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Relation	



Palladium-catalyzed formation and reactions of iodo- and bromosiloxane intermediates

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1. Introduction

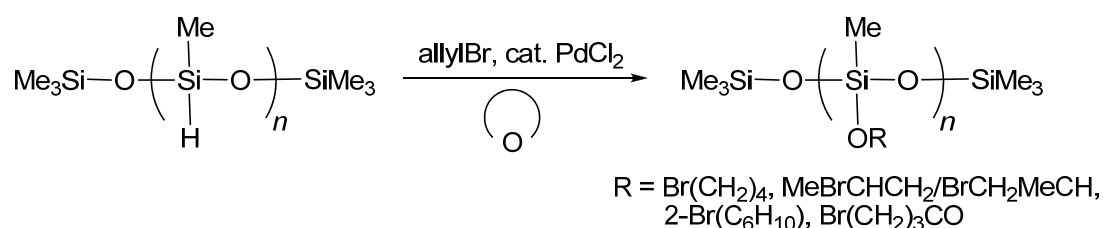
Iodo- and bromosilanes are of important reagents as the building units for a variety of organosilicon compounds [1]. Generally, these Si-X bonds react readily with nucleophiles (Nu⁻) to form substituted units (Si-Nu). In addition, iodo- and bromosilanes exhibit high Lewis acidity to permit the interaction with several organic Lewis-bases. For example, they interact with cyclic ethers, giving ring-opened haloalkoxysilanes, in contrast to chloro- and fluorosilanes whose reactions do not proceed usually [2]. However, iodo- and bromosilanes usually have a strong tendency to undergo hydrolytic cleavage of the Si-halogen bond with atmospheric moisture, compared to chloro- and fluorosilanes, and they must be handled with special care. Previously, we have reported that 1:1 mixtures of hydrosilanes and MeI or allylBr behave as synthetic equivalents of the corresponding iodo- or bromosilanes, respectively, in the presence of a catalytic amount of PdCl₂ [3–7].

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Polysiloxanes are useful materials because of their functionality, such as high thermal stability, electrical resistance, and hydrophobicity [8]. We recently reported PdCl₂-catalyzed reactions of poly(hydromethylsiloxane) with allyl bromide, and cyclic ethers and a lactone, which produced poly(bromoalkoxy- and bromoalkanoyloxy-methylsiloxane)s via the intermediary formation of Br-Si bonds (Scheme 1), as a new method to introduce functional groups to the polysiloxane chains [7]. In this paper, we report the PdCl₂-catalyzed formation and reactions of iodo- and bromosiloxane intermediates from α,ω -dihydropoly(dimethylsiloxane) (**1**) and cyclotetra(hydromethylsiloxane) (**2**) (Chart 1). The in-situ generated iodo- and bromosiloxane intermediates readily reacted with cyclic ethers and lactones, leading to haloalkoxy- and haloalkanoyloxy-terminated polysiloxanes and -substituted cyclosiloxanes. Although the introduction of functional groups to **1** and **2**, such as by hydrosilylation, has been well studied [8-10], the present method provides a new strategy for the introduction of various substituents to the terminal positions of linear polysiloxane and to the cyclosiloxane core.



Scheme 1. Bromoalkoxylation and bromoalkanoyloxylation of poly(hydromethylsiloxane) (reference 7).

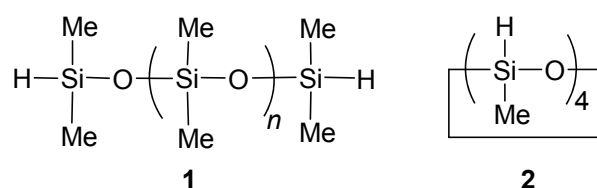


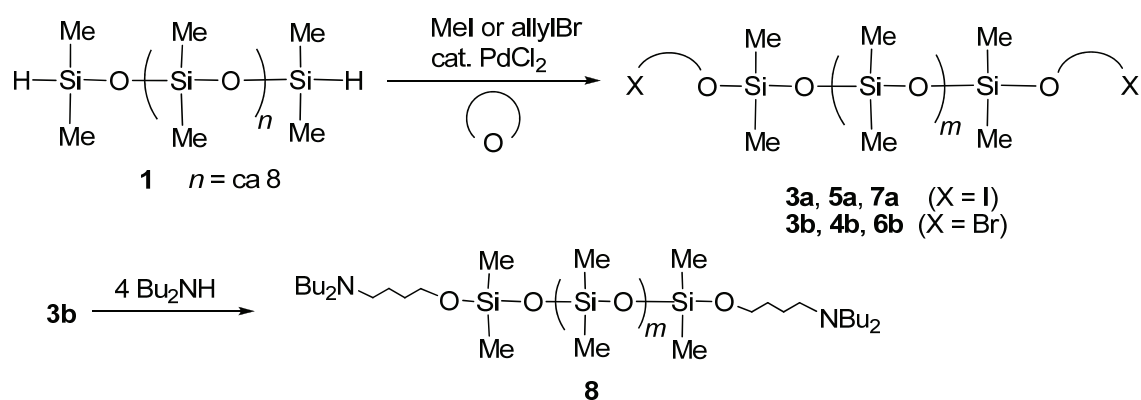
Chart 1. Structures of hydrosiloxanes **1** and **2**.

2. Results and discussion

2.1. Preparation of haloalkoxy-terminated poly(dimethylsiloxane)s

The reactions of **1** with cyclic ethers and MeI or allylBr in the presence of a catalytic amount of PdCl₂ (MeI(PdCl₂) or allylBr(PdCl₂)) were investigated and the results are summarized in Table 1 and Scheme 2. As a typical example, when a mixture of **1** with the average chain length of $n = 8$, THF (3.0 equiv for H-Si units), MeI (1.1 equiv), and a catalytic amount (1.6 %) of PdCl₂ was heated at 50 °C for 19 h, the Si-H absorption band of the FT-IR spectrum disappeared. The reaction progress could be monitored also by the ¹H NMR spectrometry. After the resulting inorganic salts and insoluble organic products were filtered, volatile substances including excess THF and MeI were evaporated under reduced pressure to give 4-iodobutoxy-terminated poly(dimethylsiloxane) (**3a**) in 76% yield. Polymer **3a** was a colorless viscous oil and soluble in common organic solvents. The structure of **3a** was verified by the ¹H and ¹³C NMR, and ESI-MS spectra. As shown in Figure 1, the Si-H bonds were wholly converted to 4-iodobutoxy units and no unidentified signals were detected in the NMR spectra. The integration ratio of the ¹H NMR spectrum indicated the average siloxane chain length of **3a** as being $m = 12.4$, which is longer than that of the starting **1**, indicating that redistribution reactions of the siloxane chains would be involved to an extent in this reaction. The ESI-MS analysis showed the signals that corresponded to (M+Na)⁺ with $m = 2-17$, of which the most intense signal appeared at that for $m = 5$. With a less amount of THF (1.5 equiv), the reaction again proceeded smoothly, but the product yield was a little lowered (71%). Similarly, dihydropolysiloxane **1** reacted with THF/allylBr(PdCl₂) under the same conditions to afford 4-bromobutoxy-terminated poly(dimethylsiloxane) (**3b**) with $m = 8.7$ (NMR) in 88% yield. The major signal in the ESI-MS was again at $m = 5$. These results are in marked contrast to the similar reactions of poly(hydromethylsiloxane) shown in Scheme 1, which gave substitution products only with allylBr(PdCl₂) [7]. No soluble products were obtained from its reactions with MeI(PdCl₂).

When **1** was treated with cyclohexene oxide/MeI(PdCl₂) under the conditions similar to those above, the expected iodocyclohexoxy-terminated poly(dimethylsiloxane) was not obtained cleanly, although no signals ascribed to the Si-H unit were detected in the FT-IR and ¹H NMR spectra of the reaction mixture. Filtration of the resulting mixture, followed by reprecipitation of the soluble organic products from ethanol/chloroform afforded a colorless viscous oil, whose ¹H NMR spectrum showed only unresolved multiple signals. In contrast to this, treatment of **1** with cyclohexene oxide/allylBr(PdCl₂) led to the formation of bromocyclohexoxy-terminated poly-(dimethylsiloxane) **4b** in 83% yield. Using toluene as the solvent did not significantly affect the results to give **4b** in slightly lower yield (80%). The reason for the different chemical behaviors of **1** depending on the halogen source is still unclear, but probably due to the higher reactivity of iodosilanes than bromosilanes. Similar dependence was observed for the reactions of poly(methylhydrosiloxane) (Scheme 1) [7].



Scheme 2. Preparation of haloalkoxy-, haloalkanoyloxy-, and aminoalkoxy-terminated poly(dimethylsiloxane)s.

Iodopentoxy-terminated poly(dimethylsiloxane) **5a** also was obtained by similar treatment of **1** with THP/MeI(PdCl₂) in 59% yield (Table 1). In this reaction, however, much longer polysiloxane ($m = 28.0$) was obtained, compared to **3a**, **3b**, and **4b**. Presumably, with less reactive THP, redistribution of the polysiloxane chain dominated

the formation of iodopentoxy units. This would be also responsible for the low yield. In fact, GC analysis of the reaction mixture indicated the formation of volatile products including cyclotetra- and cyclopenta(dimethylsiloxane) in approximately 6% and 5% yields, respectively. The yield was improved to 74% when a large excess of MeI (1.9 equiv for H-Si units) was loaded to accelerate the formation of iodosiloxane intermediates. A reaction of **1** and THP/allylBr(PdCl₂) gave a poly(dimethylsiloxane) featuring only a trace of bromopentoxy unit. The ¹H NMR spectrum of the non volatile products from this reaction indicated a very low unit ratio of bromopentoxy/Me₂SiO = 1/250.

Dihydropolysiloxane **1** reacted also with propylene oxide/allylBr(PdCl₂) to give bromopropoxy-terminated polysiloxane **6b** (*m* = 7.3) in 84% yield, as shown in Table 1. The ¹H NMR spectrum of polymer **6b** indicated that the polymer had the regioisomeric units of BrCH₂CH(Me)O- and BrC(Me)HCH₂O- in a ratio of 3:1, arising from preferential cleavage of the less hindered C-O bond. A similar reaction using MeI(PdCl₂) gave only a complex mixture, although the complete consumption of the Si-H bonds was observed.

As modification of the haloalkoxy-terminated polysiloxanes, we examined the conversion of the C-halogen bonds to C-N bonds (Scheme 2). Thus, treatment of **3b** with dibutylamine at 50 °C for 28 h gave polymer **8** (*m* = 9.8) cleanly in 77% yield from **1** as a pale yellow viscous oil (Figure 1b).

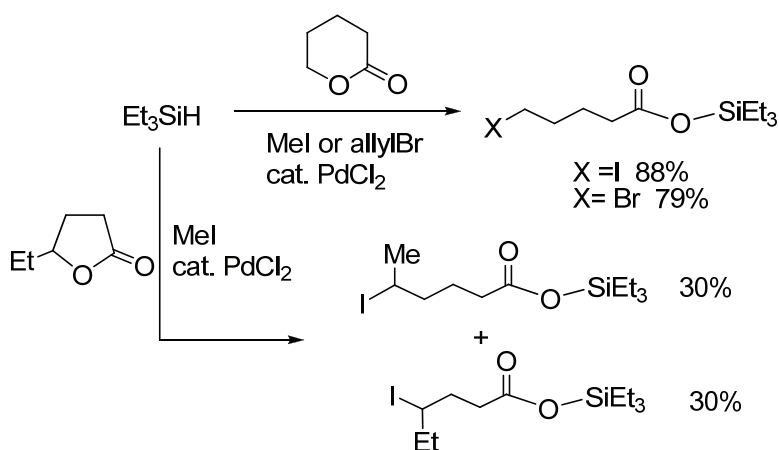
2.2. Preparation of haloalkanoyloxy-terminated poly(dimethylsiloxane)s

We next examined the introduction of haloalkanoyloxy-terminal units to poly(dimethylsiloxane). As shown in Table 1, when polymer **1** was treated with δ -valerolactone/MeI(PdCl₂) at 80 °C for 20 h, poly(dimethylsiloxane) bearing iodopentanoyloxy terminal groups (**7a**) was obtained in 37% yield. The low yield of the product was due to the formation of insoluble byproducts as a dark brown wax, which was removed by decantation from the reaction mixture, although we have not yet

obtained any direct experimental data to suggest the mechanism for the formation of the insoluble wax. The ^1H NMR spectrum of the soluble product indicated the formation of rearranged 4-iodopentanoyloxy terminal units with the average polysiloxane chain length of $m = 3.1$. No signals attributable to a simple 5-iodopentanoyloxy unit were observed in the spectrum. The yield was slightly improved to 48% by using an excess of MeI (2.1 equiv for Si-H). Similar rearrangement occurred in the reaction of Et_3SiH with γ -ethyl- γ -butyrolactone/MeI(PdCl_2), as shown in Scheme 3 [5]. However, with δ -valerolactone, no rearrangement occurred and the reaction gave triethylsilyl 5-iodo- and bromopentanoate in high yields. It has been demonstrated that the active catalysis in these reactions is not PdCl_2 , but $\text{Pd}(0)$ produced by reduction of PdCl_2 by hydrosilanes [11]. In the present system, $\text{Pd}(0)$ would possess weak but multi-site coordination with polysiloxane and provide different catalytic activity from that produced by the reduction with Et_3SiH [12]. On contrary, attempted reactions of **1** with δ -valerolactone/allylBr(PdCl_2) gave no soluble polysiloxane-containing products but afforded α,ω -bis(bromopentanyloxy)oligo(dimethylsiloxane) with the average chain length of $m = 0.6$, together with a large amount of insoluble substances. With γ -butyrolactone/MeI(PdCl_2), no soluble products were obtained, while using allylBr as the halogen source resulted in the introduction of only a trace of iodopentoxy unit (iodopentoxy/ $\text{Me}_2\text{SiO} = 1/51$), similar to the reaction with THP/allylBr(PdCl_2) described above. This is again in contrast to the reaction of poly(hydro-methylsiloxane) with γ -butyrolactone/allylBr(PdCl_2), which gave the expected poly(bromobutanoyloxymethylsiloxane) as shown in Scheme 1.

As described above, in the reactions of **1**, redistribution of the polysiloxane chains always competed with the haloalkoxylation and haloalkanoyloxylation, which would lead to the formation of volatile low molecular weight products to lower the yields. Furthermore, some other minor reactions were involved except for the reactions with THF. In fact, the NMR spectra of **3a** and **3b** showed only the signals that were expected from the halobutoxy-terminated poly(dimethylsiloxane) structures as

illustrated in Figure 1. However, the NMR spectra of **4b**, **5a**, **6b**, and **7a** showed minor unidentified signals, although the integration of these minor signals corresponded to usually less than 0.1H and 0.2H at most that was observed in the spectrum of **6b**. These minor reaction paths may be responsible for the formation of insoluble products.

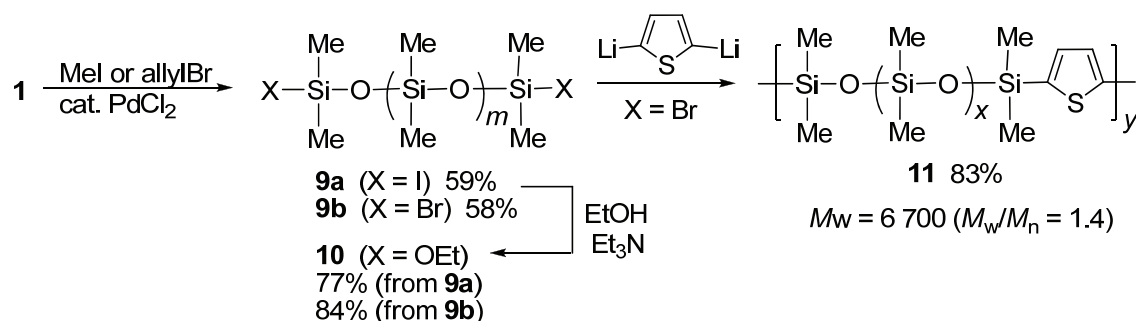


Scheme 3. Reactions of triethylsilane with lactones and MeI(PdCl_2) or allylBr(PdCl_2) (reference 5).

2.3. Characterization of α,ω -diiodo- and dibromopoly(dimethylsiloxane)s

To know about the formation of iodo- and bromopolysiloxane intermediates from **1**, we carried out the PdCl_2 -catalyzed reactions of **1** with MeI and allylBr in the absence of cyclic ethers and lactones. Treatment of **1** with MeI(PdCl_2) at 50 °C for 10 h led to disappearance of the Si-H absorption band in the FT-IR spectrum. The resulting precipitate was removed by filtration and washed with dry toluene. After removal of the solvent and volatile substances under reduce pressure, α,ω -diiodopoly-(dimethylsiloxane) **9a** (59%) was obtained as a colorless viscous oil, as shown in Scheme 4. Similar bromination of **1** with allylBr(PdCl_2) also proceeded smoothly to afford dibromide **9b** in 58% yield. Polymers **9a** and **9b** were characterized by the NMR spectrometry. However, attempted ESI-MS spectrometry revealed the signals ascribed to hydrolyzed poly(dimethylsiloxane)diols, of which the most intense ones appeared at $m = 5$ and 6 for those from **9a** and **9b**, respectively. Further information about the structures of **9a** and **9b** was obtained by quenching them with ethanol. Thus,

treatment of **9a** and **9b** with EtOH/Et₃N at room temperature afforded the corresponding α,ω -diethoxypoly(dimethylsiloxane) **10** in 77% yield from **9a** and 84% yield from **9b**. To demonstrate the synthetic utility of the present α,ω -dihalopoly(dimethylsiloxane)s, we prepared a polysiloxane-thiophene alternating polymer (**11**), as shown in Scheme 4. The molecular weight of the polymer was determined by GPC to be $M_w = 6,700$ ($M_w/M_n = 1.4$). The ¹H NMR spectrum indicated the polysiloxane chain length in **11** to be $x =$ ca 20. Anionic redistribution of polysiloxane chain would be involved in this polymerization.

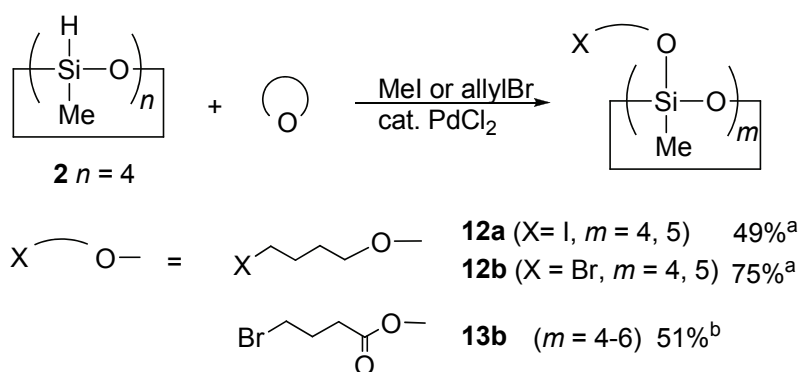


Scheme 4. Formation of α,ω -diiodo- and dibromopolysiloxanes from **1**.

2.4. Preparation of cyclo(haloalkoxy- and haloalkanoyloxysiloxane)s

We studied also haloalkoxylation and haloalkanoyloxylation of cyclo-tetra(hydromethylsiloxane) **2** with THF and γ -butyrolactone. Thus, the reactions with THF/MeI(PdCl₂) and THF/allylBr(PdCl₂) proceeded smoothly to give substitution products **12a** and **12b**, as depicted in Scheme 5. The ESI-MS of the products revealed the signals for cyclotetra- and -pentasiloxanes ($m = 4$ and 5) in a ratio of 2:1, indicating that redistribution of the siloxane framework had occurred in these reactions, as in the case of linear polysiloxane **1**. To know about the mechanism of the redistribution, we carried out a similar reaction of **2** with PdCl₂ only. However, no redistribution occurred, although black Pd(0) was found to be formed. Interaction of **2** with γ -butyrolactone gave product **13b** with $m = 4, 5,$ and 6 in a ratio of 2:1:1. On contrary, similar reactions with cyclohexene oxide, THP, propylene oxide, and δ -valerolactone

were unsuccessful and gave complex mixtures.



Scheme 5. Reactions of **2**. Conditions: Si-H of **2**/THF or δ -butyrolactone/MeI or allylBr = 1/2/1.2, at ^a80°C for 16 h and ^b50°C for 20 h. Yields are given based on **2** used.

3. Conclusions

In conclusion, we have demonstrated that mixtures of α,ω -dihydro-poly(dimethylsiloxane)s and cyclohydrosiloxanes with methyl iodide or allyl bromide behave as the synthetic equivalents of α,ω -diiodo- and dibromopoly(dimethylsiloxane)s and cyclo(iodo- and bromomethylsiloxane)s in the presence of the PdCl₂ catalyst. They reacted readily with cyclic ethers and lactones to form the corresponding haloalkoxy- and haloalkanoyloxy-substituted poly- and cyclosiloxane. The intermediary formation of α,ω -diiodo- and dibromopoly(dimethylsiloxane)s was confirmed by the NMR spectroscopy as well as by the quenching experiments with ethanol. These functionalized linear and cyclic polysiloxanes may be useful as, for example, macromonomers and coupling reagents, and monomers of ring-opening polymerization for functionalized linear siloxane high polymers, respectively. Indeed, we demonstrated the potential of α,ω -dibromopoly(dimethylsiloxane) as a macromonomer. Studies to explore further the utilities of these iodo- and bromopolysiloxanes are in progress.

4. Experimental

3.1. General procedures

All reactions were carried out in dry argon. Toluene used as the reaction solvent was distilled from sodium, and stored over activated molecular sieves until use. Hydrosiloxanes **1** and **2** were purchased from Gelest Inc and used as obtained. Cyclic ethers and lactones were dried over activated molecular sieves and used for the reactions without further purification. NMR spectra were recorded on a Varian System500 spectrometer. FT-IR spectra were measured with a Shimadzu Affinity-1 spectrometer. ESI-MS spectra were recorded on an Applied Biosystems 4000Q-TRAP spectrometer. UV spectra were measured on a Hitachi U-2910 spectrophotometer. GPC was performed with subsequently connected Shodex columns KF804 and KF806 eluting with THF using a UV detector (240 nm), and the molecular weight was calculated relative to polystyrene standards.

3.2. Preparation of haloalkoxy- and haloalkanoyloxy-terminated polysiloxanes and -substituted cyclosiloxanes

A mixture of **1** (1.03 g, 2.29 mmol, Si-H 4.58 mmol), MeI (0.72 g, 5.1 mmol), THF (0.99 g, 13.7 mmol), and PdCl₂ (0.0125 g, 0.0710 mmol) was stirred at 50 °C for 19 h, after the resulting black precipitates were filtered, the volatile substances including excess THF and MeI were evaporated under reduced process to give **3a** (2.95 g, 3.5 mmol; 76% yield). ¹H NMR (δ in CDCl₃) 0.09 (br s, inner SiMe), 0.14 (br s, terminal SiMe), 1.64 (qui, 4H, OCH₂CH₂, *J* = 7.2 Hz), 1.91 (qui, 4H, CH₂CH₂I, *J* = 7.3 Hz), 3.22 (t, 4H, CH₂I, *J* = 7.0 Hz), 3.70 (t, 4H, CH₂O, *J* = 6.0 Hz); ¹³C NMR (δ in CDCl₃) -1.1 (terminal SiMe), 0.95 (inner SiMe), 6.8 (CH₂I), 30.1 (CH₂CH₂I), 33.3 (OCH₂CH₂), 60.9 (CH₂O). Anal. Calc. C_{36.8}H_{102.4}I₂O_{15.4}Si_{14.4} (*m* = 12.4): C, 30.49; H, 7.12. Found: C, 29.92; H, 6.68%. The ¹H NMR signals are broad and the coupling constants were not exactly determined, probably due to the end-group effects, the diastereomeric environment around the Si-O-Si units, and/or hindered rotation in the polymeric system. Similar NMR feature was observed also for other products. Other haloalkoxylation and

haloalkanoyloxylation reactions of **1** and **2** were carried out as above. Data for **3b**: ^1H NMR (δ in CDCl_3) 0.09 (br s, inner SiMe), 0.12 (br s, terminal SiMe), 1.70 (qui, 4H, OCH_2CH_2 , $J = 7.3$ Hz), 1.95 (qui, 4H, $\text{CH}_2\text{CH}_2\text{Br}$, $J = 7.1$ Hz), 3.46 (t, 4H, CH_2Br , $J = 7.0$ Hz), 3.70 (t, 4H, CH_2O , $J = 6.0$ Hz); ^{13}C NMR (δ in CDCl_3) -1.1 (terminal SiMe), 1.0 (inner SiMe), 29.4 ($\text{CH}_2\text{CH}_2\text{Br}$), 31.0 (OCH_2CH_2), 33.8 (CH_2Br), 61.1 (CH_2O). Anal. Calc. $\text{C}_{29.4}\text{H}_{80.2}\text{Br}_2\text{O}_{11.7}\text{Si}_{10.7}$ ($m = 8.7$): C, 32.65; H, 7.47. Found: C, 33.23; H, 7.03%. Data for **4b**: ^1H NMR (δ in CDCl_3) 0.07-0.09 (m, inner SiMe), 0.16 (br s, terminal SiMe), 1.19-1.41 (br m, 6H, Cy), 1.65-1.83 (br m, 6H, Cy), 2.05-2.08 (br m, 2H, Cy), 2.31-2.34 (br m, 2H, Cy), 3.77-3.87 (br m, 2H, CHBr), 3.88-3.92 (br m, 2H, OCH); ^{13}C NMR (δ in CDCl_3) -0.5, -0.6 (terminal SiMe), 1.1 (inner SiMe), 23.3, 25.4, 34.4, 35.2, 58.0, 74.6 (Cy). Data for **5a**: ^1H NMR (δ in CDCl_3) 0.07-0.10 (m SiMe), 1.43-1.48 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 1.56 (qui, 4H, OCH_2CH_2 , $J = 7.0$ Hz), 1.85 (qui, 4H, $\text{CH}_2\text{CH}_2\text{I}$, $J = 7.1$ Hz), 3.19 (t, 4H, CH_2I , $J = 7.3$ Hz), 3.66 (t, 4H, CH_2O , $J = 6.5$ Hz); ^{13}C NMR (δ in CDCl_3) -1.0 (terminal SiMe), 1.0 (inner SiMe), 6.8 (CH_2I), 26.9 ($\text{OCH}_2\text{CH}_2\text{CH}_2$), 31.4 (OCH_2CH_2), 33.4 ($\text{CH}_2\text{CH}_2\text{I}$), 61.8 (CH_2O). Data for **6b**: ^1H NMR (δ in CDCl_3) 0.07-0.09 (m, inner SiMe), 0.13, 0.14 (br s, terminal SiMe), 1.29 (d, 4.5H, OCHCH_3 , $J = 6.5$ Hz), 1.68 (d, 1.5H, CHCH_3Br , $J = 6.5$ Hz), 3.27-3.29 (m, 3H, CH_2Br), 3.34-3.35 (m, 1H, OCH_2), 4.11-4.13 (m, 2H, CHBr and OCH); ^{13}C NMR (δ in CDCl_3) -0.5, -0.4 (terminal SiMe), 1.6 (inner SiMe), 22.0 (OCHCH_3), 22.3 (CHCH_3Br), 38.9 (CH_2Br), 49.1 (CHBr), 67.9 (OCH_2), 68.0 (OCH). Data for **7a**: IR 1773 cm^{-1} ($\text{C}=\text{O}$), 1157 cm^{-1} (Si-O); ^1H NMR (δ in CDCl_3) -0.06 (br s, inner SiMe), 0.17 (br s, terminal SiMe), 1.42 (d, 6H, CH_3ICH , $J = 6.5$ Hz), 1.79-1.87 (m, 2H, ICHCH_2), 2.32-2.39 (m, 2H, ICHCH_2), 2.52-2.58 (m, 4H, $\text{O}=\text{CCH}_2$), 4.62-4.69 (m, 2H, ICHCH_3); ^{13}C NMR (δ in CDCl_3) 0.4-0.8 (SiMe), 20.8, 28.6, 28.9, 29.5, 173.8. Data for **12a**: ^1H NMR (δ in CDCl_3) 0.13-0.22 (br s, 12H, SiMe), 1.62-1.67 (br s, 8H, $\text{ICH}_2\text{CH}_2\text{CH}_2$), 1.91-1.92 ((br s, 8H, ICH_2CH_2), 3.22 (br s, 8H, ICH_2), 3.72-3.79 (br s, 8H, OCH_2); ^{13}C NMR (δ in CDCl_3) -4.71 (SiMe), 29.3 ($\text{ICH}_2\text{CH}_2\text{CH}_2$), 30.8 (ICH_2CH_2), 33.6 (ICH_2), 61.4 (OCH_2). Anal. Calc. $\text{C}_{20}\text{H}_{44}\text{I}_4\text{O}_8\text{Si}_4$: C, 23.26; H, 4.30. Found: C, 23.36; H, 4.43%.

Data for **12b**: ^1H NMR (δ in CDCl_3) 0.13-0.19 (m, 12H, SiMe), 1.68-1.72 (br s, 8H, $\text{BrCH}_2\text{CH}_2\text{CH}_2$), 1.92-1.97 (br s, 8H, BrCH_2CH_2), 3.43-3.46 (br s, 8H, BrCH_2), 3.73-3.79 (m, 8H, OCH_2); ^{13}C NMR (δ in CDCl_3) -4.73 (SiMe), 29.3 ($\text{BrCH}_2\text{CH}_2\text{CH}_2$), 30.8 (BrCH_2CH_2), 33.6 (BrCH_2), 61.3 (OCH_2). Data for **13b**: IR 1726 cm^{-1} ($\text{C}=\text{O}$), 1082 cm^{-1} (Si-O); ^1H NMR (δ in CDCl_3) -0.05 (SiMe), 0.29 (br s, SiMe), 2.12-2.21 (m, 8H, BrCH_2CH_2), 2.48-2.51 (br m, 8H, $\text{O}=\text{CCH}_2$), 3.48 (t, 8H, BrCH_2 , $J = 4.5\text{ Hz}$). Anal. Calc. $\text{C}_{20}\text{H}_{36}\text{Br}_4\text{O}_{12}\text{Si}_4$: C, 26.68; H, 4.03. Found: C, 26.45; H, 4.44%.

3.3. Preparation of (dibutylamino)butoxy-terminated poly(dimethylsiloxane)

A mixture of **1** (1.0 g, Si-H 4.4 mmol unit), THF (0.90 g, 13 mmol), allylBr (0.610 g, 5.0 mmol), and PdCl_2 (0.013 g, 0.071 mmol) was stirred at 50°C for 17 h and the resulting mixture was filtered and the excess THF and allylBr were evaporated. To this was added Bu_2NH (2.0 g, 16 mmol) in 10 mL of toluene at room temperature and the mixture was stirred for 20 h. After filtration, the solvent was evaporated and the residue was analyzed as being **8** (1.5 g, 77% yield): ^1H NMR (δ in CDCl_3) 0.07 (br s, inner SiMe), 0.10 (br s, terminal SiMe), 0.90 (t, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J = 7.5\text{ Hz}$), 1.27-1.35 ((br m, 16H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42-1.53 (br m, 8H, $\text{OCH}_2\text{CH}_2\text{CH}_2$), 2.44-2.63 (br m, 12H, NCH_2), 3.66 (t, 4H, OCH_2 , $J = 6.5\text{ Hz}$); ^{13}C NMR (δ in CDCl_3) -1.1 (terminal SiMe), 1.0 (inner SiMe), 14.0, 20.7, 22.7, 28.5, 30.4, 53.6, 53.7, 61.9.

3.4. Preparation of α,ω -dihalo- and diethoxypoly(dimethylsiloxane)s

A mixture of **1** (1.00 g, Si-H 4.44 mmol unit), MeI (1.42 g, 10.0 mmol), and PdCl_2 (0.023 g, 0.13 mmol) was stirred at 50°C for 10 h and the resulting mixture was filtered in an argon atmosphere and washed with dry toluene. Evaporation of the solvents and other volatile species from the filtrate gave **9a** (0.702 g, 59% yield): ^1H NMR (δ in CDCl_3) 0.09 (br m, inner SiMe), 0.81 (s, OSiMeI); ^{13}C NMR (δ in CDCl_3) 0.93 (inner, SiMe), 9.2 (OSiMeI); ^{29}Si NMR (δ in CDCl_3) -21.9, 3.6. Polymer **9b** was obtained as above. Data for **9b**: ^1H NMR (δ in CDCl_3) 0.08 (br m, inner SiMe), 0.60 (s, OSiMeBr);

^{13}C NMR (δ in CDCl_3) 0.95 (inner, SiMe), 6.0 (OSiMeBr); ^{29}Si NMR (δ in CDCl_3) -21.9, 0.32. For ethanolysis, polymers **9a** and **9b** were poured to excess ethanol in the presence of triethylamine. After filtration of the ammonium salts, evaporation gave **10**: ^1H NMR (δ in CDCl_3) 0.08 (br m, SiMe), 1.21 (t, 6H, $\text{SiOCH}_2\text{CH}_3$, $J = 7.0$ Hz), 3.74 (q, 4H, $\text{SiOCH}_2\text{CH}_3$, $J = 7.0$ Hz). ^{13}C NMR (δ in CDCl_3) -1.0 (s, inner SiMe), 0.96 (s, terminal SiMe), 18.4 ($\text{SiOCH}_2\text{CH}_3$), 57.8 ($\text{SiOCH}_2\text{CH}_3$).

3.5. Preparation of poly[(siloxanylene)(2,5-thienylene)]

A mixture of 0.121 g (5 mmol) of 2,5-dibromothiophene and 6.21 mL (10.1 mmol) of a 1.63 M *n*-butyllithium-hexane solution was stirred in 10 mL of ether at -80 °C over 30min. The mixture was stirred at -80 °C for 2.5 h, and then 3.10 g (ca. 5 mmol) of **10b** was added to the mixture at -80 °C over 30min. The mixture was warmed to room temperature, stirred for 12h, and then hydrolyzed with water, the organic layer was separated and the aqueous layer was extracted with toluene. The organic layer and the extracts were dried over anhydrous magnesium sulfate. Evaporation of the solvent and volatile by-products under reduced pressure at room temperature to give 2.49 g (83% yield) of **11** as a colorless viscous oil: UV abs: $\lambda_{\text{max}} = 261$ nm (in THF), $\epsilon = 8700$. M_w (M_w / M_n): 6700 (1.4). ^1H NMR (δ in CDCl_3) 0.01 (br s, polysiloxane), 0.29 (br s, thienylSiMe), 7.16 (s, 2H, thiophene); ^{13}C NMR (δ in CDCl_3) 0.9, 1.8 (polysiloxane), 135.0, 135.5, 145.1 (thiophene); ^{29}Si NMR (δ in CDCl_3) -21.9, -20.4, -7.0.

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Table 1. PdCl₂-catalyzed preparation of haloalkoxy- and haloalkanoyloxy-terminated poly(dimethylsiloxane)s from **1**.

Cyclic compd (eq) ^a	RX (eq) ^a	Temp/°C (Time/h)	Product (X)	<i>m</i> ^b		Yield (%) ^c
	(3.0)	MeI (1.1)	3a (I)	12.4		76
	(1.5)	MeI (1.1)		50 (20)		71
	(3.0)	allylBr (1.1)	50 (20)	3b (Br)	8.7	88
	(3.0)	allylBr (1.1)	4b	8.9		83
	(2.8) ^d	allylBr (1.1)		50 (25)		80
	(1.9)	MeI (1.1)	5a	28.0		59
		MeI (1.9)				80 (22)
	(2.9)	allylBr (1.1)	6b	7.3		84
	(2.9)	MeI (1.2)	7a	3.1		37
		(2.1)				80 (20)

^a Relative to Si-H unit of **1**.

^b Determined by ¹H NMR analysis.

^c Isolated yield based on the polysiloxane used.

^d 15ml of toluene used as solvent.

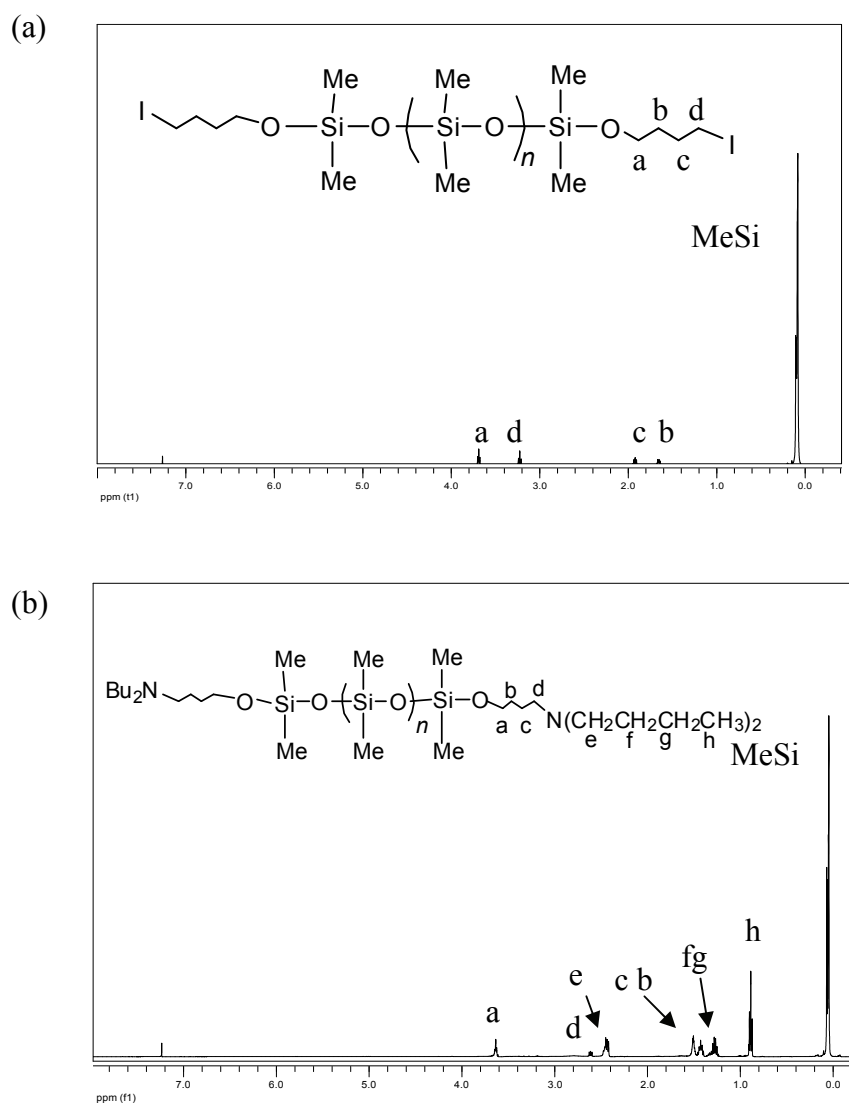


Figure 1. ^1H NMR spectra of polymers (a) **3a** and (b) **8** in CDCl_3 .