

Multi-Armed Micelles and Block Co-micelles via Crystallization-Driven Self-Assembly with Homopolymer Nanocrystals as Initiators

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S Supporting Information

ABSTRACT: We report the preparation of multi-armed micelles and block co-micelles using the crystallization-driven self-assembly of crystalline-coil polyferrocenylsilane block copolymers from nanocrystals of the homopolymer. The resulting multi-armed micelles possessed hierarchical multipod structures with monodisperse and tunable arm lengths. The termini of the arms remained active to the addition of further block copolymer unimers, and multi-armed block co-micelles with segmented arm chemistries and variable segment sequences were prepared. Coronal cross-linking followed by nanocrystal dissolution led to the release of non-centrosymmetric AB cylindrical diblock co-micelles.

Branched tetrapod or octapod-shaped nanocrystals,¹ hyper-branched colloidal nanoparticles,² and related tree-like structures³ have recently emerged as promising materials due to their potential applications in optics and electronics and as building blocks for superlattices.⁴ In contrast, the controlled preparation of branched structures based on soft matter systems remains much less developed, despite recent discoveries of “Y” junctions and some more highly branched morphologies for surfactant- or block copolymer-based micelles.^{5,6} Herein, we report the formation of multi-armed micelles through the crystallization-driven growth of cylindrical micelles from crystalline-coil diblock copolymers using nanocrystals of the homopolymer corresponding to the core-forming block. We also describe the formation of segmented arm structures including robust cross-linked multi-armed micelles, and the use of a new strategy for the preparation of non-centrosymmetric cylindrical AB block co-micelles.

We have previously demonstrated that asymmetric block copolymers with a short, crystallizable core-forming poly(ferrocenyldimethylsilane) (PFDMS) metalloblock form cylindrical micelles with a crystalline PFDMS core in a selective solvent for the complementary block.^{7,8} The termini of these cylinders remain active to the addition of further PFDMS block copolymer unimers, and controlled elongation is possible via crystallization-driven living self-assembly.⁹ Moreover, the addition of PFDMS block copolymers with a different corona-forming block or analogous materials with a poly(ferrocenyldimethylgermane) (PFDMG) core-forming block yields block co-micelles with spatially distinct coronal or core chemistries.¹⁰ However, the use of the cylindrical or platelet^{10b,c} micelle

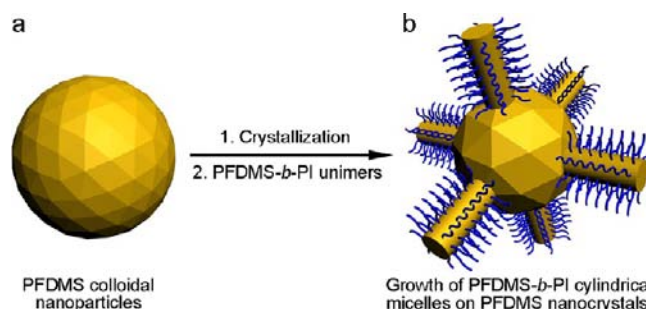


Figure 1. Schematic representation of the formation of multi-armed micelles by crystallization-driven growth of PFDMS-*b*-PI cylindrical micelles on PFDMS nanocrystals.

precursors only permits one-dimensional epitaxial growth of cylindrical micelles from the termini (along the long axis).¹¹

To facilitate the growth of branched structures, the creation of nuclei with multiple active sites for initiation is desirable. We therefore targeted the formation of PFDMS nanocrystals. However, due to the lack of a long soluble block to stabilize the discrete particles, PFDMS normally aggregates to form lamellar crystals in a non-solvent, such as hexane. Attempts to generate the targeted nanocrystal initiators by sonicating the PFDMS crystals were unsuccessful as growth at only the two ends of the fragments along the long axis was detected (Supporting Information, Figure S1). However, promisingly, we found that PFDMS initially forms colloidal nanoparticles when injected as a solution in THF into hexane (Figure S2). We postulated that these colloidal PFDMS homopolymer nanoparticles might be stabilized by the addition of PFDMS block copolymers, in a similar manner to surfactant-stabilized emulsions, and might then function as useful seeds for the growth of multi-armed micelles (Figure 1).

To evaluate this hypothesis, we injected 100 μL of PFDMS₄₃ solution (1 mg/mL in THF) into 5 mL of hexane under vigorous stirring and after 20 s added 5 μL of a unimer solution (10 mg/mL in THF) of PFDMS₅₃-*b*-PI₆₃₇ (PI = polyisoprene). Surprisingly, TEM analysis revealed the exclusive formation of platelet micelles, which can presumably be attributed to the co-assembly of PFDMS₅₃-*b*-PI₆₃₇ with PFDMS₄₃ (Figure S3a). On increasing the aging time of the PFDMS colloidal solution to 20 min, a remarkable change in the resulting micelle morphology to multi-armed structures was detected (Figure S3).

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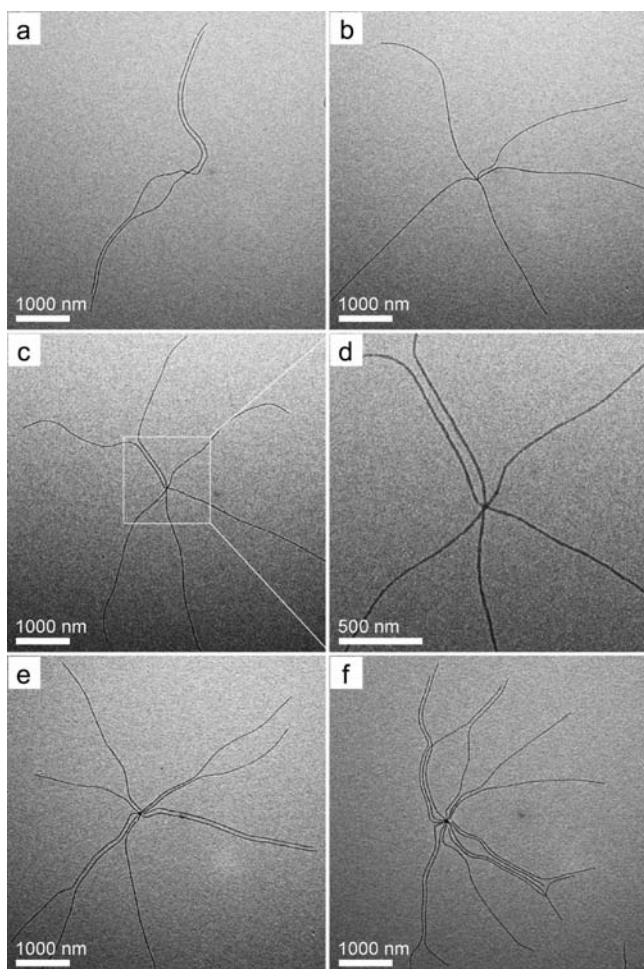


Figure 2. Representative TEM images of the M(PFDMS-*b*-PI)@PFDMS multi-armed micelles with different arm numbers co-existed in the same solution. Aging time of the PFDMS colloidal solution = 4 h.

In the optimized procedure, multi-armed micelles with uniform cylindrical micelles as arms were prepared by further increasing the aging time of the PFDMS colloidal solution to 2–4 h and, following unimer addition, subsequently leaving the quiescent solution for 24 h. The colloidal solution of multi-armed micelles was isolated by decantation from a small amount of precipitated PFDMS homopolymer crystals and the contents were then characterized by TEM and AFM. Figure 2 shows representative TEM images of the M(PFDMS-*b*-PI)@PFDMS multi-armed micelles, where M represents “micelle” and @ implies “grown from”. Multipod structures with various arm numbers, such as tetrapod, pentapod, hexapod, nonapod and tridecapod, were found to coexist in the same solution (Figures 2 and S5). Notably, the arms were of approximate lengths irrespective of the number of arms on the multi-armed micelle (Figure S6), implying that all nucleation sites on the nanocrystals are simultaneously active and thus all arms have on average the same time to grow. The length of the arms could be easily tuned by applying different ratios of PFDMS₅₃-*b*-PI₆₃₇ to PFDMS₄₃ (Figures 3 and S7), although the length was also sensitive to the aging time of the PFDMS colloidal solution. The arm number for the multi-armed micelles appeared to increase with an increase in the size of the central PFDMS nanocrystal (Figure 2). This suggests that to permit precise control over the arm number a

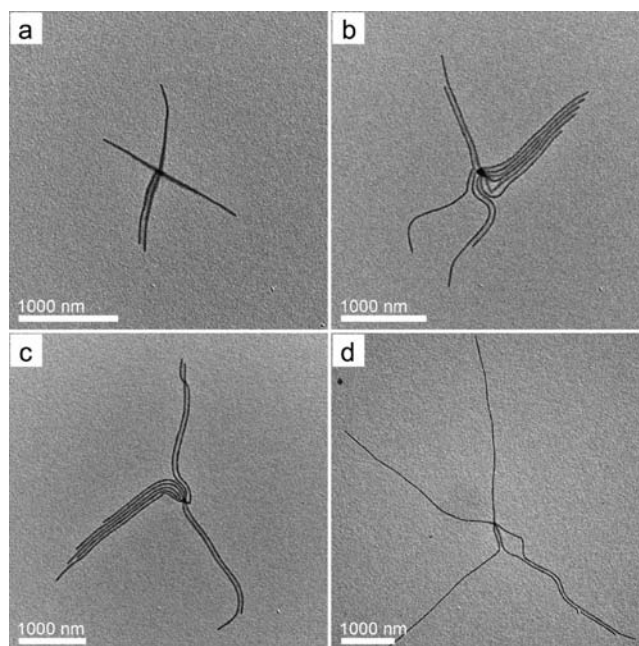


Figure 3. TEM images of the multi-armed micelles with various arm lengths obtained by adding (a) 1 μ L, (b) 2 μ L, (c) 4 μ L, and (d) 8 μ L of PFDMS-*b*-PI unimer solution to the PFDMS colloidal solution aged for 3 h, respectively. L_n = (a) 810 nm, (b) 1350 nm, (c) 2100 nm, and (d) 2960 nm.

future challenge will be the preparation of PFDMS nanocrystals that are monodisperse in size.

AFM height images and height profiles (Figure 4a–c) showed that the nanocrystal comprising the center of a decapod micelle was ca. 25 nm in height and ca. 100 nm in diameter, values that were much larger than those of the arms (ca. 7 and 50 nm, respectively). The phase image also showed that the arms were

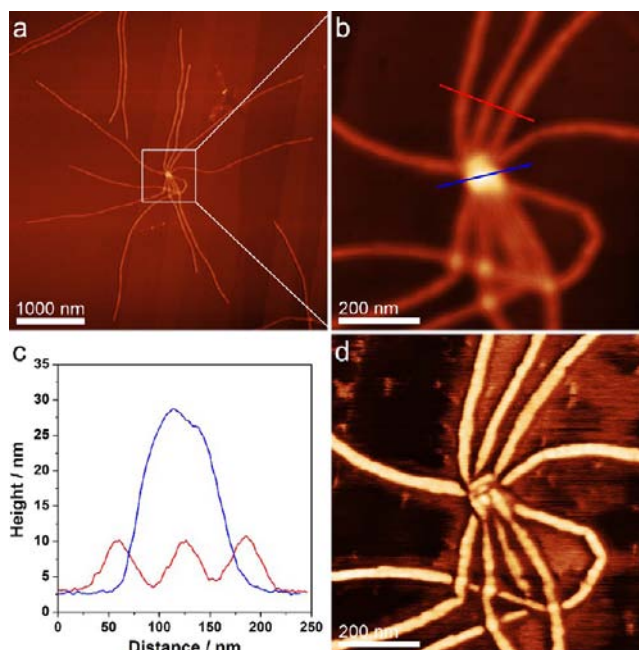


Figure 4. (a,b) AFM height images, (c) height profiles, and (d) phase image of a decapod-shaped M(PFDMS-*b*-PI)@PFDMS multi-armed micelle.

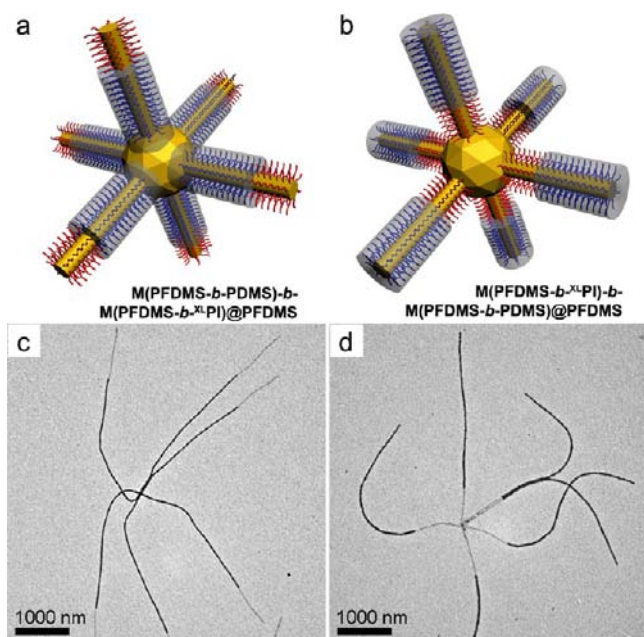


Figure 5. Pictorial representations and corresponding TEM images of (a,c) the $M(\text{PFDM}S\text{-}b\text{-PDMS})\text{-}b\text{-}M(\text{PFDM}S\text{-}b\text{-}^{\text{XL}}\text{PI})@\text{PFDM}S$ and (b,d) the $M(\text{PFDM}S\text{-}b\text{-}^{\text{XL}}\text{PI})\text{-}b\text{-}M(\text{PFDM}S\text{-}b\text{-}PDMS)@\text{PFDM}S$ multi-armed diblock co-micelles.

grown in different directions from the central PFDMS nanoparticle (Figure 4d).

It was found that for the PFDMS colloidal solutions aged for over 30 min, PFDMS crystals emerged as suspensions in the solutions while numerous small PFDMS nanocrystals still survived simultaneously (Figures S2c and S8a). To provide more insight into the kinetics of the growth process, the formation of multi-armed micelles in solution after unimer addition to PFDMS nanocrystals aged for 4 h was monitored by TEM (Figure S8). The growth of the cylindrical micelles from PFDMS nanocrystals started after only 5 min to give arms of length 320 nm (Figure S8b). Further growth led to arms with an average length of 590 nm in 20 min and 1120 nm after 1 h (Figure S8c,d).¹²

Evidence to support the epitaxial nature of the crystallization-driven growth for the formation of the multi-armed micelles was obtained from a range of control experiments. These involved the use of combinations of the colloidal solutions of homopolymers (crystalline PFDMS, PFDMG and poly(ferrocenyldiethylsilane) (PFDES) and also amorphous poly(ferrocenyldiethylmethylsilane) (PFEMS)) and added block copolymers (crystalline-coil PFDMS-*b*-PI and PFDES-*b*-PI).¹³ Growth of cylindrical micelles from the homopolymer particles was only detected in the case of the same crystalline homopolymers and core-forming blocks and heteroepitaxy was only observed in the case of PFDMG with added PFDMS-*b*-PI (Figures S9 and S10). This is consistent with previous observations that amorphous PFEMS does not allow seeded growth and that heteroepitaxy occurs only between PFDMS and PFDMG but not with PFDES due to lattice matching and/or crystallization kinetics effects.^{10b,13}

We have noted that the arms are relatively easily cleaved from the central PFDMS nanocrystal during transfer to the TEM grids, probably due to the 3D structure and the strong interfacial interaction between the arms and the carbon substrate. To make the branched structures more robust, the coronas of the multi-

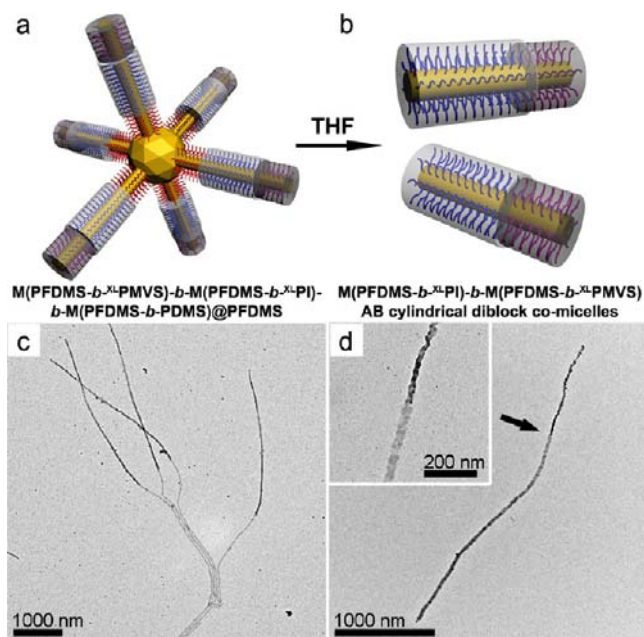


Figure 6. Pictorial representations and corresponding TEM images of (a,c) the $M(\text{PFDM}S\text{-}b\text{-}^{\text{XL}}\text{PMVS})\text{-}b\text{-}M(\text{PFDM}S\text{-}b\text{-}^{\text{XL}}\text{PI})\text{-}b\text{-}M(\text{PFDM}S\text{-}b\text{-}PDMS)@\text{PFDM}S$ multi-armed triblock co-micelles and (b,d) the non-centrosymmetric $M(\text{PFDM}S\text{-}b\text{-}^{\text{XL}}\text{PI})\text{-}b\text{-}M(\text{PFDM}S\text{-}b\text{-}^{\text{XL}}\text{PMVS})$ AB cylindrical diblock co-micelles obtained afterward by dissolution of the PFDMS-*b*-PDMS micelle segments and the PFDMS nanocrystal in THF.

armed micelles were cross-linked by Pt(0)–olefin coordination.^{10c,14} The cross-linked multi-armed micelles ($M(\text{PFDM}S\text{-}b\text{-}^{\text{XL}}\text{PI})@\text{PFDM}S$, where the superscript “XL” represents “cross-linked”) showed much improved mechanical strength and maintained their structures in good solvents for both PFDMS and PI, such as THF and toluene (Figures S11 and S12).¹⁵

The formation of multi-armed micelles by crystallization-driven self-assembly using PFDMS nanocrystals can be extended to other PFDMS block copolymers. For example, multi-armed micelles with PFDMS-*b*-PDMS (PDMS = polydimethylsiloxane) cylinders as arms were synthesized by using PFDMS₄₉-*b*-PDMS₅₀₄ in place of PFDMS₅₃-*b*-PI₆₃₇. The $M(\text{PFDM}S\text{-}b\text{-}PDMS)@\text{PFDM}S$ multi-armed micelles also showed well-defined branched structures and monodisperse arms (Figure S13). Furthermore, the termini of the arms were found to be active to the addition of further PFDMS block copolymer unimers for both the $M(\text{PFDM}S\text{-}b\text{-}PI)@\text{PFDM}S$ and $M(\text{PFDM}S\text{-}b\text{-}PDMS)@\text{PFDM}S$ multi-armed micelles. These features enabled a flexible design of the arm chemistry. Indeed, multi-armed diblock co-micelles with segmented arms can be prepared by adding PFDMS-*b*-PDMS unimers into the solution of the $M(\text{PFDM}S\text{-}b\text{-}PI)@\text{PFDM}S$ multi-armed micelles (Figure 5a,c), or alternatively, by injecting PFDMS-*b*-PI unimers into the solution of the $M(\text{PFDM}S\text{-}b\text{-}PDMS)@\text{PFDM}S$ multi-armed micelles (Figure 5b,d). The peripheral micelle segments also showed monodispersity and controlled lengths. Moreover, the segments of the arms can be selectively modified by cross-linking of the PI coronas, leading to the formation of branched segmented hybrid structures.

More complex multi-armed triblock co-micelles were prepared by further growth of the PFDMS₅₅-*b*-PMVS₈₂₅ (PMVS = polymethylvinylsiloxane) micelle segments from the $M(\text{PFDM}S\text{-}b\text{-}PI)\text{-}b\text{-}M(\text{PFDM}S\text{-}b\text{-}PDMS)@\text{PFDM}S$ multi-armed

diblock co-micelles. Both the PMVS and the PI coronas were then cross-linked by Pt(0)–olefin coordination. As shown in Figure 6c, the cross-linked PFDMS-*b*-PMVS micelle segments possessed smaller diameters (~30 nm) than those of the PFDMS-*b*-PI micelle segments (~40 nm) and also appeared darker in contrast. Thus the PFDMS-*b*-PMVS and PFDMS-*b*-PI micelle segments could be easily distinguished by TEM. Subsequent dissolution of the uncross-linked PFDMS-*b*-PDMS micelle segments and the PFDMS nanocrystals in a good solvent for PFDMS, such as THF, yielded non-centrosymmetric M(PFDMS-*b*-^{XL}PI)-*b*-M(PFDMS-*b*-^{XL}PMVS) AB cylindrical diblock co-micelles (Figure 6d).^{10d} This provides a new route to these challenging synthetic targets¹⁶ which are generally inaccessible by crystallization-driven self-assembly approaches as growth is usually observed simultaneously in two directions, which generates a center of symmetry.^{10d}

In summary, we have demonstrated that PFDMS homopolymer forms nanocrystals when aged in hexane and that PFDMS block copolymer unimers can grow from these nanocrystals through crystallization-driven self-assembly to form multi-armed micelles and block co-micelles. These nanostructures contain arms that are monodisperse in length and which possess tunable chemistries. Using multi-armed triblock co-micelles and cross-linking strategies a new route to non-centrosymmetric AB block co-micelles was established. In principle, this method should be applicable for other crystalline-coil block copolymer systems^{8,11} to create multi-armed structures using their homopolymer nanocrystals as seeds. Future work will aim to expand this approach to other materials including those with crystalline π -conjugated blocks.

■ 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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