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## **Special Issue: 1<sup>st</sup> French-Japanese Symposium: Recent Progress and Challenges in Polymer Science**

### **Editorial**

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Montpellier hosted the **1<sup>st</sup> French-Japanese Polymer Science Symposium** from January 29<sup>th</sup> to 31<sup>st</sup>, 2020. This congress was organized by Dr Sylvain Caillol, Dr Vincent Ladmira<sup>\*</sup> and Dr Julien Pinaud, from the Charles Gerhardt Institute in Montpellier, and by Prof Takashi Kato and Prof Takashi Uemura from the University of Tokyo and Prof Syuji Fujii at Osaka Institute of Technology. Under the aegis of the Groupe Français d'études et d'applications des Polymères (GFP) and the Society of Polymer Science, Japan (SPSJ), the two polymer science learned societies of France and Japan respectively, this symposium was a great opportunity for the French and Japanese delegations of eminent guest scientists and participants to meet and discuss future collaborations. Renowned French and Japanese scientists presented the results of their research in the field of polymer science in the context of crucial societal questions related to health, energy, protection of human and the environment or high performance materials, to name a few. Beyond the remarkable scientific discussions that ensued, this symposium reached its objective to facilitate the establishment of friendly and professional ties between French and Japanese researchers. The Japanese delegation was notably welcomed by the Occitanie Region and discover some of the charms of its cultural heritage as well as its high tech industry-driven development strategy. The success of this symposium, made possible thanks to the support of institutional partners such as the Institut Carnot Chimie Balard Cirimat, the Institut Charles Gerhardt, the CNRS, Montpellier University of Excellence, the University of Montpellier, the Maison de la Chimie Foundation, the CheMISyst LabEx, France Chimie Méditerranée, Montpellier Méditerranée Métropole, the French Embassy in Japan, the Occitanie Region, Chemsud, and industrial partners (Specific Polymers and COP chimie), strengthened the ties between France and Japan and marked the start of a strong impetus in the French-Japanese collaboration initiatives.

This special issue of European Polymer Journal gathers together some cutting-edge research articles which tackle current scientific and industrial challenges of Polymer Science,

such as the study of new polymerization routes or novel biobased monomers, the design of polymers as tools for investigating biological phenomena or to enable more efficient therapies and materials, better performing porous membranes or the physics of soft matter for example.

Firstly, concerning the polymerization routes, Guillaume et al. studied the ring-opening polymerization of six-membered substituted  $\delta$ -valerolactones with alkali metal alkoxides and demonstrated that the alkyl substituents on the 1- and/or 5- position on the cyclic ester ring play a major detrimental role in their ROP<sup>1</sup>. Moreover, Carlotti et al. studied the ring-opening polymerization of propylene oxide mediated with *N*-Heterocyclic carbene/Lewis acid an efficient controlling agent. They notably demonstrated that *N*-heterocyclic carbenes (NHCs) used in conjunction with triisobutylaluminum enable to efficiently trigger the controlled ring-opening polymerization of propylene oxide, improving the NHC approach for substituted epoxides<sup>2</sup>. They also reported that NHCs used in association with triethylborane (Et<sub>3</sub>B) enable to efficiently trigger the metal-free ring-opening polymerization (ROP) of propylene oxide (PO) and the synthesis of original polyether-based block copolymer<sup>3</sup>.

Block copolymers (BCP) and their self-assembly behaviour in the bulk in particular is a very active research area. Sinturel et al. studied the transition between tetragonal and hexagonal pattern in binary blends of ABC and AB block copolymers with different chain length. Hence, the thin film morphology of block copolymers binary blends based on polyisoprene (PI), polystyrene (PS) and poly(2-vinylpyridine) (P2VP) after solvent vapor annealing was investigated using AFM, GISAXS and TEM. In conclusion, PI-PS-P2VP blends in thin films offer the possibility to present non-predicted morphology<sup>4</sup>. Satoh et al. demonstrated how high  $\chi$  AB and ABA BCP comprising of oligosaccharides A block and poly(propylene oxide) B block (thus coined Sweet Pluronics) self-assembled in the bulk state into hexagonally close-packed cylinders, body-centered cubic spheres or lamellar morphologies depending on composition and annealing temperature. In addition, they showed that sub 10 nm patterning of thin films could be achieved with these sweet pluronics thus opening up application opportunities<sup>5</sup>.

Polymers also provide advantages in the field of porous materials. Semsarilar et al. reported an original research paper on amphiphilic PVDF-*b*-PEG-*b*-PVDF triblock copolymer as membrane additive. Hence, poly(vinylidene fluoride) (PVDF) ultrafiltration membranes were prepared by NIPS using a blend of a new amphiphilic PVDF-based triblock copolymer (PVDF-*b*-PEG-*b*-PVDF) and high molar mass PVDF. The PVDF-*b*-PEG-*b*-PVDF triblock copolymer additive improved the surface hydrophilicity and significantly increased the pure

water flux and permeability of the PVDF membrane, surpassing characteristics of commercial PVDF membranes<sup>6</sup>. Kato and coworkers prepared well-defined nanoporous membranes from and amphiphilic liquid crystalline taper-shaped molecules. The self-assembly of this liquid crystal into columnar structures was immobilized via ADMET polymerization and the nanopores were generated by photolysis of the *o*-nitrobenzyl ester linkage between the polymerized hydrophobic moieties and the hydrophilic triethyleneglycol groups. The resulting self-standing membranes exhibited size- and charge-dependent adsorption properties.<sup>7</sup> Le Ouay and Uemura pursued their study on the insertion of polymers into microporous flexible MOF and showed that the insertion speed was dependent on the PEG-terminus and on the terminal group concentration. This work provides important insights on the dynamics of MOF and paves the way to high performance polymer purification.<sup>8</sup>

The replacement of toxic isocyanates by less harmful substance is a crucial stake for industry. Hence, alternatives such as polyhydroxyurethanes (PHU) are gaining increasing interest in both academic and industrial communities. Caillol et al. proposed a review paper dedicated to hybrid polyhydroxyurethanes, as a solution to overcome the limitations of PHUs and reach cutting-edge properties<sup>9</sup>. Concerning biobased polymers, Hespel et al. reported the modification of cellulose fibers through metal-free click chemistry for the elaboration of versatile functional surfaces. This innovative strategy is based on a strain-promoted azide-alkyne cycloaddition under heterogeneous conditions. The metal-free click chemistry is a very attractive approach to immobilize a large diversity of molecules on a textile support, and it avoids the persistence of any metal traces on cellulose after rinsing which allows also to extend the use of the functionalized textile to biological applications without any risk<sup>10</sup>. Nicolas et al. reported optimized synthetic pathways to high purity L-phenylalanine (Phe) and L-asparagine (Asn) derived *N*-carboxyanhydrides (NCA) in one-pot processes and in a highly reproducible manner, which uses  $\alpha$ -pinene as effective acid scavenger. Then, they studied the ring-opening homopolymerizations of Asn-NCA and Phe-NCA and demonstrated strong interactions which led to formulation of nanoparticles<sup>11</sup>.

Photochemistry is an important method to foster greener approach in polymer science or to prepare smarter materials. Gimes et al. proposed the use of ketone derivatives as photoinitiators for both radical and cationic photopolymerizations of acrylate monomers under visible LED and application in 3D printing<sup>12</sup>. Takashima et al. prepared and studied a photoresponsive hydrogel from 8-arm amino-functional polyhedral oligomeric silsesquioxane and stilbene bifunctional PEG. These hydrogels displayed large and reversible deformation

upon UV-irradiation. They were also shown to lift weight with high-energy conversion ratios and power and were deemed promising actuators<sup>13</sup>. Versace et al. studied the photoinduced synthesis of antibacterial hydrogel from aqueous photoinitiating system. Hence, this new photoactivable material based on polyethylene imine with allyl functions (allylated PEI monomer) was synthesized to develop hydrogel containing quaternary ammonium groups on its surface, which demonstrated excellent anti-adherence and biocide properties against *Escherichia coli* and *Staphylococcus aureus*<sup>14</sup>.

Polymers are also very valuable tools to investigate biological properties and design functional materials for bioapplications. For example, the group of Prof. Miura synthesized a range of multiblock glycopolymers from sugar-functionalized acrylamide by RAFT polymerization and examined their molecular recognition ability with lectins.<sup>15</sup> Takai et al. also used the RAFT process to prepare PMPTSSi-*b*-PMPC-*b*-PMPTSSi (PMPTSSi = poly(3-methacryloyloxy propyltris(trimethylsilyloxy) silane) and PMPC = poly(2-methacryloyloxyethyl phosphorylcholine)) ABA triblock copolymers to study their effect of protein adhesion. The ABA block copolymers phase separated on surfaces thus generating hydrophobic PMPTSSi protein adsorption promoting domains and protein-repellant PMPC domains. Only proteins with dimensions smaller than the nanoscopic hydrophobic regions could adhere to the nanostructured surfaces.<sup>16</sup> Block copolymers can also find application as novel therapeutic solutions. Cabral et al. provided a very good example of such use of BCP with the encapsulation of fragile messenger RNA (mRNA) into polyion complex (PIC) micelles made from poly(ethylene glycol)-poly(glycidyl methyl guanidine) (PEG-PGMG) and PEG-poly(glycidyl methyl amine (PEG-PGMA)) block copolymers. These PIC micelles were proven to efficiently protect mRNA from polyanions, urea and nucleases.<sup>17</sup> Synthetic textiles with physical and/or biological properties are increasingly used in medical applications. While a simple textile coating is usually carried out to obtain biological properties, covalent grafting should be considered for long-term applications. Hence, Subra et al. have developed a new hybrid bioactive nylon whose synthesis involves a peptide sequence with a diacyl derivative. Numerous types of peptide-nylons were prepared, incorporating antibacterial peptides, which significantly inhibited *S. Aureus* proliferation. These results show that the incorporation of the peptides directly into the nylon skeleton is efficient and provides biological properties that suggest new ways of functionalizing biomedical textiles<sup>18</sup>.

Polymers are ubiquitous and versatile materials which can be endowed with numerous properties. End of life of polymers is a challenge and reversible polymers are becoming more and more attractive. Hence, Avérous et al. proposed an original article on responsive biobased

polyurethane (PU) networks crosslinked by click chemistry<sup>19</sup>. They studied the effect of the cross-linkers and backbone structures and demonstrated that these PU presented good thermal recyclability and adhesion properties, for potential industrial application adhesives or coatings, for example. The same team also studied dynamic networks based on eugenol-derived renewable monomers with reversible disulfide bonds. These reversible biobased epoxy networks demonstrated highly promising reshaping, self-healing and recycling capabilities<sup>20</sup>. Polystyrene is another widely used polymer. However, it is too brittle for certain applications. Takashima et al. showed that acetylated cyclodextrin able to form inclusion complexes with benzene rings could efficiently be used as an additive to increase polystyrene Young's modulus<sup>21</sup>. Tanaka et al. tracked the thermal motion of quantum dots dispersed in a random copolymer of n-butyl acrylate and 2-hydroxyethyl acrylate (poly(BA-r-HEA), a representative of pressure-sensitive adhesive polyacrylics) to investigate its time-dependent local rheological properties and more precisely study its spatial heterogeneity<sup>22</sup>. Fujii et al. prepared and studied millimetric swimmers composed of polyaniline (PANI) coated-air bubbles stabilized by polystyrene particles. Harnessing the light-to-heat photothermal property of PANI, these swimmers could be moved on demand on the surface of water using a near infrared laser. Using a biomimetic approach, these air bubbles were also used as adhesive to bind together hydrophobic surfaces under water<sup>23</sup>.

This special issue is a collection of highlights within the field of Polymer Science, which clearly demonstrates the increased interest in this field in both French and Japanese communities. We hope that it will inspire researchers to further develop this area and thus contribute to more sustainable society.

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- <sup>8</sup> Benjamin Le Ouay, Takashi Uemura, Terminus-dependent insertion of molten poly(ethylene glycol) into a flexible metal-organic framework, *European Polymer Journal*, 2020, 134, 109855.
- <sup>9</sup> Yvan Ecochard, Sylvain Caillol, Hybrid polyhydroxyurethanes: How to overcome limitations and reach cutting edge properties?, *European Polymer Journal*, 2020, 137, 109915.
- <sup>10</sup> Alex Meye Biyogo, Louise Hespel, Vincent Humblot, Laurent Lebrun, François Estour, Cellulose fibers modification through metal-free click chemistry for the elaboration of versatile functional surfaces, *European Polymer Journal*, 2020, 135, 109866.
- <sup>11</sup> Amaury Bossion, Julien Nicolas, Synthesis of poly(Asparagine-co-phenylalanine) copolymers, analogy with thermosensitive poly(acrylamide-co-styrene) copolymers and formation of PEGylated nanoparticles, *European Polymer Journal*, 2020, 140, 110033
- <sup>12</sup> Yangyang Xu, Guillaume Noirbent, Damien Brunel, Feiyang Liu, Didier Gimes, Ke Sun, Yijun Zhang, Shaohui Liu, Fabrice Morlet-Savary, Pu Xiao, Frédéric Dumur, Jacques Lalevée, Ketone derivatives as photoinitiators for both radical and cationic photopolymerizations under visible LED and application in 3D printing, *European Polymer Journal*, 2020, 132, 109737.
- <sup>13</sup> Motofumi Osaki, Kento Ito, Yuka Ikemoto, Hiroyasu Yamaguchi, Yoshiki Chujo, Akira Harada, Kazuo Tanaka, Yoshinori Takashima, Photoresponsive Polymeric Actuator Cross-Linked by an 8-Armed Polyhedral Oligomeric Silsesquioxane, *European Polymer Journal*, 2020, 134, 109806.
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