Macromolecules **1996,** *29,* 3123−3128 **3123**

Synthesis of Poly(silylenemethylenes) through Reactions Carried Out on Preformed Polymers. 1. Replacement of the Chloro Group in Poly[(chloromethylsilylene)methylene]

Ilya L. Rushkin and Leonard V. Interrante*

Rensselaer Polytechnic Institute, Troy, New York 12180-3590

Received November 27, 1995; Revised Manuscript Received February 9, 1996[⊗]

ABSTRACT: A new series of poly(silylenemethylenes) of the type $[Si(Me)(X)CH_2]_n$, where X = OR (R = Et, CH_2CF_3, Ph, Ac), F, and R′ (R′ = *n*-butyl, allyl), were obtained starting from the preformed $[Si(Me)(Cl)CH_2]_n$ polymer. The OR derivatives were obtained quantitatively from the $[Si(Me)(Cl)CH_2]_n$ polymer by treatment with ROH/Et_3N or NaOR. Reaction of the $[Si(Me)(Cl)CH_2]_n$ polymer with the allyl Grignard reagent also gave 100% substitution, but the reaction with the n-butyl Grignard reagent was found to proceed only to the extent of ∼70%. The novel $[Si(Me)(F)CH_2]_n$ polymer was obtained by the action of $BF_3{\cdot}Et_2O$ on the $[Si(Me)(OEt)CH_2]_n$ polymer. The atactic structures of these polymers were characterized by NMR spectroscopy, and their molecular weights and thermal properties were examined by GPC, DSC, and TGA. The $[Si(Me)(OR)CH_2]_n$ polymers were found to vary widely in terms of their hydrolytic sensitivity and glass transition temperatures.

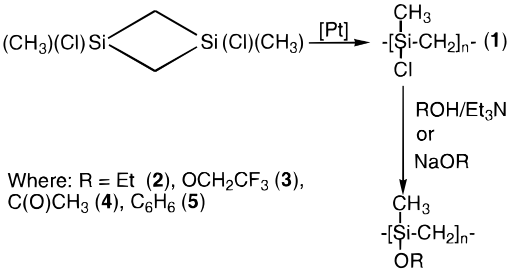
Introduction

Polymers that contain inorganic elements in their backbones can provide properties and a level of synthetic versatility that are often unachievable in all-carbon-backbone polymers. Among the best-developed examples of such “inorganic polymers” are the polysiloxanes, polyphosphazenes, and polysilanes, which have found interest as thermally stable, liquid crystalline, photoactive, semiconducting, ionically conductive, and biomedical polymers.[1]

In the 1960s, the poly(silylenemethylenes) emerged as a new class of inorganic polymers. These polymers were obtained by the ring-opening polymerization of disilacyclobutanes using heat or various late transition metal catalysts, among which platinum compounds seem to work best.[2] It was found that the Si−C backbone of these polymers provided thermal stability similar to, or even better than, that of the polysiloxanes, although the oxidative stability was lower.[2c] Moreover, the Si−C backbone offers the prospect of improved backbone hydrolytic stability over the polysiloxanes, particularly under strongly basic conditions. Thus, the availability of convenient synthetic routes to such poly(silylenemethylenes) could lead to the development of a new class of polymers that combines excellent thermal and hydrolytic stability with good synthetic versatility.

However, the early work in this area was limited to polymers with methyl or phenyl groups on silicon and was hindered by the lack of suitable high-yield synthetic routes to the appropriate disilacyclobutane monomers.[3] Prior attempts to introduce a reactive group on silicon by polymerizing a chloro- or ethoxy-substituted monomer,[2a] as well as by functionalizing poly[(dimethylsilylene)methylene][4a] or poly[(diphenylsilylene)methylenes],[4b] have resulted in low molecular weight products that have received little attention as starting materials for substitution reactions. The discovery in our laboratory that the polymerization and subsequent reduction of dichlorodimethyldisilacyclobutanes and tetrachlorodisilacyclobutanes resulted in high molecular weight polysilapropylene[5] and polysilaethylene,[6] respectively, effectively opened up some new routes to a wide range of poly(silylenemethylenes). In these cases, we have both the Si−Cl functionality of the chloropolymer intermediates and the Si−H bond in the corresponding reduced polymers as potential reactive sites for chemical substitution on Si.

Scheme 1



In a preliminary communication, we recently reported the preparation and characterization of di- and monoalkoxy-substituted poly(silylenemethylenes).[7] In particular, it was found that poly[(chloromethylsilylene)methylene] can serve as a convenient starting material for the synthesis of various alkoxy-substituted poly[(methylsilylene)methylenes]. In the current paper, we report the full details of our investigation of substitution reactions on poly[(chloromethylsilylene]methylene] as a means of preparing alkoxy-, aryloxy-, acyloxy-, fluoro-, and alkyl-substituted polymers.

Results and Discussion

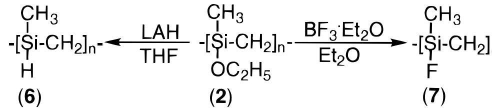
Syntheses. The parent compound for these syntheses, poly[(chloromethylsilylene)methylene] (**1**), was prepared by the ring-opening polymerization of neat 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane.[5,8] As we reported earlier,[7] the alkoxy group can be conveniently introduced by treating **1** with an alcohol/triethylamine mixture in diethyl ether or THF solution (Scheme 1). The substitution occurs stoichiometrically. Thus, the ^1H and ^{13}C NMR spectra of the products show no peaks corresponding to $-[Si(CH_3)(Cl)CH_2]-$[4] units. The same method works well for the preparation of the phenoxy-substituted polymer. It was found, however, that a more convenient route to both the phenoxy- and the acyloxy-substituted polymers is the treatment of

---

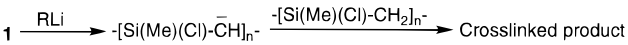
[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

0024-9297/96/2229-3123$12.00/0

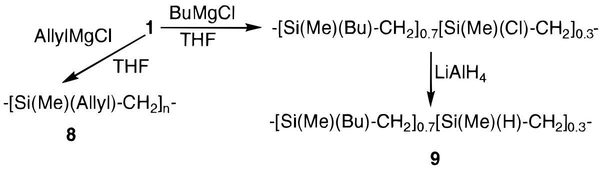
Scheme 2



Scheme 3



Scheme 4



1 with anhydrous sodium phenoxide or potassium acetate, respectively, in diethyl ether or THF. The substitution in both cases appears to be complete, based on the NMR spectra of the products. More basic alkoxides cannot be used, since traces of these in the final product catalyze exchange reactions of the alkoxy groups on silicon with water or alcohol used in the workup.[9] For example, when **1** was mixed with a solution of NaOEt in ether, followed by subsequent removal of the solvent and extraction of the polymers with hexane, attempts to precipitate the polymer from ether by addition of methanol led to >95% substitution of ethoxy groups by methoxy, as determined by NMR spectroscopy. The sensitivity toward hydrolysis of the polymers prepared by this route is also greatly increased.

In general, the stability toward hydrolysis increases from the acyloxy-substituted polymers, which can be easily cross-linked on exposure to air, to the phenoxy-substituted polymers, which survive an aqueous workup (see the Experimental Section) and remain soluble in organic solvents after at least 2 months of storage in air. Poly[(ethoxymethylsilylene)methylene] (**2**) cross-links on standing in air over a period of 1–2 days.

Further modification of polymer **2** is possible (Scheme 2). The reaction of $BF_3{\cdot}Et_2O$ with the polymer **2** in diethyl ether results in the complete substitution of the ethoxy group by fluorine[10] (Scheme 2), yielding poly[(fluoromethylsilylene)methylene] (**7**). The reduction of polymer **2** by $LiAlH_4$ in THF gives polysilapropylene (**6**).

Another reaction that was evaluated for poly[(chloromethylsilylene)methylene] was alkylation. The product obtained after treatment of **1** with BuLi or PrLi was an insoluble, presumably cross-linked, polymer. Since it is known that alkyllithium reagents can alkylate the bridging carbon in poly[(dimethylsilylene)methylene],[11] we suggest that a similar process occurs here, which leads to cross-linking through the subsequent reaction of the carbanion formed with the Si–Cl groups of other polymer chains (Scheme 3).

Alkyl Grignard reagents are, in general, insufficiently active to cause complete substitution. For example, after treating the polymer **1** with BuMgCl and then with $LiAlH_4$, a copolymer **9** was obtained (Scheme 4). About 70% of the silicons in this polymer had Bu substituents, as determined by NMR spectroscopy, with the remaining sites occupied by H. This is understandable in the context of early reports of difficulties in introducing a fourth alkyl group to sterically hindered chlorotrialkylsilanes by means of Grignard reagents.[12] The Si–H bond in this copolymer is stable toward hydrolysis, even in the presence of a strongly basic aqueous solution. Thus, after a 24 h exposure of this polymer to such a solution, it remained soluble in organic solvents, and its NMR spectra were unchanged.

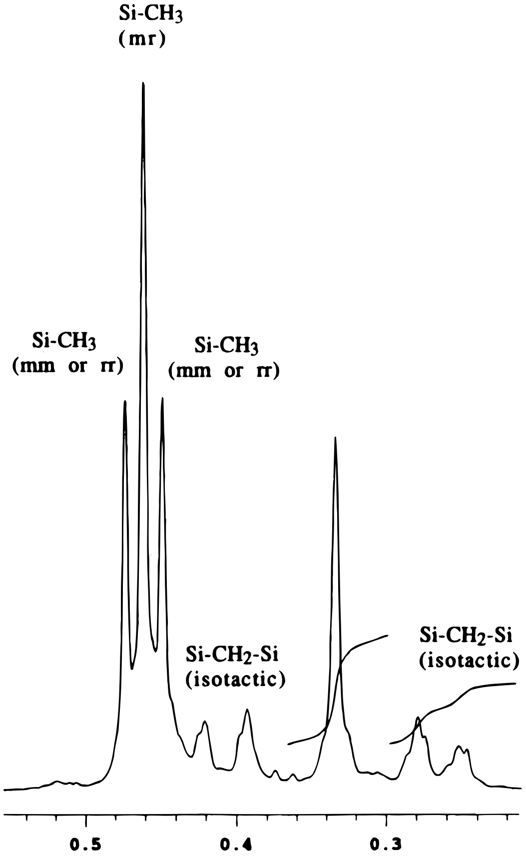


Figure 1. 500 MHz ^1H NMR spectrum of the methyl and methylene protons of the $[Si(Me)(OEt)CH_2]_n$ polymer.

Only allylmagnesium chloride was able to cause the complete substitution of the Si–Cl groups, yielding poly[(allylmethylsilylene)methylene] (**8**) (Scheme 4). Unlike BuMgCl, the allyl Grignard reagent caused a highly exothermic reaction when added to the polymer **1**.

Characterization by NMR Spectroscopy. In a general sense, the NMR spectra of the polymers synthesized resemble the spectra of poly[(chloromethylsilylene)methylene] (**1**).[4,5] As in the case of **1**, the different diastereomeric sequences formed by the chiral silicons in the polymer chain cause the splitting of the peaks of the main chain nuclei and the $SiCH_3$ group.

It has been found in the case of the polypropylenes that diastereomeric sequences with even numbers of chiral centers cause splitting of the NMR peaks due to the main chain (^{13}C) nuclei, while diastereomeric sequences with odd numbers of chiral centers split the peaks of the pendant groups.[13] Accordingly, in all of the asymmetrically substituted poly[(methylsilylene)methylenes] studied, the $SiCH_2Si$ protons show one line that can be attributed to an A_2 spectrum of syndiotactic diads and four lines due to an AB spectrum of isotactic diads (Figure 1). Since the starting monomer is a 50/50 mixture of cis- and trans-isomers, the resulting polymer can be expected to have equal numbers of iso- and syndiotactic sequences. Integration of the isotactic and the syndiotactic lines of the $SiCH_2Si$ protons gives a 1:1 ratio, confirming the expected atacticity of the polymers. In the case of the polymer **4** (R = acetoxy), each line of the isotactic diads was split into three lines by the higher order diastereomeric sequences (tetrads).

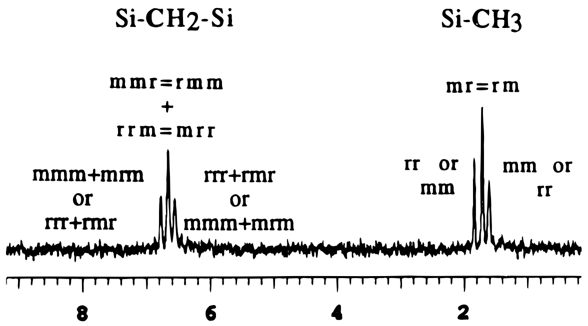


Figure 2. 125 MHz ^{13}C NMR spectrum of the methyl and methylene carbons of the $[Si(Me)(OAc)CH_2]_n$ polymer.

The $SiCH_2Si$ carbon of most of the polymers gives a broad, unresolved line in the ^{13}C NMR spectrum. In the case of the polymer **8** (R = allyl), the $SiCH_2Si$ carbon shows two lines corresponding to the syndio- and isotactic diads. Polymer **4**, on the other hand, like the parent poly[(chloromethylsilylene)methylene][4a,5] shows three lines for this carbon, with relative intensities of 1:2:1 (Figure 2). We attribute the splitting observed in these cases to sterochemical effects arising from the different possible tetrad sequences. There are eight such tetrad sequences possible: rrr, rmr, mrr = rrm, mmr = rmm, mrm, and mmm. In an atactic polymer, the probability of each tetrad is equal, so it is reasonable to assume that in the case of the polymers **1** and **4** the central peak represents the mrr = rrm and mmr = rmm tetrads, while the side peaks are caused by the overlapping mmm + mrm and rrr + rmr tetrads, respectively (Figure 2). All of the other polymers in which the methylene carbon appears as an unresolved line probably represent intermediate cases between the polymers **8** and **4**.

The $SiCH_3$ protons of all the polymers except **7**, **8**, and **9** show three lines in C_6D_6 solution, with relative intensities of 1:2:1 (Figure 1), which were assigned in the previous work[4] to mm, rm = mr, and rr triads. The ^{13}C NMR spectra of all the polymers also show the expected three lines of the triad sequences[5] for the $SiCH_3$ carbon (Figure 2). In the case of the polymer **8**, the allylic $Si\mathit{C}H_2CH{=}CH_2$ carbon resolves into three lines as well.

In the case of the polymer **7** (R = F), all the features of the NMR spectra discussed above are complicated further by short- and long-range coupling to the fluorine, so the ^{1}H NMR spectrum of the polymer **7** consists of practically unresolvable CH_3 and CH_2 overlapping multiplets. The 50 MHz ^{13}C NMR spectrum of this polymer consists of a triplet for the methylene and a doublet for the methyl carbon due to the coupling to the fluorine. The 125 MHz ^{13}C NMR spectrum shows additional splitting of all of these lines (Figure 3a). In order to establish whether this additional splitting was due to the tacticity of the polymer or to long-range coupling with fluorine, the apparently new model compound **10** was synthesized (Scheme 5). Compound **10** has no diastereomers, so the splitting due only to the coupling to the fluorine can be distinguished. In **10**, the polymer environment is simulated most closely by the middle methyl group. Since the carbon of this methyl group shows a doublet with no additional splitting in the 125 MHz ^{13}C NMR spectrum (Figure 3b), the tacticity must be the reason for the additional splitting of the methyl and methylene carbons in the 125 MHz ^{13}C NMR spectrum of polymer **7**. It should be noted that the silicon peaks in the ^{29}Si NMR spectrum of **10** do show splitting due to coupling to both the nearest and the next-nearest fluorine atoms.

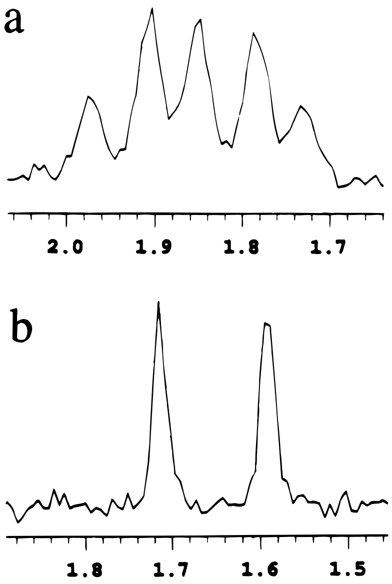
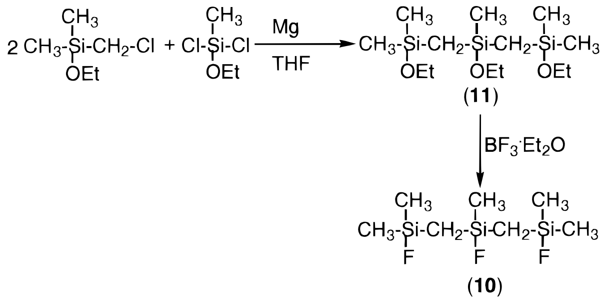


Figure 3. 125 MHz ^{13}C NMR spectrum of the (a) methyl carbon of the $[Si(Me)(F)CH_2]_n$ polymer and (b) the middle methyl carbon of model compound **10**.

Scheme 5



In general, the main chain silicon of all the polymers appears as a broad unresolved line in the ^{29}Si NMR spectra (in the case of polymer **7**, there are two lines due to the coupling to the fluorine).

The ^{1}H and ^{13}C NMR spectra of polymer **9** (the R = Bu, H copolymer) show multiple peaks due to the different combinations of $[Si(Me)(Bu)CH_2]$ and $[Si(Me)(H)CH_2]$ units. In the ^{13}C spectrum, no peaks were observed in the region between 1.5−2 and 8−7 ppm, or between 5−6 and 11−12 ppm, where $SiCH_2Si$ and $SiCH_3$ carbons, having adjacent Si−O or Si−Cl groups, respectively, should occur.[5] This indicates that practically all of the Si−Cl groups left in the polymer after the action of C_4H_9MgCl were reduced to Si−H by $LiAlH_4$. The ^{29}Si NMR spectrum shows only two peaks: the major one at 2.34 ppm for the Si−Bu and a minor one at −16.76 ppm for the Si−H groups. Again, no peaks above 10 ppm, as would be expected for Si−O or Si−Cl groups, were found.

Other Properties. The polymers synthesized were also studied by GPC, DSC, and TGA methods. The number-average molecular weights of the polymers, as measured by GPC, ranged from 7×10^3 to 30×10^3, depending on the nature of the substituents and the molecular weight of the parent poly[(chloromethylsilylene)methylene]. The polydispersities ranged from 3 to 8 (Table 1). It was noticed that the different polymerization runs with dichlorodimethyldisilacyclobutane did not yield polymers with reproducible molecular

Table 1. Physical Properties of the $[Si(Me)(R)CH_2]_n$ Polymers

polymer sample	R	M_n, $\times 10^{-3}$	M_w, $\times 10^{-3}$	T_g
2	OEt	40.3	185.4	−79
2a	OEt	7.1	41.5	−80
3	OCH_2CF_3	*a*	*a*	−50.5
4	OAc	*b*	*b*	−28
5	OPh	24.7	172.2	−17.5
6	H	12.5	47.2	−101
7	F	7.2	36.8	−76.5
7a	F	20.1	55.7	−70
7b	F	45.4	97.5	−70
7c	F	66.8	192.2	−69
8	C_3H_5	2.4	6.8	−72
9	C_4H_9, H	11.7	39.6	−71

[a] This polymer was not soluble in toluene, the solvent used for these GPC measurements. [b] This polymer was too hydrolytically sensitive for GPC measurements.

weights. The origins of these variations in molecular weight were not specifically investigated; however, neither the nature of the catalyst ($H_2PtCl_4 \cdot xH_2O$ or $(C_6H_{10})_2PtCl_4$) nor the reaction conditions employed for the polymerization appeared to have a clear effect on the molecular weight or the molecular weight distribution.

As expected for the atactic structure of these polymers,[1] their DSC curves show a clear glass transition but no melting transitions. The T_g values, as in the case of the polyphosphazenes,[1] were found to depend strongly on the nature of the side chains attached to the silicon, ranging from −17.5 °C to −101 °C. To our knowledge, the only phosphazene of the type $[P(CH_3)(OR)N]_n$ known is the one having $R = OCH_2CF_3$; interestingly, its $T_g = -50$ °C,[14] a value that is practically identical to that of poly[(trifluoroethoxymethylsilylene)methylene] (**3**). The glass transition temperatures of polymers **2** and **7** with different molecular weights are shown in the entries **2**, **2a**, and **7**−**7c** of Table 1. It is apparent that the T_g is only slightly dependent on the molecular weight of the polymer over a broad range.

In accordance with their low T_g values, the physical appearance of the polymers ranges from viscous liquids (polymers **6** and **8**) to gums (polymers **5** and **7c**). An unusually high affinity of the polymer **3** to the surface of the glass was noticed. A considerable effort was required to remove a sample from the flask.

The thermal stability of the polymers was studied by the TGA method. The TGA curves in N_2 show little or no weight loss below 300 °C and a rapid decomposition between 300 °C and 400 °C. All of the polymers except **3** and **7** leave 25−30% residue at 1000 °C. The fluorine-containing polymers volatilize completely.

Conclusions

The chief purpose of this work was to evaluate the prospect of using poly[(chloromethylsilylene)methylene] (**1**) as a convenient starting point for the synthesis of substituted poly(silylenemethylenes) by means of metathesis reactions. It was found that the Cl atoms of this polymer can be easily substituted by various OR groups, whereas its complete alkylation was achieved only by the action of the very active allyl Grignard reagent.

A basic characterization of the molecular structure of these new polymers was carried out by NMR spectroscopy, and the observed splitting of the NMR peaks could be understood in the context of their atactic structure. Also understandable in this context is the observation of glass transitions for these polymers but no melting transitions. The alkoxy polymers were found to exhibit a wide range of reactivities toward water although their hydrolytic stability is substantially lower than those of the polyphosphazenes.[15] The ethoxy polymer undergoes hydrolysis at a sufficiently convenient rate to make it potentially suitable for use in a sol−gel process for coating applications.

Apparently, the first silicon-containing polymer with a fluorine atom directly attached to the silicon was synthesized. It was found to be indefinitely stable toward hydrolysis on exposure to air and on treatment with neutral water.

Further work is under way to more completely evaluate the chemical and physical properties of these new polymers and to explore their potential application as coatings and as functional polymers.

Experimental Section

All manipulations involving air- and/or moisture-sensitive materials were performed under N_2. All ether and hydrocarbon solvents were distilled before use from their purple sodium/benzophenone solutions. Ethanol was dried before distillation by using sodium ethoxide, and triethylamine was dried with sodium. Dichlorodimethyldisilacyclobutane was prepared according to the literature method[8] and purified by distillation. Potassium acetate was purchased from Fisher and dried before use in an oven at 120 °C overnight. All other reagents were purchased from Aldrich and used without further purification.

NMR spectra were obtained on XL-200 or Unity-500 instruments. ^1H and ^{13}C spectra were referenced to the solvent peaks, ^{29}Si spectra were referenced to TMS, and ^{19}F spectra were referenced to fluorotrichloromethane. GPC was carried out in toluene solution using a Waters 600 multisolvent delivery system with a differential refractometer detector and three Ultrastyragel columns in series; molecular weights are referenced to polystyrene standards. All DSC measurements were performed by using a heating rate of 10 °C/min on a Sieko DSC 220C instrument. The T_g was determined as the inflection point in the heating portion of the DSC curve after an initial heating/cooling cycle.

Preparation of Poly[(chloromethylsilylene)methylene] (1). This polymer was prepared by the polymerization of neat dichlorodimethyldisilacyclobutane with chloroplatinic acid at 80−90 °C or with $(C_6H_8)_2Pt_2Cl_4$ at room temperature. In a typical polymerization, 2 mL of dichlorodimethyldisilacyclobutane was added via syringe to a flask containing about 2 mg of chloroplatinic acid and a magnetic stirring bar. The mixture was heated while stirring to 80−90 °C, and after an induction period of 15−30 min, the onset of polymerization was signaled by the dark color of the mixture and an increase in its viscosity. After the mixture could no longer be stirred (3−5 h), polymerization was assumed to be complete. This polymer was used directly for the various reactions described below.

Preparation of Poly[(ethoxymethylsilylene)methylene] (2) and Poly[trifluoroethoxymethylsilylene)methylene] (3). Polymer **1** (2 g) was dissolved in 30 mL of ether, and to this solution was added a 2-fold molar excess of the triethylamine/alcohol mixture (50/50 mol/mol). An immediate reaction, accompanied by the precipitation of a large amount of triethylamine hydrochloride, occurred. The mixture was refluxed overnight and filtered after cooling. The volatiles were stripped off, and the polymer was precipitated two times from an ether/methanol mixture. Polymer **2** is quite soluble in nonpolar (hexane, toluene) and polar (THF, chloroform, acetone) organic solvents, except alcohols and acetonitrile. Polymer **3** is soluble in THF and acetone and but insoluble in alcohols and acetonitrile. The yield of **2** was 1.5 g (68%); the yield of **3** was 2.4 g (71%).

For **2**: 500 MHz ^{1}H NMR (C_6D_6) δ 3.72 (q, J = 7 Hz, 2H, OCH_2CH_3), 1.25 (t, J = 7 Hz, 3H, OCH_2CH_3), 0.47, 0.46, 0.45 (3H, $SiCH_3$), 0.42, 0.39, 0.33, 0.28, 0.25 (2H, $SiCH_2Si$); 125 MHz ^{13}C NMR (C_6D_6) δ 58.04 (OCH_2CH_3), 18.83 (OCH_2CH_3), 7.51 (br, $SiCH_2Si$), 1.83, 1.79, 1.76 ($SiCH_3$); 99 MHz ^{29}Si ($CDCl_3$) δ 13.5.

For **3**: 500 MHz ^{1}H NMR (THF-d_6) δ 4.3 (q, J = 8.5 Hz, 2H, OCH_2CF_3), 5.97 (s, $SiCH_3$), 6.04, 6.01, 5.94, 5.87, 5.84 ($SiCH_2Si$); 125 MHz ^{13}C NMR (THF-d_6) δ 125.7 (q, J = 278 Hz, OCH_2CF_3), 61.57 (q, J = 36 Hz, OCH_2CF_3), 6.9 (br, $SiCH_2Si$), 0.84, 0.83 0.82 ($SiCH_3$).

Preparation of Poly[(acetoxymethylsilylene)methylene] (4). Polymer **1** (2 g, 22 mmol) was dissolved in 20 mL of THF, and 4.2 g (43 mmol) of potassium acetate was added. The reaction mixture became warm after about 5 min. After being stirred at room temperature for 1 h, the reaction mixture was refluxed overnight. The solvent was evaporated down to about 5 mL, and 40 mL of $CHCl_3$ was then added. The mixture was filtered through a Celite pad, and the volatiles were stripped off. The polymer was reprecipitated three times from an ether/hexane mixture. The yield of **4** was 1.9 g (75%).

For **4**: 500 MHz ^{1}H NMR (C_6D_6) δ 1.91 (s, 3H, $C(O)CH_3$), 0.83, 0.80, 0.69, 0.56, 0.55, 0.53 ($SiCH_2Si$ and $SiCH_3$, overlapped, 5H); 125 MHz ^{13}C NMR (C_6D_6) δ 171.04 ($C{=}O$), 22.71 ($C(O)CH_3$), 6.78, 6.66, 6.55 ($SiCH_2Si$), 1.84, 1.71, 1.61 ($SiCH_3$); 99 MHz ^{29}Si NMR ($CDCl_3$) δ 18.6.

Synthesis of Poly[(methylphenoxysilylene)methylene] (5). Procedure a. Polymer **1** (2 g, 22 mmol) was dissolved in 30 mL of toluene, and this solution was added to the solution of sodium phenolate prepared from 2.1 g (43 mmol) of phenol and 0.97 (42 mmol) of sodium in 40 mL of refluxing toluene. The reaction mixture was refluxed overnight. After cooling, it was poured into 100 mL of ice-cold water. The organic layer was separated and dried, and the toluene was stripped off. The polymer was reprecipitated three times from a 20/80 benzene/ethanol mixture. The yield was 2.2 g (69%). This polymer was found to have cross-linked after about 2 months of storage in air.

Procedure b. Polymer **1** (2 g, 22 mmol) was dissolved in 30 mL of THF, and then 2.1 g (43 mmol) of phenol was added, followed by 6 mL (43 mmol) of triethylamine. An immediate reaction was apparent by the warming of the reaction mixture and the appearance of a white precipitate. The reaction mixture was refluxed overnight, $Et_3N{\cdot}HCl$ was filtered off, and the volatiles were removed. The polymer was kept under high vacuum overnight at 60 °C. It was then precipitated three times from a benzene/ethanol mixture (20/80). The yield of **5** was 1.9 g (61%).

For **5**: 500 MHz ^{1}H NMR (C_6D_6) δ 7.07, 6.89, 6.83 (5H, OC_6H_5), 0.57, 0.50, 0.42, 0.39, 0.37 (5H, $SiCH_2Si$, $SiCH_3$); 125 MHz ^{13}C NMR (C_6D_6) δ 155.53, 129.91, 121.79, 120.43 (OC_6H_5), 8.14 ($SiCH_2Si$), 2.72, 2.65, 2.58 ($SiCH_3$); 99 MHz ^{29}Si NMR ($CDCl_3$) δ 15.25.

Synthesis of Poly[(fluoromethylsilylene)methylene] (7). Polymer **2** (4 g, 39 mmol) was dissolved in 9.7 mL (80 mmol) of $BF_3{\cdot}Et_2O$. The reaction mixture was stirred overnight, and then all the volatiles were removed under high vacuum at 60 °C overnight. The residue was dissolved in 40 mL of chloroform, and 50 mL of water was added. After being stirred for 1 h, the organic layer was separated, dried, and filtered. The solvent was removed under vacuum, and the polymer (yield, 3 g, 91%) was subjected to fractionation (see below).

Fractionation of Poly[(fluoromethylsilylene)methylene] (7). Polymer **7** (2 g) was dissolved in 25 mL of benzene. To this solution was added 55 mL of methanol, resulting in the precipitation of fraction **7d**, which was separated by centrifugation. After the addition of 10 mL more benzene, the fraction **7c** was separated. Next, addition of 15 mL of methanol precipitated the fraction **7b**. All the fractions were dried under high vacuum at 40 °C overnight.

For **7**: 500 MHz ^{1}H NMR ($CDCl_3$) δ 0.36, 0.35, 0.32, 0.31, 0.29, 0.28, 0.27, 0.25 ($SiCH_2Si$ and $SiCH_3$, overlapped); 125 MHz ^{13}C NMR ($CDCl_3$) δ 8.05 (t, J = 13.9 Hz, $SiCH_2Si$), 1.84, 1.82, 1.78, 1.7, 1.68 ($SiCH_3$); 99 MHz ^{29}Si NMR ($CDCl_3$) δ 28.59 (d, J = 279 Hz); 490 MHz ^{19}F NMR ($CDCl_3$) ϕ −148.83 (s). Anal. Calcd for **7**: C, 31.55; H, 6.62. Found: C, 31.06; H, 6.69.

Reduction of Poly[(ethoxymethylsilylene)methylene] (2). The polymer **2** (2 g, 19 mmol) was dissolved in 20 mL of THF. To this solution was added $LiAlH_4$ (0.4 g, 10 mmol) slowly. The reaction mixture was stirred at 25 °C for 24 h and refluxed for another 24 h. The reaction mixture was cooled and poured very slowly into a stirring mixture of 100 mL of 4 M HCl and 100 mL of ether cooled in an ice bath. The organic layer was separated and dried, and the solvents were stripped off, leaving 0.9 g (0.83%) of the polymer **6**. The ^{1}H and ^{13}C NMR spectra were identical to those of polysilapropylene.[4,5]

Synthesis of 2,4,6-Triethoxy-2,4,6-trimethyl-2,4,6-trisilaheptane (11). (Chloromethyl)chloroethoxymethylsilane (63 g, 0.36 mol) (prepared in 65% yield from the reaction of (chloromethyl)dichloromethylsilane with 1 equiv of ethanol) was mixed with 35 g (0.22 mol) of dichloroethoxymethylsilane (prepared in 30% yield by the reaction of ethanol with 0.6 equiv of trichloromethylsilane). This mixture was added slowly to 14 g of Mg powder suspended in 170 mL of THF. The reaction mixture was refluxed for 1 h and cooled to room temperature, and then 200 mL of hexane was added. The precipitate was filtered off, and the volatiles were evaporated on a rotary evaporator. The product was distilled at 95 °C at 0.5 mmHg. The yield of **11** was 34.5 g (66%, 97% purity by GC).

For **11**: 500 MHz ^{1}H NMR (C_6D_6) δ 3.59 (q, J = 7 Hz, 4H, $Si(OCH_2CH_3)(CH_3)_2$) and 3.58 (q, J = 7 Hz, 2H, $Si(OCH_2CH_3)(CH_3)$) overlap, 1.12 (q, J = 7 Hz, 9H, $SiOCH_2CH_3$), 0.13 (3H, $Si(CH_3)$), 0.01, 0.09 (12H, $Si(CH_3)_2$ (diastereotopic)), 0.04, 0.01, −0.02, −0.05 (4H, $SiCH_2Si$); 125 MHz ^{13}C NMR (C_6D_6) δ 57.83 ($Si(OCH_2CH_3)(CH_3)_2$), 57.77 ($Si(OCH_2CH_3)(CH_3)$), 18.44 ($Si(OCH_2CH_3)(CH_3)_2$), 18.36 ($Si(OCH_2CH_3)(CH_3)$), 5.79 ($SiCH_2Si$), 1.06 ($SiCH_3$), 0.44, 0.43 ($Si(CH_3)_2$).

Synthesis of the Model Compound, 2,4,6-Trifluoro-2,4,6-trimethyl-2,4,6-trisilaheptane (10). Compound **11** (13.7 g, 52 mmol) was mixed with 7 mL (57 mmol) of $BF_3{\cdot}Et_2O$. The reaction mixture was maintained at 50 °C for 1 h. After the mixture was cooled to room temperature, 5 mL of water and then 20 mL of hexane were added, and the mixture was stirred for another 30 min. The organic layer was carefully decanted, and the water layer was extracted by two 5 mL portions of diethyl ether. The organic layers were combined and the solvents evaporated off. The residue was fractionally distilled at 20 mmHg. The fraction with bp = 70−75 °C was collected. The yield of **10** was 5.1 g (51%, 98% purity by GC).

For **10**: 500 MHz ^{1}H NMR ($CDCl_3$) δ 0.22 (d, J = 7 Hz, 3H, $Si(F)(CH_3)$), 0.15, 0.13 (d's, J = 7 Hz, $Si(F)(CH_3)_2$), 0.025 (m, 4H, $SiCH_2Si$); 125 MHz ^{13}C NMR ($CDCl_3$) δ 7.07 (t, J = 14.4 Hz, $SiCH_2Si$), 1.66 (d, J = 15 Hz, $Si(F)(CH_3)$), 0.86, 0.81 (d, J = 15 Hz, $Si(F)(CH_3)_2$); 99 MHz ^{29}Si NMR ($CDCl_3$) δ 30.7 (d of d, J_1 = 277 Hz, J_2 = 3.7 Hz, $(CH_3)_2(F)Si$), 28.6 (d of t, J_1 = 277 Hz, J_2 = 3.6 Hz, $(CH_3)(F)Si$); 490 MHz ^{19}F NMR ($CDCl_3$) ϕ −153.7 (m, 2F, $(CH_3)_2(F)Si$), −149.5 (m, 1F, $(CH_3)(F)Si$).

Attempts To Prepare a Butyl-Substituted Poly[(methylsilylene)methylene] Using Lithium Reagents. Two equivalents of a 2.5 M solution of BuLi in hexanes was added dropwise to 30 mL of a benzene or THF solution of the polymer **1** (2 g, 22 mmol). The reaction mixture was stirred at 25 °C overnight, and then 3 mL of dry methanol was added slowly to destroy the excess BuLi. The volatiles were removed, and the residue was extracted with refluxing hexane. After the hexane extract was stripped off, no polymeric products were obtained. Extraction with benzene and chloroform gave the same result.

Preparation of Poly[(allylmethylsilylene)methylene] (8). A 2 M solution (20 mL) of allylmagnesium chloride in THF was added slowly to a refluxing solution of 2 g (22 mmol) of polymer **1** in 4 mL of THF. The mixture was stirred under reflux overnight and cooled to room temperature, and then 20 mL of hexane was added. The mixture was neutralized with a saturated solution of NH_4Cl. The organic layer was separated and dried, and the solvents were stripped off. The polymer was reprecipitated three times from an ether/methanol mixture (30/70). The yield of **8** was 1.5 g (70%).

For **8**: 500 MHz ^{1}H NMR (C_6D_6) δ 5.88 (m, 1H, $CH{=}CH_2$); 5.04 (s) and 5.01 (d, J = 8.5 Hz, 2H, $CH{=}CH_2$), 1.67 (d, J = 7.8 Hz, $SiCH_2CH{=}CH_2$), 0.23 (3H, $SiCH_3$), 0.01, −0.02, −0.04, −0.06, −0.09 (2H, $SiCH_2Si$); 125 MHz ^{13}C (C_6D_6) δ 135.3 ($CH{=}CH_2$), 113.9 ($CH{=}CH_2$), 27.23, 27.20, 27.16 ($SiCH_2$-$CH{=}CH_2$), 3.18, 3.08 ($SiCH_2Si$), 0.914 ($SiCH_3$); 99 MHz ^{29}Si NMR (C_6D_6) δ 3.1.

Synthesis of the Copolymer [Si(Me)(*n*-Bu)CH$_2$]$_m$[Si(Me)(H)CH$_2$]$_n$ (9). Polymer **1** (2 g, 22 mmol) was dissolved in 4 mL of THF. To this solution was added 40 mL of a THF solution of a butyl Grignard reagent, prepared from 1.1 g (44 mmol) of Mg powder and 4.5 mL (43 mmol) of n-C_4H_9Cl. [Notes: (a) The Grignard reagent can be alternatively prepared in situ by adding Mg and n-C_4H_9Cl to the polymer **1** dissolved in 40 mL of THF. (b) Use of higher concentrations of the Grignard reagent resulted in the polymer being precipitated out of the solution.] The reaction mixture became slightly warm after the addition. It was then refluxed overnight and then cooled to room temperature, and 0.4 g (10 mmol) of $LiAlH_4$ was added slowly. The reaction was refluxed for 48 h, cooled to room temperature, and poured slowly into a mixture of 150 mL of 4 M HCl and 100 mL of ether cooled in an ice bath. The organic layer was collected and dried, and the solvents were stripped off. The polymer was reprecipitated from an ether/methanol mixture (30/70). The yield of **9** was 1.6 g (75%).

For **9**: 500 MHz ^{1}H NMR (C_6D_6) δ 4.4 (0.27H, SiH), 1.45 (2.9H, $SiCH_2(CH_2)_2CH_3$), 1.05 (2.2H, CH_2CH_3), 0.76 (1.46H, $SiCH_2$), 0.14 (3H, $SiCH_3$), −0.5 (2H, $SiCH_2Si$); 125 MHz ^{13}C NMR (C_6D_6) δ 27.25, 27.20, 27.14 ($SiCH_2CH_2CH_2CH_3$), 26.94, 26.90, 26.83, 26.79, 26.72 ($SiCH_2CH_2CH_2CH_3$), 19.21, 18.60, 17.99 ($SiCH_2$); 13.84 (CH_2CH_3), 3.98, 3.31, 3.02, 2.97, 2.30 ($SiCH_2Si$, verified by an APT experiment), 1.33, 0.60, 0.15, −0.125 ($SiCH_3$, verified by an APT experiment); 99 MHz ^{29}Si MNR (C_6D_6) δ 2.43 (SiH), −16.76 (Si(Bu)).

Acknowledgment. Financial support from the National Science Foundation through Grant No. CHE-9520930 is gratefully acknowledged.

References and Notes

(1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992.

(2) (a) Kriner, W. A. *J. Polym. Sci., A-1* **1966**, *4*, 444. (b) Nametkin, N. S.; Vdovin, V. M.; Zav'yalov, V. I. *Dokl. Akad. Nauk SSSR, Ser. Khim.* **1965**, *162* (4), 824. (c) Levin, G.; Carmichael, J. B. *J. Polym. Sci., A-1* **1968**, *6*, 1.

(3) Nametkin, N. S.; Vdovin, V. M.; Zelenaya, A. V. *Dokl. Akad. Nauk SSSR* **1966**, *170* (5), 1088.

(4) (a) Bacque, E.; Pillot, J.-P.; Birot, M.; Dunoges, J. *Macromolecules* **1988**, *21*, 30. (b) Habel, W.; Mayer, L.; Sartory, P. *J. Organomet. Chem.* **1994**, *474*, 63.

(5) Wu, H.-J.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564.

(6) Wu, H.-J.; Interrante, L. V. *Macromolecules* **1992**, *25*, 1840.

(7) Rushkin, I. L.; Interrante, L. V. *Macromolecules*, in press.

(8) Kriner, W. A. *J. Org. Chem.* **1963**, *10*, 321.

(9) Bazant, V.; Chvalovsky, V.; Rathousky, J. *Organosilicon Compounds*; Academic Press: New York, 1965; Vol. 1, p 58.

(10) Reference 9, p 35.

(11) Seyferth, D.; Robinson, J. L.; Mercer, J. *Organometallics* **1990**, *9*, 2677.

(12) Reference 9, p 182.

(13) Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic Press: New York, 1982; p 55.

(14) Allcock, H. R.; McDonnel, G. S.; Desorcie, J. L. *Macromolecules* **1990**, *23*, 3873.

(15) Reference 1, page 90.

MA9517411