5] Report of the Conference of the Parties to the Stockholm Convention on Persistent Organic Pollutants on the work of its eighth meeting, **2017**.

# Core-shell architecture based on bio-sourced porous carbon: shape formation mechanism at the solid/liquid interface layer

Anfar Zakaria<sup>a,b,c,\*</sup>, Ait Elfakir Abdellah<sup>a,b</sup>, Jada Amane<sup>b,c,\*</sup>, and El Alem Nouredine<sup>a</sup>

<sup>a</sup> Materials and Environment Laboratory (LME), Ibn Zohr University, Agadir, 8000, Morocco

<sup>b</sup> Mulhouse Materials Science Institute – CNRS (IS2M), University Haute Alsace, F-68100, Mulhouse, France

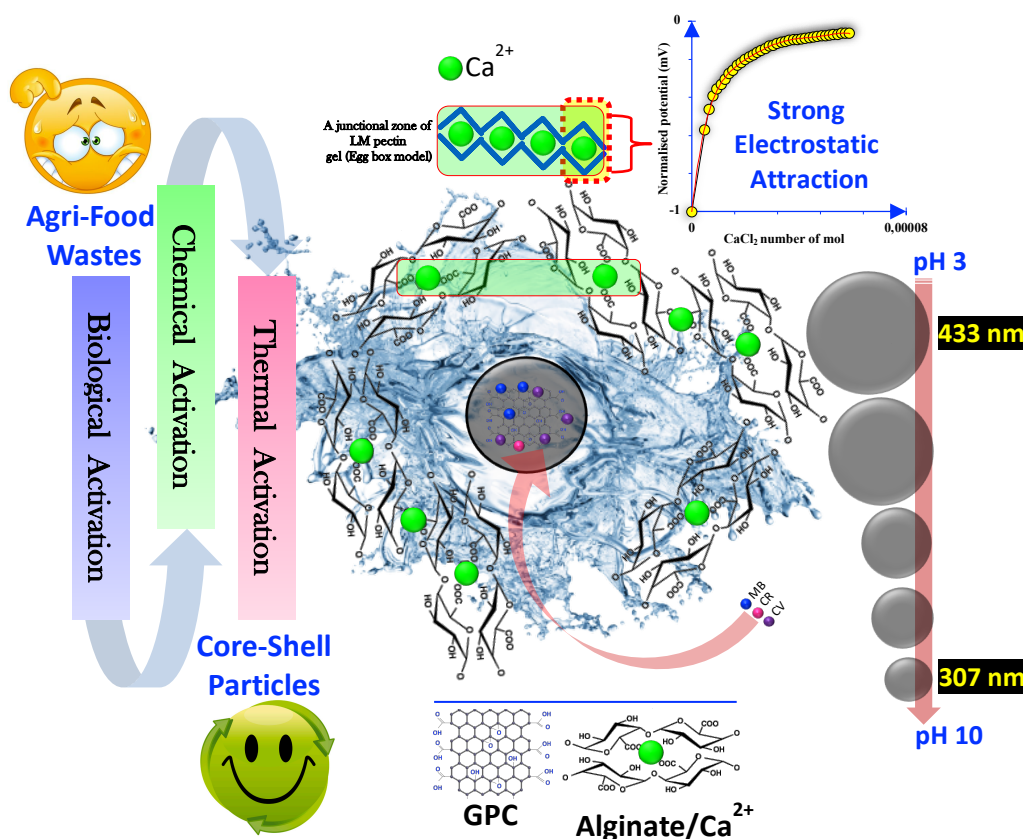
<sup>c</sup> University of Strasbourg, Strasbourg, F-67081, France

\* amane.jada@uha.fr and zakaria.anfar@uha.fr

**Key-Words:** Core-shell; porous carbon; solid/liquid; interface; bio-polymer.

## Abstract:

The overall goal of this work is to active agri-food wastes by microbial action, which makes it possible to produce a bio-digestate and energy (methane). Then, the resulted bio-digestate was transformed to porous carbon, which was used for the preparation of core-shell particles with alginate (bio-polymer) and calcium ions layer. Further, the surface charge measurements show electrostatic attraction occurring between alginate, calcium ( $\text{Ca}^{2+}$ ) ions and porous carbon, leading hence to the formation of core (PC)-shell (alginate-calcium ions) particles. However, in the absence of calcium ions, no electrostatic attraction was observed between PC and alginate. At dried state (using the Scanning Electronic Microscopy analysis (SEM) and at hydrate state (using numerical Microscopy) the designed core-shell was confirmed. The Transmission Electron Microscope (TEM) shows that the carbon particles are graphitic and porous. In addition, both Raman Spectroscopy (RS) and X-ray photoelectrons spectroscopy (XPS) show the presence of several chemical functions, especially the hydroxyl ( $-\text{O}-\text{H}$ ) and carboxylic groups ( $-\text{COO}-\text{H}$ ). In aqueous media, results shows that the PC was negatively charged, its surface charge and its particle size, were found to be very sensitive to the pH variation.



*Shape formation mechanism at the solid/liquid interface layer of core-shell architecture based on bio-sourced like graphitized porous carbon*

## ACKNOWLEDGMENT

This work was supported the framework of Franco-Moroccan cooperation, CEDocs research projects under No. 08/00057. We thank FIOUX Philippe (IS2M-Mulhouse-France) for XPS analyzes. We thank VIDAL Loïc (IS2M-Mulhouse-France) and KNOPF Stéphan (IS2M-Mulhouse-France) for SEM and TEM analyzes, respectively.



## Polymers and light

- P-29** NEW BIPHENYL AND TERPHENYL DERIVATIVES AS HIGH-PERFORMANCE PHOTOREDOX SYSTEMS DEDICATED FOR VARIOUS PHOTOPOLYMERIZATION PROCESSES  
*Wiktoria Tomal, Joanna Ortyl, Maciej Pilch, Anna Chachaj-Brekiesz*
- P-30** DIRECT LASER WRITING OF CRYSTALLIZED TiO<sub>2</sub> AND TiO<sub>2</sub>/CARBON MICROSTRUCTURES WITH TUNABLE CONDUCTIVE PROPERTIES  
*Shang-Yu Yu, Gautier Schrodj, Karine Mouglin, Joseph Dentzer, Jean-Pierre Malval, Hsiao-Wen Zan, Olivier Soppera, Arnaud Spangenberg*
- P-31** DIRECT LASER WRITING OF HYBRID SiO<sub>2</sub>/METAL OXIDE- AND METAL OXIDE MICROSTRUCTURES WITH TUNABLE OPTICAL OR MAGNETO-OPTICAL PROPERTIES  
*Xingyu Wu, Alexandra Madeira, Jeremy Riporto, François Royer, Sophie Neveu, Dominique Berling, Olivier Soppera, Arnaud Spangenberg*
- P-32** PHOTONIC PIGMENTS FROM CONTROLLED POLYMERIC NANOSTRUCTURES  
*Guillaume Moriceau, Bodo Wilts, Chris Weder, Ulli Steiner*
- P-33** DEEP-UV PHOTOINDUCED CHEMICAL PATTERNING AT THE MICRO- AND NANOSCALE  
*Benjamin Leuschel, Agnieszka Gwiazda, Wajdi Heni, Frédéric Diot, Shang-Yu Yu, Clémentine Bidaud, Laurent Vonna, Arnaud Ponche, Olivier Soppera*
- P-34** LASER POLYMER TATTOOING: A VERSATILE METHOD FOR PERMANENT MARKING ON POLYMER SURFACES  
*Po-Yi Chang, Adele Bruntz, Loïc Vidal, Pierre-Alain Vetter, Patrick Roudot, Laurent Bua, Jose Ortiz, Hsiao-Wen Zan, Olivier Soppera*
- P-35** CORE-SHELL DIBLOCK COPOLYMER NANOPARTICLES AS TEMPLATE FOR MESOPOROUS CARBONS  
*Vitalii Tkachenko, Abraham Chemtob, Julien Poly*
- P-36** MICROFLUIDIC ASSISTED SYNTHESIS OF POLYMERIC MICROFIBERS  
*Wasif Razzaq, Christophe A Serra, Delphine Chan-Seng*
- P-37** DONOR-ACCEPTOR-DONOR STRUCTURED THIOXANTHONE DERIVATIVES AS VISIBLE PHOTOINITIATORS  
*Alexandre Mau, Thi Huong Le, Fabrice Goubard, Thanh-Tuan Bui, Bernadette Graff, Celine Dietlin, Jacques Lalevée*
- P-38** TOWARDS THE DESIGN OF LIGHT-RESPONSIVE POLYMER-BASED CAPSULES FOR THE RELEASE OF BIOMOLECULES.  
*Lucas Sixdenier*

- P-39** PLASMON-TRIGGERED LIVING PHOTOPOLYMERIZATION FOR ELABORATION OF HYBRID POLYMER/METAL NANOPARTICLES  
*Farid Kameche, Wajdi Heni, Siham Telitel, Dandan Ge, Loïc Vidal, Frédéric Dumur, Didier Gignes, Jacques Lalevée, Sylvie Marguet, Ludovic Douillard, Céline Fiorini Debuischert, Renaud Bachelot, Olivier Soppera*
- P-40** USING POLYMER BASED ORGANIC PHOTODETECTOR TO FORM A LOW-COST AND SENSITIVE VERTICALLY-STACKED GASEOUS FORMALDEHYDE SENSING SYSTEM  
*Ching-Fu Lin, Hsiao-Wen Zan, Chia-Jung Lu, Hsin-Fei Meng, Olivier Soppera*
- ~~**P-41** FERROCENES AS PHOTOREDOX CATALYSTS FOR POLYMERIZATION UNDER VISIBLE TO NIR LIGHTS  
*Guillaume Noirbent, Patxi Garra, Damien Brunel, Jacques Lalevée, Frédéric Dumur, Didier Gignes*~~
- P-42** THREE-COMPONENT PHOTOCYCLIC INITIATING SYSTEM FOR EFFICIENT DLP 3D PRINTING  
*Boris Metral, Adrien Bischoff, Christian Ley, Ahmad Ibrahim, Xavier Allonas*
- ~~**P-43** DEVELOPMENT OF A PHOTOPOLYMERIZED BIO-BASED POLYESTER ACRYLATE RESIN  
*Anne-Sophie Schuller, Aymeric Champion, Xavier Allonas, Céline Croutxe-Barghorn, Christelle Delaite*~~
- ~~**P-44** SHRINKAGE OF DENTAL COMPOSITES  
*Mohammed Mouzali*~~
- P-45** DEVELOPMENT OF NEW HIGH-PERFORMANCE PHOTOINITIATING SYSTEMS FOR NEAR UV AND VISIBLE LIGHT FOR THE PHOTOPOLYMERIZATION OF MONOMERS ISSUED BY OIL INDUSTRY AND THEIR APPLICATIONS IN 3D PRINTING TECHNOLOGY, PHOTOCOMPOSITES SYNTHESIS AND HYDROGELS FORMATION  
*Mira Abdallah, Akram Hijazi, Jacques Lalevée*

# New biphenyl and terphenyl derivatives as high-performance photoredox systems dedicated for various photopolymerization processes

Wiktorija Tomal<sup>a\*</sup>, Joanna Ortyl<sup>a,b</sup>, Maciej Pilch<sup>a</sup>, Anna Chachaj-Berekiesz<sup>c</sup>

<sup>a</sup> Cracow University of Technology, Faculty of Chemical Engineering and Technology, Warszawska 24, 31 155 Cracow, Poland

<sup>b</sup> Photo HiTech Ltd., Bobrzyńskiego 14, 30-348 Cracow, Poland

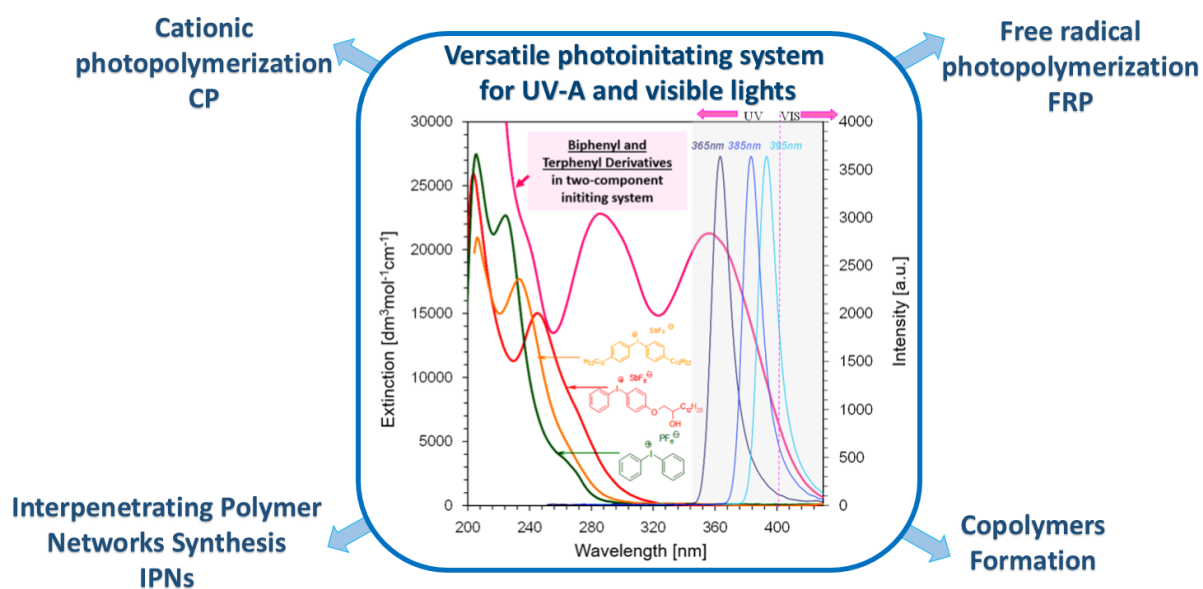
<sup>c</sup> Jagiellonian University, Faculty of Chemistry, Gronostajowa 2, 30-387 Cracow, Poland

\* wiktoriaomall@gmail.com

**Key-Words:** photo-reduction, photo-oxidation, photopolymerization, IPNs formation

## Abstract:

Photopolymerization has been the object of intense studies in past decades. The reason of its phenomena is a wide range of polymeric materials. The polymer industry is looking for fast and universal initiating systems that will allow the optimization of the production process and also improve the quality of the final product. The versatility of photoinitiators is associated in this case with the possibility of simultaneously initiating the polymerization reaction occurring via different mechanism [1].



*Comparison of the absorption characteristics of industrial photoinitiators and novel bimolecular initiating systems with the emission characteristics of UV LED diodes*

In this research, we describe bimolecular photoinitiating systems operating in the UV-A and visible light range, where 2-amino-4-methyl-6-phenyl-benzene-1,3-dicarbonitrile derivatives were selected as the effective photosensitizers. In order to verify the applicability of the biphenyl derivatives, their spectroscopic characteristics were determined. The photochemical mechanisms were studied through steady-state photolysis, fluorescence experiments, theoretical calculations of molecular orbitals, and electrochemical analysis. Last, but not least, the photopolymerization experiments was performed, including: free radical photopolymerization (FRP), cationic photopolymerization (CP) of epoxides and glycidyles, as well as a formation of interpenetrating polymer networks (IPNs) and copolymers.

## References :

[1]: Tomal, W.; Pilch, M.; Chachaj-Brekiesz, A.; Ortyl, J. Development of New High-Performance Biphenyl and Terphenyl Derivatives as Versatile Photoredox Photoinitiating Systems and Their Applications in 3D Printing Photopolymerization Processes. *Catalysts* 2019, 9, 827.

# Direct laser writing of crystallized TiO<sub>2</sub> and TiO<sub>2</sub>/carbon microstructures with tunable conductive properties

Shang-Yu Yu,<sup>a,b</sup> Gautier Schrodj,<sup>a</sup> Karine Mougín,<sup>a</sup> Joseph Dentzer,<sup>a</sup> Jean-Pierre Malval,<sup>a</sup>  
Hsiao-Wen Zan,<sup>b</sup> Olivier Soppera,<sup>\*a</sup> [Arnaud Spangenberg](mailto:Arnaud.Spangenberg@uha.fr)<sup>\*a</sup>

<sup>a</sup> *Université de Haute-Alsace, CNRS, Institut de Science des Matériaux de Mulhouse  
IS2M UMR 7361, 15 rue Jean Starcky, F 68100 Mulhouse, France*

<sup>b</sup> *Department of Photonics, College of Electrical and Computer Engineering  
National Chiao Tung University, Hsinchu, Taiwan 30010, Republic of China*

[Olivier.soppera@uha.fr](mailto:Olivier.soppera@uha.fr); [arnaud.spangenberg@uha.fr](mailto:arnaud.spangenberg@uha.fr)

**Key-Words:** femtosecond laser direct writing, metal oxide, conductive micropattern, TiO<sub>2</sub>/Carbon nanocomposites, miniaturized pressure sensor

## Abstract:

Metal oxides (MOs) are an important class of materials for optoelectronic applications. [1-2] Developing simple and versatile processes for integrating these materials at the microscale and nanoscale has become increasingly important. Solution-based processes have gained much attention during the last years due to their simplicity, cost effectiveness, vacuum-free processes, and high versatility. However, in solution-based processes, thermal annealing is required to eliminate the solvent and organic ligands that are complexed on metal ions and to obtain material and phase compositions with suitable properties. This step is typically conducted at temperatures ranging from 300 to 1000 °C. Thus, such a fabrication strategy can be difficult to apply in the case of multistep integration processes involving different materials. In this context, laser processing of MOs presents many advantages due to the control of the laser–matter interaction in space and time. [3] Laser curing allows a fast treatment that can be confined to a limited volume by focusing the laser beam.

In the present work, near-infrared femtosecond laser irradiation was successfully used to prepare amorphous or crystallized TiO<sub>2</sub> microstructures in a single step using a direct laser writing (DLW) approach from a TiO<sub>2</sub> precursor thin film doped with a suitable dye. [4] The laser-induced chemical modification was investigated by coupling photostructuring experiments and Raman microspectroscopy. When laser writing is conducted under a nitrogen atmosphere, simultaneous to the crosslinking of the Ti oxide precursor, the graphitization of the organic species embedded in the initial film is observed. In this case, a carbon network is generated within the TiO<sub>2</sub> matrix, which significantly increases the conductivity. Since the TiO<sub>2</sub>/C nanocomposite exhibits piezoresistive behavior, a miniaturized pressure microsensors has been realized as a proof of concept.

## References :

- [1] S. B. Ogale, T. V. Venkatesan, M. Blamire, *Functional Metal Oxides: New Science and Novel Applications*, Wiley-VCH, Weinheim, Germany **2013**.
- [2] Y. Wang, I. Fedin, H. Zhang, D. V. Talapin, *Science* 2017, **357**, 385.
- [3] H. Palneedi, J. H. Park, D. Maurya, M. Peddigari, G.-T. Hwang, V. Annapureddy, J.-W. Kim, J.-J. Choi, B.-D. Hahn, S. Priya, K. J. Lee, J. Ryu, *Advanced Materials* 2018, **30**, 1705148.
- [4] S. Y. Yu, G. Schrodj, K. Mougín, J. Dentzer, J. P. Malval, H. W. Zan, O. Soppera and A. Spangenberg, *Advanced Materials*, 2018, **30**, 1805093.

# Direct Laser Writing of Hybrid SiO<sub>2</sub>/Metal Oxide- and Metal Oxide Microstructures with Tunable Optical or Magneto-Optical Properties

Xingyu Wu <sup>a</sup>, Alexandra Madeira <sup>b</sup>, J  r  my Riporto <sup>c</sup>, Jean-Pierre Malval <sup>a</sup>, Olivier Soppera <sup>a</sup>, Agn  s B  e <sup>b</sup>, Vincent Dupuis <sup>b</sup>, Emilie Gamet <sup>c</sup>, Marie-Fran  oise Blanc-Mignon <sup>c</sup>, Damien Jamon <sup>c</sup>, Fran  ois Royer <sup>c</sup>, Sophie Neveu <sup>b</sup>, Dominique Berling <sup>\*a</sup>, Arnaud Spangenberg <sup>\*a</sup>.

<sup>a</sup> IS2M UMR7361, 15, rue Jean Starcky, 68057 Mulhouse

<sup>b</sup> PHENIX UMR8234, 4 place Jussieu, 75252 Paris

<sup>c</sup> LaHC UMR5516, 18 rue du Professeur Benoit Lauras, 42000 Saint-Etienne

\* dominique.berling@uha.fr; arnaud.spangenberg@uha.fr

**Key-Words:** direct laser writing, nanocomposite, metal oxide, magnetic nanoparticle, magneto-optical properties

## Abstract:

Microstructuration of hybrid SiO<sub>2</sub>/metal oxides and metal oxides based materials plays an important role to obtain functional devices with good optical, magnetical, electrical and/or mechanical properties<sup>[1,2]</sup>. For instance, microstructures with tunable electrical and optical properties were successfully fabricated by a direct laser writing (DLW) approach using near infrared femtosecond laser irradiation, but they were limited to 2D microstructures<sup>[3]</sup>. For 3D microstructures, Ovsianikov et al. have proposed to tune the refractive index by varying the content of a SiO<sub>2</sub> precursor in zirconium sol-gel matrixes<sup>[4]</sup>. However, only examples of microstructures with a high Si content in the matrix were shown, limiting the positive impact of Zr on the final optical properties. In our present work, by adjusting the molar ratio of Si/Zr (or Ti) and the content of magnetic nanoparticles (NPs), microstructures with good optical or magneto-optical properties are fabricated using DLW. The laser induced chemical modification, the influence of thermal annealing and the possibility to modulate the optical and magneto-optical properties are investigated by coupling photostructuration experiments, Raman/FTIR spectroscopies, ellipsometry and magneto-optical characterization. First, the refractive index of films with different contents of Zr or Ti (Si:Zr molar ratio 4:1, 1:1 and 1:4; Si:Ti molar ratio 4:1, 0:1, without NPs) have been measured and are found to be tunable from 1.5 to 1.73. Besides, for all these formulations, fabrication of 2D microstructures is successfully performed. Finally, functionalized magnetic CoFe<sub>2</sub>O<sub>4</sub> NPs with a diameter of 8 nm are inserted into these matrixes. This ferrofluid has good magneto-optical properties (quality factor  $F \sim 2.5$  %/dB at 1500 nm). After doping with NPs, 2D and 3D microstructures are also obtained. For instance, Figure 1 (left) exhibits a grid with a minimum period of 1.6  $\mu\text{m}$  for a Si:Ti (4:1) matrix containing 0.4 % vol NPs. Figure 1 (right) presents array of pillars with high aspect ratios ( $\sim 11$  before thermal annealing) based on a zirconium sol-gel matrix (Si:Zr molar ratio 4:1). Pillars comprising NPs have been also elaborated and impact of the thermal annealing on the 2D and 3D microstructures has been investigated.

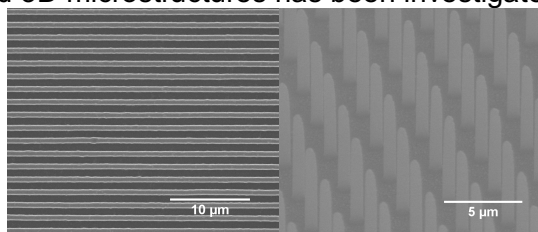


Figure 1. Left: SEM image of grid of parallel lines made by titanium matrix (Si:Ti molar ratio 4:1 with 0.4% vol NPs); Right: pillars made by zirconium sol-gel matrix (Si:Zr molar ratio 4:1)

## References:

- [1] : Y. Wang, I. Fedin, H. Zhang, D. V. Talapin, *Science* **2017**, 357, 385  
 [2] : H. Palneedi, J. H. Park, D. Maurya, M. Peddigari, G.-T. Hwang, V. Annapureddy, J.-W. Kim, J.-J. Choi, B.-D. Hahn, S. Priya, K. J. Lee, J. Ryu, *Advanced Materials* **2018**, 30, 1705148  
 [3] : S. Y. Yu, G. Schrodj, K. Mougine, J. Dentzer, J. P. Malval, H. W. Zan, O. Soppera and A. Spangenberg, *Advanced Materials*, **2018**, 30, 1805093

[4] : A. Ovsianikov, J. Viertl, B. Chichkov, M. Oubaha, B. MacCraith, I. Sakellari, A. Giakoumaki, D. Gray, M. Vamvakaki and M. Farsari, *Acs Nano*, **2008**, **2**, 2257-2262

# Photonic Pigments from Controlled Polymeric Nanostructures

Guillaume Moriceau<sup>a, b</sup>, B.D. Wilts<sup>a</sup>, C. Weder<sup>b</sup>, U. Steiner<sup>a</sup>

<sup>a</sup> Soft Matter Physics - Adolphe Merkle Institute, University of Fribourg, Switzerland

<sup>b</sup> Polymer Chemistry & Materials - Adolphe Merkle Institute, University of Fribourg, Switzerland

[guillaume.moriceau@unifr.ch](mailto:guillaume.moriceau@unifr.ch)

**Key-Words:** Structural color, polymer self-assembly

## Abstract:

Nature provides a vast array of structural models that have long inspired the development of novel bio-inspired functional materials. By controlling the structure of matter at the 100 nm level, light interference can occur, leading to the iridescent and non-iridescent vivid colors of butterflies, beetles or birds, to name few (Fig. 1 shows the example of color tuning in a jewel beetle). [1] Typical photonic structures found in nature include gratings, multilayers, packed spheres, and tree-like structures. Recently, structural color has received increasing interests due to its potential for industrial applications in paints, sensors, displays, and solar cells. [2] Photonic pigments may provide a promising alternative to commonly employed chemical dyes or pigments as it provides a platform with bright and long-term stable colors, and has a lower the impact on the environment (lower toxicity). The photonic properties of these materials solely rely on the precise control over the composition and morphology, requiring periodic arrangements on the length scale of visible light to establish interactions with light. Polymers are interesting commodity materials offering a diversity of composition (monomers, homo/block copolymer) and molecular structure (linear, non-linear), which gives access to a wide range of chemical and physical properties (e.g. phase separation, stimuli-responsiveness, phase transition, dielectric contrast). Combining polymer self-assembly and solution processing provides an efficient and scalable platform to achieve biomimicking morphologies (spherical, lamellar, cylindrical, gyroid) with control over structural parameters (periodicity, refractive index, long range order). However, the typical block copolymer unit cell dimension ( $\leq 100$  nm) is too small to achieve photonic properties and require the use of either high molecular weight copolymers or swelling of the structure using solvents, homopolymers or organic/inorganic additives. Poly(styrene-*b*-vinyl pyridine) copolymer (PS-PVP) is a robust system that gives access to diverse and controlled morphologies with tunable symmetries and stimuli-responsive properties of interest for nanophotonics and sensing. [3-5] Our goal is to exploit the self-assembly of PS-PVP systems and explore the swelling and processing methods to obtain easily scalable spherical photonic pigments (Fig 1).

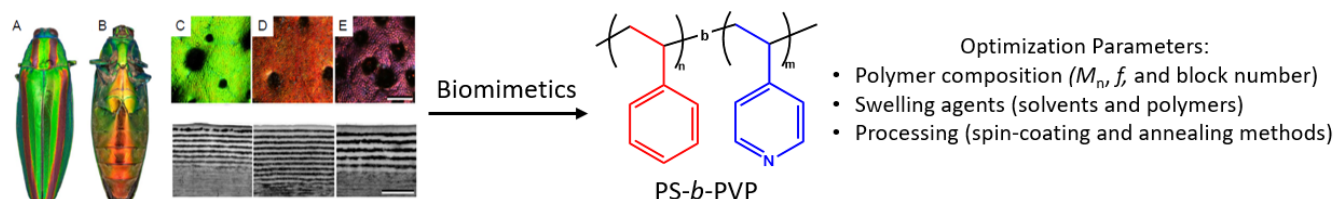


Figure 1. A-B) Dorsal, and ventral view of a Japanese Jewel beetle (*Chrysochroa fulgidissima*), C-E) Green, orange, and purple areas (100  $\mu\text{m}$ ) and their respective TEM sections 1  $\mu\text{m}$ .<sup>1</sup>

## References:

- [1] F. Schenk et al., *Bioinspir. Biomim.*, 2013, **8** (4) 045002
- [2] M. Stefik et al., *Chem.Soc.Rev.*, 2015, **44** (15) 5076-5091
- [3] S. Valkama et al., *Nature Materials*, 2004, **3** (12) 872-876
- [4] A. Noro et al., *Macromolecules*, 2016, **49** (23) 8971-8979
- [5] Y. Yang et al., *Adv. Mat.*, 2018, **30** (21) 170734

# Deep-UV photoinduced chemical patterning at the micro- and nanoscale

Benjamin Leuschel, Agnieszka Gwiazda, Wajdi Heni, Frédéric Diot, Shang-Yu Yu, Clémentine Bidaud, Laurent Vonna, Arnaud Ponche & Olivier Soppera

<sup>a</sup>Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

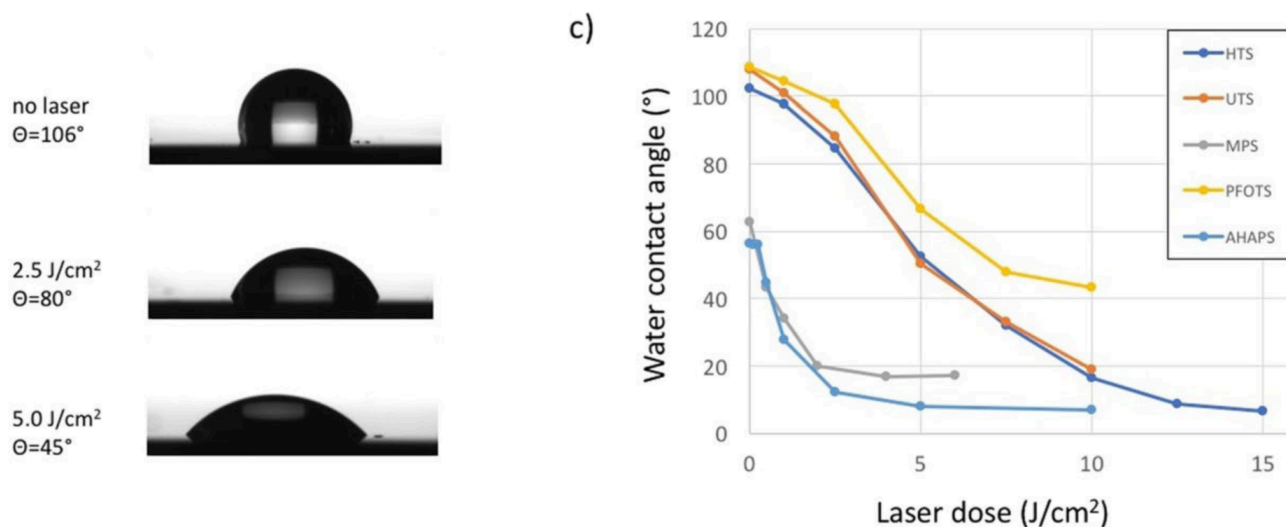
<sup>b</sup>Université de Strasbourg, France

\* Email address: [olivier.soppera@uha.fr](mailto:olivier.soppera@uha.fr)

**Key-Words:** Nanopatterning, surface chemistry, photochemistry, self-assembly

## Abstract:

Deep-UV (DUV) laser patterning has been widely used in recent years for micro- and nanopatterning, taking advantage of the specific properties of irradiation with high-energy photons. In this study, we show the usefulness of DUV laser patterning for preparing surfaces with controlled chemical properties at the micro- and nanoscale. Our motivation was to develop a simple and versatile method for chemical patterning at multiscale (from mm to nm) over relatively wide areas (mm<sup>2</sup> to cm<sup>2</sup>). We first investigated the modification of polymer surfaces under our irradiation conditions (ArF laser) using AFM, XPS and contact angle measurements. Photopatterning was then demonstrated with minimum feature sizes as small as 75 nm, and we showed the possibility to locally tune the chemistry. Finally, we used these chemically patterned surfaces for directed self-assembly of several types of objects, such as block copolymers, sol-gel materials and liquids by vapor condensation.



**Fig. Modification of the contact angle with water after DUV irradiation, illustrating the possibility to tune the surface properties from hydrophobic to hydrophilic [1]**

## References :

- [1] Leuschel, B.; Gwiazda, A.; Heni, W.; Diot, F.; Yu, S. Y.; Bidaud, C.; Vonna, L.; Ponche, A.; Haidara, H.; Soppera, O., Deep-UV photoinduced chemical patterning at the micro- and nanoscale for directed self-assembly. *Scientific Reports* **2018**, *8*, 15.



# Laser Polymer Tattooing: A Versatile Method for Permanent Marking on Polymer Surfaces

Po-Yi Chang<sup>a,b,f</sup>, Adèle Bruntz<sup>a,b</sup>, Loïc Vidal<sup>a,b</sup>, Pierre-Alain Vetter<sup>c</sup>, Patrick Roudot<sup>d</sup>, Laurent Bua<sup>d</sup>, Jose Ortiz<sup>e</sup>, Hsiao-Wen Zan<sup>f</sup>, and Olivier Soppera<sup>a,b,\*</sup>

<sup>a</sup>Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>b</sup>Université de Strasbourg, France

<sup>c</sup>IREPA Laser Illkirch-Graffenstaden 67400, France

<sup>d</sup>Tiflex Poncin 01450, France

<sup>e</sup>Valeo Visibility Bobigny 93012, France

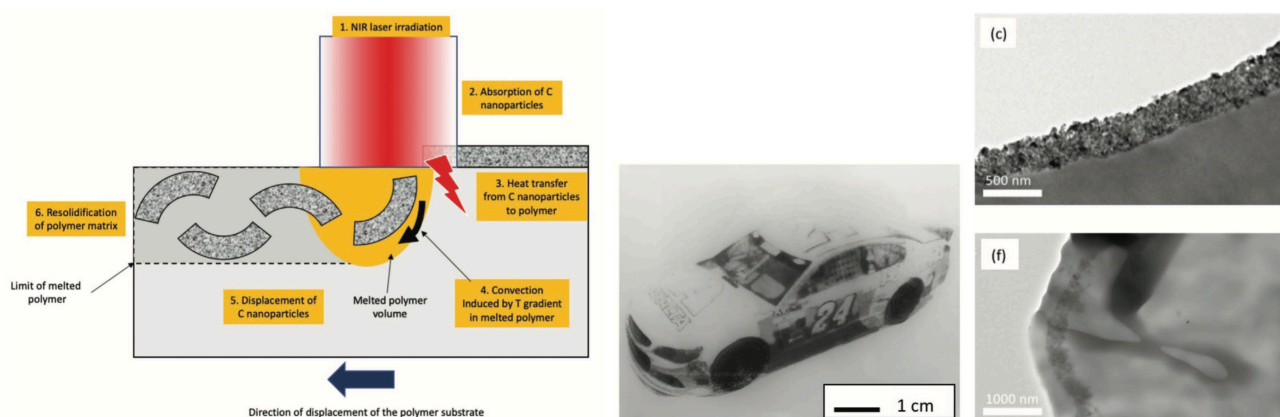
<sup>f</sup>Department of Photonics and Institute of Electro-Optical Engineering National Chiao Tung University Hsinchu, Taiwan 30010, Republic of China

\* Email address: [olivier.soppera@uha.fr](mailto:olivier.soppera@uha.fr)

**Key-Words:** Polymer marking, nanoparticles, laser, ink-jet

## Abstract:

A versatile and efficient method for the permanent marking of polymer surfaces that combines inkjet deposition and near-infrared (NIR) laser curing is investigated. The NIR laser treatment forces the ink particles to migrate into the upper layers of the polymer. This results in the fixation of a permanent grayscale image that can be applied to various polymers, such as polypropylen, which is widely used in industry but still difficult to mark. The physico-chemical processes induced by laser curing are investigated by electronic and optical microscopy. The dependence of the thickness of the deposited ink and the laser power on the contrast of marking are also studied. A mechanism implying fast laser-induced melting of the polymer surface followed by displacement of carbon nanoparticles by convection is proposed. Finally, a comparison of the aging properties of samples prepared by this process and standard UV ink is proposed to illustrate the interesting nature of this new polymer marking process. Integrating the ink under the surface of the polymer, as in a skin tattooing procedure, by laser curing is an efficient way to generate permanent images on polymer surfaces.



**Fig. Schematic view of the Laser Polymer Tattooing process; example of image printed in polypropylen; TEM images of the ink layer as deposited and after laser treatment showing the migration of the Black Carbon nanoparticles migration [1]**

## References :

- [1] Chang, P.-Y.; Bruntz, A.; Vidal, L.; Vetter, P.-A.; Roudot, P.; Bua, L.; Ortiz, J.; Zan, H.-W.; Soppera, O., Laser Polymer Tattooing: A Versatile Method for Permanent Marking on Polymer Surfaces. *Macromol Mater Eng* **2019**, 1900402.

# Core-Shell Diblock Copolymer Nanoparticles as Template for Mesoporous Carbons

Vitalii Tkachenko,<sup>a,b\*</sup> Julien Poly,<sup>a,b</sup> Abraham Chemtob<sup>a,b</sup>

<sup>a</sup> Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France

<sup>b</sup> Université de Strasbourg, France

\* vitalii.tkachenko@uha.fr

**Key-Words:** polymer nanoparticles, self-assembly, RAFT, mesoporous carbons, photopolymerization

## Abstract:

Polymerization-induced self-assembly (PISA) has emerged as a standard methodology for producing well-defined block copolymer nanoparticles of various morphologies, ranging from conventional spheres to vesicles or fibers. However, PISA has been developed mostly using thermal radical initiators. Much less investigated is photo-induced PISA despite many distinctive advantages compared to the thermal method.<sup>1</sup> We present herein an original photo-PISA process relying on a photo-mediated RAFT mechanism, which proceeds at ambient temperature, under visible light, and without the need of any external initiator (see Figure 1a).<sup>2</sup> Herein, we demonstrated that the copolymer nanoparticles could act as soft templates for the synthesis of mesoporous carbon materials from phloroglucinol and glyoxylic acid in methanol solution. A micro- and mesostructured cellular foam is obtained having uniform, interconnected and narrowly distributed mesopores ranging between 15 and 30 nm in diameter, a specific surface area up to 719 m<sup>2</sup> g<sup>-1</sup>, and a total pore volume of 0.4 – 1.3 cm<sup>3</sup> g<sup>-1</sup>. The mesopore size can be controlled by adjusting the diameter of the PS core (16 – 29 nm), while the wall thickness can be tailored independently by varying the size of the solvated PHEA shell (5 – 25 nm). An increase of PHEA block's DP from 25 to 85 gradually extends the stabilizing shell dimension, thus increasing the wall thickness up to 10 nm, and causing the shift from interconnected to isolated mesopores (see Figure 1b).

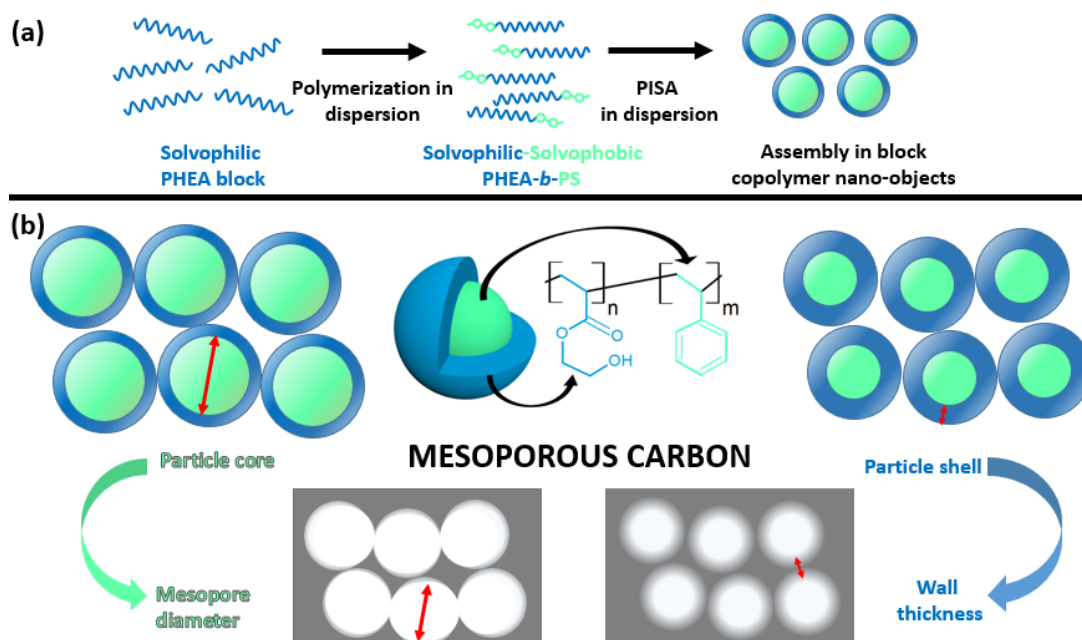


Figure 1 (a) Simplified scheme of the synthesis of poly(hydroxyethyl acrylate) macro-CTA via photomediated RAFT polymerization. Subsequent chain extension via dispersion photo-PISA of styrene. (b) Adjusting pore size by changing the PS core diameter, while the wall thickness controlled by the extent of the stabilizing PHEA shell

## References:

[1]: J. Rieger, *Macromol. Rapid Commun.*, 2015, **36**, 1458–1471

[2]: V. Tkachenko, C. Matei Ghimbeu, C. Vaultot, L. Vidal, J. Poly and A. Chemtob, *Polym. Chem.*, 2019, **10**, 2316–2326

# MICROFLUIDIC ASSISTED SYNTHESIS OF POLYMERIC MICROFIBERS

Wasif Razaq, Christophe A. Serra\*, Delphine Chan-Seng\*\*

<sup>a</sup> Université de Strasbourg, CNRS, ICS UPR 22, F-67000 Strasbourg, France

\* ca.serra@unistra.fr / \*\*delphine.chan-seng@ics-cnrs.unistra.fr

**Key-Words:** Microfibers, microfluidics, wet spinning

## Abstract:

Microfibers have excellent potentials for biomedical applications such as tissue engineering, wound dressing, cell encapsulation, drug delivery and microvascular graftings[1]. Microfluidic wet spinning has emerged as an outstanding and simple technique for the production of micro- and nanofibers with controllable size and morphology[2]. In a microfluidic T-junction (Fig. 1), the core fluid composed of the fiber material and the sheath fluid consisting in poly(ethylene glycol) (PEG, with a molecular weight of 300 g/mol) flow in a capillary of small diameter (e.g. 50  $\mu\text{m}$ ) and around that capillary respectively. Both fluids come into contact at the exit of the capillary where the shear forces induced by the high flow rate of the sheath flow elongate the core fluid into a continuous thread of small diameter which upon downstream UV irradiations gives rise to a microfiber[3] having a diameter ranging from c.a. 3 to 108  $\mu\text{m}$ . In this study, we produce poly(ethylene glycol) diacrylate (PEG-DA) microfibers using a simple microfluidic capillary-based device (Fig.1) and observed the impact of flow rates of sheath ( $Q_s$ ) and core ( $Q_c$ ) fluids on the diameter of the microfibers. We also propose to establish an empirical relationship of the fiber's diameter with different dimensionless numbers comprising parameters such as flow rates, viscosity and capillary number of the core and sheath phases. It was found that the fluid flow rates ratio ( $Q_s/Q_c$ ) is a characteristic dimensionless parameter which mainly determine the diameter of the fibers.

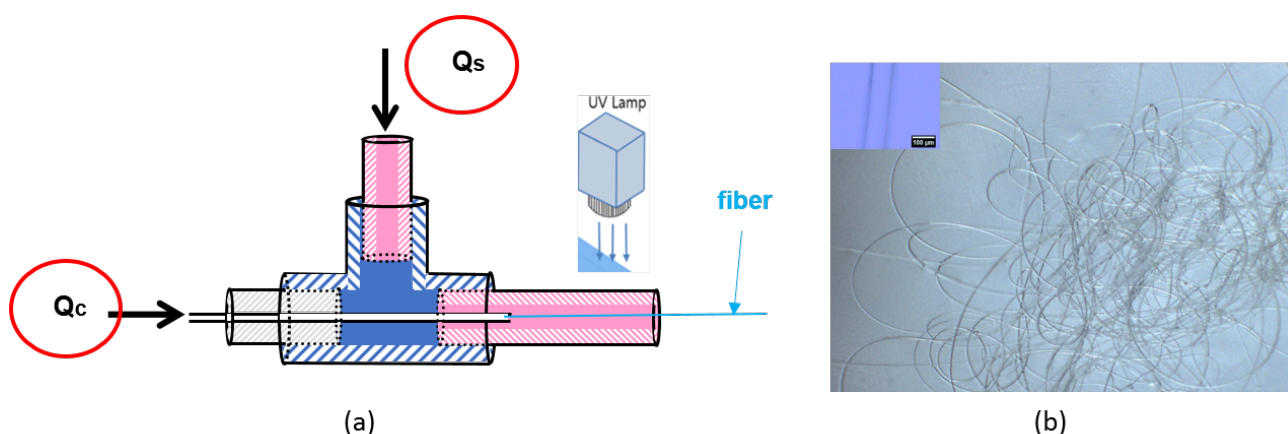


Fig.1.(a) Schematic drawing of the capillary-based microfluidic device used for producing microfibers. (b) Microscopic image of the PEG-DA fibers

## References :

- [1] : J. Cheng; Y. Jun; J. Qin; and S. H. Lee, *Biomaterials*, 2017, **114**, 121-143
- [2] : Y. Jun; E. Kang; S. Chae; and S. Hong Lee, *Lab Chip*, 2014, **14**, 2145-2160
- [3] : Y. Yu; L. Shang; J. Guo; J. Wang; and Y. Zhao, *Nature Protocols*, 2018, **13**, 2557-2579

# Donor-acceptor-donor structured thioxanthone derivatives as visible photoinitiators

Alexandre Mau<sup>a,b</sup>, Thi Huong Le<sup>c</sup>, Thanh-Tuân Bui<sup>c</sup>, Fabrice Goubard<sup>c</sup>, Bernadette Graff<sup>a,b</sup>, Céline Dietlin<sup>a,b</sup> and Jacques Lalevée<sup>\*a,b</sup>

<sup>a</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>b</sup> Université de Strasbourg, France

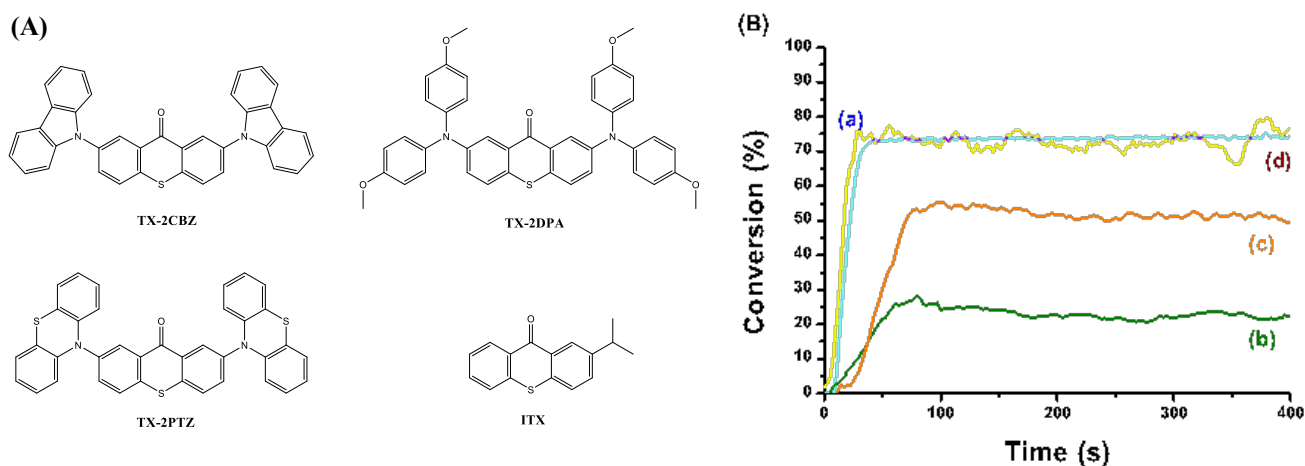
<sup>c</sup> Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 mail Gay Lussac, 95000 Neuville-sur-Oise, France

\* Corresponding author: jacques.lalevee@uha.fr

**Key-Words:** thioxanthone derivatives, photopolymerisation, visible light photoinitiator, interpenetrated polymer networks

## Abstract:

Polymerisation initiated by visible light has been an important issue over the past two decades. Multiple photoinitiators and photoinitiating systems have been established to initiate either free radical polymerisation or cationic polymerisation under mild condition (room temperature, visible light). Over the years, several photoinitiating systems were obtained by modifying an already well-known photoinitiator absorbing in near UV such as thioxanthone. In this work, three donor-acceptor-donor structured compounds based on thioxanthone with different electron donor substituents are investigated as photoinitiators. The reactivity and efficiency of the thioxanthone derivatives have been compared with a commercial type II photoinitiator 2-isopropylthioxanthone (ITX) in the case of free radical polymerisation, cationic polymerisation and interpenetrated polymer networks synthesis for 25  $\mu\text{m}$  or 1.4 mm thick sample upon a 405nm LED irradiation. They are incorporated into either, a two-component system with an iodonium salt or an amine, or a three-component system with an iodonium salt and an amine. The optical properties of these thioxanthone derivatives has been investigated and a mechanistic studies realised.



(A) Chemical structure of the investigated thioxanthone derivatives and the standard photoinitiator

(B) Polymerisation profiles (acrylate function conversion vs irradiation time) of TMPTA upon irradiation with a LED at 405 nm, start at 10 s, 50 mW.cm<sup>-2</sup>; sample thickness = 1.4 mm. Photoinitiating systems: (curve a) TX-2CBZ/EDB (0.07/1.9 w/wt%), (curve b) TX-2DPA/EDB (0.22/2.0 w/wt%), (curve c) TX-2PTZ/EDB (0.18/2.0 w/wt%) and (curve d) ITX/EDB (0.19/2.0 w/wt%)

# Towards the design of light-responsive polymer-based capsules for the release of biomolecules.

Lucas SIXDENIER <sup>\*a</sup>, Christophe TRIBET <sup>a</sup>, Emmanuelle MARIE <sup>a</sup>

<sup>a</sup> PASTEUR, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris, France

\* lucas.sixdenier@ens.fr

**Key-Words:** Light-responsive capsules, thermoresponsive polymers, gold nanoparticles.

## Abstract:

The on-demand release of pre-encapsulated bioactive molecules are increasingly required to precisely probe and unveil complex interactions in living matter, such as cell intercommunications. Light-responsive vesicular systems that can burst under laser illumination are promising systems for a spatiotemporally precise control of molecular cues delivery. If polymers are generally good candidates for the design of rigid capsules, light-responsive polymers are either complex to synthesize or hard to properly assemble into vesicles. To circumvent these issues, we focused on an alternative approach using temperature as an intermediary stimulus. This strategy relies on the combination of gold nanoparticles that can convert light into heat via plasmon resonance and a thermoresponsive polymer scaffold that breaks at high temperature. To optimize the physico-chemistry of the system, we first focus on the well-known poly(N-isopropylacrylamide) (PNIPAM), a model thermoresponsive polymer which exhibits a Lower Critical Solution Temperature (LCST) transition in water from a soluble state at low temperature to an insoluble state at high temperature. In our strategy, polymers vesicles are formed using a water-in-perfluorocarbon oil emulsion as a template. For that, PNIPAM chains are grafted on a poly(L-lysine) (PLL) cationic backbone that adsorbs at the water/oil interface via ionic interactions with an anionic perfluoro-surfactant present in the oil phase. Preliminary results show evidences for (i) the formation of a corona of PLL-PNIPAM copolymer at the water/oil interface, (ii) the temperature-induced transition of PNIPAM chains at the interface, (iii) the ability to photo-trigger the transition of bulky PNIPAM in emulsion when combined with gold nanoparticles.

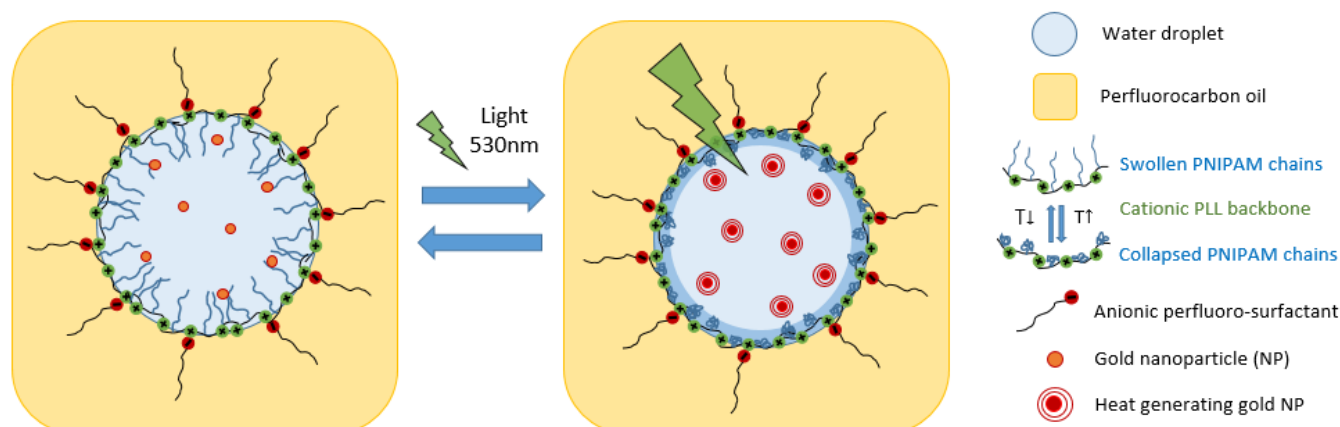


Figure 1 – Schematic of the strategy for the design of light-responsive polymer capsules based on the combination of a thermoresponsive polymer located at the interface of a water-in-oil emulsion and gold nanoparticles generating heat in the water droplet under laser illumination.

# Plasmon-triggered living photopolymerization for elaboration of hybrid polymer/metal nanoparticles

Farid Kameche <sup>a</sup>, Wajdi Heni <sup>a</sup>, Siham Telitel <sup>a</sup>, Dandan Ge <sup>b</sup>, Loïc Vidal <sup>a</sup>, Frédéric Dumur <sup>c</sup>, Didier Gigmes <sup>c</sup>, Jacques Lalevée <sup>a</sup>, Sylvie Marguet <sup>d</sup>, Ludovic Douillard <sup>e</sup>, Céline Fiorini-Debuisschert <sup>e</sup>, Renaud Bachelot <sup>b,f</sup> and Olivier Soppera <sup>a\*</sup>

<sup>a</sup> Institut de Science des Matériaux de Mulhouse (IS2M), CNRS UMR 7361, Université de Haute-Alsace, Mulhouse, France.

<sup>b</sup> Light, nanomaterials, nanotechnologies (L2n) Laboratory, ICD CNRS, Université de Technologie de Troyes, 10004 Troyes, France.

<sup>c</sup> Aix Marseille Univ, CNRS, ICR UMR 7273, Marseille, F-13397, France

<sup>d</sup> NIMBE, CEA, CNRS Université Paris-Saclay, CEA Saclay, F-91191 Gif-sur-Yvette, France.

<sup>e</sup> SPEC, CEA, CNRS Université Paris-Saclay, CEA Saclay, F-91191 Gif-sur-Yvette, France.

<sup>f</sup> Sino-European School of Technology, Shanghai University, 200444, Shanghai, China

\* olivier.soppera@uha.fr

**Key-Words:** Nanofabrication; near-field photopolymerization; gold nanoparticles; nanoplasmonic; living radical photopolymerization

## Abstract:

Reversible deactivation radical polymerization (RDRP) and more precisely photoRDRP has proved to be a powerful tool for preparing polymers, with high control of the architecture and the polydispersity of the molar masses. This technique was recently used in micropatterning [1, 2, 3].

We show here that such chemical systems can be used for photopatterning at the nanoscale by coupling with surface plasmon resonance of individual gold nanoparticles. The gold nanoparticles were used as an optical near-field source to locally trigger free radical polymerization of an acrylic monomer: metal nanoparticles embedded in a photopolymer sensitive at the resonance wavelength are irradiated under the polymerization threshold but close enough to this threshold to initiate the free-radical polymerization thanks to electromagnetic near-field enhancement [4, 5].

We will report on the physicochemical and optical parameters controlling the photopolymerization process in near-field. Kinetic parameters were shown to be of paramount importance to control the polymerization in highly confined space. Different photopolymers were used in this context to finely tune the final properties of the nanoparticles. [6]

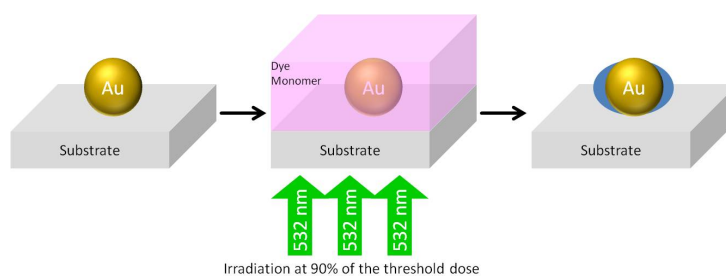


Figure 1. Experimental principle of the photopolymerization on the near-field of gold nanoparticles.

The authors thank the Agence Nationale de la Recherche (ANR), under Grant HAPPLE (ANR 10BS1001602) for financial support.

## References :

- [1] Telitel, S. et al., *Advanced Materials Interfaces*, 2014, **1** (5), 5.
- [2] Telitel, S. et al., *Polymer Chemistry*, 2015, **6** (4), 613-624.
- [3] Baron, M. et al., *Journal of the American Chemical Society*, 2018, **140** (9), 3339-3344.
- [4] Zhou, X. et al., *Journal of Optics*, 2014, **16**, 114002.
- [5] Deeb, C., *Journal of the American Chemical Society*, 2011, **133**, 10535-10542.
- [6] Kameche, F. et al., submitted.

# Using polymer based organic photodetector to form a low-cost and sensitive vertically-stacked gaseous formaldehyde sensing system

Ching-Fu Lin<sup>a</sup>, Hsiao-Wen Zan<sup>a\*</sup>, Chia-Jung Lu<sup>b\*</sup>, Hsin-Fei Meng<sup>c</sup>, Olivier Soppera<sup>d,e</sup>

<sup>a</sup> Department of Photonics and Institute of Electro-Optical Engineering, College of Electrical and Computer Engineering, National Chiao Tung University, Hsinchu, Taiwan

<sup>b</sup> Department of Chemistry, National Taiwan Normal University, Taipei, Taiwan

<sup>c</sup> Institute of Physics, National Chiao Tung University, Hsinchu, Taiwan

<sup>d</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

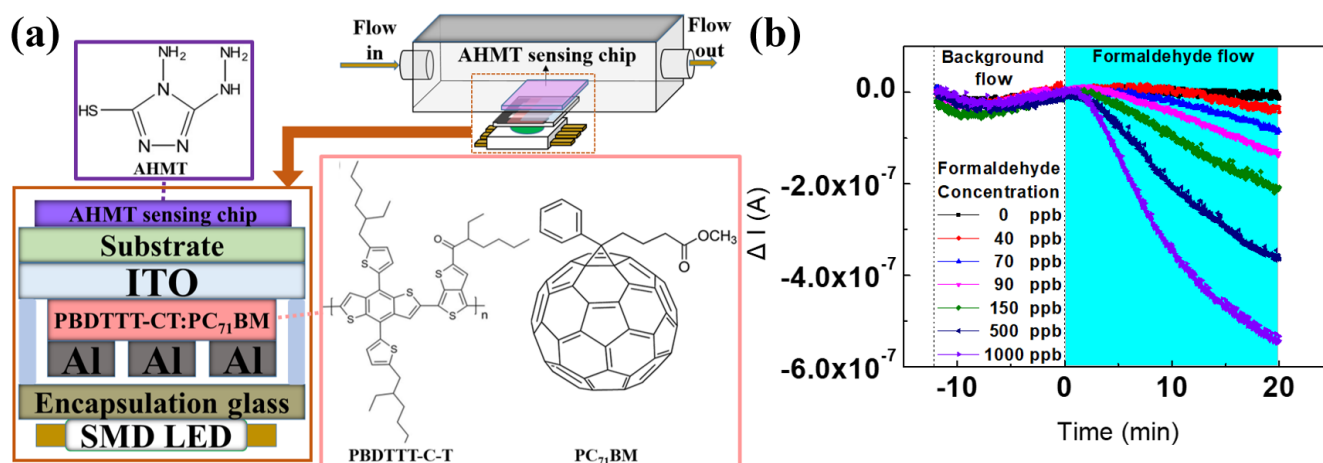
<sup>e</sup> Université de Strasbourg, France

\* Email address: [hsiaowen@mail.nctu.edu.tw](mailto:hsiaowen@mail.nctu.edu.tw) and [cjlu@ntnu.edu.tw](mailto:cjlu@ntnu.edu.tw)

**Key-Words:** colorimetric type, finger type, formaldehyde sensing, organic photodetector

## Abstract:

In this work, we mainly demonstrated a vertically-stacked gaseous formaldehyde(HCHO) sensing system. This stacked system was constructed by a special finger-type organic photodetector(OPD), a colorimetric 4-amino hydrazine-5-mercapto-1,2,4-triazole(AHMT) sensing paper[1], and a commercial surface mount device(SMD) LED. As the polymer material 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b :4,5-b'] dithiophene (PBDTTT-C-T) mixing with phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) to form the blending active layer, using solution process to construct the OPD could be available. Based on the high visible light sensitivity, and the semi-transparent structure of the OPD, a vertically-stacked gaseous HCHO sensing system could be finally realized, which contained a tiny OPD/LED stacked size of 0.8 cm x 0.5 cm. This system not only could reach a wide detection range of 40 ppb to 1 ppm in 20 min, which reached the safety criterion from World Health Organization (WHO)[2], but also could perform a long operating time around 60 days after calibration.[3]



**Fig. (a)The material and design of vertically-stacked gaseous HCHO sensing system (b) The dynamic gaseous HCHO sensing comparison**

## References :

- [1] K. Kawamura, K. Kerman, M. Fujihara, N. Nagatani, T. Hashiba, E. Tamiya. *Sensors and Actuators B: Chemical*, (2005), 105(2), 495-501.
- [2] A. Allouch, M. Guglielmino, P. Bernhardt, C. A. Serra, & S. Le Calvé, *Transportable, fast and high sensitive near real-time analyzers: formaldehyde detection. Sensors and Actuators B: Chemical*, (2013), 181, 551-558.
- [3] C. F. Lin, H. W. Zan, C. J. Lu, H. F. Meng & O. Soppera, *A low-cost miniaturized colorimetric sensor with vertically-stacked semi-transparent finger-type organic photo detector for formaldehyde sensing. Organic Electronics*, 73, 115-121, (2019).

# THREE-COMPONENT PHOTOCYCLIC INITIATING SYSTEM FOR EFFICIENT DLP 3D PRINTING

Boris Metral, Adrien Bischoff, Christian Ley\*, Ahmad Ibrahim, Xavier Allonas

Laboratoire de Photochimie et d'Ingénierie Macromoléculaires  
 Université de Haute-Alsace, 3b rue A. Werner 68093 MULHOUSE France  
 \*christian.ley@uha.fr

**Key-Words:** Photopolymerization, photocyclic initiating system, 3D printing, digital light processing.

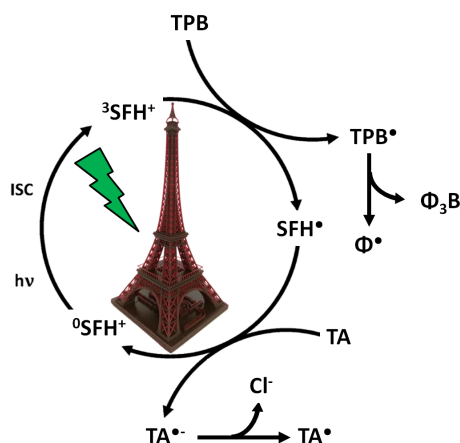
## Abstract:

Vat photopolymerization technologies are emerging quickly in the field of additive manufacturing<sup>[1,2]</sup>. To follow this fast expansion of the market, highly efficient and affordable photosensitive resins are necessary. In this work, we introduce a new three-component photoinitiating system (3K PIS) based on the Safranin O (SFH<sup>+</sup>) dye which has been identified as a very efficient initiator in several 3K PIS for photopolymerization processes<sup>[3-6]</sup>.

The dye is combined with a Tetraphenylborate salt (TPB) as electron donor and a Triazine derivative (TA) as electron acceptor to form a photochemical regenerating cycle. The photocycling mechanism is explored via laser flash photolysis (LFP) and the photopolymerization is investigated through Real-Time-Fourier Transform Infrared spectroscopy (RT-FTIR). Infrared experiments with several irradiances allow disclosure of an empirical model predicting conversion as a function of time and light intensity.

Following this, cure depth experiments are conducted in agreement with Jacobs' equation<sup>[7]</sup> and the resin 3D printing parameters, i.e. critical energy ( $E_c$ ) and penetration depth ( $D_p$ ), are established. These parameters are linked to RT-FTIR data, resulting in the determination of the critical time ( $t_c$ ) and the conversion at gel point<sup>[8]</sup>.

Finally, high resolution complex pieces are printed with the resin which composition was tailored in accordance with our studies, demonstrating the viability of this formulation in DLP 3D printing.



*Photocyclic initiating system in DLP 3D printing of Eiffel Tower*

## References:

- [1] A. Shkolnik, H. John and A. El-Sibani (Envisiontec GmbH), US7790093, 2010
- [2] J. R. Tumbleston, D. Shirvanyants, N. Ermoshkin, R. Januszewicz, A. R. Johnson, D. Kelly, K. Chen, R. Pinschmidt, J. P. Rolland, A. Ermoshkin, E. T. Samulski and J. M. DeSimone, *Science*, 2015, **347**, 1349-1352
- [3] A. Ibrahim, B. El Fouhaili, A. C. Yong, C. Ley and X. Allonas, *Can. J. Chem.*, 2015, **93**, 1-9
- [4] C. Ley, C. Carré, A. Ibrahim and X. Allonas, *J. Photopolym. Sci. Technol.*, 2017, **30**, 393-398
- [5] M. L. Gómez, C. M. Previtali and H. A. Montejano, *Polymer*, 2007, **48**, 2355-2361
- [6] W. G. Santos, C. C. Schmitt and M. G. Neumann, *J. Photochem. Photobiol., A*, 2013, **252**, 124-130
- [7] P. F. Jacobs in *Rapid Prototyping & Manufacturing: Fundamentals of StereoLithography*, American Society of Manufacturing Engineers, Dearborn, Michigan 1992, pp. 87-91
- [8] B. Metral, A. Bischoff, C. Ley, A. Ibrahim and X. Allonas, *ChemPhotoChem*, 2019, **11**, 1109-1118



# “Development of New High-Performance Photoinitiating Systems for Near UV and Visible light for the Photopolymerization of Monomers Issued by Oil Industry and their Applications in 3D Printing Technology, Photocomposites Synthesis and Hydrogels Formation”

Mira Abdallah <sup>1 a,b,c</sup>, Akram Hijazi <sup>2 c</sup>, Jacques Lalevée <sup>3 \*a,b</sup>

<sup>a</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>b</sup> Université de Strasbourg, France

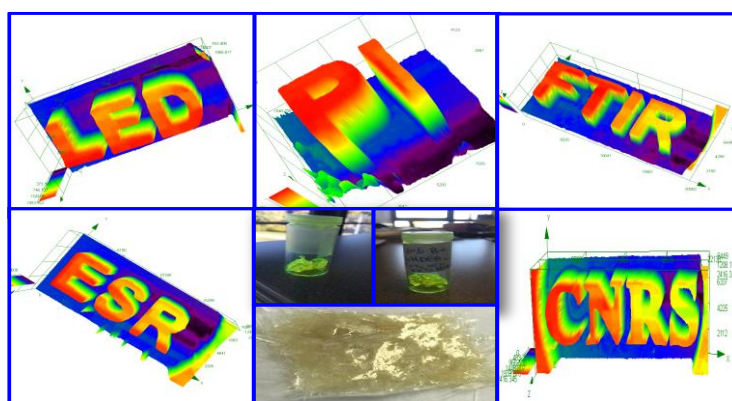
<sup>c</sup> EDST, Université Libanaise, Campus Hariri, Hadath, Beyrouth, Liban

\* jacques.lalevee@uha.fr

**Key-Words:** Light Emitting Diode, Photocomposite, Photopolymerization, 3D Printing

## Abstract:

This work focuses on the design of new high-performance photoinitiating systems in order to initiate both the free radical polymerization (FRP) and the cationic polymerization (CP) under mild irradiation conditions. In fact, the different photosensitive systems studied in this work are of different nature. For example, it can be divided into three main categories: synthesized organic compounds, commercial organic compounds, and co-initiators. Some of the photoinitiators are evaluated as photoredox catalysts. The basic idea of this PhD work is moving towards the introduction of Light Emitting Diodes (LEDs) as unharmed and economical sources of irradiation. As a matter of fact, it is a big challenge to find new photoinitiators able to generate reactive species using this low power irradiation source. Prior to the use of a safe irradiation source, the goals of this thesis range from testing the photoinitiating ability of the different photoinitiators in different kinds of monomer for different types of polymerization upon irradiation with the LED at 405 nm using RT-FTIR technique, to study their photophysical and photochemical properties which pave the way to unambiguously understand the interactions that take place in the excited states leading to the photochemical mechanism, and finally their applications in diverse regions of modern technologies: for instance 3D printing technology, synthesis of thick and filled glass fiber photocomposites with an excellent depth of cure, formation of hydrogels. The photophysical and photochemical properties are studied based on several techniques such as UV-visible spectroscopy, spectrofluorimeter, cyclic voltammetry (CV) and electron spin resonance (ESR).



*The use of the investigated photoinitiators in several regions of modern technologies: 3D Printing, Hydrogels Formation and Photocomposites Synthesis.*

## References:

- [1] : M. Abdallah; A. Hijazi; B. Graff; J.P. Fouassier; G. Rodeghiero; A. Gualandi; F. Dumur; P.G. Cozzi; J. Lalevée, *Polym. Chem.* 2019, **10**, 872-884
- [2] : M. Abdallah; H. Le; A. Hijazi; M. Schmitt; B. Graff; F. Dumur; T.T. Bui; F. Goubard; J.P. Fouassier; J. Lalevée, *Polymer* 2018, **159**, 47-58
- [3] : M. Abdallah; A. Mousawi; M. Nechab; A. Hijazi; J.P. Fouassier; F. Frédéric Dumur; J. Lalevée, *ChemPhotoChem* 2019, **3**, 1-10
- [4] : M. Abdallah; D. Magaldi; A. Hijazi; B. Graff; F. Dumur; J.P. Fouassier; T.T. Bui; F. Goubard; J. Lalevée, *J. Polym. Sci. A: Polym. Chem.* 2019, under press.

## Polymer interfaces and (nano)composites

- P-46** SURFACE CHANGES OF AN EPDM BY PLASMA TREATMENT  
*Florian Ponzio, Julie Lecomte, Pierre Lespade, Florence Bally-Le Gall, Vincent Roucoules*
- P-47** KIDNEY-TARGETED DRUG DELIVERY SYSTEMS: FROM THIOLATED CHITOSAN POLYELECTROLYTE TO LAYER-BY-LAYER REDOX-RESPONSIVE SELF-ASSEMBLY CAPSULES  
*Fannie Le Floch, Benjamin Carbonnier, Sabrina Belbekhouche*
- P-48** NANODIAMONDS COATED BY A LAYER OF POLYETHYLENE IMINE: AN EFFICIENT MATERIAL FOR OPTICAL POWER LIMITING  
*Morgane Guerchoux, Manon Dandois, Olivier Muller, Vincent Pichot, Mazheva Guillevic, Cordula Hege, Philippe Fioux, Denis Spitzer, Lionel Merlat*
- P-49** CONTROLLING SIZE AND FLUORESCENCE OF DYE-LOADED POLYMER NANOPARTICLES THROUGH POLYMER DESIGN  
*Antoine Combes, Vitalii Rosiuk, Anne Runser, Yuliia Koval, Denis Dujardin, Andrey Klymchenko, Andreas Reisch*
- P-50** DIELS-ALDER REACTION ON FUNCTIONAL SURFACES: TOWARDS THE DESIGN OF SMART BIOSENSORS  
*Jamerson Oliveira, Loïc Jierry, Vincent Roucoules, Florence Bally-Le Gall*
- P-51** HYBRID SEMI-CONDUCTING MATERIALS BASED ON ANILINE AND/OR 2-METHOXY ANILINE: SYNTHESIS, CHARACTERIZATION AND ELECTROACTIVE EFFECT  
*Abdelbassat Kenane, Ahmed Yahiaoui, Aïcha Hachemaoui, Ali Mustapha Benquider, Oana Rasoga, Aurelian Catalin Galca, Anca Stanculescu*
- P-52** REMOVAL OF CUPRIC IONS FROM WATER BY USING CELLULOSE NANOFIBERS AS ADSORBENT AND COPPER CARBONATE FORMATION BY PRECIPITATION METHOD  
*Amane Jada, Safa Ladhari*
- P-53** ELECTROCHEMICAL SENSORS BASED ON CONDUCTING POLYMERS  
*Boris Lakard, Emmanuel Contal, Sophie Lakard, Claire Magnenet, Marcel Bouvet*
- P-54** METALLIC NANOPARTICLES IMMOBILIZED AT THE PORE SURFACE OF POLYMERS: TOWARD EFFICIENT AND VERSATILE SUPPORTED CATALYTIC SYSTEMS  
*Benjamin Le Droumaguet, Romain Poupart, Benjamin Carbonnier, Daniel Grande*
- P-55** DEVELOPMENT OF NEW POLYOXOMETALATES/POLYMER FOR PHOTODEGRADATION OF ORGANIC POLLUTANTS  
*Chaima Brahmi, Jacques Lalevée, Latifa Bousselmi, Mahmoud Bentifa*

- P-56** LIGHT-ASSISTED SYNTHESIS OF METAL NANOPARTICLES AND NANOCOMPOSITES: AN EFFICIENT GREEN APPROACH TO OBTAIN SMART NANOMATERIALS  
*Marine Dabert, Lavinia Balan, Mohamed Zaier, Samar Hajjar-Garreau, Loïc Vidal*
- P-57** SURFACE COLOR ON DEMAND: CHAMELEON EFFECT  
*Karine Mougin*
- ~~**P-58** ELECTROSPUN PBAT NANOFIBERS DEGRADATION MEDIATED BY AQUEOUS ENVIRONMENT  
*Gabriela Ramos Chagas, Guilherme Kretzmann Belmonte, Daniel Weibel, Lénaïk Bélec, Jean-François Chailan, Christine Bressy*~~
- P-59** THERMOPLASTIC ELASTOMER FILAMENTS FOR MULTI-POLYMER STRUCTURES BY FUSED DEPOSITION MODELING  
*Jennifer Villamil Jiménez, Abdelali El Akroud, Sandrine Hoppe, Hakim Boudaoud, Cécile Nouvel*
- P-60** RECYCLING OF OPAQUE PET BY REACTIVE EXTRUSION  
*Thibault Parpaite, Nicolas Logié, Khadidja Chaar*
- ~~**P-61** HETEROGENEOUS CELLULOSE FUNCTIONALIZATION THROUGH METAL-FREE CLICK CHEMISTRY  
*Alex Meye-Biyogo, Louise Hespel, Vincent Humblot, Laurent Lebrun, François Estour*~~
- P-62** PHOTOACTIVE POM/POLYMER NANOCOMPOSITES FOR PHOTODEGRADATION OF ORGANIC DYES  
*Mariem Ghali, Mahmoud Benlifa, Latifa Bousselmi, Jacques Lalevée*
- P-63** GRAFTING STYRENE SULFONATE GROUPS ON BIODEGRADABLE POLYMER TO ENHANCE BIOACTIVITY AND HYDROPHILICITY THROUGH OZONE-INDUCED MECHANISM  
*Ngoc Tuan Nguyen, Andre Rangel, Veronique Migonney*
- P-64** THE EFFECT OF DAMPING ON VIBRATIONS OF STRENGTHENED BEAMS BY COMPOSITE COATS UNDER MOVING LOAD  
*Youcef Khadri, Sabiha Tekili, Yacine Kermi*

# Surface changes of an EPDM by plasma treatment

Florian Ponzio<sup>a,b\*</sup>, Julie Lecomte<sup>b</sup>, Pierre Lespade<sup>b</sup>, Florence Bally-Le Gall<sup>a</sup>, Vincent Roucoules<sup>a</sup>

<sup>a</sup> Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>b</sup> IRT Saint Exupéry, Arts et Métiers ParisTech, Campus de Bordeaux-Talence, 33405 Talence, France

\* florian.ponzio@uha.fr

**Key-Words:** surface modification, EPDM, plasma process, adhesion

## Abstract:

Elastomers are an important class of materials used in several fields of applications like automotive or aerospace for their good elasticity, high deformation rate and especially their heat and ozone resistance properties. However they display limited adhesion properties. There are different possibilities to improve adhesion between two polymeric materials including chemical bonding, physical interactions, chain interdiffusion or mechanical interlocking. In this work we focus on the formation of new chemical bonds between an elastomer and an adhesive *via* plasma treatments and particularly on the grafting of amines functions on the surface of an EPDM in order to get robust assemblies.

Low pressure cold plasma treatment is an interesting technique for the functionalization of polymer surfaces because of its versatility, environmental friendly use (no solvent) and preservation of bulk properties of thermosensitive materials<sup>1,2</sup>. Depending on the operating parameters of plasma treatment (power delivered to precursor gas, gas flow rate, pressure, nature of the gas, location of the substrate in the reactor), it is possible to control the relative importance of etching phenomena, chemical groups grafting, crosslinking reactions, or deposition of a polymer coating. Here we focus on the understanding of surface modification mechanisms implied during plasma functionalization of EPDM with N<sub>2</sub> or N<sub>2</sub>/H<sub>2</sub> mixture<sup>3</sup>.

EPDM substrates were treated with N<sub>2</sub> or N<sub>2</sub>/H<sub>2</sub> under various conditions and their surfaces were characterized by means of contact angle measurement, X-ray photoelectron spectroscopy (XPS) and atomic force microscopy. In addition, the plasma gas phase was analyzed by optical emission spectroscopy (OES). The increase of the power and treatment time resulted with both gas in a decrease of the water contact angle of the EPDM surface, originating from an increased grafting of polar groups at the surface, and particularly amine functions. These results were in good agreement with the OES analysis of plasma species during the functionalization process. This study has enabled to correlate the presence of some plasma species with final surface physico-chemical properties, which offers interesting perspectives to optimize the plasma treatment and ultimately control adhesion properties of the EPDM with the adhesive.

## References :

- [1] : Roucoules, V., Siffer, F., Ponche, A., Egurrola, U., Vallat, M. F, 2007, *Journal of Adhesion*, 83(10), 875-895.
- [2] : Henry, A., Vallat, M. F., Noël, C., Belmonte, T., Roucoules, V, 2015, *Plasma Processes and Polymers*, 12(10), 1139-1152.
- [3] : Moraes, J. H., da Silva Sobrinho, A. S., Maciel, H. S., Dutra, J. C. N., Massi, M., Mello, S. A. C., Schreiner, W. H. (). *Journal of Physics D: Applied Physics*, 2007, 40(24), 7747.

# Kidney-Targeted Drug Delivery Systems: From Thiolated Chitosan Polyelectrolyte to Layer-by-Layer Redox-Responsive Self-assembly Capsules

Fannie Le Floch <sup>\*a</sup>, Benjamin Carbonnier <sup>a</sup>, Sabrina Belbekhouche <sup>a</sup>

<sup>a</sup> CNRS, Univ Paris Est Créteil, ICMPE, UMR7182, 94320 Thiais, France affiliation 1

\* fannie.le-floch@u-pec.fr

**Key-Words:** chitosan - redox responsive - capsule - thiol/disulfide - Layer-by-Layer

## Abstract:

Targeted therapy in acquired podocyte diseases, especially minimal change nephrotic syndrome still represents a challenge. A specific protein (c-mip, c-maf inducing protein) is known to play a pivotal role in podocyte diseases. [1] During this talk, a new therapeutic approach will be presented and consists in a self-assembly templating method to obtain smart capsules. This approach implies the use of chitosan derivative and a tailor made-DNA coding against c-mip. Chitosan presents the interest of (i) being an adjunctive treatment for chronic renal failure, (ii) owing polyelectrolyte properties and (iii) being easily chemically modify.

A key challenge for the application of LbL engineered capsules as responsive drug delivery system is to stabilize them at physiological conditions while also being able to trigger film disassembly with an external stimulus or in an intracellular environment, releasing the entrapped drug. In this respect, reductive reactions employing disulfide-thiol chemistry is particularly promising because disulfide linkages are cleaved to corresponding thiols in response to reducing agents. [2] In this context, we will show how selective and controlled thiolation of chitosan via Traut's reagent allows meeting all these criteria (Figure 1). [3]

One challenge is to reach a balance between sufficient thiolation of chitosan for the stimuli-response and the conservation of its polyelectrolyte properties, essential for the elaboration of LbL multilayers vectors.

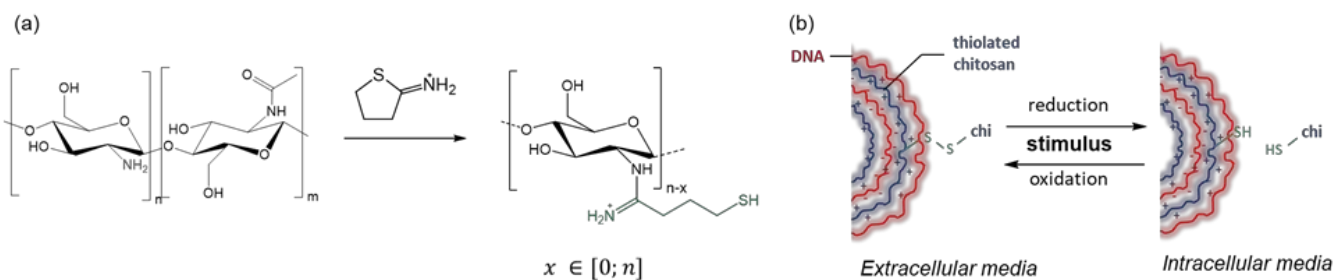


Figure 1: (a) chemical modification of chitosan by addition of 2-iminothiolane (Traut's reagent) [3] and (b) redox-responsive vectors DNA-chitosan (red : DNA - blue : thiolated chitosan). Disulfide bonds are formed between thiolated units of chitosan. These bonds are reduced in intracellular media and the LbL engineered capsule is destabilized to release DNA.

## References :

- [1] : SY. Zhang ; A. Pawlak A, *Sci Signal*, 2010, **3**, 123  
 [2] :G. Saito;, J. A. Swanson, *Advanced drug delivery reviews*, 2003, **55**, 199  
 [3] :I. M. N. Vold; B. E. Christensen, *Carbohydrate Research*, 2005, **340**, 679

# Nanodiamonds coated by a layer of polyethylene imine: an efficient material for optical power limiting

Morgane Guerchoux<sup>1\*</sup>, Manon Dandois<sup>1</sup>, Olivier Muller<sup>1</sup>, Vincent Pichot<sup>2</sup>, Mazheva Guillevic<sup>2</sup>, Cordula Hege<sup>1</sup>, Philippe Fioux<sup>3</sup>, Denis Spitzer<sup>2</sup>, Lionel Merlat<sup>1</sup>

<sup>1</sup> RIM "Radiation Interaction with Matter", French-German Research Institute of Saint-Louis, 5 rue du Général Cassagnou, 68301, Saint-Louis cedex, France

<sup>2</sup> NS3E "Nanomatériaux pour Systèmes Sous Sollicitations Extrêmes" UMR 3208 ISL/CNRS/UNISTRA, French-German Research Institute of Saint-Louis, 5 rue du général Cassagnou, 68301, Saint-Louis, France

<sup>3</sup> IS2M "Institut de Science des Matériaux de Mulhouse" UMR7361 CNRS  
15, rue Jean Starcky, 68057, Mulhouse, France

\*Corresponding author: morgane.guerchoux@isl.eu

**Key-Words:** Nanodiamonds, polyethylene imine, optical limitation, optical filters, nonlinear threshold

## Abstract:

Detonation Nanodiamonds (DNDs) show a real interest in the field of optical limitation. Since the development of increasingly compact laser sources emitting short intense radiations, it has become essential to develop suited protection means. By virtue of their interesting nonlinear optical properties, DNDs are perfectly suited for optical limitation. In other words, they contribute to limit the amount of the transmitted laser energy [1-4].

In this study, we have first elaborated DNDs coated with polyethylene imine (PEI) by electrostatic interaction and second, we have investigated their nonlinear optical properties. To synthesize the nanohybrid particles, blend mixing with different loads of PEI have been achieved, followed by a filtration and a drying step.

The zeta potential measurements reveal the evolution of the charge surface of the DNDs as a function of the PEI concentration. While the charge surface of the DNDs is negative due to the oxygenated functional groups, the cationic PEI polymer allows to change it to a positive one. XPS Spectroscopy has been used to confirm the PEI interactions with the DNDs.

Optical limitation measurements have been carried out in water suspensions as well as in solid filters using PMMA as a host. The assessment of the transmittance in the nonlinear regime has been revealed that the DNDs-PEI nanohybrids show the highest sensitivity compared to the pure DNDs. Regarding the laser beam attenuation, either of the system under study exhibited the same level of performance.

DNDs-PEI nanohybrids have been successfully synthesized by electrostatic interaction. Their optical limitation properties are better than those of unmodified DNDs. Besides, solid-state nanohybrids have been showed encouraging properties. Further research will be conducted to understand the mechanisms governing our observations like nonlinear absorption or nonlinear refraction, by means of open vs close Z-scan experiments.

## References:

- [1]: V. Pichot, O. Muller, A. Seve, *Scientific Reports*, 2017, **7**:14086
- [2]: O. Muller, V. Pichot, L. Merlat, *Applied Optics*, 2006, **55**, 3801-3808
- [3]: S. Josset, O. Muller, Loïc Schmidlin, *Diamond & Related Materials*, 2013, **32**, 66-71
- [4]: V. Pichot, M. Guerchoux, O. Muller, *Diamond & Related Materials*, 2019, **95**, 55-59

# CONTROLLING SIZE AND FLUORESCENCE OF DYE-LOADED POLYMER NANOPARTICLES THROUGH POLYMER DESIGN

Vitalii Rosiuk, Anne Runser, [Antoine Combes](#), Yuliia Koval, Denis Dujardin, Andrey S. Klymchenko, Andreas Reisch

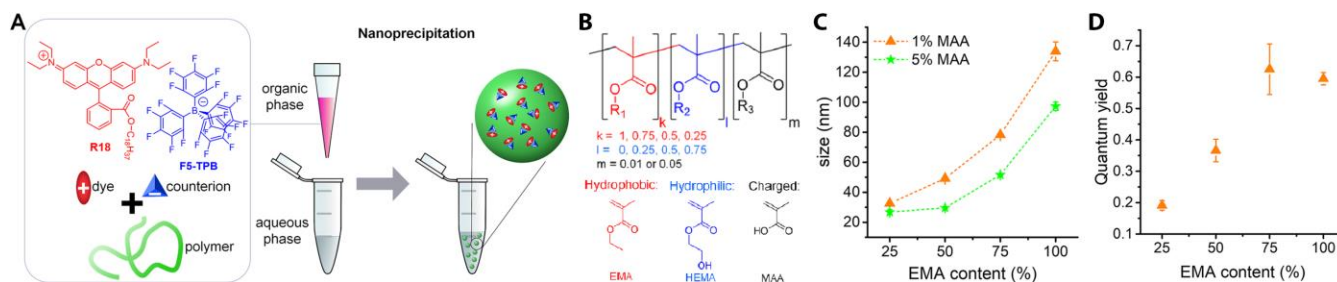
Laboratoire de Bioimagerie et Pathologies, CNRS UMR 7021, Université de Strasbourg, Faculté de Pharmacie, 67401 Illkirch Cedex, France.

antoine.combes@etu.unistra.fr

**Key-Words:** nanoparticles, polymer, nanoprecipitation, fluorescence, bioimaging

## Abstract:

Nanoprecipitation is a straightforward yet powerful technique to synthesize polymer nanoparticles loaded with various biologically active compounds or contrast agents.<sup>[1,2]</sup> Particle formation in this approach is kinetically controlled, and various assembly parameters have been used to control the size and properties of the formed nanoparticles. Here, the influence of the nature of the polymer on the formation of nanoparticles in nanoprecipitation was studied systematically by varying the hydrophobicity and charge over a broad range. For this, methacrylate copolymers with different types and fractions of hydrophobic, hydrophilic, and charged side groups were synthesized. Nanoprecipitation of these polymers showed that particle size increases with increasing global hydrophobicity of the polymers, while hydrophilic and charged groups<sup>[3]</sup> reduce it. In this way, we achieved control over particle size from ~10 to 200 nm. Furthermore, the effect of the polymer nature on the photophysical properties of nanoparticles loaded with a fluorescent dye, a rhodamine B derivative with a bulky hydrophobic counterion (R18-F5-TPB),<sup>[4]</sup> was studied. The hydrophobic/hydrophilic balance of the polymer modulated to a large extent the spectral properties and fluorescence quantum yield of the dye encapsulated at high concentration, reflecting changes in the dye aggregation within the polymer matrix. Thus, we showed how polymer chemistry can tune kinetically controlled formation of nanoparticles and encapsulation of the load. The concepts introduced here should be valuable tools for the design of nanoparticles for imaging and drug-delivery applications.<sup>[5]</sup>



(A) Schematic view of the assembly of dye-loaded polymer NPs through nanoprecipitation; (B) Part of the monomers used in the design of copolymers; (C) Influence of copolymer composition on size of particles for HEMA/EMA/MAA copolymers; (D) Influence of copolymer composition on quantum yield of particles for HEMA/EMA/MAA copolymers.

## References :

- [1] : E. Lepeltier; C. Bourgeaux; P. Couvreur; *Adv. Drug Deli. Rev.*, 2014, **71**, 86
- [2] : W. S. Saad; R. K. Prud'homme; *Nano Today*, 2016, **11**, 212
- [3] : A. Reisch *et al*; *Adv. Funct. Mater.*, 2018, **28**, 1805157
- [4] : A. Reisch; A. S. Klymchenko; *Small*, 2016, **12**, 1968
- [5] : V. Rosiuk; A. Runser; A. Klymchenko; A. Reisch; *Langmuir*, 2019, **35**, 7009

**Acknowledgements:** This work was supported by the Agence National de Recherche JC/JC grant ANR-16-CE09-0007, the European Research Council ERC Consolidator grant BrightSens 648528, and by the Fondation pour la Recherche en Chimie, Strasbourg, LabEx CSC (ANR-10-LABX-0026\_CSC).

# Diels-Alder reaction on functional surfaces: towards the design of smart biosensors

Jamerson C. de Oliveira<sup>\*a</sup>, Loïc Jierry<sup>b</sup>, Vincent Roucoules<sup>a</sup>, Florence Bally-Le Gall<sup>a</sup>

<sup>a</sup> Institut de Science des Matériaux de Mulhouse, UMR 7361 - CNRS/UHA, 15 rue Jean Starcky - 68057 Mulhouse Cedex

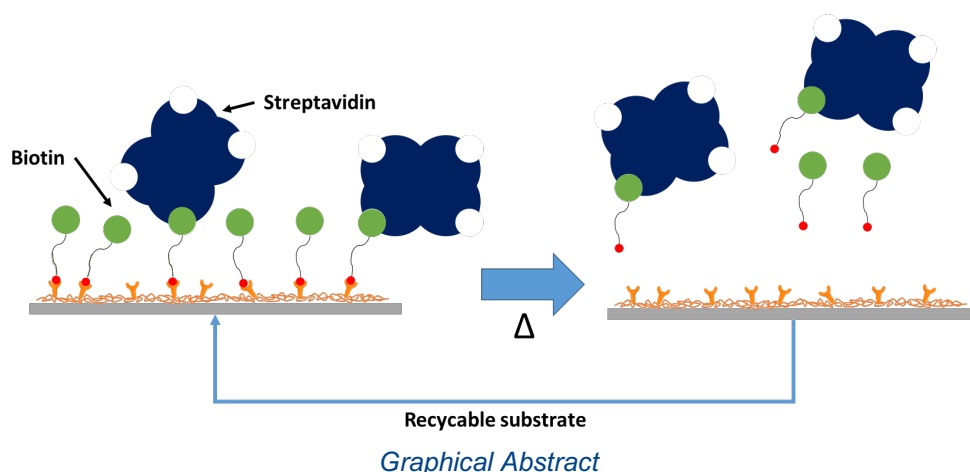
<sup>b</sup> Institut Charles Sadron, UPR22-CNRS, 23 rue du Loess - BP 84047 67034 Strasbourg Cedex 2

\* jamerson.oliveira@uha.fr

**Key-Words:** interfacial Diels-Alder reaction, plasma polymerization, biomolecules

## Abstract:

The potential use of Diels-Alder reaction to design thermoresponsive materials is experiencing growing interest. The applications of that chemistry ranges from remendable polymer networks<sup>1</sup> to the reversible attachment of biomolecules onto surfaces controlled by the surrounding temperature<sup>2</sup>. Our research group already explored the possibility of using interfacial Diels-Alder reaction on functionalized plasma polymer surfaces<sup>3</sup>. In the present work, we have evaluated the possibility of applying Diels-Alder chemistry for the controlled immobilization and release of biomolecules to a functionalized plasma polymer surface. More specifically, the goal is to control the attachment of a diene-functionalized biotin, capable of specific conjugation with streptavidin, onto a dienophile (maleimide) rich surface. For this purpose, biotin was first modified with fulvene. Fulvene was selected as the diene because it is expected to undergo retro-Diels-Alder reaction at moderate temperature, which is required to consider any application involving biomolecules. The diene functionalized biotin was analysed via <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectrometry. The functionalization of silicon wafers (used as model substrates) with maleimide moieties was done via plasma polymerization of maleic anhydride followed by a two-step post-functionalization process. Functionalized surfaces were brought in contact with the fulvene-terminated biotin and were characterized via XPS and contact angle measurements. After FITC-streptavidin conjugation with biotin, the samples were analysed via fluorescence microscopy. The observation of fluorescence, analysed against control experiments, indicated that the Diels-Alder between the functionalized surface and biotin occurred as expected. Investigations on the reversibility of the system are ongoing. These results are the first steps for the fabrication of smart sensors of biomolecules.



## References :

- [1] : M.M. Diaz; J. Brancart; G. Van Assche; B. Van Mele, *Polymer*, 2018, 153, 453-463.  
 [2] : M. Abu-Laban et al., *Journal of Colloid and Interface Science*, 2018, 526, 312-321.  
 [3] : M. Vauthier et al., *The Journal of Physical Chemistry C*, 2019, 123, 4125-4132.



# HYBRID SEMI-CONDUCTING MATERIALS BASED ON ANILINE AND/OR 2-METHOXY ANILINE: SYNTHESIS, CHARACTERIZATION AND ELECTROACTIVE EFFECT

Abdelbassat Kenane \* <sup>a, b</sup>, Ahmed Yahiaoui <sup>a</sup>, Aicha Hachemaoui <sup>a</sup>, Ali Mustapha Benquider <sup>a</sup>,  
Oana Rasoga <sup>b</sup>, Aurelian Catalin Galca <sup>b</sup>, Anca Stanculescu <sup>b</sup>.

<sup>a</sup> *Laboratoire de Chimie Organique Macromoléculaire et des Matériaux. (LCOMM), University of Mascara, Algeria.*

<sup>b</sup> *National Institute of Material Physics, 405A Atomistilor, 077125 Magurele, Romania.*

\* Email address: a.kenane@univ-mascara.dz

**Key-Words:** Nanocomposite, modified montmorillonite clay, oxidation, in-situ chemical polymerization, optical gap.

## Abstract:

In the last decade, an increased interest in hybrid semi-conducting materials of polyaniline and/or derivatives composites with montmorillonite (Mt) have been observed, a conductive or semi-conductive polymer nanocomposites have been used in a wide range of application specially in rechargeable batteries, energy storage devices, electronic and optical devices [1-2].

In this work the nanocomposites like polyaniline/montmorillonite-Cetrimonium bromide (Pani/Mt-CTAB), poly (2-methoxy aniline)/ montmorillonite-Cetrimonium bromide (poly(2-Met-ani)/Mt-CTAB) and polyaniline-co-2-methoxy aniline/ montmorillonite-Cetrimonium bromide (poly(ani-co-2-Met-ani)/Mt-CTAB) have been studied.

The hybrid composites are synthesized by in-situ chemical polymerization method of aniline and/or 2-metoxyaniline into the interlayer space of modified montmorillonite clay(Mt-CTAB) using ammonium persulfate (APS) as oxidizing agent [3].

These synthesized nanocomposites have been analyzed by several characterization methods such as Fourier transform infrared spectroscopy (FTIR) and UV-Vis spectroscopy to study the chemical structure of nanocomposites. The interactions between organic and inorganic compounds are studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The cyclic voltammetry (CV) is used to examine the electrical properties.

The obtained results are encouraging and we believe that the studied materials can be useful in the field of photovoltaic devices.

## References:

- [1] : P. M. Visakh; G. Markovic; D. Pasquini, Book Series: Woodhead Publishing in Materials, 2017, 1-329
- [2] : M. Daud, M.S. Kamal, F. Shehzad, M.A. Al-Harhi, Carbon N. Y., 2016, 104, 241–252
- [3] : P. Bober, J. Stejskal, M. Špírková, M. Trchová, M. Varga, J. Prokeš, Synth. Met., 2010, 160, 2596-2604

# Removal of cupric ions from water by using cellulose nanofibers as adsorbent and copper carbonate formation by precipitation method

Ladhari Safa<sup>a,b</sup> and Jada Amane<sup>a,b,\*</sup>

<sup>a</sup>Mulhouse Materials Science Institute – CNRS (IS2M), University Haute Alsace, F-68100, Mulhouse, France

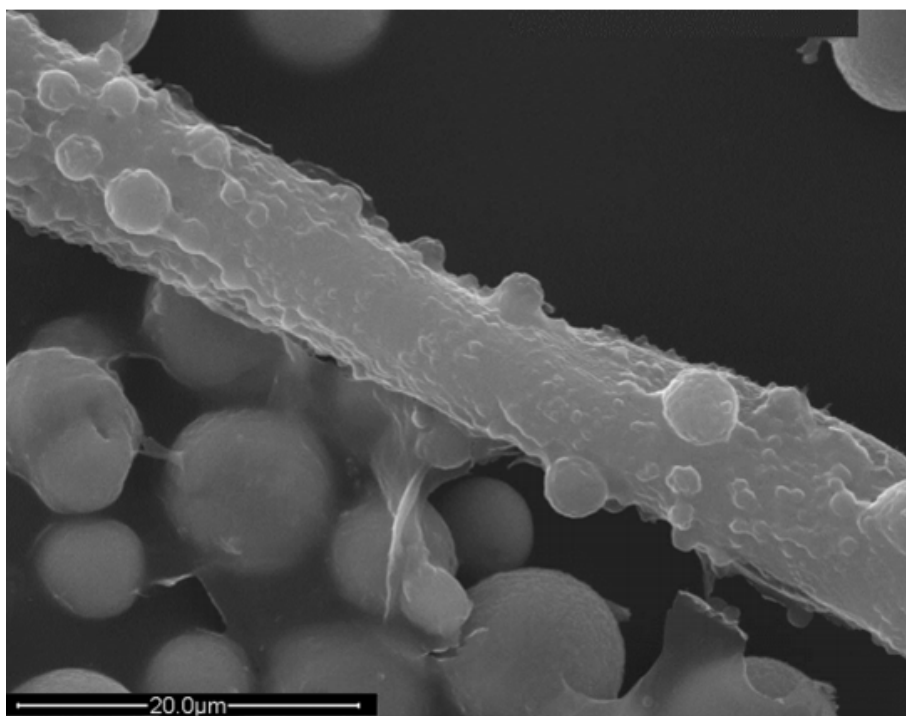
<sup>b</sup>University of Strasbourg, Strasbourg, F-67081, France

\* amane.jada@uha.fr

**Key-Words:** Cellulose Nanofibers; cupric ions; solid/liquid; interface; copper carbonate.

## Abstract:

The overall goal of this work is to active agri-food wastes by microbial action, which makes it possible to produce a bio-digestate and energy (methane). Then, the resulted bio-digestate was transformed to porous carbon, which was used for the preparation of core-shell particles with alginate (bio-polymer) and calcium ions layer. Further, the surface charge measurements show electrostatic attraction occurring between alginate, calcium ( $\text{Ca}^{2+}$ ) ions and porous carbon, leading hence to the formation of core (PC)-shell (alginate-calcium ions) particles. However, in the absence of calcium ions, no electrostatic attraction was observed between PC and alginate. At dried state (using the Scanning Electronic Microscopy analysis (SEM) and at hydrate state (using numerical Microscopy) the designed core-shell was confirmed. The Transmission Electron Microscope (TEM) shows that the carbon particles are graphitic and porous. In addition, both Raman Spectroscopy (RS) and X-ray photoelectrons spectroscopy (XPS) show the presence of several chemical functions, especially the hydroxyl (-O-H) and carboxylic groups (-COO-H). In aqueous media, results shows that the PC was negatively charged, its surface charge and its particle size, were found to be very sensitive to the pH variation.



*SEM image of CNF covered by  $\text{CuCO}_3$  particles*

# ELECTROCHEMICAL SENSORS BASED ON CONDUCTING POLYMERS

Boris Lakard<sup>a,\*</sup>, Emmanuel Contal<sup>a</sup>, Sophie Lakard<sup>a</sup>, Claire Magnenet<sup>a</sup>, Marcel Bouvet<sup>b</sup>

<sup>a</sup> Institut UTINAM, UMR CNRS 6213, Univ. Bourgogne Franche-Comté, Besançon, France

<sup>b</sup> ICMUB, UMR CNRS 6302, Univ. Bourgogne Franche-Comté, Dijon, France

\* boris.lakard@univ-fcomte.fr

**Key-Words:** Conducting Polymers, Electrochemistry; Chemical Sensors

## Abstract:

Over the last years, we have prepared a large number of original polymers, based on pyrrole [1], aniline [2] or carbazole monomers [3], and then validated them in applications ranging from micromanipulation to sensors in liquid and gaseous environments. Conductive polymers present strong advantages to satisfy all the performance criteria of a chemical sensor (sensitivity, selectivity, and stability in time). Indeed, conductive polymers present the advantage, compared with smaller molecules, to offer a high sensitivity towards analytes thanks to the presence of numerous reactive groups in their backbone. Moreover, recent progress regarding synthesis of polymers has allowed the preparation of polymers presenting a structure and a design specifically adapted to the analytes to detect, thus leading to more selective sensors.

In addition, hybrid materials can be prepared by combining heterocyclic monomers and macrocycles such as phthalocyanines or porphyrines. This strategy was used to prepare hybrid films composed of polypyrrole and sulfonated cobalt phthalocyanine [4,5]. Thanks to the use of these hybrid materials as sensitive layers, we were able to obtain ammonia sensors presenting remarkable sensitivities and limits of detection (the characteristics of the sensors were far better with a sensitive layer made of the hybrid material than with a sensitive layer consisting in a film of polypyrrole or a film of phthalocyanine taken separately). Chemical potentiometric biosensors based on electrodeposited conducting polymers, such as substituted polypyrroles and polyanilines, were also prepared. The resulting sensors operated in liquid and allowed the obtention of pH or urea sensors having a good sensitivity, a good stability in time and a good reproducibility.



*Image of a polypyrrole-based gas sensor*

## References :

- [1] : S. Lakard; J. Husson; S. Monney; C.C. Buron; B. Lakard, *Progress in Organic Coatings*, 2016, **99**, 429-436.
- [2] : J. Husson; S. Lakard; S. Monney; C.C. Buron; B. Lakard, *Synthetic Metals*, 2016, **220**, 247-254.
- [3] : E. Contal; C.M. Sougueh; S. Lakard; A. Et Taouil; C. Magnenet; B. Lakard, *Frontiers in Materials*, 2019, **6**, 131.
- [4] : T. Patois; J.B. Sanchez, P. Fievet; O. Segut; V. Moutarlier; M. Bouvet; B. Lakard, *Talanta*, 2013, **117**, 45-54.
- [5] : T. Sizun; T. Patois; M. Bouvet; B. Lakard, *Journal of Materials Chemistry*, 2012, **22**, 25246-25253.

# METALLIC NANOPARTICLES IMMOBILIZED AT THE PORE SURFACE OF POLYMERS: TOWARD EFFICIENT AND VERSATILE SUPPORTED CATALYTIC SYSTEMS

Benjamin Le Droumaguet<sup>\*a</sup>, Romain Poupart<sup>a</sup>, Benjamin Carbonnier<sup>a</sup>, Daniel Grande<sup>a</sup>

<sup>a</sup> Université Paris-Est, ICMPE UMR 7182 CNRS-UPEC, 2-8 rue Henri Dunant, 94320 Thiais, France

\* [ledroumaguet@icmpe.cnrs.fr](mailto:ledroumaguet@icmpe.cnrs.fr)

**Key-Words:** porous polymers, metallic nanoparticles, hybrid materials, heterogeneous supported catalysis

## Abstract:

This communication highlights the design and synthesis of new hybrid materials named as metallic nanoparticles@porous polymers, consisting of porous polymers in which metallic nanoparticles are immobilized, and their further use as efficient supported catalysts. After the elaboration of the porous polymeric matrix, the pore surface can suitably be chemically modified so as to ensure dense and homogeneous adsorption of metallic nanoparticles. Such nanoparticles may be either prepared through an in-situ strategy, *i.e.* *via* reduction of corresponding metallic salts, or used after performing them according to an ex-situ strategy.

First, macroporous polymeric monoliths have successfully been prepared into fused-silica capillaries (internal diameter  $\approx$  100  $\mu$ m). Their subsequent chemical modification with suitably chosen molecules containing chelating groups (*e.g.*, -COOH, -NH<sub>2</sub>) has allowed for tight adsorption of metallic nanoparticles of diverse nature (Cu, Au, Pt). Model catalytic reactions, such as nitroarene reduction, have been investigated *via* flow-through processes. [1, 2] A second part of the work has been focused on the development of ordered nanoporous bulk materials. Such porous polymers have been engineered from newly synthesized polystyrene-block-poly lactide copolymer precursors possessing a cleavable chemical junction between both blocks. [3] After proper orientation of the diblock copolymers and removal of the poly lactide sacrificial block under specific conditions for the selective cleavage of their block junction, these novel nanoporous frameworks possess pore walls lined with functional groups (*e.g.*, -SH, -NH<sub>2</sub>) that can notably chelate gold nanoparticles, and thus can be used as efficient catalytic supports. Interestingly, C-C homocoupling of benzenboronic acid derivatives, hydride-mediated reduction of nitroaromatic compounds, and especially unprecedented “one-pot” cascade reactions consisting of the latter consecutive reactions (Fig. 1) have successfully been monitored by different chromatographic and spectroscopic techniques.

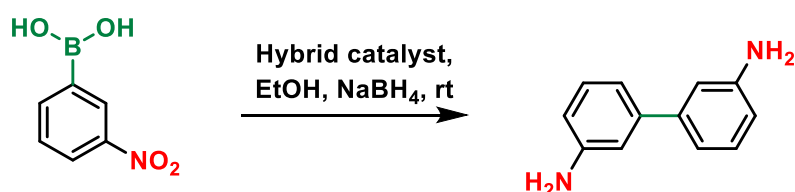


Fig. 1: Catalytic cascade reaction occurring at the surface of the hybrid catalyst

## References :

- [1] : R. Poupart, B. Le Droumaguet, M. Guerrouache, B. Carbonnier, *Mater. Chem. Phys.*, 2015, **163**, 446-452  
 [2] : R. Poupart, N. E. H. Djerir, D. Chellapermal, M. Guerrouache, B. Carbonnier, B. Le Droumaguet, *RSC Adv.*, 2016, **6**, 13614-13617  
 [3] : R. Poupart, A. Benlahoues, B. Le Droumaguet, D. Grande, *ACS Appl. Mater. Interfaces*, 2017, **9**, 31279-31290

# Development of new polyoxometalates/polymer for photodegradation of organic pollutants

Chaima Brahmi<sup>1,2,3</sup>, Jacques Lalevée<sup>1,2</sup>, Mahmoud Bentifa<sup>3</sup>, Latifa Bousselmi<sup>3</sup>

<sup>1</sup>University of Haute-Alsace, CNRS, IS2M UMR 7361, F-68100, Mulhouse, France

<sup>2</sup>University of Strasbourg, 4 rue Blaise Pascal, F-68081, Strasbourg, France

<sup>3</sup>Wastewaters and Environment Laboratory, Center for Water Research and Technologies CERTE, BP 273, Soliman 8020, Tunisia

<sup>4</sup>University of Carthage, National Institute of Applied Sciences and Technology, North Urban Center, Tunis 1080, Tunisia

Correspondence to: M. Bentifa (E-mail: mahmoud.bentifa@certe.rnrt.tn) and J. Lalevée (E-mail: jacques.lalevee@uha.fr)

**Key-Words:** Photopolymerization, photocatalysis, Polyoxometalate(POM) /Polymer composites, organic pollutants.

## Abstract:

The water is the most important resource for living species. However potable water which is indispensable for every human being represents only 1% of surface water from lakes and rivers [1]. To satisfy the demands of people for clean and safe water, new technologies for wastewater treatment have been developed. Hence photocatalysis has emerged as a green chemical approach for such treatment. In this context we developed a new regenerable composites POM/polymer characterized by photocatalytic properties which are synthesized by photopolymerization process under mild irradiation conditions [2]. Furthermore, the photocatalytic ability of these new hybrid materials has been applied for water treatment in order to remove different emergent pollutants such as pesticides, dyes, pharmaceutical and organic compounds. The POM excited by the irradiation could oxidize directly the pollutants adsorbed on its surface or generate highly reactive chemicals such as OH radicals which promotes the degradation [3]. In order to increase the conversion rates of these pollutants, different sources of irradiation have been used. The most efficient was the Omni-cure lamp. In addition, the use of thin composites which has a greater specific surface area than the thick ones made it possible to achieve high conversion rates of these organic molecules. Pollutants degradation mechanisms as well as identification of the photoproducts will be discussed using mass spectroscopy technique.

## References :

- [1]: S.S. Shinde; C.H.Bhosale; K.Y.Rajpure , *Journal of Photochemistry and photobiology B ; Biology* , 2014, **141**, 186-191.
- [2]: M.Ghali; C.Brahmi; M.Bentifa; F.Dumur; S.Duval; C.Simmonet-Jégat; F.Morlet-Savary; S.Jellali; L.Bousselmi; J.Lalevée , *Journal of Polymer Science Part A: Polymer Chemistry*, 2019, **57**, 1538-1549
- [3]: R. Palmisano; L.Campanella; B. Ambrosetti , *International Journal of Environmental Analytical Chemistry*, 2015, **2** , 2380-2391.

# Light-assisted synthesis of metal nanoparticles and nanocomposites: an efficient green approach to obtain smart nanomaterials

Marine Dabert<sup>a,b</sup>, Mohamed Zaier<sup>a</sup>, Samar Hajjar-Garreau<sup>a</sup>, Loïc, Vidal<sup>a</sup>, Lavinia Balan<sup>a,b\*</sup>

<sup>a</sup> Institut de Sciences des Matériaux de Mulhouse, CNRS UMR 7361, 15 rue Jean Starcky, 68057, Mulhouse

<sup>b</sup> Université d'Orléans, Conditions Extrêmes Matériaux Haute Température et Irradiation CNRS UPR 3079, F-45000, Orléans, France

\*Contact to: e-mail: [lavinia.balan@cnrs-orleans.fr](mailto:lavinia.balan@cnrs-orleans.fr), phone: +33(0)238255655

**Key-Words:** nanocomposites, metal nanoparticles, photo-induced material

## Abstract:

Metal nanoparticles show potential applications in various fields including but not limited to medicine, catalysis, optics or electronics. Combining the intrinsic characteristics of metal nanoparticles with those of polymers opens up new vistas in the quest for materials with very innovative properties. In this context, metal/polymer nanocomposite materials were developed through a simple, rapid and green approach based on the photoreduction of a metal precursor and photopolymerization of a blend of monomers [1].

Silver nanofilms were directly generated on a variety of substrates through this environmentally friendly approach, which uses a simple UV source does not involve any reducing or stabilizing agent and does not require any thermal activation. Top-coated films of unprotected silver nanoparticles were generated from a hydroalcoholic AgNO<sub>3</sub> solution or an acrylate monomer formulation, directly on glass substrates or food packaging plastic wraps.

The metal nanoparticles and metal/polymer nanocomposites film obtained in this way were characterized and the influence of several parameters (fluence, exposure, silver ions concentration and nature of the free radicals generator) on their formation was evaluated [2]. This photoinduced synthesis offers substantial advantages since it combines the characteristic features of light activation i.e. versatility and convenience of the process, high spatial resolution and reaction controllability (intensity and wavelength), with the simplicity of the colloidal approach. Moreover, the use of amplitude masks or interferometric devices to shape up the light beam used to induce the photoreduction of silver cations provides a very powerful and versatile means to spatially manipulate metal nanoparticles (Ag, Au, ...) [3].

## References :

- [1] : Zaier M, Vidal L, Hajjar-Garreau L, Balan L Scientific Reports 7, (2017) 12410.
- [2] : Zaier M, Vidal L, Hajjar-Garreau S, Bubendorff J-L, Balan L Nanotechnology 28, (2017) 10.
- [3] : Schejn A, Ott M, Dabert M, Vidal L, Balan L Materials & Design 160, (2018) 74-83

# Surface Color on Demand : Chameleon Effect

[Karine Mougin](#)<sup>a\*</sup>, Hendrik Hoelscher<sup>b</sup>

<sup>a</sup> Institut de Science des Matériaux de Mulhouse, UMR 7361 CNRS-Université de Haute Alsace, 15 Rue Jean Starcky, 68057 Mulhouse, France.

<sup>b</sup> Institut für Mikrostrukturtechnik (IMT), Karlsruher Institut für Technologie (KIT), Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

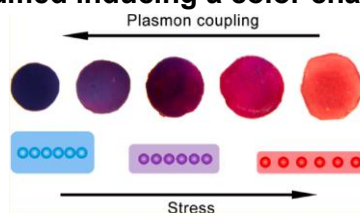
\* Karine.mougin@uha.fr

**Key-Words:** nanoparticle, color-changing material, nanostructuration

## Abstract:

Colors affect our everyday life as they provide critical functions in both recognition and communication. Nearly all artifacts of our everyday are manufactured from polymers colored by dyes. This approach allows an endless variety of colors and the colors of housewares, cloth, cars, and interior decoration offered by industry. And yet, **each individual item** is produced in **one** color, which cannot be changed after its production. This is a serious problem for manufacturers, as some goods cannot be sold anymore when their color is outdated. This issue can also cause **tremendous costs** and **waste** if products cannot be recycled and have to be deposited. *So, it is of high interest to add color-changing surfaces to the portfolio of manufacturing.* In nature, changing colors are frequently observed in the animal's world for camouflage by misleading natural enemies or for courting by standing out from the environment. The most prominent examples are chameleons that are able to exhibit complex and rapid color changes during social interactions due to dispersion/aggregation of pigment within dermal chromatophores. A direct copy nature is not typically practical for everyday items but is **the inspiration of our approach to create color change in polymeric material.**

The idea was to create a novel hybrid material able to color change of surfaces at will. The key element of this novel technology is based on the combination of two phenomena observed in the nature and transferable to material science: plasmonic and structural colors. The developed functional nanomaterial is composed of colloidal metallic nanoparticles (NPs) that are properly synthesized and assembled into latex to ensure a variety of plasmonic colors under mechanical stresses. **By changing height and width of a latex film and/or the size of nanostructures through the shape memory effect, the distance between the nanoparticles are modified inducing a color change in the composite material [1].**



*Figure 1: Basic principle of a colorimetric stress memory sensor developed by Han et al. [1]. Gold nanoparticle chains embedded in a polymer matrix. Applying stress to the film increases the distance of the gold nanoparticles resulting in a color change of the sample. (Reproduced from [1])*

To enhance the color palette of this stimuli-responsive nanocomposite, its surface will be later structured with diverse diffractive nano & micropatterns.

**As result, combining the color emission of the nanoparticles with the structural colors will allow enhancing specific wavelengths and the palette of reachable colors.** The specificity mechanical properties of the latex ensure the outstanding reversibility of color by properly controlling the reassembly of the nanoparticles inside and on the surface of the material.

## References :

[1] X. Han, Y. Liu, Y. Yin, *Nano Letters*, 2014, 14, 2466.

# Thermoplastic elastomer filaments for multi-polymer structures by fused deposition modeling

Jennifer Villamil Jiménez <sup>a,b</sup>, Abdelali El Akroud <sup>a,b</sup>, Sandrine Hoppe <sup>a</sup>, Hakim Boudaoud <sup>b</sup>,  
Cécile Nouvel <sup>a,\*</sup>

<sup>a</sup> LRGP Laboratoire Réactions et Génie des Procédés, UMR CNRS-Université de Lorraine 7274, Nancy F-54000

<sup>b</sup> ERPI Équipe de Recherche sur les Processus Innovatifs (EA 6737), Université de Lorraine, F-54000 Nancy

\* cecile.nouvel@univ-lorraine.fr

**Key-Words:** Additive fabrication, 3D printing, adhesion, interfaces, formulation

## Abstract:

In recent years, additive manufacturing techniques have attracted increasing interest in many industrial and research areas [1]. They produce three-dimensional shapes by successive deposition of material to obtain small series of complex objects. Additive processes provide many advantages (possibility to tailor made objects on demand, sometimes cheaper and faster processes than traditional techniques ...) [2-3]. Nevertheless, a certain number of scientific and technological barriers remain to overcome, like materials availability, 3D architectural design and reliability of the process, etc. [1,4]. Currently among the additive manufacturing techniques, Fused deposition modeling (FDM) is the most used because of the easiness of implementation [2-4]. It consists to extrude a thermoplastic (TP) or a thermoplastic elastomer (TPE) polymer filament through a moving and heated printer head.

By now, the studies of the mechanical properties of 3D printed objects are rather limited and are mainly focused on the measurement of the properties at macroscopic scale [4-6]. Printing parameters [4], filament composition [5] and printing orientation [6] affect the interfacial adhesion between the polymer layers and thus the mechanical properties of the final objects. Nevertheless, there is no reported work with specific study of interfacial adhesion. The challenge is even more difficult for the elaboration of multi-material polymer objects combining a flexible TPE polymer and a TP structural polymer because of the lack of affinity between polymer layers. This explains the very rare reports on such objects [7-9]. The biggest barrier to overcome is the improvement of the interfacial adhesion between polymers which has never been studied.

This work is focused on the formulation of a TPE filament more compatible with PLA and on the evaluation of its mechanical performance. The improvement of TPE compatibility with PLA should provide a better interfacial adhesion for FDM printed objects. Extrusion conditions for native TPE and charged TPE were optimized to obtain filaments with regular diameter and without bubbles inside. Printability of all filaments was checked thanks to the optimization of the printing parameters in order to produce high quality mono- and multi-polymer objects. Mechanical and hardness tests made it possible to evaluate the properties of the formulated TPE by comparison with native TPE. A discriminative test to measure the interfacial adhesion of multi-polymer FDM-printed objects was set up thanks to the printing of different multi-material models, including one originally inspired from standard T-Peel test for tape-adhesives. All of this made it possible to confirm the lower adhesion of PLA/TPE interface compared to PLA/PLA and to evaluate the performance of new formulated TPE filaments.

## References :

- [1] : N. Guo and M.C. Leu. Mech. Eng., 2013, **8**, 215-243.
- [2] : S. Singh, S. Ramakrishna and R. Singh. J. Manuf. Process., 2017, **25**,185-200.
- [3] : S. Ligon, R. Liska, J. Stampfl, M. Gurr, and R. Chem. Rev., 2017, **117**, 10212-10290.
- [4] : F. Cruz, H. Boudaoud, S. Hoppe S. and M. Camargo. Addit. Manuf., 2016, **6**, 87-105.
- [5] : A. R. Torrado Perez, D. A. Roberson and R. B. Wicker, J Fail. Anal. and Preven., 2014, **14**, 343-353.
- [6] : S. Guessasma, H. Nouri and F. Roger. Polymers., 2017, **9**, 1-16.
- [7] : L.R. Lopes, A. F. Silva and O.S. Carneiro. Addit. Manuf., 2018, **23**, 45-52.
- [8] : K. Estelle, D. Blair, K. Evans and B. Gozen. J. Manuf. Process. 2017, **28**, 500-507.
- [9] : R. Singh, R. Kumar, I. Farina, F. Colangelo, L. Feo and F. Fraternali. Polymers., 2019, **11**, 62.



# Recycling of opaque PET by reactive extrusion

Khadija Char 1<sup>a</sup>, [Nicolas Logié](#) 2<sup>\*b</sup>, [Thibault Parpaite](#) 3<sup>\*a</sup>

<sup>a</sup> PMC Group, Institut Charles Sadron, CNRS-UPR 22, 23 rue du Loess, 67034, Strasbourg, Cedex 2, France

<sup>b</sup> Cetim Grand Est, Site de Strasbourg, 24 Rue d'Alsace, 67400 Illkirch-Graffenstaden

\*thibault.parpaite@ics-cnrs.unistra.fr, \*nicolas.logie@cetimgrandest.fr

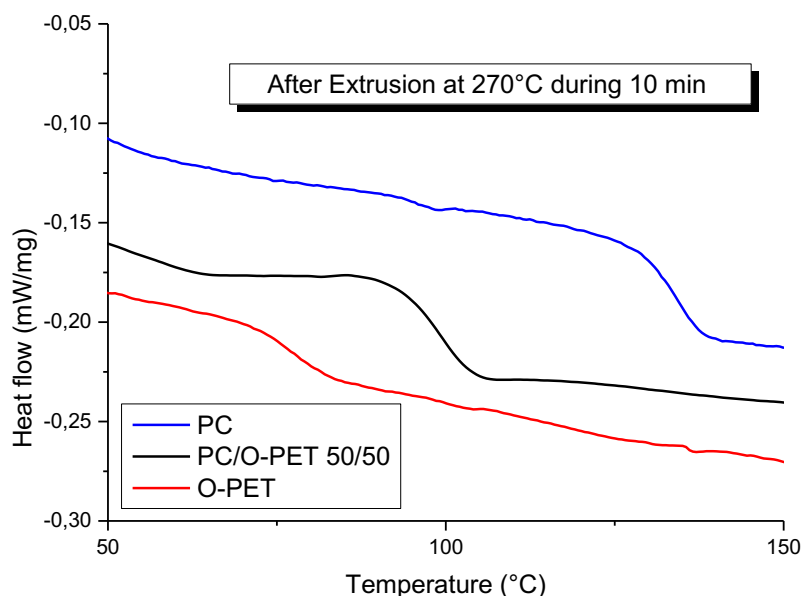
**Key-Words:** Recycling, Transesterification, opaque PET, Polymer blends, reactive extrusion

## Abstract:

Due to better processability, mechanical properties and productivity compare to conventional low density poly(ethylene) (LDPE), the use of opaque poly(ethylene terephthalate) (O-PET) in the milk bottle market continue to increase fastly. O-PET milk bottles are lighter and free of aluminum opercule. Nevertheless, the titanium dioxide nanoparticles (TiO<sub>2</sub> NPs) used as opacifier disturb the well-establish flow of recycle transparent PET from water bottle [1].

Our project proposes to investigate new valorization solution in order to prepare the upcoming increase volume of O-PET end of life bottle. While TiO<sub>2</sub> NPs are an issue in the current situation, they could be used advantageously as catalyst in different process like reactive extrusion [2].

In this work, PC/O-PET 50/50 w/w blends were first produced using twin-screw mini-extruder. The results show that the presence of TiO<sub>2</sub> NPs effectively acts as catalyst in the reaction of transesterification between ester functions of PET and carbonate functions of PC during extrusion. Miscible blends exhibiting only one glass transition temperature were obtained (see Figure below).



*DSC curves of PC, O-PET and the resulting transesterified 50/50 w/w blend with only one intermediate T<sub>g</sub>*

The influence of process parameters such as temperature, time of mixing but also type of flow (shear vs elongational) was investigated. Finally, the ability to use these PC-co-PET copolymers as compatibilizing agent in industrial twin-screw extruder is also discussed.

## References :

[1] : Maryon Pailleux. (2016). Cahier des charges: Etude de débouchés au recyclage des PET opaques

[2] : Pilati, F., Marianucci, E., & Berti, C. (1985). Study of the reactions occurring during melt mixing of poly(ethylene terephthalate) and polycarbonate. *Journal of Applied Polymer Science*, 30(3), 1267–1275.

# Photoactive POM/polymer nanocomposites for photodegradation of organic dyes

Mariam Ghali<sup>a,b,c,d</sup>, Chaima Brahmi<sup>a,b,c,d</sup>, Mahmoud Bentifa<sup>c</sup>, Frédéric Dumur<sup>e</sup>, Fabrice Morlet-Savary<sup>a,b</sup>, Latifa Bousselmi<sup>c</sup>, Jacques Lalevée<sup>\*a,b</sup>

<sup>a</sup> University of Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

<sup>b</sup> University de Strasbourg, France

<sup>c</sup> Wastewaters and Environment Laboratory, Center for Water Research and Technologies CERTE, BP 273, Soliman 8020, Tunisia

<sup>d</sup> University of Carthage, National Institute of Applied Sciences and Technology, North urban center, Tunis 1080, Tunisia

<sup>e</sup> Aix Marseille Univ, CNRS, ICR, UMR7273, F-13397 Marseille, France

\* jacques.lalevee@uha.fr

**Key-Words:** Photopolymerization, POM/polymer composite, photocatalyse, Photodegradation

## Abstract:

Polyoxometalates (POMs) are a class of inorganic transition metal-oxide cluster with different structures and properties [1] known with their strong oxidizing ability upon near UV illumination [2]. In this study, we introduce new POM/polymer nanocomposites synthesized by photopolymerization under soft conditions for photocatalytic applications.  $H_3PMo_{12}O_{40}$  was incorporated into polymeric network to overcome his high solubility into aqueous and organic media and ensure processable photocatalytic process for wastewater treatment. Herein, we would like to explore the effect of POM incorporation on the free radical polymerization of acrylate TMPTA under visible light irradiation and investigate the photocatalytic ability of POM/polymer nanocomposites for organic dyes removal under near UV irradiation. Interestingly, these new POM/polymer nanocomposites proved efficient photocatalytic properties with regenerable and processable photocatalytic process.[3]

## References:

[1]: E. Papaconstantinou, « Photochemistry of polyoxometallates of molybdenum and tungsten and/or vanadium », *Chem. Soc. Rev.*, 1989, **vol. 18**, p. 1.

[2]: A. Hiskia, A. Mylonas, et E. Papaconstantinou, « Comparison of the photoredox properties of polyoxometallates and semiconducting particles », *Chem. Soc. Rev.*, 2001, **vol. 30**, no 1, p. 62-69.

[3]: M. Ghali *et al.*, « New hybrid polyoxometalate/polymer composites for photodegradation of eosin dye », *J. Polym. Sci. Part Polym. Chem.*, 2019, **vol. 57**, p.1538 -1549.

# GRAFTING STYRENE SULFONATE GROUPS ON BIODEGRADABLE POLYMER TO ENHANCE BIOACTIVITY AND HYDROPHILICITY THROUGH OZONE-INDUCED MECHANISM

Ngoc-Tuan Nguyen, Andre Rangel, Veronique Migonney \*

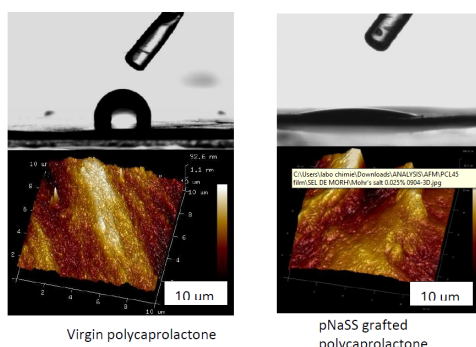
Laboratory of Chemistry, Structures, Properties of Biomaterials and Therapeutic Agents, UMR CNRS 7244, Paris 13 University, France

\* veronique.migonney@univ-paris13.fr

**Key-Words:** Degradable polymeric material, polycaprolactone, grafting from, bioactivity, hydrophilicity

## Abstract:

Functionalization long-term degradable polymers as poly ( $\epsilon$ -caprolactone) by bio-functional groups allow improving cell adhesion and proliferation for new tissue engineering scaffolds. Towards this goal, PCL substrate activated by ozonation to introduce peroxide and carbonyl groups on the surface which participated to initiate the grafting process of poly (sodium styrene sulfonate) (pNaSS) from PCL surface. Through ozone oxidation, the PCL surface was basically more hydrophilic, especially after hydrolysis. The wettability of the material increased and the surface tension was observed by contact angle measurement (CA). Besides that, pNaSS grafted exhibits styrene sulfonate groups assessed and demonstrated for its bioactivity enhancement; pNaSS grafting rate was measured by toluidine blue colorimetric method and identified by infrared spectra (FTIR). Biological assessment of pNaSS functionalized PCL was carried by using fibroblast cells. The results show that cell adhesion, morphology, and proliferation were significantly higher on pNaSS grafted PCL when compared to virgin PCL. In addition, the morphology and surface mechanical properties of grafted polycaprolactone were analyzed by atomic force microscopy (AFM) and Peakforce quantitative nanomechanical properties (Peakforce QNM). It was observed that the grafting induced the decrease of Young's surface modulus and a soft surface as seen in Peakforce QNM map. The resulting grafted branches of pNaSS covalently bond to PCL allows exhibiting high bioactivity and is promising toward the development of bio-integrated biological substitutes.



Contact angle (water) and AFM 3D image ( $10 \times 10 \mu\text{m}^2$ ) of PCL and pNaSS grafted PCL

## Références :

- [1] : M. Ciobanu, A. Siove, V. Guegen, L.J. Gamble, D.G. Castner, and V. Migonney, *Biomacromolecules*, 2006, **7**, 755-760
- [2] : G. Rohman, S. Huot, M. Vilas-Boas, G. Radu-Bostan, D.G. Castner and V. Migonney, *J Mater Sci: Mater Med*, 2015, 26-206.
- [3] : K. Fujimoto, Y. Takebayashi, H. Inoue and Y. Ikada, *Journal of Polymer Science: Part A: Polymer Chemistry*, 1993, **31**, 1035-1043.

# THE EFFECT OF DAMPING ON VIBRATIONS OF STRENGTHENED BEAMS BY COMPOSITE COATS UNDER MOVING LOAD

Khadri Youcef<sup>1\*a</sup>, Tekili Sabiha<sup>1b</sup>, Karmi Yacine<sup>1c</sup>

[speaker must be underlined]

<sup>1</sup>Laboratoire de Mécanique Industrielle, Université Badji Mokhtar BP 12 Annaba, 23000, Algérie,  
Email: [khadri152000@yahoo.fr](mailto:khadri152000@yahoo.fr)

**Key-Words:** Vibrations, Beams, Strengthened, Composite, Moving load, Damping

## Abstract:

The use of composite materials in modern engineering has increased considerably in recent years. As the composite materials offer many desirable structural properties such as lightweight and high strength, they are used to increase the rigidity of civil engineering structures such as girders, rails, crane and bridges for high speed trains, subjected to moving loads[1-2]. In this study, the dynamic response of strengthened beams by composite coats under action of the moving loads. As the main goal of this study, the damped dynamic response of the composite beam is modeled as the Rayleigh damping which is widely used in structural dynamics. The effects of various parameters such as load speed and position, the thickness ratio and fiber orientation of composite coats on natural frequencies mode and dynamic responses is parametrically studied. An aluminum beam is strengthened by composite coats made from composite material, carbon/epoxy and with a thickness ( $H - h$ ), as shown in Fig. 1.

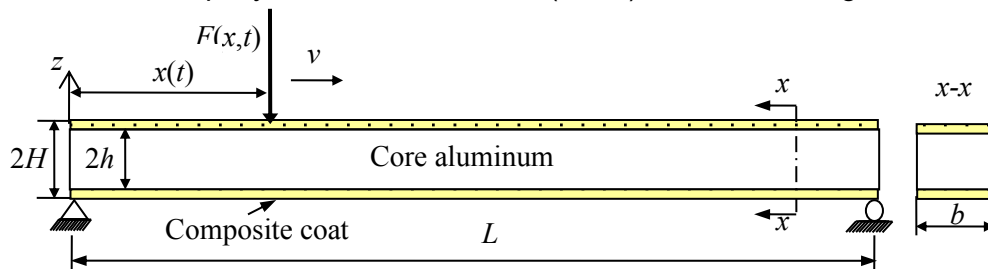


Fig. 1 A simply supported strengthened beams under a force moving

In the framework of the beam theory, in this case the fundamental equations of laminates are simplified as [3]:

$$\rho_s \frac{\partial^2 w}{\partial t^2} + \frac{\partial^2}{\partial x^2} \left( bD_{11} \frac{\partial^2 w}{\partial x^2} \right) = F(x,t) \quad (1)$$

It may be noted here that for uniform composite beam and for each uniform segment of an externally tapered composite beam,  $bD_{11}$  is constant. The equation of motion with damping matrix is as follows:

$$[K]\{q\} + [C]\{\dot{q}\} + [M]\{\ddot{q}\} = \{F(x,t)\} \quad (2)$$

The Rayleigh damping with constant damping ratio is used for dynamic analyses. The differential equation (2) is solved by using the implicit time integration Newmark- $\beta$  method with parameters  $\gamma = 0.5$  and  $\beta = 0.25$ . The beam has length,  $L = 500$  mm, width  $b = 25$  mm, thickness  $H = 4$  mm, under load  $F = 100$  N as show in Fig.1. The material of the core is aluminum and faces are made from AS4/3501-6 Carbon/Epoxy composite material (Table 1).

Table 1 Material property for the coat and core of the beam

Layer Material	Core Aluminum	Coats Carbon/Epoxy
$\rho_{c,f}$ (kg/m <sup>3</sup> )	2800	1580
$E_{11}$ (GPa)	70	147
$E_{22}$ (GPa)	70	9
$G_{12}$ (GPa)	27	5
$\nu_{12}$	0.29	0.3

The DAF is defined as the ratio of the maximum dynamic displacement to the static displacement. The effect of damping ratio on the response dynamic of the beam with different orientation of fiber and  $h/H = 0.75$ , is analyzed and shown in Figs. 2a and 2b. Fig. 2a shows the time history of dynamic deflections vs. force non-dimensional horizontal position at velocity of moving load  $v = 15$  m/s, for different coated beams,  $\theta = 0^\circ$ . It can be indicated that the maximum deflection at the beam center is 2.6, occurs when the moving force passes the position of 0.47 of the beam length. From Fig.2b one observes that in under critical region the damping ratio does not have a great effect on DAF. For damping ratio  $\xi = 0.0, 0.005, \text{ and } 0.01$ , the dynamic amplification factor values of strengthened beam are very close. The exponential decay in the dynamic amplification factor can be observed for the damping ratios greater than or equal to 0.05.

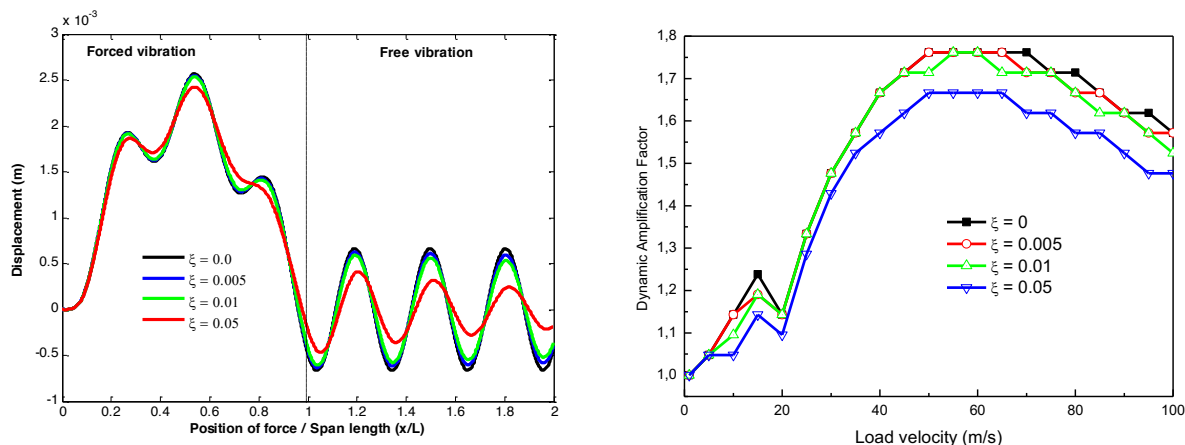


Figure 1. Dynamic responses of the strengthened beams by composite coats under moving load for different damping ratio. ((a). transverse displacement, (b). dynamic amplification factor)

Based on obtained results followings are concluded: DAFs decrease with the increase in the damping ratio; however, for speed ranges above the critical speed, the damping ratio has a significant effect on DAF compared to lower speeds; the exponential decay in the dynamic amplification factor can be observed for the damping ratios greater than or equal to 0.05; the critical speed increased with the increase of the thickness of the composite coat and it decrease, in general, with the increase of fiber orientation; thus by using the composite coats; we can augment the critical velocity considerably.

## References :

- [1] Hamada A. Vibration and damping analysis of beams with composite coats, Composite Structures, 32, pp. 33-38, 1995.
- [2] Khadri Y., Tekili S., Daya E. M., Daouadji A., Merzoug B., Dynamic analysis of train-bridge system and riding comfort of trains with rail irregularities, Journal of Mechanical Science and Technology, (2013) Vol. 27 (4) pp 951-962, 2013.
- [3] Jean-Marie Berthelot, Dynamic of composite materials and structures, ISMANS, Institute for Advanced Materials and Mechanics, Le Mans, France, 2010.



# Sponsors

---

