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Modifiable Siloxane-Containing Polymers Via Hydrosilylation Polymerization

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Introduction

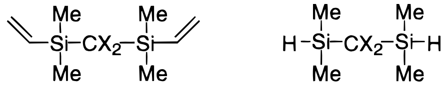
Numerous types of organosilicon polymers have attracted much research interest due to their potentially useful properties. For example, the preparation, characterization, and applications of poly(siloxanes),[1] poly(carbosilanes),[2] poly(carbosiloxanes),[3] and poly(silanes)[4] have been extensively documented in the literature. Recent research has focused on developing methods for modifying these polymers in order to prepare a variety of substituted derivatives with altered properties. Different approaches used to modify organosilicon polymers have included free-radical hydrosilylation of polysilanes,[5] nucleophilic substitution in poly(chlorosilylenemethylenes),[6] hydrosilylation of poly(silylenemethylenes),[7] and deprotonation of poly(carbosilanes).[8]

We have recently initiated an investigation into the synthesis of new modifiable organosilicon polymers via hydrosilylation polymerization. Hydrosilylation polymerization has been utilized extensively in the synthesis of both poly(carbosilanes)[9] and poly(carbosiloxanes).[3] These polymerizations usually proceed cleanly with a minimum of side reactions and can yield polymers of reasonably high molecular weight provided that the stoichiometry of the starting monomers is close to exact. In this report we outline the synthesis and characterization of new halogenated poly(carbosiloxanes), as well as preliminary results indicating that these unique polymers can be successfully and easily modified. An additional benefit of this system is that the chemical substitutions can be brought about by either modifying the preformed polymer or by polymerizing the substituted monomers.

Results and Discussion

As part of our investigation into the synthesis of modifiable organosilicon polymers, we recently reported a general synthetic route to a variety of bis(trialkylsilyl)dihalomethane compounds,[10] of which compounds **1** and **2** seemed to be ideal monomers for hydrosilylation polymerization (Scheme 1). Unfortunately, hydrosilylation polymerizations between **1** and **2** were not successful in the presence of a platinum catalyst. However, after testing various combinations of monomers, we discovered that hydrosilylation polymerization occurred between **1-Cl$_2$** and 1,1,3,3-tetramethyldisiloxane or between **1-Cl$_2$** and 1,1,3,3,5,5-hexamethyltrisiloxane to yield polymers **3-Cl$_2$** and **4-Cl$_2$**, respectively, in quantitative yield (Scheme 2). Immediately after polymerization, the polymers were viscous, transparent oils. Polymer **3-Cl$_2$**, however, slowly crystallized on standing.

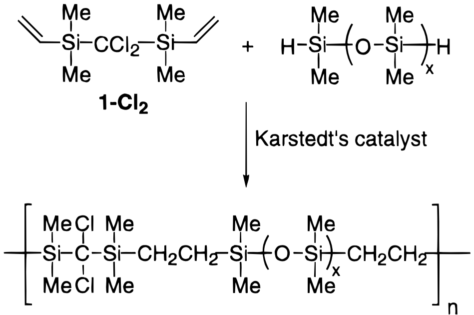
Scheme 1



1-Br$_2$; X = Br
1-Cl$_2$; X = Cl

2-Br$_2$; X = Br
2-Cl$_2$; X = Cl

Scheme 2



1-Cl$_2$

3-Cl$_2$; x = 1
4-Cl$_2$; x = 2

Polymers **3-Cl$_2$** and **4-Cl$_2$** were characterized using ^{1}H and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis, and gel permeation chromatography. The ^{1}H NMR spectra show a lack of end group resonances and also indicate that the polymerizations proceeded cleanly with a minimum of side reactions. An expanded view of the ^{1}H NMR spectrum for polymer **3-Cl$_2$** is shown in Figure 1(a). GPC molecular weight data are listed in Table 1 (entries 1 and 2). On repeating these polymerizations, we found the GPC data to be consistent from batch to batch as long as we utilized a starting monomer molar ratio as close to 1:1 as possible. These molecular weight data in addition to the lack of visible end groups in the ^{1}H NMR spectra suggest that cyclization during polymerization cannot be ruled out. Indeed, during the preparation of polymer **4-Cl$_2$**, small amounts of crystalline material were isolated, which were determined by X-ray crystal diffraction analysis to be small cyclic compounds.[11]

The next step in our investigation was to show that the polymers we obtained could indeed be modified in a relatively facile manner. Previous work has shown the $-SiCCl_2Si-$ moiety in small molecules to be very reactive toward a variety of reagents, particularly organolithium compounds.[12] To demonstrate that this chemistry is applicable to the same moiety in polymers, we performed two basic reactions on polymer **3-Cl$_2$** outlined in Scheme 3. In both cases, reaction did proceed as expected. The ^{1}H NMR spectrum of polymer **3-Cl(Me)** obtained from the reaction of **3-Cl$_2$** with 1 equiv of methyllithium exhibited a new peak at δ 1.53 due to the added methyl group (Figure 1c). However, the integration indicated that approximately 25% of the CCl_2 groups remained unreacted. Utilizing an excess of methyllithium decreased the amount of unreacted CCl_2 groups in **3-Cl(Me)**. The ^{1}H NMR spectrum of **3-Cl(SiMe$_2$H)**, on the other hand, indicated that nearly complete substitution occurred. However, unidentified side reactions may also have occurred during this reaction, evidenced by the presence of several minor new peaks in the spectrum (around δ 0.0). It is also apparent that some cleavage of the polymer backbones took place in these reactions, as evidenced by a decrease

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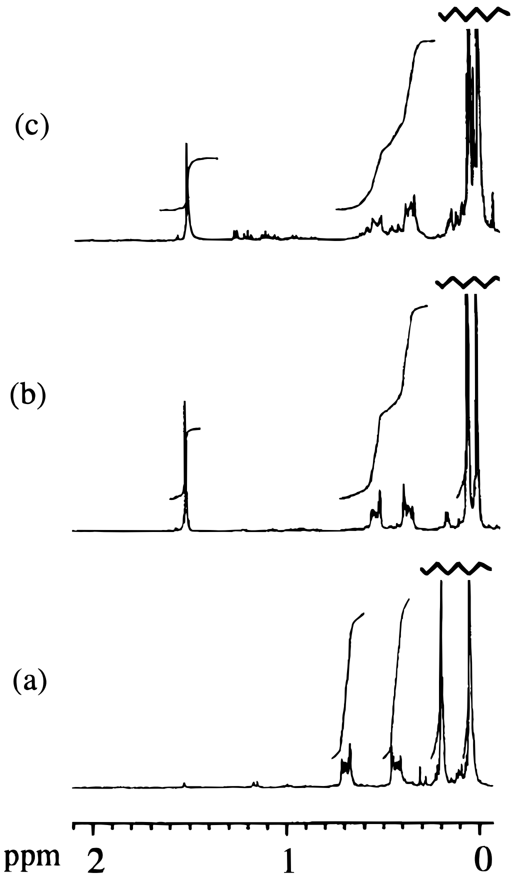


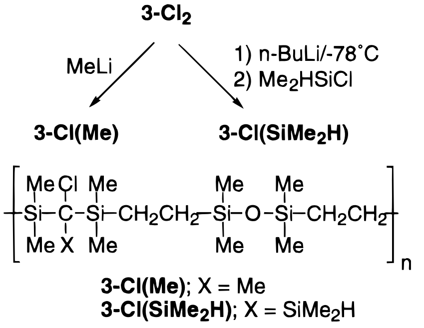
Figure 1. ^{1}H NMR spectra of (a) polymer **3-Cl$_2$**, (b) polymer **3-Cl(Me)** prepared via modification of monomer, and (c) polymer **3-Cl(Me)** prepared via modification of polymer (1.0 equiv of MeLi).

Table 1. GPC Molecular Weight Data (Referenced to Polystyrene Standards)

entry	polymer	M_n	M_w
1	**3-Cl$_2$**	8600	14500
2	**4-Cl$_2$**	16500	26700
3	**3-Cl(Me)**[a]	4800	7700
4	**3-Cl(Me)**[b]	3200	5600
5	**3-Cl(SiMe$_2$H)**	4400	6700
6	**3-Cl(Me)**[c]	7800	13100

[a] From reaction of **3-Cl$_2$** with 1 equiv of methyllithium. [b] From reaction of **3-Cl$_2$** with 1.5 equiv of methyllithium. [c] Prepared from the monomer modification route.

Scheme 3



in the GPC molecular weight values (Table 1, entries 3–5).

As an alternative to chemically modifying the preformed polymers, we investigated the possibility of modifying the monomer, **1-Cl$_2$**, prior to polymerization. The advantage of this method is that the resulting polymer would possess essentially 100% substitution and would be free of contaminants from polymer modification reactions. To illustrate the feasibility of this approach, we first prepared $(CH_2{=}CHSiMe_2)_2CClMe$ in 54% isolated yield from the reaction of **1-Cl$_2$** with methyllithium. Subsequent hydrosilylation polymerization utilizing $(CH_2{=}CHSiMe_2)_2CClMe$ and 1,1,3,3-tetramethyldisiloxane as monomers proceeded smoothly, yielding polymer **3-Cl(Me)** in quantitative yield as a viscous oil. The ^{1}H NMR spectrum of **3-Cl(Me)** (Figure 1b) prepared using this approach indicated that this product was considerably cleaner than polymer **3-Cl(Me)** prepared by the polymer modification route. The molecular weight data is also similar to that obtained for polymer **3-Cl$_2$** (Table 1, entry 6). The limitation of this method is that the choice of substitution on the monomer is restricted to groups that would not be reactive under the hydrosilylation polymerization conditions. For example, polymer **3-Cl(SiMe$_2$H)** would be difficult to obtain via this route since the $-SiMe_2H$ group in $(CH_2{=}CHSiMe_2)_2CCl(SiMe_2H)$ would be active during the polymerization.

Conclusions

In summary, the preparation of new halogenated siloxane-containing polymers has been successfully demonstrated. Substituted derivatives of these polymers can be obtained by modifying the polymers directly or by modifying the monomers prior to polymerization. These routes make the synthesis of a wide range of substituted polymers feasible. The incorporation of different functional groups into these polymers is currently under investigation in our laboratory.

Experimental Section

Materials and General Information. Unless otherwise noted, all reactions were carried out in a nitrogen atmosphere. Compound **1-Cl$_2$**, $(CH_2{=}CHSiMe_2)_2CCl_2$, was prepared in 91% yield via the deprotonation of dichloromethane with LDA in the presence of vinyldimethylchlorosilane.[10] $(CH_2{=}CHSiMe_2)_2CClMe$ was prepared from methyllithium and **1-Cl$_2$**, according to a literature procedure used for the preparation of $(Me_3Si)_2CClMe$.[13] 1,1,3,3-Tetramethyldisiloxane, 1,1,3,3,5,5-hexamethyltrisiloxane, and Karstedt's catalyst in xylene (platinum–divinyltetramethyldisiloxane complex, Pt–DVTMDSO) were obtained from Gelest, Inc. and used as received. *n*-Butyllithium was obtained from Aldrich as a 2.5 M solution in hexane. Methyllithium was obtained from Acros/Fisher as a 1.6 M solution in ethyl ether. Elemental analyses were obtained from E+R Microanalytical Laboratory, Corona, NY. All NMR spectra were obtained on a Bruker AVANCE 400-MHz spectrometer using $CDCl_3$ as solvent. Gel permeation chromatography measurements were performed on a Waters Associates GPC II instrument using 500, 10^4, 10^5, and 10^6 Å μ-Styragel columns and UV or refractive index detectors. The operating conditions consisted of a flow rate of 1.5 mL/min of unstabilized HPLC-grade THF containing 0.1% tetra-*n*-butylammonium bromide [$(n\text{-}Bu)_4NBr$], a column temperature of 30 °C, and a sample injection volume of 0.05 to 0.1 mL of a 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the molecular weight range of ca. 10^3 to 10^6.

Preparation of Polymer 3-Cl$_2$. A 100-mL Schlenk flask containing a magnetic stir bar was charged with **1-Cl$_2$** (3.0 g, 0.0118 mol) followed by 2 drops of Pt–DVTMDSO and 1,1,3,3-tetramethyldisiloxane (1.59 g, 0.0118 mol). The mixture was freeze–thaw-degassed two times. The reaction mixture was then vigorously stirred while heated in an oil bath at 45 °C. The reaction progress was measured by monitoring the disappearance of the Si−H absorbance in the IR spectrum. The reaction was complete after 3 days, yielding polymer **3-Cl$_2$** as a viscous, transparent oil in quantitative yield. $M_n = 8641$, $M_w = 14\,508$, polydispersity = 1.68. Repeat polymerizations yielded polymers with similar molecular weights. ^{1}H NMR (400 MHz), δ: 0.045 (s, 12H), 0.19 (s, 12H), 0.43 (m, 4H), 0.68 (m, 4H). ^{13}C NMR (100 MHz), δ: −4.83 ($SiCH_3$), −0.600 ($SiCH_3$), 5.02 (CH_2), 10.1 (CH_2), 74.9 (CCl_2). IR (NaCl, neat, cm^{-1}): 2956 (s), 2922 (m), 1406 (m), 1253 (s), 1136 (m), 1055 (s), 836 (s), 790 (s). Anal. Calcd: C, 40.28; H, 8.32; Cl, 18.29. Found: C, 40.43; H, 8.54; Cl, 18.15.

Preparation of Polymer 4-Cl$_2$. This polymerization was carried out using the **3-Cl$_2$** preparative procedure. The following reagents were used: **1-Cl$_2$** (3.0 g, 11.85 mmol), $HSiMe_2OSiMe_2OSiMe_2H$ (2.47 g, 11.85 mmol), and Pt−DVTMDSO (2 drops). Polymer **4-Cl$_2$** was obtained as a viscous colorless oil in quantitative yield. $M_n = 16\,500$, $M_w = 26\,700$, polydispersity = 1.62. Repeat polymerizations yielded polymers with similar molecular weights. ^{1}H NMR (400 MHz), δ: 0.015 (s, 6H), 0.067 (s, 12H), 0.20 (s, 12H), 0.45 (m, 4H), 0.69 (m, 4H). ^{13}C NMR (100 MHz), δ: −4.84 ($SiCH_3$), −0.752 ($SiCH_3$), 1.05 ($SiCH_3$), 4.98 (CH_2), 9.97 (CH_2), 74.8 (CCl_2). Anal. Calcd: C 39.01, H 8.29, Cl 15.35; found, C 39.22; H 8.03, Cl 15.29.

Preparation of Polymer 3-Cl(SiMe$_2$H) from Polymer 3-Cl$_2$. A 100-mL Schlenk flask containing a magnetic stir bar was charged with polymer **3-Cl$_2$** (2.73 g, 7.04 mmol) and 50 mL of THF. The flask was cooled in a dry ice/acetone bath and then *n*-BuLi (2.9 mL, 7.25 mmol) was added via syringe. The reaction mixture was stirred for an additional 3 h in the cold bath, at which point chlorodimethylsilane (0.68 g, 7.19 mmol) was added. The reaction mixture was stirred in the cold bath for 30 min and then stirred at room temperature overnight. After an aqueous workup, evaporation of the organic layer gave a brown viscous oil. The oil was redissolved in ether and decolorizing carbon was added. The mixture was filtered, and all volatiles were removed by heating under vacuum at 70 °C overnight. Polymer **3-Cl(SiMe$_2$H)** was obtained as a viscous oil in 92% yield. $M_n = 4400$, $M_w = 6700$, polydispersity = 1.52. The ^{1}H NMR spectrum for this product was slightly messy with many small peaks in the region δ 0.0−0.5 in addition to single peaks at δ 0.031, 0.14, and a doublet at δ 0.24. The Si−H resonance appears at δ 4.13 as a multiplet.

Preparation of Polymer 3-Cl(Me) from Polymer 3-Cl$_2$ (1 equivalent of MeLi). A 100-mL Schlenk flask containing polymer **3-Cl$_2$** (1.43 g, 3.68 mmol), 25 mL of Et_2O, and a magnetic stir bar was cooled in an ice bath. Methyllithium (2.3 mL, 3.68 mmol) was added via syringe. The reaction mixture was allowed to warm to room temperature and stirred overnight. After an aqueous workup, evaporation of the organic layer followed by heating under vacuum at 70 °C afforded polymer **3-Cl(Me)** as a pale yellow, viscous oil (1.01 g, 75%). $M_n = 4800$, $M_w = 7700$, polydispersity = 1.59. The reaction of polymer **3-Cl$_2$** with 1.5 equiv of MeLi is carried out in a similar manner. See Figure 1c for an expanded ^{1}H NMR spectrum of this product.

Preparation of Polymer 3-Cl(Me) via Hydrosilylation Polymerization. This polymerization was carried out using the **3-Cl$_2$** preparative procedure. The following reagents were used: $(CH_2{=}CHSiMe_2)_2CClMe$ (1.0 g, 4.30 mmol), $(HSiMe_2)_2O$ (0.58 g, 4.30 mmol), and Pt-DVTMDSO (2 drops). Polymer **3-Cl(Me)** was obtained as a viscous, pale gray oil in quantitative yield. $M_n = 7800$, $M_w = 13\,100$, polydispersity = 1.68. ^{1}H NMR (400 MHz), δ: 0.037 (s, 12H), 0.076 (d, 12H), 0.39 (m, 4H), 0.53 (m, 4H), 1.5 (s, 3H). ^{13}C NMR (100 MHz), δ: −4.99 ($SiCH_3$), −4.91 ($SiCH_3$), −0.602 ($SiCH_3$), 5.04 (CH_2), 10.3 (CH_2), 22.7 (CH_3C), 48.8 (CCl). Anal. Calcd: C, 45.79; H, 9.61; Cl, 9.65. Found: C, 45.90; H, 9.70; Cl, 9.93.

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