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## Future directions at the frontier of polymer science and biology

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The field of polymer science has continuously grown over the past century, since the discovery of polymers. Macromolecules are nowadays an essential piece of our life and are found in large range of different applications, from construction, materials, composites, food, health and personal care, among others. The research field is rather matured and structured, with a unique balance between fundamental research and more applied science, with a great involvement of companies. Many important challenges are still to be addressed, especially when polymers are considered at the interface with biology. This is exactly what a journal such as *Biomacromolecules* is focusing on since two decades now.<sup>1</sup>

During Spring 2018, the first Bordeaux Polymer Conference (BPC 2018)<sup>2</sup> gathered the top specialists from all over the world, offering them the opportunity to present their most recent research findings and to discuss the latest ideas, discoveries and innovations in the field of Polymer Science and Engineering. This first edition, which gathered 600 participants, was organized by the Laboratoire de Chimie des Polymères Organiques (LCPO)<sup>3</sup> in Bordeaux on May 28-31, 2018. Several symposia were featured, covering most of the different aspects of polymer science, including (1) Polymerization mechanism and catalysis, (2) Macromolecular engineering, (3) Green polymers, (4) Polymer self-assembly and (5) Interactions of polymers in life sciences and electronics.

This Special Issue includes 25 papers (4 reviews and 21 original research manuscripts) that were presented at BPC 2018. These papers are covering a wide range of research topics of

interest to the readership of *Biomacromolecules*, including biomaterials design, renewable materials, polymer micelles and vesicles, nanoparticles, hydrogels and nanogels for nanomedicine, green approaches for polymer design, biobased nanocomposites, bio-sourced amphiphiles, biocompatible and functional emulsions, macromolecular engineering for biomaterial design, DNA- and protein-based bioconjugates, design of polymer interface for controlled interaction with living organisms, bioadhesives, antimicrobial polymers and surfaces. Altogether, these contributions are providing a brilliant overview of the current state-of-the-art in the field and are highlighting exciting future emerging challenges and opportunities at the frontier of polymer science and life science, in a broad manner.

A first set of manuscripts focuses on the **elaboration of bio-based and renewable materials and biomaterials**. Sylvain Caillol et al.<sup>4</sup> give a comprehensive overview on the recent advances about the synthetic pathways reported to provide suitable monomers from fatty acids and their derivatives for radical polymerization together with the different application of the resulting bio-based polymeric materials. Karen Wooley et al.<sup>5</sup> highlight the chemical diversity of the natural product magnolol for the synthesis of renewable, degradable neolignan thermosets with tunable thermomechanical characteristics and antioxidant activity. The group of K. Masami<sup>6</sup> presents a series of cinnamic monomers, which can be derived from naturally occurring phenylpropanoids that were radically copolymerized by NMP or RAFT with vinyl monomers. The solution properties of the resulting copolymers were studied. Interestingly, H. Cramail et al.<sup>7</sup> present the synthesis and self-assembly of Xylan-based amphiphiles. Xylan oligomers were conjugated to lipid derivatives by click chemistry and the resulting amphiphiles were self-assembled using microfluidic approach into vesicles that can be used to load antifungal molecules. In another example, Z. Li et al.<sup>8</sup> evidenced the preparation of amphiphilic poly(ethylene glycol)-*b*-poly( $\gamma$ -butyrolactone) diblock copolymer via ring opening polymerization catalyzed by a cyclic trimeric phosphazene base or alkali alkoxide. The catalytic/initiating organic systems showed moderate control on the ring opening polymerization of  $\gamma$ -butyrolactone ( $\gamma$ BL) and successfully produced PEG-*b*-P $\gamma$ BL diblock copolymers with varied molecular weights and relatively narrow molecular weight distributions. In another study, S. Anastasiadis et al.<sup>9</sup> studied the structure and dynamics of two bio-based polyester polyols in the bulk and close to surfaces in polymer / layered silicate nanocomposites.

Another series of manuscript are illustrating the interest and impact of **polymers in the field of biology, biomedicine and nanomedicine**. In a first paper the groups of A. Alexander and M. Meier<sup>10</sup> present the synthesis of amphiphilic star-shaped block copolymers containing thioether groups, which could be oxidized to sulfones in order to further tune the polarity of the polymer chains, via the Passerini reaction. The resulting amphiphilic copolymers were demonstrated to act as unimolecular micellar encapsulants that can be used as a promising

nanomedicine. In another paper, J. van Hest et al.<sup>11</sup> demonstrated the generation of well-defined nanotubes based on polymersomes. The resulting nanotubes were extensively characterized and successfully loaded with model drugs, providing a promising platform for implementation in biomedical applications in which discrete structure and functionality are essential features. Z. Zhong et al.<sup>12</sup> reported that smart polymersomes based on PEG-*b*-poly(trimethylene carbonate-co-dithiolane trimethylene carbonate) dually functionalized with cRGD and fusogenic GALA peptides enable  $\alpha_v\beta_3$ -specific and high-efficiency cytosolic delivery of cytochrome C, highlighting the therapeutic interest of such a strategy. U. Schubert et al.<sup>13</sup> reported the synthesis of pH-sensitive nanogels, which are based on the monomer *N*-[(2,2-dimethyl-1,3-dioxolane)methyl]acrylamide (DMDOMA) bearing an acid cleavable acetal group. In vitro studies revealed a good compatibility of the unloaded nanogel and the capability of the doxorubicin loaded nanogel to mediate cytotoxic effects in a concentration and time-dependent manner with an even higher efficiency than the free drug. D. Gigmes and T. Trimaille<sup>14</sup> developed interesting an injectable and biodegradable hydrogel based on an amphiphilic PNIPAAm-*b*-PLA-*b*-PEG-*b*-PLA-*b*-PNIPAAm pentablock copolymer synthesized by ring-opening polymerization/nitroxide-mediated polymerization (ROP/NMP) combination. The hydrogel was shown to be cytocompatible (neuronal cells, in vitro) and injectable, displaying highly attractive features for use in brain/soft tissue engineering as well as in drug delivery. H.-A. Klok et al.<sup>15</sup> presented a first proof-of-concept that demonstrates the feasibility of NanoSIMS to monitor the intracellular localization of polymer conjugates using poly(*N*-(2-hydroxypropyl) methacrylamide)) as a prototypical polymer–drug conjugate. J. Nicolas et al.<sup>16</sup> evidenced the successful copolymerization of 2-methylene-1,3-dioxepane (MDO) and different vinyl ether (VE) monomers by free-radical radical ring-opening copolymerization. The different copolymers were formulated into nanoparticles. Their stability, hydrolytic and enzymatic degradability and cell viability were evaluated, demonstrating the interest of these original polymer structures.

Another series of papers are dealing with **proteins, DNA and bioconjugates**. The group of R. Mezzenga<sup>17</sup> first reviewed the current knowledge regarding the conformational flexibility of fibronectin, with an emphasis on how it regulates the ability of fibronectin to interact with various signaling molecules and cell-surface receptors and to form supramolecular assemblies and fibrillar structures. In a nice collaborative contribution, K. Barner-Kowollik, D. Ng and T. Weil<sup>18</sup> described a convenient, light-mediated approach toward DNA–polymer conjugates via the grafting-from approach. S. Lecommandoux et al.<sup>19</sup> presented the synthesis and original thermoresponsive behavior of hybrid diblock copolypeptides composed of synthetic poly(L-glutamic acid) and recombinant elastin-like polypeptides.

The **surface and interfacial properties of polymers and nanoparticles with biology** was also illustrated in this special issue. In this context, K. Matyjaszewski et al.<sup>20</sup> first proposed an

extensive review on molecular bottlebrushes as building blocks for the design of unique polymeric materials whose physical and biological properties are fundamentally governed by their densely grafted structures. D. Mecerreyes et al.<sup>21</sup> presented an interesting overview of the emerging strategies developed to manufacture 3D conductive scaffolds, the techniques used to fully characterize them, and the biomedical fields where they have been applied to. K. Glinel and A. Jonas<sup>22</sup> demonstrated entrapment of the commensal skin bacteria *Staphylococcus epidermidis* in mats composed of soft nanotubes made by membrane-templated layer-by-layer assembly. These patches offer a promising methodology for the fabrication of bacterial skin dressings for the treatment of skin dysbiosis while preventing adverse effects due to bacterial proliferation. B. Schmidt and M. Antonietti<sup>23</sup> proposed water-in-water Pickering emulsion stabilized by polydopamine particles that was further cross-linked via poly(acrylic acid) and carbodiimide, resulting in strengthening the stability of emulsion droplets in a colloidosome-like structure. R. Hoogenboom et al.<sup>24</sup> described a new method for the synthesis of superhydrophilic poly(2-alkyl-2-oxazoline)s from poly(2-ethyl-2-oxazoline). P. van Rijn et al.<sup>25</sup> demonstrated that poly-N-isopropylmethacrylamide based microgel coatings prepared via a spraying approach could advantageously prevent bacterial adhesion. In other interesting studies, S. Mecking et al.<sup>26</sup> developed multivalent carbohydrate-functionalized polyethylene nanocrystals and M. Stenzel et al.<sup>27</sup> evidenced that the architecture of the hydrophilic glycopolymer brush on the surface of polymeric micelles affects the interaction with cancer cells. Finally, S. Perrier et al.<sup>28</sup> explored the structure-activity relationship of synthetic homopolymers and copolymers of sodium 2-acrylamido-2-methylpropane sulfonate, with a focus on the effect of molecular weight, co-monomer type, charge dispersion and polymer architecture on protein stabilization.

This Special Issue provides a sense of up-to-date research and development of polymers at the interface with biology, with the most recent trends in the field. We are looking forward to how these exciting results that were presented during BPC 2018 develop and expand into new areas. A following-up edition of Bordeaux Polymer Conference is already expected in 2022 (BPC 2022).

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<sup>1</sup> Biomacromolecules is celebrating in 2019 the 20th Anniversary of the journal.

<https://pubs.acs.org/journal/bomaf6>

<sup>2</sup> <http://bpc2018.u-bordeaux.fr/en>

<sup>3</sup> LCPO ([www.lcpo.fr](http://www.lcpo.fr)) is a joined Research Unit from CNRS, University of Bordeaux and Bordeaux INP

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Lomege, Juliette; Lapinte, Vincent; Negrell, Claire; Robin, Jean-Jacques; Caillol, Sylvain  
DOI: [10.1021/acs.biomac.8b01156](https://doi.org/10.1021/acs.biomac.8b01156)

<sup>5</sup> Harnessing the Chemical Diversity of the Natural Product Magnolol for the Synthesis of Renewable, Degradable Neolignan Thermosets with Tunable Thermomechanical Characteristics and Antioxidant Activity

Wacker, Kevin; Weems, Andrew; Lim, Soon Mi; Khan, Sarosh; Felder, Simcha; Dove, Andrew; Wooley, Karen

DOI: [10.1021/acs.biomac.8b00771](https://doi.org/10.1021/acs.biomac.8b00771)

<sup>6</sup> Controlled Radical Copolymerization of Cinnamic Derivatives as Renewable Vinyl Monomers with Both Acrylic and Styrenic Substituents: Reactivity, Regioselectivity, Properties, and Functions

Terao, Yuya; Satoh, Kotaro; Kamigaito, Masami

DOI: [10.1021/acs.biomac.8b01298](https://doi.org/10.1021/acs.biomac.8b01298)

<sup>7</sup> Synthesis and self-assembly of Xylan-based amphiphiles: from bio-based vesicles to antifungal properties

Rosselgong, Julien; Chemin, Maud; Cabral Almada, Cedric; Hemery, Gauvin; Guigner, Jean-Michel; Chollet, Guillaume; LABAT, Gilles; da Silva Perez, Denilson; Ham-Pichavant, Frederique; Grau, Etienne; Grelier, Stéphane; Lecommandoux, Sebastien; Cramail, Henri  
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Shen, Yong; Zhang, jinbo; Zhao, Zhichao; Zhao, Na; Liu, Fusheng; Li, Zhibo

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<sup>9</sup> Structure and Dynamics of Biobased Polyester Nanocomposites

Androulaki, Krystalenia; Chrissopoulou, Kiriaki; Prevosto, Daniele; Labardi, Massimiliano; Anastasiadis, Spiros

DOI: [10.1021/acs.biomac.8b01231](https://doi.org/10.1021/acs.biomac.8b01231)

<sup>10</sup> Biocompatible unimolecular micelles obtained via the Passerini reaction as versatile nanocarriers for potential medical applications

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Oelmann, Stefan; Travanut, Alessandra; Barther, Dennis; Romero, Manuel; Howdle, Steven; Alexander, Cameron; Meier, Michael

DOI: [10.1021/acs.biomac.8b00592](https://doi.org/10.1021/acs.biomac.8b00592)

<sup>11</sup> Development of Morphologically Discrete PEG-PDLLA Nanotubes for Precision Nanomedicine

Wauters, Annelies; Pijpers, Imke; Mason, Alexander; Williams, David; Tel, Jurjen; Abdelmohsen, Loai; van Hest, Jan

DOI: [10.1021/acs.biomac.8b01245](https://doi.org/10.1021/acs.biomac.8b01245)

<sup>12</sup> Smart polymersomes dually functionalized with cRGD and fusogenic GALA peptides enable specific and high-efficiency cytosolic delivery of apoptotic proteins

Yao, Peili; Zhang, Yifan; Meng, Hao; Sun, Huanli; Zhong, Zhiyuan

DOI: [10.1021/acs.biomac.8b01243](https://doi.org/10.1021/acs.biomac.8b01243)

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Wei, Peng; Gangapurwala, Gauri; Pretzel, David; Leiske, Meike; wang, limin; Hoepfener, Stephanie; Schubert, Stephanie; Brendel, Johannes; Schubert, Ulrich

DOI: [10.1021/acs.biomac.8b01228](https://doi.org/10.1021/acs.biomac.8b01228)

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DOI: [10.1021/acs.biomac.8b01372](https://doi.org/10.1021/acs.biomac.8b01372)

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