Palladium-catalyzed synthesis of poly(bromoalkoxy- and bromoalkanoyloxy-methylsiloxane)s from poly(hydromethylsiloxane)s

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Abstract
Palladium-catalyzed synthesis of poly(bromoalkoxymethyl- and bromoalkanoyloxy-methylsiloxane)s from poly(hydromethylsiloxane)s was studied. Treatment of poly(hydromethylsiloxane)s with mixtures of allyl bromide and cyclic ethers in the presence of a catalytic amount of PdCl$_2$ gave the corresponding poly[(bromoalkoxy)methylsiloxane]s in good yield. A similar reaction with γ-butyrolactone produced poly[(bromobutanoyloxy)methylsiloxane], although the polymer was highly moisture-sensitive and could not be separated from the reaction mixture. Transformation of the bromoalkoxy unit in the resulting siloxane polymer into an aminoalkoxy group was also examined.

Keywords: Polysiloxane; Palladium catalyst; Cyclic ether; Lactone; Bromosilane; Ring opening

1. Introduction
Bromosilanes are important reagents in organic synthetic chemistry [1]. The high Lewis acidity of bromosilanes allows them to interact with ether, ester, and acetal to cleave C-O bonds. For example, bromosilanes readily react with cyclic ethers and lactones to give bromoalkoxy- and bromoalkanoyloxy silanes as the ring-opened bromosilated products. However, unless they are kinetically stabilized by a bulky protecting group, bromosilanes are usually highly moisture-sensitive and therefore,
must be handled with special care, in contrast to chloro- and fluorosilanes. Recently, we have demonstrated that 1 : 1 mixtures of hydrosilanes and allyl bromide behave as synthetic equivalents of the corresponding bromosilanes in the presence of a catalytic amount of PdCl₂ [2-4], as illustrated in Scheme 1.

\[
\text{Et}_3\text{SiH} + \text{allyl bromide} \xrightarrow{\text{cat. PdCl}_2} \text{Br} \text{-} \begin{array}{c}
\text{OSiEt}_3
\end{array}
\]

Scheme 1.

In this paper, we report the PdCl₂-catalyzed synthesis of poly(bromoalkoxy- and bromoalkanoyloxymethylsiloxane)s from poly(hydromethylsiloxane)s, presumably via the formation of a poly(bromomethylsiloxane) intermediate. The introduction of functionalities into polyhydrosiloxanes, such as by hydrosilation, has been well explored [5,6]. The present method provides a novel strategy for the introduction of various alkoxy and alkanoyloxy substituents into poly(siloxane)s.

2. Results and discussion

2.1. Model reactions

First, we examined model reactions using dihydrotetramethyldisiloxane (1) as the reactant. When compound 1 was treated with a mixture of propylene oxide (3 equiv) and allyl bromide (2 equiv) in the presence of PdCl₂ (1 mol%) at room temperature, bis(bromopropyl)tetramethyldisiloxane (2a) was obtained in 58% yield as a mixture of regioisomers (Scheme 2). In this reaction, cleavage of the less hindered C-O bond occurred preferentially, forming BrCH₂CH(Me)O- and BrC(Me)HCH₂O- units in a ratio of 7:3. The rather low yield of this reaction may be due to hydrolysis of the product during purification by column chromatography. Indeed, GC-MS analysis of the reaction mixture indicated the formation of 2a almost quantitatively. A similar reaction of cyclohexene oxide also proceeded smoothly to give bis(bromocyclo-
hexyloxy)tetrakis(2b) in 55% isolated yield. In contrast to the reactions of these oxiranes, ring opening of THF competed with the redistribution reactions of the disiloxane chain under the same conditions, giving a mixture of bis(bromobutoxy)siloxane oligomers (2c), as shown in Scheme 3.

Scheme 2.

Scheme 3.

2.2. Reactions of poly(methylsiloxane)

We next examined the bromoalkoxylation of poly(hydromethylsiloxane) (3a) (Scheme 4). Polymer 3a was treated with mixtures of cyclic ethers, allyl bromide, and PdCl₂ catalyst at room temperature and the reaction was monitored by ¹H NMR and IR measurements. The reaction proceeded smoothly and Si-H bonds were wholly converted into the corresponding bromoalkoxy units, as illustrated in Figure 1 (a) and (b). No signals corresponding to Si-H units were detected in the ¹H NMR spectra of the reaction mixtures. Hydrolysis of the resulting mixture with aqueous NaHCO₃, followed by reprecipitation of the organic products from methanol-chloroform afforded corresponding poly[(bromoalkoxy)methylsiloxane(s) (4a-c) in moderate yields (Table 1).
The $^1$H and $^{13}$C NMR spectra of polymer 4a indicated that the polymer had regioisomeric units of BrCH$_2$CH(Me)O- and BrC(Me)HCH$_2$O- in a ratio of 7:3. In this reaction, the less hindered C-O bond was cleaved preferentially, in accordance with the model reaction of 1.

![Chemical structure](image)

Scheme 4.

<table>
<thead>
<tr>
<th>Table 1: Reactions of hydrosiloxane polymers with ethers</th>
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<tbody>
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<td>polym (Mn)</td>
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<tr>
<td>----------------</td>
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<tr>
<td>3a (1800)</td>
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<td>3b (2000)</td>
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$^a$ After reprecipitation. $^b$ Determined by GPC, relative to polystyrene standards.

Poly(dimethylsiloxane-co-hydromethylsiloxane) (3b) also underwent substitution reaction with propylene oxide smoothly to give polymer 4d. However, in this reaction, heating the reaction mixture at 50°C was necessary to promote the conversion. The
rather low yield of 4d may be due to its high solubility. A large amount of a low-molecular-weight fraction was presumably removed by reprecipitation as the methanol-soluble fraction. The $^1$H NMR spectrum of the reaction mixture again indicated the complete transformation of Si-H bonds into Si-bromopropoxy units.

The interaction of 3a with $\gamma$-butyrolactone under the same conditions led to the formation of partly bromobutanoyloxy-substituted polymer (4e), as shown in Scheme 5. The $^1$H NMR spectrum of the reaction mixture indicated that no Si-H groups remained in the mixture and only Si-bromobutanoyloxy units were formed in approximately 68% yield. Presumably, the rest of the Si-H units were converted into Si-Br units. This seems to be the reason for the high moisture sensitivity of 4e. The lower Lewis basicity of lactone ring oxygen than cyclic ether would be responsible for the lower reactivity of lactone in the present reaction system. Polymer 4e could not be separated from the reaction mixture. All attempts at purification resulted in the formation of insoluble substances, probably by hydrolysis of Si-Br bonds forming cross-linked siloxane units.

![Scheme 5](image)

As can be seen in Table 1, the molecular weights of the polymers, determined by GPC, were much higher than those expected on the basis of the molecular weights of the starting polysiloxanes. It seems likely that some hydrolysis of Si-bromoalkoxy units occurred during purification, forming cross-linked siloxane units. To separate these polymers from the reaction mixtures, washing the mixtures with aqueous NaHCO$_3$
could not be avoided. Without this process, the polymers underwent further hydrolysis with atmospheric moisture presumably catalyzed by a trace of acid, leading to the formation of large amounts of insoluble substances. Polymer 4c obtained by the reaction with THF was highly moisture-sensitive. In fact, polymer 4c became insoluble unless reprecipitation was carried out in a dry atmosphere. Polymer 4e was even more moisture-sensitive and therefore, its purification by reprecipitation could not be performed as mentioned above. Combustion elemental analysis of polymer 4c indicated lower carbon content than the theoretical value, probably due to partial hydrolysis of bromobutoxy-Si bonds. On the other hand, the carbon contents of 4a and 4b were determined to be a little higher than the theoretical ones. Trace amounts of hydrosilated 2-propoxy and cyclohexyloxy units may be involved. Although we do not have any direct evidences for the formation of hydrosilated units, similar hydrosilation turned out to compete bromosilation as a minor path, in the PdCl2-catalysed reactions of Et3SiH/allyl bromide with lactones [4].

In conclusion, we demonstrated that mixtures of poly(hydrosiloxane)s and allyl bromide behave as synthetic equivalents of poly(bromosiloxane)s in the presence of a catalytic amount of PdCl2, which react with cyclic ether and lactone. The resulting poly(bromoalkoxysiloxane)s would be useful as precursors of variously substituted polysiloxanes. For example, bromoalkoxypolysiloxane (4c) reacted with dibutylamine to produce polymer 5 having aminoalkoxy units (Scheme 6 and Figure 1 (c)). In this reaction, only partially substituted polymers were obtained even with a large excess of the amine. Presumably, the dibutylamine groups sterically covered the reactive bromide centers in the polymer rods.
3. Experimental section

3.1. General

All reactions were carried out in dry nitrogen. THF and toluene used as reaction solvents were distilled from sodium/benzophenone and sodium, respectively, and stored over activated molecular sieves until use. Hydrosiloxanes 1, 3a, and 3b, ethers, and γ-butyrolactone were dried over activated molecular sieves and were used for the reactions without further purification. NMR spectra were recorded on a JEOL model LA400 spectrometer. GPC was performed with subsequently connected Shodex columns KF806 and KF804 using THF as the eluent, and recorded with a GL-Science RI detector. VPO was carried out on a Gonotec model OSMOMAT070 system using chloroform as solvent.

3.2. Model reactions

A mixture of 0.674 g (5.02 mmol) of 1, 0.869 g (15.0 mmol) of propylene oxide, 1.22 g (10.1 mmol) of allyl bromide, and 9.1 mg (0.0513 mmol) of PdCl₂ was stirred at room temperature for 12 h. GLC analysis of the mixture indicated that almost all of the starting disiloxane was consumed at this stage. The mixture was filtered and the filtrate was washed with aqueous NaHCO₃ to remove trace acids. After being dried over anhydrous magnesium sulfate, the solvent was evaporated and the residue was subjected to recycling preparative GPC to give compound 2a as a mixture of regioisomers in 58% yield. Attempted isolation of the isomers failed and compound 2a
was analyzed as a mixture. The incorporation ratio of the regioisomers was determined to be BrCH₂CH(Me)O⁻ : BrC(Me)HCH₂O⁻ = 7:3. Data for 2a: MS m/z 335 (M⁺-OCH₂CHCH₃). ¹H NMR (δ in CDCl₃) 0.13, 0.136, 0.141 (s, 12H, CH₃Si), 1.29 (d, 2.1H, OCHCH₃, J = 6.3 Hz), 1.67 (d, 0.9H, CH(CH₃)Br, J = 6.8 Hz), 3.27 (dd, 0.7H, CH₂Br, J = 10.0, 5.6 Hz), 3.34 (dd, 0.7H, CH₂Br, J = 10.3, 5.6 Hz), 3.70 (dd, 0.3H, OCH₂, J = 10.8, 7.3 Hz), 4.02-4.10 (m, 0.3H, CHBr), 4.07-4.15 (m, 0.7H, OCH). ¹³C NMR (δ in CDCl₃) -1.08, -1.06, -0.54, -0.51, -0.46, -0.43 (CH₃Si), 22.1 (OCHCH₂), 22.3 (BrCH(CH₃)), 38.9 (BrCH₂), 49.1 (BrCH), 68.0 (OCH₂), 68.1 (OCH). Anal. Calcd for C₁₀H₂₄Br₂O₃Si₂: C, 29.42; H, 5.93. Found: C, 29.24; H, 5.92.

Compound 2b was obtained in a similar fashion to that above. Data for 2b: MS m/z 375 (M⁺-CH₃). ¹H NMR (δ in CDCl₃) 0.14, 0.17 (s, 12H, CH₃Si), 1.23-1.44 (m, 3H, Cy), 1.63-1.84 (m, 3H, Cy), 2.04-2.07 (m, 1H, Cy), 2.30-2.35 (m, 1H, Cy), 3.80 (ddd, 1H, CHBr, J = 12.4, 8.4, 4.0 Hz), 3.89 (ddd, 1H, OCH, J = 10.4, 8.2, 4.2 Hz). ¹³C NMR (δ in CDCl₃) -0.4, -0.3, (CH₃Si), 23.3, 25.5, 34.5, 35.3 (Cy), 58.1 (CHBr), 74.7 (HCO). Anal. Calcd for C₁₆H₃₂Br₂O₃Si₂: C, 39.35; H, 6.60. Found: C, 39.58; H, 6.71.

Compound 2c was highly moisture-sensitive and could not be purified by chromatography. Subjecting 2c to chromatography always resulted in the formation of polysiloxane with loss of bromobutoxy groups. Therefore, 2c was analyzed after usual workup of the reaction mixture as above, including filtration of the reaction mixture, hydrolysis with aqueous NaHCO₃, drying over anhydrous magnesium sulfate, and removal of volatile substances under reduced pressure in this order. GC-MS analysis of 2c indicated the existence of oligosiloxanes Br(CH₂)ₙO(SiMe₂O)ₙ(CH₂)ₙBr (n = 1-9). The average number of n was determined to be approximately 1.6 from the integration ratio of ¹H NMR signals of 2c. Data for 2c: ¹H NMR (δ in CDCl₃) 0.075, 0.082, 0.10, 0.108, 0.111, 0.13, 0.15, 0.155, 0.161 (m, 9.6H, Si-Me), 1.72 (m, 4H, OCH₂CH₂), 1.96 (m, 4H, CH₂CH₂Br), 3.45 (t, 4H, CH₂Br, J = 14.0 Hz), 3.70 (t, 4H, OCH₂, J = 13.0 Hz).
3.3. Preparation of bromoalkoxy polymers from 3a

A mixture of 0.290 g (4.83 mmol units) of polymer 3a, 0.843 g (14.5 mmol) of propylene oxide, 0.591 g (4.89 mmol) of allyl bromide, and 12.5 mg (0.0705 mmol) of PdCl$_2$ was stirred at 50°C for 12 h. The mixture was filtered and the filtrate was washed with aqueous NaHCO$_3$. After drying over anhydrous magnesium sulfate, the solvent and volatile substances were removed under reduced pressure. The residue was reprecipitated from ethanol/chloroform to give 0.277 g (44% yield) of polymer 4a as a colorless viscous oil: GPC Mw = 19,900, Mw/Mn = 2.8. $^1$H NMR ($\delta$ in CDCl$_3$) 0.13 (br s, terminal SiMe$_3$), 0.21 (br s, 3H, SiCH$_3$), 1.32 (d, 2.1H, OCH(CH$_3$), $J = 6.1$ Hz), 1.67 (d, 0.9H, CH(CH$_3$)Br, $J = 6.6$ Hz), 3.30-3.38 (br m, 1.4H, CH$_2$Br), 3.76-3.80 (br m, 0.3H, OCH$_2$), 3.92-3.96 (br m, 0.3H, OCH$_2$), 4.07-4.09 (br m, 0.3H, CHBr), 4.18-4.25 (br m, 0.7H, OCH). $^{13}$C NMR ($\delta$ in CDCl$_3$) -5.7, -5.0 (CH$_3$Si), 20.5 (OCH(CH$_3$)), 20.8 (CH(CH$_3$)Br), 37.2 (CH$_2$Br), 47.1 (CHBr), 66.5 (OCH$_2$), 66.8 (OCH). Anal. Calcd for Me$_3$SiO(C$_4$H$_9$BrO$_2$Si)$_{35.2}$SiMe$_3$: C, 24.83; H, 4.75. Found: C, 26.82; H, 5.11. The theoretical values of elemental analysis were calculated based on the degree of polymerization estimated by GPC molecular weight (Mn).

Other polymer reactions were carried out in a similar fashion to that above. Data for 4b: GPC Mw = 11,400, Mw/Mn = 2.4. $^1$H NMR ($\delta$ in CDCl$_3$) 0.13 (br s, terminal SiMe$_3$), 0.24 (br s, 3H, SiCH$_3$), 1.15-1.50 (br m, 3H, Cy), 1.50-2.00 (br m, 3H, Cy), 2.05-2.25 (br m, 1H, Cy), 2.25-2.50 (br m, 1H, Cy), 2.50-2.75 (br m, 1H, Cy), 3.75-4.25 (br m, 2H OCH, CHBr). $^{13}$C NMR ($\delta$ in CDCl$_3$) -3.0 (Si-CH$_3$), 22.9, 24.9, 33.6, 34.5, 57.3, 74.2 (Cy). Anal. Calcd for Me$_3$SiO(C$_7$H$_{13}$BrO$_2$Si)$_{19.6}$SiMe$_3$: C, 35.86; H, 5.74. Found: C, 36.46; H, 5.45. Data for 4c: GPC Mw = 25,600, Mw/Mn = 2.2. $^1$H NMR ($\delta$ in CDCl$_3$) 0.11 (br s, terminal SiMe$_3$), 0.13 (br s, 3H, SiCH$_3$), 1.60-1.80 (br m, 2H, OCH$_2$CH$_2$), 1.92 (br qui, 2H, CH$_2$CH$_2$Br, $J = 7$ Hz), 3.42 (t, 2H, CH$_2$Br, $J = 6.8$ Hz), 3.65-3.85 (br m, 2H, OCH$_2$). $^{13}$C NMR ($\delta$ in CDCl$_3$) -4.3 (CH$_3$Si), 29.3 (OCH$_2$CH$_2$), 30.8 (CH$_2$CH$_2$Br), 33.6 (CH$_2$Br), 61.2 (OCH$_2$). Anal. Calcd for Me$_3$SiO(C$_5$H$_{11}$BrO$_2$Si)$_{54.2}$SiMe$_3$: C, 28.70; H, 5.35.
3.4. Preparation of bromopropoxy copolymer 4d

A mixture of 0.833 g (11.9 mmol Si-H units) of 3b, 0.626 g (10.8 mmol) of propylene oxide, 0.460 g (3.80 mmol) of allyl bromide, and 6.1 mg (0.034 mmol) of PdCl₂ was stirred at 50°C for 17 h. After similar workup to that for 4a, reprecipitation of the organic products from methanol/chloroform gave 0.202 g (16% yield) of 4d as a colorless viscous oil: GPC $M_w = 13,800$, $M_w/M_n = 1.6$. $^1$H NMR ($\delta$ in CDCl₃) 0.03, 0.06, 0.068, 0.09 (br s, 3H, SiCH₃), 1.29 (br d, 2.1H, OCH(CH₃), $J = 6.0$ Hz), 1.67 (br d, 0.9H, CH(CH₂)Br, $J = 6.5$ Hz), 3.15-3.45 (br m, 1.4H, CH₂Br), 3.60-3.85 (br m, 0.3H, OCH₂), 3.85-4.00 (br m, 0.3H, OCH₂), 4.00-4.10 (br m, 0.3H, CHBr), 4.10-4.30 (br m, 0.7H, OCH). $^{13}$C NMR ($\delta$ in CDCl₃), -4.2, -3.5, -3.3, -1.1 (CH₃Si), 21.8 (OCH(CH₂)), 22.3 (CH(CH₂)Br), 38.6 (CH₂Br), 48.6 (CHBr), 67.9 (OCH₂), 68.3 (OCH). Anal. Calcd for Me₃SiO[(C₂H₆OSi)₀.₃(C₄H₉BrO₂Si)₀.₇]: C, 30.32; H, 7.19. Found: C, 30.08; H, 7.11.

3.5. Preparation of bromobutanoyloxy polymer 4e

A mixture of 0.415 g (6.92 mmol units) of 3a, 0.600 g (6.97 mmol) of γ-butyrolactone, 0.836 g (6.91 mmol) of allyl bromide, and 12.3 mg (0.0693 mmol) of PdCl₂ was stirred at 50°C for 11 h. At this stage, all detectable Si-H bonds were consumed and approximately 68% of the Si-H bonds were converted into Si-bromobutanoyloxy groups. Polymer 4e was highly moisture-sensitive and could not be purified. Data for 4e: $^1$H NMR ($\delta$ in CDCl₃) 0.15 (br s, 3H, SiCH₃), 2.18 (qui, 2H, OCOCH₂CH₂, $J = 6.8$ Hz), 2.57 (t, 2H, OCH₂, $J = 7.1$ Hz), 3.48 (t, 2H, CH₂Br, $J = 6.4$ Hz). IR (in KBr) 1100 (Si-O), 1716 cm⁻¹ (C=O). Leaving the polymer to stand in air led to the formation of insoluble materials whose IR spectra showed increased intensity of Si-O stretching vibrations and the appearance of a new band at approximately 3350 cm⁻¹ due to O-H stretching.

3.6. Formation of polymer 5
A mixture of 0.570 g (9.50 mmol units) of polymer 3a, 2.042 g (28.3 mmol) of THF, 1.172 g (9.69 mmol) of allyl bromide, and 16.0 mg (0.0902 mmol) of PdCl₂ was stirred at 50°C for 12 h. At this stage, quantitative conversion of the Si-H bond into an Si-bromobutoxy unit was confirmed by analyzing the 1H NMR spectrum of the reaction mixture. To this was added 2.461 g (19.03 mmol) of dibutylamine. After reacting at room temperature for 24 h, 0.614 g (4.75 mmol) of dibutylamine was further added to the mixture. To this was added 50 mL of hexane and the resulting precipitate was removed by filtration. The filtrate was washed with water and the organic layer was dried over anhydrous magnesium sulfate. After removal of the solvent and volatile substances under reduced pressure, the residue was reprecipitated from methanol/THF to give 0.723 g (31% yield) of polymer 5 as a colorless viscous oil: VPO Mₙ = 5600. 1H NMR (δ in C₆D₆) 0.27 (br s, 9H, terminal SiMe₃), 0.51 (br s, 3H, SiCH₃), 0.75-1.20 (br m, 6H, NCH₂CH₂CH₂CH₂CH₃), 1.25-2.20 (br m, 16H, OCH₂CH₂CH₂CH₂N(CH₂CH₂CH₂CH₃)₂), 2.20-2.60 (br m, 6H, NCH₂), 3.55-4.20 (br, 2H, OCH₂). 13C NMR (δ in C₆D₆) -37, 14.5, 21.0, 24.4 (OCH₂CH₂CH₂CH₂NCH₂CH₂CH₃), 30.2, 31.0 (OCH₂CH₂CH₂CH₂NCH₂CH₂), 31.3 54.3, 54.6 (NCH₂), 62.8 (OCH₂). Signals of the bromobutoxy unit were also observed in 1H and 13C NMR spectra at essentially the same chemical shifts as those of 4c. The incorporation ratio of bromobutoxy and dibutylaminobutoxy units was determined to be 3:7 by integration of the signals in the 1H NMR spectrum of 5.

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References


Figure 1. $^1$H NMR spectra of polymers 3a, 4c, and 5 in C$_6$D$_6$. 