Moderating the Reactivity of Living Anionic Poly(ferrocenyldimethylsilane) with a Diphenylethylene Chain End: Synthesis and Characterization of Polystyrene−Polyferrocenylsilane Graft Copolymers

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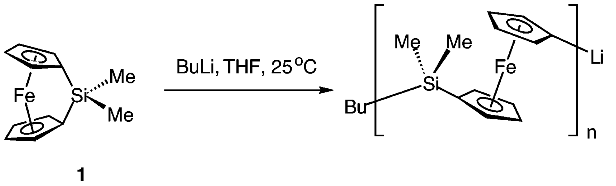
ABSTRACT: The synthesis and characterization of poly(styrene-*g*-ferrocenyldimethylsilane), the first organic−organometallic graft copolymer, are reported. This was permitted by the discovery that 1,1-diphenylethylene (DPE) can effectively cap the living anionic polyferrocenylsilane generated by the ring-opening polymerization (ROP) of the dimethyl-substituted [1]ferrocenophane **1** using *n*-BuLi as the initiator. The resultant living DPE-capped polymer was then reacted with the chloromethyl functionalities of poly(styrene-*co*-chloromethylstyrene) (PS-*co*-PCMS) (**3**) to afford the polystyrene−polyferrocenylsilane graft copolymers **5a** and **5b**. These graft copolymers were then analyzed using differential scanning calorimetry and wide-angle X-ray scattering which indicated that the materials are essentially amorphous, with at most a very low degree of crystallinity. Cyclic voltammetry of **5b** in CH_2Cl_2 showed a well-resolved wave voltammogram with a redox coupling ΔE of ca. 0.23 V, characteristic of the presence of significant Fe- - -Fe interactions in the grafted organometallic side chains. Polymer **5b** was also characterized by thermogravimetric analysis which indicated that the material is thermally stable to weight loss up to ca. 300 °C.

Introduction

The development of metal-containing polymers is of considerable interest, as such materials potentially possess unusual and useful properties.[1] Although synthetic routes to organic polymeric materials are well established, the equivalent chemistry for inorganic and organometallic polymers is in its elementary stages. One well-developed route to organometallic polymers involves the ring-opening polymerization (ROP) of [1]-ferrocenophanes to afford high molecular weight, redox-active polyferrocenylsilanes (PFSs) that possess interesting semiconductive and preceramic properties.[2−4] Incorporation of segments of PFS into block copolymer systems provides access to materials with a wide variety of solution and solid-state morphologies with potential as functional nanostructured materials.[5,6] In this regard, we have previously studied linear block copolymers such as poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFDMS-*b*-PDMS) that form cylindrical or ribbonlike structures in selective solvents due to the crystallization of the PFDMS block.[7] Polysiloxanes with very short PFDMS grafts (ca. 5 repeat units) have been previously prepared by a metal-catalyzed ROP procedure.[8] Here, we report the first synthetic methodologies for the preparation of PFS-based graft copolymers with an organic backbone. We anticipate that the copolymers containing PFDMS grafts would be interesting systems in which to probe the possibility of side-chain crystallization[9] by methods such as differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS).

Scheme 1. Living Anionic Polymerization of a Sila[1]ferrocenophane



Results and Discussion

Synthesis of Poly(chloromethylstyrene) Derivatives. It is well established that [1]ferrocenophanes such as **1** can undergo living anionic polymerization to afford polyferrocenylsilanes of controlled molecular weight and narrow polydispersity (PDI) (Scheme 1).[10] Depending on the terminating agent used, the polymers can also be end-functionalized. In this regard, we have previously shown that small molecules containing a reactive silicon−chlorine bond (e.g., Me_3SiCl) can be used to terminate the anionic polymerization of [1]-ferrocenophanes.[10] Moreover, there are literature examples of anionic polymerization of organic monomers that are terminated by the addition of a moiety containing a reactive benzyl chloride group.[11]

We therefore thought it possible to extend this literature methodology to PFSs and to potentially use the benzyl chloride groups of poly(chloromethylstyrene) (PCMS) to terminate the anionic polymerization of [1]-ferrocenophanes.

A series of chloromethylstyrene-based polymers were synthesized using radical-initiated polymerization in the presence of 1,1-diphenylethylene (DPE).[12] The addition of DPE to a conventional radical polymerization results in a controlled behavior for the polymerization.[13] The

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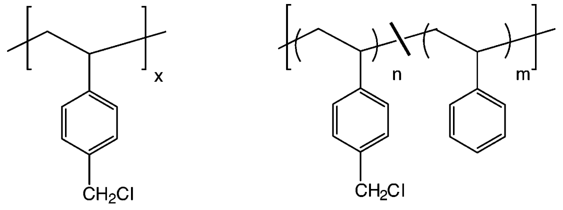


2

% of CH_2Cl groups = 48 %

3

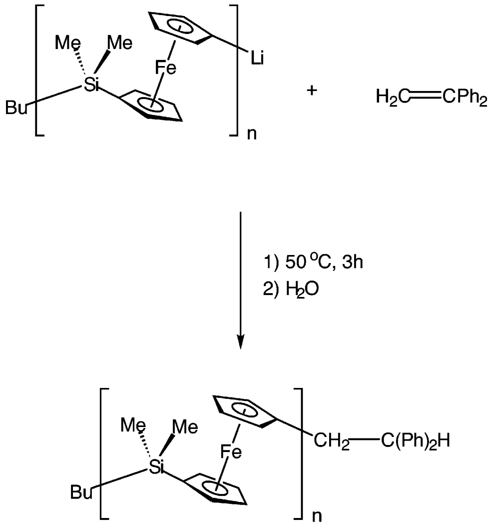
Figure 1. Structures of PCMS-based polymers.

resultant polymers possess a radical DPE end group, and termination occurs when these radicals couple. The polymers that were chosen for investigation were either a PCMS homopolymer (**2**) or, alternatively, a 1:1 copolymer of chloromethylstyrene and styrene (**3**) in order to lower the number of reactive sites available for grafting (Figure 1).

Attempted Reactions of Living Poly(ferrocenyldimethylsilane) with Poly(chloromethylstyrene). In our first experiments, we attempted the direct reaction of living anionic PFDMS with **2** and **3** at room temperature in THF. ^1H NMR analysis of the products indicated that no grafting reaction had occurred. We then attempted to increase the reactivity of the benzyl chloride groups of **3** with the addition of catalytic amounts of CsI. Chloride−iodide exchange reactions have been successfully used in other capping reactions of living anionic chain ends and benzyl chlorides.[14] In our case, the PS-based product obtained by reacting living PFDMS with **3** in the presence of CsI was insoluble. We presume that cross-linking occurs due to lithium−halogen exchange reactions of the CH_2Cl groups, followed by interchain nucleophilic substitution reactions. This type of exchange has been a well-documented problem in anionic grafting reactions.[15]

Synthesis of 1,1-Diphenylethylene-Capped Poly(ferrocenyldimethylsilane). It has been previously shown that poly(styrenyl)lithium and poly(isoprenyl)lithium can be quantitatively grafted onto poly(chloromethylstyrene) without lithium−halogen exchange if the living polymer chain ends have been reacted with DPE to afford the diphenylmethyl anion.[16] We have also previously reported that the propagation of styrene with lithium as a counterion in THF at room temperature is much faster than the initiation of styrene monomer by living PFS.[10] DPE is structurally similar to styrene but does not propagate anionically when present in low concentration. We therefore thought it possible to react living anionic PFS with DPE to similarly obtain the living DPE chain end (Scheme 2). Two equivalents of DPE were added to a solution of living PFDMS in THF at room temperature, and the reaction was heated to 50 °C for 3 h[17] before termination with water to afford **4**. The degree of DPE end-capping was determined by ^1H NMR spectroscopy to be virtually quantitative by comparing the integration of the Me resonance of the n-butyl initiator group to those of the DPE end group. Remarkably, despite the elevated temperature for the capping reaction (50 °C), no significant broadening of the molecular weight distribution was detected (PDI for **4** was <1.1).[17]

Scheme 2. Synthesis of DPE-Capped PFDMS



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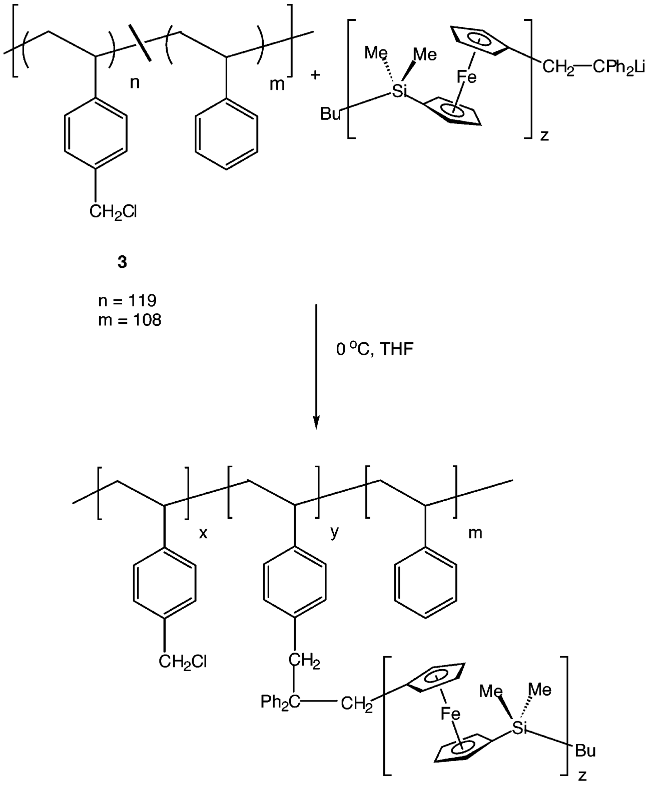
Scheme 3. Synthesis of Graft Copolymers 5a and 5b



5a, 5b

5a: x = 104, y = 15, z = 12

5b: x = 100, y = 19, z = 17

Synthesis of Graft Copolymers. To synthesize PS-based PFDMS graft copolymers, the same approach (but without termination) was used to obtain PFDMS with a living DPE chain end. Once the DPE had reacted with living PFDMS for 3 h at 50 °C, the solution was cooled to 0 °C. This solution was then added to a THF solution of **3** (also at 0 °C) and was allowed to warm to room temperature (Scheme 3). Evidence for successful grafting was detected using GPC. Two peaks in the GPC trace were observed. One was of low molecular weight ($M_n = 2880$), corresponding to ungrafted PFDMS chains. A higher molecular weight peak ($M_n = 67\ 000$) was also observed and is of significantly higher molecular weight than the ungrafted copolymer **3** ($M_n = 29\ 400$, PDI =

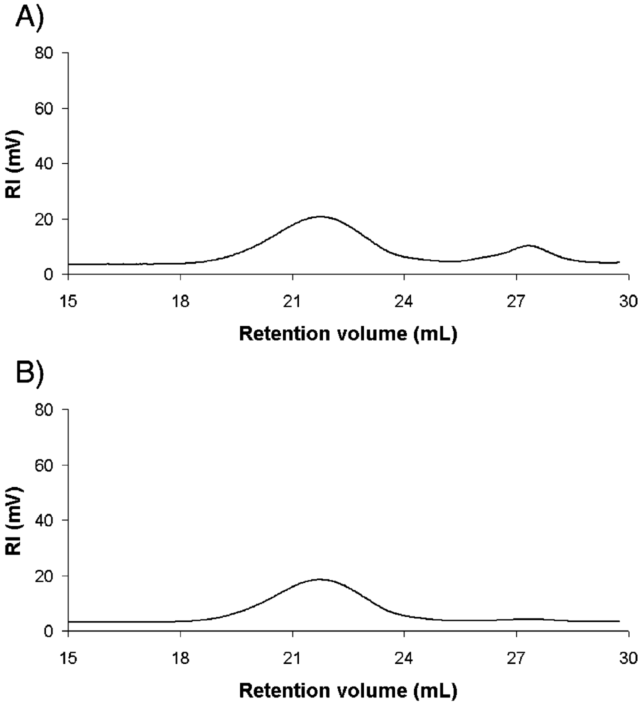


Figure 2. GPC analyses of (A) unpurified graft copolymer **5a** with ungrafted PFDMS homopolymer and (B) purified graft copolymer.

1.54) (Figure 2A). This higher molecular weight fraction corresponds to a grafting density of 15 PFDMS chains onto the PCMS-based copolymer. Subsequent precipitation of the polymer from THF into hexanes was repeated until no residual ungrafted PFDMS was detected by GPC, and pure graft copolymer **5a** was isolated (Figure 2B).

To achieve improved grafting density onto poly(styrene-*co*-chloromethylstyrene) (**3**), the analogous reaction was performed with a variation in reaction times. DPE was added to the living anionic PFDMS chains in THF 20 min after their initiation, and the solution was stirred at 50 °C for 1 h. At that time, the temperature was reduced to 0 °C, and polymer **3** was added in the same solvent. The graft copolymer **5b** was obtained following repeated precipitation into hexanes. GPC analysis showed that the number-average molecular weight (M_n) of the ungrafted PFDMS homopolymer was 4060 while the molecular weight of the graft copolymer was $M_n = 101\,480$, corresponding to a total of 19 PFDMS grafts onto the polymer main chain. ^{1}H NMR characterization of **5b** confirmed the attachment of PFDMS grafts onto the polymer backbone due to the appearance of the PFDMS-based cyclopentadienyl resonances at 4.05–4.26 ppm as well as the DPE phenyl resonances at 7.15 ppm. By comparing the integration of residual unreacted chloromethyl functionalities to that of the aromatic hydrogens of the PS-*co*-PCMS backbone, the degree of substitution of PFDMS grafts can be estimated at approximately 23% (ca. 27 PFDMS grafts out of a possible 119). This value is comparable to that obtained by GPC (ca. 19 PFDMS grafts out of a possible 119). This relatively low grafting efficiency may be a result of steric effects.

Thermal Analysis and WAXS Studies of Graft Copolymers 5a and 5b. The thermal behavior of graft copolymers **5a** and **5b** as well as PS-*co*-PCMS **3** was investigated using differential scanning calorimetry (DSC). The amorphous polymer **3** possessed a glass transition temperature (T_g) at 107 °C. Samples of **5a** and **5b** were first annealed at 80 °C under vacuum for 24 h before analysis. DSC was obtained at a scan rate of 10 °C/min from −10 to 160 °C, and in this temperature range, the only observed thermal transition was the T_g of the PFDMS grafts at 34 °C. No T_c or T_m was observed which would indicate the presence of crystallinity. Moreover, the T_g of the PS-based graft copolymer backbone was not observed, presumably due to the proportion of the polymer vs PFDMS side chains in **5a** and **5b**. WAXS analysis of **5a** and **5b** after annealing at 80 °C for 24 h displayed a broad peak. In a control experiment, a sample of **5b** was heated above the melt transition of PFDMS homopolymer ($T_m \sim 145$ °C) for 24 h and immediately quenched in liquid nitrogen in order to impede any potential crystallization of the PFDMS grafts. WAXS analysis of this second sample also afforded a broad peak. Overall, these results indicate a negligible, or at most a very low, degree of crystallinity (Figure 3). The apparent lack of crystallinity is not surprising due to the relatively low graft density of the PFDMS chains.

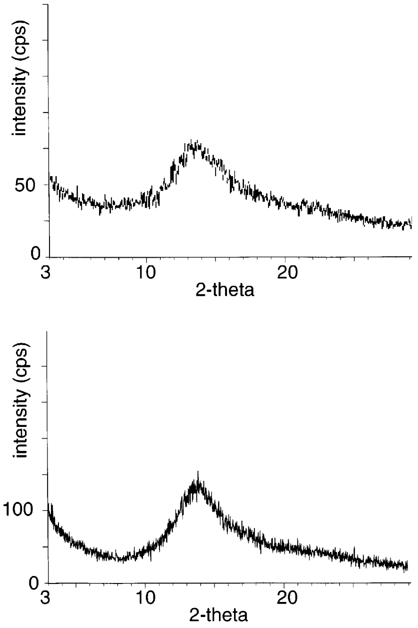


Figure 3. WAXS analysis of graft copolymer **5b**. The top trace is that of polymer **5b** after heating above the T_m of the PFDMS side chains, followed by rapid quenching with liquid nitrogen. The bottom trace is that of polymer **5b** after annealing at 80 °C for 24 h.

Thermogravimetric analysis (TGA) revealed a 10% weight loss by 400 °C and a ceramic yield of 22% at 1000 °C (Figure 4). Previous TGA studies of PFDMS hompolymer have shown that the polymer is thermally stable up to ca. 350 °C.[18] An initial weight loss of 50% occurred between 350 and 525 °C, followed by a subsequent weight loss of 14% between 575 and 650 °C. The ceramic yield at 1000 °C was found to be 36%. The thermal degradation of poly(chloromethylstyrene) and polystyrene has previously been studied.[19] Polystyrene was found to be thermally stable up to 300 °C, while poly(chloromethylstyrene) begins to decompose at approximately 285 °C with 70% weight loss having occurred by 560 °C. For polymer **5b**, the percent composition by weight of PFDMS side chains is 71% vs the PS-based backbone (29%). Therefore, assuming a negligible ceramic yield of PS-*b*-PCMS at 1000 °C, a ceramic

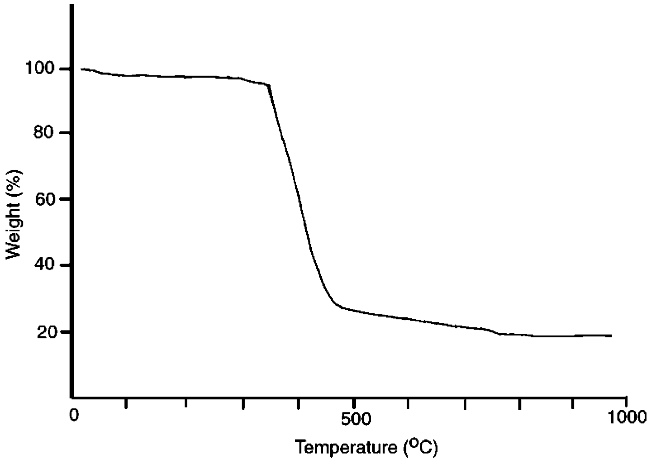


Figure 4. TGA of graft copolymer **5b** under an N_2 environment (heating rate = 10 °C/min).

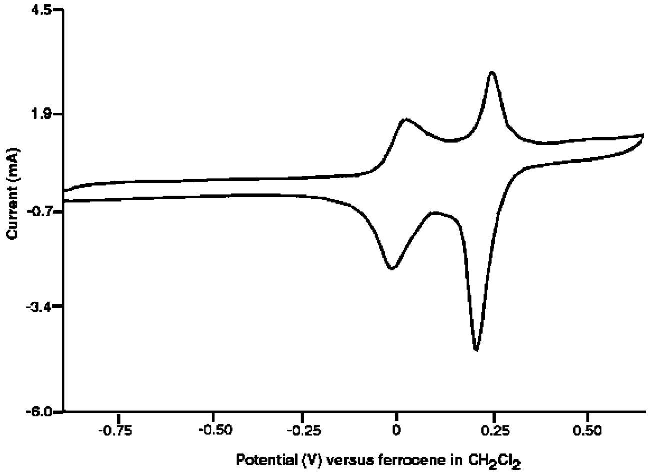


Figure 5. CV analysis of graft copolymer **5b** in CH_2Cl_2 (scan rate = 200 mV/s).

yield of approximately 26% should be obtained for **5b**, which is in reasonable agreement with the experimentally obtained value of 22%.

Cyclic Voltammetry of Graft Copolymer 5b. Polyferrocenylsilanes are redox active as the Fe(II) centers in the metallocene units can be oxidized to a cationic Fe(III) state. Previous cyclic voltammetry (CV) studies of polyferrocenylsilanes have shown the presence of two reversible oxidation waves in a 1:1 ratio, indicating the presence of iron−iron interactions along the polymer main chain.[20] This typical two-wave reversible pattern was also observed for graft copolymer **5b** in CH_2Cl_2 (Figure 5). The well-defined appearance of the waves may be due to the solubilizing effect of the PS-based backbone in CH_2Cl_2, as typically, wave shape can be significantly modified by electrode absorption in the case of PFS homopolymers.[21−23] The $E_{1/2}$ values for the first and second oxidation waves were $E_{1/2}(1) = +0.02$ and $E_{1/2}(2) = +0.25$ V (versus ferrocene), with a peak separation of a $\Delta E_{1/2}$ of 0.23 V. This peak separation is indicative of the degree of interaction between the metal centers and is consistent with the values previously reported for PFS homopolymers (0.16−0.29 V).[2,20−23] The two-wave pattern in the CV can be attributed to the fact that oxidation of alternating iron sites occurs first (at $E_{1/2}(1)$). Subsequent oxidation of the iron centers in between occurs at a higher potential ($E_{1/2}(2)$) as oxidation must occur adjacent to two previously oxidized sites (Figure 6).

Summary

The first examples of organic-organometallic polyferrocenylsilane-based graft copolymers have been synthesized by reacting living diphenylethylene-capped poly(ferrocenyldimethylsilane) with poly(styrene-*co*-chloromethylstyrene). In contrast to PFDMS homopolymers and block copolymers, the PFDMS side chains of these graft copolymers were found to possess a negligible, or at most a very low, degree of crystallinity by DSC and WAXS. The lack of crystallinity may be a function of the low grafting density of the PFDMS side chains onto the PS-based backbone. The synthesis of living DPE-capped PFDMS is a significant synthetic achievement, as this methodology may potentially provide access to block copolymers that have previously been unobtainable. For example, reducing the nucleophilicity of living anionic PFS chains by reacting them with sterically bulky DPE may allow subsequent reaction with functionalized monomers (e.g., acrylates) without undesirable side reactions. Work to explore these new possibilities is underway and will be reported in due course.

Experimental Section

All chemicals were purchased from Aldrich unless otherwise noted. THF was distilled from Na/benzophenone immediately prior to use. 12-Crown-4 was distilled and stored in a glovebox. *n*-Butyllithium (1.6 M in hexanes) was used as received from Aldrich. Tetramethylethylenediamine (TMEDA) was dried over sodium and distilled. Dilithioferrocene·$^2/_3$TMEDA was synthesized following the method of Bishop et al.[24] Chloromethylstyrene and styrene were purified as previously published.[12] The syntheses of the monomer **1** and of the polymers **2** and **3** were all performed following literature procedures.[2,12,13]

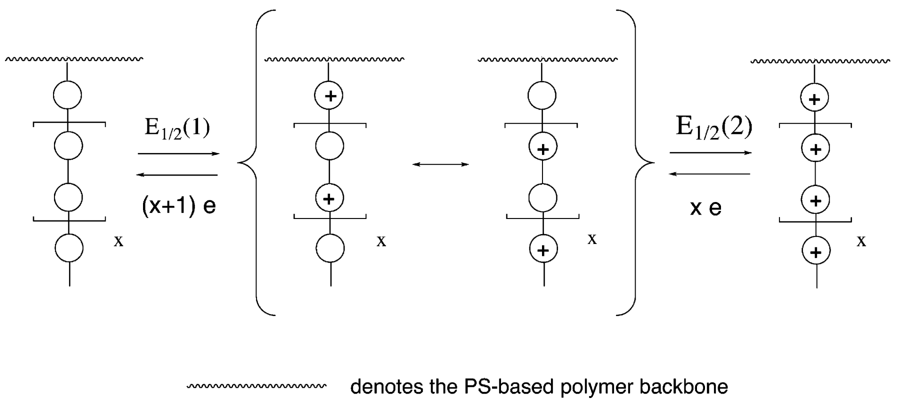


Figure 6. Schematic representation of the redox behavior of graft copolymer **5b**. $E_{1/2}(1) = +0.02$ V; $E_{1/2}(2) = +0.25$ V.

All reactions were performed under an inert atmosphere (prepurified N_2 or Ar) using either standard Schlenk techniques or a MBraun glovebox, and ^{1}H NMR spectra were recorded on a Varian Unity 400 spectrometer and referenced to either residual C_6H_6 at 7.15 ppm or CH_2Cl_2 at 5.3 ppm. Molecular weight estimates were obtained using gel-permeation chromatography (GPC) using a Waters Associates 2690 separations module equipped with a column heater, Ultrastyragel columns with pore sizes of 10^3-10^5 Å, in-line degasser, and a differential refractometer. The GPC possesses a triple detection system (refractive index, light scattering, viscosity) such that absolute molecular weights are reported for homopolymers. A flow rate of 1.0 mL/min was used and the eluent was THF. Polystyrene standards purchased from American Polymer Standards were used for calibrating the instrument response. Differential scanning calorimetry was performed using a TA Instruments differential scanning calorimeter. The instrument was calibrated at 10 °C/min using a traceable indium reference standard that has a melting point of 156.6 °C and heat of fusion of 28.71 J/g. Thermogravimetric analyses (TGA) were performed using a TA Instruments Q500 analyzer under a N_2 atmosphere at a scan rate of 10 °C/min. WAXS analyses were recorded by a Siemens D500 diffractometer equipped with a Cu Kα X-ray source. Cyclic voltammetry (CV) was performed using an Epsilon EC instrument equipped with a Pt electrode and an AgCl reference electrode. The polymer solution was prepared using CH_2Cl_2 (previously dried over CaH_2 and distilled under N_2) and $[NBu_4][PF_6]$ (previously recrystallized from EtOH and vacuum-dried). The polymer concentration was 3×10^{-4} M while the concentration of $[NBu_4][PF_6]$ was 0.1 M. All measurements were made under a N_2 atmosphere at a scan rate of 200 mV/s, and decamethylferrocene was added as an internal standard at the end of the experiment. Conversion of the reported potentials from the scale of decamethylferrocene to that of ferrocene involves the subtraction of 0.48 V.

Synthesis of PCMS-Based Polymers 2 and 3. Both the PCMS homopolymer **2** and the PS-*co*-PCMS copolymer **3** were synthesized by AIBN initiated free-radical polymerization in the bulk to which DPE was added. For **2**: $M_n = 32\,300$, PDI $= 1.52$. For **3**: $M_n = 29\,400$, PDI $= 1.54$, ratio PCMS:PS = 1:1.1.

Synthesis of DPE-Capped Polyferrocenylsilane 4. 290 mg (1.20 mmol) of **1** was dissolved in 3 mL of THF, and 75 μL of *n*-BuLi (0.12 mmol) was added to the solution as an initiator for the anionic polymerization of **1**. After 30 min at room temperature, 42 μL (0.24 mmol) of DPE was added, and the reaction mixture was heated to 50 °C for 3 h. During this time, the color of the solution changed from pale orange to dark red. To terminate the reaction, 0.5 mL of water was added, and the polymer was precipitated in methanol and dried under vacuum (270 mg, 85%). ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 0.21$ (s, Bu$-$Si(CH_3)$_2$), 0.49 (s, Si$-$$CH_3$), 0.62 (br, Bu), 0.88 (br, (Me of Bu), 1.35 (br, Bu), 3.42 (br, H), 4.04$-$4.25 (m, Cp), 7.05$-$7.42 (m, Ph). GPC: $M_n = 3580$, $M_w = 3660$, PDI $= 1.02$.

Synthesis of Poly(styrene-*co*-chloromethylstyrene-*graft*-ferrocenyldimethylsilane), 5a. In 4 mL of THF, 363 mg (1.50 mmol) of **1** was dissolved. 94 μL (0.15 mmol) of *n*-BuLi was added to this solution. After 30 min at room temperature, 53 μL of DPE (0.30 mmol) was added, and the solution was heated to 50 °C. Over the next 3 h, the solution changed from pale orange to deep red in color. 25 mg (~0.1 mmol of benzyl chloride functionalities) of **3** in 3 mL of THF was added to the solution dropwise at 0 °C. During this addition, the color of the solution changed to pale orange. The temperature of the solution was maintained at 0 °C for 3 h, and the reaction was left with stirring for 16 h. The resultant polymer was isolated by repeated precipitation into hexanes. Yield 20$-$25%. ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 0.22$ (s, Bu$-$Si(CH_3)$_2$), 0.48 (s, Si$-$$CH_3$), 0.65 (br, Bu), 0.89 (br, Bu), 1.33 (br, Bu), 1.33$-$1.80 (br, $-CH_2-CH$(Ph)$-$ + ($-CH_2-$C(Ph)$_2-$), 3.80 (br, CH_2Cl), 4.03$-$4.29 (m, Cp), 6.27 (br, aromatic PS-*co*-PCMS), 7.12 (br, $-$C(Ph)$_2$). GPC: $M_n = 67\,000$, $M_w = 101\,170$, PDI $= 1.51$.

Synthesis of Poly(styrene-*co*-chloromethylstyrene-*graft*-ferrocenyldimethylsilane), 5b. The synthesis of this graft copolymer is analogous to that of **5a** until the addition of DPE (53 μL, 0.30 mmol) to the living polymer solution which was performed after 20 min. The solution slowly changed color from pale orange to deep red; after 1 h, the temperature of the solution was reduced to 0 °C, and 25 mg of **3** (~0.1 mmol of benzyl chloride functionalities) in THF was added. The solution color changed from deep red to orange during this addition. The temperature of the solution was maintained at 0 °C for 3 h, and the reaction was left with stirring for 16 h. The graft copolymer **5b** was obtained upon repeated precipitation of a concentrated graft copolymer solution in THF into hexanes. Yield 20$-$25%. ^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 0.23$ (s, Bu$-$Si(CH_3)$_2$), 0.47 (s, Si$-$$CH_3$), 0.63 (br, Bu), 0.90 (br, Bu), 1.35 (br, Bu), 1.35$-$1.83 (br, $-CH_2-CH$(Ph)$-$ + ($-CH_2-$C(Ph)$_2-$), 3.88 (br, CH_2Cl), 4.05$-$4.26 (m, Cp), 6.30 (br, aromatic PS-*co*-PCMS), 7.15 (br, $-$C(Ph)$_2$). GPC: $M_n = 101\,480$, $M_w = 147\,150$, PDI $= 1.45$.

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