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Branched Cylindrical Micelles via Crystallization-Driven Self-Assembly

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Supporting Information

ABSTRACT: We report the preparation of branched micelles by the growth of thinner-core cylindrical micelles at the termini of the thicker-core cylindrical micelle seeds through crystallization-driven self-assembly of polyferrocenylsilane block copolymers. The branched micelles possessed structures with monodisperse middle segments and, in most cases, two branches at the seed terminus. After cross-linking of the coronas, the branched micelles become resistant to dissolution in good solvents for both blocks and can be manipulated as colloidally stable nanomaterials.

Amphiphilic species such as small-molecule surfactants and block copolymers self-assemble into micelles in selective solvents.[1] Over the past few decades, the self-assembly of block copolymers has enabled the formation of an impressive and diverse array of micellar morphologies, including spherical micelles, cylindrical/wormlike micelles, vesicles, etc.[2] However, although branched structures are ubiquitous in natural systems and are important for many functions, compared to the recent achievements in the fabrication of ordered branched inorganic nanomaterials,[3] the controlled formation of branched structures in soft matter systems is much less developed. Thus, although it is known that the branching of the wormlike micelles is responsible for the novel rheological properties of some surfactant solutions,[4] there are only a few reports on the preparation of branched wormlike micelles of block copolymers. These pioneering reports describe systems that involve a very narrow window of phase space and self-assembly conditions and no significant control over the branching degree and junction location.[2,5] Herein, we report a significant advance in the preparation of branched cylindrical micelles by taking the advantage of crystallization-driven self-assembly (CDSA) of crystalline-coil polyferrocenylsilane block copolymers. We also demonstrate that by using shell-cross-linking procedures, swellable, colloidally stable branched nanomaterials are formed.

Polyferrocenylsilane block copolymers[6] with asymmetric structures containing a shorter, crystallizable core-forming poly(ferrocenyldimethylsilane) (PFDMS) metalloblock are known to form cylindrical micelles with a crystalline PFDMS core in a selective solvent for the complementary block.[7] An interesting feature of these fiber-like micelles is that their termini remain active to the addition of further PFDMS block copolymer unimers and controlled elongation is possible.[8] This process, which has been termed CDSA, also appears to be potentially applicable to a wide range of other crystalline-coil block copolymers.[9] Using CDSA we and others have been able to control micelle lengths[8,9] and to prepare block co-micelles with tunable and spatially distinct coronal or core chemistries.[10] In addition, scarf-like micelles can be prepared through the use of approximately rectangular platelet micelles as seeds,[10b] and surfaces with grafted micelle brush layers,[10b] multiarmed micelles,[11] and fibers with grafted perpendicular arms[12] can be grown from homopolymer films, nanocrystals, and fibers, respectively. Here we demonstrate a new concept that allows further morphological control and the formation of branched structures. Our approach involves, first, the use of asymmetric PFDMS diblock copolymers with very different degrees of polymerization of the core-forming metalloblock to form cylindrical micelles with variable core diameters. In a second step, we then show that the ends of the cylinders with a higher core diameter can be used as initiators for the growth of multiple cylinders of lower core diameter, thereby permitting a new synthetic approach to branched cylindrical micelles.

Our strategy started from the core diameter control of cylindrical micelles of PFDMS diblock copolymers. While much previous attention has been paid to the contour length control, adjustment of the core diameter of the cylindrical micelles is virtually unexplored. Previous studies have indicated that the PFDMS chains in cylindrical PFDMS-*b*-PI (PI = polyisoprene) micelles pack in a lattice with 2D pseudo-hexagonal symmetry perpendicular to the long axis of the micelle and span the diameter of the crystalline central core region. This is assumed to be accompanied by chain-folding in a relatively amorphous outer core region close to the core/corona interface.[13] Based on this model, the core diameter would be expected to increase with an increase in the chain length of the PFDMS block and with a decrease in the degree of chain folding. Since chain folding in these systems is likely to be affected by a complex range of parameters, including the solvent and temperature, the nature of the coronal block, the block ratio, and the overall molar mass, we approached core diameter control by focusing on tuning the length of the PFDMS block while keeping the self-assembly conditions constant.

We employed two well-defined PFDMS diblock copolymers, namely PFDMS_{48}-*b*-P2VP_{414} (P2VP = poly(2-vinylpyridine); subscripts refer to the number-average degree of polymerization) and PFDMS_{20}-*b*-P2VP_{140} (Scheme S1). Cylindrical micelles were prepared by dissolving the diblock copolymers in

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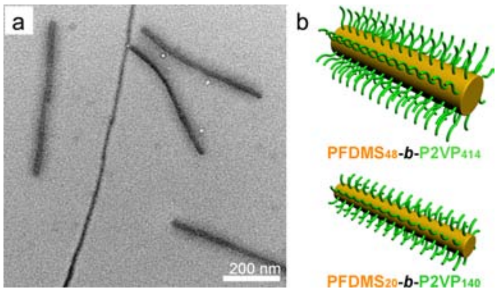

Figure 1. (a) TEM image of a mixture of the cylindrical micelles of PFDMS$_{48}$-*b*-P2VP$_{414}$ and PFDMS$_{20}$-*b*-P2VP$_{140}$. (b) Schematic representation of the cylindrical micelles.

isopropanol, which is a selective solvent for the P2VP block. To prepare monodisperse samples of cylinders, the cylindrical micelles were sonicated and then annealed at a higher temperature according to previously published self-seeding protocols (see Supporting Information (SI) for details).[8c,14]

As anticipated, TEM and AFM analysis (see SI for details) revealed that PFDMS$_{48}$-*b*-P2VP$_{414}$ formed substantially thicker cylindrical micelles than PFDMS$_{20}$-*b*-P2VP$_{140}$, with approximately half the degree of polymerization for the PFDMS core-forming block (Figures S1 and S2). To illustrate these results we obtained a higher magnification TEM image of a deliberately created mixture of short PFDMS$_{48}$-*b*-P2VP$_{414}$ and long PFDMS$_{20}$-*b*-P2VP$_{140}$ cylindrical micelles (Figure 1). For the short PFDMS$_{48}$-*b*-P2VP$_{414}$ cylindrical micelles, the electron dense PFDMS cores could be clearly identified from the lighter P2VP coronas and were measured to be 20 nm in average diameter. For the long PFDMS$_{20}$-*b*-P2VP$_{140}$ cylindrical micelles, the P2VP coronas were hardly detectable, presumably as a result of their lower degree of polymerization, and the average diameter of the PFDMS core was estimated to be ~10 nm. Given that the average distance between two adjacent ferrocenyldimethylsilane units in the PFDMS chain is ~0.65 nm,[13] the contour length of chain-extended PFDMS block would be ~31 and ~13 nm for PFDMS$_{48}$-*b*-P2VP$_{414}$ and PFDMS$_{20}$-*b*-P2VP$_{140}$, respectively. This indicated that the PFDMS chains were hardly folded in the core, especially for PFDMS$_{20}$-*b*-P2VP$_{140}$, although chain folds may exist in the outer core region near the core/corona interface (Figure S3).

As noted above, multiple cylindrical micelles can grow simultaneously from the edges of the platelet micelle seeds or from the surface of the PFDMS nanocrystals.[10b,11] This suggested that the number of cylindrical micelles grown from the termini of a single cylindrical seed micelle by CDSA would depend on the active exposed area. We hypothesized that the use of a cylindrical micelle with a thicker PFDMS core as the seed should allow the growth of multiple cylindrical micelles with a thinner PFDMS core to form a branched structure (Figure 2). To this end, we used the PFDMS$_{48}$-*b*-P2VP$_{414}$ cylindrical micelles as the seeds and to the seed solution (in isopropanol) subsequently added the unimers of PFDMS$_{20}$-*b*-P2VP$_{140}$ (in a small amount of THF, a good solvent for both blocks).

Analysis by TEM and AFM (Figure 3) was performed after 1 day on aliquots of the resulting solution after solvent evaporation. This showed the presence of predominantly (94%) branched cylindrical micelles with a thicker middle segment derived from the seeds and multiple thinner branches at the two ends (Figure 3a,b). The remaining species (6%) were linear cylindrical micelles in which the thicker, seed-derived middle segment possessed a single thinner cylinder at each end (Figure 3c). It can be seen from the high-magnification TEM image (Figure 3a, inset) that the branches grew at the termini of the cylindrical seed micelles. The branches were also reasonably monodisperse in contour length (L_n = 590 nm, L_w/L_n = 1.07, where L_n is number-average length and L_w is weight-average length), confirming an efficient living CDSA process.[8b] The core diameter of the branches (~10 nm) was comparable with that of PFDMS$_{20}$-*b*-P2VP$_{140}$ cylindrical micelles (Figure 1a), which indicated that the living CDSA of PFDMS$_{20}$-*b*-P2VP$_{140}$ was not significantly altered by using the thicker core seeds as initiators. The dramatic difference in the cross-section size of the middle segment (~20 nm height, 120 nm width) and the branches (~10 nm height, 60 nm width) was also confirmed by the AFM height profiles (Figure 3d), which was in accordance with the data of the original PFDMS$_{48}$-*b*-P2VP$_{414}$ and PFDMS$_{20}$-*b*-P2VP$_{140}$ cylindrical micelles (Figure S2).

It was found that the number of branches at each end of the branched cylindrical micelles was not constant (Figures 3 and

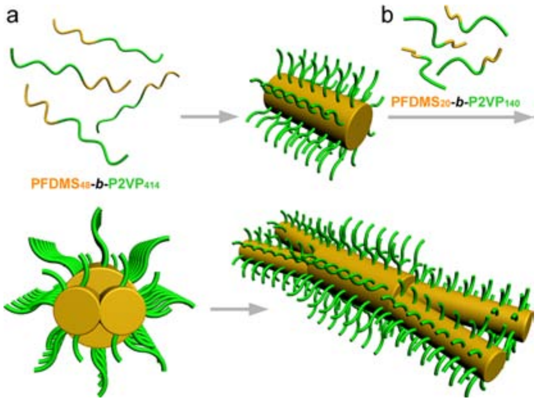

Figure 2. Schematic representation of the formation of branched cylindrical micelles. (a) Formation of cylindrical micelle seeds with thicker cores derived from PFDMS$_{48}$-*b*-P2VP$_{414}$. (b) Subsequent growth of multiple thinner-core cylindrical micelle branches by CDSA on addition of PFDMS$_{20}$-*b*-P2VP$_{140}$ unimers.

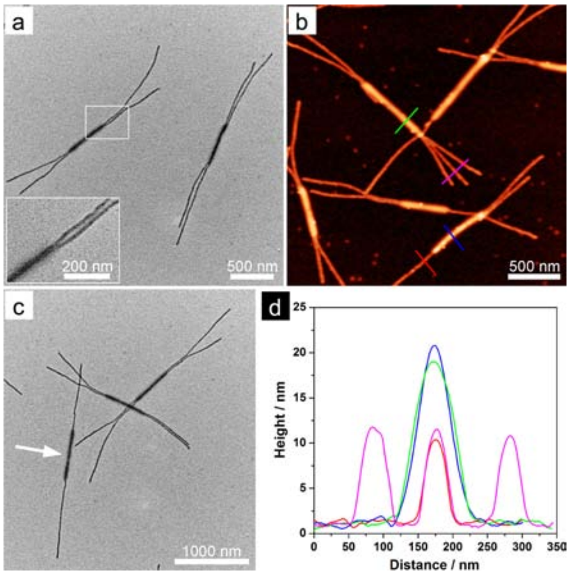

Figure 3. (a) TEM images, (b) AFM height image, and (d) height profiles of branched cylindrical micelles. (c) TEM image showing the coexistence of linear cylindrical micelles (noted by arrow).

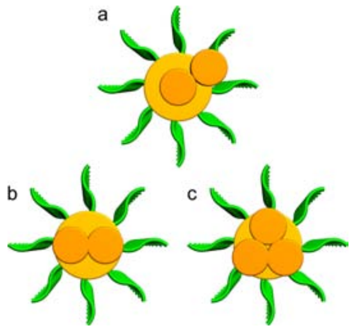

Figure 4. Possible mechanism for the determination of degree of branching of the branched cylindrical micelles. The crystalline cores of the branches are depicted by darker orange color, and the P2VP coronas on the branches are left out for clarity.

S4). As illustrated in the distribution chart shown in Figure S4, ~25% of the total termini of the $PFDMS_{48}$-*b*-$P2VP_{414}$ seed micelles had only one grown $PFDMS_{20}$-*b*-$P2VP_{140}$ cylindrical micelle, ~60% of them had two branches, and ~15% had three or more. Originally, we assumed that such a distribution of the degree of branching would be a consequence of the random variation in the active area of the termini of the seed micelles as the diameter and crystalline region of the PFDMS core may slightly change and interference from the P2VP coronas may also exist. However, we noted that the PFDMS cores were quite uniform in diameter for all of the seed micelles and more importantly, the single $PFDMS_{20}$-*b*-$P2VP_{140}$ cylinder or the bundle of the branches appeared to grow at the center of the termini of the seed micelles (Figures 3 and S4). We thus postulated that the degree of branching would be alternatively determined by the competitive initiation of $PFDMS_{20}$-*b*-$P2VP_{140}$ cylinders at different positions of the termini of the seed micelles. Since the core diameter of the $PFDMS_{20}$-*b*-$P2VP_{140}$ cylindrical micelles was around half of that of the $PFDMS_{48}$-*b*-$P2VP_{414}$ seed micelles, when the first $PFDMS_{20}$-*b*-$P2VP_{140}$ cylindrical micelle grows at the center of a terminus of one seed micelle, the growth of the second $PFDMS_{20}$-*b*-$P2VP_{140}$ cylinder on the remaining available space in the form of a ring (of width ~0.5 × core diameter of the $PFDMS_{20}$-*b*-$P2VP_{140}$ cylinders) would be unfavorable (Figure 4a). On the other hand, if the first $PFDMS_{20}$-*b*-$P2VP_{140}$ cylinder grows mainly on one side of the crystalline terminus of the seed micelle, the growth of the second $PFDMS_{20}$-*b*-$P2VP_{140}$ cylinder at the other side would be possible (Figure 4b). Moreover, if the $PFDMS_{20}$-*b*-$P2VP_{140}$ cylinders grow along the edge of the crystalline terminus of the seed micelle, growth of more branches would be also possible (Figure 4c). It should be noted that the initiation of the branches at different seeds was relatively fast (<1 min) and growth of the subsequent branches at the same terminus started very shortly thereafter (Figure S5).

The use of PFDMS-*b*-P2VP seeds with a long PFDMS block that has more than twice the degree of polymerization as that for the added unimers was of key importance for the formation of branched cylindrical micelles. Control experiments involving the addition of $PFDMS_{34}$-*b*-$P2VP_{272}$ unimers to the seed solution of $PFDMS_{48}$-*b*-$P2VP_{414}$ cylindrical micelles or the addition of $PFDMS_{20}$-*b*-$P2VP_{140}$ unimers to the seed solution of $PFDMS_{34}$-*b*-$P2VP_{272}$ cylindrical micelles failed to give branched structures but produced instead only linear cylindrical micelles, although again the end segments were thinner than the seed-derived middle segment (Figure S6).

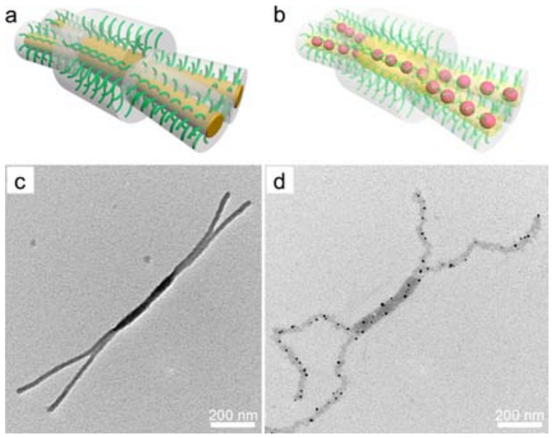

Figure 5. Graphical representations and TEM images of (a,c) rigid shell-cross-linked, branched cylindrical micelles with crystalline cores from isopropanol and (b,d) flexible Ag nanoparticle-encapsulated branched cylindrical micelles with swollen cores from dichloromethane. The Ag nanoparticles are depicted as red spheres in (b).

Cross-linking of the core or corona/shell of micelles is a well-established method for the generation of micelles with improved stability.[15] Cylindrical micelles of PFDMS block copolymers with vinyl group-functionalized coronas have been previously proven to be cross-linkable via Pt(0)-promoted hydrosilylation with 1,1,3,3-tetramethyldisiloxane (TMDS)[16] or Pt(0)-olefin coordination.[10c] To make robust branched structures, the P2VP coronas of the branched cylindrical micelles were cross-linked by the addition of Karstedt's catalyst in the presence of various silanes, presumably through the formation of small Pt nanoparticles (~2.0 nm in average diameter, Figure S7)[17] and their coordination by the pyridyl groups on P2VP (see SI for details).[18,19] The shell-cross-linked branched cylindrical micelles (Figure 5a,c) were resistant to dissolution and maintained their structures in good solvents for both blocks (THF and dichloromethane), although the rigid crystalline PFDMS cores were solvated and thus the micelles became more flexible (Figure 5d and Figure S8).

We have previously reported that silver nanoparticles can be encapsulated in shell-cross-linked cylindrical micelles of PFDMS block copolymers via an in situ reduction of Ag^+ ions by the Fe(II) moieties of the swollen redox-active PFDMS core and consequently create 1D arrays of nanoparticles along the micelle cylinders.[20] In an analogous manner, the encapsulation of silver nanoparticles in the shell-cross-linked branched cylindrical micelles can be expected. Indeed, after dispersal in dichloromethane to swell the PFDMS core followed by pre-oxidation of the PFDMS block by "magic blue" $[(p\text{-}BrC_6H_4)_3N][SbF_6]$, and then the addition of $Ag[SbF_6]$ (see SI for details), the shell-cross-linked branched cylindrical micelles encapsulated silver nanoparticles (~5−13 nm in diameter) inside both the middle $PFDMS_{48}$-*b*-$P2VP_{414}$ segment and the $PFDMS_{20}$-*b*-$P2VP_{140}$ branches, facilitating the formation of branched 1D arrays of metal nanoparticles (Figures 5b,d and S13).

In summary, we have demonstrated that branched cylindrical micelles can be prepared by a CDSA approach involving the addition of PFDMS-*b*-P2VP with a short PFDMS block (which forms cylinders with a thin core) to a cylindrical micelle seed with a thick core formed by PFDMS-*b*-P2VP with a long PFDMS block. Branched 1D arrays of silver nanoparticles can be prepared through in situ redox chemistry in the shell-cross-linked branched cylindrical micelles. Due to the uniform branched structure, the reactive P2VP coronas, the redox-active PFDMS cores, and the tunable lengths of the middle segment and the branches, the branched cylindrical micelles provide a promising scaffold for the fabrication of a variety of other branched nanomaterials. For example, we are currently exploring the formation of branched nanotubes by etching the PFDMS core from their inorganic replicas. Future work will also aim at the preparation of hyperbranched micelles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional results. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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