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Synthesis and Solution Self-Assembly of Coil−Crystalline−Coil Polyferrocenylphosphine-*b*-polyferrocenylsilane-*b*-polysiloxane Triblock Copolymers

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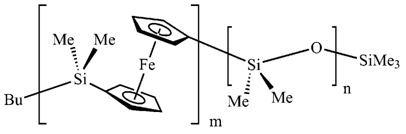
ABSTRACT: A series of well-defined coil−crystalline−coil PFP-*b*-PFS-*b*-PDMS triblock copolymers (PFP = poly(ferrocenylphenylphosphine), PFS = poly(ferrocenyldimethylsilane), and PDMS = poly(dimethylsiloxane)) of narrow polydispersity (PDI 1.04−1.06) with short PFP blocks of variable length and PFS:PDMS ratios of ca. 1:5−1:12 were prepared by sequential anionic ring-opening polymerization of the [1]phosphaferrocenophane fcPPh (fc = Fe(η-C_5H_4)$_2$), the [1]silaferrocenophane fcSiMe$_2$, and the cyclic siloxane [Me$_2$SiO]$_3$. Hexane is a selective solvent for PDMS in these ABC triblock copolymers. In the case of the very short PFP blocks (DP $\leqslant$ 6), self-assembly afforded cylindrical micelles with an organometallic core and a PDMS corona. For the sample with the longest PFP block (DP = 11), we found spherical micelles. These results are consistent with increased disruption of the crystallization of the PFS block as the PFP block is increased in length, favoring formation of spherical rather than low curvature cylindrical structures. Results of wide-angle X-ray diffraction measurements support this conclusion.

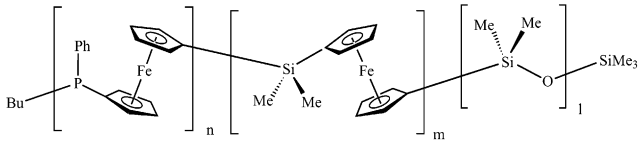
Introduction

Self-assembly of block copolymers provides a powerful route to nanostructured materials in both solution and the solid state.[1,2] The micellization of organic diblock copolymers in a selective solvent for one or the blocks is currently attracting intense attention as a route to supramolecular structures with applications as nanoparticles.[2] The incorporation of metallic elements into self-assembled micellar structures adds new possibilities which should complement those available with well-studied all organic analogues.[3]

Well-defined polyferrocene block copolymers are accessible via the living anionic ring-opening polymerization (ROP) of [1]ferrocenophanes,[4] and self-assembly of these materials offers potential access to supramolecular structures with redox activity, high refractive index contrast, and preceramic properties.[5] We have previously shown that crystalline−coil poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS-*b*-PDMS), diblock copolymers (block ratio 1:6) form cylindrical micelles with an organometallic core and a polysiloxane corona in selective solvents for the PDMS block such as hexanes.[6] As PFS homopolymers become semiconducting on oxidative doping[7] and also function as high yield precursors to ceramics,[8] these cylinders are of interest as semiconducting nanowires and as nanoscopic etching resists.[9] We have previously proposed that the formation of cylindrical structures rather than the spherical micelles expected on the basis of the block asymmetry is a result of the tendency of the PFS block to crystallize which favors the formation of low-curvature structures.[10] The extension of this concept to ABC triblock copolymer systems offers further opportunities for crystallization-directed micellar morphology control. Recently, we studied ABA crystalline−coil−crystalline triblock copolymers, PFS-*b*-PDMS-*b*-PFS, with broad polydispersity.[11] We explained the novel flowerlike morphologies observed in terms of the influence of the crystallization of the PFS block.[11,12] In this paper we explore the self-assembly of well-defined ABC triblock copolymers conceptually derived from the PFS-*b*-PDMS system where a short, amorphous atactic poly(ferrocenylphenylphosphine) (PFP) block is also attached to the PFS segment.



PFS-b-PDMS



PFP-b-PFS-b-PDMS

Results and Discussion

Synthesis of the Copolymers. The copolymers were synthesized by living anionic ROP initiated by *n*-BuLi with sequential monomer addition (see Scheme 1). The strategy for this synthesis is based upon our previous experience with the individual [1]ferrocenophane monomers **1** and **2**, which we have shown undergo living ROP when treated with butyllithium.[4] Thus, the polymerization of **1** and **2** to form the PFP and PFS blocks was carried out at 23 °C for (5 min for **1**, 30 min for **2**). Then the polymerization to form the PDMS block was carried out at 0 °C for 20 h. On the basis of the changes in color of the solution, from the initial deep red color characteristic of the strained monomers to orange-yellow typical for ring-opened polyferrocenes, we inferred that there was quantitative conversion of **1** and **2** during the polymerization reactions. The well-defined nature of the PFP-*b*-PFS-*b*-PDMS triblock copolymers was demon-

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Scheme 1

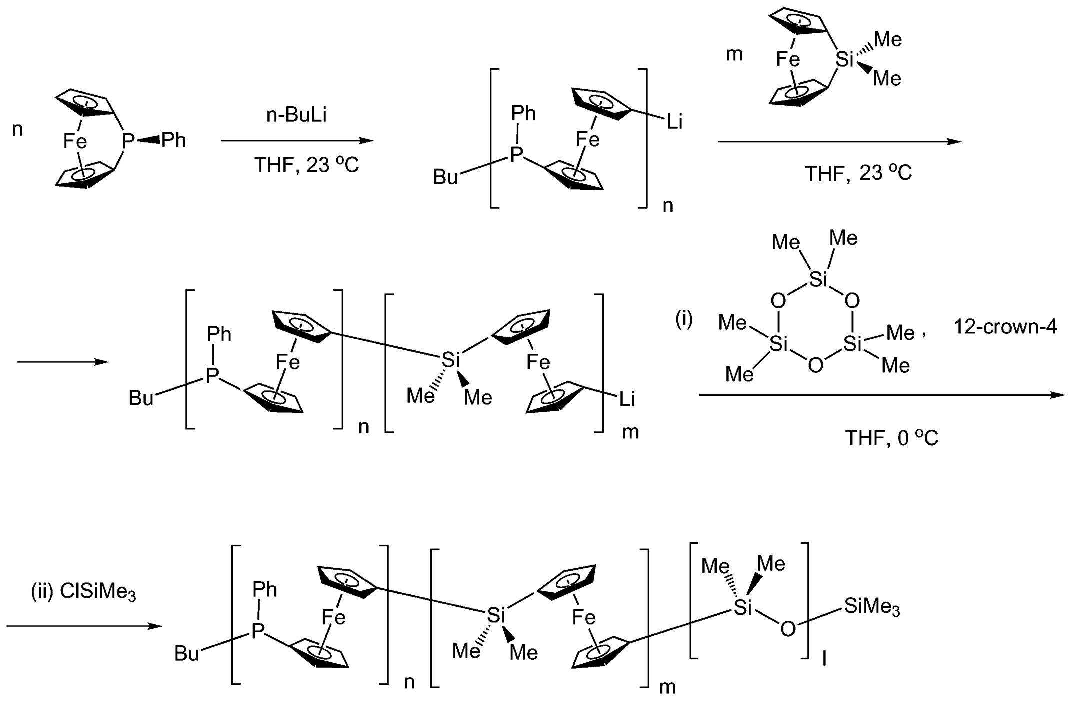
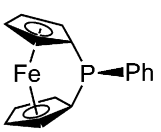


Table 1. M_n, PDI, Block Ratio, and Micelle Morphology for PFP-*b*-PFS-*b*-PDMS Triblock Copolymers in Hexane Characterized by GPC, ^{1}H, ^{31}P NMR, and TEM

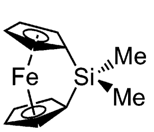
no.	block copolymers	PFP_n-PFS_m block	$PFP_n-PFS_m-PDMS_l$		
		M_n/PDI[a]	M_n/PDI[a]	n:m:l[b]	morphology[c]
1	1/40/304	10400/1.10	40500/1.04	1:40:304	cylinders
2	2/45/300	13400/1.01	38300/1.05	2:45:300	cylinders
3	6/45/220	13000/1.06	31200/1.06	6:45:220	cylinders
4	11/50/600	15000/1.06	74300/1.04	11:50:600	spheres

[a] GPC results with polystyrene standards. [b] Evaluated from ^{1}H and ^{31}P NMR integration. [c] Self-assembly in hexane as observed by TEM.

strated by the low polydispersities measured by GPC and also by ^{1}H NMR and ^{31}P NMR analysis. These results are listed in Table 1. In the text, the different block copolymers are denoted by PFP_n-*b*-PFS_m-*b*-$PDMS_l$, where n, m, and l represent the repeat units for the PFP, PFS, and PDMS block, respectively.



1



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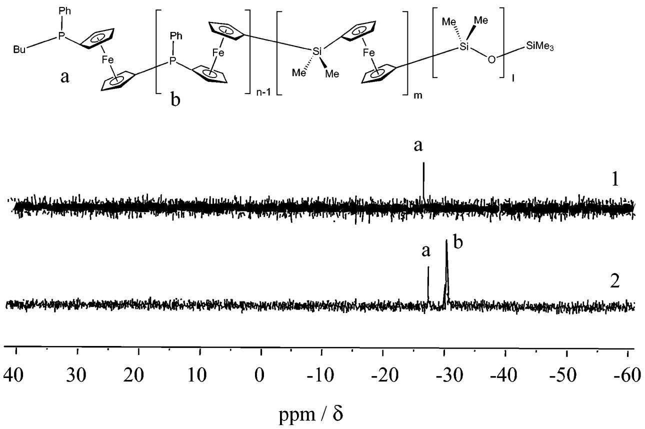

Figure 1. ^{31}P NMR spectra for PFP_1-*b*-PFS_{40}-*b*-$PDMS_{304}$ (1) and PFP_6-*b*-PFS_{45}-*b*-$PDMS_{220}$ (2).

The GPC data in Table 1 show that both the PFP−PFS diblock and PFP-*b*-PFS-*b*-PDMS triblock copolymers have narrow molecular weight distribution (M_w/M_n < 1.10) characteristic of living anionic polymerization. Because M_n values measured by GPC are based on polystyrene standards, they do not reflect the true M_n values of the block copolymers. To overcome this problem, we characterized the absolute block lengths and block ratios of PFP-*b*-PFS-*b*-PDMS by ^{31}P and ^{1}H NMR, treating the PFP segment as the block copolymer end group. We took advantage of the fact that two resonances can be detected in the ^{31}P NMR spectrum of the PFP block (see Figure 1). According to our previous study,[4d] the peak at −27 ppm (see Figure 1a) was assigned to a single phosphorus in the ring-opened monomer unit next to the initiator moiety (*n*-BuP(Ph)-Cp). A second signal at around −31 ppm (see Figure 1b) was attributed to the phosphorus atoms in the main-chain ferrocenylphosphine units. By end-group analysis, the number of PFP repeat units, n, in the polymer can be deduced from the integration of these two peaks. The results obtained are in good agreement with the fcP/BuLi reactant ratio in each case. When 1 equiv of **1** was added to the BuLi initiator, *n*-BuP(Ph)fcLi was formed exclusively and quantitatively as inferred by the appearance of single peak at −27 ppm. This result indicates that the reaction of BuLi with **1** is much faster than the reaction of the *n*-BuP(Ph)fcLi anion with **1**. This experiment provides evidence for very fast initiation in the ROP of ferrocenophane monomers with butyllithium and helps us to understand why we obtain polymers characteristic of good living character.

Figure 2 shows a ^{1}H NMR spectrum of PFP_6-*b*-PFS_{45}-*b*-$PDMS_{220}$ and peak assignments. Signals due to the phenyl group attached to phosphorus are clearly visible at δ 7.3 and δ 7.5. Based on the absolute number of

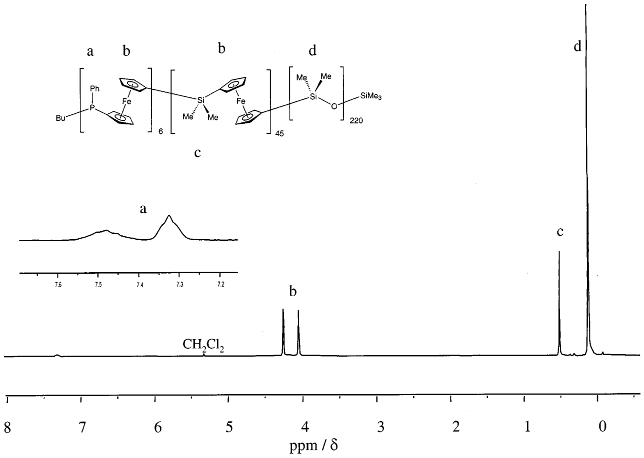

Figure 2. ^{1}H NMR spectrum of PFP$_6$-*b*-PFS$_{45}$-*b*-PDMS$_{220}$ in CD$_2$Cl$_2$.

repeats unit of PFP deduced from the ^{31}P NMR spectrum, the overall composition of the polymer was calculated from the integrals of peaks representative of the PFS and PDMS blocks. For this purpose we chose as the reference the peak integrals of phenyl protons of the PFP block. We compared them with the SiMe$_2$ protons associated with the PFS block (δ = ca. 0.50 ppm) and those associated with PDMS (e.g., δ = ca. 0.15 ppm). For the results of these calculations see Table 1.

Micellization of PFP-*b*-PFS-*b*-PDMS. Self-assembly of the ABC triblock copolymers was studied in hexane. Hexane is a non-solvent for both PFP and PFS but a good solvent for PDMS. All micelle samples were prepared by slow addition of hexane to solutions of the polymer (1% w/v) in THF, a good solvent for all three blocks. THF was removed by slow dialysis against hexane. The micellar morphology was visualized by using TEM to analyze an aerosol-sprayed sample after solvent evaporation; the results are summarized in Table 1. In these experiments, we took advantage of the fact that the Fe-rich core of the self-assembled structures provides sufficient contrast with the carbon film substrate that it can be visualized in the TEM images without the need for staining.[4b,6] In these images, the PDMS component is not visible.

The length of the PFP end block influences the type of structures formed by the PFP-*b*-PFS-*b*-PDMS block copolymers in hexane. In Figure 3 we compare the morphologies for the micelles formed by three block copolymers with 1, 6, and 11 repeat units for the PFP block. Both PFP$_1$-*b*-PFS$_{40}$-*b*-PDMS$_{304}$ and PFP$_6$-*b*-PFS$_{45}$-*b*-PDMS$_{220}$ form cylinders, as shown in Figure 3a,b. The widths and lengths of these cylinders are similar to those obtained with PFS$_{50}$−PDMS$_{300}$ diblock copolymer in hexane,[6] suggesting that short PFP (DP = 6) end blocks have little effect on the overall micelle structure. Micelle solutions of PFP$_{11}$-*b*-PFS$_{50}$-*b*-PDMS$_{600}$ with 11 PFP repeat units do not contain cylindrical structures.[13] Only spheres are seen in the TEM images (cf. Figure 3c). This observation suggests that the presence of the longer PFP chain disrupted the crystallization of the PFS blocks in the micelle core.

In this context, it is also noteworthy that the effect of PFP units on the micelle structure was also detected in the sample of the cylinder-forming triblock PFP$_6$-*b*-PFS$_{45}$-*b*-PDMS$_{220}$ at elevated temperatures. On heating the cylindrical micelles to 70 °C for 30 min, the formation of irregularly shaped aggregates was observed (see Figure 4). This again can be explained by the disruptive influence of PFP on the crystallization of PFS, as cylindrical micelles of the diblock copolymer PFS−PDMS (PFS:PDMS = 1:6) without a PFP end block remain intact upon heating at 80 °C.[6]

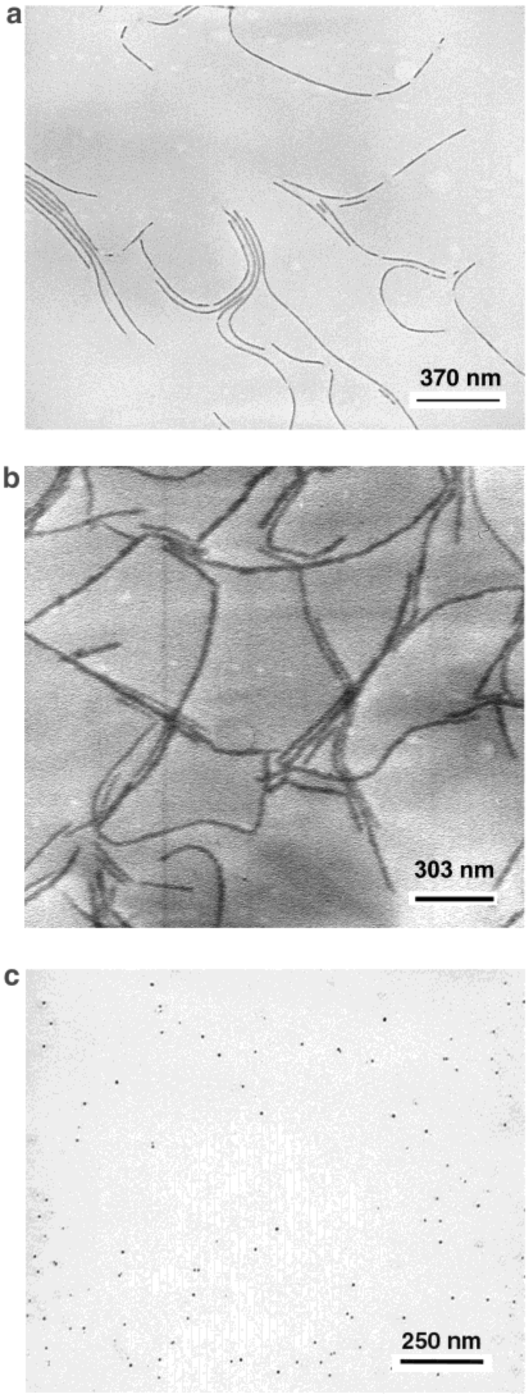

Figure 3. TEMs of micelles associated in hexane from PFP$_1$-*b*-PFS$_{40}$-*b*-PDMS$_{304}$ (a), PFP$_6$-*b*-PFS$_{45}$-*b*-PDMS$_{220}$ (b), and PFP$_{11}$-*b*-PFS$_{50}$-*b*-PDMS$_{600}$ (c).

To test the idea that the presence of the PFP block in the self-assembled structure could affect the crystallinity of the micelle core, we carried out wide-angle X-ray scattering (WAXS) measurements on films prepared from the micelles in hexane. The samples were prepared by casting a solution of the micelles in hexane onto an aluminum substrate and allowing the solvent to evaporate at ambient temperature. In Figure 5 we present

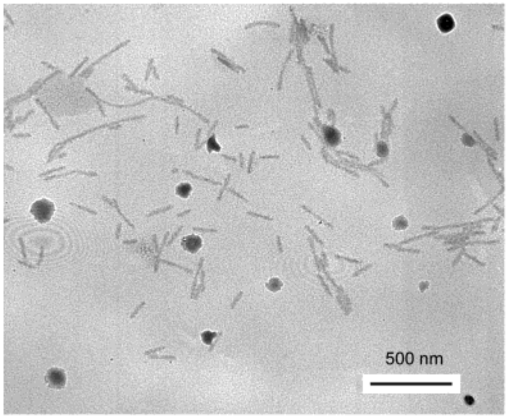

Figure 4. TEM illustrating the effect of heating on cylindrical micelles of PFP_6-*b*-PFS_{45}-*b*-$PDMS_{220}$ in hexane at 70 °C for 30 min.

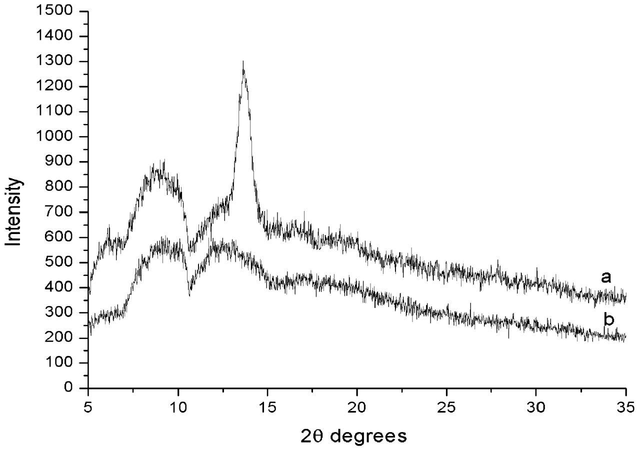

Figure 5. WAXS pattern for (a) the cylindrical micelles of PFP_6-*b*-PFS_{45}-*b*-$PDMS_{220}$ and (b) spherical micelles of PFP_{11}-*b*-PFS_{50}-*b*-$PDMS_{600}$.

the WAXS pattern of both the wormlike micelles of PFP_6-*b*-PFS_{45}-*b*-$PDMS_{220}$ and the spherical micelles of PFP_{11}-*b*-PFS_{50}-*b*-$PDMS_{600}$. The WAXS pattern obtained from the wormlike micelles PFP_6-*b*-PFS_{45}-*b*-$PDMS_{220}$ has a peak at 6.4 Å. This peak appears at the same *d* spacing as that found in PFS homopolymer, confirming the crystalline nature of the PFS in this sample.[12] The absence of higher-order peaks may indicate less well-defined crystals than in the homopolymer. In contrast, only an amorphous halo was observed in the WAXS spectrum of the film prepared from the solution of spherical micelles of PFP_{11}-*b*-PFS_{50}-*b*-$PDMS_{600}$. These results support the concept that crystallization plays a key role in the formation of cylindrical micelles in PFS block copolymers.

Summary

In conclusion, the ABC block polymers PFP-*b*-PFS-*b*-PDMS were synthesized via anionic ring-opening polymerization using sequential monomer addition. Because of its atacticity, the PFP block is amorphous, whereas the PFS block is crystalline at room temperature. These triblock copolymers form micelles in hexane, a solvent selective for the PDMS block. When the PFP block is very short (DP = 1 or 6), the polymer forms flexible wormlike micelles. A triblock copolymer with a longer PFP block (DP = 11) forms starlike spherical micelles.[13] Films show a peak in the WAXS spectrum characteristic of a crystalline PFS block for the wormlike structures. There is no evidence of crystallinity in the spherical micelles. We infer that the longer PFP block interferes with crystallization of the PFS block.

An interesting and as yet unanswered question is the location of the PFP component in these self-assembled micellar structures. The question is particularly important because the PFP segments present in these materials can coordinate to transition metals.[4d] Studies of metal coordination to PFP-*b*-PFS-*b*-PDMS, and the types of nanostructures they form, are currently in progress.

Experimental Section

Materials and Characterization. The [1]ferrocenophanes $fcSiMe_2$ (**2**) and fcPPh (**1**) were synthesized according to the procedures reported previously.[4] Monomer **1** was purified by repetitive sublimation plus recrystallization from hexanes until no spurious peaks appeared in a close inspection of the ^1H NMR spectrum. Monomer **2** was purified by repeated crystallization from hexane to ensure purity that was judged similarly. Hexamethylcyclotrisiloxane $[Me_2SiO]_3$, 12-crown-4-ether, and *n*-butyllithium (1.6 M in hexane) were purchased from Aldrich. $[Me_2SiO]_3$ was stirred over CaH_2 for 12 h in pentane, the solvent was removed by static vacuum, and the $[Me_2SiO]_3$ was obtained by sublimation at room temperature under static vacuum. 12-Crown-4-ether was distilled from CaH_2 and stored in a glovebox at −30 °C; tetrahydrofuran was distilled from Na/benzophenone under prepurified N_2 immediately prior to using.

The ^1H NMR and ^{31}P NMR were recorded on a Varian Gemini 300 spectrometer with deuterated methylene chloride or deuterated benzene as solvent. Apparent molecular weights and the molecular weight distributions were characterized by gel permeation chromatography (GPC) with polystyrene standards.

Transmission electron microscopy (TEM) measurements were carried out on a Hitachi model 600 electron microscope operating at 75 kV. The sample was prepared as follows. Thin carbon films (ca. 5 Å) were grown on mica as a support. Then 25 μL of a block copolymer micelle solution was sprayed onto the carbon film. Each carbon film was floated off the mica support in water and deposited onto a 300 mesh Gilder copper grid. The sample was air-dried before introduction into the electron microscope. Staining of the sample was unnecessary as the electron density of the Fe-rich blocks led to sufficient contrast against the carbon film for imaging.

Synthesis of PFP-*b*-PFS-*b*-PDMS Triblock Copolymers. Samples of poly(ferrocenylphenylphosphine-*b*-ferrocenyldimethylsilane-*b*-dimethylsiloxane) were synthesized by living anionic polymerization through sequential monomer addition. The polymerization was carried out under an inert atmosphere, Ar, in a flamed and vacuum-dried glass reactor equipped with a three-way stopcock and a rubber septum. A representative experimental procedure to synthesize PFP_1-*b*-PFS_{40}-*b*-PFS_{304} follows. **1** (12 mg, 0.04 mmol) was polymerized first in THF (5 mL) at 23 °C using *n*-butyllithium (25 μL, 0.04 mmol) as initiator. Five minutes later, the solution changed from deep red to orange, indicating quantitative conversion of monomer **1**. Then the ferrocenyldimethylsilane monomer **2** (388 mg, 1.6 mmol) was added as solid. As in previous studies, 0.5 h was sufficient for quantitative polymerization of the ferrocenyldimethylsilane monomer. At this point, an aliquot of the reaction mixture was drawn out for the analysis of this organometallic diblock. Then $(Me_2SiO)_3$ (776 mg, 3.5 mmol) was added to the solution of living polymer along with 100 μL of 12-crown-4. The reaction flask was immediately removed from the glovebox and placed on a Schlenk line under prepurified Ar and cooled to 0 °C. The reaction was left for 20 h at 0 °C and was terminated be the addition of a few drops of Me_3SiCl. The block copolymer was precipitated into methanol in the presence of triethylamine, isolated, and dried under vacuum for 24 h; yield 0.90 g (76%).

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(13) Although the PFS:PDMS block ratio (1:12) is larger in this case compared to the other samples (1:5−1:8) we note that asymmetric crystalline-coil PFS-*b*-PDMS diblock copolymers with block ratios of up to 1:18 also form cylindrical structures in n-hexanes but in these cases the structures are tubular. See: (a) Raez, J.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 10381. (b) Raez, J.; Manners I.; Winnik, M. A. *Langmuir* **2002**, *18*, 7229.

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