Final Draft

of the original manuscript

Lendlein, A.; Feng, Y.; Grijpma, D.W.; Zhao, Y.:

Smart Materials.

In: ChemPhysChem. Vol. 19 Weinheim: Wiley-VCH, 2018. 16, 1938 - 1940.

First published online by Wiley-VCH: 13.07.2018

https://dx.doi.org/10.1002/cphc.201800578

Smart Materials

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Smart Materials are able to respond to changes in their environment in a predetermined way. Research in this field of functional materials is often motivated by potential applications. Smart polymers are especially of technological significance in view of the grand global challenges including energy generation and storage, sustainability, and healthcare. Being smart also involves the individual tailoring of properties and functions to specific purposes. Therefore, smart materials' design requires an immensely broad approach. In this special issue, emphasis is given to responsive polymers, shape-memory polymers, nano-/micro-sized polymeric objectives, and application-driven materials. In addition, fabrication schemes of smart materials are considered.

Responsive Polymers

Among all the intelligent materials, polymers may be most readily responsive to the environmental stimulation, as their functional groups can be tailored to accommodate

to a fascinating range of stimulation modes. Song and coworkers (DOI: 10.1002/cphc.201701367) found that the spontaneous emission of the perovskite embedded in polymer opal structures exhibits clear amplified signatures. Wang's team (DOI: 10.1002/cphc.201800095) showed how to obtain a low background for early diagnosis of diseases through electrochemically responsive superhydrophilic surfaces exhibiting specific cell capture and release with high yields and extremely low nonspecific adhesion. While some polymers modify their behavior in reaction to a given trigger, most processes in daily life are reliant on responsiveness to multiple stimuli. Gianneschi, Abbott and coworkers (DOI: 10.1002/cphc.201800106) taught how to manipulate multi-scale responses of liquid crystals by interfacial assemblies of cleavable homopolymers with mesogenic side chains that can be split upon exposure to either H_2O_2 or UV light. Wang's group (DOI: 10.1002/cphc.201701145) constructed photo and thermal dually responsive smart surfaces by grafting silicon nanowire arrays onto a copolymer of spiropyran and N-isopropylacrylamide to overcome the low efficiency of cancer-cell capture and release by single-responsive smart surfaces. Deng, Zhong and coworkers (DOI: 10.1002/cphc.201701367) developed integrated multifunctional micelles through co-self-assembly of poly(ethylene glycol)-b-poly(l-lysine) derivatives with natural ferulic acid or lipoic acid. Apart from the potential applications in biomedicine, the petroleum industry is undoubtedly another promising arena to embrace the use of responsive polymers, so as to satisfy the variation of temperature and salinity when going deep into the underground formation. Su and Feng (DOI: 10.1002/cphc.201800190) reviewed the cutting-edge development of unique thermos-viscosifying polymers and their up-to-date laboratory trials at various stages of oil and gas production.

Shape-memory Polymers

A method that allows controlled manipulation and shape-memory effect (SME) quantification of individual micro and nano-objects in analogy to macroscopic thermomechanical test procedures is introduced by Lendlein *et al.* (DOI: 10.1002/cphc.201701362). An atomic force microscope is applied to address individual electro-spun poly(ether urethane) (PEU) micro- or nanowires freely suspended between two micropillars on a micro-structured silicon wafer substrate. An excellent shape-memory performance of PEU microwires (diameter of 1.0 ± 0.2 µm) becomes apparent (high strain fixity and recovery ratios) with this technique and the switching temperature could be adjusted by variation of the deformation temperature. A single PEU nanowire with a diameter of 98 ± 27 nm exhibited an impressive maximum recovery stress of $\sigma_{max} = 33.3 \pm 0.1$ MPa.

Efficient indirect heating of thermally triggered shape-memory polymers could be realized by incorporation of polydopamine particles (PDAP) in polyurethanes. The PDAPs, which exhibit strong NIR absorption, high photothermal conversion efficiency, and photostability, can form hydrogen bonds with the polyurethane matrix. A SME in a composite material containing only 0.01 wt% PDAP could be induced within 60 s

exposure time to NIR irradiation (Xia *et al*., DOI: 10.1002/cphc.201800022).
A multiple SME with three temporary shapes besides the permanent shape could be programmed in a ternary polymeric composite. Mather and coworkers created the polymeric material with three separated thermal transitions by the combination of two fabrication methods. An electrospun mesh from poly(ε-caprolactone) was embedded in a polymeric matrix. This matrix consists of two phases, which form by phase separation when the exopy monomer component reacts in presence of polymethylmethacrylate (DOI: 10.1002/cphc.201800389).
Antimicrobial effects were implemented in polymeric foams in addition to several other functions such as shape-memory capability, cytocompatibility, and blood-clotting function. It is also expected that these materials have anti-oxidant properties. The new level of multifunctionality was achieved by covalently incorporating cinnamic acid units in shape-memory polymer. Potential applications for these multifunctional scaffolds can be found in medicine, e.g., as hemostats in current hemorrhage treatments (Maitland *et al*., DOI: 10.1002/cphc.201701015).

Nano-/micro-sized polymeric objectives

Polymeric objectives at the nano- or microscales could be imparted with various kinds of smart properties. Philip G. Jessop and coworkers (DOI: 10.1002/cphc.201701303) explored the effects of smart "switchable water" on the aqueous solubility of organic compounds and indicated that aqueous solutions containing water-soluble amine additives have CO_2-switchable properties; this could allow the preparation of switchable aqueous two-phase systems. Two other researches focused on the two-phase interactions were also carried out. Ge *et al.* (DOI: 10.1002/cphc.201700838) synthesized amphiphilic Janus microparticles using a double-core capillary, which could aggregate directionally between the sides of the water-oil interface. In studying the phase separation in emulsion droplets, Man *et al.* (DOI: 10.1002/cphc.201701296) fabricated microcapsules with selected additives to be templates for use in the drug-delivery industry. Additionally, the non-spherical alginate microparticles fabricated by Scott Tsai and coworkers (DOI: 10.1002/cphc.201701094) using electrospraying could also show potential as drug carriers. These shape-controllable, biocompatible, and biodegradable microparticles could be useful in cell encapsulation and 3D cell culture. By combining emulsification and microfluidic spinning, graphene microfibers with controllable size and spacing spindle knots could be generated by Yuanjin Zhao and coworkers (DOI: 10.1002/cphc.201700939). These smart microfibers could then absorb oil by their hydrophobic surface chemistry, showing their potential in environment protection. Besides those smart microparticles, Peng *et al.* (DOI: 10.1002/cphc.201701390) summarized the recent development of nacre-inspired nanocomposites, from 1D fibers, 2D films to 3D bulks. These objects designed by

combining conventional fabrication methods with responsible building blocks and interface interactions could respond to temperature, moisture, light, strain, etc, and meet the requirement and development direction of smart materials. In conclusion, the efforts mentioned above could all provide effective inspirations for designing smart nano-/micro-sized materials in future.

Application-driven smart materials

Often, research in the field of smart materials is motivated by demands originating from potential applications. Chu and coworkers (DOI: 10.1002/cphc.201800138) have developed a simple system of hollow microgels immobilized on a non-woven filter fabric that allows facile detection of trace amounts of lead(II) ions (Pb^{2+}). The smart microgels are based on poly[(N-isopropylacrylamide)-*co*-(benzo-18-crown-6-acrylamide)] (PNB). In this system, the crown-ether component acts as a specific sensor for Pb^{2+} ions and the Poly(N-isopropylacrylamide) (PNIPAM) component as actuator. Upon recognition and capture of the ions, electrostatic repulsion forces between the crown ether/ Pb^{2+} complex results in significant swelling of the microgels. As a result, the rate of liquid flow through the device decreases, allowing the facile quantitative determination of Pb^{2+} concentrations.

Battaglia and coworkers (DOI: 10.1002/cphc.201800187) prepared polymersomes from amphiphilic polybutadiene-b-poly(ethylene oxide) (PBd-b-PEO) block copolymers and showed that the membranes of these vesicles remained stable and could compartmentalize nanoscale volumes at extreme pH gradients of 10. These biomimetic systems could be of great importance as nanoreactors and drug-delivery systems.

Anti-microRNA-155 (anti-miR-155) is an oligonucleotide with great promise for the treatment of lung cancer. However, the delivery of positively charged gene complexes using a variety of cationic materials to lung tumors in vivo was hampered by rapid removal of the complex and significant cytotoxicity. Yang *et al.* (DOI: 10.1002/cphc.201701375) used a biodegradable poly(ester amide) (PEA) based on polylactide and PEI to prepare PEA/anti-miR-155 complexes and coated the complexes with a shielding hyaluronic acid component. The hyaluronic acid itself was also modified with a lung-tumor-cell-targeting peptide. They found that these complexes were stable and had excellent compatibility with cells. Furthermore, the lung-tumor growth inhibition in vitro and in vivo was excellent.

The minireview by Zhang *et al.* (DOI: 10.1002/cphc.201800018) describes the use of mesoporous silica nanoparticles for use as drug-delivery systems. By functionalizing the surface of these nanoparticles with polymer brushes, intelligent particles with controllable release characteristics can be prepared. Examples are presented in which the switching abilities of the grafted polymers are used to allow drug delivery influenced by light, pH, temperature, ultrasound, and the presence of enzymes.

Poly(dimethyl siloxane) (PDMS) is the most commonly used material in the preparation of microfluidic and other devices by soft lithography. The polymer itself is not the most suited material for many biomedical applications because it is non-biodegradable and has limited compatibility with cells as well as sub-optimal mechanical characteristics. Schuller-Ravoo and coworkers (DOI: 10.1002/cphc.201701308) show that photo-crosslinkable networks based on poly(trimethylene carbonate) can readily be used in common microfabrication technologies to prepare microstructured surfaces and patterned surfaces for cell culturing. The polymer network was shown to perform substantially better than PDMS, making it an alternative material to PDMS in the fields of biology, medicine and tissue engineering.

Translational material research and an interdisciplinary collaboration involving material science, chemistry, engineering, physics, and computational science are promising approaches in the area of smart materials. Efficient synthesis procedures, specific processing schemes, and system engineering approaches are expected to drive innovation processes for material-based solutions, e.g., for energy harvesting and storage, flexible electronics, and healthcare technologies.
The contributions of all authors of this special issue, as well as the editorial and administrative support by Sabine Benner, HZG, and Dr. Kira Welter, Wiley-VCH, are kindly acknowledged.

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Yujun Feng is presently serving as a professor at Sichuan University. After earning his PhD in applied chemistry from Southwest Petroleum University, China, in 1999, he moved to France to undertake his post-doctoral research at the Laboratoire de Physico-Chimie des Polymères, CNRS/Université de Pau, and at the Institut Français du Pétrole (IFP). In 2004, he joined the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, and has been serving as a team leader since then. In September 2012, he was reallocated to Sichuan University where he has been focusing on smart soft materials, in particular stimuli-responsive polymers and surfactants. He has published more than 120 peer-reviewed papers in international journals and holds 8 patents. He serves as associate editors for the Journal of Surfactants and Detergents, and Current Opinion in Colloid and Interface Science.

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Yuanjin Zhao is a full professor at the School of Biological science and medical engineering of Southeast University. He received his Bachelor degree of Clinical Medicine (2006) and PhD degree of Biomedical Engineering (2011) from Southeast University in China. In 2009–2010, he worked as a research scholar in Prof. David A. Weitz's group in the School of Engineering and Applied Sciences of Harvard University. His scientific interests are focused on the microfluidic generation of biomaterials, bioinspired photonic nanomaterials, and organs-on-chips. Yuanjin Zhao has published more than 110 research papers in international journals and applied more than 70 related patents. His recent awards include

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