

# Directed Self-Assembly of Block Copolymers as a Route to Novel Hierarchical Superstructures

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## ABSTRACT

Spontaneous self-assembly of block copolymer (BCP) molecules in a block-selective solvent typically results in the formation of micelles possessing a classical spherical morphology. Inclusion of a crystallizable block in the copolymer promotes crystallization-driven self-assembly (CDSA), yielding anisotropic cylindrical micelles that can, after additional processing, possess a remarkably narrow length polydispersity. Anisotropic nanoparticles prepared from BCPs are of growing importance as building blocks for the creation of a wide range of synthetic hierarchical materials. However, the assembly of such structural units is generally limited to the use of amphiphilic interactions. In addition to CDSA to generate single cylindrical micelles, reversible coordination-driven hierarchical self-assembly can be used to produce micron-scale fibers and macroscopic films based on the association of low-polydispersity cylindrical BCP micelles. In this case, coordination of palladium metal centers to phosphine ligands immobilized within the soluble coronas of BCP micelles is observed to induce intermicellar crosslinking, affording stable linear fibers comprised of micelle subunits in a staggered arrangement. The mean length of the fibers can be readily varied by altering the micelle concentration, reaction stoichiometry or aspect ratio of the micelle building blocks. Furthermore, the fibers aggregate upon drying to form robust, self-supporting macroscopic micelle-based thin films with useful mechanical properties that are analogous to crosslinked polymer networks, but on a significantly longer length scale. A comparable hierarchical self-assembly strategy yields toroidal micelles that combine to form micron-scale superstructures. Addition of a crystallizable BCP to a solution of a toroid-forming BCP results in the formation of toroidal multimicelles, as well as single-layer hexagonal arrays of connected toroids. By controlling the ability of the BCPs to form hydrogen bonds through the introduction of hydroxyl groups on the crystallizable BCP and the accompanying level of solvophobic interactions, the BCPs can spontaneously self-assemble to form 3D periodic nanoporous superstructures. These studies demonstrate that self-assembly of BCPs into discrete, non-spherical nanostructures can be scaled up to yield materials with intriguing morphologies and useful properties.