

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

Joji Ohshita ^{*}, Ko Inata, Yuki Izumi, Atsutaka Kunai ^{*}

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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Abstract

Palladium-catalyzed synthesis of poly(bromoalkoxymethyl- and bromoalkanoyloxymethylsiloxane)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 PdCl₂ 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.

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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 bromoalkanoyloxysilanes 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.

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.

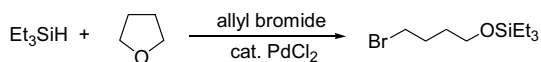
2. Results and discussion

2.1. Model reactions

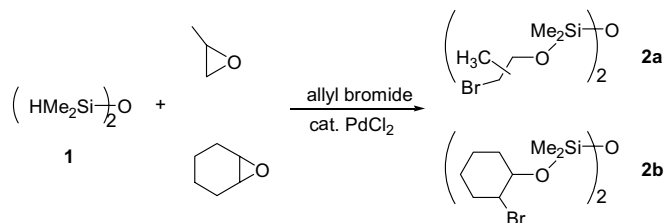
First, we examined model reactions using dihydro-tetramethyldisiloxane (**1**) as the reactant. When compound **1** was treated with a mixture of propylene oxide (3 equiv.) and allyl bromide (2 equiv.) in the presence of PdCl₂ (1 mol%) at room temperature, bis(bromopropyl)tetramethyldisiloxane (**2a**) 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

^{*} Corresponding authors.

E-mail addresses: jo@hiroshima-u.ac.jp (J. Ohshita), akunai@hiroshima-u.ac.jp (A. Kunai).



Scheme 1.

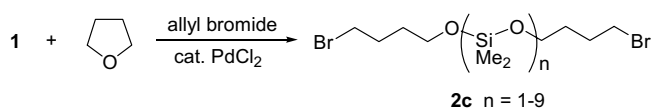


Scheme 2.

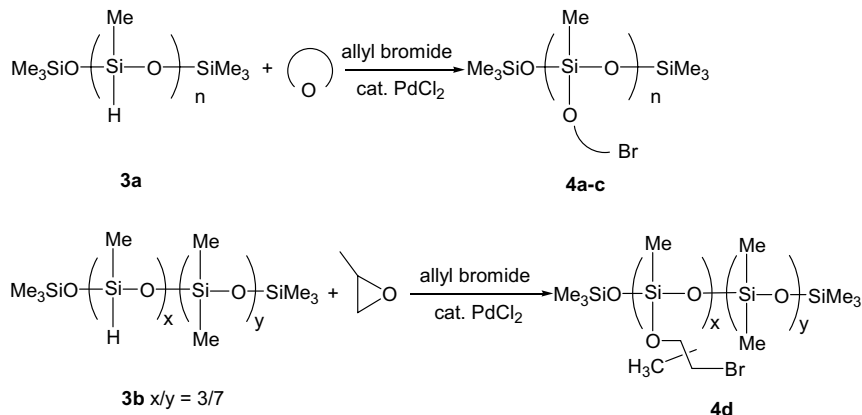
mixture indicated the formation of **2a** almost quantitatively. A similar reaction of cyclohexene oxide also proceeded smoothly to give bis(bromocyclohexyloxy)tetramethyldisiloxane (**2b**) in 55% isolated yield. In contrast to the reactions of these oxiranes, ring opening of THF competed with the redistribution reactions of the disiloxane chain under the same conditions, giving a mixture of bis(bromobutoxy)siloxane oligomers (**2c**), as shown in Scheme 3.

2.2. Reactions of poly(hydromethylsiloxane)

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



Scheme 3.



Scheme 4.

corresponding bromoalkoxy units, as illustrated in Fig. 1a 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 ethanol/chloroform afforded corresponding poly[(bromoalkoxy)methylsiloxane]s (**4a–c**) in moderate yields (Table 1). The ¹H and ¹³C NMR spectra of polymer **4a** indicated that the polymer had regioisomeric units of BrCH₂CH(Me)O- and BrC(Me)HCH₂O- 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**.

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 ethanol-soluble fraction. The ¹H NMR spectrum of the reaction mixture again indicated the complete transformation of Si–H bonds into Si–bromopropoxy units.

The interaction of **3a** with γ -butyrolactone under the same conditions led to the formation of partly bromobutanoyloxy-substituted polymer (**4e**), as shown in Scheme 5. The ¹H 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.

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

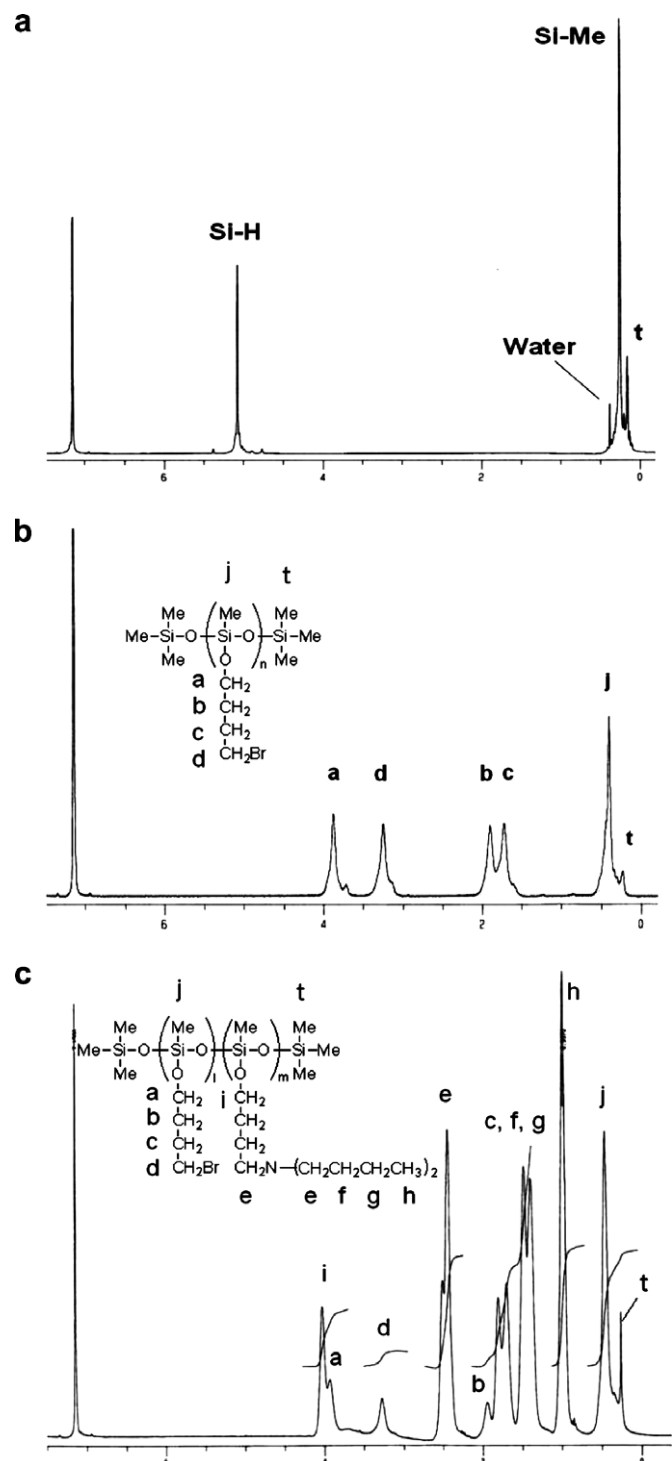


Fig. 1. ^1H NMR spectra of polymers **3a**, **4c**, and **5** in C_6D_6 .

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 sub-

Table 1
Reactions of hydrosiloxane polymers with ethers

Polymer (M_n)	Ether	Product	M_n (M_w/M_n) ^{a,b}	Yield (%) ^a
3a (1800)	Propylene oxide	4a	7100 (2.8)	44
	Cyclohexene oxide	4b	4800 (2.4)	55
	THF	4c	11 600 (2.2)	39
3b (2000)	Propylene oxide	4d	8600 (1.6)	16

^a After reprecipitation.

^b Determined by GPC, relative to polystyrene standards.

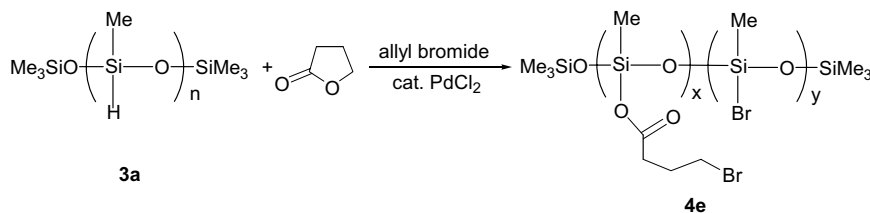
stances. Polymer **4c** obtained by the reaction with THF was highly moisture-sensitive. In fact, polymer **4c** became insoluble unless reprecipitation was carried out in a dry atmosphere. Polymer **4e** was even more moisture-sensitive and therefore, its purification by reprecipitation could not be 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 with bromosilation as a minor path, in the PdCl_2 -catalysed reactions of Et_3SiH /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 PdCl_2 , 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 aminoalkoxyl units (Scheme 6 and Fig. 1c). 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.

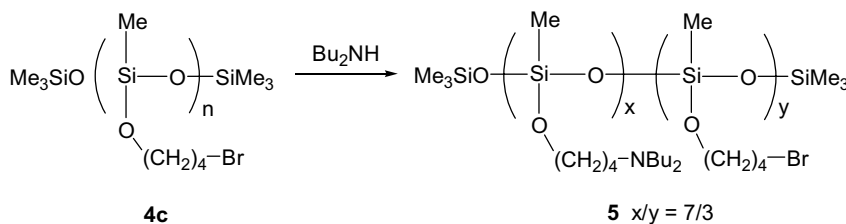
3. Experimental

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 car-



Scheme 5.



Scheme 6.

ried 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⁺ - OCH₂CH₂CH₃). 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, 0.7 H, 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 (OCHCH₃), 22.3 (BrCH(CH₃)), 38.9 (BrCH₂), 49.1 (BrCH), 68.0 (OCH₂), 68.1 (OCH). Anal. Calc. 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. Calc. 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)₄O(SiMe₂O)_{*n*}(CH₂)₄Br (*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 PdCl₂ was stirred at 50 °C for 12 h. The mixture was filtered and the filtrate was washed with aqueous NaHCO₃. 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 *M_w* = 19900, *M_w*/*M_n* = 2.8. ¹H NMR (δ in CDCl₃) 0.13 (br s, terminal SiMe₃), 0.21 (br s, 3H, SiCH₃), 1.32 (d,

2.1H, OCH(CH₃), *J* = 6.1 Hz), 1.67 (d, 0.9H, CH(CH₃)Br, *J* = 6.6 Hz), 3.30–3.38 (br m, 1.4H, CH₂Br), 3.76–3.80 (br m, 0.3H, OCH₂), 3.92–3.96 (br m, 0.3H, OCH₂), 4.07–4.09 (br m, 0.3H, CHBr), 4.18–4.25 (br m, 0.7H, OCH). ¹³C NMR (δ in CDCl₃) –5.7, –5.0 (CH₃Si), 20.5 (OCH(CH₃)), 20.8 (CH(CH₃)Br), 37.2 (CH₂Br), 47.1 (CHBr), 66.5 (OCH₂), 66.8 (OCH). Anal. Calc. for Me₃SiO(C₄H₉BrO₂Si)_{35.28}SiMe₃: 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 (*M_n*).

Other polymer reactions were carried out in a similar fashion to that above. Data for **4b** after reprecipitation from methanol/chloroform: GPC *M_w* = 11 400, *M_w*/*M_n* = 2.4. ¹H NMR (δ in CDCl₃) 0.13 (br s, terminal SiMe₃), 0.24 (br s, 3H, SiCH₃), 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), 3.75–4.25 (br m, 2H OCH, CHBr). ¹³C NMR (δ in CDCl₃) –3.0 (Si–CH₃), 22.9, 24.9, 33.6, 34.5, 57.3, 74.2 (Cy). Anal. Calc. for Me₃SiO(C₇H₁₃BrO₂Si)_{19.62}SiMe₃: C, 35.86; H, 5.74. Found: C, 36.46; H, 5.45%. Data for **4c** after reprecipitation from pentane/chloroform: GPC *M_w* = 25 600, *M_w*/*M_n* = 2.2. ¹H NMR (δ in CDCl₃) 0.11 (br s, terminal SiMe₃), 0.13 (br s, 3H, SiCH₃), 1.60–1.80 (br m, 2H, OCH₂CH₂), 1.92 (br qui, 2H, CH₂CH₂Br, *J* = 7 Hz), 3.42 (t, 2H, CH₂Br, *J* = 6.8 Hz), 3.65–3.85 (br m, 2H, OCH₂). ¹³C NMR (δ in CDCl₃) –4.3 (CH₃Si), 29.3 (OCH₂CH₂), 30.8 (CH₂CH₂Br), 33.6 (CH₂Br), 61.2 (OCH₂). Anal. Calc. for Me₃SiO(C₅H₁₁BrO₂Si)_{54.25}SiMe₃: C, 28.70; H, 5.35. Found: C, 27.84; H, 5.28%.

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 ethanol/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. ¹H NMR (δ in CDCl₃) 0.03, 0.06, 0.068, 0.074, 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(CH₃)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). ¹³C NMR (δ in CDCl₃) –4.2, –3.5, –3.3, –1.1 (CH₃Si), 21.8 (OCH(CH₃)), 22.3 (CH(CH₃)Br), 38.6 (CH₂Br), 48.6 (CHBr), 67.9 (OCH₂), 68.3 (OCH). Anal. Calc. for Me₃SiO[(C₂H₆O₂Si)_{0.3}(C₄H₉BrO₂Si)_{0.7}]_{12.87}SiMe₃: 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**: ¹H NMR (δ 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 *M_n* = 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, NCH₂CH₂CH₂CH₃), 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) –3.7, 14.5, 21.0, 24.4 (OCH₂CH₂CH₂CH₂NCH₂CH₂CH₂), 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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