Self-Organized Multicompartment Nanostructures From Triblock Terpolymers

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Compartmentalization of nanostructures is an important issue since different compartments can have different functions, e.g. loading of different payloads, such as drugs or inorganic nanoparticles. The self-assembly of triblock terpolymers (also known as ABC triblock copolymers) in solution and in the bulk are ideally suited for such a task. A typical example is polystyrene-*block*-polybutadiene-*block*-poly-(methyl methacrylate). Compartmentalization can occur either in the corona or in the core.

We have prepared corona-compartmentalized nanoparticles (Janus spheres, cylinders, or disks) by crosslinking domains in the bulk nanostructures of triblock terpolymers. These Janus micelles have superior properties as interfacial agents, as stabilizers in emulsion polymerization, as compatibilizers of polymer blends, or for the solublization of carbon nanotubes [1,2].

We present a flexible route for the hierarchical, guided self-assembly of triblock terpolymers into multicompartment micelles (MCMs) of different shapes and sizes, simply by choosing the right solvent conditions and solvent sequences. These MCMs can have spherical shapes, like hamburgers, clovers, or footballs. However, by choosing the right terpolymers composition we ca n also trigger the shapes in a way that they reversibly form worm-like structures with alternating compartments of, e.g. polystyrene and polybutadiene, with a corona of PMMA. The different compartments can be loaded with various nanoparticles [3]. Co-assembly of AB- and ABA-style building blocks for MCMs leads to new, complex linear structures at a further level of hierarchy and allows control of the chain length up to 30 µm [4].

We also demonstrate a novel, solution-based approach to Janus micelles by crosslinking the patches on a spherical MCM. In contrast to our former bulk morphology approach this new approach for the first time provides soft Janus micelles with adjustable Janus balance, i.e. adjustable fraction of polymer chains forming one face [5]. This balance is important, e.g., for their use as dispersants of carbon nanotubes.

A new miktoarm-star triblock terpolymer, having one arm each of polybutadiene, quaternized poly(2-vinylpyridine) and poly(*tert*-butyl methacrylate (µ-BVT) forms unusual assemblies in water. Depending on the nature of the counterion of the quaternized 2-vinylpyridine units, a multitude of assemblies is formed, starting from micelles over cylinders to woodlouse-shaped assemblies of lamellae [6].

References

[1] A. Walther, A.H.E. Müller *Soft Matter* **2008**, *4*, 663; *Chem. Rev*. **2013**, *113*, 5194-5261
[2] A. H. Gröschel, P. D. Petrov, T. I. Löbling, M. Müllner, F. Wieberger, C. Kuttner, A. H. E. Müller *Angew. Chem. Int. Ed*. **2013**, *52*, 3602.
[3] A. H. Gröschel, F. H. Schacher, H. Schmalz, O. V. Borisov, E. B. Zhulina, A. Walther, A. H. E. Müller *Nature Commun*. **2012**, *3*, 710.
[4] A. H. Gröschel, A. Walther, T. I. Löbling, F. H. Schacher, H. Schmalz, A. H. E. Müller, in revision
[5] A. H. Gröschel, A. Walther, T. I. Löbling, J. Schmelz, A. Hanisch, H. Schmalz, A. H. E. Müller *J. Am. Chem. Soc*. **2012**, *134*, 13850
[6] A. Hanisch, A. H. Gröschel, M. Förtsch, M. Drechsler, H. Jinnai, T. M. Ruhland, F. H. Schacher, A. H. E. Müller, *ACS Nano* **2013**, *7*, 4030; *Polymer* **2013**, *54*, 4528.