Synthesis and Self-Assembly of Poly(ferrocenyldimethylsilane-*b*-2-vinylpyridine) Diblock Copolymers

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ABSTRACT: A new class of metal-containing diblock copolymers, PFS-*b*-P2VP (PFS = poly(ferrocenyldimethylsilane), P2VP = poly(2-vinylpyridine)), with a hydrophobic organometallic block and a highly polar hydrophilic organic block were synthesized via 1,1-dimethylsilacyclobutane (DMSB)-mediated sequential anionic polymerization. In the bulk state, PFS-*b*-P2VP copolymers with a volume fraction of PFS close to 0.20 give a morphology with cylindrical domains of PFS. A remarkable difference in the morphology of PFS-*b*-P2VP micelles was observed depending on the nature of selective solvent. Simply by using different alcoholic solvents either spherical or cylindrical micelles can be selectively formed from the same copolymer. WAXS experiments indicate that the crystallinity of the core-forming PFS block may be responsible for this difference.

Introduction

Amphiphilic block copolymers with two immiscible segments can self-assemble in the bulk state to form ordered arrays of nanostructures and in block-selective solvents to yield well-defined micellar aggregates, such as spheres, cylinders, and more complex architectures.[1−4] The self-assembly of block copolymers in either the bulk state or solution provides a fascinating route to functional nanomaterials with the potential for a variety of applications. For example, the periodic domains derived from the self-assembly of block copolymers in the bulk state can be utilized to create porous membranes, lithographic templates, and photonic band-gap materials.[1,5] On the other hand, micelles formed from block copolymers in solution have been used as nanoreactors,[3] drug delivery carriers,[6] and templates for the fabrication of one-dimensional nanostructures.[7]

The incorporation of transition metals into block copolymers would be expected to allow access to a range of intriguing physical and chemical characteristics. For example, polyferrocenylsilane block copolymers[8,9] provide materials with redox[10,11] or catalytic activity,[12−14] etch resistance,[15,16] and the ability[17,18] to form magnetic ceramic nanodomains. By far the majority of the work to date with polyferrocenylsilane block copolymers has focused on materials with relatively nonpolar coblocks such as polystyrene, polyisoprene, and polysiloxanes. Introducing polarity to the coblock would be expected to increase the Flory−Huggins interaction parameter χ which would promote phase separation and influence the substrate-dependent self-assembly behavior for thin films. Our recent studies on PFS-*b*-PDMAEMA (PFS = poly(ferrocenyldimethylsilane), PDMAEMA = poly(dimethylaminoethyl methacrylate)) have shown that the presence of a polar organic block rendered these block copolymer micelles soluble in alcohols and water; however, the route leads to materials with only moderate molecular weights (ca. 10 000 g mol^{-1}) and significant polydispersity (PDI = 1.2−1.3).[19,20] In addition, the successful synthesis of PFS-*b*-PMMA (PMMA = poly(methyl methacrylate))[21−23] and well-defined materials with PEO (poly(ethylene oxide))[24] coblocks has been described. The preparation of PFS block copolymers with a highly polar block such as vinylpyridine which provides hydrophilicity and potential supramolecular interactions such as hydrogen bonding and metal coordination would represent a significant advance. In this paper, we report the first examples of polyferrocenylsilane-based block copolymers with poly(2-vinylpyridine) coblocks (PFS-*b*-P2VP) **(2)** and some interesting results on their self-assembly behavior.

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Experimental Section

Materials and Instrumentation. [1]Dimethylsilaferrocenophane (**1**) was synthesized according to previous methodology reported in the literature.[9] *n*-Butyllithium (1.6 M in hexanes, Acros) and trioctylaluminum (25 wt % in hexanes, Aldrich) were used as received. 2-Vinylpyridine (97%, Aldrich) was purified by distillation first over CaH_2. A second distillation from trioctylaluminum was performed immediately before the polymerization. 1,1-Diphenylethylene (DPE) (97%, Aldrich) was titrated with *n*-butyllithium until a deep red color sustained and then distilled under high vacuum. 1,1-Dimethylsilacyclobutane (DMSB) (Fluka) was distilled over CaH_2 twice. Lithium chloride (99.99%, Aldrich) was vacuum-dried at 120 °C overnight. THF was distilled under reduced pressure from Na/benzophenone.

The ^{1}H NMR spectra were recorded on a Varian 400 spectrometer with deuterated benzene as solvent. Molecular weights were determined by a Viscotek GPC MAX liquid chromatograph equipped with a triple detector array (model 302, Viscotek) and a UV detector (model 2501, Viscotek). Polystyrene standards (Aldrich) were used for calibration, and a solution of 2% triethylamine in THF was used as the eluent. TEM images were obtained using a Hitachi HD-2000 scanning transmission electron microscope operating at 200 kV. Energy dispersive X-ray (EDX) elemental analysis was performed using an Oxford Inca EDX system integrated in the Hitachi HD-2000 electron microscope. Samples for TEM and EDX experiments were prepared by drying a drop of solution on a Formvar and carbon-coated copper grid. Wide-angle X-ray scattering (WAXS) data were obtained using a Siemens D500 diffractometer equipped with a Cu Kα X-ray source. The samples for WAXS experiments were prepared by casting a solution of micelles 3 days after it was prepared onto a silicon wafer and allowing the solvent to evaporate at ambient temperature.

Synthesis of PFS-*b*-P2VP Block Copolymers 2a and 2b. A representative diblock copolymerization of **2a** is described. In a

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N_2-filled glovebox at room temperature, 33.0 μL of *n*-BuLi (1.6 M in hexanes) was added quickly to a stirred solution of [1]-dimethylsilaferrocenophane (194 mg, 0.80 mmol) in THF (1.5 mL). After 40 min, the color of the solution changed from red to amber, indicating complete conversion of the monomer. DPE (37.0 μL, 0.21 mmol) was then added, followed by DMSB (13.4 μL, 0.10 mmol). After the color changed from amber to deep red within a few minutes, the reaction flask was immediately removed from the glovebox and placed on a Schlenk line under prepurified Ar and cooled to −78 °C using a dry ice−acetone bath. A second flask with a solution of dried LiCl (17.9 mg, 0.42 mmol) and 2-vinylpyridine (0.69 mL, 6.4 mmol) in THF (5.6 mL) was also cooled to −78 °C before the two solutions were combined. The reaction was allowed to further proceed for 40 min at −78 °C before it was quenched by the addition of a few drops of degassed MeOH. Precipitation of the solution into hexanes followed by drying overnight under vacuum gave the product as a yellow powder (860 mg, 97%). The copolymer was purified by repeated size exclusion column chromatography (HW-55F from TOSOH, Japan) using THF as the eluent until PFS homopolymer was not detectable by a UV detector (450 nm) by GPC. ^{1}H NMR δ (ppm, C_6D_6): 0.56 (s, $Si(CH_3)_2$), 1.84−2.93 (m, CH_2 and CH, P2VP), 4.12 (m, Cp), 4.28 (m, Cp), 6.33−7.10 (m, aromatic protons, P2VP), 8.40 (m, NCHC). GPC: M_n (PDI): 4100 (1.10) for the PFS block and 19 200 (1.07) for the PFS-*b*-P2VP diblock copolymer.

Preparation of PFS-*b*-P2VP Bulk Films. The casting and annealing of **2a** and **2b** into bulk samples were conducted analogously. A representative procedure for **2a** is described. A concentrated solution of **2a** (ca. 30 mg/mL) in benzene was applied dropwise to a clean glass slide and allowed to dry in air. The resulting bulk sample (ca. 1 mm in thickness) was then dried overnight in a vacuum oven at ca. 50 °C. After the sample was thermally annealed at ca. 160 °C under vacuum for 4 days, it was rapidly removed from the oven and immersed in liquid nitrogen, which gave the bulk polymer sample as a brittle clear orange material.

Preparation of PFS-*b*-P2VP Micelles. Micelles were prepared by mixing PFS-*b*-P2VP with respective alcoholic solvents (0.5 mg/mL) at room temperature with stirring. Aliquots for TEM analysis were taken at various time intervals.

Results and Discussion

Synthesis and Characterization of PFS-*b*-P2VP Diblock Copolymers. Our attempts to prepare PFS-*b*-P2VP block copolymers via the direct sequential alkyllithium-initiated anionic polymerization of [1]dimethylsilaferrocenophane (**1**) and 2-vinylpyridine in either order were unsuccessful. However, using an analogous strategy to that employed by Rehahn for the synthesis of PFS-*b*-PMMA,[21,22] we successfully prepared PFS-*b*-P2VP (**2**), as illustrated in Scheme 1. The polymerization of **1** was performed in THF at room temperature using *n*-BuLi as initiator. An aliquot of the reaction mixture was taken for molecular weight analysis using gel permeation chromatography (GPC) before 1,1-dimethylsilacyclobutane (DMSB) and 1,1-diphenylethylene (DPE) were added. To restrict potential side reactions in the polymerization of 2-vinylpyridine,[25] the reaction mixture was cooled down to −78 °C prior to the addition of a cooled (−78 °C) solution of 2-vinylpyridine and LiCl in THF. The polymerization of 2-vinylpyridine was allowed to proceed for 40 min before the reaction mixture was quenched by adding a few drops of degassed methanol. The mixture was then precipitated in hexanes, and the block copolymer product was isolated as a yellow solid (yield 97%). The product was purified by size exclusion column chromatography using THF as the eluent.

Table 1. Characterization of the PFS-*b*-P2VP Copolymer Samples

	polymer	M_n(PFS)[a] (g/mol)	M_n(diblock)[a] (g/mol)	PDI[a]	molar block ratio[b]
2a	PFS_{17}-*b*-$P2VP_{170}$[c]	4100	19 200	1.07	1:10
2b	PFS_{22}-*b*-$P2VP_{154}$[c]	5300	20 700	1.09	1:7

[a] Determined by GPC analysis against polystyrene standards using THF with 2% of Et_3N as the eluent. [b] Determined by ^{1}H NMR integration. [c] Determined from M_n of PFS homopolymer from GPC analysis and block ratios from ^{1}H NMR analysis.

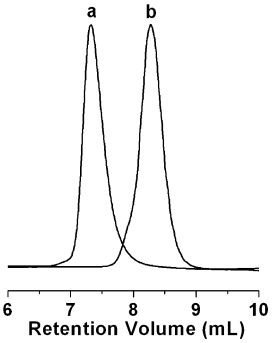
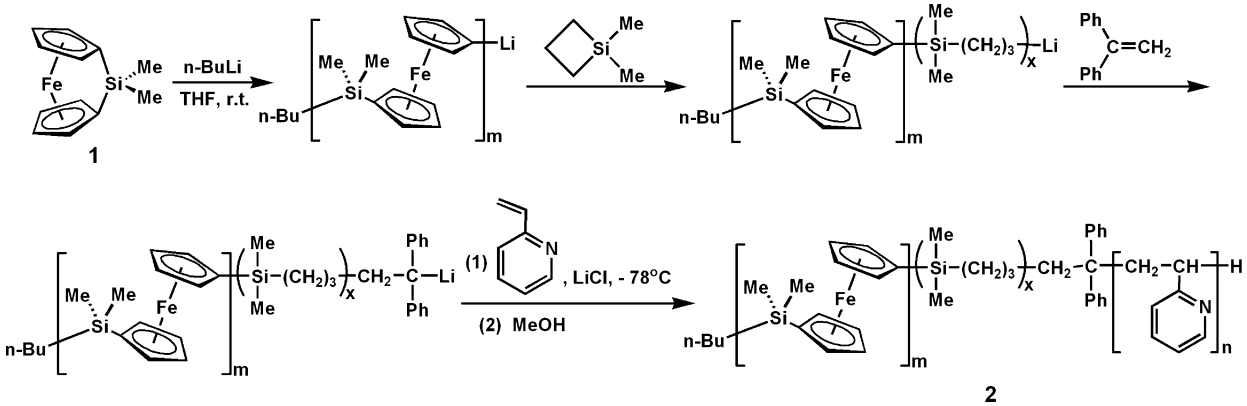


Figure 1. GPC curves (RI) of a PFS-*b*-P2VP diblock copolymer, sample **2a** in Table 1 (a), and its precursor PFS block (b).

Two samples were prepared by this method (Table 1). The molecular weights and molecular weight distributions for these samples were characterized by GPC. Shown in Figure 1 are representative GPC traces of a PFS-*b*-P2VP copolymer (**2a)** and its precursor PFS block. The polydispersity of the samples of both the PFS block and **2a** was lower than 1.10. Block ratios were calculated by comparing integrated ^{1}H NMR signals due to the PFS and P2VP blocks. The ^{1}H NMR spectrum of **2a** and the peak assignments are shown in Figure 2, from which we estimated the block ratio of PFS to P2VP for this sample to be 1:10.

Scheme 1. Synthesis of PFS-*b*-P2VP Block Copolymers



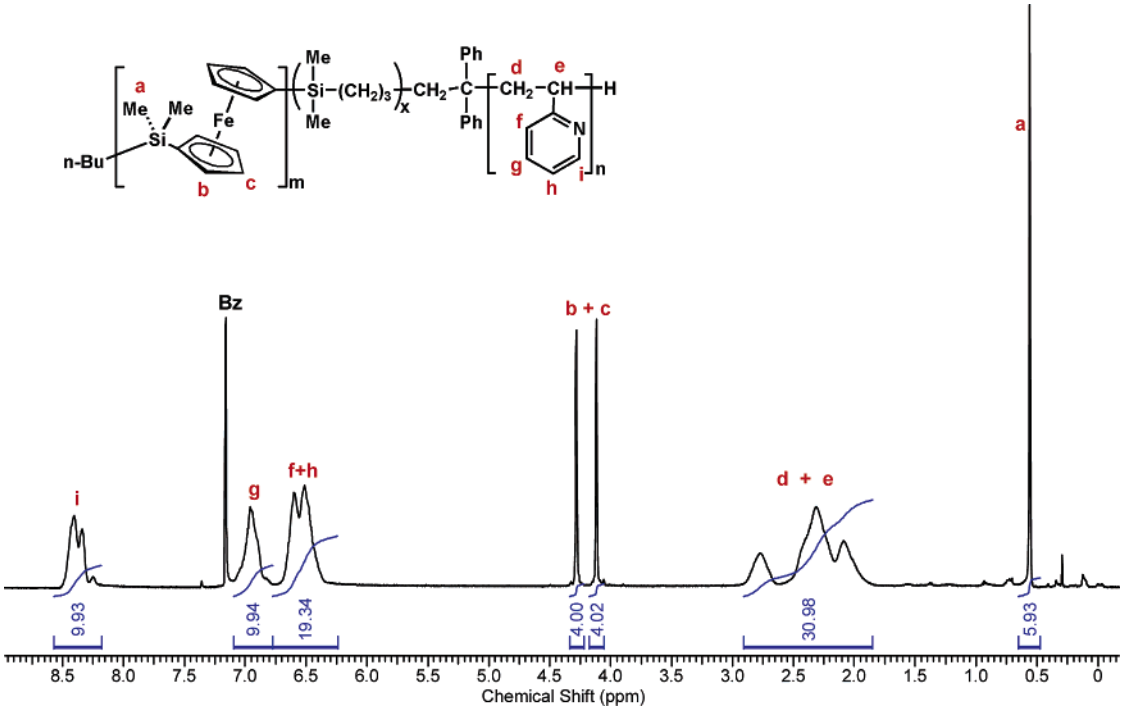


Figure 2. ^{1}H NMR spectrum of PFS-*b*-P2VP diblock copolymer, sample **2a** in Table 1 (C_6D_6, Bz = C_6H_6, 400 MHz).

In addition, the integration ratios of the aromatic to aliphatic protons on P2VP as well as methyl to ferrocenyl protons on PFS are as expected. This suggests that the block ratios derived from ^{1}H NMR spectra are reliable for determining the composition of PFS-*b*-P2VP copolymers. We deduced the assigned structural characteristics of the block copolymers by combining M_n of the first block from GPC measurements with the block ratios from ^{1}H NMR analysis, as the block ratios given by ^{1}H NMR are likely to be much more accurate than those estimated from GPC measurements. The key characterization data for two PFS-*b*-P2VP block copolymer samples are listed in Table 1.

The use of DMSB is critical to the successful preparation of PFS-*b*-P2VP diblock copolymers. It serves as a carbanion pump[26,27] that facilitates the coupling of anionic PFS chains with DPE. The latter species acts as an end-capping agent to decrease the reactivity of the living chain ends. This step is critical to restrict side reactions in the polymerization of 2-vinylpyridine. Our previous study demonstrated that the direct end-capping of PFS anions with DPE is ineffective at room temperature and requires extended reaction time at elevated temperature.[28] In contrast, when DMSB was used, the living chain ends could be trapped by DPE very efficiently at room temperature, as indicated by the color change from amber to deep red in just a few minutes.

The lack of side reactions on the pyridine ring was confirmed by the narrow molecular weight distribution of the copolymers (<1.10) as inferred from GPC measurements and by ^{1}H NMR analysis. One of the major side reactions in the anionic polymerization of 2-vinylpyridine is the nucleophilic addition of carbanions. This reaction leads to products with chemical shifts of protons on the pyridine ring appearing at 3.3−6.2 ppm.[25b] In this region we find only signals corresponding to the Cp rings (4.12 and 4.28 ppm) (Figure 2). Therefore, we conclude that the combination of DPE, LiCl and low reaction temperature is effective in suppressing these side reactions.

Self-Assembly of PFS-*b*-P2VP Diblock Copolymers in the Bulk State. In our preliminary studies of the self-assembly behavior of PFS-*b*-P2VP copolymers in the bulk state, we prepared films of PFS-*b*-P2VP by allowing the solvent (benzene) to evaporate slowly from a concentrated solution of the copolymer (30 mg/mL) cast on a glass slide. The films were then dried at 50 °C overnight in a vacuum oven and further annealed at ca. 160 °C under vacuum for 4 days. Since previous studies of other PFS block copolymers in the bulk state showed that the PFS homopolymer crystallized after 20 min in the range 80−120 °C,[29] we thought that it would be important to cool the annealed sample rapidly in order to avoid the complications brought by crystallization of PFS in our samples. After annealing, therefore, the hot glass slide with the polymer film was rapidly removed from the vacuum oven and immediately immersed in liquid nitrogen. This afforded a brittle clear orange film.

To study the morphology of the thermally quenched film by TEM, ultrathin sections were prepared by room temperature microtoming of samples mounted on an epoxy resin using cyanoacrylate glue. Shown in Figure 3A is a dark-field TEM image of an unstained section of PFS-*b*-P2VP sample **2a**. The image shows an ordered cylindrical morphology, in which we assign the bright cylindrical domains and circular cross sections to PFS and the dark intervening material to P2VP. The width of the cylindrical domains was ca. 15 nm. This assignment was confirmed by an energy dispersive X-ray spectroscopy (EDX) line scan analysis, which gives the elemental constituent change across a region by scanning the electron beam across an interactively defined line. Figure 3B presents the EDX profiles along the line across four cylindrical domains. From these profiles, we can clearly see that high contents of Fe (red line) and Si (green line) match up with the bright cylindrical domains. This demonstrates these cylindrical domains are indeed composed of PFS. Bulk films from sample **2b** also showed a similar cylindrical morphology when investigated by TEM and EDX. On the basis of ^{1}H NMR integration, we estimated that the volume fractions of PFS (ϕ_{PFS}) in samples **2a** and **2b** were ca. 0.17 and 0.22, respectively, by using a PFS density of 1.26 g/mL[30] and a P2VP density of 1.09 g/mL.[31]

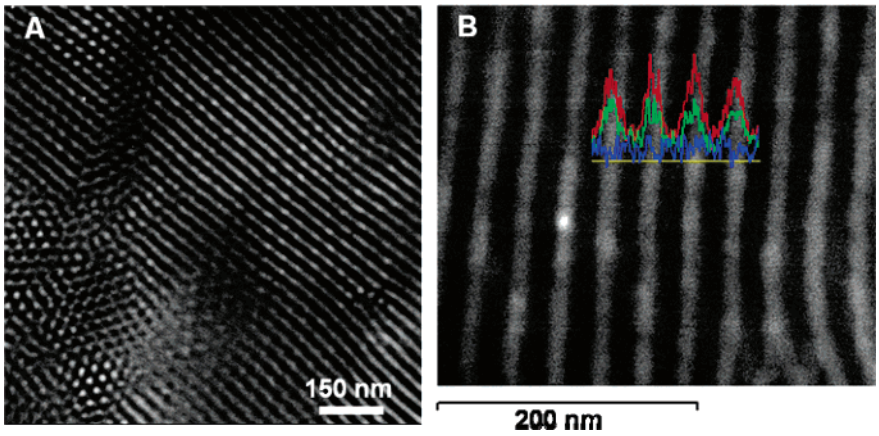


Figure 3. (A) Dark-field TEM image of a PFS_{17}-*b*-$P2VP_{170}$ (**2a**) film cast from benzene solution and annealed at 160 °C for 4 days. (B) EDX line-scan profiles on a dark-field TEM image of a PFS_{17}-*b*-$P2VP_{170}$ (**2a**) film. The red line represents Fe (Kα1), the green line represents Si (Kα1), and the blue line represents N (Kα1_2).

Self-Assembly of PFS-*b*-P2VP Diblock Copolymers in Solution. In order to study the solution self-assembly of PFS-*b*-P2VP copolymers, we prepared micelles simply by stirring the materials in P2VP-selective alcoholic solvents at room temperature. As shown in Figure 4A, only spherical micelles were present when sample PFS_{17}-*b*-$P2VP_{170}$ **(2a)** was dissolved in methanol with stirring. The relatively bright inner regions of the micelles, with a diameter of ca. 19 nm in the image, were assigned to the PFS core. In contrast, we found a dramatically different micelle morphology when the sample **2a** was dissolved in isopropyl alcohol. As shown in the TEM image in Figure 4B, long cylindrical structures formed in this solvent, with a width of ca. 10 nm and lengths of up to 10 μm. We attribute the bright inner domains to the electron-rich PFS core.

In our previous work we have observed the formation of cylindrical or platelet morphologies for asymmetric PFS block copolymers in selective *n*-alkane solvents for the complementary block. The formation of low curvature morphologies rather than the spherical structures anticipated on the basis of intercoronal repulsion effects was attributed to crystallization of the PFS core.[32−35] To examine whether crystallization of PFS played a role in the solvent-dependent morphological differences we have observed here, we conducted wide-angle X-ray scattering (WAXS) experiments on films prepared from the micelle solutions in methanol and isopropanol. As shown in Figure 5, only an amorphous halo was observed in the WAXS pattern of the film prepared from the methanol solution of spherical micelles. In contrast, the pattern for the sample prepared from isopropanol showed a strong peak corresponding to a *d*-spacing of 6.4 Å, which can be assigned, on the basis of previous studies of a model pentamer,[36] to the distance between adjacent planes containing planar zigzag PFS chains. However, the exact folding characteristics of the PFS chains in the core are still unclear at this time and are the subject of future studies. In addition, the difference between the diameter of the core of the spherical micelles (ca. 19 nm) and that of cylindrical micelles (ca. 10 nm) may also arise as a consequence of a tight folded conformation adopted by the core-forming crystalline chains as considered in the Vilgis and Halperin model.[37]

It is striking that simply changing the nature of the alcohol solvent led to such a remarkable difference in the morphology of the resulting micelles as noted from the TEM analysis. The solvent effect on micelle morphology is likely a result of a change in solvent quality for the polymer. To address this issue, we compare Hildebrand solubility parameters for the polymers

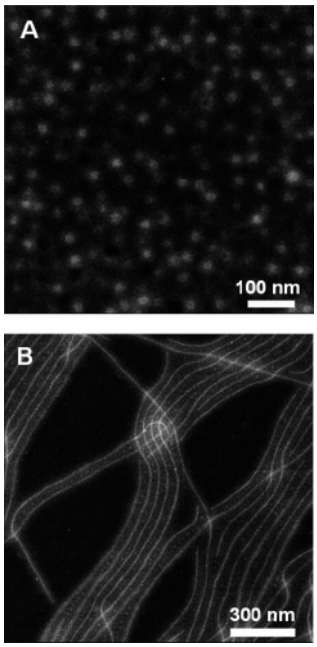


Figure 4. Dark-field TEM images of PFS_{17}-*b*-$P2VP_{170}$ (**2a**) micelles prepared from (A) methanol and (B) isopropanol.

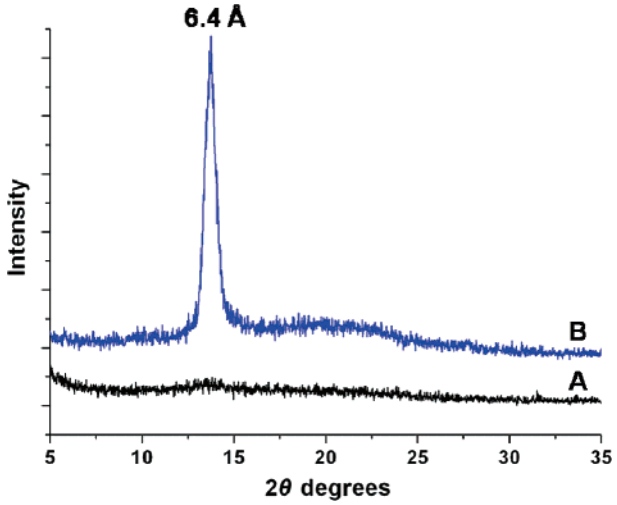


Figure 5. WAXS pattern for PFS_{17}-*b*-$P2VP_{170}$ (**2a**) micelles prepared from (A) methanol and (B) isopropanol. The samples were prepared by casting a solution of micelles 3 days after it was prepared onto a silicon wafer and allowing the solvent to evaporate at ambient temperature.

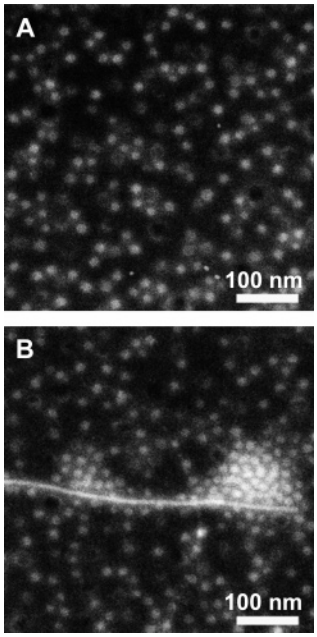


Figure 6. Dark-field TEM images of PFS_{22}-*b*-$P2VP_{154}$ (**2b**) micelles prepared from methanol after 20 min (A) and 5 h (B).

and the solvents. The solubility parameter of PFS ($\delta_{PFS} = 18.7$ $MPa^{1/2}$)[38] is closer to that of isopropanol ($\delta_{i-PrOH} = 23.5$ $MPa^{1/2}$) than to that of methanol ($\delta_{MeOH} = 29.7$ $MPa^{1/2}$).[39] We imagine that isopropyl alcohol is a better solvent for PFS than methanol, and this enhanced solubility allows the PFS chains to rearrange and crystallize more easily in this solvent. To test this idea, we carried out experiments in ethanol ($\delta_{EtOH} = 26.0$ $MPa^{1/2}$). Here we obtained the interesting result that upon dissolution the polymer formed spherical micelles, but these spheres slowly rearranged to cylinders on a time scale of weeks for the case of PFS_{17}-*b*-$P2VP_{170}$ (**2a**). For PFS_{22}-*b*-$P2VP_{154}$ (**2b**), with a block ratio of P2VP to PFS reduced from 10:1 in **2a** to 7:1 as in PFS_{22}-*b*-$P2VP_{154}$, self-assembly in ethanol resulted in long cylindrical structures immediately. When polymer **2b** was dissolved in methanol with stirring, a morphological evolution appeared to readily take place in that the initially formed spheres (Figure 6A) started to rearrange into elongated structures (Figure 6B) on a time scale of hours. This observation can be explained by the fact that the repulsion between shorter corona chains in **2b** is less than that between the longer chains in **2a**, and this lower intercoronal chain repulsion favors the change from high curvature spheres to lower curvature cylinders.[40] Detailed studies of the morphological evolution of PFS-*b*-P2VP micelles are in progress and will be published in the future.

Summary

We have demonstrated an effective synthetic approach to a new class of hydrophobic−hydrophilic polyferrocenylsilane block copolymers, PFS-*b*-P2VP. The self-assembly of PFS-*b*-P2VP copolymers in the bulk state to form hexagonal arrays of PFS cylinders in a P2VP matrix was illustrated. In solution very intriguing behavior was noted. With a 1:10 block ratio of PFS to P2VP, PFS_{17}-*b*-$P2VP_{170}$ (**2a**) showed a remarkable difference in solution self-assembly behavior when the solvent was changed from methanol (where spheres were formed) to isopropanol (where cylinders were detected). Crystallization of PFS was proposed as the driving force for the formation of nonspherical elongated structures in isopropanol. These redox-active PFS-*b*-P2VP micelles or self-assembled nanostructures appear promising for the incorporation of metal or semiconductor nanoparticles in an ordered manner, which could be very useful for fabrication of nanoscopic devices. Detailed studies of the self-assembly of PFS-*b*-P2VP block copolymers with these aims in mind are underway.

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References and Notes

(1) Alexandridis, P.; Lindman, B. *Amphiphilic Block Copolymers: Self-Assembly and Applications*; Elsevier: Amsterdam, 2000.
(2) Bates, F. S. *Science* **1991**, *251*, 898.
(3) Forster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.
(4) Discher, D. E.; Eisenberg, A. *Science* **2002**, *297*, 967.
(5) Hamley, I. W. *Angew. Chem., Int. Ed.* **2003**, *42*, 1692.
(6) Gref, R.; Minamitake, Y.; Peracchia, M. T.; Trubetskoy, V.; Torchilin, V.; Langer, R. *Science* **1994**, *263*, 1600.
(7) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, Y. Q. *Adv. Mater.* **2003**, *15*, 353.
(8) Kulbaba, K.; Manners, I. *Macromol. Rapid Commun.* **2001**, *22*, 711.
(9) Ni, Y. Z.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102.
(10) Wang, X. S.; Wang, H.; Coombs, N.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2005**, *127*, 8924.
(11) Eitouni, H. B.; Balsara, N. P. *J. Am. Chem. Soc.* **2004**, *126*, 7446.
(12) Lastella, S.; Jung, Y. J.; Yang, H. C.; Vajtai, R.; Ajayan, P. M.; Ryu, C. Y.; Rider, D. A.; Manners, I. *J. Mater. Chem.* **2004**, *14*, 1791.
(13) Hinderling, C.; Keles, Y.; Stockli, T.; Knapp, H. E.; de los Arcos, T.; Oelhafen, P.; Korczagin, I.; Hempenius, M. A.; Vancso, G. J.; Pugin, R. L.; Heinzelmann, H. *Adv. Mater.* **2004**, *16*, 876.
(14) Lu, J. Q.; Kopley, T. E.; Moll, N.; Roitman, D.; Chamberlin, D.; Fu, Q.; Liu, J.; Russell, T. P.; Rider, D. A.; Manners, I.; Winnik, M. A. *Chem. Mater.* **2005**, *17*, 2227.
(15) Cheng, J. Y.; Ross, C. A.; Chan, V. Z. H.; Thomas, E. L.; Lammertink, R. G. H.; Vancso, G. J. *Adv. Mater.* **2001**, *13*, 1174.
(16) Lu, J.; Chamberlin, D.; Rider, D. A.; Liu, M. Z.; Manners, I.; Russell, T. P. *Nanotechnology* **2006**, *17*, 5792.
(17) Kulbaba, K.; Cheng, A.; Bartole, A.; Greenberg, S.; Resendes, R.; Coombs, N.; Safa-Sefat, A.; Greedan, J. E.; Stover, H. D. H.; Ozin, G. A.; Manners, I. *J. Am. Chem. Soc.* **2002**, *124*, 12522.
(18) Temple, K.; Kulbaba, K.; Power-Billard, K. N.; Manners, I.; Leach, K. A.; Xu, T.; Russell, T. P.; Hawker, C. J. *Adv. Mater.* **2003**, *15*, 297.
(19) Wang, X. S.; Winnik, M. A.; Manners, I. *Macromol. Rapid Commun.* **2002**, *23*, 210.
(20) Wang, X. S.; Winnik, M. A.; Manners, I. *Macromolecules* **2005**, *38*, 1928.
(21) Kloninger, C.; Rehahn, M. *Macromolecules* **2004**, *37*, 1720.
(22) Kloninger, C.; Knecht, D.; Rehahn, M. *Polymer* **2004**, *45*, 8323.
(23) Korczagin, I.; Hempenius, M. A.; Vancso, G. J. *Macromolecules* **2004**, *37*, 1686.
(24) Gohy, J. F.; Lohmeijer, B. G. G.; Alexeev, A.; Wang, X. S.; Manners, I.; Winnik, M. A.; Schubert, U. S. *Chem.—Eur. J.* **2004**, *10*, 4315.
(25) (a) Quirk, R. P.; Corona-Galvan, S. *Macromolecules* **2001**, *34*, 1192. (b) Clegg, W.; Dunbar, L.; Horsburgh, L.; Mulvey, R. E. *Angew. Chem., Int. Ed.* **1996**, *35*, 753.
(26) Sheikh, M. R. K.; Imae, I.; Tharanikkarasu, K.; LeStrat, V. M. J.; Kawakami, Y. *Polym. J.* **2000**, *32*, 527.
(27) Sheikh, R. K.; Tharanikkarasu, K.; Imae, I.; Kawakami, Y. *Macromolecules* **2001**, *34*, 4384.
(28) Power-Billard, K. N.; Wieland, P.; Schafer, M.; Nuyken, O.; Manners, I. *Macromolecules* **2004**, *37*, 2090.
(29) Lammertink, R. G. H.; Hempenius, M. A.; Manners, I.; Vancso, G. J. *Macromolecules* **1998**, *31*, 795.
(30) (a) Lammertink, R. G. H.; Hempenius, M. A.; Thomas, E. L.; Vancso, G. J. *J. Polym. Sci., Part B: Polym. Phys.* **1999**, *37*, 1009. (b) Rider, D. A.; Cavicchi, K. A.; Power-Billard, K. N.; Russell, T. P.; Manners, I. *Macromolecules* **2005**, *38*, 6931.
(31) Schulz, M. F.; Khandpur, A. K.; Bates, F. S.; Almdal, K.; Mortensen, K.; Hajduk, D. A.; Gruner, S. M. *Macromolecules* **1996**, *29*, 2857.

(32) Massey, J. A.; Temple, K.; Cao, L.; Rharbi, Y.; Raez, J.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 11577.
(33) Raez, J.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **2002**, *124*, 10381.
(34) Wang, X. S.; Winnik, M. A.; Manners, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 3703.
(35) Cao, L.; Manners, I.; Winnik, M. A. *Macromolecules* **2002**, *35*, 8258.
(36) Rulkens, R.; Lough, A. J.; Manners, I.; Lovelace, S. R.; Grant, C.; Geiger, W. E. *J. Am. Chem. Soc.* **1996**, *118*, 12683.
(37) Vilgis, T.; Halperin, A. *Macromolecules* **1991**, *24*, 2090.
(38) Kulbaba, K.; MacLachlan, M. J.; Evans, C. E. B.; Manners, I. *Macromol. Chem. Phys.* **2001**, *202*, 1768.
(39) *Polymer Handbook*, 4th ed.; John Wiley & Sons: New York, 2005.
(40) Yu, Y. S.; Zhang, L. F.; Eisenberg, A. *Macromolecules* **1998**, *31*, 1144.

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