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A Competing Hydrogen Bonding Pattern to Yield a Thermo-Thickening Supramolecular Polymer

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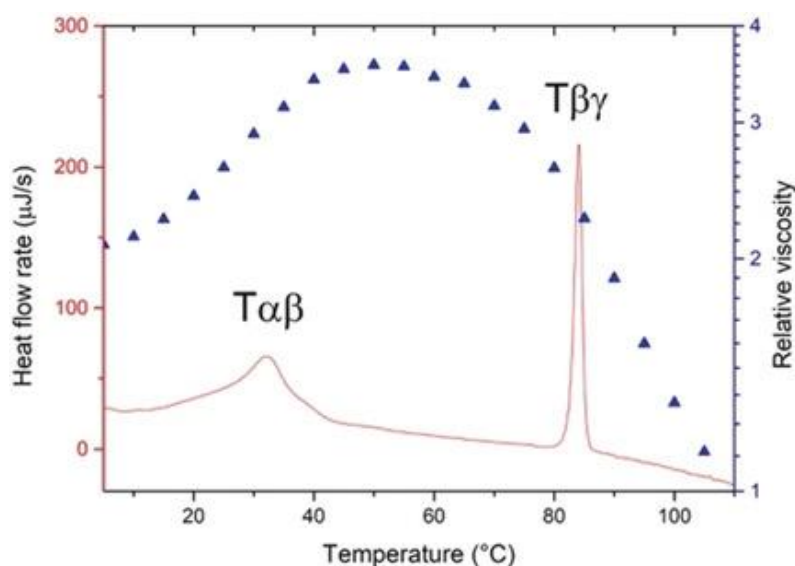
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Introduction of competing interactions in the design of a supramolecular polymer (SP) creates pathway complexity. ^[1] Ester–bis-ureas contain both a strong bis-urea sticker that is responsible for the build-up of long rod-like objects by hydrogen bonding and ester groups that can interfere with this main pattern in a subtle way. ^[2] Spectroscopic (FTIR and CD), calorimetric (DSC), and scattering (SANS) techniques show that such ester–bis-ureas self-assemble into three competing rod-like SPs. The previously unreported low-temperature SP is stabilized by hydrogen bonds between the interfering ester groups and the urea moieties. It also features a weak macroscopic alignment of the rods. The other structures form isotropic dispersions of rods stabilized by the more classical urea-urea hydrogen bonding pattern. The transition from the low-temperature structure to the next occurs reversibly by heating and is accompanied by an increase in viscosity, a rare feature for solutions in hydrocarbons.



An ester–bis-urea self-assembles into three competing rod-like structures in non-polar solvents. ^[3]

Références :

[1] F. Helmich, C. C. Lee, M. M. L. Nieuwenhuizen, J. C. Gielen, P. C. M. Christianen, A. Larsen, G. Fytas, P. E. L. G. Leclère, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem., Int. Ed.* **2010**, 49, 3939–3942.

[2] M. Dirany, V. Ayzac, B. Isare, M. Raynal, L. Bouteiller, *Langmuir* **2015**, 31, 11443–11451.

[3] Ayzac, V., Sallembien, Q., Raynal, M., Isare, B., Jestin, J., Bouteiller, L. *Angew. Chem. Int. Ed.* **2019**, 1433-7851

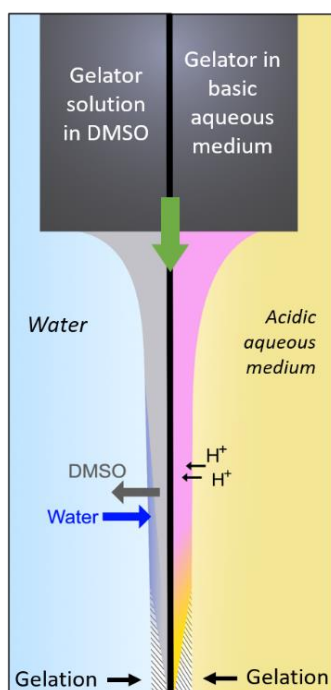
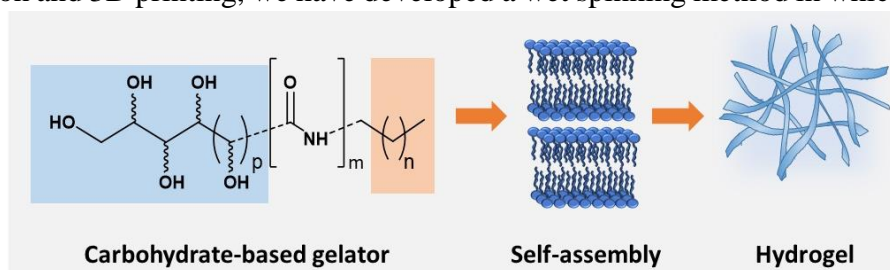
Wet spinning of carbohydrate supramolecular hydrogels: From solvent conditions to only aqueous conditions

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Small amphiphile molecules with a carbohydrate polar head, a fatty chain, and amide linkers self-assemble through non-covalent bonds in supramolecular fibers in water, leading to the formation of hydrogels. We have previously shown that some of them, N-alkyl-D-galactonamides, are biocompatible and can be used as new fibrous scaffolds for 3D cell culture (1). These hydrogels cannot be injected directly because they are not thixotropic and they are mechanically fragile. To make them suitable for injection and 3D printing, we have developed a wet spinning method in which the gelation is triggered by injecting a solution of the gelator in a good solvent into a bath of water. The very fast self-assembly of the molecules in contact with water leads to a quick setting of the gel (2).



In wet spinning conditions, long filaments of gel are formed. The first method consists in solubilizing the gelator in dimethylsulfoxide (DMSO) which is one of the scarce good solvents of these molecules (2). In order to get rid of this organic solvent, we explored the possibility to dissolve the gelator in a strongly basic aqueous solutions. Despite the absence of obvious acido-basic groups in N-alkyl-D-galactonamides, the molecules dissolve in strongly basic aqueous medium, mediated by the deprotonation of sugar hydroxyls. The injection of this solution in an acidic aqueous solution triggers the gelation in gel filaments, in the same way as for DMSO/water exchange. A well-defined base to acid transition can be visualized along the jet thanks to colored pH indicators and compared with the gelation onset.

As a result, we showed that N-alkyl-D-galactonamides can still give hydrogel filaments in only aqueous conditions. These conditions are interesting to avoid the use of an organic solvent in the context of green chemistry. In these new conditions, the wet spinning of these hydrogels could be used to support the formation of other colloidal objects triggered by acido-basic reactions. They could be transposed also to 3D printing (3).

References

- [1] Chalard, A.; et al. Simple Synthetic Molecular Hydrogels from Self-Assembling Alkylgalactonamides as Scaffold for 3D Neuronal Cell Growth. *ACS Appl. Mater. Interfaces*, **10**, 17004–17017, **2018**.
- [2] Chalard, A.; et al. Wet Spinning and Radial Self-Assembly of a Carbohydrate Low Molecular Weight Gelator into Well Organized Hydrogel Filaments. *Nanoscale*, **11**, 15043–15056, **2019**.
- [3] Andriamiseza, F. et al. 3D Printing of Biocompatible Low Molecular Weight Gels: Imbricated Structures with Sacrificial and Persistent N-Alkyl-d-Galactonamides. *Journal of Colloid and Interface Science*, **617**, 156–170, **2022**.

Poly(styrene-co-benzyl methacrylate)-b-poly[(ethylene glycol) methyl ether acrylate] star and linear block copolymers as solid electrolytes for Lithium-ion batteries

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Abstract:

Block copolymers (BCP) are of particular interest to improve performances of lithium-ion batteries because of their nanostructured morphologies and the possibility to decouple antagonist properties such as ion conductivity and mechanical strength. Herein, the controlled synthesis and characterization of a series of star ($f = 4$) and linear block copolymers, poly(styrene-co-benzyl methacrylate)-b-poly[(ethylene glycol) methyl ether acrylate] solid electrolytes, are reported. The self-assembly of the block copolymers is influenced by the presence of lithium salt and has been studied by atomic force microscopy (AFM), transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). Dynamic rheological testing verifies that these BCPs films are mechanically robust, and impedance spectroscopy reveals remarkable ionic conductivities. Finally, all those experimental results will be discussed to point out the structure/properties relationship.

Catalyst-free transesterification vitrimers: the remarkable activating effect of Fluorine.

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Vitrimers¹ are polymer networks in which associative exchange reactions can take place under specific conditions, and confer reprocessability to the insoluble materials.² Recently, catalyst-free vitrimers have emerged as a new generation of vitrimers able to overcome potential leaching, ageing and sintering issues of catalysts and to ensure the preservation of the vitrimer properties after numerous reshaping processes.³

Here, we present a novel approach to prepare catalyst-free transesterification vitrimer. The transesterification reactions usually catalyzed using an organometallic complex or a nucleophile, are, in our materials, activated by the presence of fluorinated groups located at the alpha or beta position of the ester groups (Figure1). Due to the high electron-withdrawing effect of fluorine, these activating groups not only vastly accelerate the network formation (acid ring opening reaction of epoxydes) but also strongly promote the transesterification reactions at relatively low temperature (150°C), thus allowing easy reshaping of polymer networks. This original approach, very efficient for transesterification vitrimers, is likely also applicable to other Covalent Adaptable Networks relying on other exchange reactions.

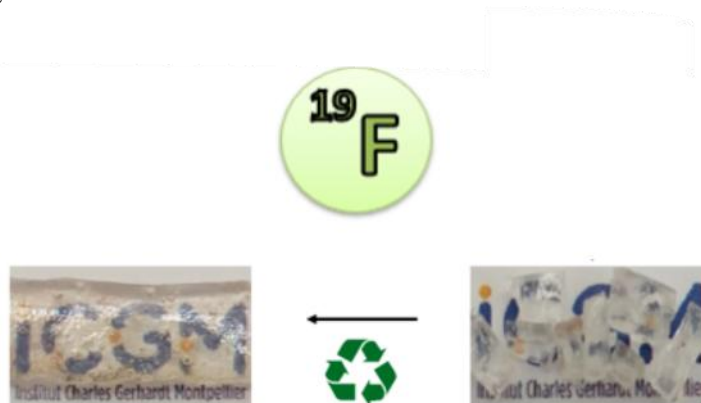


Figure 1: Reshaping of crosslinked epoxy-acid network via transesterification activated by Fluorine atoms.

Références :

- [1] N. J. Van Zee, R. Nicolaÿ, *Prog. Polym. Sci.* **696** 104, No. 101233, **2020**.
 [2] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, L. *Science* **334**, 965–968, **2011**.
 [3] F. Cuminet, S. Caillol, E. Dantras, E. Leclerc, V. L Admiral, *Macromolecules* **54**, 3927–3961, **2021**.

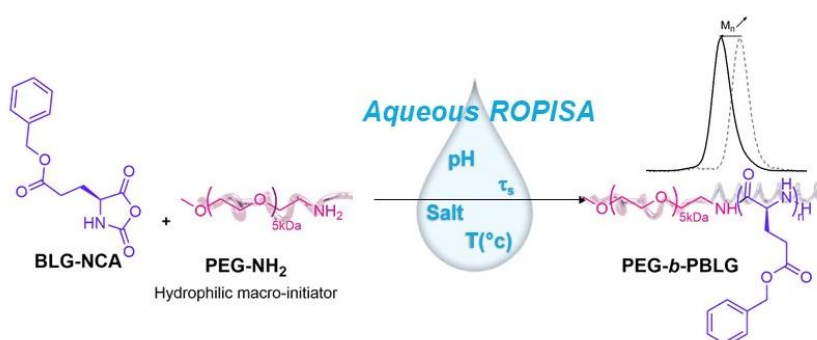
Key reaction conditions in aqueous ROPISA of N-carboxyanhydrides H. Beauseroy^a, S. Antoine^a, S. Lecommandoux^a, C. Bonduelle^a

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Polypeptides are promising polymers made of amino acids offering several interesting features including (i) imparting chemical functionality by taking advantage of the wide scope of naturally available monomer units; (ii) improving chemical and enzymatic degradability; and (iii) providing metabolizable building blocks.¹ Polypeptide polymers are usually synthesized by ring-opening polymerization (ROP) of N-carboxyanhydride (NCA). NCA polymerization still suffers from significant limitations including tedious monomer purification steps, significant sensitivity to moisture, and processing in anhydrous solvents. Recent progresses have nevertheless been impressive: efforts have focused on promoting the polymerization with more reactive initiators and using heterogeneous processes including emulsion polymerization.²

While NCAs are known to degrade in the presence of water, we recently reported the ROP of NCAs in buffered aqueous solution using a hydrophilic macroinitiator leading to well-defined copolymers which simultaneously form anisotropic nano-objects. In this process, the NCAs hydrolysis is avoided through a combination of rapid copolymerization and monomer protection by spontaneous *in situ* self-assembly.^{3,4} Although the mechanism of this ROPISA process is until now poorly understood, in this talk, we present the influence of several key parameters on the copolymer formation. We developed a comprehensive study by implementing ROPISA with an α -amino-poly(ethylene glycol) (PEG-NH₂) as a macroinitiator and γ -benzyl-L-glutamate NCA (BLG-NCA) as a monomer. The impact of the pH, the solids content, the buffer nature and the reaction temperature on the control of the polymerization were examined. We found that controlling the pH and the buffer concentration was particularly important to avoid unwanted NCAs hydrolysis and water-initiated ROP. The solid content displayed a low-limit value, below which the polymerization was no longer controlled. These results provide a better understanding of ROPISA which will allow us to adapt this process to other macroinitiators and NCAs.



Scheme 1: Ring-opening polymerization induced self-assembly (ROPISA) of BLG-NCA monomer, initiated by a α -amino-poly(ethylene glycol), in different aqueous media

References :

- [1] Song, Z.; Tan, Z.; Cheng, J. *Macromolecules*, **52** (22), 8521–8539, **2019**.
- [2] Song, Z.; Han, Z.; Lv, S.; Chen, C.; Chen, L.; Yin, L.; Cheng, J. *Chem. Soc. Rev.*, **46** (21), 6570–6599, **2017**.
- [3] Grazon, C.; Salas-Ambrosio, P.; Ibarboure, E.; Buol, A.; Garanger, E.; Grinstaff, M. W.; Lecommandoux, S.; Bonduelle, C. *Angew. Chem. Int. Ed.*, **59** (2), 622–626, **2020**.
- [4] Grazon, C.; Salas-Ambrosio, P.; Antoine, S.; Ibarboure, E.; Sandre, O.; J. Clulow, A.; J. Boyd, B.; W. Grinstaff, M.; Lecommandoux, S.; Bonduelle, C. *Polym. Chem.* **12**, 6242–6251, **2021**.

Study of flame-retardant thermoplastics for the numerical simulation of thermoforming process.

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To face low cost airline companies competition, conventional airline companies focus on modernizing and upgrading their planes and especially the business class cabin. This results into an ever greater requirement on the quality of interior parts, mainly made of flame-retardant thermoplastics, manufactured by thermoforming [1]. The perfect mastery of this process is therefore essential for aeronautical subcontractors. For this, numerical simulation is a valuable tool.

In this work, two flame-retardant polymers based on polycarbonate and PVC acrylic were fully characterized in terms of thermal, mechanical, and rheological properties in order to provide the necessary input data for numerical simulation :

- (i) Deformations in uniaxial elongation near thermoforming temperature were investigated for both polymers with an Sentmanat Extensional Rheometer (SER). This data will feed visco-elastic models such as K-BKZ model [2] in order to describe the polymers deformations during thermoforming process
- (ii) Dynamic Mechanical Analysis in temperature were used to describe mechanical properties near the rubber plating and the evolution of the glassy transition temperature as a function of the heating speed in order to understand the behavior of the material during heating.
- (iii) In order to evaluate the friction between polymer and thermoforming molds, additional friction measurements between polymers and different surface roughness aluminum were made. Temperatures from 25°C to above glass transition were investigated using a rotary rheometer according to the HEGEMANN [3] method.

Références :

- [1] J. JAMMET, F. PINSOLLE, *Thermoformage*, Techniques de L'ingénieur, **2019**
- [2] B. BERNSTEIN, E. A. KEARSLEY, and L. J. ZAPAS, *Transactions of The Society of Rheology*, vol. 7, p. 391–410, **1963**
- [3] B. HEGEMANN, *Thermoforming Quarterly*, vol. 22, p. 10-13, **2003**

RAFT Polymerization of *N*-Methyl-*N*-Vinylacetamide and Related Double Hydrophilic Block Copolymers

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Poly(*N*-vinylamide)s are water-soluble polymers known for decades as aqueous formulation additives for diverse applications.^[1] They can be categorized into two families depending on the either cyclic or non-cyclic nature of the amide group of their constitutive monomers.

Among the non-cyclic derivatives, industrial *N*-vinylformamide (NVF), *N*-vinylacetamide (NVA) and *N*-methyl-*N*-vinylacetamide (NMVA) are precursors of homopolymers and copolymers that are widely used in various applications, often in their polyvinylamines form. Unlike their cyclic counterparts, only a few studies report their reversible-deactivation radical polymerization.^[2,3] Moreover, surprisingly no general study could be found on their Reversible Addition–Fragmentation chain-Transfer (RAFT) polymerization. Only a few works dealt with the use of the RAFT polymerization of NVF and NVA,^[4,5] but only for accessing diblock copolymers and without any convincing proof of the controlled character of polymerization.

Here, studies on the bulk RAFT polymerization of NMVA were conducted using xanthate and dithiocarbamate chain transfer agents at 35°C, with a purposely high $[V-70]_0/[RAFT\ agent]_0$ ratio. Cyanomethyl *O*-ethyl carbonodithioate and cyanomethyl diphenylcarbamodithioate allowed the synthesis of poly(*N*-methyl-*N*-vinylacetamide) (PNMVA) with predetermined M_n and relatively low dispersities ($\mathcal{D} < 1.5$). A good thiocarbonylthio end-group fidelity was revealed by ¹H NMR, mass spectrometry, chain extension experiment and block copolymer synthesis. Two double hydrophilic poly(ethylene oxide)-*b*-poly(*N*-methyl-*N*-vinylacetamide) (PEO-*b*-PNMVA) and poly(*N*-isopropylacrylamide)-*b*-poly(*N*-methyl-*N*-vinylacetamide) (PNIPAAm-*b*-PNMVA) diblock copolymers were successfully synthesized, the latter exhibiting a Lower Critical Solution Temperature (LCST) with reversible formation of colloidal aggregates in water.

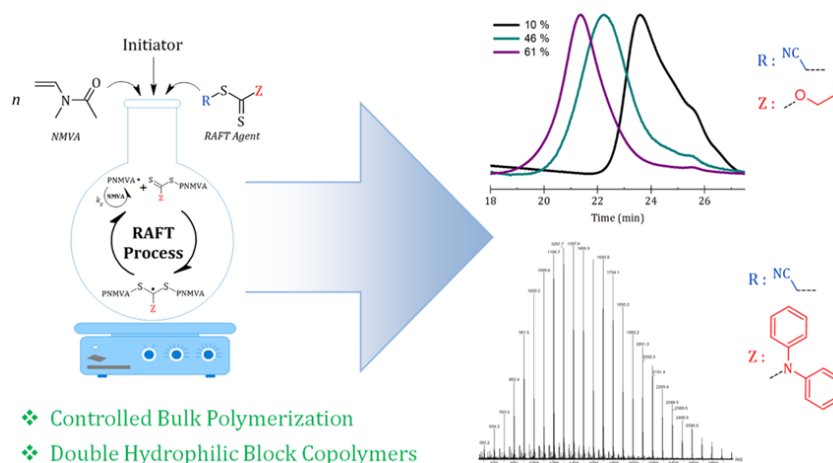


Figure 1: General description of the RAFT polymerization of NMVA and characterization by mass spectrometry and size exclusion chromatography.

Références :

- [1] Y.E. Kirsh, *Water Soluble Poly-N-Vinylamides: Synthesis and Physicochemical Properties.*; Wiley, **1998**
- [2] M. Dréan, P. Guégan, C. Detrembleur, C. Jérôme, J. Rieger, A. Debaigne, *Macromolecules*, **49**, 4817-4827, **2016**
- [3] W. Fan, S. Yamago, *Angew. Chem. Int. Ed.*, **58**, 7113-7116, **2019**
- [4] L. Shi, T.M. Chapman, E.J. Beckman, *Macromolecules*, **36**, 2563-2567, **2003**
- [5] Y. Lou, D.J. Shi, W.F. Dong, M.Q. Chen, *Adv. Mater. Res.*, **645**, 10-14, **2013**

Waterborne Organic Semiconductor Dispersions for Photovoltaics

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The growing demand for energy worldwide appears as a top priority for the next decades. The use of carbon-neutral energy sources appears as mandatory, especially in a context of sustainable development. Organic photovoltaics (OPV) is as a strong candidate, harvesting the energy provided by the sun through flexible, transparent and low-cost solar cells. However, the processing of OPV devices still needs to address some issues, such as the use of organic and hazardous solvents in order to process the active layer. Their elimination is next step for large scale production and would help to reduce the potential risk towards human health or the environment.

A new way to design OPV appeared two decades ago, in which the active material are dispersed as nanoparticles in water or ethanol, and not solubilised in an organic solvent (Figure 1).¹ To do so, several post-polymerization preparation techniques are investigated, mainly the miniemulsion and the nanoprecipitation. In 2018, a record in efficiency of 7.5% for water-based solar cells showed the potential of the nanoparticle approach for OPV.² More recently, the use of the same approach was imagined for other way to produce and store energy.³

However, new challenges need to be addressed in order to reach the efficiencies obtained with more classical OPV. For instance, the internal morphology and the size of the nanoparticle strongly influence the final performances. Another limitation lies in the insulating behaviour of surfactants, mandatory to reach stable and concentrated dispersions.

We aim to present our results related to the P3HT:PC₆₁BM system, which is a reference system in OPV. Nanoparticle dispersions are prepared through nanoprecipitation, and the addition of a surfactant during the preparation step enables the generation of stable and strongly concentrated dispersions, suited for film deposition. A special interest is given to the nanoparticle morphology and the optimization of the experimental conditions to achieved highly concentrated nanoparticle dispersions. In order to characterize them, Dynamic Light Scattering, Cryo-TEM, UV-Visible spectroscopy, Photoluminescence and Atomic Force Microscopy were used, as well as the integration of nanoparticles in devices.

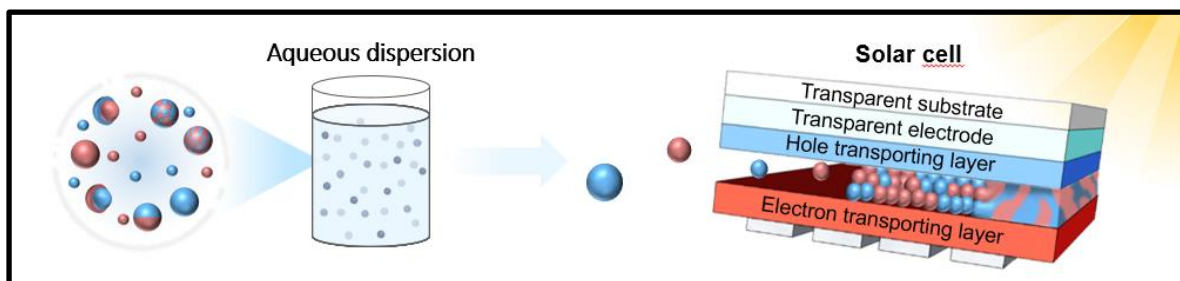


Figure 1: Schematic representation of the nanoparticle approach for the deposition of the active layer in organic solar cells.

Références :

- (1) Holmes, A.; Deniau, E.; Lartigau-Dagron, C.; Bousquet, A.; Chambon, S.; Holmes, N. P. *ACS Nano*, 15, 3, 3927–3959, **2021**.
- (2) Xie, C.; Heumüller, T.; Gruber, W.; Tang, X.; Classen, A.; Schuldes, I.; Bidwell, M.; Späth, A.; Fink, R. H.; Unruh, T.; McCulloch, I.; Li, N.; Brabec, C. J. *Nat. Commun*, 9 (1), 5335, **2018**.
- (3) Holmes, N. P.; Chambon, S.; Holmes, A.; Xu, X.; Hirakawa, K.; Deniau, E.; Lartigau-Dagron, C.; Bousquet, A. *Curr. Opin. Colloid Interface Sci.*, 56, 101511, **2021**.

Tuning the dielectric response of PVDF-based copolymer films by the optimization of the ink formulation and printing process.

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This study aims to establish the correlation between the printing process and the electroactive properties of the PVDF-based copolymer films deposited by the doctor-blade technique. A first study was dedicated to the formulation of PVDF-based copolymer inks, varying the solvent and concentration, in order to evaluate the viscoelastic properties of the inks during the film deposition. Accordingly, the viscoelastic characteristics of the inks under shear were evaluated by rheological measurements and the rheological behavior was linked to the PVDF-based copolymer chain conformation/aggregation in solution using cryo-microscopy and light scattering measurements.

In a second step, the deposition of PVDF-based copolymer films was performed by doctor-blade using different shear rates and temperatures in order to generate homogeneous layers for further structural and functional characterization. The effects of the different processing parameters and physical-chemical ink characteristics were then linked to the morphology, crystallinity and electroactive properties of the films. Surface characterization techniques like AFM qualitatively demonstrated the modification of the textures of the films with the processing parameters (in particular with the formation of extended fibrillar structures). Such relationships between the ink formulation and the film structural properties were also demonstrated by other quantitative techniques such as WAXS, RAMAN, and DSC which provided information on the crystalline structure of the PVDF-based copolymer films. Finally, the final electroactive properties of the films were measured using dielectric spectroscopy and polarization loops in order to rationalize the relationships between the printing process and the functional electroactive properties.

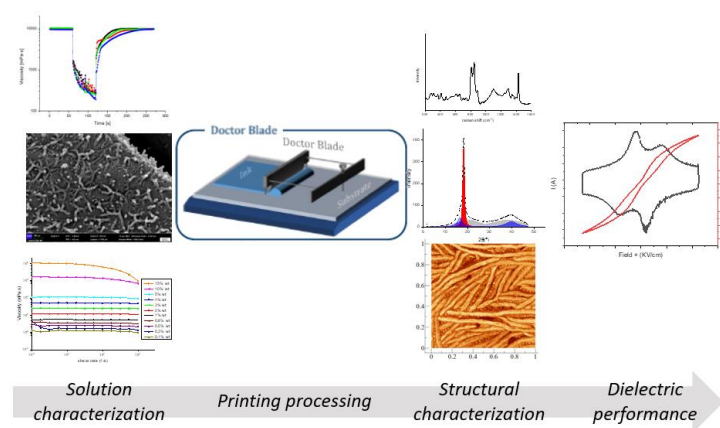


Figure 1 schematic illustration of the methodology used to establish the structure/property relationships for the formation of PVDF-based copolymer films by doctor-blade.

References

- [1] A. Glasser, E. Cloutet, G. Hadziioannou, H. Kellay, Chemistry of Materials 31(17),6936-6944 **2019**
- [2] F. Le Goupil, F. Coin, N. Pouriamanesh, G. Fleury, G. Hadziioannou ACS Macro Letters 10 (12), 1555-1562 **2021**
- [3] McGinn,C. and Al. ,J. Appl. Phys, 128, 225304 (2020).

Photo-Polymerization Induced Microphase Separation from Acrylic Block Copolymers

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Photo-polymerization allows to obtain a solid-like polymer materials in few minutes from a monomer mixture as initial resin. This rapid implementation will be a real advantage if similar properties are achieved, compared with other processes such as thermal polymerization which can take several hours. Moreover, light curing can offer a spatial control which is of interest to achieve materials with complex shapes. For those reasons, photo-polymerization is more and more used nowadays, with a significant development for 3D Printing [1, 2].

However, the development of nanostructured polymer materials generated by photo-polymerization or 3D Printing remains a real challenge to cater for both time scales of self-assembly and photo-polymerization. The aim of our project is to control the morphology of photo-polymerized and 3D Printed samples using the photo-Polymerization Induced Microphase Separation (photo-PIMS) process [3], in order to obtain rubber-toughened acrylic materials. A way to control the morphology (macro and/or micro phase separation) is the addition of a pre-synthesized block copolymer in the liquid monomer, in order to drive the phase separation during the photo-polymerization process.

The block copolymer synthesis will be presented with a full characterization (*Fig. 1*) as well as the effect of the pre-synthesized block copolymers on the phase separation during photo-polymerization.

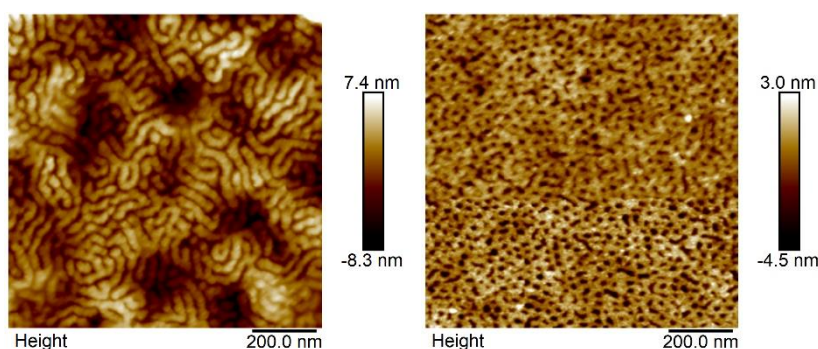


Figure 1: AFM height images of synthesized block copolymers with weight ratios of hard/soft blocks of 50/50 (left) and 70/30 (right)

References

- [1] A. Bagheri, J. Jin, *ACS Appl. Polym. Mater.* **1**, 593–611, **2019**
- [2] Y. Zhang, Y. Xu, A. Simon-Masseron, J. Lalevée, *Chem. Soc. Rev.* **50**, 3824–3841, **2021**
- [3] J. Lequieu, A. J. D. Magenau, *Polym. Chem.* **12**, 12–28, **2021**

Sustainable synthesis of polymer networks

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The awareness of environmental deterioration and our dependency on depleting fossil feedstocks forces research to find innovative solutions in order to design a more sustainable future.^[1] Improving the sustainability of polymer networks is a crucial challenge in polymer science, due to their important role in industry. Their traditional syntheses conflict with several principles of *Green Chemistry* as the employed monomers are petroleum-based, their production involves the use of toxic reagents and their permanently cross-linked structures impede their chemical recycling and reshaping. These aspects will be addressed in the presentation using lignin-derived phenolic compounds and terpene-based derivatives as renewable feedstocks. The use of safer synthetic procedures will be illustrated by (i) the development of an enzymatic dimerization process for the sustainable production of biobased biphenyl compounds^[2] and (ii) the replacement of classic toxic allylation procedures by more sustainable catalytic alternatives using palladium nanoparticles stabilized by poly(vinylpyrrolidone) as highly efficient catalysts for the Tsuji-Trost reaction^[3]. An approach to enhance the recyclability of thermoset materials by the design of biobased cleavable monomers will also be exposed. In this work, vanillyl alcohol was modified by an allylation and, in some cases, epoxidation procedure. In order to introduce recyclability into the final polymer networks, the modified vanillin building blocks were subsequently coupled to form dimeric structures bearing cleavable linker groups. The dienes were later polymerized by thiol-ene reaction with a myrcene-based trithiol to prepare transparent cross-linked films. The diglycidyl ethers were investigated as substitutes of bisphenol A for the preparation of epoxy resins by combination with limonene-based monomers. Finally, different degradation conditions were explored to establish a protocol for the controlled degradation of the cross-linked polymers. In a first step, the cleavable monomers were used as model systems to identify suitable degradation conditions. Subsequently, the most promising conditions were transferred to the polymer films to prove the degradability of the polymer network.

Références :

- [1] A. Llevot, P.-K. Dannecker, M. von Czapiewski, L. C. Over, Z. Söyler, M. A. R. Meier, *Chemistry – A European Journal*, **22**, 11510, **2016**
- [2]. A. Llevot, E. Grau, S. Carlotti, S. Grelier and H. Cramail, *Journal of Molecular Catalysis B: Enzymatic*, **125**, 34-41, **2016**
- [3] A. Llevot, B. Monney, A. Sehlinger, S. Behrens and M. A. R. Meier, *Chemical Communications*, **53**, 5175-5178, **2017**.

Coordination adaptable networks : zirconium carboxylates

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Vitrimers are associative covalent adaptable networks (CAN) with dynamically exchangeable crosslinks above a defined temperature.^[1] To date, all feature organic crosslinks whereas vitreous silica that has inspired them is inorganic. Metal-organic frameworks (MOFs) are well-known 3D materials with metal complexes or clusters as crosslinks, but are not adaptable. We introduce a new vitrimer family, coordination adaptable networks (CooANs), where the vitrimer properties originate from degenerative ligand exchange on a metallic crosslink. Our initial studies have focused on the $[\text{Zr}_6(\text{O})_4(\text{OH})_4]$ unit as crosslink, which is common in MOF chemistry,^[3] and a 2-ethylhexyl methacrylate/2-carboxyethyl acrylate (90:10) copolymer^[2] as matrix. Note that $[\text{Zr}_6(\text{O})_4(\text{OH})_4]$ -crosslinked polymer networks have been obtained by radical copolymerization of MMA or styrene with $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{O}_2\text{CMeCH}=\text{CH}_2)_{12}]$,^[4] but the absence of free acid functions negates their possible reshaping. Using $[\text{Zr}_6(\text{O})_4(\text{OH})_4(\text{O}_2\text{CMe})_{12}]$ as crosslink source, a series of transparent flexible materials (Zr-CooAN-x) were obtained by carboxylic acid exchange at various COOH/Zr ratios ($x = \text{percent loading} = 5, 10, 15, 25, 50$). These materials exhibit low temperature reshaping without significant change of properties, as confirmed by DSC, DMA, TGA, IR and frequency sweep measurements. Parallel studies carried out with well-defined dicarboxylate linkers, $\text{HO}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2\text{H}$ ($n = 4$, adipic acid; $n = 8$, sebacid acid) indicate that only up to eight carboxylates are able to bind to the Zr_6 crosslinks in the network.

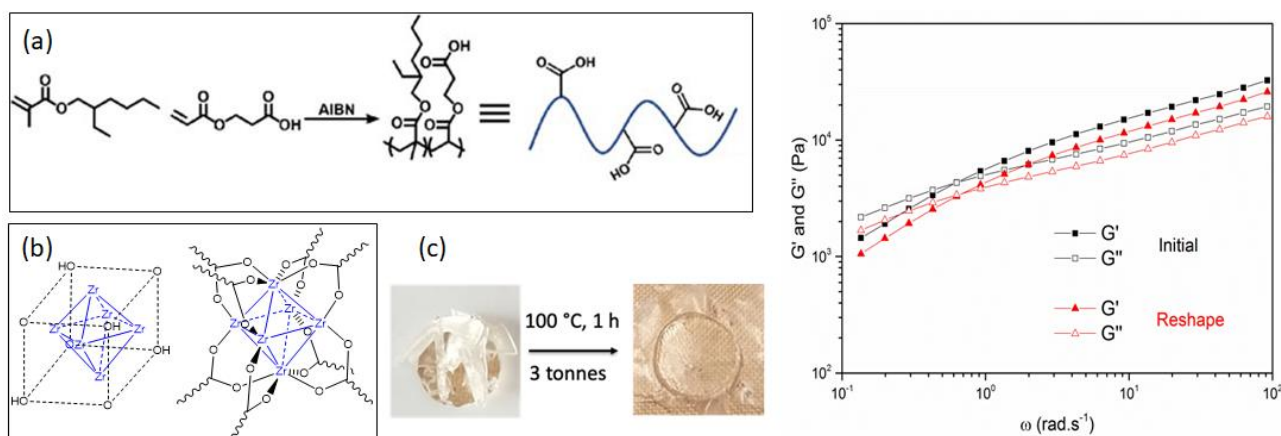


Figure 1:(a) Polymer; (b) Crosslinks used in the vitrimer synthesis; (c) Pristine and reshaped Zr-CooAN-25; (d) Frequency sweeps for Zr-CooAN-10

Références :

- [1] D. Montarnal, M. Capelot, F. Tournilhac, L. Leibler, *Science*, 334, 965-968, **2011**.
 [2] Y. Vidavsky, S. Bae, M. N. Silberstein, *J. Polym. Sci., Polym. Chem.*, 56, 1117-1122, **2018**.
 [3] a) J. H. Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.*, 130, 13850-13851, **2008**; b) T. Ntep, H. Reinsch, B. Moll, E. Hasturk, S. Goekpinar, H. Breitzke, C. Schlusener, L. Schmolke, G. Buntkowsky, C. Janiak, *Chem. Eur. J.*, 24, 14048-14053, **2018**.
 [4] a) G. Trimmel, P. Fratzl, U. Schubert, *Chem. Mater.*, 12, 602-604, **2000**. b) Y. Gao, F. R. Kogler, U. Schubert, *J. Polym. Sci., Polym. Chem.*, 43, 6586-6591, **2005**.

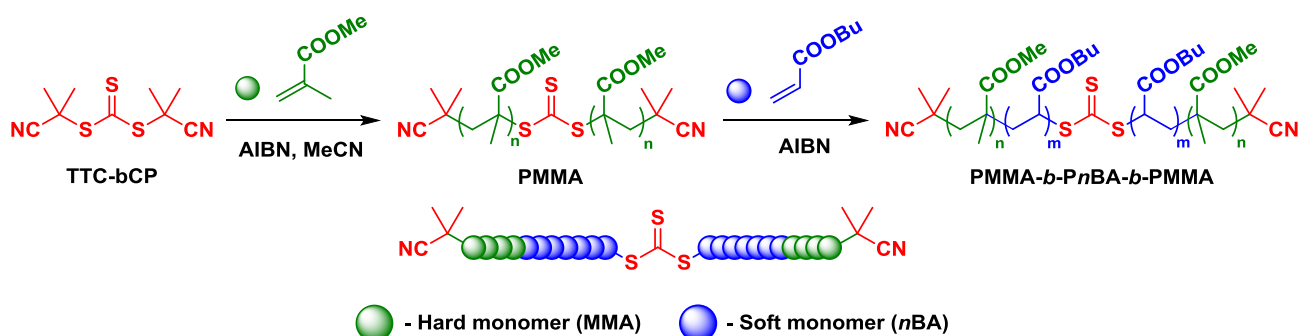
New symmetrical trithiocarbonate: from unprecedented RAFT control to thermoplastic elastomer materials

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We report a new symmetrical trithiocarbonate (TTC-bCP) [1] with the best leaving group ever reported for reversible addition-fragmentation chain transfer (RAFT) polymerization. This trithiocarbonate RAFT agent is particularly suited for the synthesis of narrowly dispersed poly(meth)acrylates of controlled molar mass. As an example, it allowed the preparation of a high molar mass ($M_n \sim 135 \text{ kg mol}^{-1}$) methyl methacrylate-*n*-butyl acrylate-methyl methacrylate triblock copolymer with unprecedented control ($\mathcal{D} = 1.04$) in reversible-deactivation radical polymerization. Furthermore, these well-defined triblock copolymers with thermodynamically immiscible soft and hard blocks exhibit thermoplastic elastomer (TPE) properties. The nature of (meth)acrylate monomers and molar masses of the hard and soft blocks can be easily varied thanks to RAFT polymerization, allowing the synthesis of all-(meth)acrylic TPEs with tailored properties.



Scheme 1. PMMA-PnBA-PMMA triblock copolymer synthesis mediated with TTC-bCP RAFT agent.

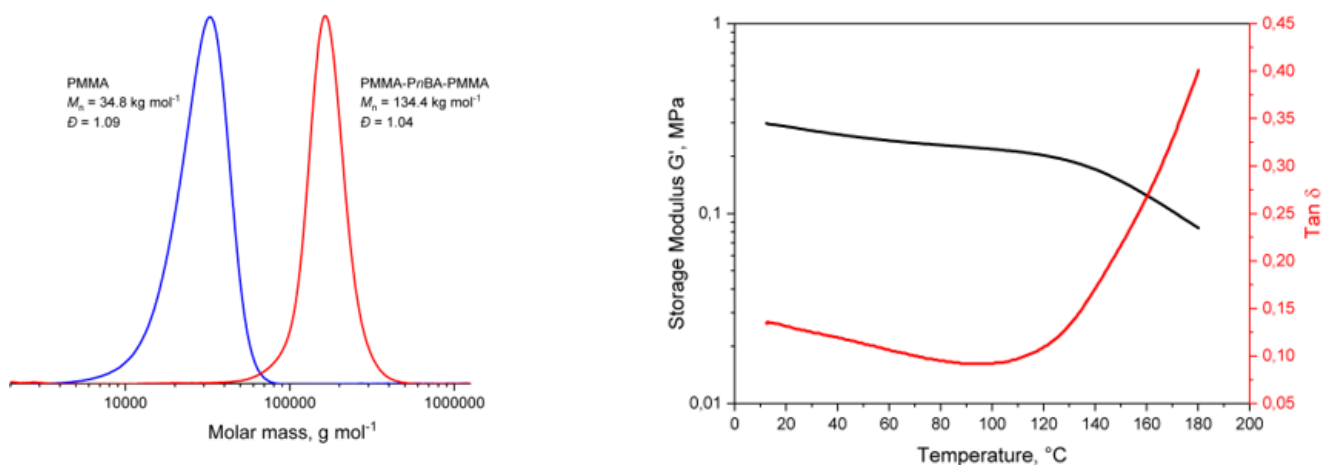


Figure 1. SEC traces (left) and temperature dependence of G' and $\tan \delta$ (right) of PMMA-PnBA-PMMA triblock copolymer.

References:

- [1] O. Ivanchenko, et al, *J. Am. Chem. Soc.*, 143, 20585-20590, **2021**

Gd³⁺/ Poly(ethylene oxide)-*b*-poly(acrylic acid-*co*-vinylphosphonic acid) hybrid polyionic complexes for MRI contrast agents : influence of the charged block composition on physical properties

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Magnetic resonance imaging (MRI) is one of the most common non-invasive medical imaging techniques for detecting a variety of diseases (brain tumor, breast cancer, multiple sclerosis, etc.). In order to increase image resolution and get more information from this method, so-called contrast agents (CAs) are used. CAs most often contain metal atoms (e.g. Gd³⁺) that shorten longitudinal T₁ relaxation time, making the MRI image brighter.¹ The main limitation of the use of Gd³⁺ is its toxicity and bioaccumulation in the body. Therefore, for clinical use, gadolinium must be associated with various complexes to avoid the release of the free ion. However, some of the commercialized chelate complexes are rapidly excreted from the body, capable of losing gadolinium ions, and also they have low relaxation values on modern MRI devices with high magnetic fields.²

We focus on the preparation of gadolinium-based CAs with anionic-neutral double hydrophilic block copolymers (DHBCs), by simply adding metal ion to the polymer to spontaneously obtain micelle-like nanostructures called hybrid polyionic complexes³ (HPICs) (Fig.1a). After first reports on Gd³⁺/poly(ethylene oxide)-*b*-poly(acrylic acid) (PEO-*b*-PAA) HPICs,³ we here consider vinylphosphonic acid as AA comonomer in reversible addition-fragmentation chain transfer (RAFT)-derived PEO-*b*-P(AA-*co*-VPA) DHBCs with different compositions of the AA/VPA block (Fig. 1b).

HPICs were obtained for all polymer compositions, their stability was tested in aqueous and NaCl solutions and at different pH values. Relaxation values and other physicochemical characteristics were determined. It was found that using pure PAA as the ionizable block gave the highest relaxation values but at the same time the lowest stability at low pH. In contrast, the use of VPA, gave higher stability, but lower relaxation.

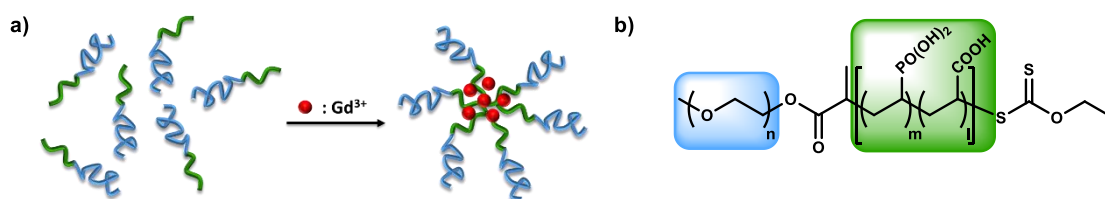


Figure 1: (a) Schematic representation of HPICs formation by adding Gd³⁺ to the DHBCs. (b) Chemical structure of the DHBCs with neutral (blue) and ionizable (green) blocks

To conclude, a compromise between the colloidal stability of Gd³⁺-based HPICs, in particular at low pH, and an acceptable level of relaxivity properties can be reached by varying the AA/VPA composition of the DHBC.

[1] E. Kanal, *Magnetic Resonance Imaging Clinics of North America*, **20**, 625–631, **2012**

[2] J. S. McDonald, R. J. McDonald, *Magnetic Resonance Imaging Clinics of North America*, **28**, 497–507, **2020**

[3] C. Frangville, Y. Li, C. Billotey, D. R. Talham, J. Taleb, P. Roy, J.-D. Marty, C. Mingotaud, *Nano Lett.*, **16**, 4069-4073, **2016**

Physico-chemical and morphological characterization of *Oreochromis niloticus*, *Salmo salar*, *Labeo rohita* and *Sardina pilchardus* fish scales

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The United Nation's Food and Agriculture Organization (FAO) 2020 report on "The State of World Fisheries and Aquaculture" [1] estimates that processing fish generate up to 70% of wastes. Among those, fish scales represent a large portion of the waste that is thrown away.

In this context, the aim of the present work is to characterize and understand the composition and the physico-chemical and morphological properties of different fish scales in order to valorize them into novel polymeric or hybrid materials. To do so, the focus will be placed on 2 main axes: (i) characterization of the selected fish scales in order to understand their physico-chemical and morphological properties (very few studies have tackled this aspects for sardine and salmon); (ii) extraction and characterization of the organic part (collagen) and the mineral part (hydroxyapatite). This study focuses on 4 fish species: *Oreochromis niloticus* or "tilapia", *Salmo salar* or "salmon", *Labeo rohita* or "rohu carp" and *Sardina pilchardus* or "sardine".

The physico-chemical characterization regroups TGA for the thermal degradation behavior, SEM and optic microscopy for the morphological properties, FTIR spectroscopy and SDS-PAGE for the chemical composition. In this communication, the difference in the ratio organic/mineral content within the different species of fish scales; the thermal behavior patterns; the organization of the collagen fibers made from bundles of small fibrils (Figure 1); and the type of collagen will be presented and discussed. Results from this study already gave useful insights for the development of new biobased material.



Figure 1: Biopolymeric fibers (collagen) from a cross-sectional view of *Oreochromis niloticus* scale

Références :

[1] FAO, *The State of World Fisheries and Aquaculture 2020*, ¹⁸ Sustainability in action, Rome, 2020

Synthesis of biobased amphiphilic copolymers as stabilizers of oil-in-water emulsions

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An emulsion is a metastable mixture of two or more non-miscible liquids generally stabilised by fossil-based emulsifiers, either surfactant molecules or amphiphilic copolymers or even particles. The slower desorption of macromolecular stabilizers from the interface of the oil/water drops makes them interesting candidates compared to molecular surfactants to improve the kinetic stabilization of the emulsions.¹ Pickering emulsions stabilized by particles are even more kinetically stable but amphiphilic stabilizers are still of interest for particle-free formulations required for some applications.

Since the last decade, there has been a growing interest in developing alternatives to fossil resources to prepare innovative formulations involving biomass feedstock. Our project aims at investigating the ability of biobased amphiphilic copolymers to stabilize efficiently oil-in-water emulsion. Early studies showed that hydrophobically modified poly(acrylic acid) (HMPAA) involving fossil-based alkyl pendant chains were efficient amphiphilic copolymers to stabilize dodecane-in-water emulsions.² In the present work, terpenes were chosen as aliphatic biomass not in competition with food supply chain to derivatize hydrophilic poly(acrylic acid) backbone to produce amphiphilic copolymers⁴. Note that the precursors for the synthesis of acrylic acid monomer can now be produced from biomass.⁵ Sunflower oil were used to prepare the biobased emulsions.

The objective of the present work is to investigate how the structural parameters of the biobased HMPAA will affect the stability and features of the emulsions: polymerization degree of PAA chain, substitution degree, concentration of copolymers in emulsion, concentration of buffer solution, and pH). Two kinds of amphiphilic polymers were targeted with either ester or amide bond between PAA and terpene chain. For that purpose, PAA backbone was synthesized by reversible addition fragmentation polymerization to control the molar mass of the hydrophilic backbone and assess its impact on stabilization of emulsion. Polyesters will be synthesized by direct esterification between PAA and terpene alcohol. Regarding polyamides, more stable to hydrolysis, an intermediate step of modification of the terpene is necessary⁶. The aim of this study is to determine the optimum structural parameters providing a long-term stability over several months to the emulsions.

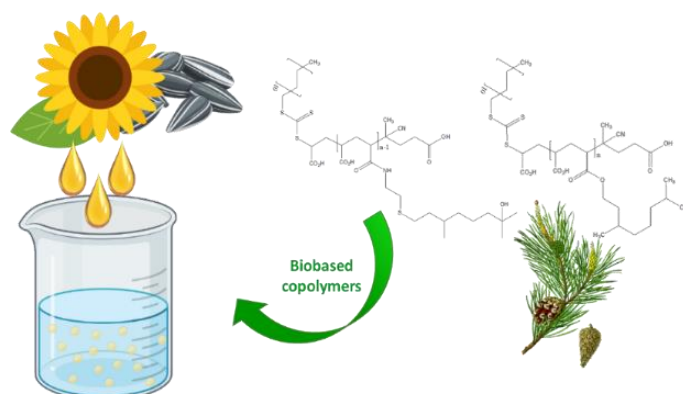


Figure 1: Sunflower oil-in-water emulsion with terpene-based amphiphilic copolymers as emulsifier

Références :

1. Atanase, L. I.; Riess, G. *Polymer International* **2011**, *60*, 1563-1573.
2. Perrin, P.; Lafuma, F. *Journal of colloid and interface science* **1998**, *197*, 317-326.
4. Atanase, L. I.; Larraya, C.; Tranchant, J. F.; Save, M. *European Polymer Journal* **2017**, *94*, 248-258.
5. Meng, X.-s.; Tsobanakis, P.; Malsam, J.; Abraham, T. WO 2005/003074 A1, 2005.
6. Alvès, M.-H.; Sfeir, H.; Tranchant, J.-F.; Gombart, E.; Sagnon, G.; Caillol, S.; Billon, L.; Save, M. *Biomacromolecules* **2014**, *15*, 242-251.

Use of Emulsion Templating to Obtain Porous Polymeric-Based Materials from Kraft Black Liquor

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Kraft black liquor is a cheap by-product of paper industry mainly composed of an alkaline solution of lignin and hemicellulose fragments. This solution has been successfully emulsified in presence of a chlorinated solvent (*i.e.* 1,2-dichloroethane) as well as epichlorohydrin (as a crosslinker) to give materials with a porosity up to 70 %v of the total volume.[1] Different methods of emulsification have been tried. On the one hand, a conventional stirred reactor with an anchor-type impeller. On the second hand, a “laboratory-made” two-syringes emulsification device has been used to shear the emulsion.[2] Both materials have been calcinated in an oven to give porous carbonaceous foams (CarboHIPE), with a total specific area up to 1000 m².g⁻¹. [3] Such specific area could be increased by the presence of metallic nanoparticles at the surface. With these particles, these carbon-based materials could be used in catalysis or hydrogen storage.

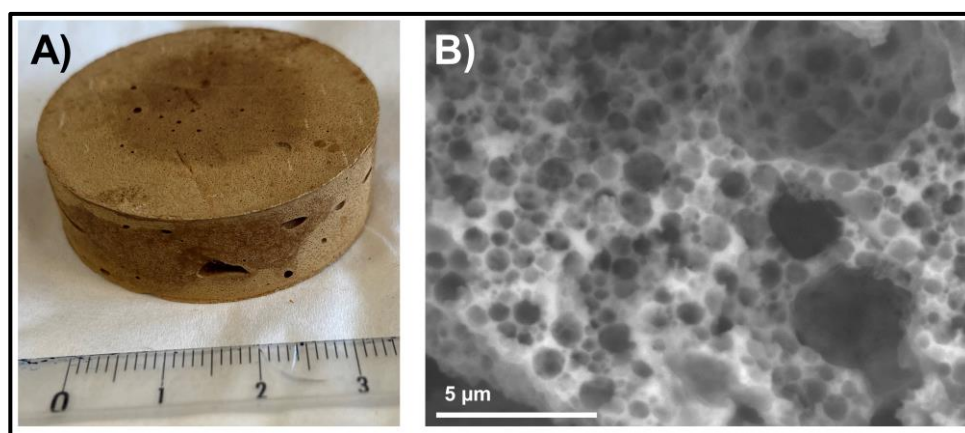


Figure 1: A) Photograph of a Kraft black liquor-based HIPE sample (ruler in centimeter) & B) SEM picture of the sample porosity

Références :

- [1] A. Foulet, M. Birot, G. Sonnemann, H. Deleuze, *Reactive and Functional Polymers*, **90**, 15-20, **2015**
- [2] O. Lépine, M. Birot, H. Deleuze, *Colloid and Polymer Science*, **286**, 1273-1280, **2008**
- [3] A. Foulet, M. Birot, R. Backov, G. Sonnemann, H. Deleuze, *Materials Today Communications*, **7**, 108-116, **2016**

Rationally designed bis-carbene building blocks for functional polymer synthesis

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Singlet carbenes have undergone considerable developments over the past three decades, on the one hand as transition metal ligands, on the other as organic catalysts in (macro)molecular chemistry [1,2,3]. In the context of polymer chemistry, polymerization of bis-carbene through dimerization reaction has been reported [4,5,6] but their use as true monomeric specie remains underexplored. In this work, we aim to explore the reactivity of acyclic amino-aryl bis-carbenes as true monomers in insertion reaction with difunctional partners. Presence of tertiary amino groups in the polymer backbone offer the possibility of tuning the physical-properties by a structural variation of the bis-carbene. This type of carbenes is known to selectively dimerize accessing to new amino containing poly(*p*-phenylene vinylene)s (N-PPVs) [7]. The objective here is to avoid the dimerization reaction and access a wide range of hybrid polymers through insertion reaction. Model molecular compounds will therefore be established and transposed later to difunctional models. Model reactions are required to master the precursor reactivity and overcome dimerization, promoting then insertion into various bonds (O-H, Si-H, C-H...). Hence, we propose here a new methodology to access this type of polymers involving a previous study of the reactivity towards different partners.

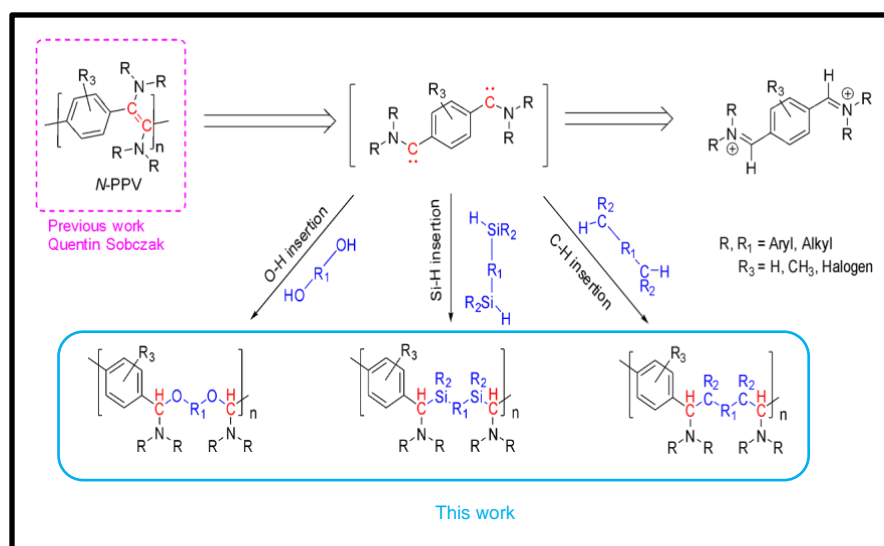


Figure 1: Synthetic strategy for new acyclic amino aryl polymers

References:

- [1] A. Igau, H. Grutzmacher, A. Baceiredo, G. Bertrand, *J. Am. Chem. Soc.*, **110**, 6463–6466, **1988**
 [2] A. J. III. Arduengo, R. L. Harlow, M. A. Kline, *J. Am. Chem. Soc.*, **113**, 361–363, **1991**

-
- [3] W. A. Herrmann, *Angew. Chem. Int. Ed.*, **41**, 1290–1309, **2002**
- [4] J. W. Kamplain, C. W. Bielawski, *Chem. Commun.*, **16**, 1727–1729, **2006**
- [5] A. G. Tennyson, B. Norris, C. W. Bielawski, *Macromolecules*, **43**, 6923–6935, **2010**
- [6] B. M. Neilson, A. G. Tennyson, C. W. Bielawski, *J. Phys. Org. Chem.*, **25**, 531–543, **2012**
- [7] Q. Sobczak, A. Kunche, D. Magis e, *Nat. Commun.*, **12**, 4093, **2021**
- Sobczak, A. Kunche, D. Magis, D. Sosa Carriso, K. Miqueu, J-M. Sotiropoulos, E. Cloutet, C. Brochon, Y. Landais, D. Taton, J. Vignolle, *Nat. Commun.*, **12**, 4093, 2021

Study of the impact of flour mixing on prolamin assemblies within the gluten by force flow fractionation

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Gluten is a three-dimensional network made up of the cereal's reserve proteins (prolamins) : glutenins and gliadins. Glutenins form the network and give gluten its elastic properties, while gliadins, monomeric objects, are responsible for the viscous properties of gluten. Traditionally these proteins, insoluble in water, are extracted from solutions containing surfactants and a sonification step. This efficient extraction technique tends to denature the conformation and molar mass of the proteins. A soft extraction was implemented using a "good solvent" extraction method (water/ethanol, 50/50 v/v) allowing for the extraction of prolamins with limited denaturation^{1,2}. Thanks to this soft-extraction coupled to the force flow fractionation methods (AsFIFFF), it was possible to study the whole population of proteins present in the extract and to study their structures. The presence of assemblies composed mainly of glutenins and ω -gliadins in the gluten network was revealed³. Moreover, Ramos et al., 2021 showed that the rheological properties of a gluten gel is impacted by the content of assemblies present in the gel⁴. In order to better understand the dynamics around these assemblies, different extracts of prolamins from flour and gluten were studied. The first AsFIFFF analyses show differences in profiles depending on the source of prolamin, with notably a lower population of assemblies for flour proteins than for gluten proteins. This difference in population can be explained by the mixing of the dough when obtaining the gluten. Based on these results, the flours were mixed at different times in order to measure the impact of mixing. Thus, the fractograms obtained in AsFIFFF show a correlation between the rate of assemblies and the mixing time of the dough. Moreover, the content of assemblies is directly related to the level of glutenins present in the extract. Mixing the dough also seems to impact the conformation and structure of the assemblies present.

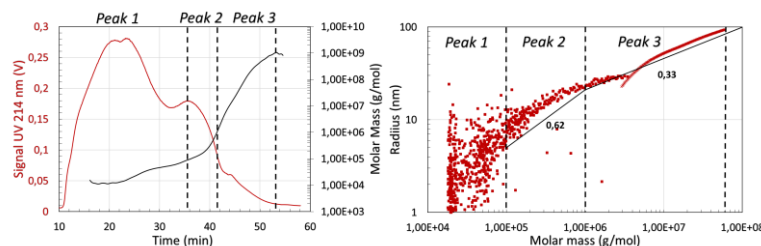


Figure 1: Fractogramme d'un extrait de protéines issue de gluten and conformation of the objects regarding the radius against molar mass

Références :

- [1] Boire, A.; Menut, P.; Morel, M.-H.; Sanchez, C. Phase Behaviour of a Wheat Protein Isolate. *Soft Matter* **2013**, *9* (47), 11417.
- [2] Pincemaille, J. Interactions and Assemblies of Gluten Proteins. PhD Thesis of the University of Montpellier. **2018**
- [3] Morel, M.-H.; Pincemaille, J.; Chauveau, E.; Louhichi, A.; Violleau, F.; Menut, P.; Ramos, L.; Banc, A. Insight into Gluten Structure in a Mild Chaotropic Solvent by Asymmetrical Flow Field-Flow Fractionation (AsFIFFF) and Evidence of Non-Covalent Assemblies between Glutenin and ω -Gliadin. *Food Hydrocolloids* **2020**, *103*, 105676..
- [4] Ramos, L.; Banc, A.; Louhichi, A.; Pincemaille, J.; Jestin, J.; Fu, Z.; Appavou, M.-S.; Menut, P.; Morel, M.-H. Impact of the Protein Composition on the Structure and Viscoelasticity of Polymer-like Gluten Gels. *J. Phys.: Condens. Matter* **2021**, *33* (14), 144001.

Correlation between the macromolecular architecture of electroactive fluorinated copolymers and the semi-crystalline structure

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The objective of this Ph.D. thesis is to correlate the macromolecular architecture and the semi-crystalline structure of electroactive fluorinated polymers with their dielectric and electroactive properties in order to integrate them in devices benefiting from the ferroelectric and electrocaloric effects [1]–[3]. The investigated materials are VDF-based terpolymers.

In a first step, we highlighted the impact of the casting process (solution entanglement density, casting temperature and time) and annealing conditions (aging, temperature) on the semi-crystalline structure and the final functional properties of these materials. To evaluate these effects, X-ray scattering (SAXS-WAXS), FTIR, RAMAN, solid state NMR, dielectric spectroscopy and polarization cycles measurements as well as DSC were used, and the characteristic transitions, crystalline phases and electroactive behavior were determined as regard to the processing conditions.

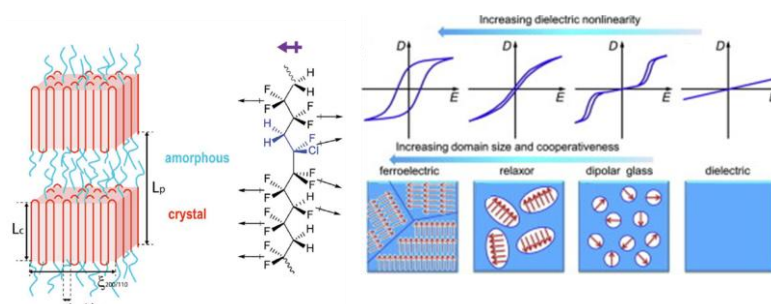


Figure 1: Left: schematic illustration of the crystalline lamellae and the chain conformation of *P(VDF-ter-TrFE-ter-CTFE)*. Right: Different dipole and ferroelectric domain structures and the corresponding electroactive responses in $D-E$ loops

Afterwards, the macromolecular sequence of fluorinated copolymers as well as the heterogeneity in composition will be deciphered using a combination of ^1H - and ^{19}F - NMR. Following this preliminary results, an in-depth rationalization of the semi-crystalline structure of these copolymers was established by WAXS in order to determine the relationships between the macromolecular sequencing (and its defects) and the crystalline structure of such fluorinated copolymers. Overall, this study is designed to establish the relationships between the macromolecular architecture of electroactive copolymers and their crystalline structure in thin film in order to obtain generate dielectric and electroactive functionalities for targeted applications.

References

- [1] F. Bargain, P. Panine, F. Domingues Dos Santos, and S. Tencé-Girault, *Polyme.*, 105, 144–156, 2016.
- [2] T. Soulestin, V. Ladmiral, F. D. Dos Santos, and B. Améduri, *Prog. Polym. Sci.*, 72, 16–60, 2017.
- [3] F. Le Goupil *et al.*, *Adv. Funct. Mater.*, 31, 2007043, 2021.

Formation and Photo-Fenton Performance of polymeric micelles containing Iron ions

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Recently, hybrid organic–inorganic nanomaterials based on polymers have attracted great attention, and show outstanding potential to combine different properties in one material.^{[1],[2]} Easy-to-prepare and stable nanostructured catalyst are synthesized thanks to an innovative strategy based on hybrid micelles called hybrid polyionic complexes (HPICs). These HPICs were obtained through the complexation of iron III ions with double-hydrophilic block copolymers. The Photo-catalytic activity of these nanostructures is evaluated through the degradation of naphthol blue black induced by a Photo-Fenton process. The kinetic of degradation with this nanocatalyst is slightly slower than in traditional homogeneous Fenton reaction (as expected with such hybrid architecture). Chemical and colloidal stabilities as well as the recyclability of the HPIC nanocatalyst are largely improved opening new opportunities for recoverable photocatalysts.

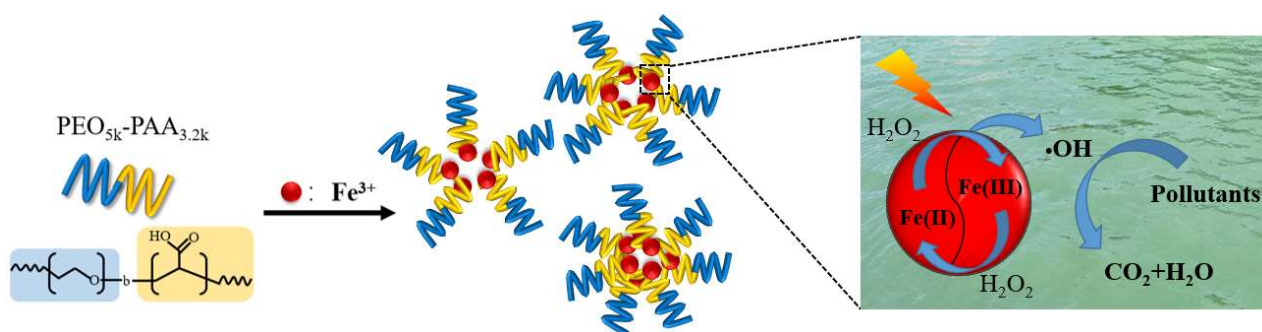


Figure 1: Schematic diagram of the synthesis and catalytic mechanism of HPICs.

Références :

- [1] Shifrina. Z. B, Matveeva. V, Bronstein. L. M, *Chem. Rev.*, **120**, 1350, **2020**
 [2] Nabiyan. A, Max. J, Schacher. F. H, *Chem. Soc. Rev.*, **51**, 995, **2022**

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