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Virtual special issue "Biomimetic Polymers"

Without macromolecules, life would not have evolved. The whole cell machinery relies on macromolecular compounds, such as DNA, RNA, proteins, and peptides. Moreover, biopolymers such as polysaccharides or lignin play important roles as structural components of living systems. Natural macromolecules have sophisticated functions and properties that have so far been rarely achieved in synthetic systems. That is why synthetic polymer chemists often look into nature for inspiration how to design functional polymers, or to mimic the function of natural systems with synthetic ones. Moreover, with the advent of biotechnology, the boundaries between natural and synthetic polymers become fluid. For example, the recombinant expression and engineering of genes allows using recombinant proteins in materials applications. The aim of this special issue of the *European Polymer Journal* is to highlight examples of research in the field of biomimetic and bioinspired polymer chemistry in order to showcase current trends and to emphasize the opportunities of biomimetic and bioinspired functional materials for novel applications.

A classic example for a source of bioinspiration are the proteins of the mussel foot, which adhere strongly to surfaces in wet condition. Messersmith and coworkers review polymers that are inspired by this and other tricks of marine organisms to create adhesives for medical applications [1]. Scheibel and coworkers investigate the question how mussels control the oxidation and reduction of 3,4-dihydroxyphenylalanine (DOPA) residues in their proteins, which is key to the adhesion properties of the mussel foot proteins [2]. To this end, they recombinantly expressed a mussel protein that can suppress DOPA oxidation. Not only the mussel foot, but also the byssal threads of mussels have fascinating properties. They exhibit high toughness and can self-heal. Harrington and coworkers developed a model polymer network composed of star-shaped PEG with peptides at the chain ends to investigate the role of histidin-rich domains in the self-assembly and self-healing of proteins in the byssal threads [3].

In general, structural proteins are widespread in nature. One class of structural proteins that has been used since ancient times for man-made materials is silk. Nowadays, silk fibroin is intensively investigated as material for biomedical applications because it is biocompatible, biodegradable, and has low immunogenicity. The processing of soluble silk fibroin into insoluble fibers is an essential process both in nature and during the preparation of fibroin-based biomaterials. Linder, Aranko and coworkers investigate the effect of dextran as a crowding agent during silk fibroin coacervation and show that the crowding agent drastically reduces the concentration at which the protein aggregates [4]. Collagen is the most important structural protein in mammals. Collagen-mimetic peptides consist of oligomeric collagen segments and are considered model systems to study the properties and behavior of collagen. The contribution by Börner and coworkers deciphers the effect of pH-dependent switch defects in various locations of the peptide chain on the formation of the collagen triple helix [5].

Polysaccharides, including cellulose, chitin, and starch are abundantly available natural polymers that are increasingly used in materials applications. Especially cellulose nanocrystals (CNCs) and cellulose nanofibrils have attained much interest as nanoscale reinforcing agents for polymeric matrices. Ikkala and Nonappa report nanocomposite fibers that were made by wet-spinning of gel-like mixtures of methylcellulose and CNCs [6]. The fibers showed high ductility and high modulus of toughness and represent an interesting example of a high performance material made from renewable feedstock. Rowan and coworkers made CNC-reinforced polymer nanocomposites by UV-induced crosslinking of allyl-functionalized CNCs with a tetra-functional thiol reagent in a poly(vinyl acetate) matrix [7]. Not only did they use naturally occurring CNCs, but they also mimicked the mechanical gradient of squid beaks by modulation of the UV-light intensity. The study elucidates the effect of processing conditions on the properties of the resulting material. Similar to the squid beak, the remarkable mechanical properties of the jaw of polychaete worms are due to a gradient of hardness along the length of the jaw. It is caused by a gradient in the density of metal-ligand coordination crosslinks. Taking inspiration from this structure, Korely and coworkers designed semi-interpenetrating networks in which a gradient of supramolecular metal-ligand crosslinks allowed to modulate the materials' capability to dissipate energy at various locations in the material [8].

A possibility to mimic the globular structure of enzymes and their catalytic activity is to collapse polymer chains into single–chain nanoparticles (SCNPs). Berda and his group report poly(oxanorbornene imide) single-chain nanoparticles by intra-chain radical polymerization of side groups [9]. Pomposo and coworkers folded copolymers of oligo (ethyleneglycol) methyl ether methacrylate (OEGMA) and 2-acetoacetoxy ethyl methacrylate (AEMA) into SCNPs by coordination of iron ions to the ligand groups [10]. The latter particles possess peroxidase-like activity and were used as biomimetic catalysts to synthesize the conducting polymer poly(3,4-ethylenedioxythiophene) (PEDOT) by step-growth oxidative polymerization. A remarkable feature of enzymes and antibodies is their high affinity and selectivity towards specific compounds. Bossi and coworkers synthesized antibody mimicking molecularly imprinted nanogels by copolymerization of an excess of the crosslinker bisacrylamide with various acrylamide, acrylate and methacrylate monomers in the presence of the peptide Troponin I [11], which is a biomarker of cardiac failure. The nanoparticles had nanomolar dissociation constants for the template and, on average, one binding site per particle. Such particles could be useful to capture biomarkers from blood samples and, thereby, facilitate diagnostics.

The last set of papers in this special issue covers amphiphilic block copolymers. They have been extensively investigated as macromolecular mimics of lipids due to their ability to self-assemble into

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biomimetic membranes. Palivan, Meier, and coworkers give an excellent overview over the field [12]. Their review covers polymersomes and planar block copolymer membranes, as well as methods to permeabilize block copolymer membranes and to reconstitute membrane proteins. Moreover, the authors discuss applications of polymersomes as nanoreactors, artificial organelles and rudimentary mimics of cells. Bruns and coworkers present a new type of amphiphilic block copolymer in which the popular stimuli-responsive spiropyran motive is located at the junction of the blocks [13]. These polymers might be used for self-assembled biomimetic membranes, whereby the location of the stimuli-responsive group could influence self-assembly of the block copolymers and the permeability of the resulting membrane in unique ways.

Synthetic polymeric materials are far from achieving the level of sophistication in function and structure that arose in biological systems during millions of years of evolution. Thus, a myriad of opportunities exist for chemists, physicists and biologist to design and produce novel materials with advanced functionalities if they follow the design principles found in biology. We therefore hope that the collection of reviews and original research articles in this special edition will inspire the reader to pursue activities in the vast field of biomimetic, bioinspired, and bio-based polymer chemistry.

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