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Loos, Katja

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Editorial

Editorial: Self-assembly

Self-assembly is the spontaneous and reversible organization of molecular entities by noncovalent interactions [1]. Certain materials self-organize into useful hierarchical architectures, that in the world of macromolecules lead to unique structures and functionalities that can be used both in technical and biological applications [2]. The driving force for self-assembly of polymers is the system's tendency to lower the associated surface free energy per chain. Based on polymer self-assembly, many interesting one-, two- and three-dimensional morphologies, such as spherical micelles, cylinders, rods, and vesicles, have been observed and already successfully used to study the relationship between structure and morphology, and their subsequent application in the fields of electronics [3], membranes [4,5], templating [6,7,8,9] etc.

Block copolymers are known to spontaneously form ordered structures at the nano-to mesoscale [10]. Although the number of different morphologies is rather limited in diblock copolymer systems, their phase behavior becomes increasingly more complex with each additional building block or non-covalent additive added to the system [11,12]. This special issue on polymer self-assembly compiles new synthetic approaches towards polymer systems that can self-organize into interesting structures in bulk, in thin films, and in solution; their applications and novel characterization approaches are included. In addition, this issue's feature article reports how multiple intermolecular interactions such as hydrogen bonding, π - π stacking, metal-ligand coordination, hydrophobic interactions and host-guest interactions can be used to guide the third-order structure of synthetic polymers into an impressive range of morphologies [13]. The reversible and tunable nature of such noncovalent interactions endows these supramolecular assemblies with the important properties of reversibility and stimuli-responsiveness. By careful choice of both the copolymer and, in many cases, the small organic surface-active compound, fascinating morphologies can appear in supramolecular comb-shaped block copolymers [14].

Block copolymers in bulk can, for instance, be used as a material for mechanically demanding switchable devices. Highly amphiphilic and multiple stimuli-responsive polystyrene-*b*-poly[2-(*N*-morpholino)ethyl methacrylate] block copolymers were designed by Abetz and coworkers to respond towards temperature, pH, and kosmotropic as well as chaotropic salts [15]. Hayes et al. reported that microphase-separated supramolecular polyurethanes can be used to produce elastic materials at room temperature whose properties can be easily varied by their composition [16].

Thin films of (block co)polymers are interesting material systems for nanofabrication since they can form well-defined periodic

nanostructures by microphase separation [17]. However, attaining a specific morphology with the required orientation can be challenging. In this respect, fascinating morphological transitions were observed by Reiter et al. in thin Langmuir monolayers of a rod-like polypeptide (poly- γ -benzyl-L-glutamate) as a function of increasing surface density [18]. Kamperman and coworker were able to show, that the morphological behavior of polystyrene-*b*-poly(*N*-isopropylacrylamide)-*b*-polystyrene during selective solvent annealing is highly interesting and that thin films of this material might be suitable for thermo-responsive nanofiltration and biomedical membranes [19]. Asymmetric poly(isoprene-*b*-styrene-*b*-4-vinylpyridine) block copolymers were synthesized by Wiesner et al. and proved suitable for the production of high-quality pH-responsive isoporous ultrafiltration membranes [20] via non-solvent induced phase separation processes [21]. By depositing negatively charged polyelectrolytes into the positively charged cylinder gaps of two-dimensionally confined "dots" pattern - built by hexagonally-packed cylinder block copolymer films - Müller, Shenhar and coworker were able to produce polyelectrolyte nanostructures that adopted a toroidal ("doughnut") shape, that eventually, after increased exposure time to the polyelectrolyte solution, reached the final shape of the deposited polyelectrolyte transitions from a doughnut to a hemisphere. The reported results could lead a way to advanced patterned multilayers that can be used in smart coating systems [22].

When block copolymers are dissolved in a selective solvent, the core blocks tend to aggregate to minimize contact with the solvent, while the corona blocks tend to expand and stay in contact with the solvent. Governed by a delicate balance of the free energy contributions from each block together with the overall entropic properties, block copolymers spontaneously self-assemble into various different structures [23,24]. Hadjichristidis et al. synthesized amphiphilic polymethylene-*b*-poly(ethylene glycol) diblock copolymers, with different hydrophobic chain lengths, that self-assembled into spherical micelles in aqueous solutions, whose size was found to be dependent on the polymethylene block length [25]. Further molecular design - as reported by Laschewsky, Gradzielski and coworker - towards hydrophobically end-capped linear triblock copolymers as well as of three-arm and four-arm star block copolymers of *N,N*-dimethylacrylamide and *N,N*-diethylacrylamide results in an interesting temperature-dependent associative behavior [26]. Förster et al. could show that block copolymer micelles and vesicles can be further manipulated and tailored using a combination of microfluidic flow-focusing and capillary interdiffusion experiments, that give important insights - not only on the

self-assembly pathways of block copolymers into vesicles, but also on the related time-scales and intermediate structures and might pave the way to more defined polymer micelle and vesicle systems in the future [27].

Characterization of polymer self-assembly can be very tedious and usually requires expensive instrumentation and therefore new approaches can have an immediate impact on the field. In this context, **Wilson, van Hest**, and coworker report a combination of multi-angle light scattering and quasi-elastic light scattering with which they were able to accurately assess the inherent shape ratio of differently shaped polymersomes such as spheres, prolates and discs by accurately determining of both the radius of gyration and the hydrodynamic radius [28]. Furthermore, iPAINT super-resolution microscopy was used by **Voets et al.** as a powerful tool to study morphological transitions from spherical to ellipsoidal micelles complex coacervate core micelles based on a flexible cationic diblock copolymer poly(*N*-methyl-2-vinylpyridinium)-*b*-poly(ethylene oxide) and a stiff anionic polyfluorene derivative [29].

The synthesis of all-covalent block copolymer materials can be a very challenging task. By moving to supramolecular chemistry these preparation methods can be avoided while maintaining the same kind of macromolecular complexity [13]. Very interesting Janus nanostructures from the bulk, including Janus cylinders, nanoporous Janus membranes, and Janus sheets were for instance observed by **Ikkala, Gröschel** and coworker using rod-like 4-(4-pentylphenylazo)phenol as supramolecular amphiphiles to tailor the morphologies of polystyrene-*b*-poly(4-vinylpyridine)-*b*-poly(*tert*-butyl methacrylate) ABC triblock terpolymers [30]. In this context, **Binder et al.** report a very interesting new system, that is based on a series of complex supramolecular dendritic polymer networks in the melt state, that are generated by the association between tri-barbiturate functionalized poly(*n*-butyl acrylate), and several different *bis*-Hamilton wedge functionalized polymers that forms a dendritic phase segregated structure, held together solely by specific H-bonding moieties in the sense of a key/lock system [31]. Biological recognition pattern, such as for instance the lectin binding properties, can be further used to tremendously broaden the self-assembly of polymers as reported by **Lecommandoux et al.**, that studied the self-assembly of poly(lysine)-*b*-poly(*benzyl-L*-glutamate) copolypeptides functionalized by introducing galactose and lactose moieties on the copolypeptide's hydrophilic block [32].

Polymer self-assembly also offers excellent opportunities for the production of nanoparticle structures with excellent structure control at the nanoscopic level, which is important for their future applicability [33]. PS-*b*-P4VP@SiO₂ core-shell particles could, for instance, be prepared using polystyrene-*b*-poly(4-vinylpyridine) block copolymers as templates via an acid catalyzed sol-gel process – as reported by **Horechyy, Stamm, Fery** and coworker [34]. **Bettinger, Bockstaller, Matyjaszewski** and coworker were able to show, that by tethering polymer chains on ZnO particles via various routes the dispersibility of this important bandgap semiconductor material in various polymeric matrices was improved tremendously [35]. When grafting light-responsive polymers onto gold nanoparticles **Vana et al.** could trigger the aggregation of the polymer-gold hybrid particles by UV-light [36]. Very interesting crosslinked poly(ionic liquid) nanoparticles were synthesized by **Yuan et al.** via aqueous dispersion polymerization of 1,2,4-triazolium ionic liquid monomers [37,38] in the presence of a dication crosslinker and a fascinating array of shapes and highly ordered inner mesostructures was observed. The system is even able to readily disperse multi-walled carbon nanotubes in water and

organic media [39,40,41].

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Katja Loos
Macromolecular Chemistry and New Polymeric Materials, Zernike
Institute for Advanced Materials, University of Groningen, The
Netherlands
E-mail address: k.u.loos@rug.nl.

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