Transition Metal-Based Polymers with Controlled Architectures: Well-Defined Poly(ferrocenylsilane) Homopolymers and Multiblock Copolymers via the Living Anionic Ring-Opening Polymerization of Silicon-Bridged [1]Ferrocenophanes

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Abstract: The living anionic ring-opening polymerization (ROP) of the methylated silicon-bridged [1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiMe_2$ **1** initiated by *n*-BuLi, PhLi, FcLi (Fc = $Fe(\eta\text{-}C_5H_4)(\eta\text{-}C_5H_5)$), and 1,1′-dilithioferrocene, $fcLi_2 \cdot {}^2/_3TMEDA$ (fc = $Fe(\eta\text{-}C_5H_4)_2$) in THF at 20 °C has allowed the preparation of well-defined poly(ferrocenyldimethylsilanes) $[Fe(\eta\text{-}C_5H_4)_2SiMe_2]_n$ **4** with control of molecular weights, narrow polydispersities, and controlled end-group structures. The living anionic ROP of **1** has also been used to prepare a variety of novel, well-defined organometallic/organic/inorganic multiblock copolymers constructed from a combination of poly(ferrocenyldimethylsilane) (PFS), polystyrene (PS), and poly(dimethylsiloxane) (PDMS). The materials prepared included PFS-b-PDMS diblock copolymers (**7a** and **7b**), PDMS-b-PFS-b-PDMS triblock copolymers (**8a** and **8b**), a PS-b-PFS diblock copolymer (**10a**), a PS-b-PFS-b-PDMS triblock copolymer (**11**), a PS-b-PFS-b-PDMS-b-PFS-b-PS pentablock copolymer (**12**), a PFS-b-PS-b-PFS triblock copolymer (**15**), and a PDMS-b-PFS-b-PS-b-PFS-b-PDMS pentablock copolymer (**16**). These materials were studied by cyclic voltammetry which afforded two reversible oxidation waves characteristic of redox-coupling arising from interactions between the skeletal iron atoms in the ferrocenylsilane blocks. The multiblock copolymers were also characterized by DSC which showed the presence of individual thermal transitions for each block which indicated that they were incompatible. In addition, the morphology of a film of PS-b-PFS (**10a**) was investigated by TEM which showed a high degree of phase separation leading to the formation of microdomains of polystyrene and poly(ferrocenyldimethylsilane).

Introduction

Well-characterized, high molecular weight transition metal-based polymers are attractive materials because of their potentially novel physical and catalytic properties and their possible applications.[1−4] However, in general, most synthetic routes to these materials involve polycondensation reactions which often utilize difunctional monomers (e.g., dilithiated species) which are poorly-defined or difficult to purify.[3] Although exceptions exist, the resulting polymers are usually of low molecular weight and therefore do not permit access to the advantageous processability characteristics of macromolecules. In addition, many of the transition metal-based polymers reported in the literature are insoluble and poorly characterized. As a consequence of these synthetic problems it is therefore not surprising that high molecular weight examples of these materials with well-defined and controlled architectures[5] (e.g., monodisperse polymers and multiblock structures) are virtually nonexistent.[6−8]

Chain growth polymerization represents a promising alternative method for accessing transition metal-based macromolecules which circumvents the stringent stoichiometry and conversion requirements which often impede the preparation of high molecular weight polymers via condensation routes.[3] For example, homopolymers and block copolymers with ferrocene units in the side group structure have been synthesized *via* the living metathesis polymerizations of norbornene derivatives and acetylenes containing ferrocenyl substituents.[7] In addition, the preparation of poly(vinylferrocene) *via* the living anionic

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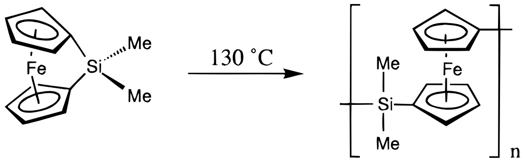
polymerization of vinyl ferrocene at low temperatures has also been reported.[8] The ferrocene units in the side group structure of the resulting materials behave as independent, electronically isolated units. Thus, the iron atoms do not interact with one another, and the electrochemical behavior of the polymers is quite similar to that of ferrocene itself.

We are particularly interested in the development of ring-opening polymerization (ROP) routes to transition metal-based polymers in which the metal atoms are in close proximity to one another in the main chain. This may permit interactions which lead to interesting electronic or magnetic properties. In 1992 we reported the discovery that strained, ring-tilted silicon-bridged [1]ferrocenophanes (e.g., **1**) undergo thermal ROP to yield high molecular weight ($M_n > 10^5$) poly(ferrocenylsilanes) (e.g., **2**) in which the iron atoms exhibit redox-coupling and clearly interact with one another.[9,10] Subsequent papers have described the extension of this thermal ROP route to other strained [1]- and [2]metallocenophanes and have also detailed the interesting electrochemical, preceramic, morphological, and (when oxidized) magnetic properties that the resulting polymers (e.g., **2**) possess.[11−19]



1 **2**

Although the thermal ROP route to polymers such as **2** is convenient, no control over molecular weight is possible, and the molecular weight distributions of the polymer products are fairly broad. In addition, termination processes operate, and thus no possibility exists to prepare materials such as block copolymers.[20] We have therefore explored the use of alternative methods for the ROP of **1**.[21] The living anionic ROP of hexamethylcyclotrisiloxane, [Me$_2$SiO]$_3$,[22,23] is well-known and has been used to prepare materials with a variety of architectures. Anionically-induced ROP has also been established for a range of organosilicon rings, including cyclosilapentenes and cyclosilabutanes[24,25] and cyclotetrasilanes.[26,27] This prompted us to explore the reaction of **1** with anionic initiators. We found that equimolar quantities of **1** and ferrocenyllithium FcLi afforded linear oligo(ferrocenylsilanes) with between 2 and 9 repeat units.[28] We have subsequently found that in the presence of small quantities of anionic initiators anionic ROP occurs and living polymerizations are possible.[29] To our knowledge, this process represents the first living polymerization of a metal-containing monomer to afford polymers with transition metal atoms in the main chain. In this paper we report full details of our work on the living anionic ROP of **1** including the preparation and characterization of a variety of unprecedented block copolymer structures.

Experimental Details

Equipment and Materials. All the reactions were performed under an inert atmosphere (prepurified N$_2$ or Ar) using either standard Schlenk techniques or a Vacuum Atmospheres glovebox. All of the living anionic polymerization reactions were performed in a Vacuum Atmospheres glovebox purged with prepurified N$_2$. THF was distilled from Na/benzophenone immediately prior to use. All the chemicals were purchased from Aldrich unless otherwise noted. Hexanes were distilled from Na immediately prior to use. Me$_3$SiCl and Me$_2$SiCl$_2$ were distilled immediately prior to use. Distilled H$_2$O was degassed prior to use. Styrene was distilled under reduced pressure from CaH$_2$ and CuCl twice prior to use. Hexamethylcyclotrisiloxane, [Me$_2$SiO]$_3$, was sublimed at room temperature under a static vacuum prior to use. 12-Crown-4 was dried using activated molecular sieves and was then stored in a glovebox. The monomeric [1]silaferrocenophane **1** was prepared by a modification of a previously reported procedure.[30] *n*-BuLi (1.6 M in hexanes) and PhLi (1.8 M in hexanes) were titrated prior to use by addition from a 1000 μL syringe to menthol and 1,10-phenanthroline as an indicator. Ferrocenyllithium, FcLi,[31] and 1,1′-dilithioferrocene, fcLi$_2$·$^2/_3$TMEDA[32] were prepared by literature methods and were recrystallized from THF at −40 °C prior to use. Lithium naphthalide (THF solution) was freshly prepared by reacting naphthalene (0.705 g, 5.5 mmol) with lithium metal (38 mg, 5.5 mmol) in 20 mL of THF under argon at room temperature. The concentration of the lithium naphthalide solution was established based on the M_n of polystyrene which was formed using this solution as an initiator.

The 200- or 400-MHz ^{1}H-NMR spectra and 50.3- or 100.5 MHz ^{13}C-NMR spectra were recorded with a Varian Germini 200 or a Varian

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XL 400 spectrometer, respectively. The 79.5-MHz ^{29}Si-NMR spectra were recorded on a Varian XL 400 spectrometer utilizing a DEPT pulse sequence (proton decoupled) with a $^2J_{Si-H}$ coupling of 6.7 Hz and were referenced externally to $SiMe_4$. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates Liquid Chromatograph equipped with a 510 HPLC pump, U6K injector, ultrastyragel columns with a pore size of 10^3 and 10^5 Å, and a Waters 410 differential refractometer. A flow rate of 1.0 mL/min was used, and samples were dissolved in a solution of 0.1% tetra-*n*-butylammonium bromide in THF. The GPC was calibrated by nine monodisperse (PDI < 1.1) polystyrene standards (retention time (min)/M_w: 10.8/1.0 $\times 10^6$, 11.2/6.0 $\times 10^5$, 12.0/2.0 $\times 10^5$, 13.7/6.3 $\times 10^4$, 15.2/2.0 $\times 10^4$, 16.5/9.0 $\times 10^3$, 17.4/4.0 $\times 10^3$, 18.1/2.0 $\times 10^3$, 19.1/1.0 $\times 10^3$). Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

Cyclic voltammograms were recorded with a PAR Model 273 potentiostat. A Pt working electrode, and a Ag wire reference electrode in a Luggin capillary were used. All potentials are relative to the ferrocene/ferrocenium ion couple at 0.00 V, which was used as an internal reference. CH_2Cl_2 and MeCN solvents were freshly distilled from P_2O_5, anhydrous grade $[Bu_4N][PF_6]$ (Aldrich) was used as supporting electrolyte (0.100 M), and the analyses were carried out under prepurified N_2. Cyclic voltammograms of the block copolymers were obtained using 10 mg of sample dissolved in 10 mL of solution comprising 4:1 (by volume) CH_2Cl_2:MeCN at scan rates of 25, 50, 100, 250, 500, and 1000 mVs^{-1} at 22 °C.

A Perkin-Elmer DSC-7/Unix instrument equipped with a TAC 7 instrument controller was used to study the thermal behavior. The thermograms were calibrated with the melting transitions of *n*-heptane or *n*-decane and indium and were obtained at a heating rate of 10 °C/min from −160 °C to 150 °C. A Perkin-Elmer TGA-7/Unix instrument equipped with a TAC-7 instrument controller was used to study the polymer thermal stability. Thermograms were calibrated with the magnetic transitions of Nicoseal and Perkalloy and were obtained at a heating rate of 10 °C/min under N_2.

Electron photomicrographs were obtained on a HITACHI Model H-600 AB transmission electron microscope with a 100 kV, 25 μÅ beam current. Ultrathin sections of cast films of **10a** were cut to ca. 70 μm thickness.

Synthesis of [1]Silaferrocenophane 1. Over a period of 5 min 4.6 mL of Me_2SiCl_2 (38 mmol) was added dropwise to a suspension of 10.0 g of $fcLi_2 \cdot {}^2/_3$TMEDA (36.4 mmol) in 500 mL of diethyl ether at −30 °C during which the reaction mixture changed from orange-yellow to red. The reaction mixture was then slowly left to warm to 20 °C over 2 h and filtered, and solvent and excess Me_2SiCl_2 were removed under vacuum. The crude product was then sublimed at room temperature onto a cold probe. Thus 6.98 g (79%) of red crystalline [1]ferrocenophane **1** was obtained.

Further purifications to obtain a product of “high purity” suitable for living anionic polymerizations consisted of alternating recrystallizations from hexanes (−15 °C) and high vacuum sublimations (0.005 mm, 40 °C) until no impurities could be observed by ^{1}H-NMR (generally three recrystallizations and three sublimations were required). ”High purity” implies that no signals other than those for the [1]ferrocenophane and benzene were observed in a 20× expansion of the vertical scale of the ^{1}H-NMR spectrum of a solution containing 10 mg of [1]silaferrocenophane **1** in 0.5 mL of C_6D_6. ^{1}H-NMR (200 MHz, C_6D_6) is included for comparison: 0.51 (s, 6H, Me), 4.08 (t, J_{H-H} = 1.7 Hz, 4H, Cp), 4.48 (t, J_{H-H} = 1.7 Hz, 4H, Cp) ppm.

Anionic ROP of [1]Silaferrocenophane 1 Initiated by FcLi. FcLi was generated *via* the reaction of 1:2 mol ratio of FcHgCl:*n*-BuLi in THF for 5 min.[31] The ROP reaction was carried out by the rapid addition of the 0.40 M FcLi solution in THF to a solution of **1** in 2 mL of THF. The reaction was terminated by the addition of a few drops of H_2O or 10 μL (0.079 mmol) of Me_3SiCl. The polymer product **4** was isolated by precipitation into hexanes and was dried under high vacuum for 18 h. (Table 1).

Anionic ROP of [1]Silaferrocenophane 1 Initiated by PhLi. The reaction was carried out by the addition of PhLi (0.18 M in THF) to a solution of **1** in 2 mL of THF. The reaction was terminated by the addition of a few drops of H_2O. The polymer product **4** was isolated by precipitation into hexanes and was dried under high vacuum for 18 h (Table 2).

Table 1. Anionic ROP of **1** Initiated by 0.40 M FcLi

run	M:I	monomer used (mg)	initiator used (μL)	reaction time (min)	M_n calculated ($\times 10^3$)	M_n found ($\times 10^3$)	PDI	isolated yield (%)
1	20:1	44	23	15	4.8	4.0	1.02	50
2	35:1	50	15	15	8.5	7.9	1.11	61
3	50:1	49	10	15	12	13	1.26	64

Table 2. ROP of **1** Initiated by 0.18 M PhLi

run	M:I	monomer used (mg)	initiator used (μL)	reaction time (min)	M_n calculated ($\times 10^3$)	M_n found ($\times 10^3$)	PDI	isolated yield (%)
1	52:1	50	22	15	13	18	1.25	85
2	91:1	100	25	15	22	34	1.19	76

Table 3. Anionic ROP of **1** Initiated by 0.18 *n*-BuLi

run	M:I	monomer used (mg)	initiator used (μL)	reaction time (min)	M_n calculated ($\times 10^3$)	M_n found ($\times 10^3$)	PDI	isolated yield (%)
1	10:1	44	100	15	2.4	1.8	1.10	45
2	20:1	50	57.4	15	4.8	3.8	1.08	63
3	40:1	50	28.7	15	9.7	8.1	1.05	65
4	75:1	100	30.6	15	18	14	1.05	45
5	100:1	150	34.4	60	24	22	1.05	62
6	130:1	200	35.3	60	31	30	1.05	59
7	170:1	200	27.0	90	41	47	1.08	68
8	208:1	260	28.7	90	50	54	1.09	56
9	259:1	260	23.0	90	63	83	1.10	54

Table 4. Further Addition of Monomer **1** to the Polymerization Solution[a]

run	M:I	monomer used (mg)	initiator used (μL)	reaction time (min)	M_n calculated ($\times 10^3$)	M_n found ($\times 10^3$)	PDI	isolated yield (%)
1a	47:1	49	27	15	11	12	1.15	
1b	48:1	50		15	23	27	1.15	95
2a	50:1	50	23	15	12	16	1.20	
2b	57:1	57		15	26	27	1.47	97

[a] The runs 1a and 2a were initiated by 0.16 M *n*-BuLi and 0.18 M PhLi, respectively. Runs 1b and 2b represent the experiments after the addition of more monomer **1** to the products from run 1a and 1b, respectively.

Anionic ROP of [1]Silaferrocenophane 1 Initiated by *n*-BuLi. The reaction was carried out by the addition of *n*-BuLi (0.18 M in hexanes) to a solution of **1** in 2 mL of THF. The reaction was terminated by the addition of a few drops of H_2O. The polymer product **4** was isolated by precipitation into hexanes and was dried under high vacuum for 18 h (Table 3).

Further Addition of Monomer 1 to the Living Polymerization Solution. After the first part of the polymerization was complete (in 2 mL of THF) a few drops of the reaction solution were precipitated into hexanes to run a GPC. An additional amount of monomer **1** was then added into the living polymer solution. After full conversion as judged by a color change from red to amber, the resulting living polymer was quenched by the addition of few drops of H_2O. The polymer product **4** was isolated by precipitation into hexanes and was dried under high vacuum for 12 h (Table 4).

Anionic ROP of [1]Silaferrocenophane 1 Initiated by $fcLi_2 \cdot {}^2/_3$TMEDA. Based on X-ray diffraction studies we assumed $^2/_3$ equiv of TMEDA chelating to $fcLi_2$.[33] A solution of 0.046 M $fcLi_2 \cdot {}^2/_3$TMEDA in THF was stored in a glovebox at −40 °C and used within one week.

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Table 5. Anionic ROP of **1** Initiated by 0.046 M fcLi$_2$·$^2/_3$TMEDA

run	M:I	monomer used (mg)	initiator used (μL)	reaction time (min)	M_n calculated ($\times 10^3$)	M_n found ($\times 10^3$)	PDI	isolated yield (%)
1	45:1	50	100	15	11	8	1.09	84
2	95:1	53	50	15	23	18	1.07	100
3	136:1	50	33	20	33	27	1.06	46
4	180:1	100	50	50	44	34	1.10	75
5	272:1	100	33	60	66	51	1.22	100
6	355:1	190	48	90	86	70	1.09	69

The polymerization **1** (in 2 mL of THF) was initiated by the addition of 0.046 M fcLi$_2$·$^2/_3$TMEDA. After 30 min the living polymer **5** was terminated by the addition of a few drops of H_2O to yield poly(ferrocenylsilane) **6** which was isolated by precipitation into hexanes and dried under high vacuum for 12 h (Table 5).

Synthesis of the Diblock Copolymers PFS$_{20}$-PDMS$_{39}$ (7a) and PFS$_{50}$-PDMS$_{99}$ (7b). A similar procedure was used for the synthesis of **7a** and **7b**, and a representative procedure is given for the synthesis of **7a**.

A solution (26 μL) of *n*-BuLi in hexanes (1.6 M, 0.042 mmol) was injected into a red solution of 200 mg (0.83 mmol) of [1]silaferrocenophane **1** in 2 mL of THF. The solution gradually changed from red to amber over 5 min. After 15 min 186 mg of $[Me_2SiO]_3$ (0.84 mmol) was added and stirred an additional 30 min. The reaction was then quenched by the addition of 20 μL (0.15 mmol) of Me_3SiCl, and the polymer **7a** was isolated by precipitation into methanol and filtration, and was then dried under high vacuum for 18 h. Thus 302 mg (78%) of the yellow powdery diblock copolymer **7a** was isolated. $M_w = 8.9 \times 10^3$, $M_n = 7.7 \times 10^3$, PDI = 1.15, (calculated $M_n = 7.7 \times 10^3$).

For **7b**: 200 mg of [1]silaferrocenophane **1** (0.83 mmol), 10 μL of 1.6 M *n*-BuLi (0.016 mmol), 186 mg of $(Me_2SiO)_3$ (0.84 mmol), and 10 μL Me_3SiCl (0.070 mmol) were used. The yellow powdery copolymer **7b (**278 mg**,** 72%) was isolated; $M_w = 2.4 \times 10^4$, $M_n = 2.1 \times 10^4$, PDI = 1.13, (calculated $M_n = 1.9 \times 10^4$).

For **7a** and **7b**: ^{29}Si-NMR (79.5 MHz, C_6D_6) 7.6 ($-OSiMe_3$), 0.7 $-(\eta\text{-}C_5H_4)_2FeSiMe_2O-$, -1.9 $BuMe_2Si-$, -6.4 $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_x$, and -21.4 ppm $[Me_2SiO]_{3y}$. ^{13}C-NMR (100.6 MHz, C_6D_6) 73.7 (Cp), 72.1 (Cp, *ipso*-C), 71.8 (Cp), 1.4 $[Me_2SiO]_{3y}$ and -0.5 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$. ^{1}H-NMR (400 MHz, C_6D_6) 4.10, 4.26 (Cp), 0.54 $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$, and 0.28 ppm $[Me_2SiO]_{3y}$. ^{1}H-NMR integration gave for **7a** $x = 20$, $y = 13$ and for **7b** $x = 50$, $y = 33$. Anal. Calcd for **7b**: C, 49.7; H, 6.7. Found: C, 49.6; H, 6.7.

Synthesis of the Triblock Copolymers PDMS$_{72}$-PFS$_{48}$-PDMS$_{72}$ (8a) and PDMS$_{108}$-PFS$_{100}$-PDMS$_{108}$ (8b). A 0.040 M solution of fcLi$_2$·$^2/_3$TMEDA in THF was prepared and stored at -40 °C. A similar procedure was used for the synthesis of **8a** and **8b**, and a representative procedure is given for the synthesis of **8a**.

A 0.040 M solution (52 μL) of fcLi$_2$·$^2/_3$TMEDA in THF (2.1×10^{-3} mmol) was injected into a solution of 25 mg of [1]silaferrocenophane **1** (0.10 mmol) in 2 mL of THF. The reaction mixture gradually changed from red to amber over 10 min. The reaction was allowed to stir for ca. 15 min. One drop of 12-crown-4 and 2 mL of THF was then added to the solution before the addition of 24 mg of $(Me_2SiO)_3$ (0.11 mmol). The reaction mixture became increasingly viscous and was almost immobile after 30 min. After the addition of 25 μL (0.20 mmol) of Me_3SiCl the reaction mixture immediately became mobile again. The resulting polymer **8a** was isolated by precipitation into methanol and filtration and was dried at high vacuum for 18 h. Thus 20 mg (21%) of the orange-yellow powdery triblock copolymer **8a** was isolated. $M_w = 1.6 \times 10^4$, $M_n = 1.4 \times 10^4$, PDI = 1.15, (calculated $M_n = 1.9 \times 10^4$).

For **8b**: 52 μL of 0.040 M fcLi$_2$·$^2/_3$TMEDA (2.1×10^{-3} mmol) in THF, 52 mg of [1]silaferrocenophane **1** (0.21 mmol), 45 mg of $(Me_2SiO)_3$ (0.20 mmol), and 25 μL of Me_3SiCl (0.20 mmol) was used. The orange-yellow powdery triblock copolymer **8b (**40 mg, 28%) was isolated. $M_w = 3.0 \times 10^4$, $M_n = 2.7 \times 10^4$, PDI = 1.09, (Calculated $M_n = 3.6 \times 10^4$).

For **8a** and **8b**: ^{29}Si-NMR (79.5 MHz, C_6D_6) 7.6 ($-OSiMe_3$), 0.7 $-(\eta\text{-}C_5H_4)_2FeSiMe_2O-$, -6.4 $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_x$ and -21.4 ppm $[Me_2SiO]_{3y}$. ^{13}C-NMR (100.6 MHz, C_6D_6) 73.7 (Cp), 72.1 (Cp, *ipso*-C), 71.8 (Cp), 1.4 $[Me_2SiO]_{3y}$ and -0.5 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$. ^{1}H-NMR (200 MHz, CD_2Cl_2) 4.02, 4.23 (Cp), 0.47 $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$ and 0.10 ppm $[Me_2SiO]_{3y}$. ^{1}H-NMR integration gave for **8a** $x = 24$, $y = 24$ and for **8b** $x = 50$, $y = 36$.

Synthesis of the Diblock Copolymers PS$_{100}$-PFS$_{98}$ (10a) and PFS$_{90}$-PS$_n$ (10b). For **10a**: 48.5 μL of a *n*-BuLi solution (0.18 M , 8.7×10^{-3} mmol) was injected into a solution of 100 μL of styrene (0.87 mmol) in 2 mL of THF upon which the typical yellow color of living polystyryl anions could be observed. After 5 min 205 mg of the [1]silaferrocenophane (**1**) (0.85 mmol) was added. The solution changed gradually from red to amber over 15 min. The living polymer **9** was terminated by the addition of two drops of H_2O, and polymer **10a** was isolated by precipitation into hexanes, filtration and drying at high vacuum for 18 h. The yellow powdery diblock copolymer **10a** (203 mg, 69%) was isolated. $M_w = 4.4 \times 10^4$, $M_n = 4.0 \times 10^4$, PDI = 1.08, (Calculated $M_n = 3.4 \times 10^4$).

For **10b**: *n*-BuLi 48.5 μL, 0.18 M (8.7×10^{-3} mmol) was rapidly injected into a red solution of 200 mg of the [1]silaferrocenophane **1** (0.82 mmol) in 2 mL of THF upon which the solution gradually changed from red to amber over 15 min. Then 100 μL (0.87 mmol) of styrene was injected into the living poly(ferrocenyldimethylsilane) solution. After stirring for an additional 15 min the reaction was terminated by the addition of two drops water. Precipitation in hexanes, filtration and drying under high vacuum for 18 h yielded 245 mg (84%) of the light orange-yellow powdery product **10b** for which a bimodal molecular weight distribution was observed by GPC. Higher molecular weight fraction $M_w = 2.4 \times 10^5$, $M_n = 1.8 \times 10^5$, PDI = 1.32; lower molecular weight fraction $M_w = 2.2 \times 10^4$, $M_n = 2.2 \times 10^4$, PDI = 1.02.

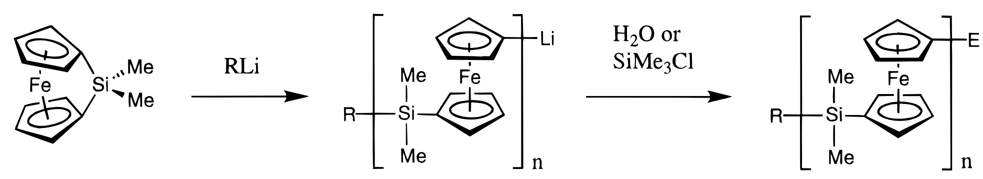
For **10a** and **10b**: ^{29}Si-NMR (79.5 MHz, CD_2Cl_2) -1.2 $-(\eta\text{-}C_5H_4)_2FeSiMe_2CHPh$, and -4.6 ppm $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_y$. ^{13}C-NMR (100.6 MHz, CD_2Cl_2) 147.0$-$145.0 (Ph, *ipso*-C), 128.3 (Ph, m), 128.0 (Ph, o), 126.0 (Ph, p), 73.5 (Cp), 72.0 (Cp C-Si), 71.6 (Cp), 47.0$-$40.9 (CH_2), 40.8 (C*H*Ph) and -0.9 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$. ^{1}H-NMR (300 MHz, CD_2Cl_2): 6.60, 7.10 (br. Ph), 4.23, 4.03 (Cp), 1.82 (br, CHPh), 1.45 (br, CH_2) and 0.48 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_y$. ^{1}H-NMR integration gave for **10a** $x = 100$, $y = 98$. Anal. Calcd for **10a**: C, 69.5; H, 6.4. Found: C, 68.8; H, 7.0.

Synthesis of the Pentablock Copolymers *n*-Bu-PS$_{100}$-PFS$_{38}$-PDMS$_{120}$-PFS$_{38}$-PS$_{100}$-*n*-Bu (12). BuLi (8.3×10^{-3} mmol, 52 μL, 0.16 M) in hexanes was rapidly injected into a solution of 95 μL styrene (0.83 mmol) in 4 mL of THF upon which a yellow color appeared immediately. After 5 min 98 mg of [1]silaferrocenophane **1** (0.40 mmol) was added at once with stirring. The reaction mixture changed from red to amber in 15 min. One drop of 12-crown-4 and 4 mL of THF was added before the quick addition of 95 mg of $(Me_2SiO)_3$ (0.43 mmol) upon which the reaction mixture became increasingly viscous. After 30 min, a few drops of the reaction mixture were precipitated into hexanes. The molecular weight of this precipitated triblock copolymer **11** was estimated by GPC. $M_w = 2.6 \times 10^4$, $M_n = 2.3 \times 10^4$, PDI = 1.11 (calculated $M_n = 3.3 \times 10^4$). While stirring, to the remaining reaction mixture was slowly added 7.0 μL of 0.60 M Me_2SiCl_2 (4.2×10^{-3} mmol) in hexane over a period of 15 min. The resulting polymer **12** was isolated by precipitation into methanol and filtration and was dried under high vacuum for 18 h. Thus 176 mg (63%) of the yellow powdery ABCBA pentablock copolymer **12** was isolated. $M_w = 7.7 \times 10^4$, $M_n = 6.0 \times 10^4$, PDI = 1.28, (calculated $M_n = 4.8 \times 10^4$).

For **12**: ^{29}Si-NMR (79.5 MHz, CD_2Cl_2) 2.5 $-(\eta\text{-}C_5H_4)_2FeSiMe_2O-$, -1.2 $-(\eta\text{-}C_5H_4)_2FeSiMe_2CHPh$, -4.6 $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_y$ and -19.6 ppm $[Me_2SiO]_{3z}$. ^{13}C-NMR (100.6 MHz, CD_2Cl_2) 147.0$-$145.0 (Ph, *ipso*-C), 128.3 (Ph, m), 128.0 (Ph, o), 126.0 (Ph, p), 73.5 (Cp), 72.0 (Cp, *ipso*-C), 71.6 (Cp), 47.0$-$40.9 (CH_2), 40.8 (C*H*Ph), 1.2 $[Me_2SiO]_y$ and -0.9 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$. ^{1}H-NMR (200 MHz, CD_2Cl_2) 7.10, 6.60 (br, Ph), 4.23, 4.03 (Cp), 1.82 (br, C*H*Ph), 1.45 (br, CH_2), 0.48 $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_y$, and 0.08 ppm $[Me_2SiO]_{3z}$. ^{1}H-NMR integration gave for **12** $x = 100$, $y = 38$, $z = 20$.

Synthesis of the Triblock Copolymers PFS$_{35}$-PS$_{86}$-PFS$_{35}$ (15). The concentration of the lithium naphthalide initiation solution used in this experiment was back calculated from the polymerization of styrene at -40 °C. A THF solution (4 mL) of 100 μL (0.87 mmol) of styrene at -40 °C was added quickly to a solution of 14 μL of the prepared deep blue lithium naphthalide solution upon which the styrene solution turned

Scheme 1



1 **3** **4**

R = Fc, Ph , or *n*-Bu

E = H or SiMe$_3$

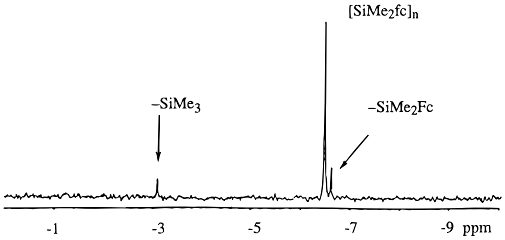


Figure 1. 79.8 MHz ^{29}Si-NMR spectrum of trimethylsilyl terminated poly(ferrocenylsilane) **4** (R = Fc, E = SiMe$_3$, $M_n = 4.0 \times 10^3$), PDI = 1.02 in C_6D_6.

yellow immediately. After stirring for 15 min the living polystyrene was terminated by the addition of a few drops of H_2O and isolated by precipitation into hexanes. GPC analysis gave $M_n = 4.2 \times 10^4$, PDI = 1.10, from which the initial lithium naphthalide initiation solution was calculated to be 0.15 M.

Lithium naphthalide in THF (0.010 mmol, 70 μL, 0.15 M) was rapidly injected into a solution of 100 μL of styrene (0.87 mmol) in 4 mL of THF at −40 °C after which the solution became deep yellow immediately. After warming to room temperature 205 mg (0.85 mmol) of [1]silaferrocenophane **1** was added at once while stirring. The resulting red solution gradually changed to amber over 15 min. After 20 min the living polymer **14** was terminated by the addition of 2 drops of H_2O and polymer **15** was then isolated by precipitation into methanol, filtration, and was dried under high vacuum for 18 h. Thus 251 mg (85%) of the orange-yellow powdery BAB triblock copolymer **15** was isolated. $M_w = 3.1 \times 10^4$, $M_n = 2.8 \times 10^4$, PDI = 1.11 (calculated $M_n = 2.6 \times 10^4$).

For **15**: ^{29}Si-NMR (79.5 MHz, CD_2Cl_2) −1.2 $-(\eta\text{-}C_5H_4)_2FeSiMe_2$-CHPh and −4.6 ppm $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_y$. ^{13}C-NMR (100.6 MHz, CD_2Cl_2) 147.0−145.0 (Ph, *ipso*-C), 128.3 (Ph, m), 128.0 (Ph, o), 126.0 (Ph, p), 73.5 (Cp), 72.0 (Cp, *ipso*-C), 71.6 (Cp), 47.0−40.9 (CH_2), 40.8 (C*H*Ph), and −0.9 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$. ^{1}H-NMR (200 MHz, CD_2Cl_2): 7.10, 6.70 (br, Ph), 4.25, 4.05 (Cp), 1.85 (br, CHPh), 1.50 (br, CH_2) and 0.50 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_y$. ^{1}H-NMR integration gave for **15** $x = 43$, $y = 35$. Calcd C, 70.5; H, 6.5. Found: C, 69.4; H, 6.4.

Synthesis of the Pentablock Copolymers Me_3Si-$PDMS_{111}$-PFS_{47}-PS_{86}-PFS_{47}-$PDMS_{111}$-$SiMe_3$ (16). Lithium naphthalide in THF (0.010 mmol, 70 μL, 0.15 M) was rapidly injected into a solution of 100 μL of styrene (0.87 mmol) in 4 mL THF at −40 °C resulting in a deep yellow color. After warming to room temperature 237 mg of [1]silaferrocenophane **1** (0.98 mmol) was added at once while stirring. The red reaction mixture gradually changed to amber over 15 min. One drop of 12-crown-4 and 2 mL of THF was then added to the reaction mixture followed by the addition of 198 mg of $[Me_2SiO]_3$ (0.89 mmol). The reaction mixture became increasingly viscous until it was almost immobile after 30 min. Then 2 drops of Me_3SiCl were added upon which the reaction mixture immediately became mobile again. The resulting polymer **16** was isolated by precipitation into methanol and drying under high vacuum for 18 h which yielded 367 mg (68%) of the yellow powdery pentablock copolymer **16**. $M_w = 6.2 \times 10^4$, $M_n = 5.3 \times 10^4$, PDI = 1.17 (calculated $M_n = 4.8 \times 10^4$).

For **16**: ^{29}Si-NMR (79.5 MHz, C_6D_6) 7.6 $-OSiMe_3$, 0.7 $-(\eta\text{-}C_5H_4)_2$-$FeSiMe_2O-$, −1.2 $-(\eta\text{-}C_5H_4)_2FeSiMe_2CHPh$, −6.4 $[(\eta\text{-}C_5H_4)_2FeSiMe_2]_y$ and −21.4 ppm $[Me_2SiO]_{3z}$. ^{13}C-NMR (100.6 MHz, CD_2Cl_2) 147.0−145.0 (Ph, *ipso*-C), 128.3 (Ph, m), 128.0 (Ph, o), 126.0 (Ph, p), 73.5 (Cp), 72.0 (Cp, *ipso*-C), 71.6 (Cp), 47.0−40.9 (CH_2), 40.8 (C*H*Ph), 1.2 $[Me_2SiO]_{3z}$, and −0.9 ppm $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_x$. ^{1}H-NMR (200 MHz, CD_2Cl_2) 7.10, 6.60 (br. Ph), 4.23, 4.13 (Cp), 1.82 (br, CHPh), 1.45 (br, CH_2), 0.48 $[(\eta\text{-}C_5H_4)_2FeSi\mathit{Me}_2]_y$ and 0.08 ppm $[Me_2SiO]_{3z}$. ^{1}H-NMR integration gave for **16** $x = 43$, $y = 47$, $z = 37$.

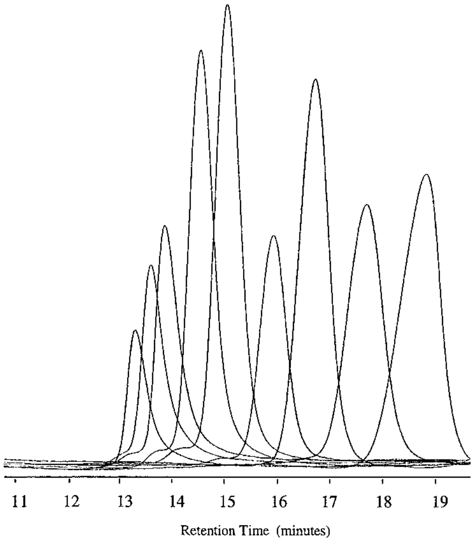


Figure 2. GPC traces of polymer **4** (R = *n*-Bu, E = H) initiated by *n*-BuLi with different mole ratios of monomer:initiator.

Results and Discussion

A living polymerization system should be free of chain transfer and termination reactions.[34,35] This represents an ideal case, as in real systems chain-breaking reactions do exist. Recently, Matyjaszewski proposed a quantitative ranking for “living” systems.[36] Our approach toward investigating the livingness of the anionically initiated [1]silaferrocenophane system was to carry out several experiments which included (i) the generation of a plot of M_n versus the monomer: initiator ratio to show that it is linear; (ii) further addition of monomer to the living polymer solution to demonstrate that the expected molecular weight increase is observed, and (iii) demonstrations of synthetic control of the end group structures and the synthesis of block copolymers with narrow molecular weight distributions.

Anionic ROP of [1]Silaferrocenophane 1 with the Different Initiators. Reaction of **1** with FcLi in THF at 25 °C for 15 min followed by quenching of the living polymer **3** with either H_2O or Me_3SiCl yielded the H or $SiMe_3$ terminated poly(ferrocenyldimethylsilane) **4** (E = H, $SiMe_3$, respectively) (Scheme 1). The molecular weights of **4** could be controlled from $M_n = 4.0 \times 10^3 - 1.3 \times 10^4$ with narrow polydispersities ($M_w/M_n = 1.02 - 1.26$) by varying the monomer:initiator ratio from 20:1 to 50:1. Our experiments are documented in Table 1. The polymer products **4** gave ^{29}Si-, ^{1}H-, and ^{13}C NMR

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(34) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; p 338.

(35) Szwarc, M. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 141.

(36) Matyjaszewski, K. *Macromolecules* **1993**, *26*, 1787.

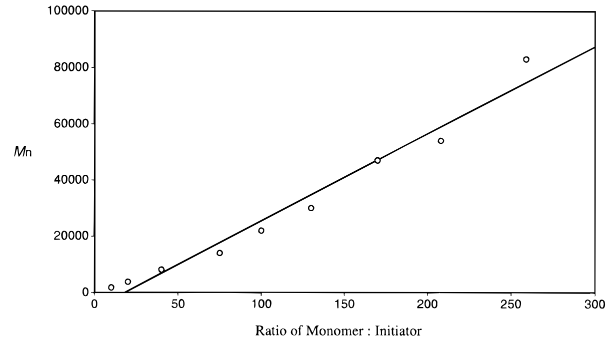
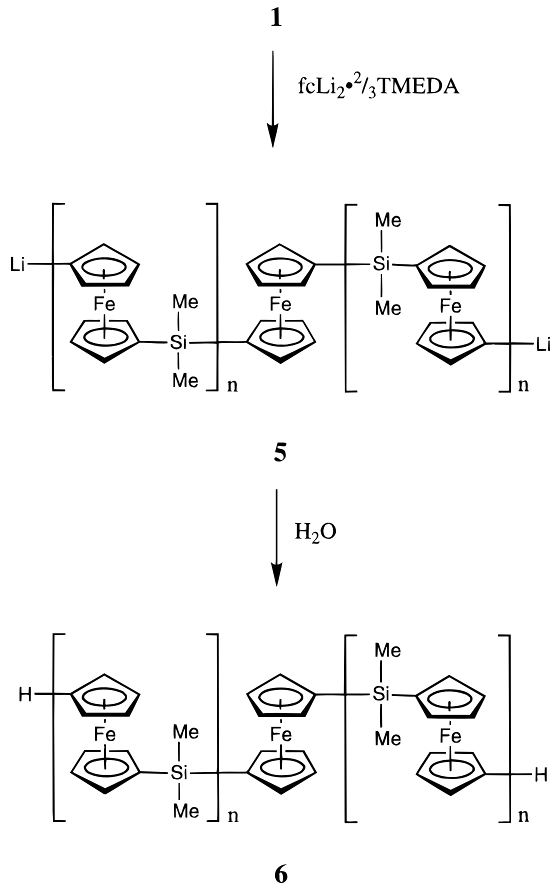


Figure 3. A plot of the mole ratio of monomer:initiator versus M_n for the *n*-BuLi initiated synthesis of poly(ferrocenyldimethylsilane) **4** (R = *n*-Bu, E = H).

Scheme 2



spectra which were identical to those previously reported[9] for **2** formed by thermal ROP. In addition, end groups were detected by ^{29}Si-NMR. As shown in Figure 1, for low molecular weight, FcLi-initiated, and Me_3SiCl terminated species, resonances at −3.1 and −6.6 ppm were assigned to the terminal $-SiMe_3$ and $FcSiMe_2-$ groups, respectively.

Reaction of **1** with PhLi under similar conditions yielded monodisperse (M_w/M_n = 1.19 and 1.25) poly(ferrocenyldimethylsilane)s **4** (R = Ph, E = H). Control of molecular weights was achieved between $M_n = 1.8 \times 10^4$ and 3.4×10^4 by using monomer:initiator ratios of 52:1 and 91:1. The significant difference between the predicted and the found M_n value suggests that the PhLi solution had a lower concentration than calculated (Table 2).

With *n*-BuLi optimal control of the anionic polymerization of **1** was achieved (Table 3). By varying the monomer:initiator ratio from 10:1 to 259:1 monodisperse poly(ferrocenylsilanes) (PDI = 1.05−1.10) with molecular weights ranging from $M_n = 1.8 \times 10^3 - 8.3 \times 10^4$ were obtained (Figure 2). The plot of M_n versus mol ratio of monomer:initiator is shown in Figure 3. The linear relation suggests the existence of a living system under the experimental conditions. A noticeable feature is that concentrations of impurities that react rapidly with *n*-BuLi become significant when the synthesis of polymers with more than 250 repeat units was attempted. Thus the found molecular weight of the polymer becomes higher than the predicted value (eg., M_n(found) = 8.3×10^4 versus M_n(calc) = 6.3×10^4 for a 259:1 monomer:*n*-BuLi ratio), while no significant increase in polydispersity was detected (Table 3, run 9).

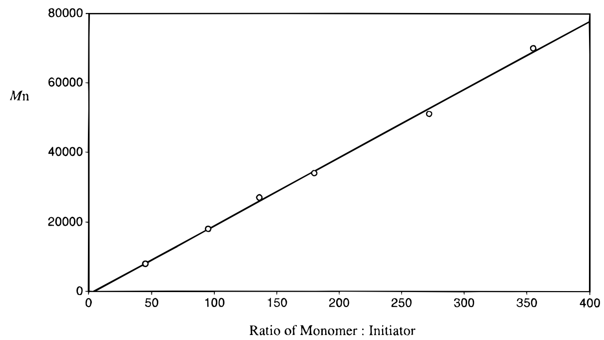


Figure 4. A plot of the mole ratio of monomer:initiator versus M_n for the $fcLi_2{\cdot}{}^2/_3$TMEDA initiated synthesis of poly(ferrocenyldimethylsilane) **6**.

In separate experiments, treatment of the intermediate polymer **3** with additional monomer **1** followed by quenching with H_2O led to polymers **4** which showed the expected increase in molecular weight characteristic of a living process (Table 4).

In addition to monofunctional initiators, we also studied difunctional initiators such as 1,1′-$fcLi_2$ (fc = $(\eta\text{-}C_5H_4)_2Fe$) for the anionic ROP of **1** (Scheme 2). Previous X-ray structural characterization showed that when complexed to TMEDA this species possesses a $fcLi{\cdot}{}^2/_3$TMEDA stoichiometry in the solid state.[33] Reaction of **1** with 1,1′-$fcLi_2{\cdot}{}^2/_3$ TMEDA under similar conditions to those described above yielded monodisperse poly(ferrocenyldimethylsilane) **6** (PDI = 1.06−1.22) with control of molecular weights between $M_n = 8.0 \times 10^3$ and 7.0×10^4 by varying the monomer:initiator ratio from 45:1 to 355:1 as shown in Table 5.

The plot of M_n versus mol ratio of monomer:initiator is shown in Figure 4. A good linear relation was found which suggests that a living system exists under the experimental conditions.

Synthesis of Block Copolymers. One of the distinctive and most useful features of living anionic polymerizations is the ability to synthesize block copolymers with different combinations of the chain segments. Styrene and the cyclic siloxane $[Me_2SiO]_3$ represent two of the most widely studied monomers for living anionic polymerizations. *n*-Butyllithium and sodium naphthalide and its derivatives[37−39] are examples of excellent initiators for these systems.[40] Thus, they were chosen as the monomers and initiators in the block copolymer studies described in this paper.

(i) Synthesis and Characterization of the Diblock Copolymers PFS$_{20}$-PDMS$_{39}$ (7a) and PFS$_{50}$-PDMS$_{99}$ (7b). In order to demonstrate that the living anionic ROP of **1** can be exploited to prepare novel, well-defined polymer structures we initially

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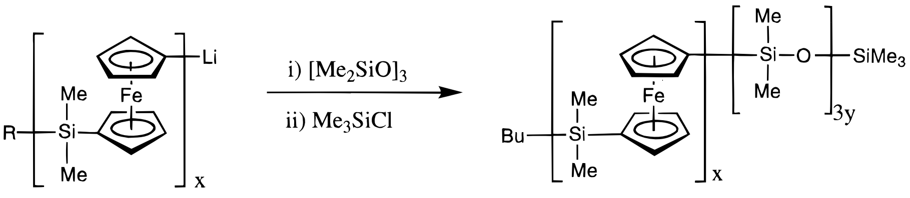
[37] Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983; p 201.

[38] Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.

[39] Szwarc, M. *Nature* **1956**, *178*, 1168.

[40] (a) Quirk, R. P. *Adv. Polym. Sci.* **1984**, *56*, 70. (b) Szwarc, M. *Makromol. Chem., Rapid Commun.* **1992**, *13*, 141. (c) Webster, O. W. *Science* **1991**, *251*, 887.

Scheme 3



3

7a x = 20, y = 13
7b x = 50, y = 33

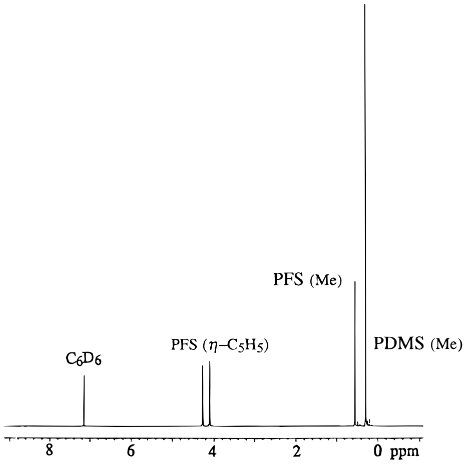


Figure 5. 400 MHz ^{1}H-NMR spectrum of the PFS-b-PDMS diblock copolymer **7b** in C_6D_6.

targeted poly(ferrocenylsilane)-poly(dimethylsiloxane) block copolymers **7**. Thus, the living polymer **3** (R = *n*-Bu) was reacted (THF, 25 °C) with the strained cyclotrisiloxane $[Me_2SiO]_3$[41] for 30 min. Subsequent addition of Me_3SiCl yielded the yellow copolymers **7a** and **7b** which were isolated by precipitation into methanol (Scheme 3).

The block copolymers **7a** and **7b**, which in contrast to the poly(ferrocenylsilane) **2** are soluble in hexanes, were structurally characterized by ^{1}H-, ^{13}C-, and ^{29}Si-NMR as well as by elemental analysis. The ^{1}H-NMR spectra of **7a** and **7b** (Figure 5) showed resonances at 4.10, 4.26, and 0.54 ppm for the poly(ferrocenyldimethylsilane) block and a resonance at 0.28 ppm which was assigned to the poly(dimethylsiloxane) block. Significantly, the ^{29}Si-NMR spectra of these copolymers showed not only the two expected resonances for the poly(ferrocenylsilane) at -6.4 ppm and the polysiloxane segments at -21.4 ppm but also small peaks arising from groups located at the start ($BuMe_2Si-$) and end ($-OSiMe_3$) of the polymer chains together with a crossover group ($-fcSiMe_2O-$) between the ferrocenylsilane and polysiloxane segments (Figure 6).

The molecular weights of the block copolymers **7a** and **7b** were estimated to be $M_n = 7.7 \times 10^3$, PDI = 1.15 and $M_n = 2.1 \times 10^4$, PDI = 1.13, respectively, and analytical data were consistent with the assigned structures. Based on ^{1}H-NMR integration, it seems that not all of the $[Me_2SiO]_3$ monomer was consumed to form the block copolymers. The existence of polymer-ring equilibria could be an explanation for the incomplete incorporation of the $[Me_2SiO]_3$ monomer into the poly(dimethylsiloxane) block.[42,43] In other words, the rate of chain growth for the hexamethylcyclotrisiloxane competes with a depolymerization process.

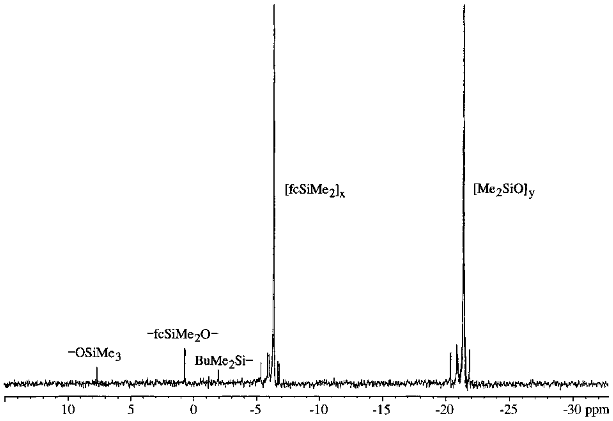


Figure 6. 79.8 MHz ^{29}Si-NMR spectrum of the PFS-b-PDMS diblock copolymer **7b** in C_6D_6.

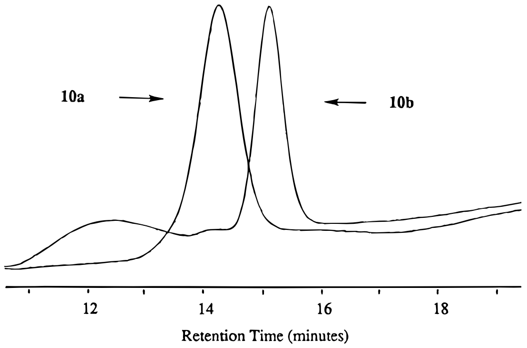


Figure 7. GPC traces of block copolymers **10a** and **10b**.

(ii) Synthesis and Characterization of the Triblock Copolymers $PDMS_{72}$-b-PFS_{48}-b-$PDMS_{72}$ (8a) and $PDMS_{108}$-b-PFS_{100}-b-$PDMS_{108}$ (8b). We also synthesized triblock copolymers using $fcLi_2$ as initiator. When $[Me_2SiO]_3$ was added to the solution of **5**, a gel was formed presumably due to the aggregation of the lithium silanolates. This significantly decreases the rate of a chain growth of the poly(dimethylsiloxane) block.[44] Previous work by Boileau et al. indicated that the reactivity of $[Me_2SiO]_3$ toward anionic ROP in solution was greatly enhanced in the presence of cryptated silanolate ion pairs.[45] In our studies, we chose 12-crown-4 as the coordination reagent for Li^+. Thus, a small amount of 12-crown-4 was added before the addition of $[Me_2SiO]_3$ in order to suppress the aggregation of lithium silanolates. This appeared to be effective as no gel formation took place although the solution viscosity still increased significantly during the reaction.

By reaction of the difunctional living poly(ferrocenylsilanes) **5** with $[Me_2SiO]_3$ followed by the addition of Me_3SiCl the yellow triblock copolymers **8a** and **8b** were formed. These were

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(41) Noshay, A.; McGrath, J. E. *Block Copolymers, Overview and Critical Survey*; Academic Press: New York, 1977; p 187.

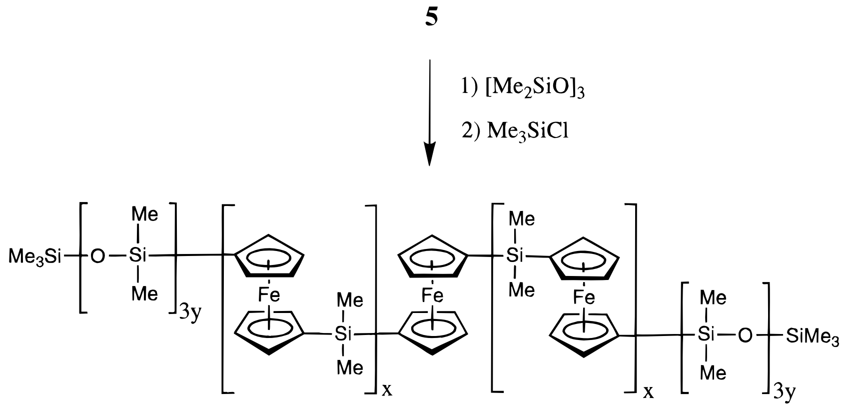
(42) Jones, F. R. *Eur. Polym. J.* **1974**, *10*, 249.

(43) Morton, M.; Bostick, E. E. *J. Polym. Sci., Part A* **1964**, *2*, 523.

(44) Zilliox, J. G.; Roovers, J. E. L.; Bywater, S. *Macromolecules* **1975**, *8*, 573.

(45) Boileau, S. In *Ring-Opening Polymerization*; McGrath, J. E., Ed.; American Chemical Society: Washington, DC, 1985; Vol. 286, p 23.

Scheme 4



8a x = 24, y = 24
8b x = 50, y = 36

isolated by precipitation into methanol (Scheme 4). The molecular weights of the block copolymers **8a** and **8b** were estimated to be $M_n = 1.4 \times 10^4$ (PDI = 1.15) and $M_n = 2.7 \times 10^4$ (PDI = 1.09), respectively. The ^{29}Si-NMR spectra of these copolymers showed two very intense resonances for the poly(ferrocenylsilane) block (at −6.4 ppm) and the polysiloxane segments (at −21.4 ppm) and, in addition, small peaks arising from groups located at the end of the polymer chains ($-OSiMe_3$) together with crossover groups between the poly(ferrocenylsilane) and polysiloxane segments ($-fcSiMe_2O-$). Additional characterization by ^{1}H- and ^{13}C-NMR as well as by elemental analysis yielded data which were also consistent with the assigned structures.

(iii) Synthesis and Characterization of the Diblock Copolymers PS$_{100}$-b-PFS$_{98}$ (10a) and PFS$_{90}$-b-PS$_n$ (10b). The synthesis and study of organic-organometallic block copolymers represents a virtually unexplored area.[7] Living anionic ROP of [1]silaferrocenophanes offers an attractive route toward the synthesis of this type of polymer. We synthesized the block copolymer polystyrene-b-poly(ferrocenyldimethylsilane) **10a** by the sequential addition of **1** to a solution of living lithium polystyrene in THF (Scheme 5). The color change from red to amber was used to detect the end of the reaction. Polymerization was terminated by the addition of H_2O, and the block copolymer was obtained by precipitation from hexanes. GPC analysis showed that **10a** possessed a narrow molecular weight distribution (PDI = 1.08, Figure 7).

The ^{29}Si-NMR spectrum of the copolymer **10a** in CD_2Cl_2 shows the expected intense resonance for the poly(ferrocenylsilane) block at −4.6 ppm and also small peaks arising from crossover groups between styrene and ferrocenyldimethylsilane units at −1.2 ppm. Characterization by ^{1}H- and ^{13}C-NMR as well as by elemental analysis also yielded data consistent with the assigned structure. The ^{1}H- and ^{13}C NMR spectra showed that the block copolymer **10a** contained atactic polystyrene,[46] which is common for the anionic polymerization of styrene in THF at room temperature.[47]

The attempted synthesis of the diblock copolymer **10b** starting with living poly(ferrocenyldimethylsilane) (Scheme 6) resulted a bimodal molecular weight distribution for the product (see Figure 7). The high molecular weight fraction consisted of a block copolymer with a very long polystyrene block. This is due to the slow initiation of styrene by the living polymer **3**. Once initiated, rapid chain propagation of polystyrene occurred to generate a poly(ferrocenylsilane)-polystyrene block copolymer with long polystyrene blocks that show a molecular weight distribution that is typical for a slow initiation process (for **10b** $M_w/M_n = 1.33$).[48] The low molecular weight fraction was mainly the poly(ferrocenylsilane) homopolymer, which had insufficient time to initiate the styrene polymerization. Thus, it appears from these results that the propagation of polystyrene with lithium as counter ion in THF at room temperature is much faster than the initiation of styrene monomer by the living poly(ferrocenylsilane) **3**.

(iv) Attempted Synthesis of the Pentablock Copolymer *n*-Bu-PS$_{100}$-b-PFS$_{38}$-b-PDMS$_{120}$-b-PFS$_{38}$-b-PS$_{100}$-b-*n*-Bu (12). To further demonstrate the control over polymer architecture based on the living polymerization of [1]dimethylsilaferrocenophane **1** we were interested in the preparation of block copolymers with an organic-organometallic-inorganic-organometallic-organic structure. The general method investigated to prepare these materials was through a coupling process,[41] using a three-stage protocol to prepare a living triblock copolymer which is then "coupled" by a reaction with Me_2SiCl_2 to form the pentablock structure (Scheme 5). Before the addition of $[Me_2SiO]_3$ to the solution of the living diblock copolymer **9**, 12-crown-4 was added. After the addition of $[Me_2SiO]_3$ the solution viscosity increased dramatically until it became almost immobile after 30 min. A few drops of this solution were precipitated into hexanes to estimate its molecular weight by GPC. The remaining living polymer ends were then "coupled" by the reaction with Me_2SiCl_2. This resulted in a significant decrease of the solution viscosity. The pentablock product **12** was isolated by precipitation into hexanes. Polymer **12** showed a significant increase of the estimated molecular weight (a doubling would be expected) compared to the triblock precursor. Thus for polymer **12** $M_n = 6.0 \times 10^4$ (PDI = 1.28), whereas for **11** $M_n = 2.3 \times 10^4$ (PDI = 1.11). The significant broadening of the molecular weight distribution and the presence of a low molecular weight shoulder (20−30% by area) on the GPC traces of **12** suggested that in addition to the pentablock copolymer uncoupled impurities of triblock copolymer were also present. This type of behavior is found to be a common problem in multiblock copolymer synthesis.[37,49] The ^{1}H- and ^{13}C-NMR spectra of **12** were consistent with the presence of a backbone containing polystyrene, poly(ferrocenyldimethylsilane), and poly(dimethylsiloxane) segments. The ratio of the different

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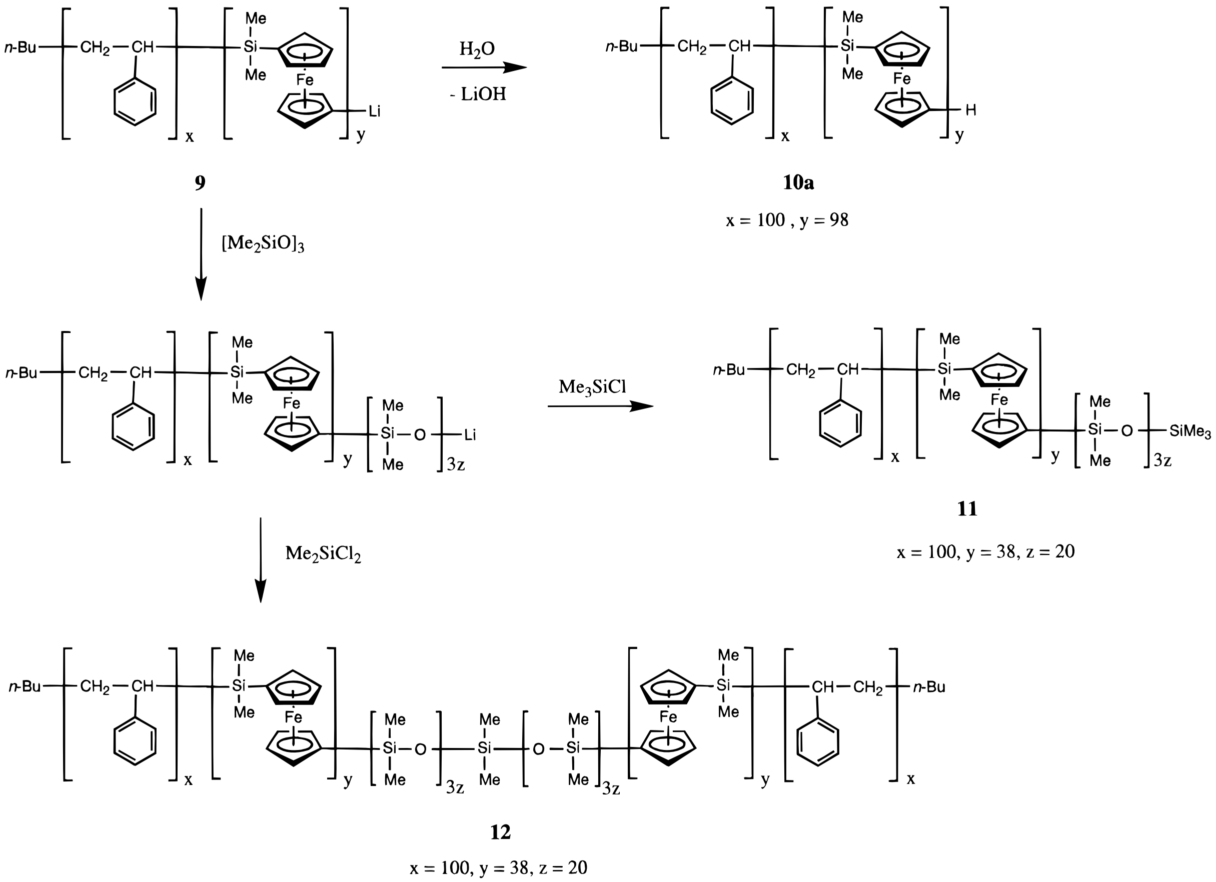
(46) Pham, S. T.; Pëtiaud, R.; Waton, H.; Llauro-Darricades, M.-F. *Proton and Carbon NMR Spectra of Polymers*; Penton Press, London: Boca Raton, FL, 1991.

(47) Kern, R. J. *Nature* **1960**, *187*, 410.

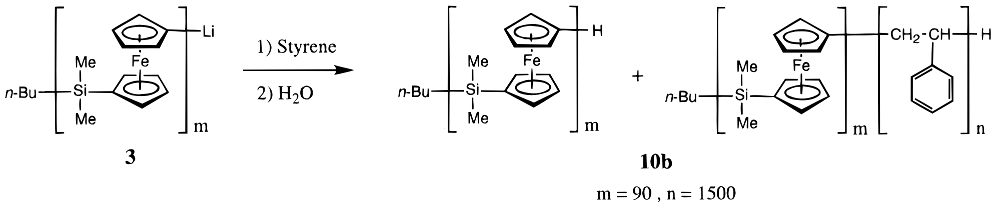
(48) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.

(49) Bates, F. S. *Science* **1991**, *251*, 898.

Scheme 5



Scheme 6



blocks was calculated based on ^{1}H-NMR integration. The ^{29}Si-NMR spectrum of this copolymer in CD_2Cl_2 showed very intense resonances for the poly(ferrocenylsilane) and the polysiloxane segments (-4.6 and -19.6 ppm respectively) and, in addition, small peaks corresponding to the crossover groups between the poly(ferrocenylsilane) and polysiloxane segments ($-fcSiMe_2O-$ at 2.5 ppm) and for the environments between the polystyrene and the poly(ferrocenylsilane) segments ($-fcSiMe_2CHPh-$ at -1.2 ppm).

(v) Synthesis and Characterization of the Triblock Copolymers PFS$_{35}$-b-PS$_{86}$-b-PFS$_{35}$ (15) and the Pentablock Copolymer Me$_3$Si-PDMS$_{111}$-b-PFS$_{47}$-b-PS$_{86}$-b-PFS$_{47}$-b-PDMS$_{111}$-SiMe$_3$ (16). Sodium naphthalide was first reported as an initiator for living anionic polymerizations in 1956.[38,39] It is well-known that block copolymers such as polyisoprene-b-polystyrene-b-polyisoprene can be quantitatively synthesized at -80 °C using this species. We attempted to synthesize triblock copolymers using sodium naphthalide as initiator in THF at -40 °C. The results showed that the expected copolymer possessed a bi- or trimodal molecular weight distribution, which suggested that with sodium as counter ion, anionic polymerization of **1** might not be living. Next we tried the readily accessible lithium naphthalide initiator at -40 °C which was first reported in a patent for the block copolymer synthesis of polyisoprene-polystyrene-polyisoprene.[50] Since no experimental details were available, prior to the synthesis of the block copolymer, we performed an anionic polymerization of styrene initiated by lithium naphthalide at -40 °C in THF solution. This was successful and polystyrene produced by this method had $M_n = 4.2 \times 10^4$, PDI = 1.10. The concentration of the lithium naphthalide was then back calculated based on the molecular weight formed. The triblock copolymer **15** was prepared using the reaction sequence described in Scheme 7 and possessed a narrow molecular weight distribution (PDI 1.11) with $M_n = 2.8 \times 10^4$ which was close to the calculated value of $M_n = 2.6 \times 10^4$ (Figure 8).

Further reaction of the difunctional triblock living system **14** with $[Me_2SiO]_3$ followed by termination with Me_3SiCl produced the pentablock copolymer **16** with $M_n = 5.3 \times 10^4$ (see GPC traces in Figure 8). This multiblock copolymer has a narrow molecular weight distribution ($M_w/M_n = 1.17$) and based on the GPC area calculation it contains less than 20% of triblock copolymer **15** as an impurity.

The ^{1}H- and ^{13}C NMR spectra confirmed the presence of polystyrene and poly(ferrocenylsilane) units for polymer **15**. In addition, the ^{1}H-, ^{13}C-, and ^{29}Si-NMR spectra confirmed the

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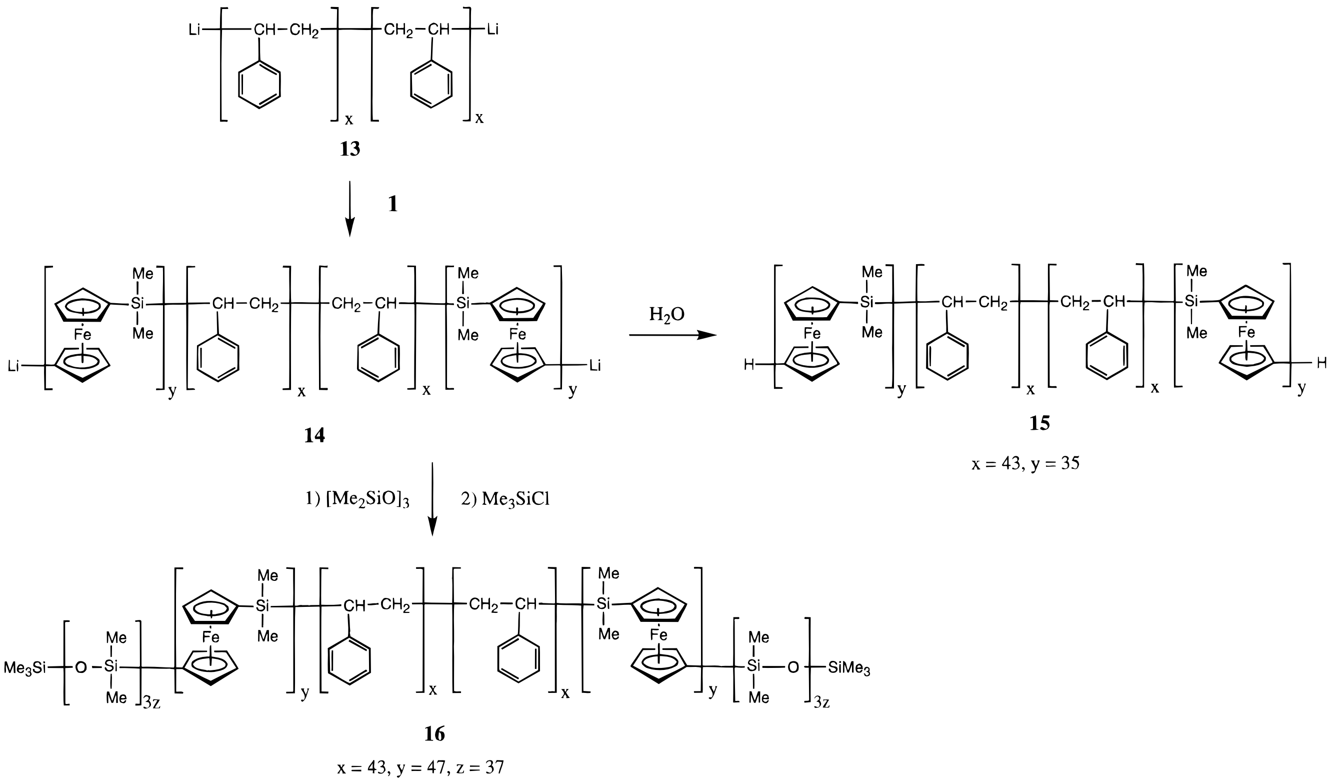
(50) Dunlop Co. Ltd. French Patent 1,566,887 1969, *Chem. Abstr.* **1970**, *72*, 4219n.

Scheme 7



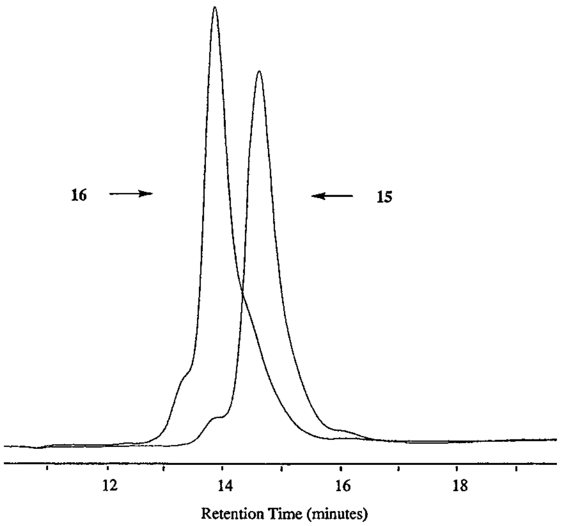


Figure 8. GPC traces of block copolymers **15** and **16**.

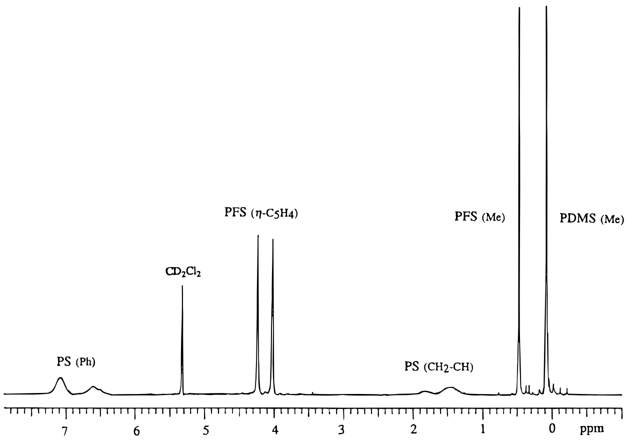


Figure 9. 200 MHz ^{1}H-NMR spectrum of pentablock copolymer PDMS-b-PFS-b-PS-b-PFS-b-PDMS **16** in CD_2Cl_2.

presence of polystyrene, poly(ferrocenylsilane), and polysiloxane segments for polymer **16** (see Figure 9). The ^{1}H- and ^{13}C-NMR spectra also showed that block copolymers **15** and **16** contain atactic polystyrene blocks.

The ^{29}Si-NMR spectra of the pentablock copolymer **16** in C_6D_6 showed the expected resonances for the poly(ferrocenylsilane) and polysiloxane segments (−6.4 and −21.4 ppm respectively) and, in addition, small peaks for end groups ($-OSiMe_3$ at 7.6 ppm), crossover groups between the poly(ferrocenylsilane) and polysiloxane segments ($-fcSiMe_2O-$ at 0.7 ppm), and for crossover groups between the polystyrene and poly(ferrocenyldimethylsilane) blocks ($-fcSiMe_2CHPh-$ at −1.2 ppm).

Electrochemical Properties of the Block Copolymers. Cyclic voltammetric data for selected block copolymer samples is listed in Table 6. In general, adsorption on the electrode was found to be significant. Less adsorption was detected for diblock copolymers **7a** and **7b**, poly(ferrocenyldimethylsilane)-b-poly(dimethylsiloxane), in comparison to the rest of the block copolymers synthesized. The addition of MeCN was necessary in order to obtain well-defined waves and minimize adsorption of the oxidized polymer on the electrode. Two waves of approximately equal intensity were then observed. For all of the polymer samples measured, two redox couples were detected which were separated by $\Delta E_{1/2} = 0.27-0.29$ V. For each block copolymer and for both oxidation waves, plots of i_{pk} (peak current) vs the square root of the scan rate were linear over the range of scan rates employed (25−1000 mV^{-1}), indicating that the electron transfer is diffusion controlled.

This electrochemical behavior has been found to be similar to that for poly(ferrocenyldimethylsilane) homopolymer[9,12] and has been explained by the existence of interactions between the iron centers. This leads to oxidation of alternating ferrocenyl moieties in the poly(ferrocenylsilane) backbone which makes the subsequent removal of electrons from the remaining intermediate iron(II) centers more difficult.

Table 6. Electrochemical Data for Selected Block Copolymers

sample	$E_{1/2}(1)^a$ (V)	$E_{1/2}(2)^a$ (V)	ΔE^b (V)
7a	0.00	0.27	0.27
7b	0.00	0.28	0.28
8b	−0.08	0.21	0.29
10a	−0.10	0.19	0.29
12	−0.01	0.28	0.29
15	0.00	0.28	0.28
16	0.00	0.28	0.28

[a] Cyclic voltammogram of block copolymer 10 mg in a 10 mL solution of 4:1 (by volume) CH_2Cl_2:MeCN at a scan rate of 250 mV s^{-1} at 22 °C. $E_{1/2}(1)$ and $E_{1/2}(2)$ refer to the half-wave potentials for the first and second oxidation waves. [b] $\Delta E = E_{1/2}(2) - E_{1/2}(1)$.

Table 7. Glass Transition Temperatures for Poly(ferrocenyldimethylsilane) **4** (R = *n*-Bu, E = H) as a Function of Chain Length

polymer	M_n ($\times 10^3$)	PDI	T_g (°C)
1	1.8	1.10	8
2	3.8	1.08	18
3	8.1	1.05	29
4	14	1.05	31
5	22	1.05	33
6	30	1.05	34
7	47	1.08	34
8	54	1.09	34
9	83	1.10	34

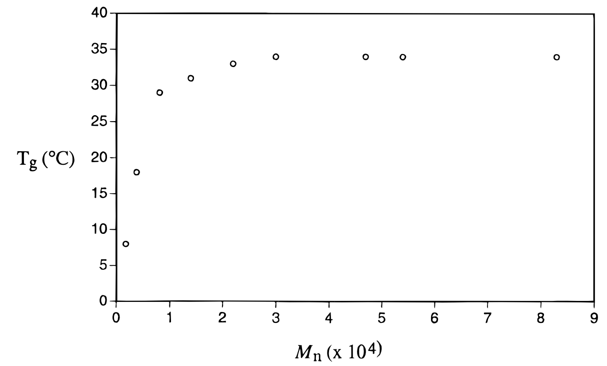


Figure 10. Plot of T_g versus M_n for poly(ferrocenyldimethylsilane) **4** (R = *n*-Bu, E = H).

Table 8. DSC Analysis for the Block Copolymers

sample	T_g (°C) PDMS block	T_c (°C) PDMS block	T_m (°C) PDMS block	T_g (°C) PFS block	T_g (°C) PS block	T_m (°C) PFS block
7a	−125	100	−45	35		128
7b	−127	100	−45	35		136
8b	−125	−93	−49	34		134
10a				27	99	127
12	−127	−100	−41	32	103	
15				34	99	119
16	−122	−100	−45	31	88	

Thermal Transition Behavior and Thermal Stability of the Block Copolymers. The glass transition temperatures (measured by DSC) of monodisperse poly(ferrocenyldimethylsilane) samples synthesized by living anionic ROP as a function of M_n are shown in Table 7. The T_gs clearly increase from 8 °C to 33 °C as the M_n value increases from 1.8×10^3 to 2.2×10^4 (Figure 10). Above $M_n = 2.2 \times 10^4$ (ca. 90 repeating units) the same glass transition temperature as for high molecular weight ($M_n > 10^5$) poly(ferrocenyldimethylsilane) **2** was detected. This observed correlation between the T_g and M_n of the poly(ferrocenyldimethylsilane) is similar to the general behavior found for other polymer systems.[51]

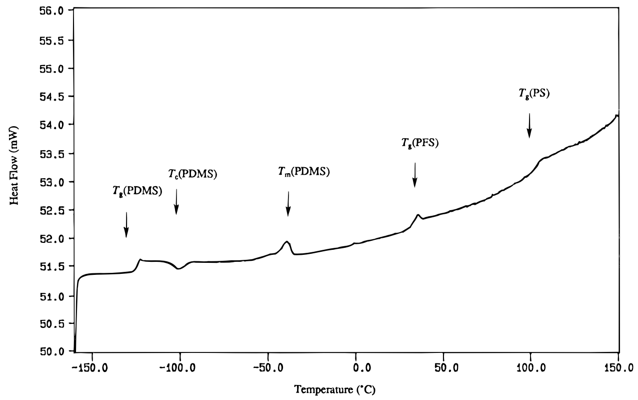


Figure 11. DSC trace of pentablock copolymer PS-b-PFS-b-PDMS-b-PFS-b-PS **12** (heating rate of 10 °C min^{-1}).

Table 9. TGA Data for Poly(ferrocenyldimethylsilane) **4** (R = *n*-Bu, E = H) and for selected Block Copolymers

polymer	T_1^a (°C)	$T_{10\%}^b$ (°C)	$T_{50\%}^b$ (°C)	T_2^c (°C)	ceramic yield (%) at 900 °C
4[d]	370	465	500	570	30
7b	310	455	525	630	29
8b	305	425	510	605	38
10a	370	435	460	555	30
12	305	420	475	615	25
15	370	450	475	560	25
16	305	390	490	610	27

[a] Temperature at which initial weight loss occurs. [b] $T_{10\%}$ and $T_{50\%}$ correspond to the temperatures at which the polymer sample has lost 10% and 50%, respectively, of the initial mass. [c] Temperature where no further weight is lost. [d] Poly(ferrocenyldimethylsilane) **4** (R = *n*-Bu, E = H), $M_n = 8.9 \times 10^4$, PDI = 1.10.

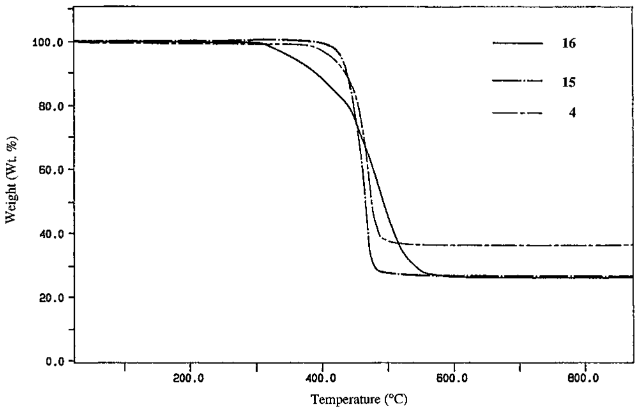


Figure 12. Selected TGA traces for block copolymers (heating rate of 10 °C min^{-1}).

The thermal transition behavior of the copolymers was also investigated by DSC. The results are compiled in Table 8. The copolymers **7a**, **7b**, **8b**, **12**, and **16** containing poly(dimethylsiloxane) blocks possessed glass transitions, crystallization transitions, and melting transitions at −122 °C to −127 °C, −93 °C to −100 °C, and −41 °C to −49 °C, respectively. These are similar to the thermal transitions found for poly(dimethylsiloxane) homopolymer.[52] For all of the block copolymers synthesized, the glass transition temperature of the poly(ferrocenyldimethylsilane) block was in the range of 31−35 °C which is also similar to the T_g found for poly(ferrocenyldimethylsilane) homopolymer (33 °C).[53] The glass transition temperatures of the polystyrene blocks for copolymers **10a**, **12**,

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(51) Young, R. J.; Lovell, P. A. *Introduction to Polymers;* 2nd ed.; Chapman & Hall: London, 1991; pp 299.

(52) *Silicon-Based Polymer Science*; Zeigler, J. M.; Fearon, F. W. G., Eds.; American Chemical Society: Washington, DC, 1990.

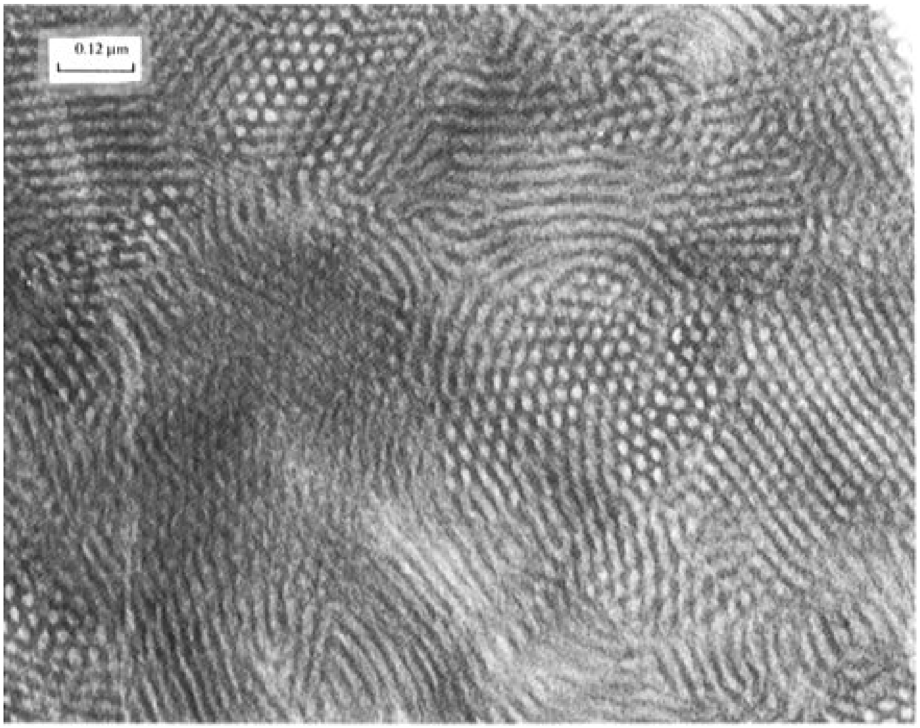

Figure 13. Transmission electron photomicrograph of the PS-b-PFS block copolymer **10a**.

15, and **16** ranged from 88 °C to 103 °C and are also within the range found for polystyrene homopolymer.[54] A typical DSC trace is shown for the pentablock copolymer **12** in Figure 11. All the glass transitions were in a similar range to those of the corresponding homopolymers which strongly suggested that the blocks were incompatible.[41,49] Such behavior has been previously noted for the block copolymer polystyrene-b-poly(dimethylsiloxane).[23] Thus, in the solid state, the formation of microscopic heterogeneties in composition would be expected. Interestingly, the melting transition of poly(ferrocenyldimethylsilane) was only detected by DSC for samples **7a**, **7b**, **8b**, **10a**, and **15**, and values from 119 °C to 136 °C were observed.

Thermogravimetric analysis (TGA) data at a heating rate of 10 °C/min for selected polymers under N_2 is listed in Table 9, and some representative traces are shown in Figure 12. The block copolymers without siloxane units such as **15** showed similar weight loss versus temperature increase which suggested a similar decomposition behavior to the homopolymer **4** (R = *n*-Bu, E = H). In contrast, the block copolymers with siloxane segments (e.g., **16**) underwent initial weight loss at ca. 300 °C, ca. 50 °C lower then for homopolymer **4** (R = *n*-Bu, E = H), whereas the end of weight loss at ca. 600−630 °C was at least 50 °C higher than for the polymers without polysiloxane blocks. Thus, poly(dimethylsiloxane) containing block copolymers show a broader temperature range of weight loss in comparison to the studied block copolymers without polysiloxane segments.

Morphological Studies of the Block Copolymer 10a by TEM. In order to obtain additional insight into the morphology of the block copolymers, the PS-b-PFS block copolymer **10a** was studied as a representative example by transmission electron microscopy (TEM). An electron photomicrograph of an ultrathin section of a film of block copolymer **10a** cast from THF is shown in Figure 13. A staining process, necessary for most block copolymers[41] was not needed in this case as the presence of a metal such as iron leads to efficient scattering of the electron beam. Thus the polystyrene region is white, and the poly(ferrocenyldimethylsilane) region is black. Based on the transmission electron photomicrograph, two different types of domains were observed: First, a phase separation resulting in the formation of approximately spherical polystyrene domains with a diameter of ca. 30−40 nm dispersed within a matrix of poly(ferrocenyldimethylsilane). Second, a phase separation resulting in the formation of a lamellar microphase. The thickness of each layer was ca. 30−40 nm for the polystyrene regions and 20−30 nm for poly(ferrocenyldimethylsilane) regions. Regions between these two extremes were also observed (see Figure 13). The morphology represents a network structure, where the small polystyrene domains act as network junctions for the poly(ferrocenyldimethylsilane).[23,41] Since the two blocks are highly incompatible, the interface between micro domains of the two chains is sharp.[49] The formation of the observed structure may be a result of the presence of blocks of equal length and the narrow polydispersities of the polymer sample.[49]

Summary

Our results demonstrate that the anionic ROP of [1]silaferrocenophanes in THF initiated by organolithium reagents represents a living system at room temperature. Under the conditions studied we estimate our system to be inbetween class 4 and 5 based on Matyjaszewski's classification of the "livingness" of polymerizations.[36] The living anionic polymerization of **1** allows access to a variety of transition metal-containing polymers with controlled architectures. Thus, organometallic/organic/inorganic multiblock copolymers with narrow molecular weight distributions have been synthesized and characterized. The comparative reactivity of the three living systems studied in this paper followed the sequence of PS > PFS > PDMS.

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(53) Foucher, D. A.; Ziembinski, R.; Tang, B. Z.; Macdonald, P. M.; Massey, J.; Jaeger, R.; Vancso, G. J.; Manners, I. *Macromolecules* **1993**, *26*, 2878.

(54) *Encyclopedia of Polymer Science and Engineering,* 2nd ed.; John Wiley & Sons, Inc.: New York, 1987; Vol. 16, p 1.

DSC studies showed that the copolymers constructed from PS, PFS, and PDMS segments possess highly incompatible blocks in the solid state. This situation was confirmed by TEM studies of the polystyrene-poly(ferrocenyldimethylsilane) diblock copolymer **10a**.

Work is now focused on exploring the properties of the block copolymer materials in both the solid state and also in solution where the formation of novel redox active micelle structures might be anticipated. Our results concerning these studies will be reported in due course.

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