Polymer Self-Assembly

Redox-Active Organometallic Vesicles: Aqueous Self-Assembly of a Diblock Copolymer with a Hydrophilic Polyferrocenylsilane Polyelectrolyte Block**

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The formation of nanoscopic aggregates via the self-assembly of block copolymers in a selective solvent for one of the blocks is currently a flourishing area of polymer and materials science.[1] While early studies of such systems reported mainly spherical micelles, more recent efforts have yielded an interesting variety of other morphologies such as cylinders, vesicles, and lamellae, as well as more complex structures particularly in systems containing a short, corona-forming polyelectrolyte block.[2] Diblock copolymers capable of self-assembling in water are of intense interest due to their potential applications as nanocontainers for drug delivery technologies and as emulsifiers for heterogeneous catalysis.[3,4] Although the aqueous self-assembly of organic diblock copolymers has been well studied and copolymers with polyelectrolyte blocks have received particular attention in this vein,[4] analogous investigations of metal-containing block copolymers are extremely rare.[5] Micelles derived from a metal-containing block copolymer offer potentially interesting redox tunability, in addition to conductive and preceramic characteristics.[5,6] In this communication, we report on the molecular self-assembly of a water-soluble block copolymer possessing a hydrophilic organometallic polyferrocene polyelectrolyte block. This chemical constitution results in the formation of novel redox-active vesicles with a metal-containing block on both the outside and inside of the nanoscale aggregates. In addition, our studies demonstrate how sample preparation can influence the complex morphologies of such aqueous colloidal systems as discerned by transmission electron microscopy (TEM).

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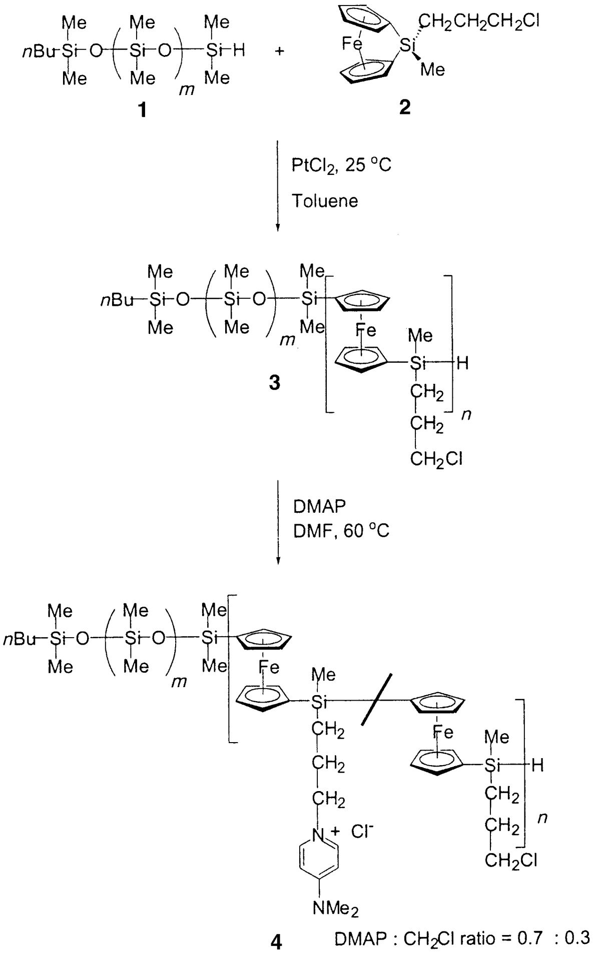
Previous work has demonstrated that polyferrocenylsilane (PFS) block copolymers[7] form a variety of micellar morphologies.[8] To generate vesicles via aqueous self-assembly, we targeted a block copolymer with a hydrophilic PFS block and a hydrophobic polydimethylsiloxane (PDMS) co-block. We also utilized the synthetic design strategy suggested by the recent work of Eisenberg and co-workers,[9] who elucidated a mechanism for the thermodynamic stabilization of block copolymer vesicles. In their studies, they demonstrated that the curvature of poly(styrene-*b*-acrylic acid) (PS-*b*-PAA) vesicles was stabilized by preferential segregation of long hydrophilic PAA chains towards the outside of the vesicle and short PAA chains towards the inside of the vesicle. This chain arrangement generated greater interchain repulsion between PAA chains outside than inside the vesicle. The polydispersity of the hydrophilic PAA block was believed to be of crucial importance in the formation of such structures (even though the molecular-weight distribution was narrow). In this work, a hydrophobic PDMS block was synthesized by anionic polymerization so that it was nearly monodisperse. However, we chose to prepare the hydrophilic PFS block by Pt-catalyzed ring-opening polymerization (ROP), which is known[10] to yield polymers with polydispersity indices (PDIs) in the range of 1.3 to 1.5. Thus, we anticipated that the resultant polydispersity of the hydrophilic PFS block would help promote the formation of the desired vesicular morphology.

Specifically, the PDMS-*b*-PFS diblock copolymer **4** (block ratio 2.9:1, $\bar{M}_n \approx 8600$, PDI ≈ 1.5) employed in this work was synthesized according to Scheme 1.[11] First, the chloropropyl-substituted ferrocenophane **2** was induced to undergo transition-metal-catalyzed ROP in the presence of Si–H-terminated polydimethylsiloxane **1** ($\bar{M}_n = 3110$, PDI = 1.19), which was prepared by anionic polymerization. The PDMS telechelic functioned as a capping group for the growing PFS chain to yield the diblock copolymer **3** ($\bar{M}_n = 7490$, PDI = 1.49). Second, the latter material was then treated with dimethylaminopyridine (DMAP) to yield the final PDMS-*b*-PFS diblock copolymer **4** containing a hydrophilic PFS polyelectrolyte block with 70 % substitution by DMAP.[11]

Self-assembly of **4** was initiated via direct dissolution in water. Solutions of block copolymer **4** were initially investigated by dynamic light scattering (DLS), which revealed an average hydrodynamic diameter of 84 nm for a 0.5 mg mL^{-1} solution of **4**. The morphology of **4** in a 0.5 mg mL^{-1} aqueous solution was also investigated by TEM. Specimens were prepared either by an "as-dropped" method or by freeze-drying. In the former, a drop of solution was placed on a carbon-coated copper grid and excess liquid was blotted away with filter paper. In the sample prepared by this method, spherical and compound aggregates with diameters ranging from 12 to 50 nm were observed (Figure 1 a). These diameters most likely correspond to aggregates that collapsed during drying. Since contrast in phase-contrast TEM is attributed to differences in electron density, the dark regions in the TEM images are assigned to the water-soluble PFS block. A small population of cylindrical aggregates with widths of ≈ 30 nm and lengths that varied from 140 to 230 nm were also observed. Freeze-drying was performed by first placing a drop of solution on a carbon-coated copper grid resting on a metal block cooled by liquid nitrogen (LN2). Once the drop was solidified, it was immediately placed in a Schlenk tube under vacuum (≈ 0.003 mm Hg) until the solvent was completely removed. Surprisingly, the samples prepared in this fashion using LN2 as the cryogen displayed a variety of structural elements, which include ribbons, vesicles, strands of hollow hoops, and pearl necklaces (Figure 1 b). The strands of hollow hoops and ribbon morphologies extended for several tens of microns, while vesicular structures ranged from several hundreds of nanometers to several microns in diameter. It must be recognized, however, that the observed sizes of the aggregates are substantially greater than those expected on the basis of the companion DLS data. In light of this result, we postulated that the methods of sample preparation used may dramatically influence the observed morphologies, which constitutes the first time that this effect has been observed in our studies regarding the self-assembly of polyferrocene-based diblock copolymers. We therefore undertook more detailed studies to address this issue.



Scheme 1. Synthesis of **4**.

Samples of **4** identical to those used in the DLS studies were used to explore the influence of TEM sample preparation on the observed aggregate morphology. First, solutions of **4** were freeze-dried in liquid ethane (LE) as a quenching medium. Plunging into LE (bp = −88 °C) supercooled to

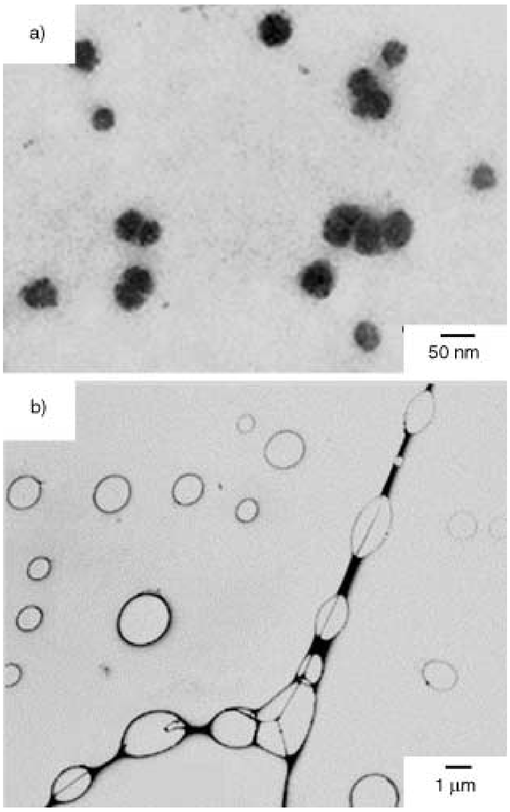


Figure 1. TEM images of block copolymer **4** (0.5 mg mL^{-1} in water) wherein the sample was prepared by a) the "as-dropped" method, and b) freeze-drying using liquid nitrogen as the quenching agent.

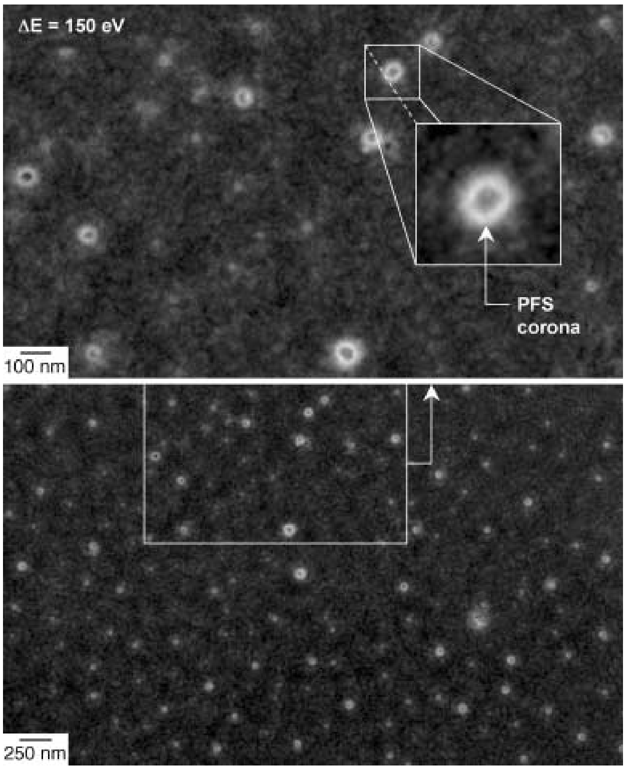


Figure 2. Energy-filtered TEM image of block copolymer **4** (0.5 mg mL^{-1} in water). The sample was prepared by quenching in liquid ethane.

-196 °C provides a cooling rate in excess of 15000 K s^{-1}, in marked contrast to LN2 (bp = -196 °C), which cools at a much slower rate of $\approx$1000 K s^{-1}.[12] The difference in cooling rate is attributed to the insulating liquid nitrogen vapor layer that forms and surrounds the sample during immersion into the liquid reservoir, since LN2 is at its normal boiling point. This vapor layer slows the rate of heat exchange between the sample and cryogen (thereby permitting water crystallization and probable morphological alteration), but does not occur in the case of LN2-cooled LE since the ethane is at a temperature below its normal freezing point (-183 °C). By using LE instead of LN2 as a quenching medium, water crystallization in ultrathin aqueous films should be altogether avoided, in which case the intrinsic polymer morphology is expected to remain intact. This is essentially the same methodology used to investigate the complex morphological characteristics of aqueous polymer solutions in situ (at cryogenic temperatures) by cryo-TEM.[13] Care was exercised to ensure that the sample temperature did not rise during freeze-drying so that neither water crystallization (at a transition temperature[14] of -125 °C) nor aggregate reorganization could occur as the water was removed by sublimation.

Transmission electron microscopy of polymer **4** after rapid quenching in LE and subsequent freeze-drying revealed the presence of vesicular-like aggregates with diameters measuring 85 nm on average (Figure 2). This structure-sensitive image was obtained using energy-filtered TEM.[15] In this imaging mode, electrons inelastically scattered due to carbon at an energy loss (ΔE) of $\approx$150 eV are effectively removed from image formation so that contrast is generally enhanced and non-carbonaceous elements appear highlighted. Thus, the light circular features in Figure 2 clearly identify the water-soluble PFS block. The relatively low-magnification image provides evidence that this morphology is representative, whereas the enlargements permit more detailed analysis of the aggregates. Recall, for instance, that the PDMS block is relatively short and that it is likewise composed of a non-carbonaceous element. Taken together, these two attributes explain why the PDMS-rich core of the copolymer bilayer comprising each vesicular aggregate is undetectable in Figure 3. The bilayer measures on the order of 15–20 nm in thickness, which compares well with four times the copolymer gyration radius, estimated to be $\approx$4 nm. It is further satisfying that the size of the vesicular aggregates gleaned from this TEM analysis is in favorable quantitative agreement with the corresponding measurement obtained by DLS.

This comparison clearly demonstrates that the method of sample preparation dramatically affects the solution aggregate morphology observed by TEM. Relative to our previous studies of the solution self-assembly of polyferrocene-based block copolymers, this is the first detailed study in which the solvent is water instead of a volatile organic solvent. Therefore, factors such as solvent crystallization, surface tension, and the rate of solvent evaporation during sample preparation become increasingly important, as rearrangement of the aggregate structure can occur if the matrix crystallizes during quenching or freeze-drying, or a receding solvent front forms

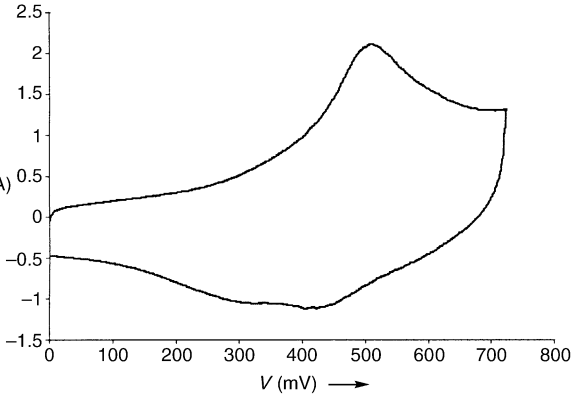


Figure 3. Cyclic voltammogram of **4** in 0.01 M aqueous NaCl. The scan rate was 100 $mV\,s^{-1}$.

during solvent removal. Solvent surface-tension effects constitute an especially important consideration when aqueous polymer solutions are prepared by placing a small sample volume onto a carbon-coated grid and allowing the (liquid) water to evaporate at ambient temperature. To preclude artifacts arising from such preparation, aqueous polymer solutions have been quenched and freeze-dried at LN2 temperature. Due to the low heat-transfer efficacy of LN2 relative to LE, water crystallization during quenching becomes a critical factor that could potentially promote gross alteration of the solution morphology. For this reason, LE is a far more suitable cryogen for preparing aqueous TEM samples than LN2. During solvent sublimation, the solution structure ideally should not be able to rearrange. It is, however, important to prevent the sample from warming up during freeze-drying so as to avoid morphological deformation due to solvent crystallization. Special care may further be required to ensure that sample temperature remains not only low, but also consistent. Finally, it is important to note that, due to the chemical nature of the diblock copolymer **4** (e.g., the glass-transition temperature of PDMS is −123 °C), our material is relatively fluid, which would not be expected to help preserve the structural integrity of complex morphologies during TEM sample preparation.

On the basis of previous work,[16] which established that low-molecular-weight ferrocene-based surfactants can be reversibly opened and reformed by sequential oxidation and reduction of the ferrocene units, the PDMS-*b*-PFS vesicles described herein may provide access to aggregate structures with redox-tunable encapsulation properties. To examine the redox chemistry of the vesicles, cyclic voltammetric studies have been performed on a 10^{-4} M solution of the vesicles in 0.1 M aqueous NaCl. Reversible oxidation of the ferrocene units in the PFS block is apparent from the detection of a single reversible oxidation wave (Figure 3).[17] This result underscores the interesting potential of these novel supramolecular vesicular assemblies as switching materials.

In summary, a water-soluble PDMS-*b*-PFS diblock copolymer prepared by combining both anionic and transition-metal-catalyzed ring-opening polymerization techniques has been found to form nanoscale vesicular aggregates upon direct dissolution in water. The mean diameter of these aggregates (≈85 nm) is in favorable agreement with that derived from dynamic light scattering. The method of TEM sample preparation has been shown to drastically affect the observed aggregate morphology. Contrary to the water-soluble PFS-containing block copolymers investigated thus far, self-assembly of materials such as **4** is of considerable interest since the electroactive PFS block, rather than the organic block, is hydrophilic and in aqueous media constitutes the aggregate corona. The potentially redox-tunable encapsulation properties of these structures are currently under study.

Experimental Section

4:[11] The chloropropyl-substituted ferrocenophane **2**[18] was subject to ROP in toluene over 24 h using a catalytic amount of $PtCl_2$ in the presence of Si−H-terminated polysiloxane **1**. The solution was then precipitated into an excess of MeOH and dried in vacuo to yield diblock copolymer **3** as a viscous amber fluid (GPC in THF versus polystyrene standards: $M_n = 7490$, PDI = 1.49). The diblock copolymer **3** was heated at 60 °C over 5 days in DMF with excess 4-dimethylaminopyridine (DMAP). The DMF was removed by vacuum distillation and the crude product was dissolved in distilled water and dialyzed against distilled water for 3 days to eliminate small-molecule impurities. The product was then dried at 100 °C to afford **4** as an amber viscous fluid (yield ≈20 %). ^1H NMR analysis showed that 70 % of the Cl substituents of the CH_2Cl groups of **4** had been replaced by DMAP under these reaction conditions. The approximate molecular weight and polydispersity of **4** ($M_n = 8600$, PDI = 1.5) was calculated from that for **3** assuming negligable chain cleavage during the substitution step.[19]

3: ^1H NMR (C_6D_6, 400 MHz): $\delta = 0.03$–0.31 (br, $SiMe_2O$), 0.41 (s, SiMe), 0.55 (t, CH_2 (*n*Bu)), 0.87–0.89 (m, CH_2 + CH_2 (*n*Bu)), 1.32 (m, CH_2CH_3 (*n*Bu)), 1.70 (br, CH_2), 3.18 (br, CH_2Cl), 3.95–4.19 ppm (m, Cp). ^{13}C NMR (C_6D_6, 100 MHz): $\delta = -3.0$ (SiMe), −1.3 to −1.7 ($SiMe_2O$), 14.0 (*n*Bu), 14.2 ($SiCH_2$), 18.3 (*n*Bu), 25.9 (*n*Bu), 26.8 (*n*Bu), 28.2 (CH_2), 48.2 (CH_2Cl), 70.5 (ipso-Cp), 71.9–74.0 ppm (Cp). ^{29}Si NMR (C_6D_6, 79.3 MHz): $\delta = 7.6$ (*n*Bu$SiMe_2O$), 0.1 ($SiMe_2fc$), −5.4 (fcSi(Me)$CH_2CH_2CH_2Cl$), −17.7 (fcSi(Me)($CH_2CH_2CH_2Cl$)H), −21.5 to −22.2 ppm ($SiMe_2O$). GPC: $M_n = 7490$, $M_w = 11\,200$, PDI = 1.49.

4: ^1H NMR ([D_7]DMF, 400 MHz): $\delta = -$ 0.20–0.37 (br, $SiMe_2O$), 0.54–0.64 (s, SiMe + $SiCH_2$ (*n*Bu)), 0.82–1.18 (br, $SiCH_2$ + CH_2 (*n*Bu)), 1.41 (br, CH_2CH_3 (*n*Bu)), 1.80–2.05 (br, $\mathit{CH_2}CH_2N$ + $\mathit{CH_2}CH_2Cl$), 3.28 (s, $N(CH_3)_2$)), 3.50 (H_2O), 3.71 (br, CH_2Cl), 4.09–4.55 (br, Cp + CH_2N), 7.24 (br, aromatic DMAP), 8.62–8.90 ppm (br, aromatic DMAP). ^{13}C NMR ([D_7]DMF, 100 MHz): $\delta = -$ 2.4 ($SiCH_3$), 1.1–1.9 ($SiMe_2O$), 13.3 (*n*Bu), 14.7 ($SiCH_2$), 18.9 (*n*Bu), 26.5 (*n*Bu), 27.4 (*n*Bu), 29.2 (CH_2), 40.7 ($N(CH_3)_2$), 49.5 (CH_2Cl), 60.8 (CH_2N), 71.5 (*ipso*-Cp), 72.6 (Cp), 74.6 (Cp), 108.9 (aromatic DMAP), 143.8 (aromatic DMAP), 157.4 ppm (aromatic DMAP). ^{29}Si NMR ([D_7]DMF, 79.3 MHz): $\delta = -5.4$ and −5.0 (fcSi(Me)-$CH_2CH_2CH_2Cl$ + fcSi(Me)$CH_2CH_2CH_2N$), −23.0 to −21.5 ppm ($SiMe_2O$).

The copolymer gyration diameter was estimated to be 7–10 nm based on light-scattering studies of PFS materials.[20]

Microscopy and Light Scattering: Solutions of polymer **4** were prepared by dissolving the sample in water at a concentration of 0.5 $mg\,mL^{-1}$ and filtering the solution with a 0.2 μm filter. Scattering intensity was recorded at a scattering angle of 90°. TEM was performed with comparably prepared solutions at the same concentration. Samples were prepared by three methods. In the first, a drop of solution was placed on a carbon-coated copper grid and excess solution was removed by blotting with filter paper. In the second method, a drop of solution was placed on a carbon-coated copper grid lying on a metal block cooled by LN2. Once the drop was solidified, it was immediately placed in vacuo until the solvent was completely removed. The third method involved placing a 2 µL drop of sample onto a carbon-coated copper grid that was then rapidly plunged into LE at −196 °C. The sample was then freeze-dried by placing the resultant vitrified sample on a metal block kept in equilibrium with LN2 and placed under vacuum until the solvent was fully sublimed. TEM images were obtained on a Phillips CM12 electron microscope operated at an accelerating voltage of 120 kV (for samples of **4** quenched in LN2 or prepared by the "as-dropped" method) or a Zeiss EM902 electron spectroscopic microscope operated at an accelerating voltage of 80 kV and $\Delta E = 150$ eV (for samples of **4** quenched in LE).

Electrochemistry: Cyclic voltammetry was performed on a BAS 1000 B/W instrument with a Ag/AgCl electrode as a reference. The solution was $\approx 10^{-4}$ M of **4** in 0.01 M aqueous NaCl. The peak potentials were 0.51 V (ox) and 0.42 V (red).

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[1] a) M. Antonietti, C. Göltner, *Angew. Chem.* **1997**, *109*, 944; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 910; b) P. Alexandridis, R. J. Spontak, *Curr. Opin. Colloid Interface Sci.* **1999**, *4*, 130; c) P. Alexandridis, B. Lindman, *Amphiphilic Block Copolymers: Self-Assembly and Applications*, Elsevier, Amsterdam, **2000**. d) S. Förster, B. Berton, H. P. Hentze, E. Krämer, M. Antonietti, P. Lindner, *Macromolecules* **2001**, *34*, 4610.

[2] For examples of recent work on nonspherical morphologies of block copolymers in solution, see a) L. Zhang, A. Eisenberg, *J. Am. Chem. Soc.* **1996**, *118*, 3168; b) K. Yu, C. Bartels, A. Eisenberg, *Langmuir* **1999**, *15*, 7157; c) X. H. Yan, G. J. Liu, F. T. Liu, B. Z. Tang, H. Peng, A. B. Pakhomov, C. Y. Wong, *Angew. Chem.* **2001**, *113*, 3705; *Angew. Chem. Int. Ed.* **2001**, *40*, 3593; d) Y. Y. Won, H. D. Davis, F. S. Bates, *Science* **1999**, *283*, 960; e) S. Stewart, G. Liu, *Angew. Chem.* **2000**, *112*, 348; *Angew. Chem. Int. Ed.* **2000**, *39*, 340; f) L. Zhang, A. Eisenberg, *Science* **1995**, *268*, 1728; g) J. P. Spatz, S. Mössmer, M. Möller, *Angew. Chem.* **1996**, *108*, 1673; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1510.

[3] a) A.-Y. A. I. Lebdeh, P. M. Budd, V. M. Nace, *J. Mater. Chem.* **1998**, *8*, 1839; b) R. Gref, Y. Minamitake, M. T. Peracchia, V. Trubetskoy, V. Torchilin, R. Langer, *Science* **1994**, *263*, 1600.

[4] a) S. Y. Liu, S. P. Armes, *Angew. Chem.* **2002**, *114*, 1471; *Angew. Chem. Int. Ed.* **2002**, *41*, 1413.b) S. Y. Liu, N. C. Billingham, S. P. Armes, *Angew. Chem.* **2001**, *113*, 2390; *Angew. Chem. Int. Ed.* **2001**, *40*, 2328; c) V. Bütün, S. P. Armes, N. C. Billingham, Z. Tuzar, A. Rankin, J. Eastoe, R. K. Heenan, *J. Am. Chem. Soc.* **2001**, *123*, 9910; d) A. V. Kabanov, T. K. Bornich, V. A. Kabanov, K. Yu, A. Eisenberg, *J. Am. Chem. Soc.* **1998**, *120*, 9941; e) J. Zhu, A. Eisenberg, R. B. Lennox, *J. Am. Chem. Soc.* **1991**, *113*, 5583; f) F. Henselwood, G. Liu, *Macromolecules* **1997**, *30*, 488; g) J. F. Gohy, N. Willet, S. Varshney, J. X. Zhang, R. Jerome, *Angew. Chem.* **2001**, *113*, 3314; *Angew. Chem. Int. Ed.* **2001**, *40*, 3214; h) K. L. Wooley, *Chem. Eur. J.* **1997**, *3*, 1397.

[5] Recent works on the self-assembly of metal-containing block copolymers include a) S. J. Hou, W. K. Chan, *Macromol. Rapid Commun.* **1999**, *20*, 440; b) S. J. Hou, K. Y. K. Man, W. K. Chan, *Langmuir* **2003**, *19*, 2485; c) C. M. Park, J. E. McAlvin, C. L. Fraser, E. L. Thomas, *Chem. Mater.* **2002**, *14*, 1225; d) J. F. Gohy, B. G. G. Lohmeijer, S. K. Varshney, U. S. Schubert, *Macromolecules* **2002**, *35*, 7427; e) J. F. Gohy, H. Hofmeier, A. Alexeev, U. S. Schubert, *Macromol. Chem. Phys.* **2003**, *204*, 1524.

[6] I. Manners, *Science* **2001**, *294*, 1664.

[7] a) R. Rulkens, Y. Z. Ni, I. Manners, *J. Am. Chem. Soc.* **1994**, *116*, 12121; b) Y. Ni, R. Rulkens, I. Manners, *J. Am. Chem. Soc.* **1996**, *118*, 4102.

[8] a) J. A. Massey, K. N. Power, M. A. Winnik, I. Manners, *Adv. Mater.* **1998**, *10*, 1559; b) J. A. Massey, M. A. Winnik, I. Manners, V. Z.-H. Chan, J. M. Ostermann, R. Enchelmaier, J. P. Spatz, M. Möller, *J. Am. Chem. Soc.* **2001**, *123*, 3147; c) J. Raez, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2002**, *124*, 10381.

[9] a) L. Luo, A. Eisenberg, *J. Am. Chem. Soc.* **2001**, *123*, 1012; b) D. E. Discher, A. Eisenberg, *Science* **2002**, *297*, 967.

[10] a) P. Gómez-Elipe, P. M. Macdonald, I. Manners, *Angew. Chem.* **1997**, *109*, 780; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 762; b) P. Gómez-Elipe, R. Resendes, P. M. Macdonald, I. Manners, *J. Am. Chem. Soc.* **1998**, *120*, 8348.

[11] K. N. Power-Billard, I. Manners, *Macromol. Rapid Commun.* **2002**, *23*, 607.

[12] P. Echlin, *Low-Temperature Microscopy and Analysis*, Plenum, New York, **1992**.

[13] P. Terech, A. de Geyer, B. Struth, Y. Talmon, *Adv. Mater.* **2002**, *14*, 495.

[14] J. R. Harris, *Negative Staining and Cryoelectron Microscopy: The Thin Film Techniques*, Bios Scientific, Oxford, **1997**.

[15] a) A. Du Chesne, *Macromol. Chem. Phys.* **1999**, *200*, 1813; b) R. Thomann, R. J. Spontak in *Science, Technology and Education of Microscopy: An Overview* (Ed.: A. Mendez-Vilas), Formatex, Badajoz, Spain, **2003**, pp. 249–254.

[16] a) Y. Kakizawa, H. Sakai, A. Yamaguchi, Y. Kondo, N. Yoshino, M. Abe, *Langmuir* **2001**, *17*, 8044; b) T. Saji, K. Hoshino, S. Aoyagui, *J. Am. Chem. Soc.* **1985**, *107*, 6865.

[17] The presence of a single wave is anticipated based on the formation of ion pairs between ferrocenium units and the chloride anions in the supporting electrolyte, which reduces any metal–metal interactions present: see a) R. Rulkens, A. J. Lough, I. Manners, S. R. Lovelace, C. Grant, W. E. Geiger, *J. Am. Chem. Soc.* **1996**, *118*, 12683; b) F. Barriere, N. Camire, W. E. Geiger, U. T. Mueller-Westerhoff, R. Sanders, *J. Am. Chem. Soc.* **2002**, *124*, 7262.

[18] K. N. Power-Billard, T. J. Peckham, A. Butt, F. Jäkle, I. Manners, *J. Inorg. Organomet. Polym.* **2000**, *10*, 157.

[19] Halide substitution reactions on PFS materials have previously been shown to take place without any significant molecular-weight decline. See, for example, a) K. N. Power-Billard, I. Manners, *Macromolecules* **2000**, *33*, 26; b) D. L. Zechel, K. C. Hultszch, R. Rulkens, B. Balaishis, Y. Ni, J. K. Pudelski, A. J. Lough, I. Manners, *Organometallics* **1996**, *15*, 1972.

[20] J. A. Massey, K. Kulbaba, M. A. Winnik, I. Manners, *J. Polym. Sci. Polym. Phys. Part B* **2000**, *28*, 3032.