Self-Assembly of a Novel Organometallic−Inorganic Block Copolymer in Solution and the Solid State: Nonintrusive Observation of Novel Wormlike Poly(ferrocenyldimethylsilane)-*b*-Poly(dimethylsiloxane) Micelles

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Abstract: The novel organometallic−inorganic diblock copolymer, poly(ferrocenyldimethylsilane)-*b*-poly(dimethylsiloxane) (PFS-*b*-PDMS) (block ratio = 1.0:6.0) (M_n = 35 100 g/mol with a narrow molecular weight distribution M_w/M_n = 1.10 based upon gel permeation chromatography in THF using polystyrene standards) forms long rodlike micelles in hexane solution. After the solvent was evaporated, transmission electron microscopy (TEM) and atomic force microscopy (AFM) showed that individual cylindrical micellar structures form with the iron-rich, organometallic PFS core encased in a sheath (corona) of PDMS. The block copolymer forms hexagonally packed cylinders in the bulk, and exposure to warm hexane causes the cylinders to disperse in the solvent. Both static and dynamic light scattering (SLS and DLS) were used to establish that the micelles are flexible rods which are stable in hexane even at 80 °C. The as-prepared sample possessed an aggregation number of ca. 2000 polymer molecules. Ultrasonication (60 W) in hexane led to the generation of short cylinders with an aggregation number of ca. 700. Since PFS can be oxidized to a semiconductive state and PDMS is an insulator, these rodlike micellar structures have the potential to function as nanoscale self-insulated wires.

Introduction

The incompatibility of the constituent segments is known to facilitate the self-assembly of block copolymers into a variety of morphologies in the solid state.[1] In addition, spherical micelles have been observed in many studies of block copolymers in solution where the solvent preferentially solvates one of the blocks. Although there are several reports in the literature of the formation of cylindrical micelles[2−10] from block copolymers, such systems are uncommon, and understanding of them remains poor. Many of the early reports of nonspherical micelles were complicated by the so-called anomalous effect in which certain block copolymer solutions would exhibit a milky opalescence with a large angular dissymmetry at concentrations or temperatures near the onset of micellization.[6] Nevertheless, there are examples supported by TEM images, particularly from Price[4,7] involving the formation of a web of block copolymer micelles when solutions are evaporated onto a TEM grid. The more recent experiments by Antonietti et al.,[5] by Liu and co-workers,[2], by Möller et al.,[10] and by Eisenberg[3] provide well-documented examples of systems that form cylindrical structures reversibly in solution under the conditions of micelle formation. Cylinder formation with surfactants is driven by a balance between two factors, phase separation of the lyophobic tails of the surfactant, leading to formation of a space-filling insoluble phase, and the surface area occupied by the headgroups. The energy of curvature is smaller along the cylinder than at the hemispherical ends, providing a driving force for the formation of (in principle, infinitely) long cylinders.[11]

High molecular weight poly(ferrocenylsilanes) are a novel class of transition metal based polymers which have recently become readily available via the ring-opening polymerization (ROP) of monomeric silicon-bridged [1]ferrocenophanes.[12−14] These materials possess interacting metal atoms in the polymer main chain and are currently under investigation as, for example, charge-transport materials and as precursors to ferromagnetic ceramics (including superparamagnetic nanostructures) by pyrolysis.[15,16] Block copolymers containing poly(ferrocene) seg-

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ments offer unique possibilities for the preparation of self-assembled architectures with novel properties in both the solid state and in solution.[14,19] The recent discovery of the living anionic ROP of [1]ferrocenophanes has, for the first time, permitted access to a range of multiblock copolymers containing skeletal transition metal atoms.[18−20] Phase separation of these materials in the solid state affords nanoscale redox-active domains which should be of considerable interest.[14,19] Phase separation of the organometallic−organic diblock copolymer poly(ferrocenylsilane)-*b*-polystyrene (PFS-*b*-PS) in the solid state has been previously studied by TEM.[19] In this paper, we report the first detailed studies of the solution and solid-state behavior of the organometallic−inorganic block copolymer, poly(ferrocenylsilane)-*b*-poly(dimethylsiloxane) (PFS-*b*-PDMS) and discuss characterization of the resulting nanostructures.

Experimental Section

Equipment and Materials. Butyllithium (1.6M in hexanes), dimethyldichlorosilane, chlorotrimethylsilane, and hexamethylcyclotrisiloxane were all purchased from Aldrich. Me_3SiCl and Me_2SiCl_2 were distilled prior to use. $(Me_2SiO)_3$ 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. Distilled water was degassed prior to use. The 12-Crown-4 was purchased from Aldrich, distilled from CaH_2, and stored in a glovebox at −30 °C. Tetrahydrofuran, hexanes, and diethyl ether were 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 (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 as the solvent in all cases.

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.

Dynamic light scattering experiments were carried out on a wide angle laser light scattering photometer from Brookhaven Instruments Corporation. A 5-mW vertically polarized He−Ne laser from Spectra physics was the light source. The solutions were filtered through disposable 0.5-μm filters from Millipore into glass scattering cells with a diameter of 12.3 mm. The cells were placed into the BI-200SM goniometer and sat in a vat of thermostated toluene which matched the index of refraction of the glass cells. The angular range of the goniometer was 7−162°. The scattered light was detected by a photomultiplier interfaced to the BI-2030AT digital correlator with 136 channels and measured the correlation function in real time. The instrument was controlled by a 486AT computer. The data were analyzed by software supplied by Brookhaven.

Static light scattering experiments were also carried out on the same instrument as that used for the dynamic light scattering measurements. A larger quartz cell was used, with a diameter of 22 mm. Toluene was used as a reference for the Rayleigh ratio ($R_\Theta = 14 \times 10^{-6}$ cm^{-1}).

Transmission electron micrographs were obtained on a Hitachi model 600 electron microscope. Atomic force images were obtained using a Nanoscope III microscope (Digital Instruments) in tapping mode with a silicon cantilever with a resonance frequency of 300−380 kHz.

Synthesis of [1]Silaferrocenophane Monomer. Over a period of 5 min, neat Me_2SiCl_2 (9.2 mL, 76 mmol, 16% excess) was added dropwise to a suspension of 20.0 g of dilithioferrocene·tmeda (64 mmol) in 400 mL of diethyl ether at −76 °C. The reaction was allowed to warm to room-temperature overnight; over this time the color changed from orange-yellow to red. The solvent, excess Me_2SiCl_2, and TMEDA were removed by vacuum (10^{-3} mmHg) over 24 h and hexanes added. The solution was filtered to remove LiCl, and the hexanes were removed. The product was vacuum-sublimed (10^{-3} mmHg) onto a cold probe (5 °C) at room-temperature, yielding 12.3 g (yield = 80%) of red crystalline [1]silaferrocenophane. ^1H NMR (200 MHz, C_6D_6, δ) data: 0.51 (s, 6H, Me), 4.08 (t, $J_{H-H} = 1.7$ Hz, 4H, Cp), 4.48 (t, $J_{H-H} = 1.7$ Hz, 4H, Cp) ppm.

Further purification was necessary to obtain monomer of sufficient purity to be initiated anionically. This process consisted of repetitive sublimation plus recrystallization from hexanes until no spurious peaks appeared in the ^1H NMR spectrum with the vertical scale increased 20 times, relative to the Me (0.51 ppm) peak. This cycle was usually repeated a minimum of three times. The reaction could be easily scaled up to produce ca. 80 g of monomer.

Synthesis of the Diblock Copolymer PFS-*b*-PDMS. This polymer was prepared by a modification of the previously published route.[19] Before the anionic polymerization of [1]silaferrocenophane was attempted, the purity of the THF was confirmed. To a volume of THF that was the same as that used for the subsequent reactions was added a few milligrams of 1,10-phenanthroline as an indicator. BuLi was then added dropwise until the solution turned slightly pink. In successful polymerizations, this volume was an order of magnitude less than the minimum initiator volume to be used. In a glovebox at room temperature, 56 μL of 1.45 M BuLi (8.1×10^{-5} mol) in hexanes was added quickly to a stirred solution of 1.014 g of [1]silaferrocenophane (4.19×10^{-3} mol) in THF (18 mL). After 40 min, the solution changed from a red to a deep amber color, and then 2.073 g of $(Me_2SiO)_3$ (9.33×10^{-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 it showed a marked decrease in viscosity. 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 2.491 g (yield = 81%). ^1H NMR (200 MHz, C_6D_6, δ) data: 0.54 (s, $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_x$), 4.10 (s, Cp), 4.26 (s, Cp), and 0.28 (s, $[Me_2SiO]_{3y}$).

Static Light Scattering. SLS experiments were carried out to determine the weight-averaged molecular weight, M_w, the radius of gyration, R_G, and the second virial coefficient, A_2. The values were obtained by the Rayleigh−Debye relationship

$$\frac{Kc}{R_\theta} = \left(\frac{1}{M_w} + 2A_2c + 3A_3c^2 + ...\right)\left(1 + \frac{16\pi^2}{3\lambda^2} {R_G}^2 \sin^2\frac{\theta}{2}\right) \qquad (1)$$

where c is the concentration, R_θ is the measured Rayleigh ratio, and K is an optical constant defined as

$$K = [4\pi^2 n^2/N_A \lambda_0^4](\mathrm{d}n/\mathrm{d}c)^2 \qquad (2)$$

where n in the refractive index of the solvent, λ_0 is the wavelength of the laser light in a vacuum, N_A is Avogadro's number, and dn/dc is the refractive index increment of the solution. Refractive index increment measurements were performed at five different concentrations in hexane at 23 °C. A value of dn/dc at 632.8 nm of 0.08938 mL/g was obtained.

Dynamic Light Scattering. In dynamic light scattering, the experimentally determined intensity autocorrelation function is related to the autocorrelation function representative of the motions of the particles

$$G^{(2)}(\tau) = {I_\theta}^2\left[1 + \left|\frac{G^{(1)}(\tau)}{G^{(1)}(0)}\right|^2\right] = {I_\theta}^2[1 + \mathrm{e}^{-2Dq^2\tau}] \qquad (3)$$

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where the normalized intensity autocorrelation function, which is determined experimentally, can be expressed as an exponential with a decay of Γ,

$$g^{(1)}(\tau) = \frac{G^{(1)}(\tau)}{G^{(1)}(0)} = Ae^{-\Gamma\tau} \tag{4}$$

Real systems can rarely be described by a single decay, and often a cumulant expansion is used, where the logarithm of $g^{(1)}(\tau)$ is expanded in a power series in terms of the delay time τ,

$$\ln g^{(1)}(\tau) = -\Gamma_1\tau + (\Gamma_2/2!)\tau^2 - (\Gamma_3/3!)\tau^3 + ... \tag{5}$$

where Γ_1 is the first cumulant, Γ_2 the second cumulant, and so forth. Finally, once Γ_1 is determined, the concentration and angular dependence can be expressed as

$$\frac{\Gamma_1}{q^2} = D_{z,0}(1 + k_D c + ...)(1 + C\bar{R}_g{}^2 q^2 + ...) \tag{6}$$

where $D_{z,0}$ is the diffusion coefficient, C is a parameter that is characteristic of the molecular architecture, k_D is the effective interaction parameter, and q is the magnitude of the scattering vector.

From the diffusion coefficient, the effective hydrodynamic radius, R_H can be determined from the Stokes−Einstein relation

$$R_H = \frac{kT}{6\pi\eta D_z} \tag{7}$$

where η is the solvent viscosity.

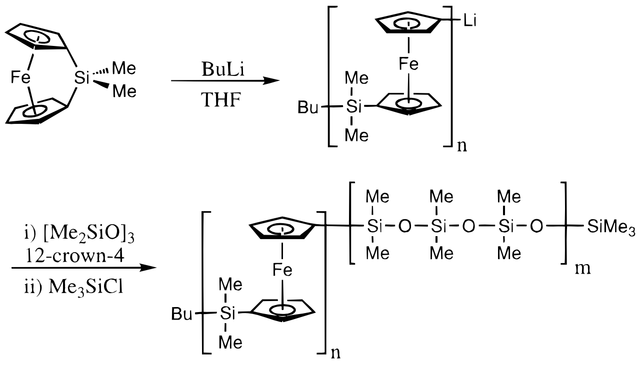
Preparation of Samples for TEM and AFM. Thin carbon films (ca. 5 Å) were grown on mica as a support, and then 25 μL of a dilute solution of the block copolymer in hexane (ca 0.2%) was aerosol-sprayed onto the carbon film. Each carbon film was floated off the mica support in water and deposited onto a 300 mesh Gilder copper grid. The sample was air-dried before introduction into the electron microscope. No staining of the sample was necessary. Samples for AFM were prepared in an analogous manner, except that the solution was aerosol-sprayed directly onto a freshly cleaved mica surface which was then mounted for imaging.

Results and Discussion

The study of structures with nanometer dimensions and their use in the fabrication of nanoscale devices is of considerable scientific and technological interest.[21−24] Block copolymers containing organometallic segments offer potential access to interesting nanostructures via a self-assembly approach. Here we describe a material which forms flexible cylindrical structures with a diameter on the order of tens of nanometers. This material, poly(ferrocenylsilane)-*b*-poly(dimethylsiloxane) (PFS-*b*-PDMS), a diblock copolymer with an organometallic block and an inorganic block, can be prepared as long rodlike micelles in aliphatic hydrocarbon solution and laid down as individual cylinders on a solid support. The cylinders have an iron-rich, potentially semiconductive core of PFS, surrounded by an insulating sheath (corona) of PDMS.

1. Synthesis of PFS-*b*-PDMS Copolymer. The diblock copolymer PFS-*b*-PDMS was prepared by the addition of hexamethylcyclotrisiloxane $[Me_2SiO]_3$ to a solution of living poly(ferrocenyldimethylsilane) synthesized by the initiation of the silicon-bridged [1]ferrocenophane with *n*-butyllithium (see Scheme 1).[18,19] After the reaction was terminated with trimethylchlorosilane and the copolymer was precipitated into methanol, the resulting block copolymer was isolated as an amber, rubbery solid. Analysis of the polymer by ^{1}H NMR indicated that the PDMS block had a degree of polymerization 6.0 times that of the PFS block, compared to the stoichiometric ratio of monomeric reactants of 6.6:1. Analysis of the polymer by gel permeation chromatography (GPC) in THF gave a narrow band with a (nominal) number average molecular weight (M_n) of 35 100 g/mol based upon polystyrene (PS) standards and a narrow molecular weight distribution ($M_w/M_n = 1.10$). The M_n value is close to that predicted from the reaction stoichiometry (38 100 g/mol).

Scheme 1



PFS-b-PDMS

An aliquot of the PFS block, isolated from the polymerization reaction before copolymerization, gave M_n = 7750 g/mol and M_w/M_n = 1.07 (vs PS standards). From this result and NMR integration on the block copolymer, the molecular weight of the latter is 22 000 g/mol^{-1}. This result is, however, consistent with previous light-scattering studies of various ferrocene-based homopolymers where the absolute molecular weight determined from light scattering was always ca. 30% greater than that determined by GPC (vs polystyrene standards).[13] However, we have been unsuccessful in obtaining an absolute molecular weight of the block copolymer. Attempts to characterize the PFS homopolymer by light scattering were frustrated by the tendency of the homopolymer to form a small amount (ca. 1%) of aggregates that could be detected in the CONTIN analysis of dynamic light scattering (DLS) experiments and which could not be removed or which rapidly reformed when the solution was filtered. This aggregation may be related to the relative ease of oxidizing the ferrocenyl groups in the polymer or to the self-charging phenomena described by Xu and Chu.[25]

2. Solvent Cast Films of PFS-*b*-PDMS. The morphology of a block copolymer in the bulk ranges from spheres to cylinders to lamella, depending on the relative ratios of each block.[17] TEM studies showed that PFS-*b*-PDMS self-assembles in the bulk state to form cylinders in a hexagonal array, as is expected for diblock copolymers whose components have a volume ratio in the range of 18 to 40%.[17] These bulk samples can be prepared by solvent casting from tetrahydrofuran, a good solvent for both blocks. The self-assembly process may be aided by the fact that both components of the block copolymer have relatively low glass transition temperatures (T_g(PDMS) = −123 °C, T_g(PFS) = 34 °C). The "as-cast" film exhibits randomly oriented cylindrical domains with a local hexagonal structure (parts A and B of Figure 1). Annealing the film at ca. 120 °C leads to a rearrangement of the structure (parts C

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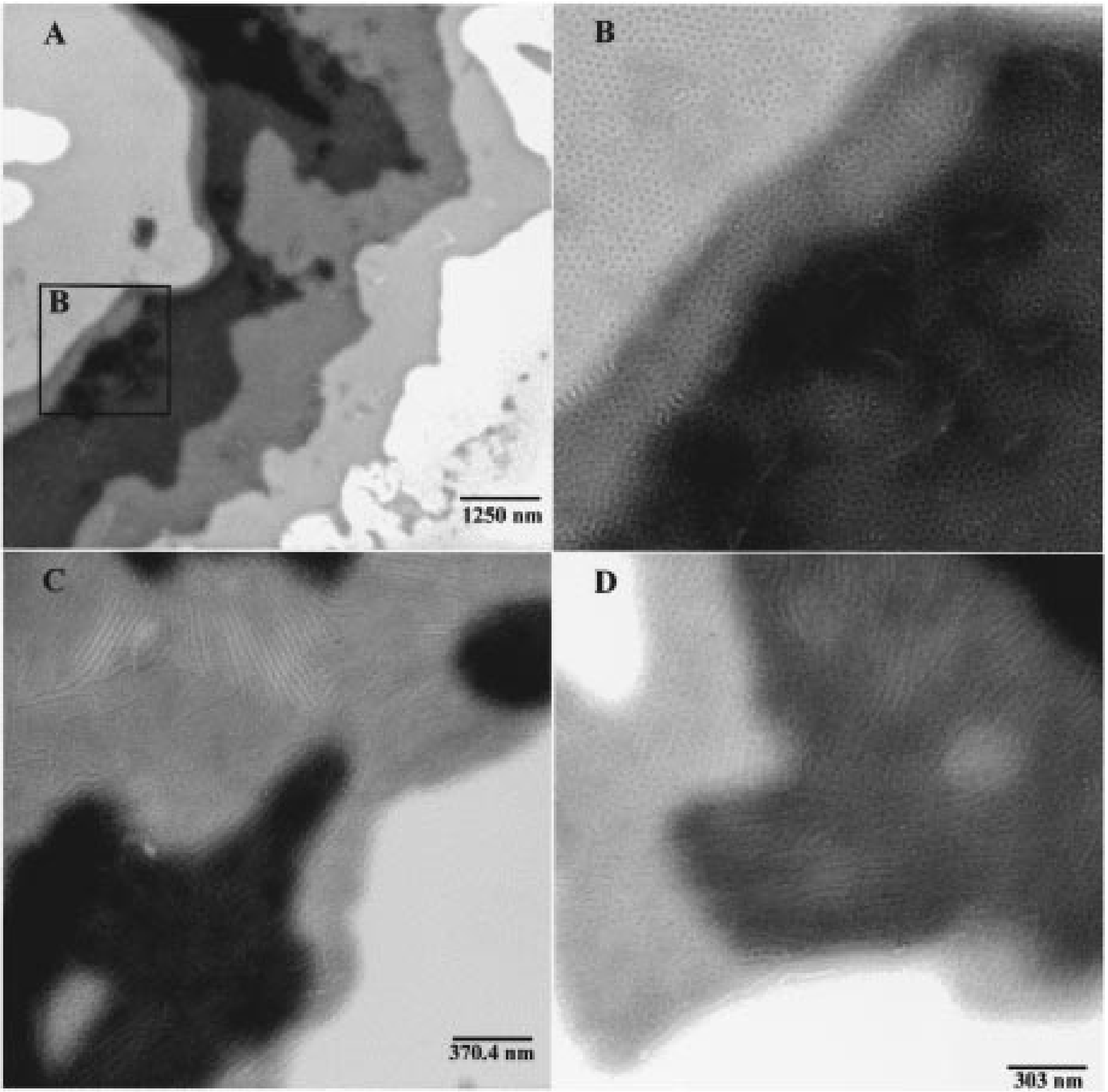

Figure 1. (A) A TEM of a film of PFS-*b*-PDMS formed by aerosol-spraying a dilute solution from THF onto a thin carbon film supported on mica. The film was not annealed. It was not necessary to stain the film since iron is in the backbone of PFS. The film displays local hexagonal packing of cylinders perpendicular to the substrate. (B) Enlarged area from Figure 1A clearly showing local hexagonal packing of the cylinders. Some cylinders lying on their side are also visible in the lower left of the micrograph. (C) and (D) show the effect of annealing the film at 120 °C for 24 h. The cylinders are now parallel to the substrate.

and D of Figure 1) with a greater tendency for the cylinders to lie parallel to the substrate.[26]

3. Cylindrical Micelle Formation in Hexane; TEM and AFM Studies. When a bulk polymer sample is heated with *n*-hexane in a sealed vial at 80 °C, the cylinders are solubilized and can be laid down on a solid support. These cylindrical structures can be visualized by TEM under remarkably mild conditions. Because of the iron rich block, it was not necessary to stain the samples to obtain contrast. In fact, no invasive sample preparation was required; therefore, only the pristine sample was imaged. Various images are shown in parts A−D of Figure 2. One sees that when the polymer is more concentrated, one can obtain films which are close-packed, two-dimensional arrays of cylinders. More dilute solutions lead to isolated cylinders. The individual micelles appear to be flexible and to have contour lengths on the order of 440 nm. They vary somewhat in contour length but have a uniform thickness of ca. 20 nm.

AFM was used to study the morphology of the polymeric micelles in solution. An image obtained is shown in Figure 3, which corresponds to a 5 μm × 5 μm scan. The average contour length of the cylindrical micelles is 388 nm. The average width is 68 nm. The length of the cylindrical micelles agrees well with the lengths found in the TEM images. The widths measured by AFM, however, are considerably larger than those seen in TEM images. Since there is no indication of contrast between the core and the corona in the TEM images, the micrographs are most likely images of the electron-rich core only, whereas the AFM image shows the wider corona surface of the wormlike micelle.

4. Light Scattering Studies of Cylindrical Micelles of PFS-*b*-PDMS in Hexane. The PFS-*b*-PDMS solutions used to

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[26] In the bottom right of Figure 1A, there are cylindrical micelles lying on their side. They are clear under higher magnification of the micrograph.

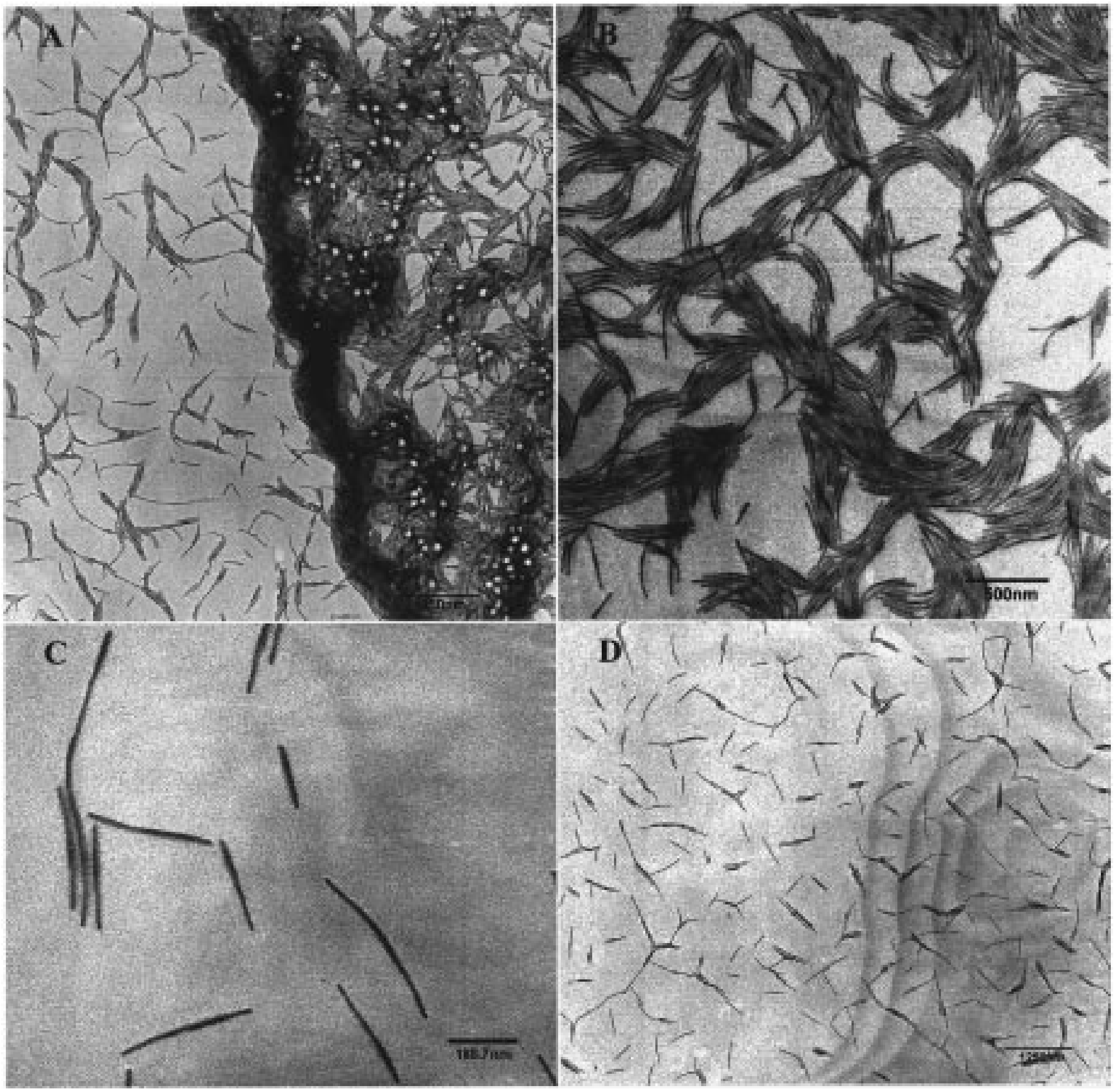

Figure 2. Various TEMs of PFS-*b*-PDMS, which self-assembles in hot hexane to form wormlike micelles with a core rich in iron. They have an average contour length of 440 nm and an average diameter of 20 nm. Samples were prepared by aerosol-spraying a dilute solution from hexane onto a thin carbon film supported on mica. It was not necessary to stain the samples because of the iron-rich core. The micrographs show regions where the cylinders are starting to pack and form a two-dimensional film and regions where there are isolated worms.

obtain the TEM images in Figure 2 were also examined by static and dynamic light scattering (SLS and DLS, respectively).[27,28] Micelle-like aggregates were observed even at very low concentrations (10^{-3} g/L), indicating that the critical micelle concentration of the polymer is sufficiently low that the onset of association can be neglected in the interpretation of the scattering data. As we demonstrate below, the aggregates examined here are in fact “frozen micelles,” whose structures depend on the method of sample preparation. These aggregates do not equilibrate on an experimentally accessible time scale.

DLS results are presented in Figure 4, and we obtain a $D_{z,0}$ value for the micelles of 9.7×10^{-8} cm^2/s. This corresponds to an effective hydrodynamic radius R_H, of 72 nm calculated from the Stokes−Einstein relationship. The hydrodynamic radius does not change significantly when measured at 80 °C (the temperature was maintained for ca. 3 h) or when a sample is cycled repeatedly through temperatures from 20 to 80 °C. Algorithms to deconvolute the autocorrelation function (GENDIST and CONTIN) indicate a unimodal size distribution, but these distributions are broader than those obtained for spherical block copolymer micelles in other systems formed through closed association.[29] There was no indication of a second slow relaxation mode characteristic of rodlike structures, resulting from the coupling of the translational and rotational diffusion.[30] This result indicates that the wormlike structures identified in the TEM images are flexible in solution.

The ratio Γ_2/Γ_1^2 is a useful measure of size polydispersity for unimodal distributions. For monodisperse spheres Γ_2/Γ_1^2 has a value of ca. 0.01, and starlike spherical micelles of narrow size distribution are typically characterized by Γ_2/Γ_1^2 values of

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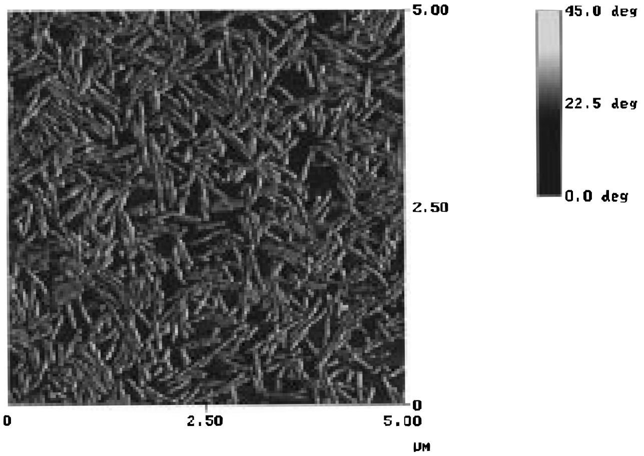

Figure 3. AFM phase image obtained using a Nanoscope III microscope (Digital Instruments) in tapping mode with a silicon cantilever with a resonance frequency of 300−380 kHz. The sample is identical to the one used to obtain the TEM images from Figure 2.

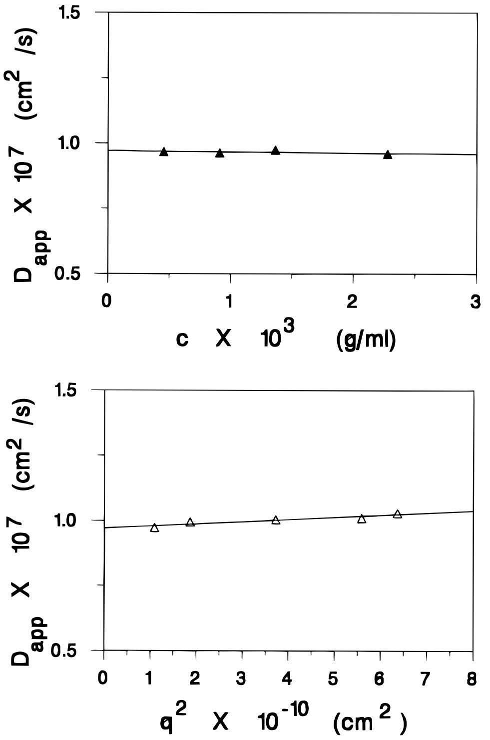

Figure 4. Angular (extrapolated to zero concentration) and concentration (extrapolated to zero angle) dependence of the DLS data for the wormlike micelles (nonsonicated sample).

0.04 to 0.07.[2,6] We find $\Gamma_2/\Gamma_1^2 = 0.11$, consistent with wormlike micelles[6] with a distribution of contour lengths as observed in the TEM images. The slope C of the angular dependence of the normalized DLS signal (eq 6) is related to the shape of the diffusing species. We find $C = 0.01$ smaller than the theoretical value for a Gaussian chain ($C = 0.17$) and consistent with the predicted value for a rodlike, wormlike, or elliptical structure ($C = 0.03$).

SLS experiments presented in Figure 5 reveal the apparent molecular weight of the micelles (M_w) to be 8.4×10^7 g/mol (with $A_2 = 1.4 \times 10^{-6}$). When compared to the molecular weight of the block copolymer itself, we estimate a mean aggregation number of about 2000.[31] This is a very large aggregation number compared to the 50 to 150 polymers per micelle found typically for spherical block copolymer micelles.[29] The rms radius of gyration, R_G for this sample is 87 nm. Both R_H and R_G values are significantly smaller than that of the contour length of the micelles seen in the TEM images, again indicating that the cylindrical micelles have considerable flexibility in solution.

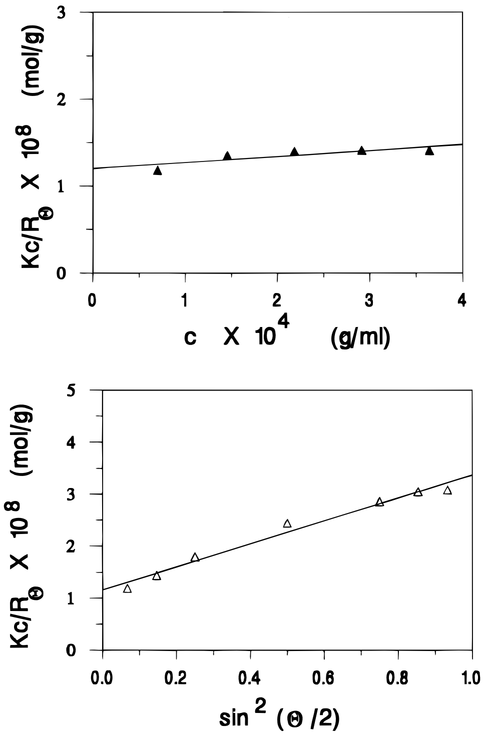

Figure 5. Angular (extrapolated to zero concentration) and concentration (extrapolated to zero angle) dependence of the SLS data for the wormlike micelles. (nonsonicated sample).

The ratio R_G/R_H is sensitive to the inner density profile of the particle structure.[5,32] The theoretical value for monodisperse impermeable spheres is 0.775, whereas that for a Gaussian random coil is close to 1.5. For elliptical structures, the magnitude of the R_G/R_H ratio depends strongly on the axial ratio, and for the specific case of cylinders of length L and thickness d, this ratio is given by the expression

$$R_G/R_H = \frac{1}{\sqrt{3}}(\ln (L/d) + 0.38) \qquad (8)$$

Our value of $R_G/R_H = 1.2$ corresponds to an aspect ratio, $L/d = 5.5$, about three times smaller than that observed in the TEM micrographs but compares well with a value of 5.7 calculated from the AFM image. Liu et al.[2] reported R_G/R_H values near 1.25 for cylindrical micelles of poly(styrene-*b*-2-cinnamoylethyl methacrylate) with a cross-linked core in toluene, and Antonietti et al.[5] found values of 1.1 for poly(styrene-*b*-4-vinylpyridine) in solvents selective for polystyrene. Taken together, all of our light scattering data provide strong evidence for the existence of large wormlike micelles in solution.

5. Light Scattering and TEM on Sonicated PFS-*b*-PDMS Solutions in Hexane. To investigate the stability of these wormlike micelles in hexane, the solutions were subjected to (relatively low intensity) ultrasonication with a 60-W sonication bath. The solutions were monitored by DLS at a scattering angle of 90°. The time dependence of R_H is plotted in Figure 6, where one sees that the size decreases to an asymptotic value of 35

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[31] The ratio of M_w for the micelle to M_w of the polymer, estimated from the GPC analysis, is equal to 2100.

[32] Schmidt, M.; Stockmayer, W. H. *Macromolecules* **1984**, *17*, 509.

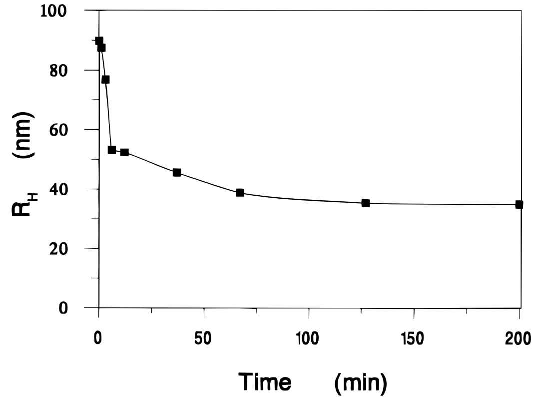

Figure 6. The change in hydrodynamic radius, R_H with time caused by sonication of the worms in Figure 2 is shown. R_H was calculated from the Stokes−Einstein relationship, $R_H = kT/(6\pi\eta D_z)$. The diffusion constant, D_z was determined from the relation $D_z = \Gamma_1/q^2$ at a fixed scattering angle of 90°, where Γ_1 is the first cumulant calculated from the experimentally measured autocorrelation function by a cumulant expansion (see eq 5) and q is the magnitude of the scattering vector. The radius decreases with sonication time to a constant value of 35 nm. The line is to guide the eye.

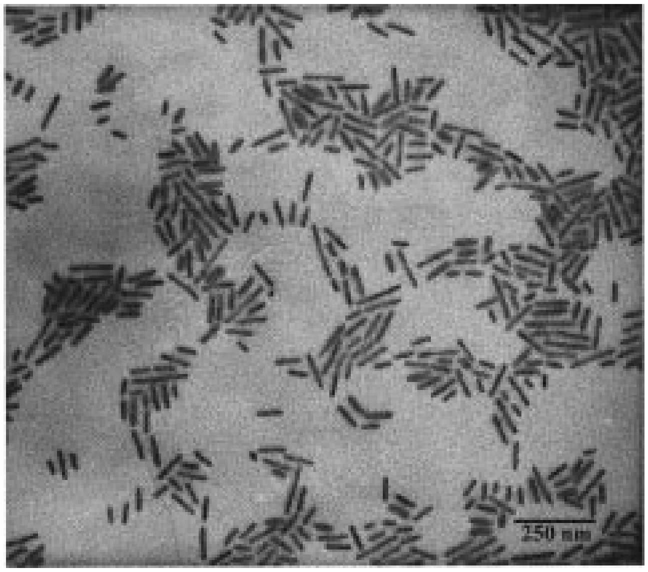

Figure 7. A TEM of PFS-*b*-PDMS, which was sonicated for 3 h after dissolution in hot hexane to form wormlike micelles with a core rich in iron. The length of the worms decreased to 77 nm with a narrower distribution of contour lengths after sonication. Samples were prepared by aerosol-spraying a dilute solution from hexane onto a thin carbon film supported on mica. It was not necessary to stain the samples because of the iron-rich core.

nm. The structures produced in this way remain stable even after they are reheated to 80 °C. A representative TEM image is shown in Figure 7. The micelles retain their wormlike morphology, but are significantly shorter and more uniform in length than the original samples. Here we find an average contour length of 77 nm and a diameter very similar to that of the original sample.

These sonicated solutions provide an interesting comparison to the as-prepared micellar solutions described above. DLS measurements presented in Figure 8 show that the now smaller micelles are characterized by a diffusion coefficient of 2.0 × 10^{-7} cm^2/s, which corresponds to an effective hydrodynamic radius of 35 nm. As with the unsonicated samples, Laplace inversion of the autocorrelation function gave a unimodal distribution of micelle sizes. Here $\Gamma_2/\Gamma_1^2 = 0.03$ is consistent with a narrow size distribution as seen in the TEM images. Static light scattering presented in Figure 9 showed that the M_w had decreased to 2.7 × 10^7 g/mol, corresponding to an aggregation number of 700, indicating that sonication had reduced the micelle size by a factor of 3. The change in R_G/R_H from 1.2 to 0.88 is also consistent with a strong decrease in the particle

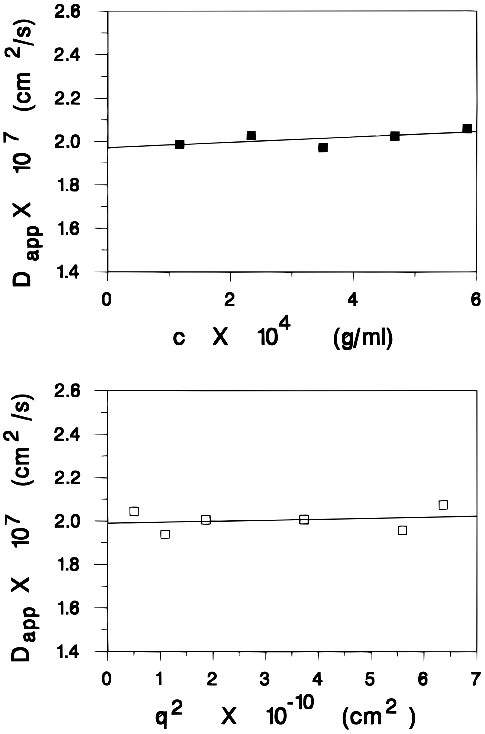

Figure 8. Angular (extrapolated to zero concentration) and concentration (extrapolated to zero angle) dependence of the DLS data for the wormlike micelles (sonicated sample).

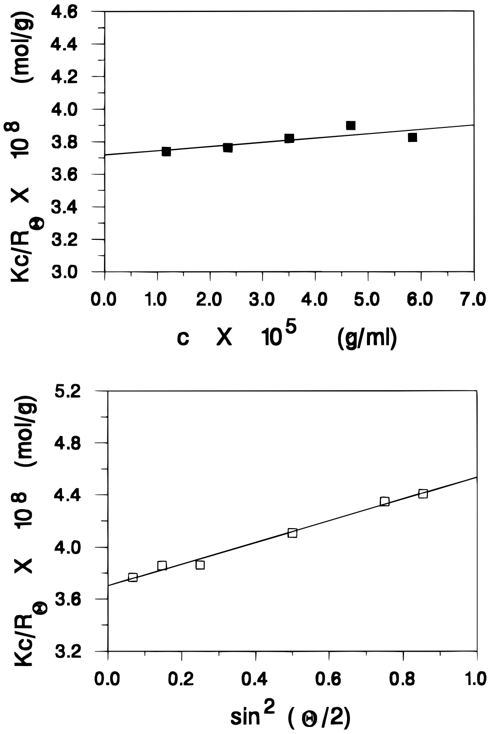

Figure 9. Angular (extrapolated to zero concentration) and concentration (extrapolated to zero angle) dependence of the SLS data for the wormlike micelles (sonicated sample).

asymmetry. The aspect ratio calculated from eq 8 is 3.1, very similar to the value of 3.8 calculated from the TEM micrographs.

Summary

Self-assembly of a novel organometallic−inorganic block copolymer has been studied in solution and in the solid state. The PFS-*b*-PDMS micelles we describe have a structure in solution of a cylindrical core consisting of PFS surrounded by a swollen corona of PDMS chains. These PDMS hairs provide steric stability to the structure and prevent aggregation of the insoluble PFS cores. Upon drying, the PDMS chains collapse to form a solid continuous insulating sheath. There is some indication from the TEM images (Figure 2) of the tendency for the cylinder ends to associate. For systems in dynamic equilibrium, as for example in some micellar solutions,[33] evolution of the structure to form long cylinders is to be expected because the unfavorable energy associated with the sharper curvature of the ends of the cylinder dominates over the small gain in translational entropy associated with smaller structures.[34] For PFS-*b*-PDMS, the structures in solution are frozen because of the insolubility of the PFS core. In the solid state, welding of the chain ends is more facile. This offers the possibility of connecting the wormlike micelles into extended wires. Since the micelles themselves are prepared by solubilization of structures present in bulk, their length is presumably limited only by the spacing between grain boundaries. Processing strategies such as shear alignment should provide a means of producing micelles with longer contour lengths.[35]

The formation of cylinders in bulk depends only upon the composition of the block copolymers. Varying the polymer overall chain length while preserving the composition should allow one to control the thickness of the iron-rich PFS core. Moreover, thermolysis of the PFS homopolymer in the bulk yields ferromagnetic iron silicon carbide ceramics.[16] Pyrolysis of the bulk or micellar cylindrical structures described here may generate magnetic nanowires with a silicon oxide coating.[14,16b] In addition, films of PFS homopolymer show interesting hole transport properties and isotropic semiconductivity (10^{-3} to 10^{-4} S cm^{-1}) upon oxidation.[15] Thus, upon oxidation of the core, the novel wormlike micellar aggregates should produce structures which have the potential to function as self-insulated semiconducting nanowires. Experiments aimed at translating these possibilities to practice are in progress.

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