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Multigeometry nanoparticles and higher-order assemblies from block copolymer blends via kinetic control and chemical modification

JIAHUA ZHU, Department of Materials Science and Engineering, University of Delaware, SHIYI ZHANG, KAREN WOOLEY, Department of Chemistry, Texas A&M University, DARRIN POCHAN, Department of Materials Science and Engineering, University of Delaware — Multigeometry micellar structures, due to segregation of unlike hydrophobic domains trapped within the same micelle core, have been produced via self-assembly of block copolymer mixtures in tetrahydrofuran/water solution. The mixture is composed of two block copolymers with distinctive hydrophobic blocks but the same poly(acrylic acid) (PAA) hydrophilic block. By taking advantage of the complexation in the hydrophilic corona between the acid side chains of the PAA block and added organoamine molecules, unlike hydrophobic blocks can be trapped in the same micelle core. Locally, the unlike hydrophobic blocks can segregate into compartments and even express different interfacial curvatures, or geometries, within the same nanoparticle. Through controlled kinetic pathways, block copolymer design and mixing ratios, both micelle compartment size and shape can be controlled to generate sphere-sphere, sphere-cylinder, cylinder-cylinder, cylinder-bilayer, and bilayer-bilayer blended multigeometry nanoparticles. Furthermore, higher order assembly behavior of the micelles has been investigated by taking advantage of chemical modification on the hydrophilic PAA shells. New mixtures using functionalized-PAA-containing block copolymers produce nanoparticles with a compartmentalized surface. These patchy surfaces can be used as templates for asymmetric hybrid nanoparticles, but also as building blocks for hierarchical assembly of the nanoparticles to produce one-dimensional arrays or three dimensional networks.

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