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Progress on Stimuli-Responsive Polymers

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Polymers have evolved to become much more than plastics. This is especially true for polymers or copolymers that respond to external stimuli and have accordingly found increased attention across several disciplines and play a significant role in advancing materials sciences. Probably the most well-known responsive polymer is poly(*N*-isopropoyl acrylamide) (PNIPAM), which demonstrates a lower critical solution temperature and has become the lead material for a versatile and vibrant field in polymer science. The success and utility of PNIPAM has triggered the search for new stimuli-responsive—"smart"—polymers that respond to temperature, pH-changes, gases, light, redox, salts, mechanical stress, electric or magnetic fields, etc.

With a plethora of controlled and living polymerization techniques and creative approaches to post-polymerization modification, functional polymers are now accessible which allow the combination of several responsive groups to generate new examples of multi-responsive materials.

This special issue collects 19 recent developments in the area of stimuli-responsive polymers. Contributions by authors with interdisciplinary backgrounds have been collected to feature synthesis of new polymers, polymer surfaces, or detailed physico-chemical analyses of stimuli-responsive polymers to elucidate their potential in a variety of applications. The special issue contains two review articles: Marek W. Urban and co-workers summarize developments in commodity acrylics, epoxies, esters, carbonates, urethanes, and siloxane-based polymers containing responsive elements (2100054). Lei Tao and colleagues review recent advances in multifunctional phenylboronic acid-containing polymers as responsive materials (2100022).

Two contributions update the classic example of PNIPAM. Jianbo Tan and co-workers used PNIPAM in an innovative photo-PISA approach (i.e., polymerization-induced self-assembly) to prepare PNIPAM-based block copolymer assemblies (2100201); and Nathanial Corrigan and co-workers presented interesting data on the molar mass distribution on the phase-change temperature of PNIPAM (2100212). Other contributions expand the field of thermoresponsive polymers. Takaya Terashima et al. developed a cation-templated synthesis towards large in-chain ring cyclopolymers that are examples of thermoresponsive pseudo-crown ether polymers (2000670). Zhengbiao Zhang and co-workers present sequence-dependent stimuli-response in PNIPAM copolymers using 2,5-dimethylfuran/acrylonitrile adduct as a latent monomer (2000724).

Longhai Guo and colleagues prepared ABA-triblock copolymers containing thermoresponsive moieties that demonstrated an ice recrystallization inhibition activity, resulting in decreased sizes of ice crystals (2100024). Gas-responsive assemblies based on amphiphilic block copolymers were prepared by San H. Thang and co-workers; these materials showed a morphological transition from nanotubes to vesicles under gas stimulation mimicking the function of alveoli (2100019).

Dominik Konkolewicz and co-workers presented covalent adaptable networks (CANs) with dynamic properties (2100070). Because of the reversible linkages in the CANs, temperature-responsive re-healing and malleability were achieved. In addition, photoresponsive coumarin-containing CANs revealed light-mediated reconfigurability. Mechanically enhanced hydrogels are reported by Yang Li et al. (2100028). Masami Kamigaito and co-workers prepared copolymers containing poly(thioether)s and poly(vinylether)s, which self-assembled in aqueous solutions and exhibited lower critical solution temperatures that depend on the segment sequences and lengths (2100192).

Photoresponsive polymer vesicles are presented by Jinming Hu and co-workers which enabled the sequential release of nitric oxide and gentamicin to eradicate biofilms (2000759), while Richard Hoogenboom and his colleagues synthesised copolymers with responsive host–guest complexation using 1,5-dialkoxynaphthalene guest molecules and cyclobis(paraquat-*p*-phenylene) tetrachloride hosts to manipulate the copolymer phase transition temperature (2100068).

Stimuli-responsive polymers can also be attached to surfaces to control interfacial properties. In our collection, Karen Lienkamp and her colleagues developed surface-attached hydrophobically modified poly(carboxybetaine)s, which change from a protein-repellent polyzwitterion to antimicrobial and protein-adhesive polycations upon pH-change (2100051). Cyrille Boyer and co-workers present polymeric brushes with antifouling and visible light-activated bactericidal properties using surface-initiated photoinduced electron transfer-reversible addition-fragmentation

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chain transfer polymerization (SI-PET-RAFT) (2100106). Didier Gigmes et al. grafted photoresponsive polystyrene on silica nanoparticles using ortho-nitrobenzyl linkers (2100181).

Jian Zhu and co-workers polymerized (*p*-phenylseleno) styrene to obtain polymers that were selectively oxidized to selenoxide or selenone groups by H_2O_2 or NaClO (2000764), and Birgit Esser and co-workers demonstrated the potential of dibenzo[*a*,*e*]cyclooctatetraene-containing polymers as battery electrode materials, which show pseudo capacitive behaviour with Faradaic contributions (2000725). Zi-Chen Li and colleagues report on the design and synthesis of a fluoride-triggered self-immolative polyester (2100169).

In summary, this special issue is a reminder that the long-standing field of stimuli-responsive polymers continues to evolve at a rapid pace. New developments in synthesis, characterization, and processing continue to enable creative advances that pave the way for fundamental science to be applied to materials with real-world utility. We are proud to present this collection of exciting developments, and we hope that the resulting knowledge will inspire further expansion of a thriving field.

Conflict of Interest

The authors declare no conflict of interest.

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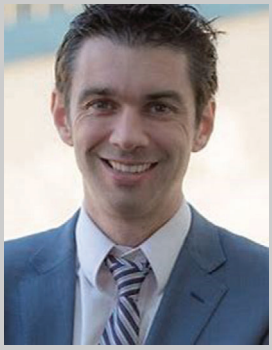
Frederik R. Wurm is currently leading the group "Sustainable Polymer Chemistry" at the Universiteit Twente (UT, Enschede, the Netherlands). The group designs materials with molecular defined functions for degradable polymers and nanocarriers for agricultural or biomedical applications and especially phosphorus-based polymers. Among these, polyphosphoesters as degradable and stimuli-responsive materials have been a major focus in the last years. He received his Ph.D. in 2009 focussing on linear-hyperbranched block copolymers (Johannes Gutenberg-University, Mainz, Germany). After a two-year stay at EPFL (Lausanne, Switzerland) as a Humboldt fellow designing new polymer-protein conjugates, he joined the Max Planck Institute for Polymer Research (Mainz) and finished his habilitation in macromolecular chemistry in 2016. In August 2020, he was appointed as a full professor at UT in the Department of Molecules and Materials. He has published more than 200 peer-reviewed articles and his research has been awarded several times, e.g., with the Reimund Stadler and the Georg Manecke Awards of the German Chemical Society (2016), the "Dozentenpreis des Fonds der deutschen chemischen Industrie" (2017) and Polymer Chemistry Lectureship (2019). He is also editor for the *European Polymer Journal*.



Cyrille Boyer received his Ph.D. from the University of Montpellier II. His Ph.D. was performed in collaboration with Solvay-Solexis for the preparation of new adhesives. At the end of his Ph.D., he undertook a position with Dupont Performance Elastomers, dealing with the synthesis of fluorinated elastomers. Later, he joined the University of New South Wales in the School of Chemical Engineering, where, in 2009, he was awarded an Australian Research Council Fellowship (ARC-APD). In 2012, Cyrille was awarded an Australian Research Council - Future Fellowship. In January 2017, Cyrille was promoted to full professor at the University of New South Wales and co-director of the Australian Centre for Nanomedicine. More recently, he has been appointed Deputy Head of School (research). Cyrille's research interests mainly cover the preparation of functional macromolecules, where he developed new polymerization techniques using photocatalysts. These macromolecules find applications in various areas, including in nanomedicine and in energy storage. The research of his group has been recognized by several research awards, including 2018 IUPAC-Polymer International Young Researcher award, 2016 ACS Biomacromolecules/Macromolecules Young Researcher Awards, 2016 Journal of Polymer Science Innovation Award, Le Fevre Memorial Prize for Chemistry; 2015 Malcolm McIntosh Prize for Physical Science (one of the six Prime Minister Prize).

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