A Convenient, Transition Metal-Catalyzed Route to Water-Soluble Amphiphilic Organometallic Block Copolymers: Synthesis and Aqueous Self-Assembly of Poly(ethylene oxide)-*block*-poly(ferrocenylsilane)

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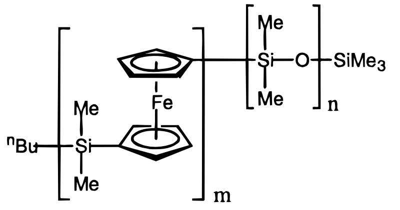
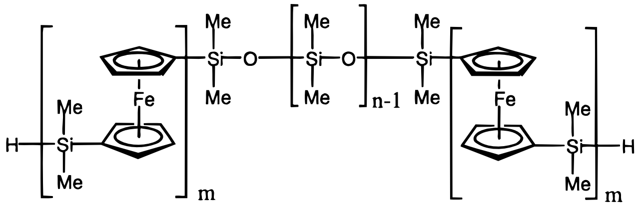
The self-assembly of block copolymers in block selective solvents is currently attracting considerable attention,[1,2] and water-soluble materials are of particular interest.[3] Block copolymers containing poly(ferrocene) segments have recently become accessible as a result of the discovery of living anionic ring-opening polymerization (ROP) of [1]ferrocenophanes.[4,5] By incorporating poly(ferrocenylsilanes) into block copolymer systems, one can potentially design phase-separated materials with interesting semiconductive or preceramic properties.[6,7] For example, as part of our work in this area, we have prepared poly(ferrocenyldimethylsilane)-*b*-poly(dimethylsiloxane) (PFS-*b*-PDMS), **1**, an AB block copolymer which self-assembles in *n*-hexane (a PDMS block selective solvent) into cylindrical wormlike micelles.[8] Transition metal-catalyzed ROP of [1]ferrocenophanes provides an alternative route to poly(ferrocene) block copolymers. For example, we have recently shown that the ABA triblock copolymer, PFS-*b*-PDMS-*b*-PFS, **2**, prepared via the Pt(0)-catalyzed ROP of strained dimethylsila[1]ferrocenophane in the presence of Si−H end-functionalized PDMS,[9] self-assembles in *n*-hexane to give interesting flowerlike micellar assemblies.[10]



1

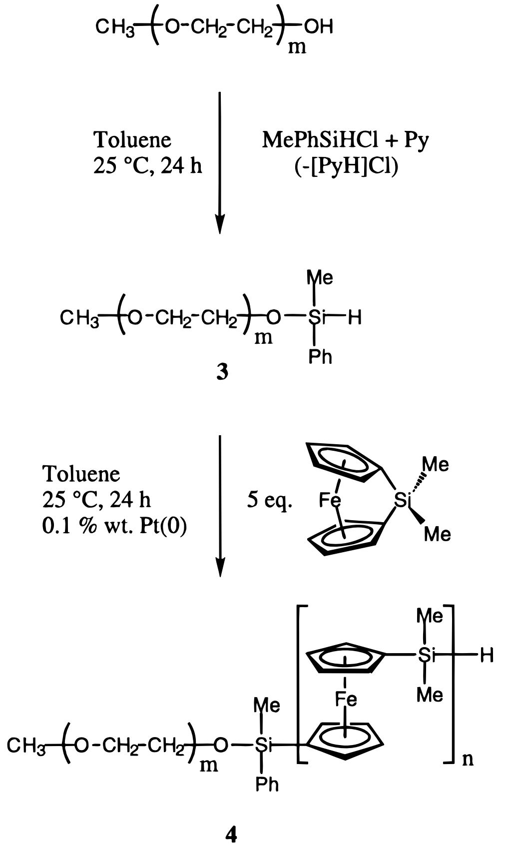
PFS-*b*-PDMS
m : n = 1 : 6



2

PFS-*b*-PDMS-*b*-PFS
m : n : m = 1 : 7 : 1

Scheme 1. Synthesis of 3 and 4



PEO-b-PFS
m : n = 4.5 : 1

The incorporation of poly(ethylene oxide), PEO, into a block copolymer is desirable as this gives access to materials that can self-assemble in aqueous media. Such materials find potential application as drug delivery agents,[11] emulsifiers for heterogeneous catalysis, and templating agents for the synthesis of mesoporous materials.[12] In this communication, we report on the synthesis and aqueous assembly of a PEO-*b*-PFS AB block copolymer. To our knowledge, this material represents the first example of a water-soluble organometallic block copolymer.

The incorporation of PEO in a block copolymer has been achieved via macromolecular condensations,[13] atom transfer radical polymerizations,[14] and the more commonly employed sequential living anionic polymerization route.[15] Given the toxic nature of monomeric ethylene oxide as well as the stringent experimental conditions required for living anionic copolymerizations, an alternative approach toward incorporating PEO in a block copolymer is desirable. The PEO-*b*-PFS diblock copolymer, **4**, used in this study was prepared via the Pt(0) (Karstedt's catalyst)-catalyzed ROP of a strained [1]ferrocenophane in the presence of Si−H end-functionalized poly(ethylene glycol) methyl ether (PEG-O-Me), **3**. This facile synthetic approach, recently applied toward the synthesis of the triblock copolymer **2**, involves a PFS chain being "grown" off of the reactive Si−H end group present in **3**.[9] The synthesis of **3** was accomplished via the condensation of PEG-O-Me (M_w = 3000, PDI = 1.13, Aldrich Chemical Co.) with ClSi-

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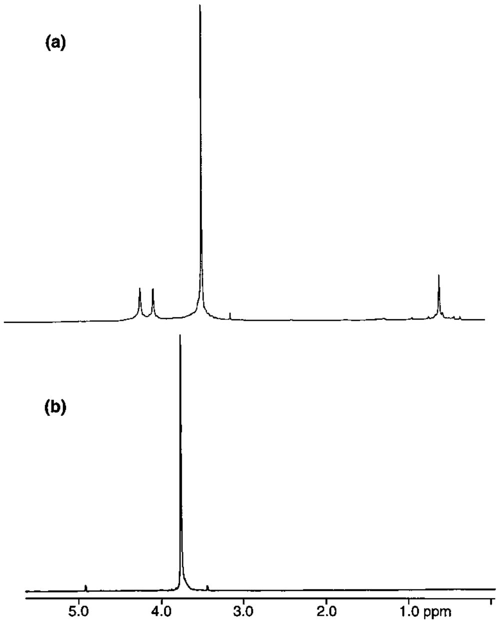

Figure 1. ^{1}H NMR spectrum (400 MHz, 20 scans) of **4** in (a) C_6D_6 and (b) D_2O.

MePhH in the presence of pyridine (Scheme 1). The Si−H source used in this synthesis possesses a bulky Si−Ph moiety which was expected to assist in sterically shielding the potentially hydrolytically sensitive Si−O−C linkage present in **4**. This approach has been shown to be successful in previous studies with polysilane-based materials.[13]

Although the materials obtained from this methodology possess molecular weight distributions broader than those observed from sequential living anionic routes (PDI typically >1.3 compared to <1.3 by living anionic ROP), previous work has shown that well-defined supramolecular aggregate formation is observed using materials with PDI values as high as 1.6.[13]

Polymer **4** was obtained in crude form as a light amber powder after precipitation into hexanes. To purify the product from unreacted **3**, aqueous solutions of **4** were prepared by first dissolving the product in THF and then adding water dropwise to the stirred solution which became turbid, indicating micelle formation. This solution was then dialyzed (M_w cutoff = 14 000) against distilled water. ^{1}H NMR analysis of the resulting purified material revealed a PEO:PFS block ratio of ca. 4.5:1, and GPC analysis (in THF) indicated a monomodal molecular weight distribution ($M_w = 6.75 \times 10^3$, PDI = 1.5). Furthermore, ^{1}H NMR analysis of **4** in D_2O revealed the absence of PFS resonances, which is consistent with micellar aggregates that possess a PFS core relatively devoid of any solvent molecules (Figure 1). The AB block nature of **4** was confirmed by ^{29}Si NMR (C_6D_6), which revealed the presence of switching groups between the PEO and PFS blocks (Figure 2).

Transmission electron microscopy (TEM) images of micelles aerosol sprayed from aqueous solutions of **4**, after solvent evaporation, revealed the presence of relatively monodisperse spherical structures with an average diameter of 50 nm (Figure 3a). In regions of concentrated micelle arrangements, the intercore distance was measured to be approximately 100−120 nm (Figure 3b). By assuming a close-packed arrangement of micelles, this value can be taken as an approximation of the average overall particle diameter. Preliminary dynamic light scattering (DLS) data revealed the average particle diameter to be ca. 150 nm. As TEM relies on contrast provided by electron density differences, this

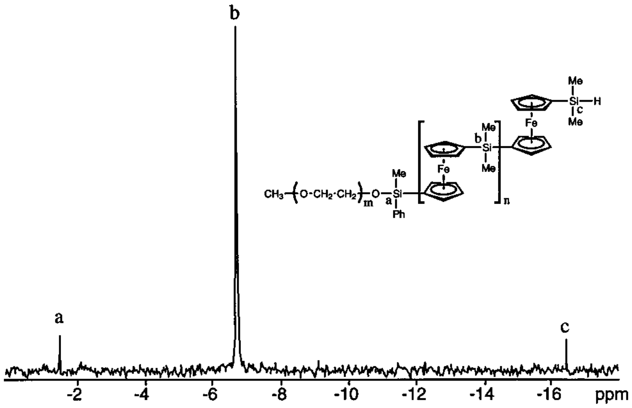

Figure 2. ^{29}Si NMR spectrum of **4** in C_6D_6.

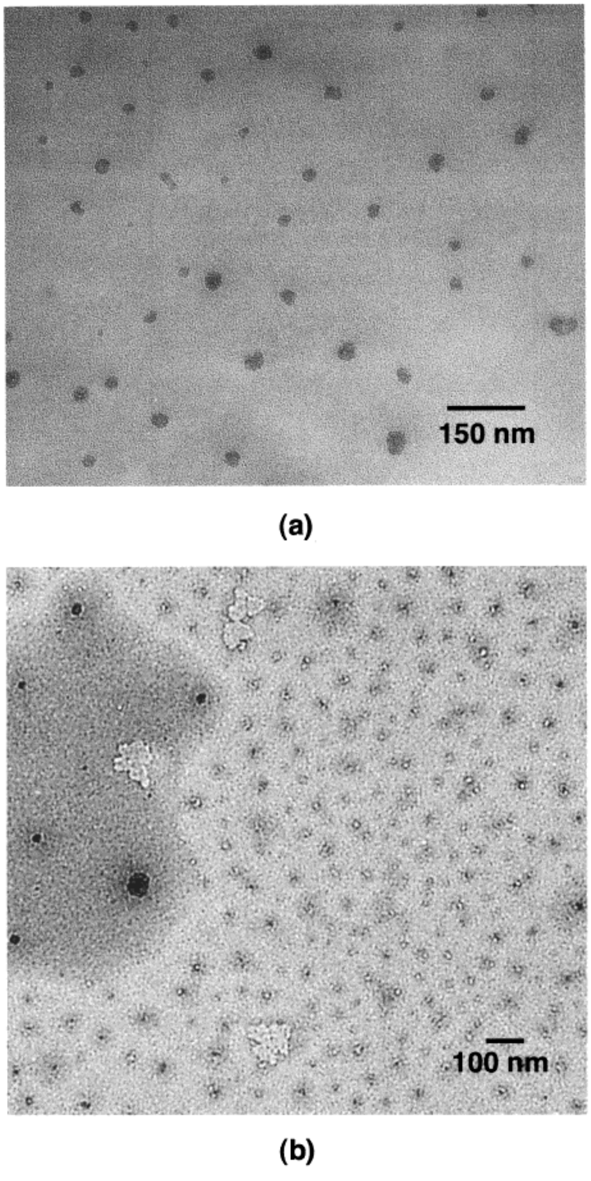

Figure 3. TEM micrographs of (a) spherical micelles of **4** and (b) concentrated close packed region of spherical micelles of **4**. TEM samples were prepared by aereosol spraying a dilute solution of **4** in water onto a thin carbon film supported on mica. The carbon film was then floated off the mica and supported on a copper grid.

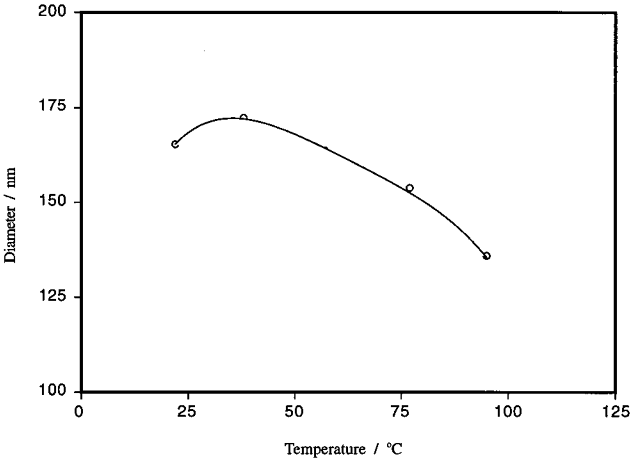

Figure 4. Effect of temperature on the average hydrodynamic diameter, as determined by DLS, of spherical micelles of **4** in water (five points shown).

technique allowed the selective imaging of the iron-containing PFS cores.

In an attempt to determine the lower critical solution temperature (LCST) displayed by **4**, a variable temperature dynamic light scattering (DLS) experiment was undertaken on aqueous micellar solutions of **4**. Between the temperatures of 22 and 95 °C, no LCST point was detected by DLS. However, the observed average hydrodynamic radius was observed to decrease from a RT value of 160 nm to 135 nm at 95 °C (Figure 4). This observation is consistent with decreasing corona–solvent interactions due to the disruption of hydrogen bonding between the solvent and micelle corona on increasing temperature.

In summary, the transition metal-catalyzed ROP of dimethylsila[1]ferrocenophane in the presence of Si–H end-functionalized PEG-O-Me affords a PEO-*b*-PFS amphiphilic AB block copolymer, **4**, which self-assembles into spherical micelles in aqueous solution. This methodology represents a facile and convenient route toward incorporating PEO into an organometallic block copolymer architecture. Furthermore, **4** represents the first example of an amphiphilic, water-soluble organometallic block copolymer. Work is currently underway in our laboratories aimed at further understanding the factors that govern the aqueous self-assembly of **4** and related materials as well as investigating the redox properties of these micellar assemblies.

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Supporting Information Available: Text detailing the synthesis and characterization of polymers **3** and **4** as well as TEM sample preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

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