Self-Organized Multi-Compartment Nanostructures From New Triblock Terpolymers

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Compartmentalization of nanostructures is an important issue since different compartments can have different functions, e.g. transport of payloads of different polarity, such as drugs or inorganic nanoparticles. Helmut Ringsdorf was probably first to propose multicompartment micelles based on block copolymers.[1] 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. Compartmentalization can occur either in the corona (e.g., Janus micelles[2]) or in the core.[3]

We present a general procedure to obtain spherical, linear, branched and cyclic multi-compartmented structures composed of many micelles of linear triblock terpolymers by using suitable combinations of solvents that are selective for the different blocks. We have shown that this approach works for at least eight different block terpolymers of largely varying structure in organic solvents or in water. We are able to predict these structures from the ratio of block lengths and the corresponding Flory-Huggins interaction parameters.[4-6]

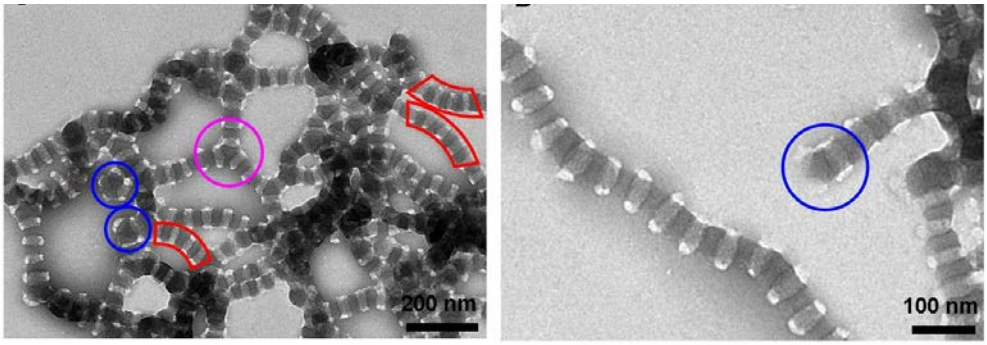

Fig. 1. RuO_4 stained TEM images of undulated cylinders of poly(*tert*-butoxystyrene)-*b*-poly(perfluoroalkyl-1,2-butadiene)-*b*-poly(*tert*-butyl methacrylate), obtained after dialysis from dioxane into ethanol.[4]

Using anionic polymerization, we have synthesized a number of new ABC triblock terpolymers, among them polybutadiene-*block*-poly(2-vinyl pyridine)-*block*-poly(*tert*-butyl methacrylate) (PB-P2VP-PtBMA; BVT). By quaternizing the P2VP block with methyl iodide and/or hydrolyzing the PtBMA block, forming poly(methacrylic acid) (PMAA), we obtain terpolymers of different degrees of amphiphilicity, which form interesting multi-compartment core micelles with an anionic corona, as evidenced by cryogenic transmission electron microscopy (cryo-TEM).[7,8]

These micelles further interact with diblock copolymers having a cationic block, e.g. poly(N,N-dimethylaminoethyl methacrylate)-*block*-poly(ethylene oxide) (PDMAEMA-PEO) forming new sunray-like or core-shell-shell-corona inter-polyelectrolyte complexes (IPECs). These complex organic nanoparticles can be loaded with metal nanoparticles to form hybrids.[9]

In addition, we obtained cylindrical nanoparticles with a double-helical P2VP shell by crosslinking the inner PB domain of bulk structures of BVT. Again, they can form hybrids by loading their shell or corona with metal nanoparticles.[10,11]

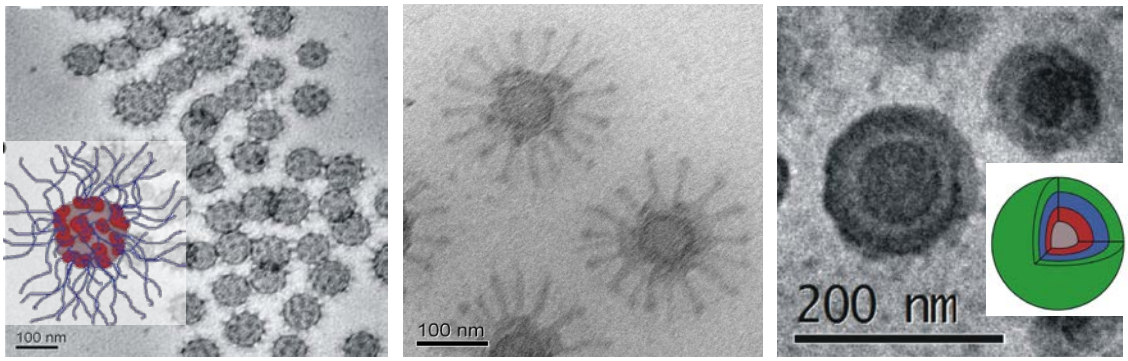

Fig. 2: PB-P2VP-PMAA micelles in water (left) and their interaction with PDMAEMA-PEO after 1 h (middle) and 10 days (right).[8,9]

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