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Ring-Opening Copolymerization of Cyclotetrasilanes and Silicon-Bridged [1]Ferrocenophanes: Synthesis and Properties of Polysilane−Poly(ferrocenylsilane) Random Copolymers

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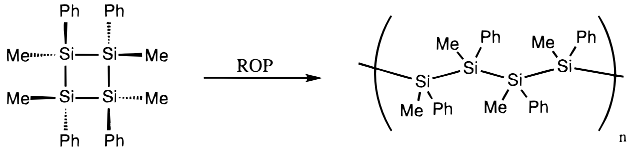
ABSTRACT: Novel poly(methylphenylsilane)−poly(ferrocenyldimethylsilane) copolymers **5a**−**d** of varying monomer composition were prepared via the thermal ring-opening polymerization of a mixture of the strained cyclic tetrasilane $[MePhSi]_4$ (**1**) and the silicon-bridged [1]ferrocenophane $Fe(\eta\text{-}C_5H_4)_2SiMe_2$ (**3**). The resulting materials were structurally characterized by ^1H and ^{29}Si NMR and also by gel permeation chromatography (GPC), pyrolysis mass spectrometry (MS), and cyclic voltammetry. GPC in THF indicated that the molecular weights of the polymers **5a**−**d** were in the range $M_n = (2.0 \times 10^4)-(8.9 \times 10^4)$ with PDI values of 2.4−3.5. Polymers **5a**−**c** were photosensitive and GPC traces of **5a**−**c** were studied both before and after irradiation of the sample with UV light ($\lambda = 340$ nm). The formation of short chain oligo(ferrocenylsilanes) after irradiation was consistent with exclusive photodegradation of the polysilane segments and indicated that the copolymers were random in nature. Pyrolysis MS of **5a**−**c** also supported a random structure. Cyclic voltammetric studies of **5a**−**c** in CH_2Cl_2 showed the presence of the characteristic two reversible oxidation waves arising from oligo(ferrocenylsilane) segments with interacting iron atoms at $E_{1/2} = 0.00$ and 0.23 V (relative to ferrocene/ferrocenium) and an irreversible oxidation with $E_p(ox) = 0.39$ V arising from the polysilane segments. UV/vis spectroscopy showed that the σ-electrons in the oligosilane segments are delocalized and that λ_{max} increased from 325 to 333 nm as the proportion of the cyclotetrasilane **1** in the initial monomer mixture increased. These values suggest that the oligosilane segments are relatively short and do not approach the limit corresponding to ca. 30 silicon atoms (M_n = ca. 3 000), which levels off at 338 nm. Attempted anionic initiation of the copolymerization of **1** and **3** was unsuccessful and led exclusively to homopolymerization. Transition metal catalyzed copolymerization of **1** and **3** using $PtCl_2$ resulted in a copolymer which was derived almost exclusively from **3**. The charge transport properties of the representative copolymer **5d** were also investigated. Films of pristine **5d** were insulating (conductivity $<10^{-14}$ S cm^{-1}) but after exposure to iodine the conductivity increased by a factor of 10^8 to $(6.5-8.2) \times 10^{-6}$ S cm^{-1}. In comparison, the conductivities of iodine-exposed films of poly(ferrocenyldimethylsilane) (**4**) and poly(ferrocenyldi-*n*-butylsilane) (**7**) were ca. 2×10^{-4} S cm^{-1}. The hole mobility of **5d** was studied by standard time of flight techniques and was found to be appreciable with a value of 4.0×10^{-6} cm^2/V s.

Introduction

Polymers with backbones constructed from main group or transition elements continue to attract considerable attention because of their unique physical and chemical properties.[1,2] Polysilanes $[SiR_2]_n$ represent a novel class of these materials, which exhibit σ-delocalization, photosensitivity, and thermochromic behavior and have potential applications as photoconductors and photoresists and as ceramic precursors.[3] These silicon-backbone polymers have been prepared via a variety of methods including Wurtz[3] and dehydrogenative coupling[4] and anionic polymerization of masked disilenes.[5] In 1991, anionic ring-opening polymerization (ROP) of cyclic tetrasilanes (e.g., **1**) to yield polysilanes such as **2** was reported.[6]



1 **2**

Poly(ferrocenylsilanes) (e.g., **4**) possess a main chain of alternating ferrocene and organosilane units and the first high molecular weight, well-characterized examples of these materials were reported in 1992.[7] The synthetic route used involved thermal ROP of strained silicon-bridged [1]ferrocenophanes such as **3**. More recently, anionic[8,9] and transition metal-catalyzed[10,11] ROP routes to these materials have also been described. Poly(ferrocenylsilanes) and related materials formed by ROP of metallocenophanes have been found to exhibit a range of interesting physical characteristics as a result of the presence of transition metals in the polymer backbone.

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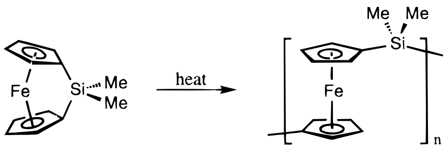
Table 1. GPC Data for Polysilane–Poly(ferrocenylsilane) Copolymers 5a–c

polymer	1:3, mol:mol	M_n(PDI)[a]	λ_{max}, nm (polysilane)[b]	M_n(PDI)[c]
4	0:1	250 000 (1. 6)		230000 (1.9)
5a	1:2	89 000 (3.5)	325	1730 (1.4)
5b	1:1	75 000 (3.1)	330	1410 (1.2)
5c	2:1	67 000 (2.4)	333	1050 (1.4)
2	1:0	91 000 (3.0)	338	

[a] Data in THF relative to polystyrene standards. [b] Data in THF. [c] M_n of the remaining oligo(ferrocenylsilane) segments after irradiation with UV light (340 nm) in THF for 18 h.

These include electroactivity, electrochromism, and the ability to function as precursors to magnetic materials on oxidation or pyrolysis.[12–16] Recent attention has focused on the interesting morphology of these polymers including liquid crystalline derivatives.[17]



3 **4**

The synthesis of high molecular weight copolymers of polysilanes and poly(ferrocenylsilanes) offers the possibility of tuning physical characteristics and of providing access to processable materials with novel combinations of properties.[18,19] Copolymers of this type might also be synthesized via the ROP of oligosilane-bridged ferrocenophanes. However, previous attempts at polymerizing species with more than one silicon atom in the bridge (e.g., the [2]ferrocenophane Fe(η-C_5H_4)$_2$-($SiMe_2$)$_2$) have been unsuccessful as a consequence of the smaller degree of strain present.[20,21] In this paper, as a follow up to our communication,[22] we report full details of an alternate approach toward the copolymerization of the cyclic silane **1** and the silicon-bridged [1]ferrocenophane **3** and studies of the properties of the resulting materials.

Results and Discussion

Thermal Copolymerization of 1 and 3. Synthesis of Copolymers 5a–c. Anionic ROP of the cyclic tetrasilane **1** was first reported around 6 years ago.[6] As a prelude to thermal copolymerization experiments with **3**, we investigated whether **1** would also thermally polymerize to afford **2**. We found that **1** polymerizes thermally at 150 °C to quantitatively afford poly(methylphenylsilane) **2**. Indeed, when the ROP of **1** was monitored by differential scanning calorimetry (DSC), a large broad exotherm at 150 °C was detected with an onset temperature of 90 °C. Integration revealed the polymerization enthalpy to be ca. 56 kJ mol^{-1}, which is less than that determined for **3** (ca. 70–80 kJmol^{-1}) by similar methods.[7]

Upon discovery that **1** undergoes thermal ROP, thermal copolymerization was attempted by heating mixtures of **1** and **3**. This resulted in the formation of random copolymers **5**. By varying the ratio of **1** and **3**, a series of copolymers, **5a**–**c**, with varying composition was obtained (Table 1). Analysis by ^{1}H-NMR spectroscopy confirmed that no unreacted monomer remained and indicated that the relative amounts of polysilane and poly(ferrocenylsilane) segments was the same in **5a**–**c** as in the initial monomer mixture (see below). The polymeric products were isolated as pale, amber powders by precipitation from THF into hexanes and were shown by gel permeation chromatography (GPC) to possess number-average molecular weights (M_n) of (6.7 × 10^4)–(8.9 × 10^4) versus polystyrene standards with polydispersities ranging from 2.4 to 3.5.

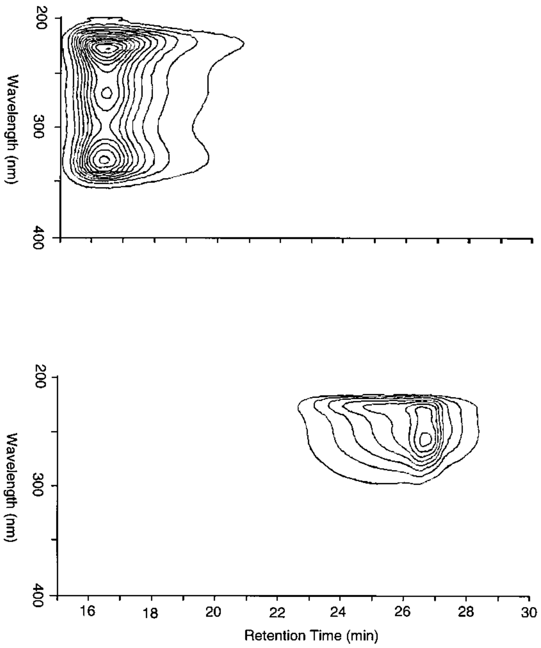
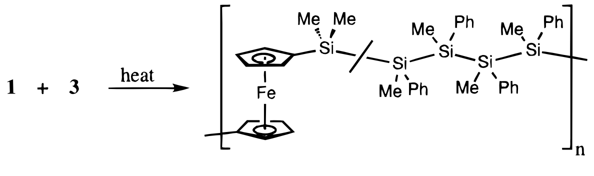


Figure 1. Three dimensional GPC (wavelength × retention time × absorption) of polymer **5c** before (top) and after (bottom) photolysis by 340-nm UV light.



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Structural Characterization of Copolymers 5a–c by Photodegradation Studies and NMR Spectroscopy. The copolymers were characterized by a number of techniques in order to elucidate their structure. Polymer molecular weights were determined by GPC with an online photodiode array detector for the simultaneous monitoring of multiple wavelengths. The GPC results are summarized in Table 1; these results conclusively showed that the copolymers are random in nature. Molecular weights are given for the polymers before and after exposure to UV light. It is well known that polysilanes undergo photodegradation upon exposure to UV radiation to give small cyclic species, while experiments with **4** show that poly(ferrocenylsilanes) are UV-stable. In a copolymer system, the polysilane segments would be expected to degrade, while the ferrocenylsilane segments should remain intact. Photodegradation experiments with **5a**–**c** in THF were carried out using 340 nm UV light for 18 h; the GPC trace of the product showed no absorption at 330 nm, indicating the absence of polysilane segments (Figure 1). For the three copolymers the molecular weights observed after photolysis (Table 1) correspond to oligomeric ferrocenylsilane segments (n = 4–7) and are related to the initial relative stoichiometries of the copolymers. This implies that, in the copolymers **5a**–**c**, the ferrocenylsilane segments are short chains.

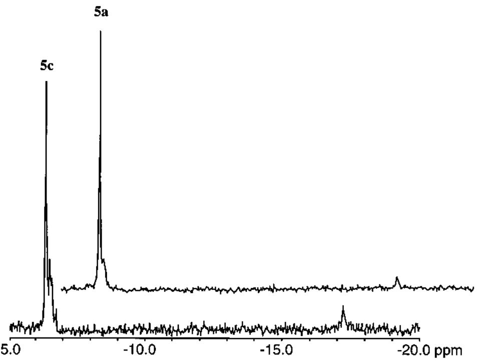
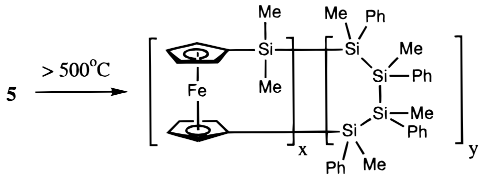


Figure 2. ^{29}Si-NMR spectrum (C_6D_6) of **5a** and **5c**.

In addition, it was easily shown that the segments derived from **1** consist of small, oligo(methylphenylsilane) units. The delocalization of the σ-electrons within the poly(methylphenylsilane) backbone causes a shift to higher wavelength of λ_{max} with increasing chain length; this reaches a maximum of 338 nm at a chain length of approximately 30 silicon atoms (or 7 or 8 units of **1**).[3] The λ_{max} values show that the methylphenylsilane segments are very short oligomeric units: as the amount of **1** incorporated in the polymer increases, λ_{max} increases as well, but does not reach its maximum value, even in the copolymer studied with the highest methylphenylsilane content. The data of Table 1 indicate that the copolymers **5a**–**c** contain short segments of methylphenylsilane and ferrocenylsilane repeat units.

Further structural characterization of the copolymers was provided by ^{1}H and ^{29}Si NMR spectroscopy. The ^{1}H NMR spectra of the copolymers (in C_6D_6) showed sharp signals for the ferrocenyldimethylsilane segments at 0.51 ppm ($SiMe_2$) and at 4.08 and 4.48 ppm (η-C_5H_4) and two broad signals for methylphenylsilane segments at −0.5 to +0.5 ppm (Me) and 6.5–7.5 ppm (Ph). As briefly mentioned above, the integration ratio of the phenyl and cyclopentadienyl regions of the ^{1}H NMR spectra of the copolymers confirmed that the relative amounts of segments of type **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}Si NMR spectroscopy (in C_6D_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 $SiMe_2$ crossover groups between the ferrocenylsilane and methylphenylsilane segments at −6.6 and −17.3 ppm, respectively. The peaks are particularly apparent in the ^{29}Si NMR spectrum of polymer **5c**, which possessed relatively short ferrocenylsilane segments; in contrast, the resonances in the corresponding spectrum of **5a** are less intense, as the oligo(ferrocenylsilane) segments are longer (Figure 2).

Characterization of Copolymers 5a–c by Pyrolysis Mass Spectrometry and TGA. When poly(ferrocenylsilanes) are heated to high temperatures under vacuum, cyclic oligomeric depolymerization products can be detected by pyrolysis mass spectrometry.[23] In the case of a copolymer, depolymerization fragments would represent parts of the initial copolymer chain; having established that the copolymer chain is random in nature, one would expect to observe cyclic depolymerization fragments containing both repeat units. In contrast, in a block copolymer, depolymerization products would consist mainly of one of the repeat units i.e., **6** ($x > 0$, $y = 0$) or **6** ($x = 0$, $y > 0$). Pyrolysis mass spectrometry was performed on polymers **5a**–**c** and gave an indication of the effect of varying ratios of the monomers on the polymer.



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Pyrolysis mass spectrometry was also performed on the homopolymers **2** and **4**. The mass spectrum of **4** identified oligomeric ferrocenylsilane units of up to the heptamer **6** ($x = 7$, $y = 0$), while the mass spectrum of **2** showed the absence of oligomeric methylphenylsilane units larger than the dimer **6** ($x = 0$, $y = 2$), a result indicative of the lower thermal stability of the Si–Si bond. In copolymer **5a**, the material rich in ferrocenylsilane repeat unit, the main depolymerization products were the cyclic ferrocenylsilane oligomers **6** ($x = 2$–7, $y = 0$), with the dimer **6** ($x = 2$, $y = 0$) being the major product. This corresponds well with the results obtained in the photodegradation experiments: following photolysis, the remaining segments (corresponding to ferrocenylsilane units) had $M_n = 1730$, which corresponds to approximately seven repeat units. There is essentially no evidence in the mass spectrum for the existence of oligosilane units after pyrolysis. However, there is evidence for some mixed oligomers: there are small peaks at $m/e = 722$, [**6** ($x = 1$, $y = 1$)], $m/e = 602$, [**6** ($x = 1$, $y = {}^3/_4$)], $m/e = 482$ [**6**($x = 1$, $y = {}^2/_4$)], and $m/e = 362$ [**6** ($x = 1$, $y = {}^1/_4$)]. Fractional values for y are a result of Si–Si cleavage not occurring preferentially at every fourth silicon and are as expected. As the amount of **1** incorporated in the copolymers is increased as in polymers **5b** and **5c**, cyclic ferrocenylsilanes **6** ($x = 2$–7, $y = 0$) are again observed but in smaller proportions. As well, more mixed oligomers are observed, up to $m/e = 1202$ ($x = 1$, $y = 2$). These mixed oligomers provided additional evidence regarding the random nature of the copolymers.

TGA was also performed in order to obtain information regarding the thermal stability of the copolymers. For this purpose and the charge transport studies (see below) an ca. 1 g sample of a new copolymer, **5d** ($M_n = 20\,000$, PDI = 2.4), was prepared containing 60% ferrocenylsilane from a 1:1.5 mol ratio of the monomers **1** and **3**. The polymer was stable to weight loss up to approximately 300 °C and the ceramic yield was 40% at 900 °C. Most of the weight loss occurred between 400 and 600 °C, apparently by two different mechanisms (indicated by a change in slope). The thermal stability observed is similar to that observed in ferrocenylsilane homopolymer **4**.[24]

Attempted Anionic and Transition-Metal-Catalyzed Copolymerization of 1 and 3. As both monomers **1** and **3** can be polymerized via anionic initiation we also investigated the synthesis of copolymers **5** via anionic copolymerization. The tetrasilane **1** undergoes ROP in the presence of *n*-butyllithium and 1,4-dipotassiooctaphenyltetrasilane[6] and the ferrocenophane **3** undergoes ROP in the presence of a variety of anionic

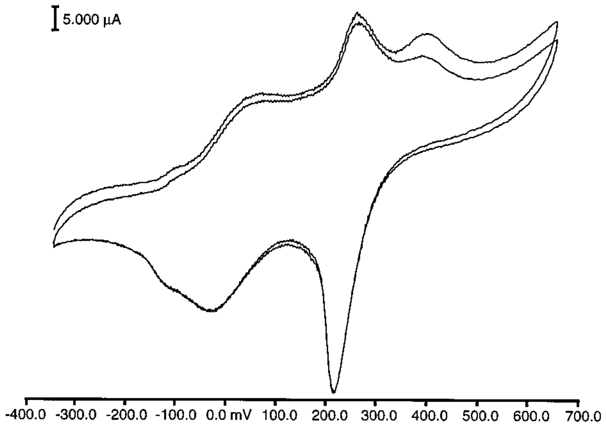


Figure 3. Cyclic voltammogram of polymer **5a**.

initiators, such as butyllithium and phenyllithium.[8,9] Copolymerization reactions were attempted with a mixture of **1** and **3** with butyllithium. However, only the homopolymer **2** was formed. Also, the synthesis of block copolymers was attempted by the addition of the second monomer to a solution of the "living" polymer derived from the anionic ROP of the first monomer with butyllithium. However, in each case, the only polymer formed was the homopolymer derived from the monomer that was initially ring-opened.

Attempts to induce the copolymerization of **1** and **3** using transition metal catalysis were also made. Various transition metal compounds, such as $PtCl_2$, $PdCl_2$, and $[Rh(cyclooctene)_2Cl]_2$, have been shown to catalyze the ROP of the ferrocenophane **3**.[10,11] Transition metal-catalyzed ring opening of **1** has also been studied;[25,26] the main product of this reaction is the cyclic dimer, the cyclooctasilane, which was generally formed in greater than 50% yield. Some higher molecular weight material was observed with less bulky catalysts, but just as a tail on the GPC traces; values of M_n were all under 1000 (representing, on average, just slightly greater than two units of **1**). Bearing this in mind, copolymerization was attempted using $PtCl_2$ as a catalyst. Experiments were attempted both at room temperature and at 60°C. With a 1:4 ratio of **1**:**3**, polymerization occurred at room temperature over a 4-day period, with incomplete conversion of **1**; the resulting polymer was found to comprise 96% **3** by ^{1}H NMR. As expected, the polymerization occurred more easily for the ferrocenophane **3**; as well, the presence of **1** inhibited the copolymerization, as transition-metal-catalyzed homopolymerization of **3** occurs within a few hours. At 60 °C, the reaction was complete in 2 h, and the polymer had the same approximate composition as the polymer derived from the room temperature copolymerization. Therefore, although **1** and **3** can copolymerize in the presence of a transition metal catalyst, the homopolymerization of **3** is much more efficient.

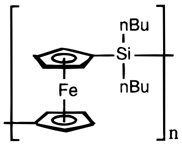
Redox and Charge Transport Properties of Copolymers 5a–d. Cyclic voltammetric studies of **5a**–**c** in CH_2Cl_2 showed the presence of two reversible oxidations at $E_{1/2} = 0.00$ and 0.23 V (relative to the ferrocene/ferrocenium couple at $E_{1/2} = 0.00$ V) arising from the oligoferrocenylsilane segments, as found previously for poly(ferrocenylsilane) homopolymers (Figure 3).[7,12] The two-wave pattern arises from initial oxidation at alternating iron sites followed by oxidation of those in between at a higher potential. This phenomenon is attributed to the presence of iron–iron interactions, which renders more difficult electron removal for an iron site which neighbors a ferrocene unit that has already been oxidized.[9] An irreversible oxidation with $E_p(ox) = 0.39$ V was also detected for **5a**–**c** and corresponds to oxidative cleavage of the polysilane segments (Figure 3).[27]

The charge transport properties of these materials were evaluated by using the copolymer **5d** ($M_n = 20\,000$, PDI = 2.4), which was prepared from a 1:1.5 mol ratio of the monomers **1** and **3**. The electrical conductivity of copolymer **5d** was examined. A pristine film of the copolymer was found to be insulating and its measured conductivity was found to be less than 10^{-14} S cm^{-1}. However, on exposure to iodine vapor the conductivity increased to values of 6.5×10^{-6} S cm^{-1} (for a 10 μm film) and 8.2×10^{-6} S cm^{-1} (for a 20 μm film). The measured conductivity of the I_2-doped films is in the semiconductor range and is similar to that reported (3.2×10^{-6} S cm^{-1}) for low molecular weight copolymers (M_n = ca. 3500) of the type $[Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_6]_x$ ($x \sim 6$) synthesized by Tanaka et al. by polycondensation routes.[18] We attribute the observed dramatic (10^8) increase in electrical conductivity to the dopant, I_2, acting as an electron acceptor.[28] Significantly, previous work by Tanaka has shown that the Si–Si bonds in the low molecular weight materials $[Fe(\eta\text{-}C_5H_4)_2(SiMe_2)_6]_x$ ($x \sim 6$) remain intact on exposure to I_2 and that the oxidative doping process is reversible and can be reproduced over several cycles.[18]

Previous work on the electrical conductivity of poly(ferrocenyldimethylsilane) (**4**) has shown that this material is insulating, but on doping with I_2 the conductivity increases into the weak semiconductor range (10^{-7}–10^{-8} S cm^{-1}).[12] In order to permit a further comparison with **5d** we also studied the conductivity of a 15-μm film of poly(ferrocenyldimethylsilane) (**4**) and poly(ferrocenyldi-*n*-butylsilane) (**7**). Pristine films of these materials were also found to possess an intrinsic conductivity of less than 10^{-14} S cm^{-1}. However, on exposure to I_2 vapor a dramatic (10^{10}) increase in electrical conductivity was observed to give values of 1.7×10^{-4} S cm^{-1} (for **4**) and 2.1×10^{-4} S cm^{-1} (for **7**). These values are almost 2 orders of magnitude higher than that of **5d** and similarly exceed those previously obtained for I_2- or TCNQ-doped poly(vinylferrocene) (ca 10^{-6}–10^{-8} S cm^{-1}) where the ferrocenyl groups are in the side group structure.[29] The conductivity of I_2-doped **4** and **7** was also higher than that of amorphous (presumably branched) I_2-doped poly(ferrocenylene) (ca. 10^{-7} S cm^{-1}).[30] However, crystalline I_2-doped samples of the latter material have been reported to possess comparable conductivities to I_2-doped **4** and **7** (1×10^{-4} S cm^{-1}) and, with TCNQ as oxidant, values of up to 4×10^{-2} S cm^{-1} have been reported.[31] The higher electrical conductivity of I_2-doped **4** in this study compared to that found previously may be due to the higher degree of crystallinity in the films used.[12,32] Thus, in this work the films were generated with the use of a motor driven blade applicator. This process imparts a shearing force which increases crystallinity by promoting the alignment of the polymer chains in the resulting polymer film.

In order to examine the charge transport characteristics of the polysilane–poly(ferrocenylsilane) copolymers in more detail, hole mobilities were also measured. The hole mobility of **5d** was investigated through the evaluation of a device obtained via the deposition of a thin film (ca. 10 μm) of **5d** onto a multilayer Mylar–

aluminum–hydroxygallium phthalocyanine substrate.[33,34] In an electric field of ca. 5.0 × 10^5 V/cm **5d** possessed an appreciable hole mobility of 4.0 × 10^{-6} $cm^2/(V\ s)$. This value is comparable to the values possessed by the composite materials currently used in xerography but falls below values of 10^{-4} $cm^2/(V\ s)$ achieved for polysilane homopolymers.[35] For comparison, and as crystalline materials could not be evaluated, the hole mobility of a film of the amorphous poly(ferrocenylmethylphenylsilane) (**8**) was also investigated and, under similar conditions to those used for **5d**, was found to possess a value of 7.0 × 10^{-6} $cm^2/(V\ s)$. Although many other factors will need to be considered, the interesting charge transport properties of **5d** and the homopolymers **4**, **7**, and **8** suggest that these materials or their analogues might be used productively in device fabrication.[35–40] Further work in this area is in progress and will be reported in the future.



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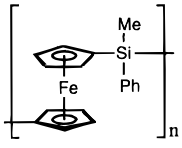

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Summary

The synthesis of a series of novel, high molecular weight polysilane–poly(ferrocenylsilane) copolymers has been achieved by thermal ring-opening polymerization of mixtures of strained cyclosilanes and [1]silaferrocenophanes. Characterization of these copolymers has shown that they are random in nature, possessing alternating short chains of each monomer. The materials are photosensitive and irradiation with UV light results in the isolation of oligo(ferrocenylsilane) segments. The polymers are also redox active and the σ-electrons in the oligosilane segments are delocalized. Thin films of these materials possess interesting charge transport properties. For I_2-doped polymers, electrical conductivities fall in the semiconducting range and the intrinsic hole mobilities are appreciable. Future work will focus on further studies of these interesting materials and their analogues including their possible use in device fabrication.

Experimental Section

Equipment and Chemicals. Equipment. Molecular weights (relative to linear polystyrene standards) were measured in THF by using a Waters GPC equipped with linear, 10^2 Å, and 10^3 Å Phenogel columns, a Waters 410 refractive index detector, and a Waters 991 photodiode array. Spectra were analyzed at the wavelength of maximum absorption (300–338 nm and 230 nm) specific for the σ–σ^* and LMCT electronic transitions of poly(methylphenylsilane) and poly(ferrocenylsilane) **4**, respectively.

Proton NMR spectra were recorded with a Varian Gemini 200 spectrometer. The 79.5-MHz ^{29}Si-NMR spectra were recorded on a Varian XL 400 spectrometer utilizing a DEPT pulse sequence (proton decoupled) with a $^2J_{Si-H}$ coupling of 6.7 Hz and were referenced externally to $SiMe_4$. The solvent was C_6D_6.

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 up to 600 °C.

Thermogravimetric analyses were performed at a heating rate of 10 °C min^{-1} under prepurified N_2 by using a Perkin Elmer TGA 7 thermogravimetric analyzer.

Cyclic voltammograms were recorded with a PAR Model 273 potentiostat. A Pt working electrode and a Ag wire reference electrode in a Luggin capillary were used. All potentials are relative to the ferrocene/ferrocenium ion couple at 0.00 V, which was used as an internal reference. CH_2Cl_2 and MeCN solvents were freshly distilled from P_2O_5, anhydrous grade $[Bu_4N][PF_6]$ (Aldrich) was used as supporting electrolyte (0.100 M), and the analyses were carried out under prepurified N_2.

Films were cast with the use of a motor driven blade applicator. The thickness of the films was measured by using a Heidenhain digital length gauge (Model MT60M, Heidenhain Corp.) and the values are accurate to ±0.5 μm.

Hole mobility was determined by conventional time-of-flight techniques.[33,34] In this technique, the drift of a sheet of holes injected from the charge generating layer (CGL) is time-resolved and the transit time was determined in order to calculate the hole mobility at an applied electric field. An electric field was applied across the device (featuring the copolymer as a charge transport layer) with a negative bias voltage (DC power supply) at the top electrode and an incident light (about 5-μs) pulse from a strobe was used to generate a sheet of charge carriers in the CGL. The duration of the light pulse (about 5 μs) was chosen to be much smaller than the typical transit time (about a millisecond in many organic and polymeric materials) so that the transport process does not interfere with the generation process.

Chemicals. Solvents were dried by using standard methods and were distilled under dinitrogen before use. All chemicals (including $PtCl_2$ powder) were purchased from Aldrich.

The ferrocenophane **3** was synthesized according to the literature reaction of dilithioferrocene·TMEDA with dichlorodimethylsilane;[32] the tetrasilane **1** was synthesized via the literature reaction of octaphenylcyclotetrasilane with triflic acid, followed by methylation with methylmagnesium bromide.[3]

Synthesis of Copolymers. *Synthesis of Polymers **5a–d** via Thermal Copolymerization.* The same procedure was used for the synthesis of the three copolymer samples; what follows is the procedure for the synthesis of polymer **5a**. An analogous method was used for the thermal ROP of **1** to afford **2**.

The ferrocenophane **3** (86 mg, 0.36 mmol) and the cyclotetrasilane **1** (75 mg, 0.16 mmol) were dissolved in hexanes, and the two solutions were mixed and transfered to a Pyrex tube. The hexanes was pumped off slowly, leaving the mixture of the two compounds. The tube was evacuated, sealed, and heated at 150 °C for 2 h. The polymer was isolated by precipitation from THF into hexanes. Yield: 118 mg (74%). ^{1}H NMR (200 MHz, C_6D_6) δ −0.5 to 0.5 (br, Si*Me*Ph), 0.51 (br, fcSi*Me*$_2$), 4.08 (br, (η-C_5H_4)$_2$FeSiMe$_2$), 4.48 (br, (η-C_5H_4)$_2$FeSiMe$_2$), 6.5–7.5 (SiMe*Ph*) ppm; ^{29}Si NMR (39.7 MHz, C_6D_6) δ = −40 to −37 (br, *Si*MePh), −6.4 (br, fc*Si*Me$_2$), −6.6 (br, fc*Si*Me$_2$fcSiMePh...), and −17.3 (br, fc*Si*Me$_2$SiMePh...) ppm.

Attempted Anionic Copolymerization. As a general procedure for the attempted anionic ring-opening copolymerizations, 200 mg (0.42 mmol) of **1** and 50 mg (0.20 mmol) of **3** were dissolved in THF and initiator (*n*-butyllithium or ferrocenyllithium) was added via syringe. (In the case of attempted block copolymerizations, the second monomer was added after the initiator.) Following the reaction, the polymer was precipitated in hexanes. This polymer was found to be the homopolymer **2** by ^{1}H NMR.

Attempted Transition-Metal-Catalyzed Copolymerization. These experiments were monitored by ^{1}H NMR. The two monomers (1.66 × 10^{-4} mol of **3**, 4.16 × 10^{-5} mol of **1**) were mixed with $PtCl_2$ (6 mg, 2.0 × 10^{-5} mol) with C_6D_6 as solvent in a NMR tube which was then sealed. For the experiment at room temperature, the reaction was monitored by NMR daily. For the experiment at 60 °C, the tube was heated in an oil bath for 2 h and the ^{1}H NMR spectrum was then obtained. The polymer was found to contain 96% **4** by ^{1}H NMR.

Charge Transport Measurements. *Electrical Conductivity Using the van der Pauw Technique.* The electrical conductivities of polymer films coated on a Mylar substrate were measured by using the van der Pauw technique.[41,42] The electrode attachment and electrical connections were accomplished with the use of sputtered gold electrode pads and commercial conducting gold epoxy. Gold electrodes were sputtered on the four corners of the films using stainless steel masks with triangular openings. A Perkin-Elmer sputtering system (Model 2400) operating at 1000 V in 12 Torr of argon was used to sputter 50−60-nm-thick gold films. Gold wire with 100-μm diameter (Aldrich Chemical Co., Milwaukee, WI) and gold wire mesh (Unique Wire Weaving Co., Inc., Hillside, NJ) were used with conducting gold epoxy (product no. 417GF, Epoxy Tech. Inc., Billerica, MA) to make electrical contacts with the sputtered pads. The thin film-gold electrode assembly was laid on a thick Teflon block with four steel contact posts. The four electrode gold wires were wrapped to the steel contact posts which were then connected to the measurement circuit. Iodine doped films were allowed to equilibrate (2−3 h) in iodine vapor at room temperature before the measurements were made.

The measurements were conducted in air at room temperature. The thick Teflon blocks with thin film conductivity specimens were placed in a Faraday cage to minimize electromagnetic interference. A HP 4140A pA meter/DC voltage source was used as a current source in the range $10^{-7}-10^{-14}$ A. Voltages were measured by using two separate Keithley 6512 Electrometers connected by using guarded triax leads. The total error in the measured conductivities was estimated to be less than 10%.

Fabrication of Hole Transport Devices. The charge transport layer, **5d** or **8**, was coated from a 10% by weight solution of the polymer in toluene with a 10-mL blade applicator onto the multilayer substrate. This substrate consisted of a 20-nm aluminum film which has been evaporated onto a poly(ethylene terephthalate) (Mylar) sheet. The aluminum sheet acts as an electrode. Coated onto this electrode was a 100-nm-thick silane layer, which functioned as a hole-blocking layer. The charge generation layer consisted of hydroxygallium phthalocyanine dispersed in poly(vinyl butaryl) which was deposited on top of the silane layer. For **5d** and **8**, a 10 μm charge transport layer was obtained.

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