Living Anionic Polymerization of Phosphorus-Bridged [1]Ferrocenophanes: Synthesis and Characterization of Well-Defined Poly(ferrocenylphosphine) Homopolymers and Block Copolymers

Timothy J. Peckham, Jason A. Massey, Charles H. Honeyman, and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto M5S 3H6, Ontario, Canada

Received August 25, 1998; Revised Manuscript Received January 13, 1999

ABSTRACT: The living anionic ring-opening polymerization (ROP) of the phosphorus-bridged [1]-ferrocenophane (η-$C_5H_4)_2$FePPh initiated by *n*-BuLi in THF at 25 °C has allowed the preparation of well-defined poly(ferrocenylphenylphosphines) [(η-$C_5H_4)_2$FePPh]$_n$ **5**, with molecular weight control, narrow polydispersities, and controlled end-group structures. Reaction of polymers **5** with sulfur allowed the synthesis of the analogous poly(ferrocenylphenylphosphine sulfides) [(η-$C_5H_4)_2$FeP(S)Ph]$_n$ **6**. Analysis of the high-molecular-weight polymers **5** and **6** (where $n = 100$) by DSC showed glass-transition temperatures of 126 and 206 °C, respectively. The absence of melt transitions and the featureless WAXS profiles indicated that the materials are amorphous. The living nature of the ROP also permitted the synthesis of well-defined block copolymers, poly(ferrocenylphenylphosphine)-*b*-poly(dimethylsiloxane) (PFP-*b*-PDMS), PFP_{11}-*b*-$PDMS_{81}$ (**7a**) and PFP_{50}-*b*-$PDMS_{141}$ (**7b**), and poly(ferrocenylphenylphosphine)-*b*-poly(ferrocenyldimethylsilane) PFP_{11}-*b*-PFS_{11} (**8**). Analysis of the block copolymer **7b** by DSC showed the presence of individual thermal transitions for each block which indicated that they were incompatible. Metal coordination studies on copolymer **7b** showed that this material coordinates $PdCl_2$, to yield the insoluble copolymer **11**, as well as $Fe(CO)_4$, which resulted in the formation of **12** which remained soluble in hexane.

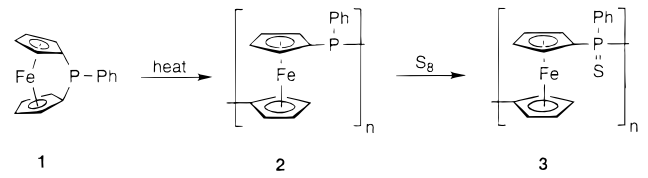
Introduction

Ring-opening polymerization (ROP) of strained [1] and [2]metallocenophanes represents a well-established route to high-molecular-weight poly(metallocenes) which have been shown to possess a range of intriguing properties.[1−4] In 1994, we reported that living anionic ROP of silicon-bridged [1]ferrocenophanes was possible.[5] This permitted molecular weight control, end-group functionalization, and access to poly(ferrocene) block copolymers, the first with skeletal transition-metal atoms.[5,6] The incompatibility of blocks in the latter leads to the formation of nanoscale, organometallic poly(ferrocene) domains in the solid state and novel micellar aggregates in solution.[3,6,7] These structures are of considerable interest because (i) poly(ferrocene) homopolymers are redox-active and become semiconductors when oxidatively doped and (ii) the pyrolysis of nanoscale domains of poly(ferrocenes) permits access to magnetic nanostructures.[8,9]

Poly(ferrocenylphosphines) such as **2** are a particularly interesting target as they are possible polymeric supports for catalysts (see Scheme 1). The preparation of materials of structure **2** were first reported via condensation routes, and coordination studies of these polymers with $Co_2(CO)_8$ and their subsequent use as hydroformylation catalysts were also described.[10,11] In 1995, we reported that high-molecular-weight poly(ferrocenylphosphines) (e.g., **2**) may be obtained via thermal ROP of strained, phosphorus-bridged [1]ferrocenophanes (**1**).[12] The polymers may be subsequently functionalized by the reaction with elemental sulfur to obtain the analogous poly(ferrocenylphosphine sulfides) (**3**).

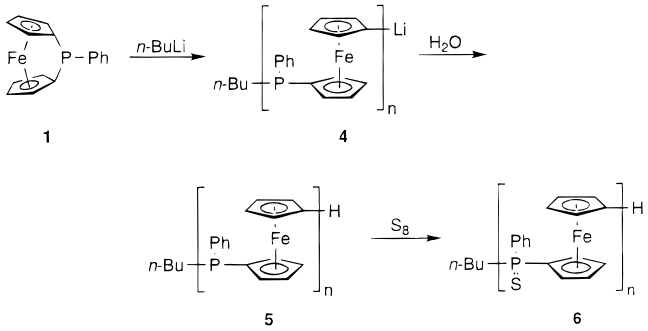
More recently, we have made a preliminary report of the living anionic ROP of the phosphorus-bridged [1]-ferrocenophane **1**.[13] In this paper, we report full details of our work in this area which has allowed access to poly(ferrocenylphosphines) with controlled molecular weights as well as the first poly(ferrocenylphosphine) block copolymers. We also report studies of the coordination of Pd and Fe moieties to the poly(ferrocenylphosphine) segment of the latter.

Scheme 1



1 2 3

Scheme 2



1 4 5 6

Results and Discussion

Anionic ROP of Phosphorus-Bridged [1]Ferrocenophane 1 with *n*-BuLi. Reaction of **1** with *n*-BuLi in THF at 25 °C for 30 min was followed by quenching of the living polymer **4** by the addition of H_2O to yield polymer **5** (see Scheme 2). As has been noted by Seyferth and by us,[12,14] poly(ferrocenylphosphine) homopolymers do not elute from a gel permeation chromatograph using THF as the elution solvent. However, these polymers

10.1021/ma981329w CCC: $18.00
Published on Web 04/10/1999

Table 1. Molecular Weights of Poly(ferrocenylphosphines) and Related Copolymers Prepared via the Living Anionic ROP of 1[a]

product	mole ratio *n*-BuLi/**1**/*x*	M_n calcd[a]	M_n found	PDI = M_w/M_n
5	1:11:-	3.6×10^3	2.4×10^3	1.08
5	1:20:-	6.5×10^3	3.9×10^3	1.08
5	1:55:-	1.8×10^4	1.3×10^4	1.11
5	1:70:-	2.3×10^4	2.7×10^4	1.17
5	1:100:-	3.2×10^4	3.6×10^4	1.25
7a[b]	1:11:27[c]	9.2×10^3	8.7×10^3	1.10
7b[b]	1:50:47[c]	2.5×10^4	2.4×10^4	1.30[d]
8[c]	1:11:11[e]	5.9×10^3	3.2×10^3	1.08
10[f]	1:11:11[e]	6.2×10^3	4.4×10^3	1.11

[a] Based on calculated weight for the analogous sulfurized polymer (**6**) except where noted. [b] Molecular weights determined (by GPC in THF vs polystyrene standards) and calculated for unsulfurized copolymer (calculated on the basis of ^{1}H NMR integration and assuming full conversion of monomer **1** into living polymer **4**). [c] $x = [Me_2SiO]_3$. [d] The higher PDI is a result of tailing in the GPC trace due to adsorption of the PFP block to the column material. [e] x = [1]dimethylsilaferrocenophane. [f] Molecular weights determined and calculated for sulfurized copolymer.

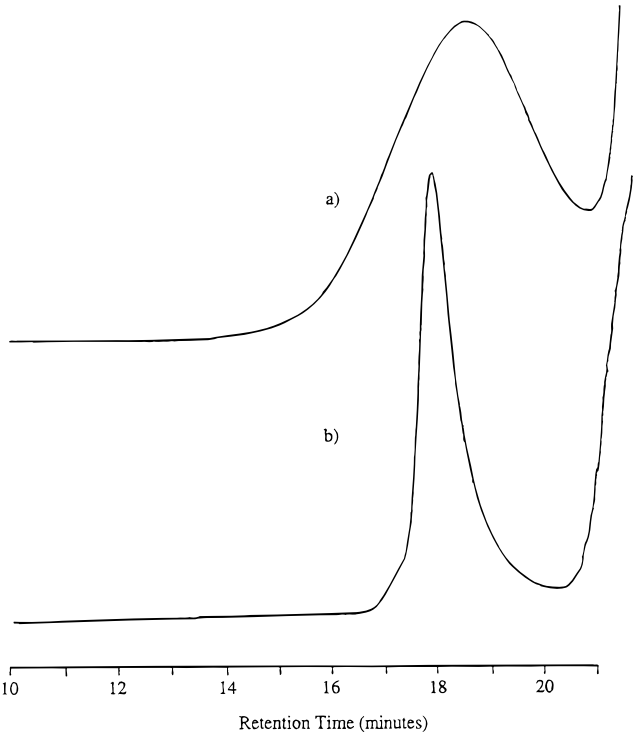


Figure 1. Comparison of GPC traces for (a) polymer **3** ($M_n = 1.8 \times 10^4$, PDI = 1.52) formed by thermal ROP of **1** followed by sulfurization (see ref 12) and (b) polymer **6** ($n = 100$) ($M_n = 3.6 \times 10^4$, PDI = 1.25) formed via living anionic ROP followed by sulfurization.

will elute once the phosphorus(III) sites have been sulfurized to phosphorus(V).[12,13] Thus, samples of all of the homopolymers were sulfurized to give poly(ferrocenylphosphine sulfides) (**6**).

The molecular weights of the polymers could be controlled from $M_n = 2.4 \times 10^3$ to 3.6×10^4 with narrow polydispersities ($M_w/M_n = 1.08-1.25$) by varying the *n*-BuLi/**1** ratio from 1:11 to 1:100. These results are summarized in Table 1. The narrow polydispersity for polymer **6** even when $n = 100$ ($M_w/M_n = 1.25$) can be seen when compared with polymer **3** produced via thermal ROP of **1** (Figure 1).[12] The polymer products **5** and **6** gave ^{31}P, ^{13}C, and ^{1}H NMR spectra which were consistent with those previously reported for **2** and **3**

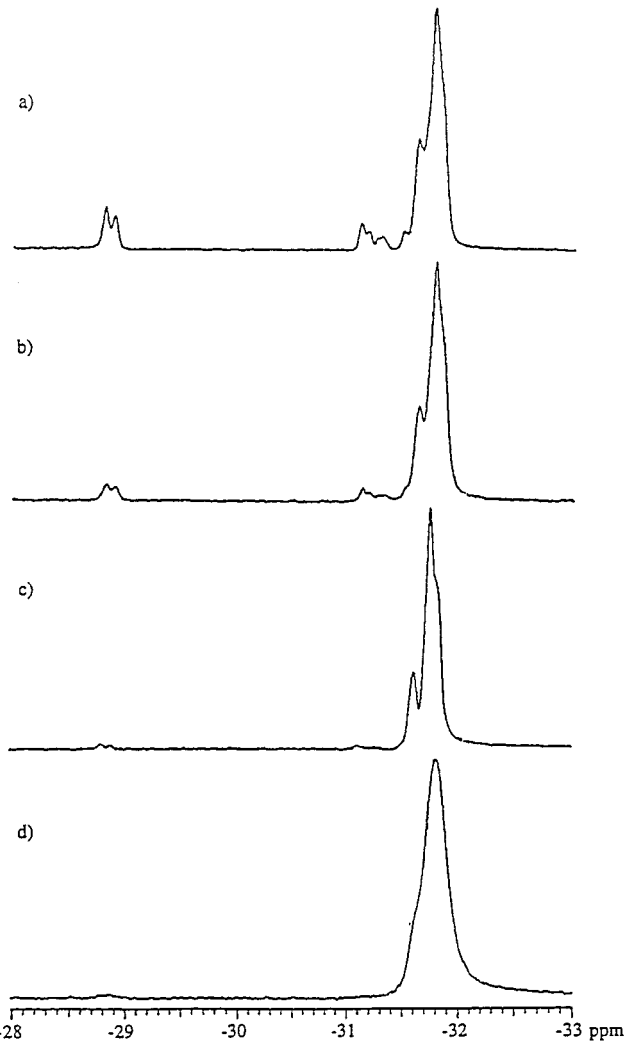


Figure 2. ^{31}P NMR spectra in C_6D_6 of polymer **5** where the **1**/*n*-BuLi ratio is (a) 11:1, (b) 20:1, (c) 55:1, and (d) 100:1.

formed by thermal ROP. The ^{31}P NMR spectra for the unsulfurized homopolymers (**5**) are shown in Figure 2. For **5** ($n = 11$), the three major resonances can be seen clearly. The resonance at −31.7 ppm was attributed to the P(III) centers in the polymer main chain and is consistent with the literature value.[14] The *n*-BuP(Ph)-Cp end group can be observed at −28.8 ppm, and we have attributed the resonance at −31.1 ppm to the penultimate main chain P(III) centers. The integration for these resonances for **5** (n = 11, 20, and 55) is consistent with the original monomer/initiator ratio in each case. The integrations of the resonances for the end groups and the main polymer chain in the ^{1}H NMR spectra are also consistent with the original monomer/initiator ratio. Similar results were observed in the NMR spectra of the sulfurized derivatives **6**.

Thermal Transition Behavior, Thermal Stability, and Morphology of 5 and 6 (Where $n = 100$). As no characterization data on the thermal properties of polymers **5** and **6** had been reported, the thermal transition behavior and thermal stabilities were analyzed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. The morphology of these polymers was also studied using wide-angle X-ray scattering (WAXS).

Analysis by DSC (Figure 3a,b) showed that both **5** and **6** were amorphous with no evidence for any melting

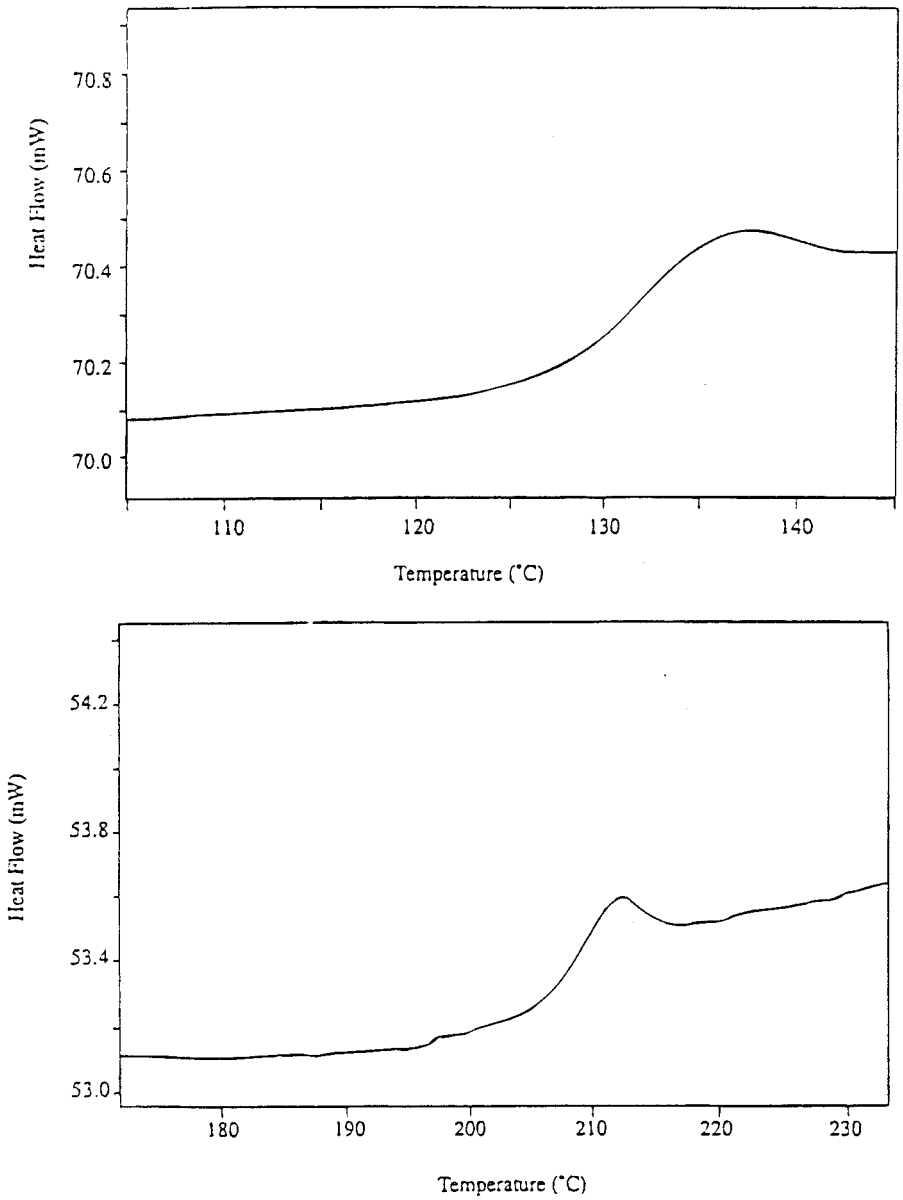


Figure 3. (a) DSC thermogram of polymer **5** ($n = 100$) (scan rate 10 °C/min). (b) DSC thermogram of polymer **6** ($n = 100$) (scan rate 10 °C/min).

transitions. Glass transitions were found, however, at 126 and 206 °C, respectively. These values suggest that the addition of a sulfur group to phosphorus in the backbone of **5** leads to a less flexible backbone in the case of **6**. It was similarly found that methylation of the phosphorus centers of **5**, to yield the polymer $\{[(\eta\text{-}C_5H_4)_2\text{-}FePPhMe][OTf]\}_n$, also led to an increase in the T_g value (to 176 °C), although it was noted that the presence of triflate counterions could also have played a role in the thermal transition behavior of this polymer.[15] The amorphous nature of the two polymers was corroborated by the results from WAXS studies which afforded diffractograms with only one broad and featureless amorphous halo at 5.2 and 7.4 Å for **5** and **6**, respectively.

Polymers **5** and **6** were found to be thermally stable up to 385 and 410 °C, respectively, by TGA analysis, with 10% weight losses having occurred by 440 and 430 °C for **5** and **6**, respectively. By 800 °C, polymer **6** had lost 50% of its weight, whereas **5** still retained 56% of its weight even at 900 °C. The weight losses by 600 °C of 30% and 33% for **5** and **6** were consistent with the loss of substituents from phosphorus and the formation of a residue derived from the unsubstituted poly(ferrocenylphosphine) backbone.

Synthesis and Characterization of the Diblock Copolymers PFP_{11}-*b*-$PDMS_{81}$ (7a), PFP_{50}-*b*-$PDMS_{141}$ (7b), and PFP_{11}-*b*-PFS_{11} (8). It was also possible to utilize the active end group of the living polymer **4** to synthesize block copolymers with either poly(siloxane) (**7a** and **7b**) or poly(ferrocenylsilane) (**8**) segments, producing materials which were soluble and insoluble in hexanes, respectively (see Scheme 3 and 4). As the homopolymer analogues of the nonpoly(ferrocene) segments of these copolymers are GPC-analyzable we attempted molecular weight analysis of the block copolymers using GPC. In contrast to the behavior of the homopolymer **5**, elution from the column was detected in each case, and monomodal molecular weight distributions were observed. In the case of the copolymers **7a** and **8**, the molecular weight distributions were narrow ($M_w/M_n = \sim 1.1$) but in the case of **7b**, a significant tailing effect was observed in the GPC trace (Figure 4). We attribute this to the presence of a longer

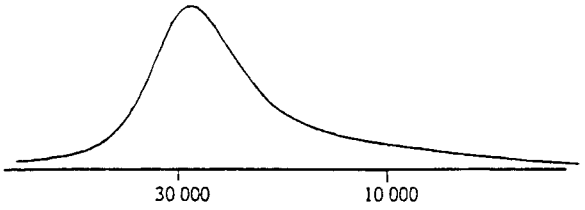
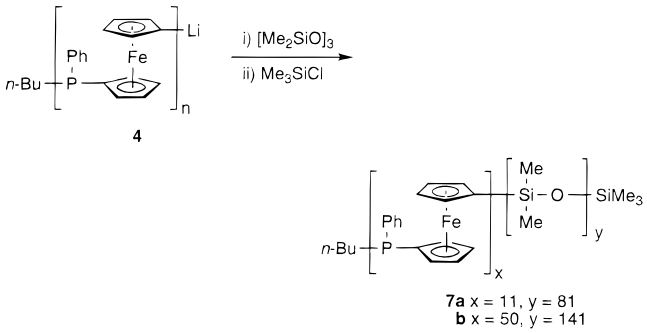


Figure 4. GPC trace of block copolymer **7b** in THF.

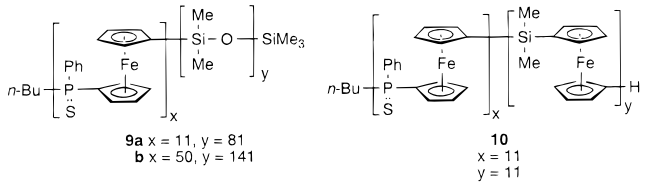
Scheme 3



poly(ferrocenylphosphine) block in this material that leads to GPC column adsorption problems. Sulfurization of the block copolymer **8** to afford **10** allowed a comparison between the molecular weights for the sulfurized and unsulfurized copolymers by GPC. We found that the unsulfurized copolymer **8** gave a lower apparent molecular weight value ($M_n = 3.2 \times 10^3$) than that for the sulfurized analogue **10** ($M_n = 4.4 \times 10^3$), presumably because of significant attractive interactions between the column material and the poly(ferrocenylphosphine) block in the former case.[16]

Block copolymers **7a** and **7b** were characterized by ^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectroscopy. In the ^{1}H NMR spectra of the copolymers, resonances were found for the phenyl (7.0−7.6 ppm) and cyclopentadienyl (3.9−4.4 ppm) protons of the poly(ferrocenylphosphine) segment as well as a silicon methyl resonance (0.28 ppm) assigned to the dimethylsiloxane block. The integrations for the ^{1}H NMR spectra were consistent with the assigned block ratios. In the ^{29}Si NMR spectra, an intense resonance detected at −21.4 ppm was assigned to the poly(siloxane) segment and small peaks to the crossover group (fc*Si*Me$_2$O) [fc = Fe(η-C$_5$H$_4$)$_2$] and the end groups (O*Si*Me$_3$). The ^{31}P and ^{13}C NMR spectra of **7a** and **7b** were also consistent with the assigned structures.

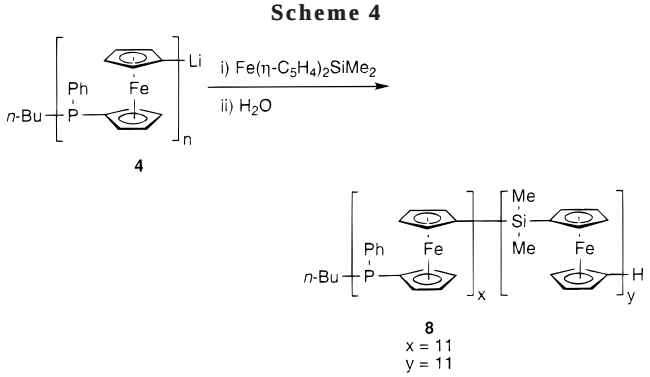
Similarly, the NMR spectra for **8** were consistent with the assigned structure as were the spectra for the sulfurized analogues for **7a**, **b** and **8** (**9a**, **b** and **10**,



respectively).[16]

Thermal Behavior of Block Copolymers 7b and 8. Copolymers **7b** and **8** were analyzed by DSC. In the case of **7b**, glass transitions were detected for both the poly(dimethylsiloxane) block ($T_g = -126$ °C) and the

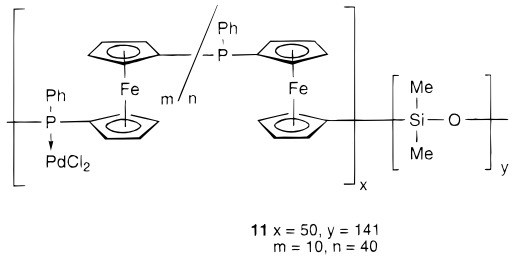
Scheme 4



poly(ferrocenylphenylphosphine) block ($T_g = 126$ °C), as well as a crystallization transition ($T_c = -107$ °C) and melting transition ($T_m = -60$ °C) for the poly(dimethylsiloxane) block. Separate thermal transitions were also observed for the poly(ferrocenyldimethylsilane)-*b*-poly(dimethylsiloxane) copolymer.[6] No transitions were detected for copolymer **8**, possibly because of the shortness of both blocks.

The thermal stability of the block copolymers was examined by TGA. Copolymer **7b** was stable up to 300 °C, whereas **8** did not begin to experience weight loss until 400 °C, with 10% weight losses having occurred at 430 and 450 °C for **7b** and **8**, respectively. On the other hand, **7b** experienced only 50% weight loss by 790 °C, whereas **8** had already lost 50% of its weight by 660 °C.

Metal Coordination Behavior of Block Copolymer 7b with PdCl$_2$ and Fe(CO)$_4$ Fragments. To explore the metal coordination behavior of copolymer **7b**, we reacted this material with Pd(1,5-cod)Cl$_2$ and Fe(CO)$_4$(THF), resulting in polymers **11** and **12**, respec-



tively. In both cases, the amount of coordination that occurred was estimated to be 20−22% (on the basis of the integration of the solution ^{31}P NMR spectra). Copolymer **11** was initially soluble in THF. However, after removal of the THF, the material was no longer found to be appreciably soluble in either THF or chloroform. Subsequent analysis by cross-polarization−magic angle spinning (CP-MAS) ^{31}P NMR spectroscopy (Figure 5) of the insoluble material revealed two resonances (at 29.6 and −33.9 ppm for phosphorus sites with coordinated and no coordinated PdCl$_2$, respectively). The chemical shift for the phosphorus sites with coordinated PdCl$_2$ corresponds reasonably well with the value for the initial solution ^{31}P NMR as well as for the model compound Fe(η-C$_5$H$_4$PPh$_2$)$_2$PdCl$_2$ (33.0 ppm).[17] An additional resonance at 6.6 ppm was also detected. We have attributed the resonances at 29.6 and 6.6 ppm to different coordination modes for phosphorus, i.e., cis and trans coordination in which the polymer chain acts as a bidentate ligand for each Pd center. As in general, the higher field resonance is due to phosphorus ligands in a trans conformation,[18] we have assigned the resonances

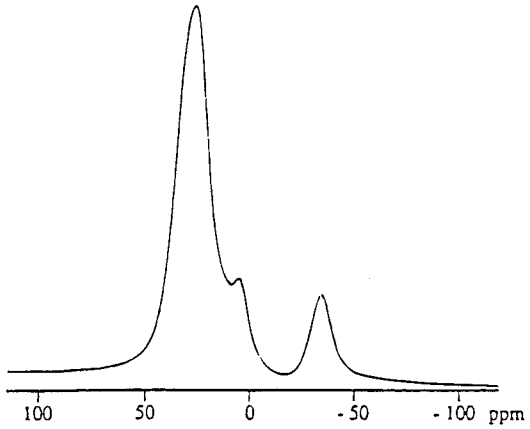
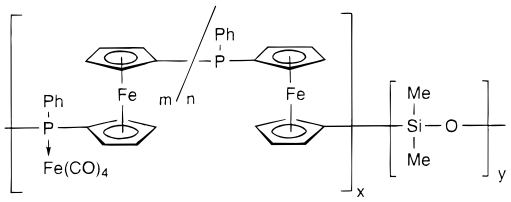


Figure 5. CP-MAS ^{31}P NMR spectrum of block copolymer **11** (spinning rate = 15 kHz).

at 29.6 and 6.6 ppm to cis and trans conformations, respectively.

The insolubility of the block copolymer may be due to cross-linking that results from coordination of Pd centers by two polymer chains rather than one. Evaporation of the reaction solvent would have led to the polymer chains being closer to one another and thus increasing the probability that Pd centers on one polymer chain could also be coordinated by phosphorus sites on a neighboring chain. It is interesting to note that the trans configuration is only observed in the insoluble fraction. Such a configuration is likely the preferred mode for cross-linking by the block copolymer as interchain linkage via cis coordination would be sterically less favorable. In addition, a cis configuration for coordination is more likely to promote solubility, which probably explains why only one conformation (presumably cis) is observed in the solution ^{31}P NMR spectrum.

In an attempt to prevent cross-linking, we also studied the metal coordination behavior of $Fe(CO)_4$ fragments which would be less likely to coordinate to more than one phosphorus site. Copolymer **12**, in contrast to **11**, was found to be very soluble in THF, chloroform, and benzene and was even found to be soluble in hexane. The solution ^{31}P NMR spectrum of **12** (Figure 6) was found to be similar to that of **11** with resonances for coordinated and uncoordinated phosphorus sites. The resonance at 25.8 ppm was attributed to monocoordination, and a very small resonance at 19.9 ppm was probably due to bidentate coordination of the polymer chain. Additional evidence for coordination of $Fe(CO)_x$ moieties to the polymer were provided by IR spectroscopy. The CO stretching region is expanded and shown in Figure 7. The intense absorbances for **12** at 2049, 1975, and 1940 cm^{-1} have been attributed to the presence of $Fe(CO)_4L$ sites (i.e., monocoordination at an axial site) where L represents coordinating phosphorus sites. The absorbance at 1884 cm^{-1} has been attributed to bidentate coordination. In both cases, these results correspond well to the IR spectra of model compounds, $Fe(CO)_4(PPh_3)$ (2049, 1973, and 1939 cm^{-1} in benzene) and *trans*-$Fe(CO)_3(PPh_3)_2$ (1885 cm^{-1} in benzene), respectively.[19] Other low intensity absorbances were also found at 2065, 1987, and 1917 cm^{-1}. We have tentatively assigned these to an equatorial coordination of the phosphine ligand to $Fe(CO)_4$. A corresponding resonance was not observed in the ^{31}P NMR spectrum. This possibly is due to the difficulty of detection by ^{31}P NMR as the overall loading of metallized sites is quite low (~20%, on the basis of integration). A tentative alternative explanation is that the polymer-bound $Fe(CO)_4$ units are fluxional on the NMR time scale and that the ^{31}P NMR resonance at 25.8 ppm represents a weighted average of the predominant axial and less favored equatorial environments.



12 x = 50, y = 141
m = 11, n = 39

Summary

The living anionic ROP of a phosphorus-bridged [1]-ferrocenophane has been achieved and has allowed access to well-defined poly(ferrocenylphosphine) homopolymers and novel block copolymers with coordinating phosphorus atoms. Glass-transition temperatures were found by DSC for high-molecular-weight (n = 100) samples of polymers **5** and **6** at 126 and 206 °C, respectively, and these materials were found to be amorphous by WAXS. Analysis of the poly(ferrocenylphenylphosphine)-*b*-poly(dimethylsiloxane) copolymer **7b** by DSC showed separate thermal transitions for each block which indicated that they were incompatible. Copolymer **7b** was also found to coordinate $PdCl_2$ (to yield insoluble copolymer **11**) as well as $Fe(CO)_4$, resulting in the formation of **12** which was still soluble in hexane.

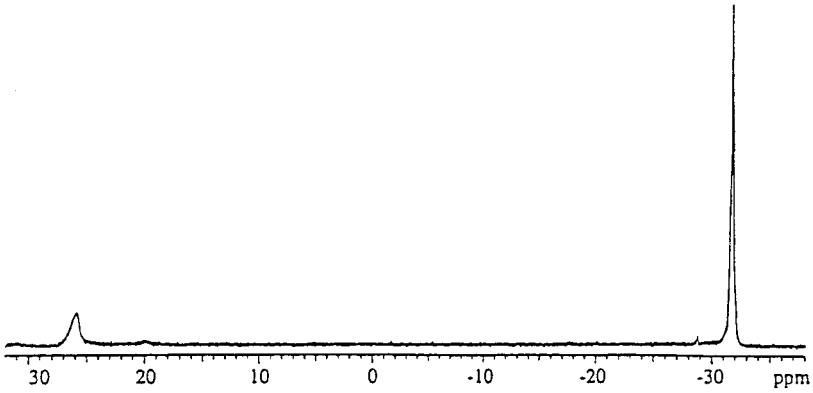


Figure 6. ^{31}P NMR spectrum of block copolymer **12** in THF.

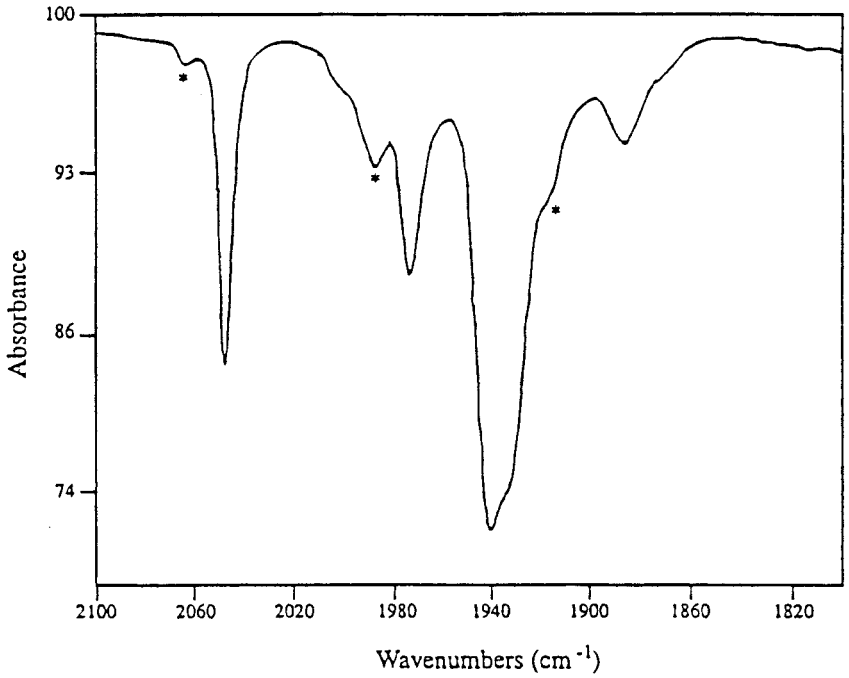


Figure 7. IR spectrum (in CCl_4) of block copolymer **12** in the CO stretching region (* = unassigned absorptions).

Future work on the block copolymers will involve the study of phase separation in the solid state to generate nanoscale organometallic domains and the formation of micellar aggregates in solution.[7] The formation of such novel structures has been previously demonstrated for poly(ferrocenylsilane)-based block copolymer materials.[6,7] On the basis of the additional possibilities offered by the coordination of transition metals to the phosphine groups, poly(ferrocenylphosphine) block copolymers permit opportunities for access to a variety of interesting new materials, e.g., highly metallized organometallic nanostructures or catalytic materials.

Experimental Section

Equipment and Materials. All reactions were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glovebox (Vacuum Atmospheres). All of the living anionic polymerization reactions were performed in an Innovative Technologies glovebox purged with prepurified nitrogen. Hexanes and THF were dried over Na/benzophenone and distilled immediately prior to use. CH_2Cl_2 was dried over CaH_2 and distilled immediately prior to use. All chemicals were purchased from Aldrich unless otherwise noted. Me_3SiCl was distilled immediately prior to use. Distilled H_2O was degassed prior to use. Hexamethylcyclotrisiloxane, $[Me_2SiO]_3$, was dried over CaH_2 and sublimed prior to use. 12-Crown-4 was distilled from CaH_2 and then stored in a glovebox. The monomeric [1]ferrocenophane **1** was prepared by a modification of a previously reported procedure.[20] *n*-BuLi (1.6 M in hexanes) was titrated immediately prior to use by the addition from a 100 μL syringe of menthol with 1,10-phenanthroline as an indicator. 1,1′-Dilithioferrocene, $fcLi_2 \cdot {}^2/_3TMEDA$ was prepared by a literature method.[21]

^1H NMR spectra at 200 or 400 MHz and ^{13}C NMR spectra at 50.3 or 100.5 MHz were recorded either on a Varian Gemini 200 or Unity 400 spectrometer. ^{29}Si at 79.5 MHz and ^{31}P NMR spectra at 121.5 MHz were recorded on a Varian Unity 400 and a Gemini 300 spectrometer, respectively. Solid-state ^{31}P CP-MAS NMR spectra at 81.0 MHz were obtained on a Bruker DSX200 spectrometer using a spinning rate of 15 kHz, a recycle delay of 10 s, and a contact time of 5 ms. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a model 510 HPLC pump, a model U6K injector, Ultrastyragel columns with pore sizes of 10^3-10^5 Å, and a differential refractometer. A flow rate of 1.0 mL/min was used, and the eluent was a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Polystyrene standards were used for calibration purposes.

A Perkin−Elmer DSC-7/Unix differential scanning calorimeter equipped with a TAC 7 instrument controller was used to study the thermal behavior. The thermograms were calibrated with the melting transitions of decane, cyclohexane, and indium and were obtained at a heating rate of 10 °C/min from −145 to 150 °C. A Perkin−Elmer TGA-7/Unix thermal gravimetric analyzer 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.

Synthesis of Phosphorus-Bridged [1]Ferrocenophane 1.[20] Over a period of 15 min, 15.9 mL (117 mmol) of $PhPCl_2$ were added dropwise to a stirred suspension of 30.0 g (109 mmol) $fcLi_2 \cdot {}^2/_3TMEDA$ in 250 mL of hexanes cooled to −30 °C. The reaction mixture was then allowed to warm to room temperature, at which point it was filtered. The solvent, TMEDA, and the small amount of excess $PhPCl_2$ were then removed under vacuum (1×10^{-3} mmHg). The ferrocenophane **1** was extracted using hexanes (250 mL) and crystallized on cooling to −55 °C. The monomer was purified by two further recrystallizations from hexanes resulting in 12.7 g (40%) of dark red crystalline **1**. This purified product was found to be suitable for living anionic polymerizations as no resonances in the ^1H NMR spectrum other than those for **1** and benzene were observed on 20× expansion of the vertical scale for a solution containing 30 mg of **1** in 0.5 mL of C_6D_6. ^1H NMR (200 MHz, C_6D_6) is included for comparison: 7.7−7.5 (m, *o*-Ph, 2H), 7.2−7.0 (m, *p*, *m*-Ph, 3H), 4.6−4.5 (m, Cp, 2H), 4.4−4.3 (m, Cp, 2H), 4.3−4.1 (m, Cp, 4H).

Examples of standard procedures for the anionic polymerization experiments are provided in the following sections.

Anionic ROP of 1 Initiated by *n*-BuLi. The reactions were carried out by the addition of *n*-BuLi (1.6 M in hexanes) to a solution of **1** in 2 mL of THF. The reaction was stirred at room temperature for 30 min before termination by the addition of a few drops of H_2O. The yellow polymer product **5** was isolated by precipitation into hexanes and filtration and was dried under high vacuum for 12 h (Table 1).

For **5** (where n = 11, 20, or 55), the following data were found. ^{31}P NMR (C_6D_6): δ −28.8 [PhP(*n*-Bu)fc−], −31.1 (−fcPPhFc), −31.7 (−fcPPhfc−) ppm. ^{13}C NMR (C_6D_6): δ = 139.9 (Ph, *ipso*-C), 134.2−134.5 (Ph), 129.0 (Ph), 79.3 (Cp, *ipso*-C), 72.0−74.8 (Cp), 69.5 [(η-C_5H_4)Fe(η-C_5H_5)] ppm. ^{1}H NMR (C_6D_6): δ = 7.6−7.7 (Ph), 7.0−7.2 (Ph), 3.9−4.4 (Cp) 1.95 ($CH_2CH_2CH_2CH_3$), 1.23−1.60 ($CH_2CH_2CH_2CH_3$,) 0.86 ($CH_2CH_2CH_2CH_3$) ppm.

For **5** (where n = 70 or 100), the NMR data was the same as per above, but there were no detectable resonances associated with either the *n*-Bu or PPhFc end groups.

Synthesis of the Poly(ferrocenylphosphine)-*b*-Poly(dimethylsiloxane) Copolymer 7a. A solution (50 μL, 0.08 mmol) of 1.6 M *n*-BuLi in hexanes was injected into a dark red solution of 260 mg (0.89 mmol) of **1** in 2 mL of THF cooled to 0 °C. The solution gradually changed from dark red to dark orange over 5 min. After 30 min, 488 mg (2.18 mmol) of hexamethylcyclotrisiloxane and 100 μL of 12-crown-4 were added, and the solution was stirred overnight. The reaction was then quenched by the addition of a few drops of Me_3SiCl and copolymer **7a** were isolated by precipitation into a 1% solution of triethylamine in methanol, filtration, and then drying under high vacuum for 12 h. The polymer was found to be a sticky yellow solid. Yield: 400 mg (83%). $M_w = 9.6 \times 10^3$. $M_n = 8.7 \times 10^3$. PDI = 1.10 (calculated $M_n = 9.2 \times 10^3$).[22]

For **7a** the following data were found. ^{31}P NMR (C_6D_6): δ = −28.8 [PhP(*n*-Bu)fc−], −31.7 (−fcPPhfc−) ppm. ^{29}Si NMR (C_6D_6): δ = 7.6 (−$OSiMe_3$), 0.5 (−fcMe_2SiO−), −21.4 (−Me_2SiO−) ppm. ^{13}C NMR (C_6D_6): δ = 139.9 (Ph, *ipso*-C), 134.5 (Ph), 129.0 (Ph), 79.3 (Cp, *ipso*-C), 72.0−74.8 (Cp), 69.5 [fcSiMe_2O−, ipso-C], 1.4 (−Me_2SiO−) ppm. ^{1}H NMR (C_6D_6): δ = 7.6−7.7 (Ph), 7.0−7.2 (Ph), 3.9−4.4 (Cp), 1.95 ($CH_2CH_2CH_2CH_3$), 1.23−1.60 ($CH_2CH_2CH_2CH_3$,) 0.86 ($CH_2CH_2CH_2CH_3$), 0.28 (−Me_2SiO−) ppm. ^{1}H NMR integration for **7a** gave x = 11 and y = 81; for **7b**, x = 50 and y = 141.

Synthesis of the Poly(ferrocenylphosphine)-*b*-Poly(ferrocenylsilane) Copolymer 8. A solution (50 μL) of 1.6 M *n*-BuLi in hexanes was injected into a dark red solution of 260 mg (0.89 mmol) of **1** in 2 mL of THF. The solution gradually changed from dark red to dark orange over 5 min. At this point, 219 mg (0.90 mmol) of [1]dimethylsilaferrocenophane was added, and the solution was stirred for a further 20 min. The reaction was then quenched by the addition of a few drops of H_2O, and polymer **8** was isolated by precipitation into hexanes and filtration and was then dried under high vacuum for 12 h. The polymer was found to be an orange-yellow powder. Yield: 470 mg (98%). $M_w = 3.5 \times 10^3$. $M_n = 3.2 \times 10^3$. PDI = 1.08 (calculated $M_n = 5.9 \times 10^3$).[22]

For **8**, the following data were found. ^{31}P NMR (C_6D_6): δ = −28.8 [PhP(*n*-Bu)fc−], −31.8 (−fcPPhfc−) ppm. ^{29}Si NMR (C_6D_6): δ = −6.4 (−fcSiMe_2fc−) ppm. ^{13}C NMR (C_6D_6): δ = 139.9 (Ph, *ipso*-C), 134.5 (Ph), 129.0 (Ph), 79.3 (Cp_2FePPh, *ipso*-C), 72.0−74.8 (Cp), 69.5 [(η-C_5H_4)Fe(η-C_5H_5)], −0.5 (−fcSiMe_2-fc−) ppm. ^{1}H NMR (C_6D_6): δ = 7.6−7.7 (Ph), 7.0−7.2 (Ph), 3.9−4.4 (Cp), 1.95 ($CH_2CH_2CH_2CH_3$), 1.23−1.60 ($CH_2CH_2CH_2CH_3$), 0.86 ($CH_2CH_2CH_2CH_3$), 0.54 (−fcMe_2Sifc−) ppm. ^{1}H NMR integration for **8**, gave x = 11 and y = 11.

Reaction of the Poly(ferrocenylphosphine) Homopolymers and Block Copolymers with Elemental Sulfur: Synthesis of the Analogous Poly(ferrocenylphosphine sulfide)s 6, 9, 10. All reactions were carried out in a similar fashion, and that for **5** is detailed as a representative example.

Polymer **5** (50 mg, 0.171 mmol) was dissolved in 2 mL of dry dichloromethane with stirring. To this solution was added elemental sulfur (5.5 mg, 0.021 mmol of S_8). The reaction mixture was allowed to stir overnight. This solution was then filtered, and the solvent was removed under vacuum. GPC analysis was then carried out, and the results are listed in Table 1. The NMR data for polymers **5** were essentially identical, and only the full data for **6** (n = 11, 20, or 55) is reported here. The NMR data for the block copolymers **9a** and **10** are also given.

For **6** (where n = 11, 20, or 55), the following data were found. ^{31}P NMR (C_6D_6): δ = 41.4 [PhP(S)(*n*-Bu)fc−], 37.9 [−fcP(S)PhFc], 37.2 (−fcP(S)Phfc−) ppm. ^{13}C NMR (C_6D_6): δ = 135.0 (Ph, *ipso*-C), 131.3 (Ph), 129.0 (Ph), 79.5 (Cp, *ipso*-C), 72.5−75.8 (Cp), 70.3 [(η-C_5H_4)Fe(η-C_5H_5)] ppm. ^{1}H NMR (C_6D_6): δ = 7.9−8.1 (Ph), 7.0−7.2 (Ph), 4.0−5.0 (Cp), 2.15 (CH_2-$CH_2CH_2CH_3$), 1.10−1.50 ($CH_2CH_2CH_2CH_3$), 0.75 (CH_2CH_2-CH_2CH_3) ppm.

For **6** (where n = 70 or 100), the NMR data was the same as per above, but there were no detectable resonances for the terminal *n*-Bu group.

For **9a**, the following data were found. ^{31}P NMR (C_6D_6): δ = 41.4 [PhP(S)(*n*-Bu)fc−], 37.2 (−fcP(S)Phfc−) ppm. ^{29}Si NMR (C_6D_6): δ = 7.6 (−$OSiMe_3$), 0.5 (−fcMe_2SiO−), −21.4 (−Me_2-SiO−) ppm. ^{13}C NMR (C_6D_6): δ = 135.0 (Ph, *ipso*-C), 131.3 (Ph), 129.0 (Ph), 79.5 (Cp, *ipso*-C), 72.5−75.8 (Cp), 70.3 [(η-C_5H_4)Fe(η-C_5H_5)], 1.4 (−Me_2SiO−) ppm. ^{1}H NMR (C_6D_6): δ = 7.9−8.1 (Ph), 7.0−7.2 (Ph), 4.0−5.0 (Cp), 2.15 ($CH_2CH_2CH_2$-CH_3), 1.10−1.50 ($CH_2CH_2CH_2CH_3$,), 0.75 ($CH_2CH_2CH_2CH_3$), 0.28 (−Me_2SiO−) ppm.

For **10**, the following data were found. ^{31}P NMR (C_6D_6): δ = 41.4 [PhP(S)(*n*-Bu)fc−], 37.8 (−fcP(S)PhfcSiMe_2−), 37.2 (−fcP(S)Phfc−) ppm. ^{29}Si NMR (C_6D_6): δ = −6.4 (−fcSiMe_2-fc−) ppm. ^{13}C NMR (C_6D_6): δ = 135.0 (Ph, *ipso*-C), 131.3 (Ph), 129.0 (Ph), 79.5 (Cp, *ipso*-C), 72.5−75.8 (Cp), 70.3 [(η-C_5H_4)-Fe(η-C_5H_5)], −0.5 (−fcSiMe_2fc−) ppm. ^{1}H NMR (C_6D_6): δ = 7.9−8.1 (Ph), 7.0−7.2 (Ph), 4.0−5.0 (Cp), 2.15 ($CH_2CH_2CH_2$-CH_3), 1.10−1.50 ($CH_2CH_2CH_2CH_3$), 0.75 ($CH_2CH_2CH_2CH_3$), 0.54 (−fcMe_2Sifc−) ppm.

Reaction of Block Copolymer 7b with Pd(1,5-cod)Cl_2. A small amount (0.113 g, 0.226 mmol of available P sites) of **7b** was dissolved in 2 mL of THF in air. To this stirred orange solution was added 0.019 g (0.067 mmol) of Pd(1,5-cod)Cl_2. The solution immediately turned red-purple, and the evolution of 1,5-cod was noted based on the characteristic odor of the material. The solution was allowed to stir for 1 h. An aliquot of this solution was analyzed by solution NMR, the results of which are described below. The solution was filtered, and the solvent was removed under high vacuum, yielding **11** as a glossy, dark red film. The compound was no longer appreciably soluble in either THF or $CDCl_3$. The sample was then analyzed by CP-MAS ^{31}P NMR, and the results are described below. Yield: 0.090 g (74%, on the basis of 20% coordinated P sites).

For **11**, the following data were found. ^{31}P NMR (THF): δ = 25.2 (with coordinated $PdCl_2$) and −31.7 (uncoordinated PPh sites) ppm. On the basis of the integration of the solution NMR spectrum, the amount of phosphorus sites with coordinated $PdCl_2$ was estimated to be 20%. CP-MAS ^{31}P NMR: 29.6 (with coordinated $PdCl_2$ in a cis conformation), 6.6 (with coordinated $PdCl_2$ in a trans conformation), and −33.9 (uncoordinated PPh sites) ppm.

Reaction of Block Copolymer 7b with $Fe(CO)_4$(THF). A small quantity (0.090 g, 0.247 mmol) of $Fe_2(CO)_9$ was suspended in 10 mL of THF, and the resulting cloudy solution was then added dropwise with stirring to 0.515 g (1.03 mmol of P sites) of **7b** dissolved in 5 mL of THF. The solution was then allowed to stir for a further 2 h and filtered. Polymer **12** was isolated by precipitation into methanol and dried under high vacuum, yielding an adhesive, orange-yellow material. After isolation, **12** was stored under nitrogen. On the basis of ^{31}P NMR analysis, the proportion of phosphorus sites with coordinated $Fe(CO)_4$ was estimated to be 22%. In contrast to **11**, **12** remained soluble in the same solvents as the parent polymer **7b**. Yield: 0.489 g (88%, on the basis of 22% coordinated P sites).

For **12**, the following data were found. ^{31}P NMR (C_6D_6): δ = 25.8 [with coordinated $Fe(CO)_4$] and −31.7 [no coordinated $Fe(CO)_4$] ppm. Additionally, there are very small resonances at 19.9 [with coordinated $Fe(CO)_3$] and −28.8 [*n*-BuP(Ph)Cp end group] ppm. The ^{1}H NMR spectrum was consistent with retention of the structure described for **7b**. IR spectrum (in CCl_4, terminal carbonyl region): 2049 (s), 1975 (s), and 1940 (vs) cm^{-1}, which are due to the CO groups of $Fe(CO)_4$(L); 1884 (s) cm^{-1} due to the CO groups of $Fe(CO)_3L_2$ where L represents P(III) sites within the polymer backbone.

Acknowledgment. This work was funded by the Natural Sciences and Engineering Research Council (NSERC). T.J.P. thanks NSERC for a graduate scholarship, and I.M. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1994−1998), NSERC for an E. W. R. Steacie Fellowship (1997−1999), and the University of Toronto for a McLean Fellowship (1997−2003).

References and Notes

(1) Foucher, D. A.; Tang, B.-Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.
(2) Manners, I. *Adv. Organomet. Chem.* **1995**, *37*, 131.
(3) Manners, I. *Can. J. Chem.* **1998**, *76*, 371.
(4) For the work of others on ring-opened poly(ferrocenes), see: (a) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926. (b) Pannell, K. H.; Dementiev, V. V.; Cervantes-Lee, F.; Nguyen, M. T.; Diaz, A. F. *Organometallics* **1994**, *13*, 3644. (c) Stanton, C. E.; Lee, T. R.; Grubbs, R. H.; Lewis, N. S.; Pudelski, J. K.; Callstrom, M. R.; Erickson, M. S.; McLaughlin, M. L. *Macromolecules* **1995**, *28*, 8713. (d) Reddy, N. P.; Yamashita, H.; Tanaka, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2263. (e) Barlow, S.; Rohl, A. L.; Shi, S.; Freeman, C. M.; O'Hare, D. *J. Am. Chem. Soc.* **1996**, *118*, 7578. (f) Buretea, M. A.; Tilley, T. D. *Organometallics* **1997**, *16*, 1507. (g) Heo, R. W.; Somoza, F. B.; Lee, T. R. *J. Am. Chem. Soc.* **1998**, *120*, 1621.
(5) Rulkens, R.; Ni, Y.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 12121.
(6) Ni, Y. Z.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102.
(7) Massey, J. A.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533.
(8) (a) Foucher, D. A.; Nelson, J. M.; Honeyman, C.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709. (b) Rulkens, R.; Resendes, R.; Verma, A.; Manners, I.; Murti, K.; Fossum, E.; Miller, P.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 8165.
(9) MacLachlan, M. J.; Aroca, P.; Coombs, N.; Manners, I.; Ozin, G. A. *Adv. Mater.* **1998**, *10*, 144.
(10) Seyferth, D.; Withers, H. P. *Organometallics* **1982**, *1*, 1275.
(11) Fellman, J. D.; Garrou, P. E.; Withers, H. P.; Seyferth, D.; Traficante, D. D. *Organometallics* **1983**, *2*, 818.
(12) Honeyman, C. H.; Foucher, D. A.; Dahmen, F. Y.; Rulkens, R.; Lough, A. J.; Manners, I. *Organometallics* **1995**, *14*, 5503.
(13) Honeyman, C. H.; Peckham, T. J.; Massey, J. A.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1996**, 2589.
(14) Withers, H. P.; Seyferth, D.; Fellman, J. D.; Garrou, P. E.; Martin, S. *Organometallics* **1982**, *1*, 1283.
(15) Peckham, T. J.; Lough, A. J.; Manners, I. *Organometallics* **1999**, *18*, 1030.
(16) In the case of the copolymers **7a** and **7b**, sulfurization (to yield **9a** and **9b**) led to some cleavage of the poly(dimethylsiloxane) block as the GPC traces for **9a** and **9b** were found to be multimodal. The integration of the ^{1}H NMR spectra of the products remained consistent with the composition calculated for **7a** and **7b**.
(17) We recorded the ^{31}P NMR spectrum ourselves in THF. The material was kindly provided by Digital Specialty Chemicals, Ltd.
(18) Pregosiu, P. S.; Kunz, R. W. *^{31}P and ^{13}C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979.
(19) Graff, J. L.; Sanner, R. D.; Wrighton, M. S. *Organometallics* **1982**, *1*, 837.
(20) The synthesis of [1]phosphaferrocenophane **1** has been previously described. See: (a) Osborne, A. G.; Whiteley, R. H.; Meads, R. E. *J. Organomet. Chem.* **1980**, *193*, 345. (b) Seyferth, D.; Withers, H. P., Jr. *J. Organomet. Chem.* **1980**, *185*, C1.
(21) Bishop, J. J.; Davison, A.; Katcher, M. L.; Lichtenberg, D. W.; Merrill, R. E.; Smart, J. C. *J. Organomet. Chem.* **1971**, *27*, 241.
(22) The calculated molecular weights for block copolymers **7a** and **7b** were based on ^{1}H NMR integration assuming full conversion of **1** to living polymer **4**.

MA981329W