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# Synthesis and Properties of Poly(ferrocenyldihydrosilane) Homopolymer and Random Copolymers

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ABSTRACT: The strained, silicon-bridged [1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiH_2$ (**4**) was prepared via the reaction of $H_2SiCl_2$ with $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA in ether at $< -78$ °C. This species was analyzed by single-crystal X-ray diffraction and was found to possess a strained, ring-tilted structure similar to those of previously reported silicon-bridged [1]ferrocenophanes [tilt angle 19.1(1)°]. Thermal ring-opening polymerization of **4** afforded the poly(ferrocenylsilane) $[Fe(\eta\text{-}C_5H_4)_2SiH_2]_n$ (**5**), which was found to be insoluble in common organic solvents. Under the same conditions, mixtures of **4** and the dimethyl analog $Fe(\eta\text{-}C_5H_4)_2SiMe_2$ (**1a**) afforded soluble copolymers **7a–c**, consisting of random ferrocenyldihydrosilane and ferrocenyldimethylsilane repeat units, as the first examples of poly(ferrocenylsilane) copolymers prepared via ring-opening polymerization. Repeat unit composition of the random copolymers could be controlled by manipulation of the monomer ratio and was readily assessed by $^1H$ NMR spectroscopy. TGA of **5** under $N_2$ at a heating rate of 10 °C/min found this material to be the most thermally stable to weight loss of all the poly(ferrocenylsilanes) yet studied with only 10% weight loss up to 600 °C and a ceramic yield of 63% at 1000 °C. Among copolymers **7a–c**, thermal stability to weight loss increased with increasing ferrocenyldihydrosilane repeat unit content. The homopolymer **5** was found to be crystalline by wide-angle X-ray scattering, and a melting transition at 165 °C was detected by DSC. Glass transitions for the essentially amorphous copolymers were observed to fall between the $T_g$ of 18 °C observed for **5** and the $T_g$ of 33 °C reported for $[Fe(\eta\text{-}C_5H_4)_2SiMe_2]_n$ (**2a**).

## Introduction

The development of polymer systems that incorporate transition metal atoms in the main-chain structure is a promising route to new, processable materials with novel and potentially useful properties.[1] Ferrocene-based polymer systems represent interesting examples of transition metal-based macromolecules.[2–9] Low molecular weight, partially characterized poly(ferrocenylsilanes) consisting of alternating ferrocene and organosilane units were first prepared in the late 1960s via the polycondensation reactions of $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA and diorganodichlorosilanes.[10] In 1992, we reported the preparation of high molecular weight poly(ferrocenylsilanes) via the thermal ring-opening polymerization (TROP) of strained, silicon-bridged [1]ferrocenophanes (Scheme 1).[11] More recently, we described the anionic and transition metal-catalyzed ring-opening polymerization of these strained monomers in solution at room temperature.[12,13]

Detailed studies of poly(ferrocenylsilanes) have focused on the variety of interesting physical properties that they exhibit.[9,14–18] A large number of silicon-bridged [1]ferrocenophanes, substituted at silicon with a variety of organic groups, have been prepared and polymerized, and clear relationships between polymer properties and the substituents at silicon have emerged. For example, in the case of poly(ferrocenylsilanes) symmetrically substituted at silicon with *n*-alkyl groups, polymer $T_g$ increases smoothly with decreasing alkyl group chain length.[15] Thus, while **2** (R, R′ = *n*-hexyl) exhibits a $T_g$ of −26 °C, **2** (R, R′ = Me) exhibits a $T_g$ of 33 °C. In addition, thermal stability to weight loss varies considerably with the substituents at silicon.[14] Thus, thermolysis of **2** (R, R′ = Ph) through 1000 °C at 10 °C/min under $N_2$ affords an Fe/C/Si ceramic product in 17% yield while identical treatment of **2a** affords a 36% yield of ceramic.

Preparation of a silicon-bridged [1]ferrocenophane with two hydrogen substituents at silicon has not yet been reported. Our interest in such a species stems from its potential to exhibit unique reactivity due to the

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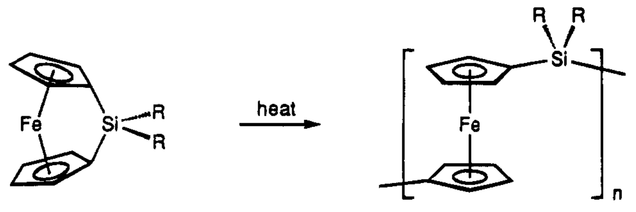
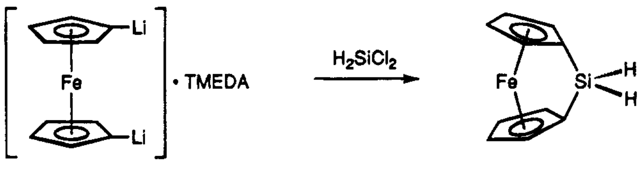
Scheme 1



**1** **2**

[e.g. **1a**/**2a** R = Me]

Scheme 2



**3** **4**

sterically unencumbered nature of the substituents at silicon and the chemical reactivity of the Si−H bonds. For example, ring-opening polymerization reactions (both thermal and anionic)[12] of this species would be expected to proceed under mild conditions because the bridging silicon atom is not sterically shielded by organic substituents and is thus readily accessible. For similar reasons, poly(ferrocenylsilane) materials prepared via TROP of this ferrocenophane might exhibit unusual properties and reactivity. For example, these polymers would be attractive as pyrolytic precursors to novel ferromagnetic Fe/C/Si ceramic materials[14] since they would be expected to afford ceramics in high yield given the possibility that the reactive Si−H functionality might participate in thermal cross-linking processes. Additionally, the presence of reactive Si−H bonds in these polymers might allow for their functionalization in a controlled manner via hydrosilylation reactions. In this paper, we describe the first preparation and structure of a dihydrosilane-bridged [1]ferrocenophane, thermal ring-opening polymerization and copolymerization reactions of this species, and properties of the resulting polymeric materials.

## Results and Discussion

**Synthesis of Monomer $Fe(\eta\text{-}C_5H_4)_2SiH_2$ (4).** Silicon-bridged [1]ferrocenophanes with organic substituents at silicon are prepared in good yield by reaction of $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA (**3**) with diorganodichlorosilanes ($RR'SiCl_2$) at −78 °C.[9,19a,b] Our initial attempts to prepare **4**, with two hydro substituents at silicon, involved similar methodology. However, slow condensation of $H_2SiCl_2$ into ethereal or hexanes slurries of $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA at −78 °C afforded only insoluble oligomeric and/or polymeric products. We reasoned that, under these reaction conditions, ferrocenophane formation and anionic ring opening might both occur readily. The desired ferrocenophane **4** might therefore be generated in the presence of lithioferrocenyl species and suffer anionically initiated ring-opening reactions.[12a] We do not observe such complications during the syntheses of silicon-bridged [1]ferrocenophanes with organic substituents at silicon because anionic ring-opening reactions of these species do not occur until temperatures well above −78 °C, whereas the sterically accessible environment of Si in **4** might result in greater susceptibility to anionic attack. Our synthetic strategy addressing these concerns involved rapid addition of a slight excess of $H_2SiCl_2$ to an ethereal slurry of $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA frozen at liquid nitrogen temperatures (−196 °C) (Scheme 2). Under these conditions, we hoped to generate **4** and consume all nucleophilic ferrocenyl−lithium species in the reaction mixture at temperatures well below those at which anionic ring-opening processes would become problematic.

Thus, an ethereal slurry of $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA was frozen with a liquid $N_2$ bath and was then treated with 1.1 equiv of $H_2SiCl_2$, which had been condensed and collected at −78 °C. The cooling bath was then removed, and the mixture was allowed to warm slowly to room temperature with vigorous stirring. As the ether melted (−116 °C), a distinct color change from yellow to deep red, consistent with ferrocenophane formation, was observed. Upon warming to room temperature, a red solution with copious quantities of white precipitate was obtained. The slurry was filtered and the filtrate was concentrated in vacuo to afford a red solid. Vacuum (0.01 mmHg) sublimation of this solid onto a water-cooled probe without application of external heat readily afforded **4** as a powdery red solid in 38% yield. We found that crude **4** was unstable in solution, readily undergoing oligo-/polymerization at temperatures as low as −30 °C. However, after purification by sublimation, **4** is stable both as a solid and in solution under an inert atmosphere.

**Characterization of Monomeric Ferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiH_2$ (4).** The identity of **4** was confirmed by $^1H$, $^{13}C$, and $^{29}Si$ NMR analysis. Analysis by $^1H$ NMR ($C_6D_6$) found triplets at 4.07 and 4.28 ppm assigned to the α and β cyclopentadienyl protons and a sharp singlet at 5.41 ppm, with $^{29}Si$ sidebands ($^1J_{H-Si}$ = 215 Hz), assigned to the $SiH_2$ group. Separation of the $^1H$ NMR signals for the α and β cyclopentadienyl protons, which is an indication of cyclopentadienyl ring tilt,was unusually small for **4** (0.21 ppm).[19] A strained structure was nevertheless suggested by $^{13}C$ NMR ($C_6D_6$) analysis, which found a high-field chemical shift (21.3 ppm) for the *ipso* cyclopentadienyl carbons, typical of strained, silicon-bridged [1]ferrocenophanes.[20] The proton-coupled $^{29}Si$ NMR spectrum ($C_6D_6$) of **4** consisted of a well-resolved triplet at −42.7 ppm with a $^1J_{Si-H}$ value of 215 Hz.

**X-ray Diffraction Study of 4.** In order to provide additional characterization of **4** and to assess possible structural effects related to the sterically undemanding hydro substituents at silicon in **4**,[21−26] we undertook a single-crystal X-ray diffraction study of this compound. Figure 1 shows the molecular structure of **4**; Table 1 lists data collection details for the analysis of **4**; and Table 2 compares important structural features of **4** and **1a**. The structure of **4** consists of tilted cyclopentadienyl rings which are eclipsed and bridged by the dihydrosilyl group. The structural features of **4** do not differ significantly from those of other strained, silicon-bridged [1]ferrocenophanes previously studied.[22,24,27] However, close inspection of the comparative data in Table 2 reveals several subtle structural differences between **4** and **1a**[22] which may be a consequence of the sterically undemanding hydrogen substituents at silicon in the former. For example, the Me−Si−Me angle in **1a** is 114.8(6)° while the H−Si−H angle in **4** is reduced to 112.8(12)° . Reduction of this angle may be a consequence of less steric repulsion between the smaller hydrogen substituents in **4**. The reduced H−Si−H angle in **4** is accompanied by scissoring, and thus the C1−Si−C6 angle in this species [97.21(7)°] is greater

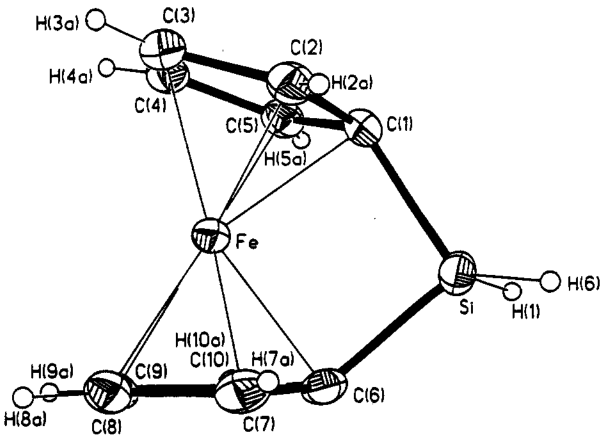


**Figure 1.** Molecular structure of $Fe(\eta\text{-}C_5H_4)_2SiH_2$ (**4**) using 50% probability thermal ellipsoids. The hydrogen atoms are given arbitrarily small thermal parameters for clarity. See Table 1 for a summary of the crystallographic data.

**Table 1. Crystal Data and Structure Refinement for 4**

| | |
|---|---|
| empirical formula | $C_{10}H_{10}FeSi$ |
| formula wt | 214.12 |
| space group | $P2_1/c$ |
| unit cell dimens | |
| $a$ (Å) | 10.629(1) |
| $b$ (Å) | 7.390(1) |
| $c$ (Å) | 11.895(1) |
| $\beta$ (deg) | 111.36(1) |
| $V$ (Å$^3$) | 870.2(2) |
| Z | 4 |
| $D_{calcd}$ (Mg/m$^3$) | 1.634 |
| crystal size (mm) | 0.48 × 0.38 × 0.12 |
| $\theta$ range (deg) | 3.31–29.99 |
| absorption coeff (mm$^{-1}$) | 1.803 |
| $F$(000) | 440 |
| refinement method | full-matrix least squares on $F^2$ |
| data/parameters | 2538/150 |
| goodness of fit | 1.012 |
| $R1$ [$I > 2\sigma(I)$] | 0.0278 |
| $wR2$ (all data) | 0.0777 |

**Table 2. Comparison of Important Structural Features of Ferrocenophanes 1a and 4**

| | 1a | 4 |
|---|---|---|
| ring tilt α (deg) | 20.8(5) | 19.1(1) |
| Cp–Si/Cp, $\beta$ (deg) | 37.0(6) | 39.1(1), 38.8(1) |
| Si–C1 (Å) | 1.851(9) | 1.882(2) |
| Si–C6 (Å) | 1.865(9) | 1.880(2) |
| C1–Si–C6 (deg) | 95.7(4) | 97.21(7) |
| C11–Si–C12/H–Si–H (deg) | 114.8(6) | 112.8(12) |
| RC1–Fe–RC2, $\delta$ (deg)[a] | 164.74(8) | 165.6(1) |
| Fe displacement (Å)[b] | 0.2164(11) | 0.205(2) |
| Fe···Si (Å) | 2.690(3) | 2.6729(6) |

[a] RC1 and RC2 are the ring centroids of cyclopentadienyl rings 1 and 2, respectively. [b] Fe displacement is the displacement of the iron atom from the line joining the RC1 and RC2.

than that in **1a** [95.7(4)°]. The C1–Si–C6 angle is closely related to the angles α (cyclopentadienyl ring tilt) and $\beta$ (between the cyclopentadienyl rings and the exocyclic bonds to Si) in silicon-bridged [1]ferrocenophanes.[24] Increases in the C1–Si–C6 angle are generally accompanied by reduced α values and increased $\beta$ values. Indeed, the increased C1–Si–C6 angle in **4**, relative to **1a**, is accompanied by a decrease in α [19.1(1)° vs 20.8(5)°] and increases in $\beta$ [39.1(1)°, 38.8(1)° vs 37.0(6)°]. In turn, for silicon-bridged [1]ferrocenophanes, increases in $\beta$ and decreases in α are generally accompanied by reduced Fe displacement from the line joining the cyclopentadienyl ring centroids (RC1, RC2), reduced Fe···Si distances, and increased RC1–Fe–RC2 angles.[24] Indeed, relative to **1a**, both Fe displacement [0.205(2) vs 0.2164(11) Å] and the Fe···Si distance [2.6729(6) vs 2.690(3) Å) are reduced in **4** while the RC1–Fe–RC2 angle is increased [165.6(1)° vs 164.74(8)°].

**Scheme 3**

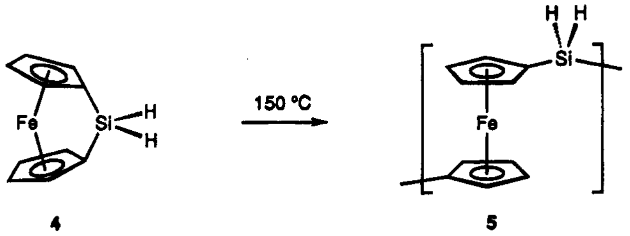
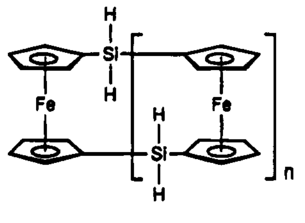


**Chart 1**



**6**

**TROP of 4: Characterization of $[Fe(\eta\text{-}C_5H_4)_2SiH_2]_n$ (5).** A preliminary study of the TROP of **4** by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min under $N_2$ revealed a sharp melting endotherm at 122 °C followed immediately by a large, broad exotherm at ca. 125–175 °C which is assigned to the TROP reaction. Based on this result, a bulk polymerization of **4** was undertaken by sealing a sample of this species in a Pyrex tube under vacuum and heating at 150 °C for 2 h. The sample rapidly melted, became more viscous, and within 10 min was immobile. A red solid was recovered which proved to be insoluble in common organic solvents (see Experimental Section). The sample was ground, extracted with THF for 24 h, filtered, and dried in vacuo to afford a 90% yield of insoluble material. Although insolubility precluded extensive characterization of the product, $^{29}Si$ CPMAS NMR, IR, elemental analysis, and pyrolysis mass spectrometry experiments were consistent with the structure of ring-opened poly(ferrocenylsilane) **5** (Scheme 3).

For example, the IR spectrum of a thin film of **5** showed a strong peak at 2137 cm$^{-1}$, assigned to Si–H stretching. Furthermore, we previously found extrusion of cyclic oligomeric species to be a characteristic thermal reaction of poly(ferrocenylsilanes).[28] When a sample of **5** was introduced into our mass spectrometer and the sample probe was heated to 600 °C, we observed peaks in the resulting spectra that could readily be assigned to cyclic oligomer species such as **6** ($n$ = 1, 2, 3).[14a]

**Thermal Ring-Opening Copolymerization of $Fe(\eta\text{-}C_5H_4)_2SiH_2$ (4) and $Fe(\eta\text{-}C_5H_4)_2SiMe_2$ (1a).** We approached the preparation of soluble polymeric materials containing dihydrosilane units via thermal ring-opening copolymerization of **4** with dimethyl analog **1a**. Our previous DSC studies of the latter ferrocenophane showed that its TROP exotherm coincides well with that of **4**.[11] Furthermore, since TROP of **1a** affords poly(ferrocenylsilane) **2a**, which is soluble in common organic solvents, we felt that a copolymer prepared via TROP of a mixture of **4** and **1a** would likewise be soluble.[11] In collaboration with Matyjaszewski and coworkers, we previously obtained random copolymers via the thermolysis of mixtures of silicon-bridged ferro-

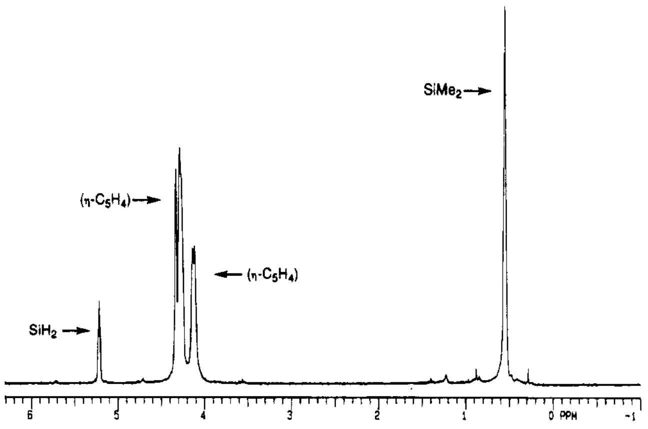


**Figure 2.** $^1$H NMR (200 MHz) of **7c**.

cenophane **1a** and the cyclic tetrasilane [SiMePh]$_4$.[29] However, to date, well-characterized copolymers from thermolysis of ferrocenophane mixtures have not been reported. A challenge of such copolymerization experiments is to be able to differentiate between a true copolymer and a blend of the two homopolymers formed by separate homopolymerizations of the two monomers. The insolubility of the ferrocenyldihydrosilane homopolymer **5** compared to the dimethyl analog **2a**, which is soluble in polar organic solvents, was expected to allow us to easily differentiate between a blend and a true copolymer of **5** and **2a** as different solubility characteristics would be anticipated. In a preliminary experiment, a 1:1 mixture of the two ferrocenophanes was sealed under vacuum in a Pyrex tube and while mixing heated slowly from 20 to 150 °C. Under these conditions we expected the melt to become homogeneous prior to the onset of TROP. The mixture increased rapidly in viscosity and became immobile after 10 min at 150 °C. Heating at this temperature was maintained for a total of 2 h. The resulting red solid was found to be readily soluble in THF, suggesting that the product was indeed a copolymer rather than a mixture of two homopolymers. A 65% yield of a fibrous, orange solid was obtained by precipitation into hexanes. GPC analysis of the copolymer in THF found it to be monomodal and of high molecular weight ($M_w = 4.2 \times 10^5$, $M_n = 1.5 \times 10^5$, PDI = 2.8).

NMR analysis of the material was consistent with copolymer structure **7** (Scheme 4), incorporating both dimethylsilane and dihydrosilane monomer units. IR analysis of a thin film of the material found a peak of medium intensity at 2134 cm$^{-1}$, assigned to Si–H stretching, but also strong peaks at 2959, 2925, and 2853 cm$^{-1}$ consistent with the presence of SiCH$_3$ groups. The $^1$H NMR spectra (in C$_6$D$_6$) of the copolymer **7c** (Figure 2) included peaks at 5.21 and 0.55 ppm assigned to SiH and SiCH$_3$ protons, respectively. Integration of these peaks suggested an approximate 2:3 distribution of dihydrosilane and dimethylsilane groups in this copolymer (i.e., $x$:$y$ = 2:3). A proton-decoupled $^{29}$Si NMR spectrum of copolymer **7c** (Figure 3) found peaks at −6.4 and −37.5 ppm assigned to methyl-substituted silicon atoms and dihydrogen-substituted silicon atoms, respectively.[11] We assigned the smaller peaks shown in the insets to crossover groups, indicating that the copolymer microstructure is random in nature.[29] The proton-coupled $^{29}$Si NMR spectrum (C$_6$D$_6$) of **7c** (Figure 4) showed a broad singlet at −6.4 ppm and a triplet ($^1J_{\text{Si-H}}$ = 200 Hz) at −37.5 ppm.

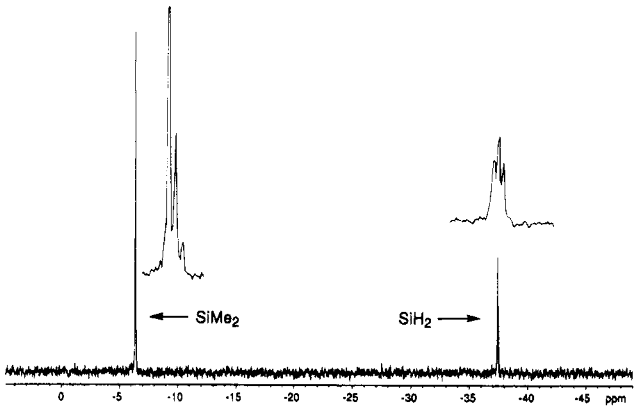
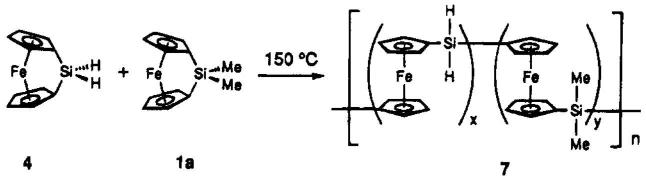


**Figure 3.** $^{29}$Si NMR (proton decoupled, 79.5 MHz) of **7c**.

**Scheme 4**



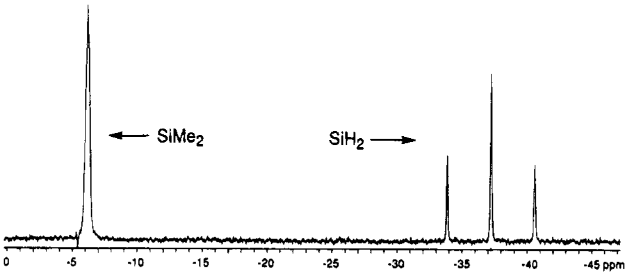


**Figure 4.** $^{29}$Si NMR (proton coupled, 59.6 MHz) of **7c**.

**Table 3. Data for Copolymers 7a–d prepared via TROP**

| copolymer | reactant ratio (**1a**/**4**) | SiMe$_2$/SiH$_2$ $^1$H NMR integral ratio theor | exp | $M_w$ | $M_n$ | PDI | % yield |
|---|---|---|---|---|---|---|---|
| **7a** | 4:1 | 12:1 | 12.2:1 | $6.2 \times 10^5$ | $4.4 \times 10^5$ | 1.4 | 96 |
| **7b** | 2:1 | 6:1 | 6.3:1 | $3.6 \times 10^5$ | $2.1 \times 10^5$ | 1.7 | 81 |
| **7c** | 1:1 | 3:1 | 2.4:1 | $3.0 \times 10^5$ | $2.0 \times 10^5$ | 1.5 | 65 |
| **7d** | 1:2 | 1.5:1 | 2.2:1 | $3.0 \times 10^4$ | $1.8 \times 10^4$ | 1.7 | 52 |

Further copolymerization experiments demonstrated that it is possible to control the ratio of dihydrosilane and dimethylsilane units in the copolymer ($x$:$y$) by manipulating the ratio of reactants. Thus, monomer mixtures with **1a**:**4** compositions of 4:1, 2:1, and 1:2 were heated at 150 °C for 2 h. The corresponding copolymers were then obtained as fibrous, orange solids by dissolution in THF, filtration, and precipitation in hexanes. Copolymer compositions could be readily assessed via integration of the resonances at ca. 5.21 (SiH$_2$) and 0.55 ppm (SiMe$_2$) in the copolymer $^1$H NMR spectra. Table 3 summarizes the results of the copolymerization experiments. For copolymers **7a–c** the theoretical and experimental $^1$H NMR data for copolymer composition are in good agreement. Furthermore, the GPC molecular weight estimates and copolymer yields for **7a–c** are typical of poly(ferrocenylsilanes) prepared via TROP.[11,15,16] These data are therefore indicative of well-behaved copolymerization reactions.

In the case of **7d**, with the highest proportion of **4** in the reactant mixture, the experimental $y$:$x$ value found for the copolymer is considerably higher than the theoretical value (i.e., the content of SiMe$_2$ units in the copolymer is high). Additionally, this material is of low molecular weight and is obtained in low yield for a poly(ferrocenylsilane) prepared by TROP. A possible explanation for these observations is that copolymers with high compositions of dihydrosilyl units suffer reduced solubility and, as a result, are removed during the filtration step of the purification. Removal of the dihydro-rich material leads to a reduction in yield. The reduced solubility of materials with greater dihydro compositions is consistent with the complete insolubility of homopolymer **5**. The materials obtained after purification consist of lower molecular weight fractions with higher compositions of $SiMe_2$ units and hence greater solubility. These results suggest that for the **1a**/**4** monomer couple, due to the insolubility of dihydrosilyl-rich materials, the preparation of copolymers in high yield and with controllable repeat unit compositions requires a reaction mixture consisting of at least 50% **1a**.

**Analysis of Poly(ferrocenyldihydrosilane) Homopolymer and Copolymers.** Homopolymer **5** and copolymers **7a–d** have been studied by DSC, wide-angle X-ray scattering (WAXS), pyrolysis mass spectrometry, and thermogravimetric analysis (TGA). Our DSC studies focused on determining the glass transition ($T_g$) and possible melt transition of **5** and assessing the effect of repeat unit composition on copolymer $T_g$. We also expected that copolymer glass transition behavior would help us to distinguish between random and block microstructure for these materials. WAXS provided additional information on polymer morphologies. Pyrolysis mass spectrometry was used to provide further information on the polymer microstructure. Our TGA studies focused on establishing the thermal stability of **5** to weight loss and assessing the effect of repeat unit composition on copolymer thermal stability to weight loss.

**a. Thermal Transition Behavior.** Poly(ferrocenylsilanes) with different substituents at silicon are usually amorphous.[16] However, many symmetrically substituted polymers possess the ability to crystallize, and particularly after annealing, samples of these materials show melt transitions by DSC analysis.[9] Poly(ferrocenylsilanes) also exhibit glass transitions with small changes in heat capacity which are readily observable by DSC.[9] As described previously, the side groups at silicon exert a considerable effect on poly(ferrocenylsilane) $T_g$. This is exemplified by the smooth increase in $T_g$ observed as the length of $n$-alkyl substituents decreases from $n$-hexyl to methyl.[15] Since the hydro substituents in **5** are the smallest yet incorporated into a poly(ferrocenylsilane) we were interested in determining the glass transition temperature of this material and probing for the possibility of a melt transition. Also, since block copolymers generally afford two $T_g$s, which are similar to the $T_g$s of the two homopolymers, while random copolymers generally afford a single $T_g$ that is located between the $T_g$s of the two homopolymers,[30] DSC analysis would be valuable in probing the microstructure of copolymers **7a–d**. Finally, if the $T_g$ of **5** differed considerably from that of **2a**, then control of the random copolymer $T_g$ might be possible by control of the dihydrosilane/dimethylsilane composition ($x$:$y$).

DSC analysis of **5** at 10 °C/min under $N_2$ revealed a weak $T_g$ at 16 °C and a strong, irreversible endothermic transition at 165 °C. Subsequent scans of the same sample showed the $T_g$ but not the strong endotherm. This behavior proved to be reproducible for all of the samples we studied. In regard to the irreversible endotherm at 165 °C, similar transitions have been observed on the initial DSC scan for annealed samples of several poly(ferrocenylsilanes) and have been assigned to melt transitions resulting from partially crystalline material.[9] In contrast to the situation for **5**, the copolymers **7** showed no evidence for a melt transition.

**Table 4. Thermal Analysis Data for 5, Copolymers 7a–d, and 2a**

| material | $T_g$ (°C) | TGA % yield at 1000 °C | material | $T_g$ (°C) | TGA % yield at 1000 °C |
|---|---|---|---|---|---|
| **5** | 16 | 63 | **7b** | 27 | 55 |
| **7d** | 21 | 59 | **7a** | 32 | 50 |
| **7c** | 22 | 52 | **2a** | 33 | 41 |

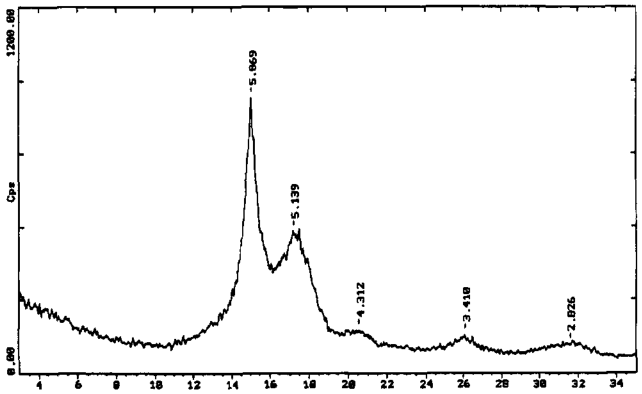


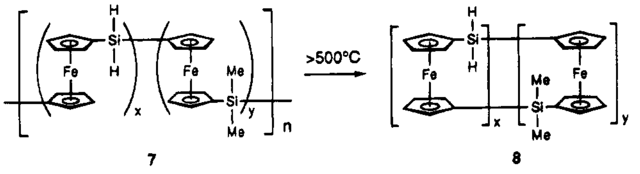
**Figure 5.** WAXS profile of $[Fe(\eta\text{-}C_5H_4)_2SiH_2]_n$ (**5**).

The $T_g$ of 16 °C observed for **5** proved to be below the $T_g$ of 33 °C previously observed for **2a**.[15] We therefore expected that $T_g$s for copolymers **7a–d** would fall between these two limits and that tuning of copolymer $T_g$ would only be possible over a narrow temperature range. DSC analysis revealed that the copolymer $T_g$s fell between the limits of the homopolymer $T_g$s and generally exhibited a single $T_g$, suggesting that they are composed of random (as opposed to blocks of) ferrocenyldihydrosilane and ferrocenyldimethylsilane repeat units.[32] Copolymer $T_g$ data are provided in Table 4. Despite the small difference between the homopolymer $T_g$s, the data in Table 4 reveal that copolymer $T_g$s do indeed show a smooth decrease with increasing copolymer dihydrosilane content.

**b. Wide-Angle X-ray Scattering (WAXS) Studies.** For samples of dimethyl substituted poly(ferrocenylsilane) **2a**, the most intense peak in the WAXS profile indicates a d-spacing between the planes of diffraction of 6.37 Å and most probably arises from planes in crystalline domains that contain the iron and the silicon atoms.[31] The existence of crystalline domains in samples of $[Fe(\eta\text{-}C_5H_4)_2SiH_2]_n$ (**5**) was indicated by WAXS (Figure 5). The most intense peak for polymer **5** was found at a $2\theta$ angle of 15.07° and corresponds to a d-spacing of only 5.87 Å, i.e., 0.50 Å smaller than that of **2a**. The most probable explanation is that the methyl groups of **2a** induce a larger separation between the polymer chains than the hydro substituents of **5**. Interestingly the WAXS profile of **7c** is consistent with this explanation and shows only a single broad peak centered at $2\theta$ = 14.5°. This corresponds to an average d-spacing of 6.04 Å, which is an intermediate value between those of homopolymers **2a** and **5**.

**c. Thermal Stability.** When poly(ferrocenylsilanes) are heated to high temperatures under vacuum, cyclic oligomeric depolymerization products (e.g., **6**) can be detected by pyrolysis mass spectrometry.[28] Depolym-

Scheme 5



erization fragments of ferrocenylsilane copolymer samples such as **8** (Scheme 5) would represent parts of the original copolymer chains and would indicate whether the copolymer is blocky or random in nature. For a block copolymer, mainly cyclic oligomer fragments containing only ferrocenyldihydrosilane or only ferrocenyldimethylsilane repeat units would be expected, whereas for a random copolymer sample, a higher content of cyclic oligomer fragments containing both repeat units (**8**) would be expected to form. Thus molecular ions of intermediate molecular weight compared to the analogous homooligomer fragments should be observed by pyrolysis mass spectrometry. Pyrolysis mass spectrometry of **7c** was carried out by an electron impact method while the sample was heated from 25 to 600 °C. Ion fragments were observed between 500 and 600 °C. Intense peaks at $m/e = 428$ for **8** ($x = 2, y = 0$) and 484 for **8** ($x = 0, y = 2$) indicated the presence of identical neighboring repeat units in the polymer sample. However, the most intense peak was at $m/e = 456$ for **8** ($x = 1, y = 1$) and clearly indicates the presence of numerous parts of the copolymer sample in which a ferrocenyldihydrosilane moiety is neighbor to a ferrocenyldimethylsilane unit. The essentially random nature of the copolymer **7c** is further supported by the observation of molecular ions **8** with varying numbers for $x$ and $y$.

We have investigated poly(ferrocenylsilanes) prepared via TROP as pyrolytic precursors to novel Fe/C/Si ceramic materials.[14] Ideally, pyrolysis of a polymeric precursor should afford the ceramic product with a minimum loss in weight, i.e., in high ceramic yield. In this regard, we have employed TGA to study the thermal behavior of a large number of poly(ferrocenylsilanes). The TGA response of these materials, particularly their TGA yield at 1000 °C (the limit of our instrument), provides a valuable measure of their thermal stability to weight loss.

Our TGA studies have shown that, under $N_2$, poly(ferrocenylsilanes) are generally stable to weight loss through ca. 300 °C. Above this temperature, they suffer weight loss through ca. 400–800 °C, ultimately forming Fe/C/Si ceramic materials in yields that vary from 20 to 60%. The ceramic materials are resistant to further weight loss through 1000 °C.[14] Our studies have also shown that the identity of the substituents at silicon greatly affects stability to weight loss.[14] For example, polymers with large organic groups at silicon (e.g., Ph) afford ceramic materials in lower overall yield than do polymers with smaller organic substituents at silicon (e.g., Me). Polymers with substituents that can be envisioned as capable of entering into thermal cross-links (e.g., vinyl) also afford higher ceramic yields. On the basis of these observations, we anticipated that the small size of the hydro substituents at silicon in **5** in conjunction with the reactivity of the Si–H bonds, which might lead to thermal cross-linking reactions, would make this material particularly stable to weight loss and thus a potentially valuable ceramic precursor.

TGA of **5** at 10 °C/min revealed this material to be the most stable to weight loss of all the poly(ferrocenylsilanes) we have studied to date. Analysis of the TGA trace of **5** showed that a 10% loss of initial sample weight was not observed until 600 °C and that heating through 1000 °C afforded a final yield of 63%. The TGA trace of **5** is shown in Figure 6. For comparison purposes, TGA traces of **2a** and copolymers **7a** and **7b** are included in Figure 6. Table 4 lists ceramic yields at 1000 °C for **5**, **2a**, and copolymers **7a–d**.

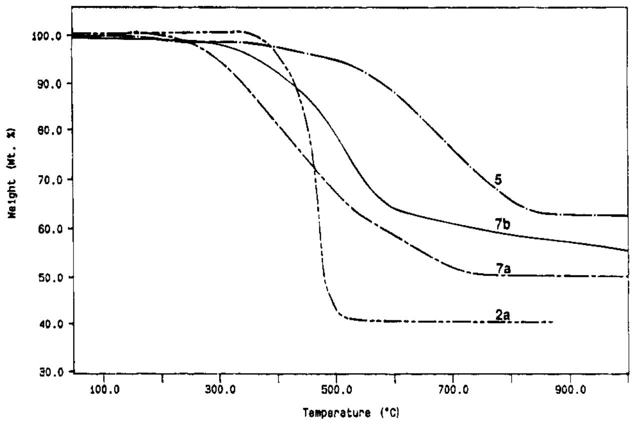


**Figure 6.** TGA traces of poly(ferrocenylsilanes) **5** and **2a** and copolymers **7a** and **7b** obtained at 10 °C/min under $N_2$.

We anticipated, on the basis of the high thermal stability of **5**, that the ceramic yield would increase with the content of dihydro units among copolymers **7a–d**. TGA of the copolymers found that indeed this was the case although the trend was not perfect (e.g., a slightly higher yield was observed for **7b** than for **7c**). Our TGA studies suggest that the identity of the substituents at silicon is related to poly(ferrocenylsilane) thermal stability in at least two ways: (1) loss of the organic substituents at silicon may be an important thermal degradation mechanism, and (2) substituents that thermally cross-link the polymer chains prevent the loss of volatile depolymerization products. Furthermore, both effects might be operative.

## Summary

In summary, we have demonstrated a low-temperature synthetic route to the strained, dihydrosilane-bridged [1]ferrocenophane **4**. TROP of this species affords an insoluble, crystalline poly(ferrocenylsilane) material **5** which exhibits high thermal stability to weight loss. Soluble, amorphous poly(ferrocenylsilanes) with controllable quantities of dihydrosilane repeat units can be prepared by thermal copolymerization of **4** with dimethyl analog **1a**. The resulting copolymers **7a–d** exhibit thermal stability to weight loss which increases with an increasing content of ferrocenyldihydrosilane units. We are currently extending our investigations to studies of the reactivity of the copolymers **7**.

## Experimental Section

$H_2SiCl_2$ was purchased from Aldrich and used without further purification. Silicon-bridged [1]ferrocenophane **1a** and dilithioferrocene·TMEDA **3** were synthesized as described in the literature.[27] IR spectra were recorded on a Nicolet Magna 550 IR spectrometer. Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact mode. Pyrolysis mass spectrometry experiments were carried out by heating the sample probe to 600 °C. Solution NMR spectra were recorded on Varian Gemini 200, Varian Gemini 300, or Varian XL 400 instruments. $^1H$ NMR spectra were referenced to residual protonated $C_6D_6$ at 7.15 ppm, and $^{13}C$

spectra were referenced to the $C_6D_6$ signal at 128.0 ppm. $^{29}$Si NMR spectra were recorded by utilizing normal (proton-coupled) or DEPT (proton-decoupled, $J_{Si-H} = 6.7$ Hz) pulse sequences. A solid state $^{29}$Si spectrum (DEPT) of **5** was obtained using a Chemagnetics CMX 300 spectrometer equipped with a Chemagnetics magic angle spinning probe doubly tuned to the resonance frequencies of $^{29}$Si (59.7 MHz). The sample was spun in a 7.5 mm o.d. zirconium rotor at a spinning rate of 6000 Hz. A single-contact cross-polarization technique was employed with a contact time of 5 ms and proton decoupling during the signal acquisition period. The proton radio frequency field strength was 50 kHz. The spectrum was acquired using a sweep width of 50 kHz, a data size of 2 Hz, and a recycle delay of 5 s. All chemical shifts were referenced to external TMS. Wide-angle X-ray scattering data were obtained at 25 °C using a Siemens D5000 diffractometer employing Ni-filtered Cu Kα ($\lambda = 1.541\ 78$ Å) radiation. Samples were scanned at step widths of 0.02° with 1.0 s per step in the Bragg angle range 3−35°. Samples were prepared by spreading finely ground polymer on grooved glass slides. DSC analyses were performed at a heating rate of 10 °C/min under prepurified $N_2$ using a Dupont Instruments DSC10 differential scanning calorimeter. Thermogravimetric analyses were performed at a heating rate of 10 °C/min under prepurified $N_2$ using a Perkin-Elmer TGA 7 thermogravimetric analyzer. Molecular weight estimates were made via gel permeation chromatography using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, Ultrastyragel columns with a pore size between $10^3$ 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 THF solution of 0.1% tetra-*n*-butylammonium bromide. Polystyrene standards were used for calibration purposes. Elemental analyses were performed by Quantitative Technologies Inc., Whitehouse, NJ.

**$Fe(\eta\text{-}C_5H_4)_2SiH_2$ (4).** A slurry of 3.17 g (10.1 mmol) of $Fe(\eta\text{-}C_5H_4Li)_2\cdot$TMEDA in 50 mL of dry ether was frozen with a liquid $N_2$ bath. The frozen slurry was then treated with 1.1 mL (1.3 g, 13 mmol) of $H_2SiCl_2$, which had been condensed at −78 °C. The liquid $N_2$ bath was removed, and the resulting mixture was allowed to warm to −78 °C. Reaction was continued at −78 °C for 1 h and then the mixture was allowed to warm to room temperature. The resulting red-orange slurry was filtered through a fritted glass disk, and the clear, red filtrate was concentrated in vacuo to afford a red, powdery solid. This solid was sublimed in vacuo (0.01 mmHg), without application of external heat, and 0.86 g (38%) of **4** was collected from the water-cooled cold finger as a powdery red solid: mp 122 °C (DSC); $^1$H NMR (200 MHz, $C_6D_6$) $\delta$ 5.41 (s, 2H, $SiH_2$), 4.28 (t, $J = 2$ Hz, 4H, Cp), 4.07 (t, $J = 2$ Hz, 4H, Cp); $^{13}$C NMR (50.3 MHz, $C_6D_6$) $\delta$ 78.3 (Cp), 76.3 (Cp), 21.3 (Cp-Si); $^{29}$Si NMR (79.5 MHz, $C_6D_6$, proton coupled) $\delta$ −42.7 (t, $J = 215$ Hz); HRMS calcd for $C_{10}H_{10}{}^{56}FeSi$ 213.9901, found 213.9895.

**$[Fe(\eta\text{-}C_5H_4)_2SiH_2]_n$ (5).** A Pyrex tube was charged with 0.20 g of **4** and was then flame sealed under vacuum (0.01 mmHg). The tube was then heated at 150 °C for 2 h. The sample melted and became viscous and then immobile over the course of 10 min. The gummy red solid product was extracted with THF for 24 h and dried in vacuo to yield 0.18 g (90%) of a red brown solid: IR (NaCl) 3089, 2137, 1422, 1381, 1365, 1166, 1032, 817 cm$^{-1}$; $^{29}$Si CPMAS NMR (59.7 MHz, proton decoupled) $\delta$ −36 (br); Pyrolysis MS *m/z* (relative intensity) 856 (43, **6**:$n = 3$), 826 (10, **6**:$n = 3$, $-SiH_2$), 642 (52, **6**:$n = 2$), 612 (15, **6**:$n = 2$, $-SiH_2$), 428 (100, **6**:$n = 1$); WAXS (d, relative intensity) $2\theta = 15.07°$ (5.87 Å, 100), 17.31° (5.12 Å, 51), 20.53° (4.32 Å, 15), 26.11° (3.41 Å, 14), 31.63° (2.83 Å, 10). Anal. Calcd for $C_{10}H_{10}FeSi$: C, 56.09; H, 4.71. Found: C, 55.83; H, 4.65.

Polymer **5** was found to be insoluble in the following solvents: THF, hexanes, acetone, toluene, methylene chloride, pyridine, 1,2-dichloroethane, benzene, chlorobenzene, *o*-dichlorobenzene, acetonitrile, dimethylformamide, aniline, anisole, nitrobenzene, $CF_3CH_2OH$, *o*-cresol, and dimethyl sulfoxide. Polymer **5** swelled slightly in THF and in hot aniline.

**$[(Fe(\eta\text{-}C_5H_4)_2SiH_2)_x(Fe(\eta\text{-}C_5H_4)_2SiMe_2)_y]_n$ (7a−d).** A representative example of the thermal copolymerization of **4** and **1a** is as follows: A Pyrex tube was charged with a mixture consisting of 0.25 g (1.2 mmol) of **4** and 0.33 g (1.4 mmol) of **1a** and then flame-sealed under vacuum. The tube was then heated slowly from room temperature to 150 °C and maintained at 150 °C for 2 h. The dark red solid product was taken up in THF, filtered through a thin pad of Celite, and precipitated into hexanes. The solid was collected by filtration and dried in vacuo to afford 0.38 g (65%) of copolymer **7c** as an orange, fibrous solid: IR (NaCl) 3090, 2959, 2925, 2853, 2134, 1427, 1251, 1168, 1038, 824, 798, 772 cm$^{-1}$; $^1$H NMR (200 MHz, $C_6D_6$) $\delta$ 5.21 (br m, $SiH_2$), 4.33−4.26 (br m, Cp), 4.14−4.12 (br m, Cp), 0.55 (br m, $SiCH_3$); $^{13}$C NMR (100.6 MHz, $C_6D_6$) $\delta$ 75.7, 75.2, 74.3, 73.8, 72.90, 72.87, 72.54, 72.52, 72.2, 72.0, 71.9, 63.8, 63.6, 63.2, 63.1 (Cp), −0.4 ($SiMe_2$); $^{29}$Si NMR (79.5 MHz, $C_6D_6$, proton decoupled) $\delta$ −6.38, −6.42, −6.48 ($SiMe_2$), −37.42, −37.45, −38.49 ($SiH_2$); $^{29}$Si NMR (59.6 MHz, $C_6D_6$, proton coupled) $\delta$ −6.4 (s, $SiMe_2$), −37.5 (t, $J = 200$ Hz, $SiH_2$); pyrolysis MS *m/z* >820 (relative intensity) 1210 (3, **8** $x = 0$, $y = 5$), 1182 (4, **8** $x = 1$, $y = 4$), 1154 (4, **8** $x = 2$, $y = 3$), 1126 (4, **8** $x = 3$, $y = 2$), 1096 (7, **8** $x = 3$, $y = 2$, $-SiH_2$), 970 (25, **8** $x = 2$, $y = 2$, $+SiMe_2$) 940 (100, **8** $x = 1$, $y = 3$), 912 (55, **8** $x = 2$, $y = 2$), 882 (70, **8** $x = 2$, $y = 2$, $-SiH_2$), 854 (33, **8** $x = 3$, $y = 1$, $-SiH_2$), 852 (39, **8** $x = 3$, $y = 1$, $-SiH_2$, −2H); pyrolysis MS *m/z* < 820 (relative intensity) 728 (24, **8** $x = 2$, $y = 1$, $+SiMe_2$), 698 (48, **8** $x = 1$, $y = 2$), 670 (33, **8** $x = 2$, $y = 1$), 640 (11, **8** $x = 2$, $y = 1$, $-SiH_2$), 484 (88, **8** $x = 0$, $y = 2$), 456 (100, **8** $x = 1$, $y = 1$), 428 (50, **8** $x = 2$, $y = 0$); WAXS (d, relative intensity) $2\theta = 14.5°$ (6.04 Å, br 100).

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**Supporting Information Available:** Complete crystal and structure refinement data, atomic coordinates and equivalent isotropic displacement parameters, bond angles and bond lengths, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and least-squares planes data for **4** (5 pages). Ordering information is on any current masthead page.

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(32) For some copolymer samples the $T_g$ appeared to consist of two overlapping transitions. This behavior suggests a significantly blocky rather than a completely random microstructure. Blocky copolymer compositions could arise from poor melt mixing of the two monomers prior to TROP. The multiple $T_g$ behavior was independent of both ferrocenyldihydrosilane/ferrocenyldimethylsilane ratios in the copolymer and sample thermal history.

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