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Hierarchical Structures

Tunable Supermicelle Architectures from the Hierarchical Self-Assembly of Amphiphilic Cylindrical B–A–B Triblock Co-Micelles**

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Amphiphilicity represents one of the most important characteristics of nature's building blocks. Amphiphilic species, such as surfactants and block copolymers, have been shown to form a rich variety of self-assembled structures, including various types of micelles, bilayers, tubes, and vesicles.[1–4] On a larger length scale, amphiphilic nanostructures, such as Janus and patchy particles,[5,6] have been recently utilized to construct a variety of fascinating colloidal materials.[7–9] A limited number of amphiphilic micelle architectures have also been prepared by methods including the self-assembly of ABC triblock copolymers, co-assembly of two different block copolymers, and nanotube-assisted synthesis, and have also been shown to provide a pathway to aggregate soft matter to form various superstructures, such as supermicelles, chains, nanotubes, and nanosheets.[10–15] Nevertheless, the state of the art with these amphiphilic building blocks mainly involves the use of spherical particles. The formation of hierarchical structures from nonspherical particles is rare, despite recent advances.[16–20] As a contribution to this emerging field, we report herein the use of the versatile new crystallization-driven living self-assembly method to access well-defined and tunable amphiphilic cylindrical B–A–B triblock co-micelles analogous to bolaamphiphiles.[21] We also describe their hierarchical self-assembly to form supermicelle architectures.

We have previously demonstrated that asymmetric block copolymers with a short, crystallizable core-forming poly(ferrocenyldimethylsilane) (PFS) metalloblock produce cylindrical micelles with a crystalline PFS core in a selective solvent for the second block.[22,23] The termini of these cylinders remain active toward the addition of further PFS block copolymer unimers and the cylindrical micelles can be controllably elongated by an epitaxial crystallization-driven growth.[24–26] Monodisperse cylindrical micelles have been obtained by the use of very small uniform crystallite seeds as initiators or through a self-seeding approach.[27,28] Moreover, the addition of PFS diblock copolymers with a different corona-forming block from that used to prepare the seed micelles has been shown to form B–A–B triblock co-micelles with spatially distinct corona chemistries.[24–26,29,30] However, to date, our work in this area has been limited to B–A–B triblock co-micelle with A and B co-blocks of similar corona polarity. The formation of amphiphilic systems would be expected to represent a challenge as a medium that functions as a good solvent for both the nonpolar and polar coronas, but not the PFS core would be needed to ensure epitaxial growth. Recently, we were able to prepare amphiphilic A–B–C block co-micelles with a long C block with a polar corona. In polar media, these materials were found to assemble into spherical supermicelles with a "shell" formed by the C segments and a "core" comprising the hydrophobic A and B blocks.[31] We now report the first examples of amphiphilic B–A–B block co-micelles and their self-assembly into spherical and, significantly, also crossed and elongated structures.

To prepare the amphiphilic cylindrical B–A–B triblock co-micelles (Figure 1), firstly, monodisperse PFS-*b*-PDMS (PDMS = polydimethylsiloxane) cylindrical micelles were prepared by adding PFS_{49}-*b*-$PDMS_{504}$ unimers in THF to a solution of small PFS_{28}-*b*-$PDMS_{560}$ crystallites (ca. 23 nm in length) in hexane.[27] These cylinders represented the non-polar A block and the length was controlled by the ratio of the PFS_{49}-*b*-$PDMS_{504}$ unimers to the small seeds (see Table S1 and Figure S1 in the Supporting Information). PFS_{48}-*b*-$P2VP_{414}$ (P2VP = poly(2-vinylpyridine)) was then added to grow the terminal B blocks. Isopropanol (*i*PrOH), a good solvent for P2VP, was added to increase the polarity of the solution. A hexane/*i*PrOH volumetric ratio of 1:3 was found to favor the growth of the PFS-*b*-P2VP micellar blocks but avoid the precipitation of the preformed PFS-*b*-PDMS micelle seeds, which might be anticipated when an excess of *i*PrOH is added.[31] The final amphiphilic cylindrical B–A–B triblock co-micelles are denoted as M(PFS-*b*-P2VP)-*b*-M(PFS-*b*-PDMS)-*b*-M(PFS-*b*-P2VP), where M represents the "micelle" segment. The B blocks with coronas of P2VP were easily distinguished by TEM (see Figure 2) and their length was controlled by the ratio of the PFS_{48}-*b*-$P2VP_{414}$ unimers to the pre-existing cylinders representing the A block (see Table S2 in the Supporting Information). The solutions in hexane/*i*PrOH mixtures were subsequently dialyzed against pure *i*PrOH to produce the supermicelles.

Figure 2 a–c shows the drop-cast TEM images of the dried triblock co-micelles with a constant B block length of 90 nm and increasing A block length of 110, 260, and 505 nm from the 1:3 hexane/*i*PrOH mixture. The TEM images were consistent with the existence of well-dispersed triblock co-

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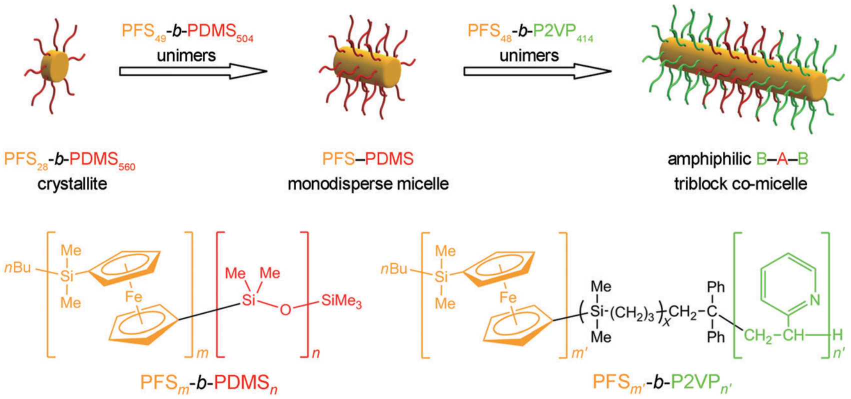

Figure 1. Graphical representation of the formation of amphiphilic cylindrical B–A–B triblock co-micelles by the crystallization-driven living self-assembly of PFS-*b*-PDMS and PFS-*b*-P2VP.

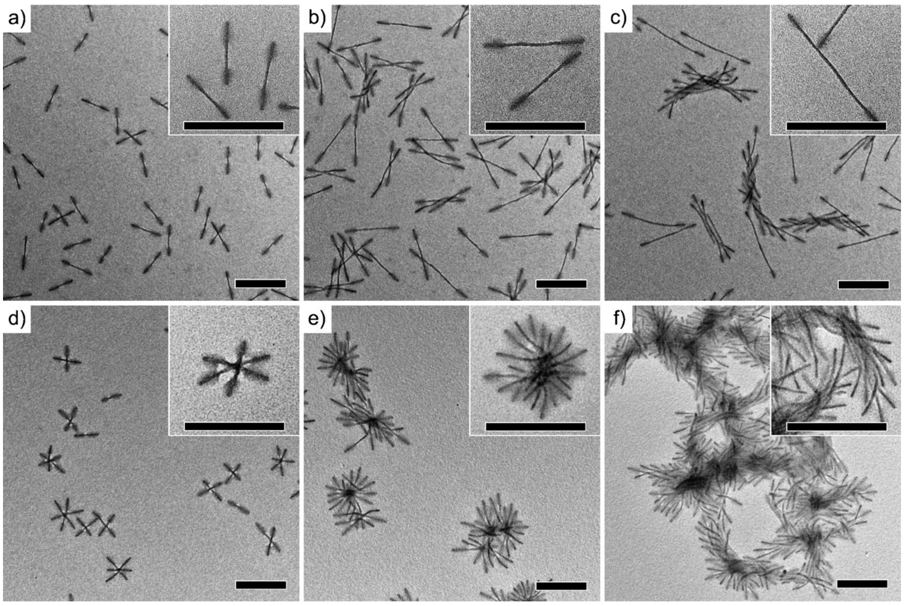

Figure 2. Drop-cast TEM images of M(PFS-*b*-P2VP)-*b*-M(PFS-*b*-PDMS)-*b*-M(PFS-*b*-P2VP) with a B block length of 90 nm and different A block lengths of a) 110, b) 260, and c) 505 nm in a 1:3 hexane/*i*PrOH mixture, and d–f) the corresponding supermicelles formed after dialysis against pure *i*PrOH. The scale bars correspond to 500 nm.

micelles in solution in the case of the short A block (110 nm; Figure 2a), although a small number of intersecting pairs were detected, which might be a drying effect. In contrast, TEM analysis of drop-cast samples of the triblock co-micelles with a longer A block (260 nm) tended to form low aggregation number self-assembled structures (Figure 2b). Interestingly, the triblock co-micelles with an A block length of 505 nm partially self-assembled into helical twisted bundles (Figure 2c; see also Figure S2 in the Supporting Information). Such bundled structures presumably reduce the unfavorable interactions between the nonpolar PDMS corona regions of the long A block and the polar *i*PrOH solvent, the dominant component of the solvent mixture.

After dialysis to form a solution in pure *i*PrOH, we anticipated that the nonpolar A blocks of neighboring triblock co-micelles would aggregate to reduce the surface free energy. In addition, the repulsion between the polar B blocks was expected to favor the formation of discrete supermicelles. Indeed, the triblock co-micelles formed a series of discrete supermicelle architectures in *i*PrOH, depending on the relative lengths of the A and B blocks (Figure 2d–f and Figure S3 in the Supporting Information). The aggregation number of the supermicelles was found to dramatically increase with an increase in the relative length of the A block (Figure 2d–f). The larger supermicelles were detected in solution by optical microscopy (see Figure S4); the supermicelles were therefore not formed by a drying effect.

The morphology of the supermicelles changed as the length of the A block was varied. The triblock co-micelles with a short A block (110 nm) self-assembled into regular crossed supermicelles, either in a crosslike or a hexagonal configuration (Figure 2d and Figure 3a). AFM images and height analysis (Figure 4) showed that the three triblock co-micelles comprise a 2D hexagonally crossed supermicelle.[32] The height of the common junction of three triblock co-micelles was estimated to be 16 nm, which is significantly less than the sum of their core diameters (each ca. 13 nm as estimated from the TEM images). This value is suggestive of a surprising degree of flattening of the micelles, presumably as a consequence of strong

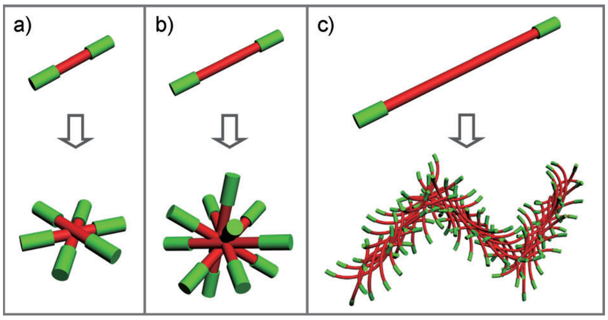

Figure 3. Illustration of the supermicelles formed by M(PFS-*b*-P2VP)-*b*-M(PFS-*b*-PDMS)-*b*-M(PFS-*b*-P2VP) with various center block lengths. For simplicity, the A and B blocks are denoted by red and green cylinders, respectively.

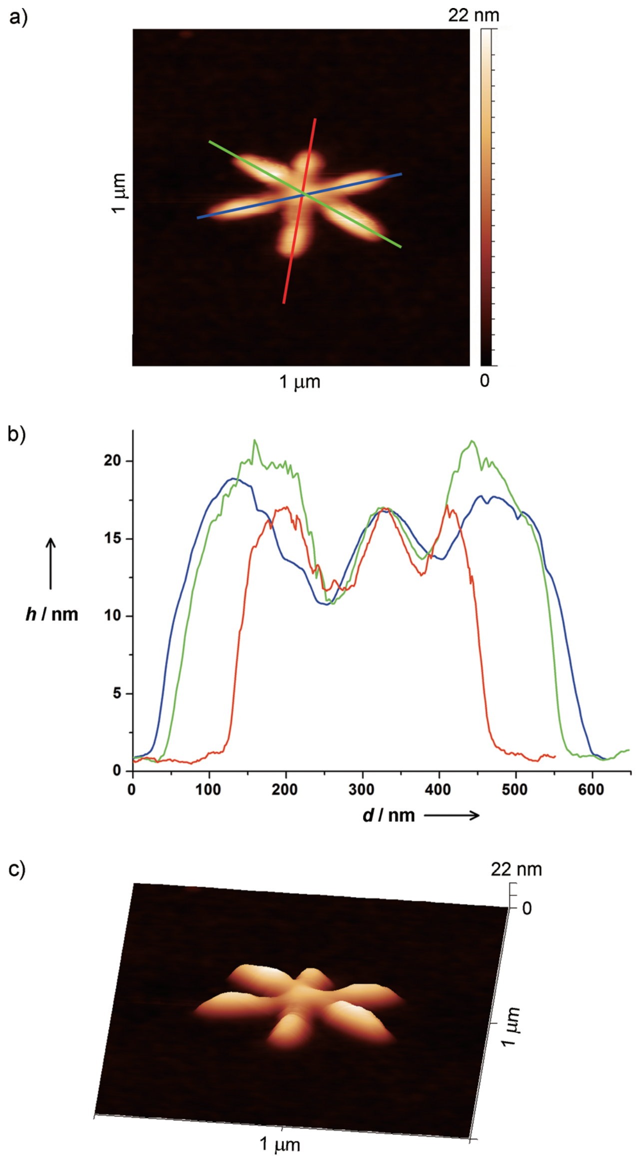

Figure 4. a) AFM height image, b) cross-sectional height profiles along the long axis of the triblock co-micelles and c) 3D view AFM height image of a hexagonally stacked supermicelle formed by M(PFS-*b*-P2VP)-*b*-M(PFS-*b*-PDMS)-*b*-M(PFS-*b*-P2VP) with A and B block lengths of 110 and 90 nm, respectively.

interfacial interaction with the silicon substrate (Figure S5 in the Supporting Information). The supermicelles formed with a longer (260 nm) A block showed a spherical morphology (Figure 2e, Figure 3b, and Figure S6). Unlike in the crossed supermicelles, the triblock co-micelles were no longer stacked center-by-center, but preferred a more flexible stacking site and slight bending of the component block co-micelles was detected. When the length of the A block was increased further to 505 nm, the triblock co-micelles were found to be substantially twisted and elongated network structures were formed (Figure 2f, Figure 3c, and Figures S7 and S14). Clearly the preferred morphology for the supermicelles changed from spherical to cylinder-like with an increase in the relative length of the A block. This behavior is reminiscent of that of small-molecule-surfactant- or block-copolymer-based micelle systems, in which the curvature of the core–corona interface decreases as the core to corona block ratio increases.[33–35]

The self-assembly of the triblock co-micelles to result in supermicelles was shown to be thermally reversible in *i*PrOH.[36] After heating a solution at 60 °C for 15 min, drop-cast TEM images obtained by drying the hot solution indicated that the supermicelle architectures had been disassembled, while the integrity of the triblock co-micelle building blocks was preserved (Figure S8a–c in the Supporting Information). This may be explained by the enhanced thermal motion and the improved solvation of PDMS corona, which disrupt the weak interactions between the triblock co-micelles. The supermicelles reformed after the solution was cooled to ambient temperature (Figure S8d–f).

Crosslinking of the core or corona of micelles is a well-established method for the generation of micelles with improved stability.[37] To stabilize the supermicelle architectures in an analogous manner, a cross-linkable A segment derived from the diblock polymer PFS-*b*-PMVS (PMVS = polymethylvinylsiloxane) was introduced to the triblock co-micelle. The A blocks in the supermicelles were then cross-linked by platinum(0)-promoted hydrosilylation of 1,1,3,3-tetramethyldisiloxane (TMDS; see Figures S9, S12, and S13 in the Supporting Information).[30,38,39] The cross-linked supermicelles were found to be thermally stable and retained their structures in the presence of nonpolar solvents (Figures S10–S13).

In summary, amphiphilic cylindrical B–A–B triblock co-micelles, in a similar fashion to bolaamphiphiles, self-assemble reversibly when placed in a polar solvent. The aggregation number, morphology, packing, and symmetry of the resulting supermicelles can be controlled by tailoring the lengths of the nonpolar (A) and polar (B) micellar blocks. In particular, regular crossed and elongated network structures are reported for the first time, and corona cross-linking renders the supermicelles resistant to thermally and nonpolar-solvent-induced disassembly. We are currently exploring the self-assembly of a wide range of other block co-micelles with variations in chemical composition, segment number, length, and sequence, in order to access a variety of new hierarchical architectures.

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