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Self-Assembly of Organometallic Block Copolymers: The Role of Crystallinity of the Core-Forming Polyferrocene Block in the Micellar Morphologies Formed by Poly(ferrocenylsilane-*b*-dimethylsiloxane) in *n*-Alkane Solvents

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Abstract: The organometallic−inorganic diblock copolymer poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFDMS-*b*-PDMS) with a 1:6 block ratio unexpectedly forms long rodlike micelles rather than spherical structures in a variety of PDMS-selective *n*-alkane solvents when the solutions are prepared at or near ambient temperature. The cylindrical structures represent the thermodynamically preferred morphology and consist of an iron-rich PFDMS core and a corona of PDMS. The length of the micelles can be varied from 70 nm to 10 μm by altering the method of sample preparation. In addition, the dimensions of the micellar core can be controlled through variations in the length of the PFDMS block, which is achieved by altering the molecular weight of the diblock copolymer while maintaining a constant block ratio. In contrast, when micelles are formed above the T_m of PFDMS (ca. 120−145 °C), spherical aggregates are formed, which suggests that crystallization of the core polymer is the driving force for the formation of wormlike micelles below T_m. Furthermore, the analogues with amorphous polyferrocene blocks, poly(ferrocenylmethylphenylsilane-*b*-dimethylsiloxane) (PFMPS-*b*-PDMS) and poly(ferrocenylmethylethylsilane-*b*-dimethylsiloxane) (PFMES-*b*-PDMS), form spherical micelles in hexane at room temperature. This lends further support to the proposition that the crystalline nature of the PFDMS block plays a pivotal role in the unexpected formation of cylindrical micelles. To provide an application of this concept, an analogous PFDMS block copolymer with polyisoprene, PI-*b*-PFDMS, was prepared and, as predicted, was found to form cylindrical micelles in hexane.

Introduction

The immiscible segments of a block copolymer are known to facilitate phase separation in the solid state, and in solution micellar aggregates will form in a solvent which preferentially solvates one of the blocks. The resulting self-assembled materials are ordered on the nanometer scale and are of considerable current interest for applications which range from electronics to drug delivery.[1] The vast majority of block copolymers that have been studied in solution form spherical micelles. In rare instances other morphologies are encountered. For example, several examples of block copolymers that form well-defined cylindrical micelles have been reported.[2−12] Well-characterized examples that have appeared recently include those reported by Bates and co-workers,[12] Antonietti et al.,[6] Liu and co-workers,[2] Möller et al.,[11] Yu and co-workers,[4] and Eisenberg and his group.[3] In general, our understanding of the factors that determine which morphology is formed is poor, and improved insight is highly desirable.

When cylindrical micelles are encountered, they are often kinetically trapped morphologies that depend strongly on the method of sample preparation. For example, Price and co-workers reported the observation of a web of wormlike micelles after a micelle solution was evaporated on a transmission electron micrograph (TEM) grid. These structures were, however, found to be in a metastable state and could be driven to a spherical morphology after the block copolymer was heated above the critical micelle temperature.[5,13] The more recent work of Eisenberg demonstrates the wide range of possible morphologies that can be obtained with block copolymer micelles, which include spheres, rods, vesicles, lamellae, and more complex architectures.[3] These aggregates however fall under the special

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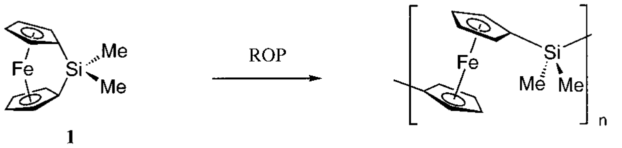
Scheme 1



case of crew-cut micelles, which have a very short corona chain. For these systems, the minimization of the interfacial energy is balanced more by an increase in the chain stretching of the core block than by an increase of the intercorona chain repulsion. The range of multiple micellar morphologies is attributed to the balancing of these forces. Bates and Scriven have suggested that micellar morphology should mirror the trends found in small-molecule surfactants,[14] namely, that reducing the volume ratio of the corona gives rise to smaller interfacial curvature, driving the transition from spherical to cylindrical micelles or even lamellar structures.

Virtually all studies of block copolymer self-assembly to date have focused on organic materials. The ring-opening polymerization (ROP) of strained monomeric silicon-bridged [1]ferrocenophanes is a well-established route to high molecular weight poly(ferrocenylsilanes) (Scheme 1), which represent rare examples of high molecular weight transition-metal-based polymers.[15−17] Poly(ferrocenylsilanes) possess interacting metal atoms along the polymer main chain and are currently being investigated as, for example, charge-transport and charge-dissipation materials and as precursors to magnetic ceramics and nanostructures.[17−21] The discovery that monomeric silicon-bridged [1]ferrocenophanes (e.g., **1**) undergo living anionic polymerization has allowed the preparation of the first block copolymers with transition-metal atoms in the main chain.[22,23] Self-assembly of these materials in the solid state and in solution allows the generation of nanoscale domains with a high transition-metal concentration.[23,24]

We have previously reported that the copolymer, poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFDMS-*b*-PDMS) (block ratio 1:6), unexpectedly forms cylindrical micelles in *n*-hexane, a selective solvent for PDMS.[24] In this paper, we demonstrate that control of the length and width of these structures is possible. In addition, we explore the reasons why the wormlike morphologies form and provide evidence that the crystallization of the micellar core is the key driving force for the formation of cylindrical micelles in this system. We also demonstrate the application of this concept to a related block copolymer (PI-*b*-PFDMS, PI = polyisoprene), which also leads to the formation of wormlike morphologies in solution.

Experimental Section

Equipment and Materials. *n*-Butyllithium (1.6 M) in hexanes, *sec*-butyllithium (1.3 M) in cyclohexane, dimethyldichlorosilane, chlorotrimethylsilane, dichloromethylphenylsilane, dichloromethylethylsilane, hexamethylcyclotrisiloxane, isoprene, and *n*-hexane were all purchased from Aldrich. Me_3SiCl, $MePhSiCl_2$, $MeEtSiCl_2$, and Me_2SiCl_2 were distilled prior to use. $(Me_2SiO)_3$ was stirred over CaH_2 for 12 h in pentane, the solvent removed by static vacuum, and the $(Me_2SiO)_3$ obtained by sublimation at room temperature under static vacuum. Isoprene was distilled from CaH_2 and stored at −30 °C. A second distillation from *n*-butyllithium was performed immediately before the polymerization. [1]Ferrocenophanes were synthesized according to previous methodology reported in the literature.[23,25] 12-Crown-4 was purchased from Aldrich, 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 use. All reactions and manipulations were carried out under an atmosphere of prepurified N_2 using either a standard Schlenk line or a glovebox (Mbraun, Vacuum Atmospheres or Innovative Technology). Anionic polymerizations carried out using a Schlenk line were under an atmosphere of prepurified Ar.

The 200 MHz ^1H NMR spectra were recorded on a Varian Gemini 200 spectrometer, with deuterated benzene or methylene chloride as the solvent.

Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a model 510 HPLC pump, a model U6K injector, Ultrastyragel columns with pore sizes of 10^3−10^5 Å, and a differential refractometer as the detector. A flow rate of 1.0 mL/min was used, and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards purchased from American Polymer Standards were used for calibration purposes.

Transmission electron micrographs were obtained on a Hitachi model 600 electron microscope. Wide-angle X-ray scattering (WAXS) diffraction analysis was performed using a Siemens D5000 $\theta/2\theta$ diffractometer with a Cu Kα source operating at 50 kV and 35 mA in step scan mode. The second beam was monochromatized by a Kevex solid-state detector.

Synthesis and Characterization of Poly(ferrocenylsilane-*b*-dimethylsiloxane) Block Copolymers. A detailed description is given for the synthesis of $PFMPS_{40}$-*b*-$PDMS_{240}$ (PFMPS = poly(ferrocenylmethylphenylsilane)). The polymers $PFDMS_{50}$-*b*-$PDMS_{300}$, $PFDMS_{75}$-*b*-$PDMS_{375}$, and $PFMES_{50}$-*b*-$PDMS_{330}$ (PFMES = poly(ferrocenylmethylethylsilane)) were synthesized by an analogous route. The notation is derived from either, in the case of the PFDMS blocks, the predicted degree of polymerization based on reaction stoichiometry or, in other cases, the GPC data, taken in combination with the calculated *n*:*m* ratios from ^1H NMR. In a glovebox at room temperature 56 μL of 1.45 M *n*-BuLi (8.1×10^{-5} mol) in hexanes was added quickly to a stirred solution of 1.09 g of methylphenylsilicon-bridged [1]ferrocenophane (3.59×10^{-3} mol) in THF (18 mL). After 35 min the solution changed from a red to a deep amber color, and then hexamethylcyclotrisiloxane (1.56 g, 7.03×10^{-3} mol) was added to the solution of living polymer along with a few drops 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. After ca. 30 min the solution became very viscous. The reaction proceeded for 20 h at 0 °C and was terminated by the addition of a few drops of Me_3SiCl, after which a marked decrease in viscosity was noted. The block copolymer was precipitated into methanol (ca. 500 mL) in the presence of triethylamine (ca. 10 mL), isolated, and dried under vacuum for 24 h, yielding 1.96 g (74%) of the desired diblock copolymer. ^1H NMR (δ, CD_2Cl_2): 0.08 (s, Si*Me*$_2$O), 0.68 (s, fcSi*Me*Ph), 0.70 (s, fcSi*Me*Ph), 0.72 (s, fcSi*Me*Ph), 3.86−4.04 (m, *fc*SiMePh), 7.38 (br, fcSiMe*Ph*), 7.60 (br, fcSiMe*Ph*).). ^{13}C NMR (δ, CD_2Cl_2): −3.4, (s, fcSi*Me*Ph), −3.3 (s, fcSi*Me*Ph), −3.2(5) (s, fcSi*Me*Ph), 1.4 (s, br, Si*Me*$_2$O), 70.4 (s, ipso-C, *fc*SiMePh), 72.1 (s, br, *fc*SiMePh), 72.5 (s, br, *fc*SiMePh), 74.3 (s, br, *fc*SiMePh), 74.5 (s, br, *fc*SiMePh), 128.2 (s, br, fcSiMe*Ph*), 129.6 (s, br, fcSiMe*Ph*), 134.7 (s, br, fcSiMe*Ph*),

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139.2 (s, br, fcSiMe*Ph*). ^{29}Si NMR (δ, CD_2Cl_2): −19.9 (s, *Si*Me_2O), −9.9 (s, fc*Si*MePh). GPC: $M_n = 29\,700$ g/mol, PDI = 1.14. ^{1}H NMR integration revealed a block ratio (molar ratio) of PFMPS:PDMS = 1:6.0.

For $PFDMS_{50}$-*b*-$PDMS_{300}$, 56 μL of 1.6 M BuLi was added to 1.01 g of **1**, and then 2.07 g of $(Me_2SiO)_3$ was added, yielding 2.49 g of amber polymeric product. GPC: $M_n = 35\,100$ g/mol, PDI = 1.10. ^{1}H NMR integration revealed a block ratio (molar ratio) of PFDMS:PDMS = 1:6.0.

For $PFDMS_{75}$-*b*-$PDMS_{375}$, 26 μL of 1.6 M BuLi was added to 0.997 g of **1**, and then 2.084 g of $(Me_2SiO)_3$ was added, yielding 2.22 g of amber polymeric product. GPC: $M_n = 48\,800$ g/mol, PDI = 1.04. ^{1}H NMR integration revealed a block ratio (molar ratio) of PFDMS:PDMS = 1:5.0.

For $PFMES_{50}$-*b*-$PDMS_{330}$, 51 μL of 1.6 M BuLi was added to 1.04 g of methylethylsila[1]ferrocenophane, and then 1.86 g of $(Me_2SiO)_3$ was added, yielding 2.07 g of the desired block copolymer. GPC: $M_n = 40\,300$ g/mol, PDI = 1.09. ^{1}H NMR integration revealed a block ratio (molar ratio) of PFMES:PDMS = 1:6.6.

Synthesis and Characterization of Poly(isoprene-*b*-ferrocenyldimethylsilane). The polymerization was carried out under a nitrogen atmosphere in a flame- and vacuum-dried glass reactor equipped with a three-way stopcock and a rubber septum. Monomer, initiator, and solvent were transferred into the polymerization reactor via a stainless steel cannula or a glass syringe. At 0 °C, 1.0 mL of 0.10 M *sec*-BuLi (1.0×10^{-4} mol) in cyclohexane was added quickly to a stirred solution of 1.00 g of isoprene (1.47×10^{-2} mol) in THF. After 2 h the silicon-bridged [1]ferrocenophane **1** (0.45 g, 1.86×10^{-3} mol) was added as a solution in THF (2 mL). The reaction mixture was warmed to room temperature, and the polymerization was allowed to continue for 1 h more before it was quenched by adding a few drops of degassed methanol. The yellow gumlike product was recovered by precipitation into methanol, filtered, and dried under vacuum for 24 h Yield: 1.2 g, 83%. ^{1}H NMR (δ, $CDCl_3$): 0.45 (s, fcSi*Me*$_2$), 0.9−2.2 (br, alkyl), 3.9−4.2 (m, *fc*SiMe_2), 4.5−6.0 (br, vinyl). GPC: $M_n = 23\,100$ g/mol, PDI = 1.10. ^{1}H NMR integration revealed a block ratio (molar ratio) of PI:PFDMS = 4.4:1.

Preparation of Samples for TEM and WAXS. Thin carbon films (ca. 5 Å) were grown on mica as a support. Then 25 μL of a dilute solution of the block copolymer in hexane (ca. 0.2%) was aerosol 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 the samples was not necessary because of the presence of iron in the core of the micelle. Samples were negatively stained using $H_3PO_4 \cdot 12WO_3 \cdot 26H_2O$ (ca. 3%) in the presence of a surfactant (bovine serum albumin). Samples for WAXS were prepared by solution casting a film of cylindrical micelles from heptane onto an aluminum substrate.

Results and Discussion

Block copolymers that contain polyferrocene segments provide a route to nanoscale organometallic domains through self-assembly either in solution or in the solid state.[23,24,26] We have previously shown that a PFDMS-*b*-PDMS diblock copolymer ($M_n = 35\,100$ g/mol, PDI = 1.10) dissolves in hot *n*-hexane to form wormlike micelles with a PFDMS core and a corona of PDMS (Figure 1).[24] In the bulk, PFDMS is an interesting material that becomes semiconducting upon oxidation and on pyrolysis yields magnetic ceramic materials containing iron nanoclusters.[17,18] The cylindrical micelles are therefore of further interest as self-insulating semiconducting nanowires upon oxidation of the core[26] or as precursors to magnetic nanowires with a silica coating following pyrolysis or reactive ion etching.[17]

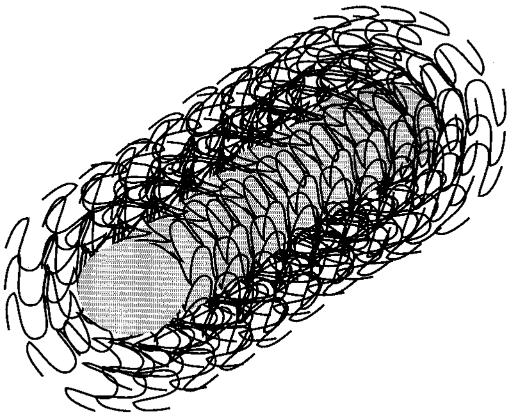

Figure 1. Schematic cross-sectional diagram of PFDMS-*b*-PDMS cylindrical micelles.

Scheme 2

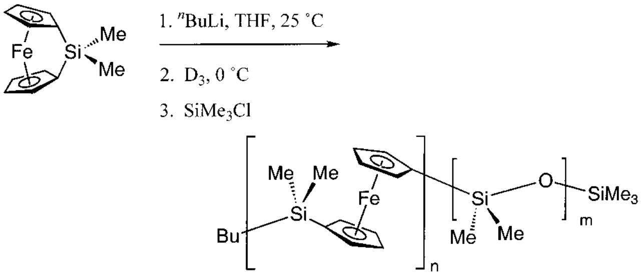

Table 1. Characterization Data for Polyferrocene Diblock Copolymers

polymer	M_n (g/mol)	M_n(core) (g/mol)	PDI	*n*:*m*
$PFDMS_{50}$-*b*-$PDMS_{300}$	35 100	7 750[a]	1.10	1:6.0
$PFDMS_{75}$-*b*-$PDMS_{375}$	48 800	13 500[a]	1.04	1:5.0
$PFMPS_{40}$-*b*-$PDMS_{240}$	29 700	12 100[b]	1.14	1:6.0
$PFMES_{50}$-*b*-$PDMS_{330}$	40 300	12 800[b]	1.09	1:6.6
PI_{188}-*b*-$PFDMS_{42}$	23 100	10 200[b]	1.10	4.4:1

[a] As determined by GPC analysis. [b] As determined by ^{1}H NMR integration.

It was therefore worthwhile to examine whether control of the micellar dimensions, both length and width, would be possible, so we investigated the micellization of the previously reported material and a new analogue with a higher molecular weight under a variety of conditions. We also envisaged that such studies would provide insight into whether the cylindrical micelles formed by direct dissolution in hot *n*-hexane represent kinetically trapped structures or the thermodynamically preferred morphology.

Control of the Dimensions of PFDMS-*b*-PDMS Micelles. (i) Synthesis of $PFDMS_{50}$-*b*-$PDMS_{300}$ and $PFDMS_{75}$-*b*-$PDMS_{375}$. Poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) diblock copolymers, $PFDMS_{50}$-*b*-$PDMS_{300}$ and the analogue $PFDMS_{75}$-*b*-$PDMS_{375}$, were prepared by sequential anionic polymerization. The ROP of **1** was initiated with *n*-butyllithium, and **1** was allowed to polymerize, after which hexamethylcyclotrisiloxane (D_3) was added to the living polymer solution. The copolymerization was terminated by the addition of a few drops of chlorotrimethylsilane, and amber rubbery solids were isolated in each case after precipitation into methanol (Scheme 2).[22,23]

The relevant physical data for each material are presented in Table 1. Analysis of $PFDMS_{50}$-*b*-$PDMS_{300}$ by ^{1}H NMR indicated that the PDMS block had a degree of polymerization 6 times that of the PFDMS block, compared to the stoichiometric ratio of the monomeric reactants of 6.6:1. For $PFDMS_{75}$-*b*-

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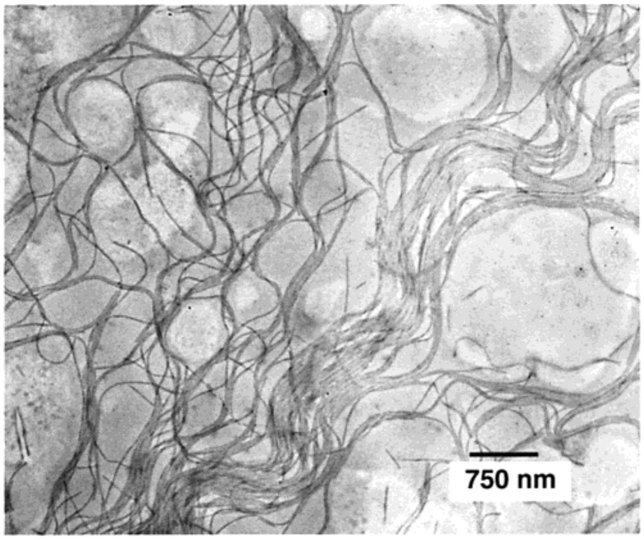

Figure 2. Transmission electron micrograph of cylindrical micelles of $PFDMS_{50}$-*b*-$PDMS_{300}$ ($M_n = 35\,100$, PDI = 1.10) prepared by the slow addition of hexane to a THF solution and subsequently aerosol-sprayed onto a TEM grid.

$PDMS_{375}$, ^1H NMR indicated that the ratio of PDMS to PFDMS was 5:1 compared to the stoichiometric ratio of the reactants of 6.8:1. The materials are almost identical in composition but differ in overall molecular weight. Analysis of the polymers by GPC in THF gave a narrow band for each polymer, with the number average molecular weight (M_n) for each being 35 100 and 48 800 g/mol, respectively (Table 1).

(ii) Micellization of $PFDMS_{50}$-*b*-$PDMS_{300}$ in *n*-Hexane. In our previous studies of the micellization behavior of $PFDMS_{50}$-*b*-$PDMS_{300}$, the micellar solutions were prepared by heating the copolymer in *n*-hexane, a solvent selective for PDMS and a precipitant for PFDMS, at 80 °C until a clear solution was obtained.[24] These micelle solutions were characterized by static and dynamic light scattering, which provided an aggregation number of ca. 2000. The light scattering results obtained also provided strong evidence that the micelles had an asymmetric geometry. TEM studies confirmed that the aggregates which formed were flexible wormlike micelles with an average contour length of 440 nm with a core diameter of 20 nm. Mild sonication of the micelle solutions reduced the length to a constant and more uniform value of 77 nm.

As $PFDMS_{50}$-*b*-$PDMS_{300}$ forms a morphology involving PFDMS cylinders in a PDMS matrix in the solid state,[24] we speculated that the wormlike morphology observed in solution may simply be frozen micelles levitated into solution. Consequently, the micelles were prepared in a different way. $PFDMS_{50}$-*b*-$PDMS_{300}$ was dissolved in THF, a solvent for both blocks. Hexane was then added slowly until the solution was ca. 95% v/v hexane. The resulting solution was placed in a conditioned dialysis tube and dialyzed against pure hexane to remove the residual THF. A typical TEM image is shown in Figure 2. Clearly from the micrograph, wormlike micelles were formed in solution. Moreover, the micelles formed were an order of magnitude longer than those formed by simply dissolving the copolymer with hot *n*-hexane. The micelles in many cases extend from one end of the micrograph to the other, having lengths on the order of tens of micrometers. Importantly, the rate of *n*-hexane addition had no effect on the observed morphology. Rapid addition of *n*-hexane (ca. 10 mL/min) and slow addition (ca. 0.01 mL/min) both resulted in cylindrical micelles with lengths on the order of tens of micrometers.

The addition of *n*-hexane to a solution of the copolymer $PFDMS_{50}$-*b*-$PDMS_{300}$ in THF was monitored by light scattering to determine the critical micelle composition. An increase in the light scattering intensity was found to occur at a composition of 54% v/v *n*-hexane in THF. This solution was allowed to stand for 3 days, after which microscopy experiments were undertaken. Again, the morphology of the micelles that formed was wormlike, with micellar lengths that extend for tens of micrometers.

In all TEM images of the wormlike micelles only the core of the micelles is observed. There is not sufficient contrast with the carbon film to observe the corona of PDMS. In an attempt to obtain further insight into the overall dimensions of the wormlike micelles, the technique of negative staining was utilized. The negative stain ($H_3PO_4 \cdot 12WO_3 \cdot 26H_2O$) in the presence of a biological surfactant completely wets the supported carbon film but does not cover any area with relief. Therefore, the area surrounding the micelles is filled with the heavy metal staining agent but does not cover the micelles themselves. Representative micrographs of cylindrical micelles formed by dissolution in hot hexane with and without negative staining are shown in parts a and b, respectively, of Figure 3. In the case of the negatively stained sample the width of the micelles was found to be 32 nm, greater than the value of 20 nm assigned to the core diameter obtained by TEM in the absence of staining.

(iii) Micellization of $PFDMS_{75}$-*b*-$PDMS_{375}$ in *n*-Hexane. To investigate the effect of molecular weight, the micellization behavior of $PFDMS_{75}$-*b*-$PDMS_{375}$ was also studied. We found that the tendency for this higher molecular weight sample to form wormlike micelles was as robust as that of $PFDMS_{50}$-*b*-$PDMS_{300}$. Simply heating the block copolymer in *n*-hexane at ca. 80 °C in a sealed vial formed cylindrical micelles that had lengths on the same order of magnitude as those of $PFDMS_{50}$-*b*-$PDMS_{300}$ prepared in the same manner. A representative micrograph is shown in Figure 4. The core of the micelles measured from the TEM image was found to be 30 nm for the higher molecular weight sample compared to 20 nm for $PFDMS_{50}$-*b*-$PDMS_{300}$. We infer from this result that the diameter of the core of the micelle depends on the molecular weight of the block copolymer.

Micellization Behavior of PFDMS-*b*-PDMS in Other *n*-Alkane Solvents and at Different Temperatures. The morphology of micelles formed by $PFDMS_{50}$-*b*-$PDMS_{300}$ in a number of different *n*-alkane solvents was also investigated. Micelles were prepared by heating the copolymer in *n*-pentane, *n*-heptane, *n*-octane, and *n*-decane at 80 °C in sealed vials. In all the solvents, the micelles formed with contour lengths in the range of 400 ± 200 nm, with diameters the same as those found in *n*-hexane (20 nm). The micelles discussed so far have all been formed in solvents below the melting transition of bulk PFDMS ($T_m = 120-145$ °C), and we therefore explored the effect of forming the micelles above T_m. $PFDMS_{50}$-*b*-$PDMS_{300}$ was heated in *n*-decane at 150 °C, forming a clear solution, which was then quenched in an ice bath and left at room temperature. In contrast to previous results, TEM images showed that the morphology of the micelles prepared above the melt temperature of PFDMS is spherical with a nominal diameter of 18 nm (Figure 5). This size is similar to the diameter found for the wormlike micelles. In contrast to solutions of the wormlike micelles, which are indefinitely stable (at least 6 months), the solution of spherical micelles in *n*-decane began to precipitate within 24 h.[27]

This result clearly points to the importance of the crystallinity of the core in determining the morphology of the micelle in

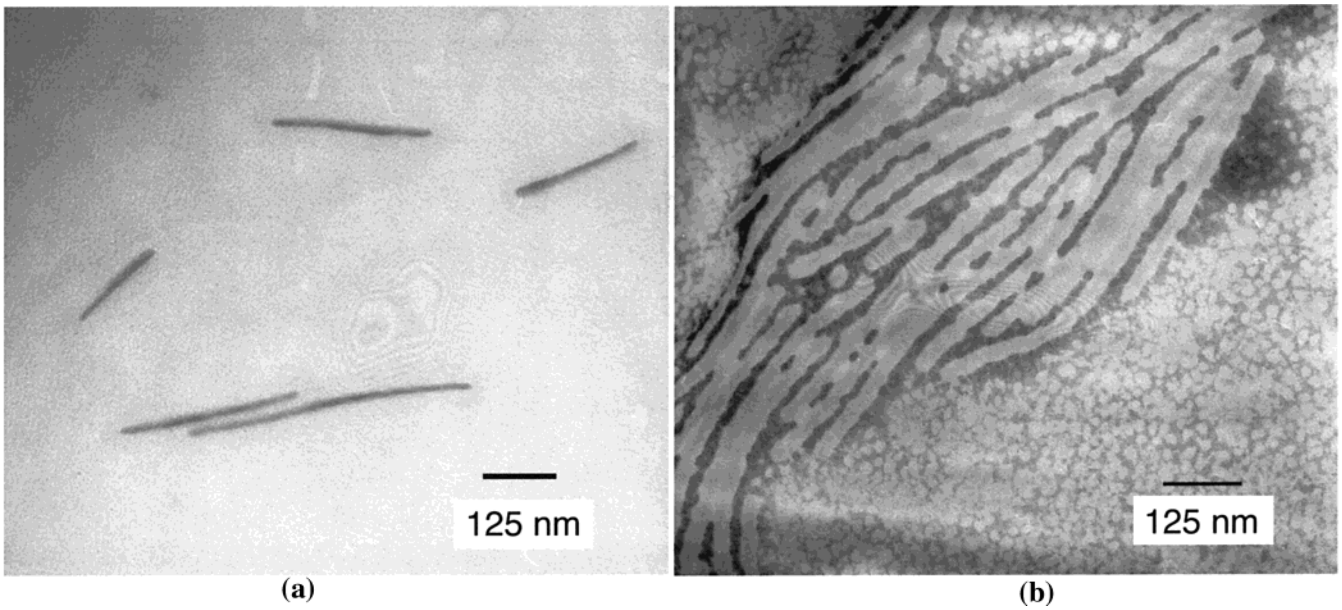

Figure 3. Transmission electron micrographs of the cylindrical micelles of PFDMS$_{50}$-*b*-PDMS$_{300}$ aerosol-sprayed from an *n*-hexane solution (a) without staining and (b) with negative staining using $H_3PO_4 \cdot 12WO_3 \cdot 26H_2O$.

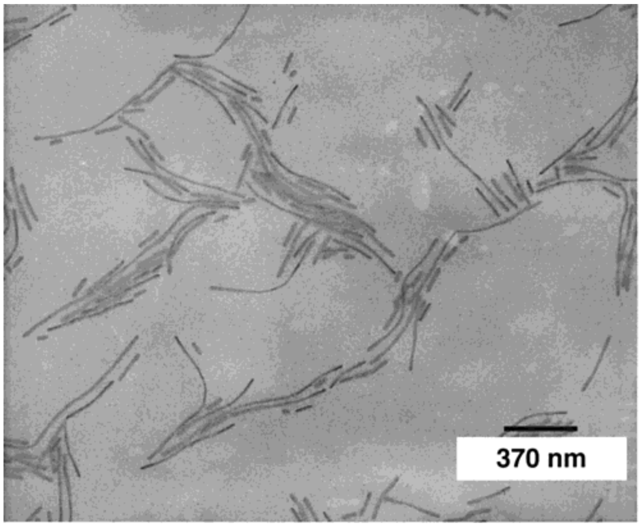

Figure 4. Transmission electron micrograph of cylindrical micelles of PFDMS$_{75}$-*b*-PDMS$_{375}$ ($M_n = 48\,000$, PDI = 1.04) aerosol-sprayed from an *n*-hexane solution.

solution. In all cases when the micelles were formed below the melt temperature of bulk PFDMS, cylindrical morphologies were observed. When the micelles were formed above the T_m, spherical micellar aggregates formed.

Wide-Angle X-ray Scattering Studies of PFDMS-*b*-PDMS Micelles: Evidence for Core Crystallinity. Films of bulk PFDMS homopolymer have previously been studied by wide-angle X-ray diffraction and are known to be semicrystalline in the bulk.[28] The analogous PFDMS pentamer has also previously been synthesized by anionic initiation of **1**, and single crystals suitable for an X-ray structural determination were obtained.[29] A powder pattern of single crystals of the pentamer is similar to the WAXS pattern for bulk PFDMS.[28] Taken together, these data provided a strong basis to infer the structure of PFDMS crystallites. The crystal structure of the pentamer consists of parallel, linear chains in which the ferrocenylsilane units have a zigzag trans planar configuration. The strongest peak in the powder pattern of the pentamer was assigned to the planes with (011) Miller indices and has a *d* spacing of 6.287 Å. The iron atoms in the polymer main chain lie in this plane, which gives rise to the strong intensity of the peak. The *d* spacing for the strongest peak in the powder pattern of high molecular weight PFDMS was 6.3 Å, which compares very well to the value for the pentamer.[29]

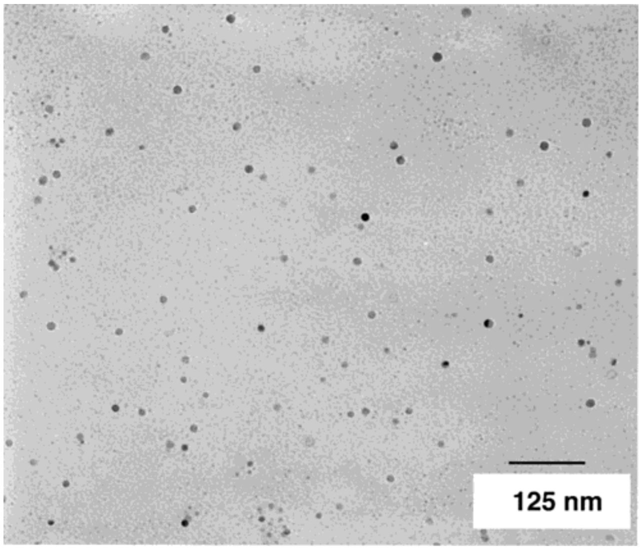

Figure 5. Transmission electron micrograph of spherical micelles of PFDMS$_{50}$-*b*-PDMS$_{300}$ ($M_n = 35\,100$, PDI = 1.10) prepared above the T_m of the PFDMS block (aerosol-sprayed from an *n*-hexane solution).

In an attempt to gain some insight into the nature of the micellar core of PFDMS-*b*-PDMS, WAXS experiments were undertaken. A film of cylindrical micelles of PFDMS$_{50}$-*b*-

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[27] Solutions that were prepared by quenching the heated solution in an ice bath immediately prior to microscopy studies also contained what appeared to be large aggregrates of the spherical micelles, which may be precursors to the precipitant observed after 24 h. Slow cooling revealed the presence of short cylindrical micelles.

[28] (a) Rasburn, J.; Peterson, R.; Jahr, T.; Rulkens, R.; Manners, I.; Vancso, G. J. *Chem. Mater.* **1995**, *7*, 871. (b) Papkov, V. S.; Gerasimov, M. V.; Dubovik, I. I.; Sharma, S.; Dementiev, V. V.; Pannell, K. H. *Macromolecules* **2000**, *33*, 7107.

[29] Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683.

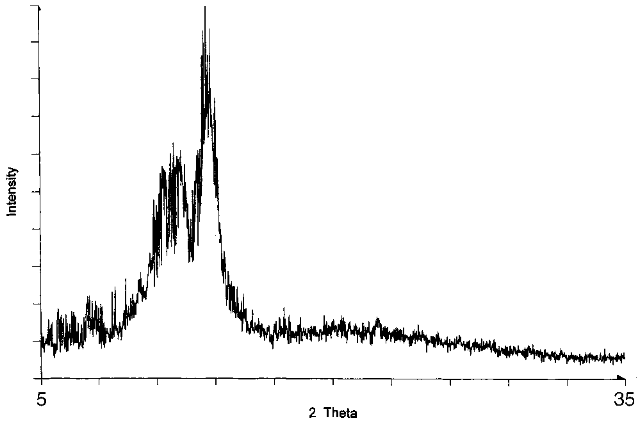
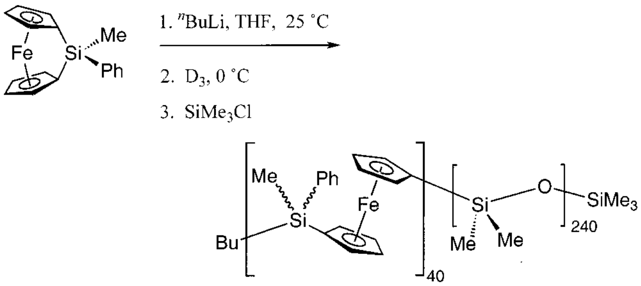


Figure 6. WAXS pattern of wormlike micelles of PFDMS$_{50}$-*b*-PDMS$_{300}$.

Scheme 3



PDMS$_{300}$ was deposited on an aluminum substrate from *n*-heptane, and the WAXS pattern in Figure 6 was obtained. The strongest peak in the powder pattern has a *d* spacing of 6.3 Å. It has been previously demonstrated that the structure for the pentamer is an excellent model for the crystallites in bulk PFDMS homopolymer.[29] With the powder pattern in Figure 6 of the micellar cores also so closely matching that of the pentamer, it is reasonable to infer a similar general crystal structure of PFDMS in the cores, namely, that the chains align preferentially with each other in an extended structure within the core. As one end of the polymer chain is confined to the PFDMS-*b*-PDMS interface because of the covalent linkage, it is also reasonable to infer that the PFDMS chains would predominately align perpendicular to the long axis of the wormlike micelle.

Core Crystallization as the Driving Force for the Formation of Wormlike Micelles. The tendency of the micellar core to crystallize with the chains aligned perpendicular to the long axis of the wormlike micelle may provide the thermodynamic driving force for the formation of the low-curvature cylindrical micelles in this system below the T_m. Current theories for the formation of block copolymer micelles in a solvent selective for one block would predict the formation of spherical micelles in the system discussed here that has a block ratio of 1:6. In our case, it is clear that the system forms cylindrical micelles below the T_m of PFDMS. This is clearly demonstrated in the case where wormlike micelles form with lengths on the order of tens of micrometers in hexane/THF mixtures at the onset of micellization. The observation that the system forms spherical micelles above the T_m of PFDMS which are then frozen in place by rapid cooling offers further evidence that the crystallization process is the driving force for the formation of wormlike micelles.

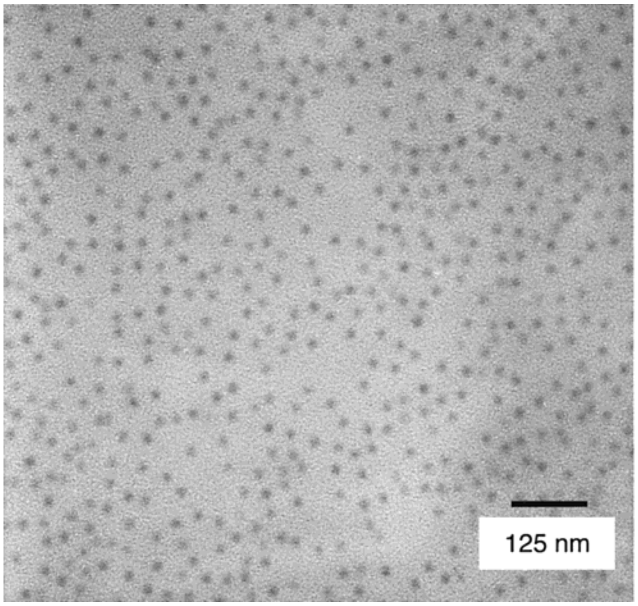


Figure 7. Transmission electron micrograph of spherical micelles of PFMPS$_{40}$-*b*-PDMS$_{240}$ (M_n = 29 700, PDI = 1.14) aerosol-sprayed from an *n*-hexane solution.

In an effort to provide further evidence for the key influence of crystallinity on the unexpected formation of the cylindrical morphologies, we synthesized two purely amorphous analogues,[25] PFMPS$_{40}$-*b*-PDMS$_{240}$ (PFMPS = poly(ferrocenylmethylphenylsilane)) and PFMES$_{50}$-*b*-PDMS$_{330}$ (PFMES = poly(ferrocenylmethylethylsilane)) diblock copolymers, and studied their micellation in *n*-hexane.

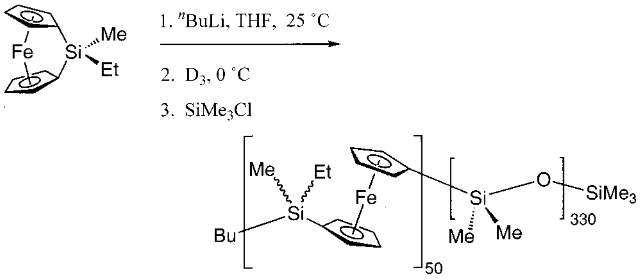
Investigation of Poly(ferrocenylsilane-*b*-dimethylsiloxane) Block Copolymers with Amorphous Poly(ferrocene) Blocks. (i) Synthesis, Characterization, and Micellization of PFMPS$_{40}$-*b*-PDMS$_{240}$. Poly(ferrocenylmethylphenylsilane-*b*-dimethylsiloxane) was synthesized by sequential anionic ROP in a similar manner to that of the corresponding PFDMS$_{50}$-*b*-PDMS$_{300}$ and PFDMS$_{75}$-*b*-PDMS$_{375}$ diblock copolymers (Scheme 3).

Of significance in the ^{1}H NMR spectrum was the presence of three Me singlets centered at δ = 0.70 in a 1:2:1 ratio indicative of the formation of an atactic poly(ferrocenylmethylphenylsilane). The lack of stereoregularity was also apparent in the ^{13}C NMR spectrum. Thus, environments assigned to the methyl carbon atoms were resolved into three distinct resonances at δ = −3.4, −3.3, and −3.2(5) attributed to the mm, mr/rm, and rr triads. GPC analysis determined an M_n value of 29 700 g/mol with a narrow molecular weight distribution (PDI = 1.14). Integration by ^{1}H NMR spectroscopy revealed that the PDMS block possessed a degree of polymerization 6 times that of the PFMPS block. Thus, the completely amorphous PFMPS$_{40}$-*b*-PDMS$_{240}$ and the crystalline PFDMS$_{50}$-*b*-PDMS$_{300}$ diblock copolymers possessed similar block ratios of ca. 1:6.

To explore the solution morphology of PFMPS$_{40}$-*b*-PDMS$_{240}$, a sample of the material was dissolved in *n*-hexane at 80 °C to afford a clear solution. Analysis of the morphology by TEM revealed the presence of spherical micelles (Figure 7).

The spherical micelles were quite uniform in size with an average core diameter of 14 nm. This is in agreement with that observed for the PFDMS$_{50}$-*b*-PDMS$_{300}$ cylindrical micelles (20 nm) and spherical micelles (18 nm) generated by forming the micelles above the T_m of the PFDMS block. Moreover, the decrease in diameter correlates with a lower degree of polymerization of the poly(ferrocenylmethylphenylsilane) block while maintaining a similar block ratio (cf. 20 nm (PFDMS$_{50}$-*b*-PDMS$_{300}$) and 30 nm (PFDMS$_{75}$-*b*-PDMS$_{375}$)). Thus, the amorphous PFMPS$_{40}$-*b*-PDMS$_{240}$ copolymer forms spherical micelles in solution.

Scheme 4



(ii) Synthesis, Characterization, and Solution Morphology of PFMES$_{50}$-*b*-PDMS$_{330}$. While the effects of a crystalline versus amorphous poly(ferrocenylsilane) block on the solution morphology have been discussed above, the influence of the glass transition temperature has not been addressed. Notably, both PFDMS-*b*-PDMS (T_g(PFDMS) = 33 °C) and PFMPS-*b*-PDMS (T_g(PFMPS) = 90 °C) possess cores in the glassy state at room temperature, which might conceivably serve to lock the morphology prior to reaching a thermodynamic equilibrium. Therefore, we synthesized a second amorphous diblock copolymer, PFMES$_{50}$-*b*-PDMS$_{330}$, in which the polyferrocene block possesses a T_g of 15 °C, which is well below room temperature.[25] Using an analogous route with the appropriate [1]ferrocenophane, the desired diblock copolymer was synthesized (Scheme 4). Analysis by GPC revealed a narrow molecular weight distribution (PDI = 1.09) with M_n = 40 300 g/mol. Integration of the methyl resonances in the ^{1}H NMR spectrum provided a block ratio of 1:6.6, from which we deduced a degree of polymerization of 50 for the PFMES block and 330 for the PDMS block. While microstructure resolution was absent in the NMR spectra, the signals were noticeably broad, indicative of an atactic polyferrocene block.

The solution morphology of PFMES$_{50}$-*b*-PDMS$_{330}$ was investigated by TEM with an analogous sample preparation as described above. As seen in Figure 8, a spherical morphology was observed. The sample is somewhat less monodisperse than the corresponding PFMPS$_{40}$-*b*-PDMS$_{240}$ diblock copolymer with an average core diameter of ca. 14 nm. These results, together with those for PFMPS-*b*-PDMS, provide further evidence that the formation of cylindrical structures for PFDMS-*b*-PDMS is indeed a consequence of crystallization of the core-forming block.

Synthesis and Micellization Behavior of Poly(isoprene-*b*-ferrocenyldimethylsilane). To investigate the generality of the effect of polyferrocene core crystallinity on observed micelle morphologies, we prepared the block copolymer PI-*b*-PFDMS (Scheme 5). The block copolymer was synthesized by living anionic polymerization through sequential monomer addition, similar to the synthesis of an analogous system reported before.[30] The polymerization of isoprene was initiated with *sec*-butyllithium, and after the polymerization was complete, a solution of **1** was added. The living block copolymer was terminated by the addition of a few drops of degassed methanol, and an amber rubbery solid was isolated in high yield after precipitation into methanol. GPC indicated a narrow molecular weight distribution (PDI =1.10) with a nominal M_n of 23 100 g/mol, and ^{1}H NMR revealed a block ratio of 4.4:1, which corresponds to the structure PI$_{188}$-*b*-PFDMS$_{42}$.

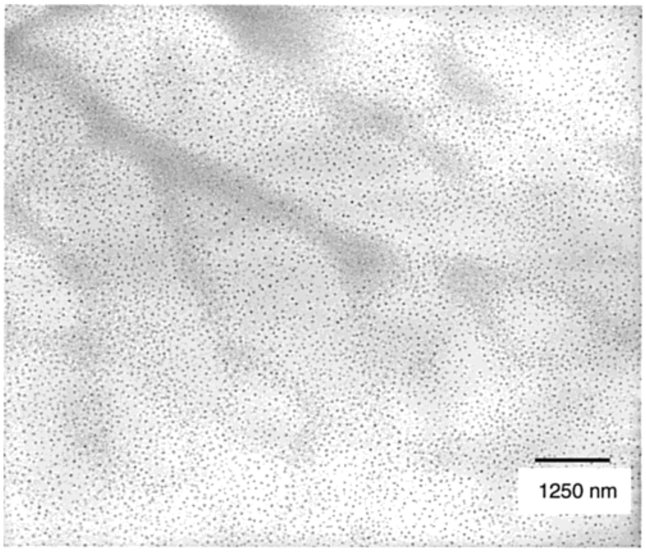
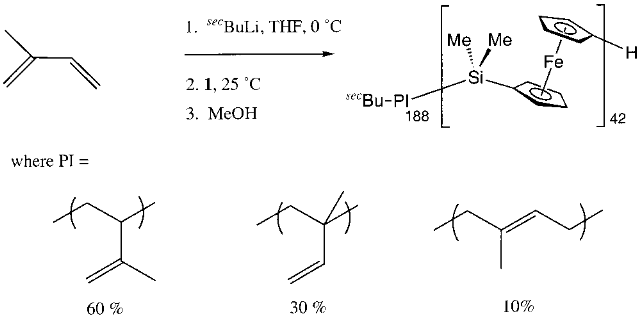


Figure 8. Transmission electron micrograph of PFMES$_{50}$-*b*-PDMS$_{330}$ spherical micelles prepared by aerosol-spraying from an *n*-hexane solution.

Scheme 5



The formation of micellar aggregates of PI$_{188}$-*b*-PFDMS$_{42}$ was studied by two different methods. First, a micelle solution was obtained by direct dissolution of PI$_{188}$-*b*-PFDMS$_{42}$ in hexane at room temperature with 1 min of mild sonication to accelerate the process. TEM revealed the presence of short cylindrical micelles (Figure 9a) with contour lengths ranging from 100 to 500 nm similar to those of PFDMS-*b*-PDMS prepared by direct dissolution at 80 °C. Second, the slow addition of hexane to a solution of PI$_{188}$-*b*-PFDMS$_{42}$ in THF and the subsequent removal of the residual THF by dialysis afforded a solution of wormlike micelles (Figure 9b) that had contour lengths that extended for tens of micrometers. This behavior is similar to that described above for the PFDMS block copolymers with PDMS, and provides convincing support for our assertion that the key driving force for the formation of cylindrical micelles in these systems is the crystalline nature of the core-forming polyferrocene block.

Summary

The self-assembly of the organometallic–inorganic block copolymer PFDMS-*b*-PDMS in *n*-alkane solvents has been studied under a variety of conditions. When the micelles are formed below the melt transition of PFDMS, wormlike micelles are observed. These structures formed regardless of the method of sample preparation, either by direct dissolution in the *n*-alkane solvent at 80 °C or by adding *n*-hexane to a solution in THF. Changing the method of sample preparation only affected the length of the micelle aggregates observed. Heating the sample

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[30] Cao, L.; Winnik, M. A.; Manners, I. *J. Inorg. Organomet. Polym.* **1998**, *8*, 215. For recent, brief reports of PI-*b*- PFDMS, see (a) Lammertink, R. G. H.; Hempenius, M.; van den Enk, J. E.; Chan, V. Z.-H.; Thomas, E. L.; Vancso, G. *J. Adv. Mater.* **2000**, *12*, 98. (b) Chen, Z.; Vaidya, N.; Cheong, T.-H.; Foster, M. D.; Quirk, R. J. P. *Polym. Mater. Sci. Eng. Prepr. (Am. Chem. Soc., Div. Polym. Mater. Sci. Eng.)* **2000**, *83*, 525.

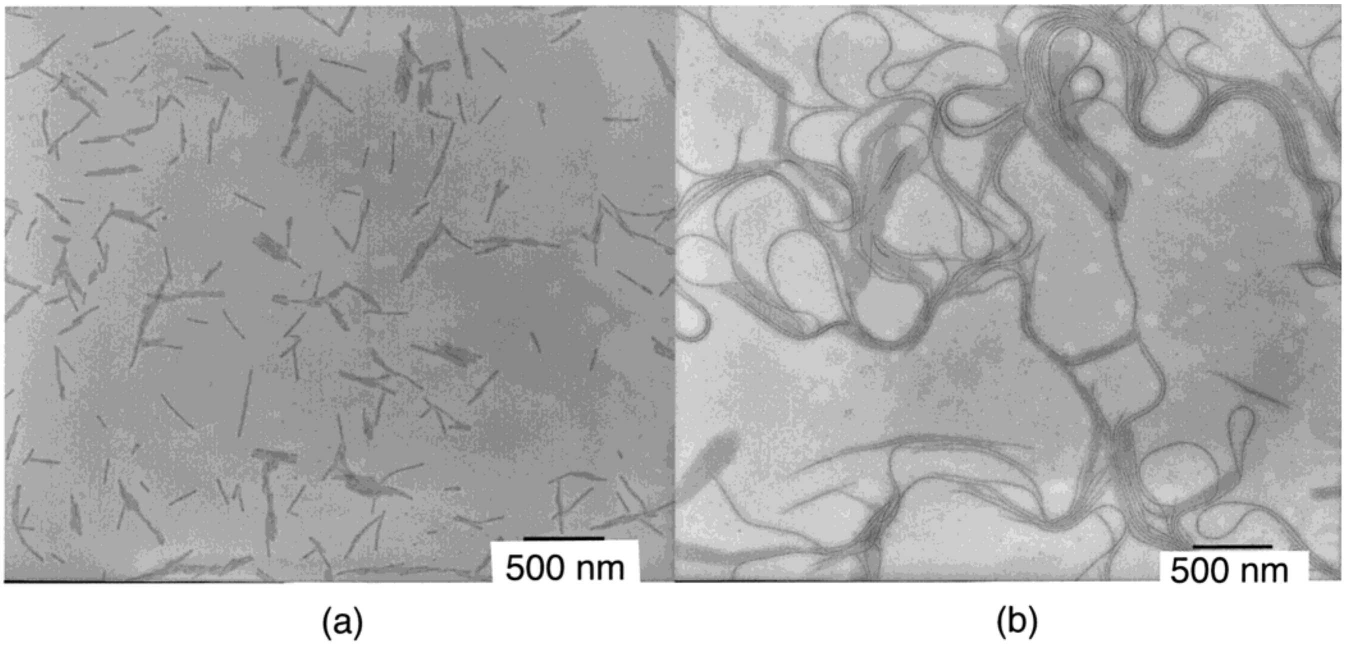

Figure 9. Transmission electron micrograph of PI-*b*-PFDMS micelles formed in hexane (a) prepared by direct dissolution and (b) prepared by the slow addition of hexane to a solution in THF.

resulted in micelles that were ca. 440 nm long, and sonication reduced the length to 70 nm.[24] The method of adding *n*-hexane to a solution in THF afforded micelles whose lengths were on the order of tens of micrometers. Moreover, changing the overall molecular weight, while maintaining the stoichiometric ratio of the respective blocks, varied the diameter of the micellar core. A feasible explanation for the formation of wormlike micelles in this system is also presented. If micelles are formed above the T_m of PFDMS (ca. 120−145 °C), spherical aggregates are formed. This suggests that the crystallization of the core is the driving force for the formation of wormlike micelles below the T_m in this system.[31] The synthesis of the amorphous analogues PFMPS$_{40}$-*b*-PDMS$_{240}$ and PFMES$_{50}$-*b*-PDMS$_{330}$ and the observation of their resulting spherical morphologies in hexane further support the finding that the energetic driving force for the formation of novel cylindrical micelles lies in the crystallization of the PFDMS core. This concept was applied successfully to a different system, PI-*b*-PFDMS, where the synthesis was tailored to afford a material in which the crystalline nature of the core would lead to the formation of wormlike morphologies in solution. It appears probable that block crystallization may allow predictable and selective formation of nonspherical micellar morphologies in other (e.g., organic) systems. Studies to test this hypothesis are underway. We are also investigating oxidation, etching, and pyrolysis of the cylindrical micellar polyferrocene structures for nanostructure applications.[17,26]

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(31) Crystallization of PFDMS blocks has also been shown to influence the properties of poly(ferrocenylsilane) block copolymers in the solid state. See, for example, Li, W.; Sheller, N.; Foster, M. D.; Balaishis, D.; Manners, I.; Annis, B.; Lin, J. S. *Polymer* **2000**, *41*, 719.