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Diblock Copolymers with Amorphous Atactic Polyferrocenylsilane Blocks: Synthesis, Characterization, and Self-Assembly of Polystyrene-*block*-poly(ferrocenylethylmethylsilane) in the Bulk State

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ABSTRACT: Living anionic ring-opening (ROP) polymerization of ethylmethylsila[1]ferrocenophane yields atactic poly(ferrocenylethylmethylsilane) (PFEMS) homopolymers with controlled molecular weights (M_n = 4000−41 400) and narrow molecular weight distributions (PDI = 1.01−1.02). A series of well-defined polystyrene-*block*-poly(ferrocenylethylmethylsilane) (PS-*b*-PFEMS) diblock copolymers was synthesized from styrene and ethylmethylsila[1]ferrocenophane via sequential anionic polymerization. The iron content was readily varied (PFEMS volume fraction = 0.07−0.68), affording high molecular weight (M_n = 38 700−149 000) iron-rich diblock copolymers with narrow molecular weight distributions (PDI = 1.00−1.07). Both the PFEMS homopolymers and the PS-*b*-PFEMS diblock copolymers were shown to be amorphous due to the atactic nature of the organometallic block. As a result, PS-*b*-PFEMS block copolymers readily undergo solid-state self-assembly in the bulk. A spectrum of nanometer-sized iron-rich morphologies has been accessed, and in many cases these arrays were found to be well-ordered over large areas.

Introduction

Diblock copolymers self-assemble in the bulk into arrays of nanometer-sized domains as a result of microphase separation of the immiscible blocks.[1,2] These arrays of nanostructures are of intense current interest for applications such as porous membranes, lithographic templates, and photonic band gap materials.[1,3] In the microphase-separated state, variations of the volume fraction (ϕ) of one of the polymer segments generates a range of different morphologies whose sizes are dictated by the block copolymer molecular weight.[4]

To date, research on self-assembled block copolymers has primarily focused on organic materials, whereas inorganic block copolymers have remained virtually unexplored. Block copolymers containing transition metals offer the prospect of additional functionality such as useful redox, photophysical, conductive, catalytic, or preceramic properties.[5−9] Polyferrocenylsilane (PFS) block copolymers are readily available via living anionic ring-opening polymerization of strained silicon-bridged [1]ferrocenophane monomers and are of interest due to the presence of iron atoms in the main chain.[10−12] These materials self-assemble in block selective solvents to afford a range of intriguing micellar morphologies such as nanoscopic cylinders, vesicles, and nanotubes with a variety of potential applications.[13−16] Self-assembly of PFS block copolymers in the solid state yields phase-separated iron-rich nanodomains and has been studied by several groups.[12,13,17−23] Thin films of PFS block copolymers are thereby attracting growing attention with respect to redox-induced morphology changes, as plasma etch resistant nanotemplates and as precursors to magnetic or catalytically active nanoparticles on pyrolysis or plasma treatment.[18−27]

To date, although PFS block copolymers with a variety of organic comonomers have been prepared, the vast majority of the studies have focused on PFS segments which possess two methyl substituents at silicon (Scheme 1). Such PFS blocks are capable of crystallizing, as shown by previous studies of the homopolymer **2** which possesses a T_m of ca. 140 °C.[28−31] Although the presence of a potentially crystalline PFS block adds further interest to many aspects of block copolymer self-assembly, complications can also arise when facile access to predictable morphologies with long-range order are desired.[21,27,32−41] Under such circumstances experimental precautions (such as quenching of PFS block copolymers in ice after annealing above the T_m) have been used to ensure that the PFS block remains amorphous.

Recently, we have briefly reported on the synthesis and self-assembly in thin films of polystyrene-*b*-poly(ferrocenylethylmethylsilane) (PS-*b*-PFEMS) which contains an amorphous PFS block by virtue of the presence of different substituents at silicon.[24,25,42] In this paper we report full details on and improvements of the synthesis and describe a systematic study of the self-assembly of this material in the bulk state.

Experimental Section

Equipment and Materials. Ferrocene was used as received from Chemische Betriebe Pluto GmbH, Herne, Germany. Tetramethylethylenediamine was obtained from Aldrich and purified by drying over CaH_2 and subsequent distillation. Dichloroethylmethylsilane was purchased from Gelest and distilled under reduced pressure. Hexanes and diethyl ether were purified using a Grubbs-type solvent system. Methanol was dried over CaH_2 and distilled prior to use. Hexanes, diethyl ether, methanol, and distilled water were deoxygenated by passing a stream of dry N_2 gas through the liquid under an inert atmosphere. Cyclohexane was washed once with 95 mol % H_2SO_4 and once with 10 mol % NaOH, rinsed with distilled water, and dried over anhydrous $MgSO_4$. Prior to use, cyclohexane and THF were distilled under reduced pressure from ^nBuLi and Na/benzophenone, respectively. Styrene monomer was dried over CaH_2 for 24 h and subsequently distilled

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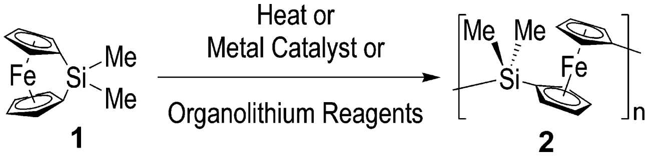
Scheme 1. Ring-Opening Polymerization of Dimethylsila[1]ferrocenophane



twice under reduced pressure prior to polymerizations. 1.6 M ^{n}BuLi in hexanes and a polystyrene homopolymer (M_n = 13 700, PDI = 1.01) were used as received from Aldrich. 1.3 M ^{sec}BuLi in cyclohexane was purchased from Acros and used as received. All polymerizations were conducted in an MBraun inert atmosphere glovebox purged with prepurified N_2.

The ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were obtained from Varian Gemini 300, Varian XL 400, or Varian Unity 500 spectrometers. Molecular weights were determined by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a Waters 410 differential refractometer and a Viscotek T60A dual detector consisting of a 90° angle laser light scattering detector (λ_0 = 670 nm), and a four capillary differential viscometer was used. Alternatively, molecular weights were determined using a Viscotek GPC MAX liquid chromatograph equipped with a Viscotek triple detector array. The triple detector array consists of a refractometer, a four-capillary differential viscometer, a 90° angle laser, and a low-angle laser (7°) light scattering detector (λ_0 = 670 nm). The triple detector system has been shown to provide absolute M_w values for PFS homopolymers,[43] and we assume that it provides accurate values of M_w/M_n. In both cases, a flow rate of 1.0 mL/min was used with THF as the eluent. Standard deviations for molecular weights and polydispersity indices were estimated by running a PS-*b*-PFEMS sample (polymer **5j**) three times. Ultrathin sections (ca. 50 nm in thickness) of bulk samples were obtained at room temperature using a Leica Ultracut UCT equipped with a glass knife and collected on carbon-coated copper grids (400 mesh). Transmission electron microscopy images were obtained using a Hitachi HD 2000 electron microscope with an accelerating voltage and current of 200 kV and 30 mA, respectively. Wide-angle X-ray scattering data were obtained using a Siemens D500 diffractometer equipped with a Cu Kα X-ray source. Small-angle X-ray data were obtained using a Molecular Metrology instrument operated with a 2-dimensional gas-filled multiwire detector and 0.030 kW microsource X-ray tube with a confocal multilayer optic to produce a focused monochromatic X-ray beam (λ = 0.154 nm). The *q* spacing was calibrated using silver behenate, and the sample-to-detector distance was 1.5 m.

Synthesis of Dilithioferrocene·Tetramethylethylenediamine. Dilithioferrocene·tetramethylethylenediamine was synthesized according to a modification of the procedure outlined by Bishop and Davison.[44] A slurry of ferrocene (100 g, 0.54 mol) was established in hexanes (1.5 L) under an inert atmosphere of dry N_2 in a 5 L flask. Dried tetramethylethylenediamine (100 mL, 0.66 mol) was added to the above via a dropping funnel followed by the dropwise delivery of chilled ^{n}butyllithium (800 mL, 1.6 M, ca. −20 °C). The reaction, which gradually changed from a dark orange slurry to a light orange suspension, was allowed to stir for 65 h. Following repeated washings of the solids with hexanes, the product was dried under dynamic vacuum (ca. 10^{-3} mmHg) overnight to afford dilithioferrocene·tetramethylethylenediamine as a peach-colored pyrophoric solid in high yield (138 g, 93%). The solid was stored under dry N_2 in a glovebox.

Synthesis of Ethylmethylsila[1]ferrocenophane (3). Dilithioferrocene·tetramethylethylenediamine (15.4 g, 49.0 mmol) was suspended in diethyl ether (ca. 350 mL), and the suspension was then chilled to −78 °C. Distilled dichloroethylmethylsilane (8.4 g, 58.8 mmol) was then added dropwise via syringe to the reaction vessel, which was then allowed to slowly warm to room temperature over 4 h, during which time the color was observed to change from orange to red. The solvent was then evaporated, and the crude solids were allowed to dry under dynamic vacuum (ca. 10^{-3} mmHg) overnight. Dissolution, filtration, and recrystallization (−55 °C) from hexanes afforded the desired ethylmethylsila[1]ferrocenophane monomer as red crystals in high yield (9.9 g, 79%). Subsequent sublimations (10^{-3} mmHg, 25 °C) and recrystallizations from hexanes yielded monomer of sufficient purity for anionic polymerization as assessed by ^{1}H NMR. ^{1}H NMR (C_6D_6, 300 MHz): δ = 0.37 (s, 3H, Si−C*H*$_3$), 0.88 (q, 2H, Si−C*H*$_2$CH$_3$), 1.13 (t, 3H, Si−CH$_2$C*H*$_3$) 3.97 (m, 4H, Cp), 4.42 (m, 4H, Cp). ^{13}C NMR (C_6D_6, 100.5 MHz): δ = −5.6 (s, br, fcSi*C*H$_3$(Et)), 5.2 (s, fcSiMe(CH$_2$*C*H$_3$)), 6.4 (s, fcSiMe(*C*H$_2$CH$_3$)), 32.9 (s, ipso-C, *fc*SiMe(Et)), 75.6 (s, *fc*SiMe(Et)), 75.9 (s, *fc*SiMe(Et)), 77.6 (s, *fc*SiMe(Et)), 77.7 (s, *fc*SiMe(Et)). ^{29}Si NMR (C_6D_6, 79.5 MHz): δ = −1.9 (s, fc*Si*Me(Et)).

Synthesis of Polyferrocenylethylmethylsilane Homopolymers (4a−4f). A representative homopolymerization to yield **4f** is described. In an inert atmosphere glovebox, ethylmethylsila[1]ferrocenophane (**3**) (0.100 g, 0.391 mmol) was dissolved in 3 mL of THF, to which was added 1.50 μL (0.391 mmol) of ^{n}BuLi (1.6 M solution in hexanes). The polymerization was allowed to proceed for 30 min, during which time the color of the solution changed from red to amber. The polymerization was terminated by the addition of a drop of deoxygenated, distilled water. Subsequent precipitation of the polymer solution into rapidly stirring methanol followed by overnight drying under dynamic vacuum (ca. 10^{-3} mmHg) afforded poly(ferrocenylethylmethylsilane) **4f** as a red-orange gum (87 mg, 87%). GPC analysis: M_n = 41 400, PDI = 1.01. ^{1}H NMR (C_6D_6, 400 MHz): δ = 0.56 (s, Si−C*H*$_3$), 1.07 (br, 2H, Si−C*H*$_2$CH$_3$), 1.13 (br, 3H, Si−CH$_2$C*H*$_3$) 4.13 (m, 4H, Cp), 4.31 (m, 4H, Cp). ^{13}C NMR (CD_2Cl_2, 100.5 MHz): δ = −3.1 (s, br, fcSi*C*H$_3$(Et)), 8.5 (s, br, fcSiMe(CH$_2$*C*H$_3$) and fcSiMe(*C*H$_2$CH$_3$)), 71.3 (s, br, ipso-C, *fc*SiMe(Et)), 71.8 (s, br, *fc*SiMe(Et)), 74.0 (s, br, *fc*SiMe-(Et). ^{29}Si NMR (CD_2Cl_2, 79.5 MHz): δ = −2.6 (s, fc*Si*Me(Et)).

Synthesis of Polystyrene-*block*-polyferrocenylethylmethylsilane (PS-*b*-PFEMS) Diblock Copolymers (5a−5m). The data for the synthetic procedure for **5a**−**5m** are outlined in Table 1. A representative diblock copolymerization of **5h** is described. Styrene (0.685 g, 6.58 mmol) was dissolved in cyclohexane (ca. 2.3 mL) and initiated with 15.1 μL of ^{sec}BuLi (1.3 M solution in cyclohexane) at ambient temperature in an inert atmosphere glovebox. The colorless solution was seen to rapidly turn orange indicative of the living polystyrenyl anions. After an hour a drop of the solution was taken for a GPC analysis followed by the rapid delivery of a solution of ethylmethylsila[1]ferrocenophane (**3**) (0.500 g, 1.95 mmol) in THF (ca. 2.2 mL). The reaction was allowed to stir for 1 h, after which ca. 0.1 mL of deoxygenated water was added to quench. Precipitation of the solution into rapidly stirring hexanes, followed by drying overnight under dynamic vacuum (ca. 10^{-3} mmHg) afforded the desired block copolymer as an orange powder (1.15 g, 97%). ^{1}H NMR (δ, C_6D_6): 0.56 (s, Si−C*H*$_3$), 1.02 (q, Si−C*H*$_2$CH$_3$), 1.18 (t, br, Si−CH$_2$C*H*$_3$), 1.59 (br, C*H*$_2$CH(Ph)), 2.09 (br, CH$_2$C*H*(Ph)), 4.10−4.16 (m, *fc*SiEtMe), 4.30 (m, *fc*SiEtMe), 6.55−7.06 (br, CH$_2$CH(*Ph*)). ^{13}C NMR (CD_2Cl_2, 100.5 MHz): δ = −3.1 (s, br, fcSi*C*H$_3$(Et)), 8.5 (s, br, fcSiMe(CH$_2$*C*H$_3$) and fcSiMe(*C*H$_2$CH$_3$)), 41.0 (s, br, CH$_2$*C*HPh) 42.5−44.5 (br, *C*H$_2$CHPh), 71.3 (s, br, ipso-C, *fc*SiMe(Et)), 71.8 (s, br, *fc*SiMe(Et)), 74.0 (s, br, *fc*SiMe(Et), 126.2 (br, CH$_2$CH*Ph*). ^{29}Si NMR (CD_2Cl_2, 79.5 MHz): δ = −2.6 (s, fc*Si*Me(Et)).

GPC aliquot analysis: M_n = 40 500, PDI = 1.04.

^{1}H NMR integration and aliquot data gave a *x*:*y* = 389:108 block ratio which corresponds to ϕ_{PFEMS} (volume fraction) of 0.36. GPC analysis: M_n = 62 500, PDI = 1.04.

For **5i**−**5m**, purification of the PS-*b*-PFEMS from quenched PS homopolymer was required and carried out as follows. The isolated polymer from the above procedure was slowly precipitated from a good solvent for both PS and PFEMS (e.g., THF) by slowly adding a nonsolvent for PFEMS (e.g., acetone) with stirring.[13] The precipitated polymer was dried overnight under vacuum (ca. 10^{-3} mmHg). The repetition of this procedure was conducted until the sample was observed to be monomodal by GPC, thus affording the desired pure PS-*b*-PFEMS diblock copolymer in moderate yields.

Table 1. Summary of Synthetic Procedure for 5a−5m

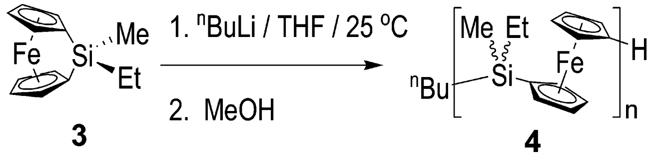
	styrene (g)	cyclohex (mL)	^{sec}BuLi (μL)	**3** (g)	THF (mL)	isolated yield (g) (% yield)	M_n PS (g/mol)[b]	x:y	ϕ_{PFEMS}	M_n PS-*b*-PFEMS[b] (g/mol) (PDI)[c]
5a	0.375	1.3	8.5	0.050	0.23	0.145 (34)	75 900	729:29	0.074	102 700 (1.02)
5b	0.375	1.3	10.5	0.050	0.23	0.405 (95)	43 900	473:20	0.078	62 300 (1.03)
5c	0.375	1.3	10.3	0.050	0.23	0.404 (95)	52 000	499:26	0.095	66 500 (1.00)
5d	0.619	2.3	12.8	0.40	1.2	0.042 (4)	46 900	450:25	0.10	61 400 (1.01)
5e	1.14	3.85	15.0	0.15	0.44	1.24 (96)	56 400	541:35	0.12	63 700 (1.00)
5f	1.14	3.9	30.0	0.488	2.2	1.44 (89)	27 400	263:44	0.25	39 900 (1.00)
5g	0.681	2.3	15.0	0.44	2.2	1.09 (97)	41 900	402:98	0.33	59 800 (1.03)
5h	0.685	2.3	15.1	0.5	2.2	1.15 (97)	40 500	389:108	0.36	62 500 (1.04)
5i[a]	0.686	2.3	14.9	0.505	2.2	0.539 (45)	47 900	460:175	0.43	140 300 (1.04)
5j[a]	0.260	1.0	15.0	0.310	0.55	0.120 (21)	20 800	200:83	0.45	155 500 (1.04)
5k[a]	0.200	0.7	3.4	0.15	0.55	0.196 (56)	56 100	539:296	0.52	239 900 (1.05)
5l[a]	0.400	1.3	6.4	0.300	1.1	0.159 (23)	60 900	585:345	0.54	232 400 (1.06)
5m[a]	0.270	1.0	15.0	0.320	0.55	0.043 (7)	18 400	176:186	0.68	124 500 (1.07)

[a] Purification of PS-*b*-PFEMS from PS is required in these cases. [b] By GPC, standard deviation estimated to be ca. 5%. [c] By GPC, standard deviation estimated to be ca. 1%.

Bulk Casting and Annealing of PS-*b*-PFEMS. The casting and annealing of **5d, 5h,** and **5k** into bulk samples were conducted analogously. The representative procedure for **5h** is described. A concentrated solution of **5h** (ca. 200 mg/mL) in toluene was applied dropwise to a clean glass slide and was slowly allowed to dry in a closed vial over ca. 5 days. The resulting bulk sample (ca. 1 mm in thickness) was then dried overnight in a vacuum oven at ca. 50 °C. Thermal annealing at ca. 190 °C for 36 h gave the bulk polymer sample as a brittle clear orange material. Small-angle X-ray scattering (SAXS) measurements on films prior to annealing and at 190 °C confirmed that the solvent casting did not result in a nonequilibrium morphology and that at the annealing temperature polymers **5h** and **5k** were in the ordered state.

For 5f + PS$_H$. A solution containing **5f** (0.010 g) and PS$_H$ (0.0015 g, M_n = 13 700, PDI = 1.01) was stirred in toluene (ca. 0.15 mL) for 4 h to ensure adequate mixing. A bulk film was then cast as above and annealed (190 °C, 36 h), resulting in a brittle clear orange sample. Small-angle X-ray scattering (SAXS) measurements at 190 °C confirmed that at the annealing temperature the polymer mixture **5f** + PS$_H$ was in the ordered state.

Scheme 2. Anionic Ring-Opening Polymerization of Ethylmethylsila[1]ferrocenophane



3 **4**

Table 2. Anionic ROP of Ethylmethylsila[1]ferrocenophane Initiated by 1.6 M ^{n}BuLi

polymer	monomer:BuLi	theor M_n	obsd M_n[a]	PDI[b]	n
4a	19.5	5000	4000	1.01	16
4b	39.1	10 000	10 100	1.01	39
4c	58.6	15 000	14 500	1.01	57
4d	78.2	20 000	20 800	1.01	81
4e	135.6	34 700	39 000	1.02	152
4f	156.3	40 000	41 400	1.01	162

[a] Standard deviation estimated to be ca. 5%. [b] Standard deviation estimated to be ca. 1%.

Results and Discussion

A living polymerization system is required to be free of chain transfer and chain termination reactions.[45,46] To investigate the living nature of the anionic ring-opening polymerization of ethylmethylsila[1]ferrocenophane (**3**), we carried out a series of experiments which allowed us to (i) plot M_n values of several homopolymers vs the monomer: initiator ratio to confirm its linearity and (ii) to show that these homopolymers and block copolymers all have narrow molecular weight distributions.

Synthesis of Ferrocenophane Monomer 3. The organometallic monomer (**3**) used in this study was prepared in two steps. First, dilithioferrocene·tetramethylethylenediamine was prepared by the reaction of ferrocene with ca. 2.4 equiv of ^{n}BuLi in the presence of the amine catalyst tetramethylethylenediamine (TMEDA). The resulting suspension was washed with hexanes and dried under reduced pressure to afford a peach-colored pyrophoric powder in large amounts and high yields. The material was stored and easily handled in an inert atmosphere glovebox where charging of reaction vessels was readily accomplished. All stoichiometric calculations were performed using a mole ratio of 1,1′-dilithioferrocene to TMEDA of 3/2 as the overall yields of subsequent reactions were improved. Second, dilithioferrocene·tetramethylethylenediamine was reacted at a subambient temperature with MeEtSiCl$_2$. The red crystalline ethylmethylsila[1]ferrocenophane monomer **3** was isolated after purification by sublimations and recrystallizations. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR spectroscopy confirmed the structure of the ethylmethylsila[1]ferrocenophane monomer by providing data typical of that for strained, ring-tilted sila[1]ferrocenophanes.[47]

Synthesis and Characterization of PFEMS Homopolymers (4a−4f). The synthetic procedure for the synthesis of PFEMS homopolymers is outlined in Scheme 2. Reaction of ethylmethylsila[1]ferrocenophane with ^{n}BuLi in THF at 25 °C for 30 min followed by quenching of the living polymer with H$_2$O yielded the H-terminated poly(ferrocenylethylmethylsilane)s **4** as amber gums in high yields. On the basis of the GPC data, the molecular weights of PFEMS were easily controlled from M_n = 4000 to 41 400 with low polydispersity indices (PDI = 1.01−1.02) by varying the monomer: initiator ratio from 20:1 to 156:1. The experimental results are reported in Table 2.

The stereoregularity of PFEMS, and thus the tacticity of the polymer, was probed using a high-resolution NMR. A 500 MHz ^{1}H NMR spectrum was obtained from the homopolymer **4f**. Shown in Figure 1 are the representative spectra of diblock copolymer **5f** (in C$_6$D$_6$) with the PFEMS SiCH_3 signal from homopolymer **4f** (in CD$_2$Cl$_2$) shown as the inset. On the basis of previous tacticity studies on polyferrocenylsilanes,[48] we assign the triad resolved methyl signals in **4f** at 0.457, 0.455, and 0.453 ppm as *mm, mr,* and *rr* (integral data: *mm*

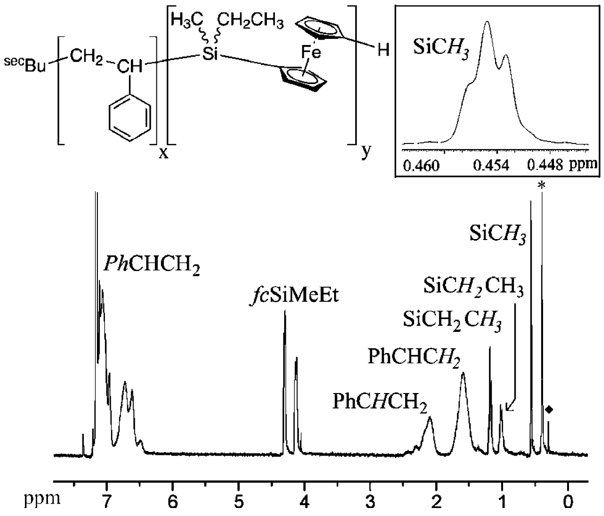


Figure 1. ^{1}H NMR of PS-*b*-PFEMS **5f** (C_6D_6, 400 MHz) (∗ = H_2O; ◆ = silicone grease) and SiCH_3 signal of PFEMS homopolymer **4f** (inset) (CD_2Cl_2; 500 MHz).

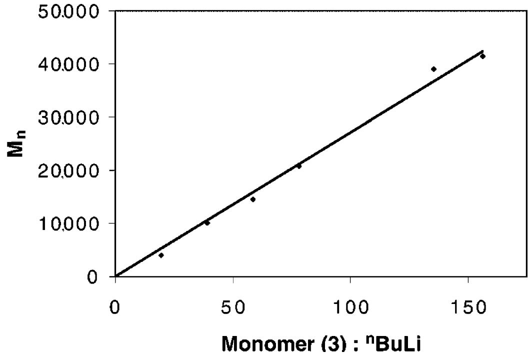


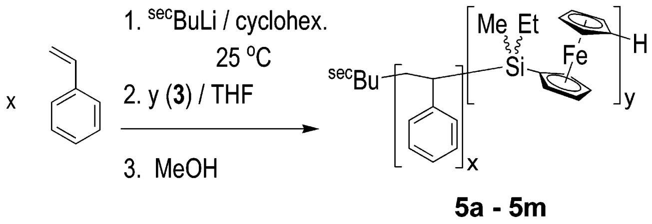
Figure 2. Plot of M_n vs monomer:initiator ratio for ^{n}BuLi-initiated synthesis of poly(ferrocenylethylmethylsilane).

$= 0.39$, $mr = 0.34$, $rr = 0.27$). The integrations for the triad signals suggested a largely atactic polymer with slight increased syndiotacticity, a stereoregularity not unlike other anionically synthesized diblock copolymers.[49] The ^{1}H NMR spectra of **5f** (in C_6D_6) showed characteristic broadening of the cyclopentadienyl proton resonances at 4.13 and 4.30 ppm and broad methyl resonance and ethyl resonances at 0.56, 1.02, and 1.18 ppm, respectively, with no triad resolution.[50]

The plot of M_n vs the monomer:initiator ratio is shown in Figure 2. The linearity of the plot suggests living character under the above experimental conditions. As is typical for anionic polymerizations, minor impurities become significant for targeted higher molecular weight samples, often resulting in difficulties in predicting molecular weights (polymer **4e** and **4f**, Table 2). Nevertheless, a controlled polymerization of **3** was possible up to a molecular weight of ca. 40 000 with near monodisperse molecular weight distributions.

Synthesis and Characterization of PS-*b*-PFEMS Diblock Copolymers (5a–5m). The synthetic procedure for the preparation of PS-*b*-PFEMS diblock copolymers **5a–5m** is outlined is Scheme 3. The sequential addition of ethylmethylsila[1]ferrocenophane monomer **3** to a living polystyrene (PS) system was anticipated to afford a narrow molecular weight distribution diblock copolymer and thus further confirm the living anionic ROP of ethylmethylsila[1]ferrocenophane. Our approach involves the initiation with ^{sec}BuLi and polymerization of styrene in cyclohexane at room temperature, where polystyrenyl anions are known to propagate in a living manner.[51] After ca. 1 h, a small sample of the living polystyrene solution was taken for molecular weight characterization against a polystyrene-based GPC calibration curve. In accordance with the optimized conditions for the anionic homopolymerization of ethylmethylsila[1]ferrocenophane, a THF solution of this monomer was used so as to establish a mixed solvent medium with increased polarity. The polymerization in this mixed solvent was allowed to proceed for ca. 1 h. Subsequent addition of deoxygenated H_2O and precipitation into rapidly stirred hexanes yielded the yellow to orange diblock copolymers in high yields (Table 2). For high PFEMS volume fraction and high molecular weight targets, impurity contamination becomes significant, resulting in multimodal molecular weight distributions. Selective precipitation of PS-*b*-PFEMS into a PS solvent and a PFS nonsolvent provided pure diblock copolymers.

Scheme 3. General Synthetic Procedure for Optimized Anionic Polymerization for PS-*b*-PFEMS Copolymers



The diblock copolymers obtained using the above synthetic procedure were all characterized by multinuclear NMR and gel permeation chromatography (GPC). Using the GPC traces from the polystyrene aliquots and a calibration curve from polystyrene standards, the number of repeat units in the polystyrene block (x) was readily determined. From ^{1}H NMR integration of the polystyrene main chain methylene protons ($\delta = 1.59$ ppm) and the ferrocenyl protons located nearest to the *ipso* cyclopentadienyl carbons ($\delta = 4.30$ ppm), the number of PFEMS repeat units (y) was accurately determined. Subsequently, from this information the absolute molecular weight for the diblock copolymer was calculated. Using a polystyrene density of 1.05 g/mL[17,52] and a PFEMS density of 1.29 g/mL[53] in combination with the ^{1}H NMR data, the volume ratio for each corresponding block was determined. Polydispersity indices were reported as recorded by GPC. All data are given in Table 3.

High yields of monodisperse PS-*b*-PFEMS diblock copolymers with no detectable PS homopolymer impurities were isolated with molecular weights up to 65 000 (Figure 3). The presence of PS homopolymer in higher molecular weight samples (ca. $M_n > 67\,000$) is presumably a result of a significant quantity of impurities leading to terminated PS chains (Figure 3b). PS-*b*-PFEMS could be easily purified from the mixture of homopolymer and diblock copolymer by selective precipitation using a nonsolvent for PFEMS and a good solvent for PS. Following reprecipitation and overnight drying under reduced pressure, pure amber PS-*b*-PFEMS diblock copolymer were isolated in moderate yields (Figure 3c). All isolated diblock polymers were observed to have narrow molecular weight distributions (PDI = 1.00–1.07), and the colors ranged from pale yellow to amber as the PFEMS volume fraction increased.

Table 3. Molecular Characterization Data for Polystyrene-*Block*-polyferrocenylethylmethylsilane Copolymers 5a–5m

polymer	M_n[a]	M_w[b]	PDI[c]	ϕ_PS[d]	ϕ_PFEMS[d]	x[e]	y[d]
5a	83 300	85 000	1.02	0.93	0.074	729	29
5b	54 400	54 700	1.01	0.92	0.078	473	20
5c	58 600	58 700	1.00	0.91	0.095	499	26
5d	53 300	53 700	1.01	0.90	0.10	450	25
5e	65 300	65 300	1.00	0.88	0.12	541	35
5f	38 700	38 600	1.00	0.75	0.25	263	44
5g	67 000	68 800	1.03	0.67	0.33	402	98
5h	68 200	70 900	1.04	0.64	0.36	389	108
5i	92 700	96 600	1.04	0.56	0.43	460	175
5j	41 900	43 400	1.04	0.54	0.45	200	83
5k	132 000	139 000	1.05	0.47	0.52	539	296
5l	149 000	158 000	1.06	0.45	0.54	585	345
5m	66 000	71 000	1.07	0.32	0.68	176	186

[a] From PS aliquot and ^{1}H NMR data. Standard deviation estimated to be ca. 5%. [b] From PS aliquot, ^{1}H NMR, and PDI data. [c] From GPC curve. Standard deviation estimated to be ca. 1%. [d] From ^{1}H NMR integration and PS aliquot data. [e] From PS aliquot data.

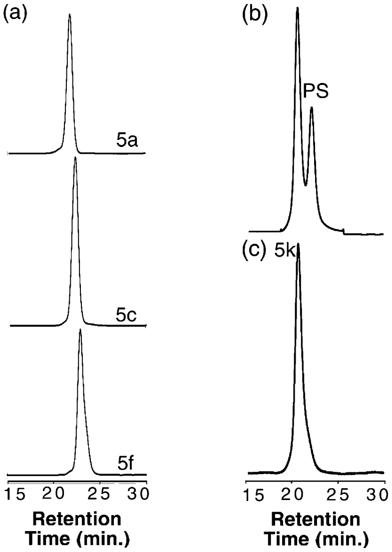


Figure 3. GPC traces of (a) PS-*b*-PFEMS diblock copolymers prepared using ^{sec}BuLi as initiator with different mole ratios of monomers: initiator (**5a, 5b, 5f**). GPC traces of (b) PS-*b*-PFEMS **5k** contaminated with PS homopolymer (c) purified PS-*b*-PFEMS **5k**.

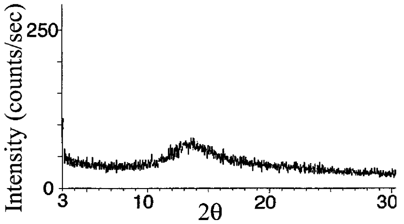


Figure 4. WAXS analysis of PS-*b*-PFEMS **5f** showing an amorphous halo centered at $2\theta = 14°$.

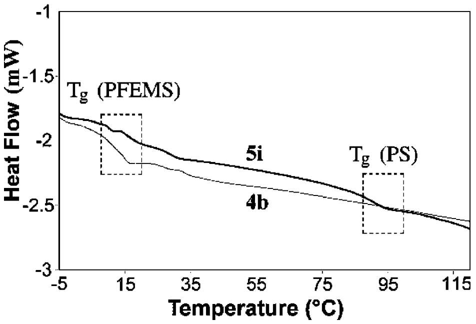


Figure 5. Differential scanning calorimetry plots of (a) PFEMS homopolymer **4b** and (b) PS-*b*-PFEMS diblock copolymer **5i**.

Bulk Morphological Studies of PS-*b*-PFEMS Diblock Copolymer by Polarizing Optical Microscopy, WAXS, DSC, TEM, and SAXS. To confirm the lack of crystallinity in PS-*b*-PFEMS materials, representative polymers, **4b** and **5f**, were investigated by polarizing optical microscopy and wide-angle X-ray scattering (WAXS), respectively. In heating **4b** and **5f** above the PFEMS glass transition and slowly cooling the sample to room temperature, favorable exothermic crystallization would be encouraged as a result of the increased chain mobility in the bulk sample. The resulting crystallites can polarize light and scatter an incident X-ray beam to wide angles, and thus macroscopic observations through crossed polars and a WAXS experiment are appropriate. Sample **4b** did not show any evidence for significant optical birefringence and confirms a lack of crystallinity at the macroscopic level. Shown in Figure 4 is the resulting WAXS plot for **5f**. Indeed, it was found that only an amorphous halo was observed at a 2θ value of 14°, thus confirming the lack of crystallites in the annealed sample.

To further confirm the lack of crystallinity in PFEMS, we investigated the thermal behavior of **4b**, a relatively low molecular weight PFEMS homopolymer (M_n = 10 100), and **5i**, a diblock copolymer having a high molecular weight PFEMS segment. Bulk samples were examined via differential scanning calorimetry (DSC) between the temperatures of −30 and 170 °C, a range known to extend over all glass transitions (T_g) and melt transitions (T_m) for alkyl-substituted PFSs.[12,22] The DSC plots (heating cycle) for polymer **4b** and diblock copolymer **5i** are shown in Figure 5. The T_m for the symmetrically methyl- and ethyl-substituted PFSs polymers are 140 and 108 °C, respectively, and thus any potential T_m for the asymmetrically substituted PFEMS polymer would likely fall in this range. A characteristic glass transition at ca. 15 °C for PFEMS was detected in both systems whereas neither an exothermic crystallization transition nor an endothermic melt transition is detected. In addition, in the case of the diblock copolymer, the signature T_g of polystyrene is observed at ca. 95 °C, well within its typical range.[54] These data in combination with the high-resolution ^{1}H NMR and the WAXS data confirm that PFEMS is amorphous and is therefore ideal for bulk self-assembly in block copolymers.

To gain insight into the morphology of PS-*b*-PFEMS diblock copolymers, polymers **5d**, **5h**, and **5k** were studied as representative examples by transmission electron microscopy (TEM) and small-angle X-ray scattering. Electron micrographs of ultrathin sections of these polymers that were slow cast from toluene or

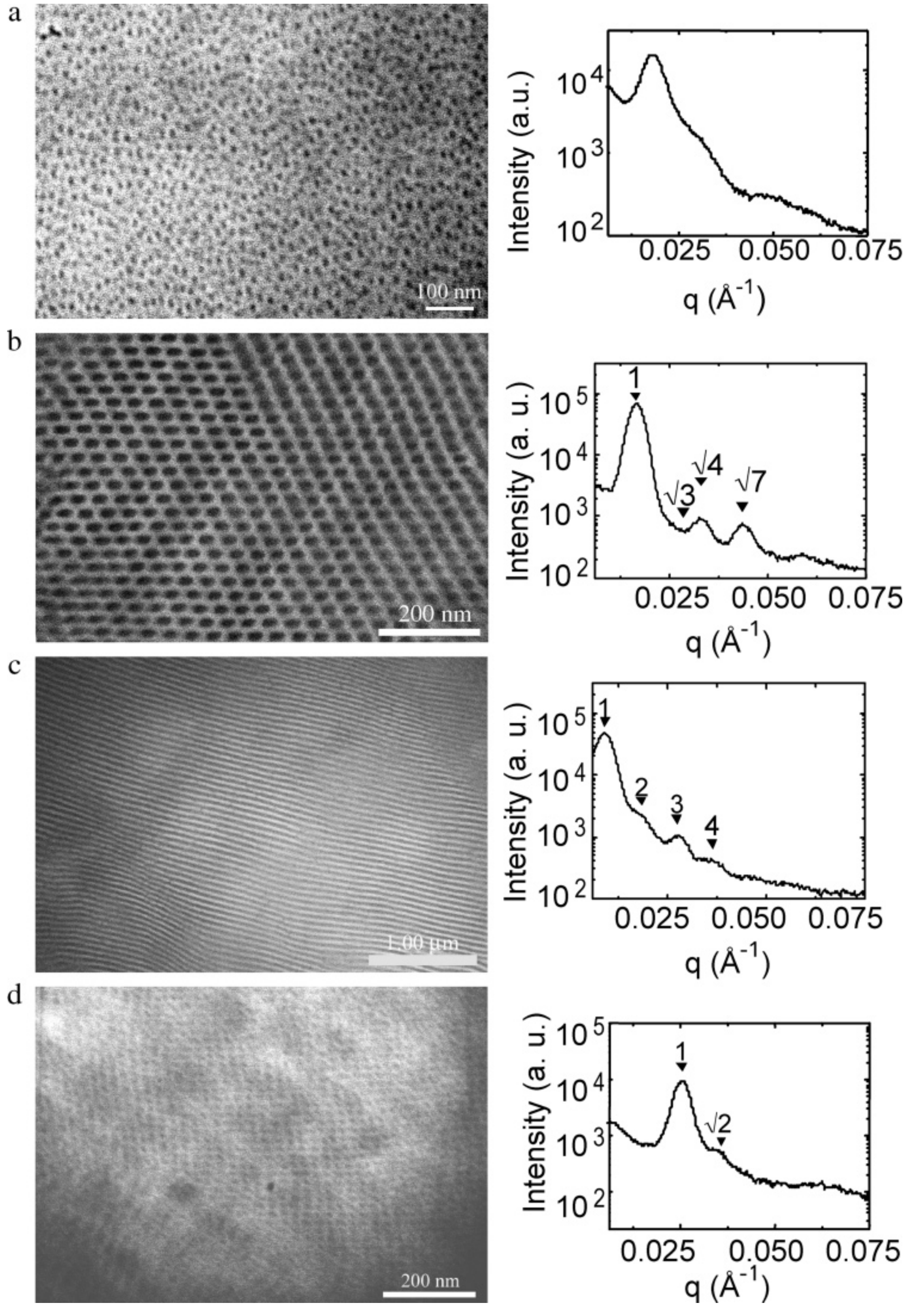


Figure 6. Transmission electron photomicrographs of microtomed bulk samples (shown on left) and small-angle X-ray scattering plots of bulk samples (shown on right) (a) **5d**, (b) **5h**, (c) **5k**, and (d) **5f** + PS_H.

benzene[55] for 1 week, dried overnight at 50 °C, and thermally annealed at 190 °C for 36 h are shown in Figure 6. Contrary to polystyrene-*block*-poly(ferrocenyldimethylsilane) (PS-*b*-PFDMS), an analogous diblock copolymer containing a potentially crystallizable polyferrocenylsilane block, no thermal quenches of the bulk samples were necessary, as the PS-*b*-PFEMS has no crystallization to hinder bulk morphological ordering. Bulk samples were mounted on a cured acrylate-based resin with a cyanoacrylate glue and allowed to dry overnight. Swelling of the bulk microstructure is thought to be negligible, as neither polystyrene nor poly(ferrocenylethylmethylsilane) homopolymers were readily soluble in the glue. Room temperature microtoming was effective, since the glassy PS phase provided sufficient integrity for these materials during the sectioning process. Preserved samples were microtomed at a thickness of ca. 50 nm, floated onto water, and subsequently transferred to a carbon-coated TEM grid by touching the grid with the floating sections. All samples were imaged without staining, as the high electron density associated with the main chain Fe atoms provided sufficient contrast for TEM micrographs. PFEMS areas are dark whereas PS areas are lighter in all TEM images.

For polymer **5d**, a diblock copolymer with a ϕ_{PFEMS} of 0.10, a disordered spherical morphology was observed. Shown in Figure 6a (left) is the TEM micrograph of a sectioned sample of **5d** which displays a disordered array of PFEMS spheres in a PS matrix. Regardless of the angle of microtoming, varied between 0° and 30°, a similar image to that shown in Figure 6a was observed, suggesting a spherical shape for the PFEMS phase. The average diameter of the PFEMS spheres was estimated to be ca. 10 nm by TEM. The azimuthally averaged SAXS intensity profile of **5d** is shown in Figure 6a (right). The features in this profile are consistent with a liquidlike packing of spheres, as previously shown by Kinning and Thomas.[56] The primary peak and shoulder at low q are due to interference between the spheres while the broad peak at higher q is due to the sphere form factor.

For polymer **5h**, a diblock copolymer with a ϕ_{PFEMS} of 0.36, a highly ordered cylindrical morphology was observed. Shown in Figure 6b (left) is the TEM micrograph of a sectioned sample of **5h** and, as mentioned, displays an ordered array of PFEMS cylinders in a PS matrix. In contrast to **5d**, a strong angular dependence of the microtoming was observed. By TEM, the average diameter of the PFEMS cylinders was estimated to be ca. 20 nm, whereas the periodicity was found to be 44 nm. The azimuthally averaged SAXS intensity profile of **5h** is shown in Figure 6b (right). As indicated on the profile, peaks are present at q/q^* ratios of 1, $\sqrt{4}$, and $\sqrt{7}$, consistent with hexagonally packed cylinders ($\sqrt{3}$ not found due to form factor cancellation).[57]

For polymer **5k**, a diblock copolymer with a ϕ_{PFEMS} of 0.52, a highly ordered lamellar morphology was observed. Shown in Figure 6c (left) is the TEM micrograph of a sectioned sample of **5k** which displays an ordered array of alternating PFEMS and PS lamellae. The average PFEMS lamella thickness, PS lamella thickness, and an average domain spacing of 46, 42, and 88 nm, respectively, were determined by TEM. The azimuthally averaged SAXS intensity profile of **5k** is shown in Figure 6c (right). As indicated on the profile peaks are present at q/q^* ratios of 1, 2, 3, and 4, consistent with a lamellar morphology.

To access a body-centered-cubic (bcc) ordered spherical morphology of PFEMS domains, the effective ϕ_{PFEMS} was tailored through the addition of homopolymer PS ($\mathrm{PS_H}$). This technique has been previously used to stabilize ordered arrays of nanostructures by inducing phase transitions associated with the forced curvature of interfaces toward the minority block's domains by spatially accommodating homopolymer in the domains of the majority block.[17,58] For polymer **5f**, a diblock copolymer with a ϕ_{PFEMS} of 0.25, an ordered cylindrical morphology was measured by SAXS. The ϕ_{PFEMS} was altered to 0.20 by addition of a $\mathrm{PS_H}$ of half the corresponding PS molecular weight found in the PS-*b*-PFEMS **5f** followed by annealing as above to afford an ordered array of PFEMS spheres in a PS matrix. Shown in Figure 6d (left) is the TEM micrograph of a sectioned sample **5f** + $\mathrm{PS_H}$ and, as mentioned, displays an ordered array of PFEMS spheres in a PS matrix. Regardless of the angle of microtoming, varied between 0° and 30°, a similar image to that shown in Figure 6d (left) was observed, suggesting a spherical shape to the PFEMS phase. The average radius of the PFEMS spheres was estimated to be ca. 5 nm by TEM. The azimuthally averaged SAXS intensity profile of **5f** + $\mathrm{PS_H}$ is shown in Figure 6d (right). This is a more well-ordered structure than sample **5d**. As a consequence, peaks at q/q^* ratios of 1 and $\sqrt{2}$ are observed, consistent with a simple cubic (sc) or bcc sphere morphology. The d_{100} plane spacings calculated from the q^* peak for the sc and bcc lattices are 25 and 35 nm, respectively. Using a 5 nm TEM measured sphere radius and the fact that a sc and bcc unit cell includes 1 and 2 spheres, respectively, the volume fraction of PFEMS in a sc lattice was estimated as 0.27, whereas that of a bcc lattice was 0.20. We therefore assign a bcc packing to the spheres as the calculated volume fraction of PFEMS matches the diluted volume fraction as above.

Summary

We have demonstrated that the anionic polymerization of ethylmethylsila[1]ferrocenophane **3** initiated with alkyllithium reagents (^{n}BuLi, polystyrenyllithium) in THF or in a mixed cyclohexane/THF solvent proceeds in a living manner at room temperature. This living anionic ring-opening polymerization permits the synthesis of high molecular weight, very low polydispersity index organic/inorganic diblock copolymers with a tunable iron content. The organometallic PFEMS homopolymers and diblock copolymers were found to be atactic by ^{1}H NMR and amorphous by DSC and WAXS. Block copolymers comprising PFEMS blocks are therefore excellent candidates for solid-state self-assembly in bulk and in thin films.[59] In this work we found that for PS-*b*-PFEMS well-ordered and well-defined nanoscale structures such as spheres, cylinders, and lamellae that are rich in iron evolved on using simple bulk annealing procedures where a low-temperature quench is avoided. The resulting morphologies and their dimension were characterized by TEM and SAXS.

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