

# Polysilane–Poly(ferrocenylsilane) Random Copolymers

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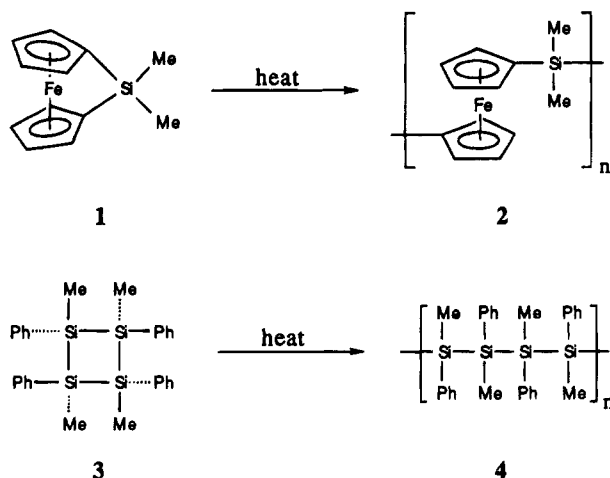
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Polymers based on inorganic elements continue to attract considerable interest because of their unique physical and chemical properties.<sup>1</sup> Polysilanes [SiR<sub>2</sub>]<sub>n</sub> represent a novel class of these materials which exhibit *o*-delocalization, photosensitivity, and thermochromic behavior.<sup>1,2</sup> Such characteristics have led to potential applications as photoconductors and photoresists. In addition, these polymers have also attracted attention as ceramic precursors.<sup>2</sup> Polysilanes have been prepared via a variety of methods including Wurtz<sup>2</sup> and dehydrogenative<sup>3</sup> coupling, anionic polymerization of masked disilenes,<sup>4</sup> and recently ring-opening polymerization (ROP).<sup>5,6</sup> In 1992 the synthesis of high molecular weight poly(ferrocenylsilanes) via the thermal ROP of silicon-bridged [1]ferrocenophanes was described.<sup>7</sup> These macromolecules possess a main chain of alternating ferrocene and organosilane units and exhibit a range of interesting properties as a result of the presence of transition metals in the polymer backbone.<sup>8</sup> The synthesis of copolymers of polysilanes and poly(ferrocenylsilanes) offers the possibility of tuning physical characteristics and of providing access to materials with unusual combinations of properties.<sup>9</sup> In this paper we report on our attempts to thermally copolymerize cyclic silanes and silicon-bridged [1]ferrocenophanes.

The [1]ferrocenophane (**1**) polymerizes thermally at elevated temperatures in the melt to yield the poly(ferrocenylsilane) (**2**).<sup>7</sup> In addition, the anionic ROP of



**3** in solution has been previously reported.<sup>5</sup> We have now found that **3** also polymerizes thermally at 150 °C to quantitatively yield poly(methylphenylsilane) (**4**). Indeed, when the ROP of **3** was monitored by differential scanning calorimetry (DSC), a large broad exotherm at 175 °C was detected with an onset temperature of 145 °C. Integration revealed the polymerization enthalpy to be ca. 56 kJ mol<sup>-1</sup>, which is less than that determined for **1** (ca. 80 kJ mol<sup>-1</sup>) by similar methods.<sup>7</sup>

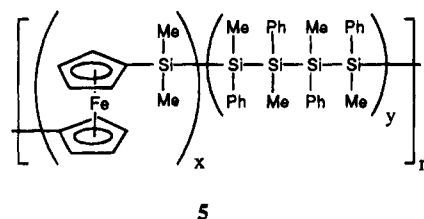
Table 1. Thermal Copolymerization Experiments Involving **1** and **3**

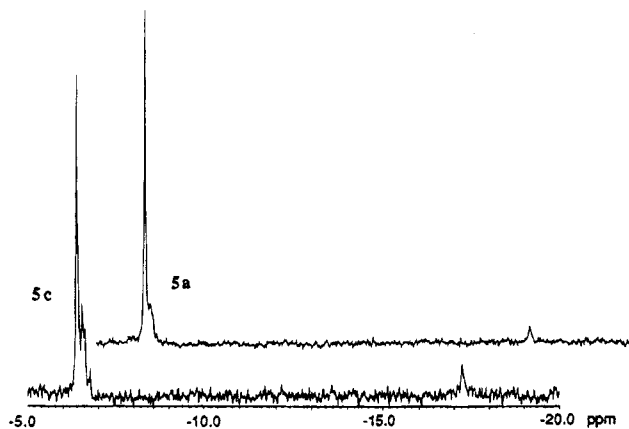
	3:1 (mol:mol)	<i>M</i> <sub>n</sub> (PDI)	<i>M</i> <sub>n</sub> (PDI) <sup>a</sup>	λ <sub>max</sub> (nm) (polysilane)	<i>T</i> <sub>g</sub> (°C) <sup>b</sup>
<b>2</b>	0:1	250 000 (1.6)	230000 (1.9)		33
<b>5a</b>	1:2.2	89 000 (3.5)	1730 (1.4)	325	69
<b>5b</b>	1:1	75 000 (3.1)	1410 (1.2)	330	
<b>5c</b>	2:1	67 000 (2.4)	1050 (1.4)	333	
<b>4</b>	1:0	91 000 (3.0)		338	

<sup>a</sup> *M*<sub>n</sub> of the remaining oligo(ferrocenylsilane) segments after irradiation with UV light (340 nm) in THF for 18 h. <sup>b</sup> Determined by DSC.

Thermal copolymerization experiments involving mixtures of **1** and **3** were carried out in various ratios (Table 1) and were performed in sealed, evacuated Pyrex tubes at 150 °C for 2 h. Under these conditions the reaction mixture transformed from a red melt into an immobile amber-colored glass. Analysis by <sup>1</sup>H NMR (in C<sub>6</sub>D<sub>6</sub>) confirmed that no unreacted monomer **1** or **3** remained. The polymeric products **5a–c** were isolated as pale amber powders by precipitation from THF into hexanes and possessed number-average molecular weights (*M*<sub>n</sub>) of 67 000–89 000 versus polystyrene standards.

Evidence that **5a–c** are true copolymers rather than blends of the two homopolymers was provided by the use of gel permeation chromatography (GPC) with an on-line photodiode array detector, which allows for the simultaneous observation of multiple wavelengths. GPC traces for **5a–c** showed two absorptions at ca. 330 and ca. 450 nm which are close to those of **4** and **2**, respectively.<sup>2,10</sup> The two traces overlapped exactly, which indicated that, unless two homopolymers with identical molecular weights were present, the two different monomers were incorporated into a single copolymer. Photochemical degradation was found to be selective for the methylphenylsilane units, leaving the ferrocenylsilane segments intact. Thus, when photodegradation of **5** was carried out in THF using 340-nm UV light for 18 h, a GPC trace of the products showed no absorption at 330 nm, indicating the absence of polysilane segments. In addition, the absorption at ca. 450 nm for the ferrocenylsilane segments shifted to a longer retention time (lower molecular weight), indicating that no high polymer remained. From the molecular weight of the degraded polymer it was possible to obtain the degree of polymerization (DP) of the ferrocenylsilane segments; in all cases this was relatively low (DP = 2–10) but an increase was detected as the amount of **1** in the initial monomer mixture was increased. The λ<sub>max</sub> for the polysilane segments increased with an increasing proportion of **3** in the monomer mixture, ranging from 325 nm for **5a** to 333 nm for **5c**. These absorption values suggest that the polysilane segments are relatively short and do not approach the limit corresponding to *M*<sub>n</sub> = 3000 where the λ<sub>max</sub> levels off at 338 nm.<sup>2</sup> These data indicated that **5a–c** are copolymers which contain short segments of polysilane and poly(ferrocenylsilane).





**Figure 1.**  $^{29}\text{Si}$  NMR spectra (39.7 MHz,  $\text{C}_6\text{D}_6$ ) of **5a** and **5c** in the ferrocenylsilane region

Further structural characterization of **5a–c** was provided by  $^1\text{H}$  and  $^{29}\text{Si}$  NMR spectroscopy. The  $^1\text{H}$  NMR spectra of **5a–c** (in  $\text{C}_6\text{D}_6$ ) showed sharp signals for the ferrocenyldimethylsilane segments at 0.51 ppm ( $\text{SiMe}_2$ ) and at 4.08 and 4.48 ppm ( $\eta\text{-C}_5\text{H}_4$ ) and two broad signals for methylphenylsilane segments at  $-0.5$  to  $+0.5$  (Me) and  $6.5\text{--}7.5$  ppm (Ph).<sup>7,11</sup> The integration ratio of the phenyl and cyclopentadienyl regions of the  $^1\text{H}$  NMR spectra of **5** confirmed that the relative amounts of **2** and **4** in the copolymers **5** were equal to the relative amounts of the two monomers **1** and **3** in the initial mixture prior to polymerization. Smaller, unresolved cyclopentadienyl resonances between 3.5 and 4.4 ppm were assigned to the ferrocenylsilane units near a juncture to a methylphenylsilane segment. Analysis of **5a–c** by  $^{29}\text{Si}$  NMR (in  $\text{C}_6\text{D}_6$ ) showed resonances for ferrocenyldimethylsilane units at  $-6.4$  ppm and a broad resonance for atactic methylphenylsilane segments from  $-37$  to  $-40$  ppm and also revealed small peaks for  $\text{SiMe}_2$  crossover groups between the ferrocenylsilane and methylphenylsilane segments at  $-17.3$  and  $-6.6$  ppm.<sup>12</sup> The peaks are particularly apparent in the  $^{29}\text{Si}$  NMR spectrum of polymer **5c** which possessed relatively short ferrocenylsilane blocks; in contrast, the resonances in the corresponding spectrum of **5a** are less intense as the ferrocenylsilane blocks are longer (Figure 1).

Cyclic voltammetric studies of **5a–c** in  $\text{CH}_2\text{Cl}_2$  showed the presence of two reversible oxidations at  $E_{1/2} = 0.00$  and  $0.23$  V<sup>13</sup> due to interacting iron atoms as found previously for poly(ferrocenylsilane) homopolymers.<sup>7,8</sup> An irreversible oxidation with  $E_p(\text{ox}) = 0.39$  V was also detected which corresponds to oxidation of the polysilane segments.<sup>14</sup>

In summary, the thermal ROP of mixtures of **1** and **3** provides a route to novel polysilane–poly(ferrocenylsilane) copolymers. It is interesting to note that these polymer structures are not available from the ROP of oligosilane-bridged  $[n]$ ferrocenophanes ( $n > 1$ ) as such species are insufficiently strained to polymerize.<sup>8</sup> The exact composition of the copolymers was found to

depend on the initial ratio of monomers **1** and **3**, but all are segmental in nature with alternating oligo(ferrocenylsilane) and oligosilane blocks. Attempts to extend the scope of this type of copolymerization reaction are underway, and we are also investigating the electronic and optical properties of the copolymers in detail.

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