NOTES

Synthesis of Polydimethylsiloxanes Containing Aminosilyl or Amidosilyl Groups at One Chain End

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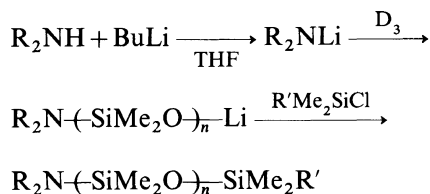Polydimethylsiloxanes (PDMS) with well-defined molecular structures prepared by non-equilibrium ring-opening polymerization of hexamethylcyclotrisiloxane (D_3) have been intensively investigated and a considerable number of reports on their syntheses, properties and applications have been published.[1] We previously reported that the lithium salt of an oligosiloxanol compound containing a vinyl or hexenyl group can act as an initiator for non-equilibrium ring-opening polymerization of D_3 to give a one-end alkenyl-functional PDMS.[2] This method was named "initiator method" because a functional alkenyl group was present in the initiator. We also reported another example in which lithium trimethylsilylacetylide was used as the initiator to form a PDMS with a trimethylsilylethynyl group at the initiation end.[3]

Organosilicon compounds bearing aminosilyl or amidosilyl groups are utilized by taking advantage of their high reactivity towards active protic compounds such as water, alcohols and silanols. For example, di- or tri-functional aminosilanes are used as cross-linking agents in silicone elastomers which cure when exposed to ambient moisture. Aminosilanes, silazanes and amidosilanes can be classified as the most versatile silylating agents for alcohols, amines or silanols.[4]

Recently, we found that the lithium salts of diethylamine or diisopropylamine can initiate the non-equilibrium polymerization of D_3 to form a PDMS containing an aminosilyl group at the initiation end. The synthetic procedure is illustrated in Scheme 1.

$$R_2NH + BuLi \xrightarrow[THF]{} R_2NLi \xrightarrow{D_3}$$

$$R_2N\text{-}(SiMe_2O)_n\text{-}Li \xrightarrow{R'Me_2SiCl}$$

$$R_2N\text{-}(SiMe_2O)_n\text{-}SiMe_2R'$$

<div align="center">Scheme 1</div>

Any functional group can be incorporated at the termination end of the PDMS as long as the corresponding chlorosilane is available.

During the course of investigating Si–N functional PDMS, we found that PDMS containing a terminal amidosilyl group can be obtained by the reaction between PDMS with a terminal chlorosilyl group and N-methyl-N-trimethylsilylacetamide.

The first part of this report describes the synthesis of one-end aminosilyl-functional PDMS initiated by the lithium salts of

dialkylamines, with the second part focusing on the synthesis of PDMS with terminal amidosilyl groups. It is expected that this class of PDMS will become quite versatile for the preparation of graft copolymers or star-shaped polymers as a consequence of the reactive terminal Si–N functional groups.

EXPERIMENTAL

General

All synthetic procedures were conducted under dry argon or nitrogen atmosphere and the glassware was dried by vacuum-heating. Tetrahydrofuran (THF) was distilled from a purple solution of THF/Na/benzophenone. Diethylamine (Et_2NH) or diisopropylamine ($isoPr_2NH$) was distilled and stored over activated molecular sieves. Hexamethylcyclo-trisiloxane (D_3) was distilled, dissolved in dry THF (50wt%), and stored over activated molecular sieves. N-Methyl-N-trimethylsilyl-acetamide (TMSNMA) and the chlorosilanes were freshly distilled before use. Butyllithium (BuLi, in hexanes) was used as purchased.

Measurements

Gel permeation chromatography (GPC) was performed on a Tosoh HLC 8020 equipped with a series of Tosoh G5000HXL and GMHXL-L columns and a refractometer. Toluene was used as the eluent and standard polydimethylsiloxane samples were used for calibration. The samples were quenched with excess MeOH prior to GPC measurements to avoid hydrolysis/condensation reactions caused by water in the eluent. Analytical gas chromatography was carried out using a Shimadzu gas chromatograph model GLC-14AH equipped with a CBM1 glass capillary column. Quantitative ^1H and ^{29}Si NMR spectra were recorded on a Bruker AC-P 300 spectrometer [300.13 MHz for ^1H; room temperature; solvent: $CDCl_3$; reference: $CHCl_3$ (^1H), $CDCl_3$ (^{13}C), Me_4Si (^{29}Si); relaxation agent: $Cr(acac)_3$ (0.02 M)]. Gas chromatog-

raphy-mass spectrometric (GC-MS) data were obtained using a Shimadzu GCMS-QP1000EX gas chromatograph-mass spectrometer.

1-Diethylamino-7-vinyloctamethyltetrasiloxane (1)

To a solution of Et_2NH (18.8 g, 0.26 mol) in THF (50 ml) at $-78°C$ was added BuLi (0.25 mol) over a period of 30 min. The mixture was allowed to warm to room temperature, mixed for further 30 min, and then cooled again with an ice bath. D_3 in THF (55 g, 0.25 mol) was added to the mixture and stirred for 30 min at $0°C$. Chlorodimethylvinylsilane (35 g, 0.29 mol) was then added to the mixture while maintaining a temperature at $0°C$. A white precipitate appeared about 30 s later, which was then removed by filtration. After evaporation of the solvent and unreacted materials under vacuum at room temperature, 1 was collected by fractional distillation. Yield 43%. bp $108°C/6$ mmHg. Purity by GC: >99%. ^1H NMR (δ, ppm): 6.18—5.68 (m, 3H), 2.82 (q, 4H), 0.98 (t, 6H), 0.14 (s, 6H), 0.06 (s, 6H), 0.04 (s, 6H), 0.03 (s, 6H). ^{29}Si NMR (δ, ppm): -4.20 (ViMe$_2$$\underline{Si}$O–), -12.15 (Et$_2NMe_2$$\underline{Si}$O–), -21.21 (ViMe$_2$SiOMe$_2$$\underline{Si}$O–), -23.22 (Et$_2$N-Me$_2$SiOMe$_2$$\underline{Si}$O–). ^{13}C NMR (δ, ppm): 139.18, 131.37, 39.30, 15.61, 0.95, 0.89, 0.05, -0.50. GC-MS m/z (relative abundance): 379 (M$^+$, 3), 364 (M$^+$ − Me, 60), 307 (27), 219 (54), 207 (100), 130 (30), 85 (37), 73 (75).

1-Diethylaminononamethyltetrasiloxane (2) was prepared in a similar way. Yield 31%. bp $60°C/0.1$ mmHg. Purity by GC: >98%. ^1H NMR (δ, ppm): 2.82 (q, 4H), 0.98 (t, 6H), 0.08 (s, 9H), 0.07 (s, 6H), 0.04 (s, 6H), 0.03 (s, 6H). ^{29}Si NMR (δ, ppm): 7.03 (Me$_3$$\underline{Si}$O–), -12.26 (Et$_2NMe_2$$\underline{Si}$O–), -21.80 (Me$_3$SiOMe$_2$$\underline{Si}$O–), -23.38 (Et$_2NMe_2$SiOMe$_2$$\underline{Si}$O–). ^{13}C NMR (δ, ppm): 39.43, 15.73, 1.68, 1.04, -0.39. GC-MS m/z (relative abundance): 367 (M$^+$, 3), 352 (M$^+$ − Me, 40), 295 (26), 207 (100), 130 (39), 73 (50).

Polymerization Initiated by LiNEt₂ (4 *in Table* 1)

To a solution of Et₂NH (0.90 g, 12 mmol) in THF (10 ml) cooled to 0°C was added BuLi (12 mmol) over a period of 2 min. After stirring at 0°C for 30 min, D₃ in THF (50 g, 225 mmol) was added to the solution in one portion. The reaction mixture was allowed to warm to room temperature and the consumption of D₃ was monitored by GC. When the consumption reached 83%, chlorodimethylsilane (2.7 g, 28 mmol) was added to the solution. The solvents and unreacted materials were removed by vacuum evaporation (up to 100°C) and LiCl was removed by filtration to give 36.7 g of polymer. Yield (based on BuLi): 85%. ¹H NMR (δ, ppm): 4.70 (m), 2.82 (q), 0.98 (t), 0.07 (s). ²⁹Si NMR (δ, ppm): −6.89, −12.11, −19.85, −21.89, −23.13.

Other polymerizations initiated by lithium diethylamide or lithium diisopropylamide were carried out in a similar manner. NMR data for **3**: ¹H NMR (δ, ppm): 6.18—5.68 (m), 2.82 (q), 0.98 (t), 0.07 (s). ²⁹Si NMR (δ ppm): −4.20, −12.22, −21.03, −22.05, −23.27. NMR data for **5**: ¹H NMR (δ, ppm): 4.70 (m), 3.20 (sept), 1.07 (d), 0.06 (s). ²⁹Si NMR (δ, ppm): −6.92, −13.84, −19.89, −21.94, −23.67.

1-(N-Methylacetamido)-7-vinyloctamethylte-trasiloxane (6)

To a flask containing 1-chloro-7-vinyloctamethyltetrasiloxane[5] (4.2 g, 12 mmol), TMSNMA (2.2 g, 15 mmol) was added with stirring at room temperature. The mixture was stirred for 30 min, during which time a slight exotherm was observed. A vacuum was then applied to the mixture to remove Me₃SiCl and unreacted TMSNMA. Hydrolysis of the product and subsequent pH measurement indicated that only a trace amount of the Si–Cl species was remaining. Yield: 98%. ¹H NMR (δ, ppm): 6.10—5.61 (m, 3H), 2.74 (s, 3H), 1.98 (s, 3H), 0.24 (s, 6H), 0.08 (s, 6H), 0.02 (s, 6H), −0.01 (s, 6H), ²⁹Si NMR (δ, ppm): −3.83 (ViMe₂$\underline{\text{Si}}$O–), −7.22 (AcMeNMe₂$\underline{\text{Si}}$O–),

−20.84 (–Me₂$\underline{\text{Si}}$O–).

Amidosilyl-Functional PDMS

To a flask containing D₃ (52 g, 230 mmol) and THF (65 ml), BuLi (22 mmol) was added in one portion with stirring at room temperature. When the consumption of D₃ reached 85%, the mixture was transferred to a separate flask containing dichlorodimethylsilane (12.9 g, 100 mmol) and THF (20 ml). The transfer was made over a period of 5 min with constant stirring. The solvents and unreacted materials were removed under vacuum at 80°C and LiCl was removed by filtration. The resulting polymer (38 g) had an M_n of 2000 and M_w of 2500 according to a GPC measurement (after quenching with excess MeOH). Thus, it was assumed that this polymer has the structure Bu(SiMe₂O)₂₇SiMe₂Cl [²⁹Si NMR (δ, ppm): 7.63, 3.58, −19.08, −21.34, −21.90, −22.52]. A flask was charged with this polymer (30 g, 15 mmol) and TMSNMA (4.6 g, 32 mmol) and heated to 50°C with stirring. After stirring for 4 h, Me₃SiCl and unreacted TMSNMA were removed by vacuum evaporation to give PDMS **7** (30 g, 99%). ¹H NMR (δ, ppm): 2.82 (s), 2.06 (s), 1.32 (m), 0.89 (t), 0.57 (t), 0.32 (s), 0.09 (s). ²⁹Si NMR (δ, ppm): 7.63, −7.22, −20.91, −21.90, −22.52.

RESULTS AND DISCUSSION

Aminosilyl-Functional PDMS
Model Compound

1-Diethylamino-7-vinyloctamethyltetrasilox-ane. Et₂N(SiMe₂O)₃SiMe₂Vi (**1**) was used as a model compound for the analogous higher polymers. ¹H and ¹³C NMR as well as GC-MS spectral data support the expected structure **1** (see EXPERIMENTAL section). Due to the lack of chemical shift data in ²⁹Si NMR analysis for this particular class of polymers, each of the four signals had to be assigned based on shift differences before and after methoxylation of the sample. The assignments thus made are shown in the experimental section. The

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Table I. Aminosilyl-functional PDMS

No.	R^a	R'^a	Theoretical[b]		GPC		n by NMR	
			n	M	M_n	M_w	^1H	^{29}Si
3	Et	Vi	32	2510	2680	3230	37	33
4	Et	H	47	3620	4220	5170	44	47
5	isoPr	H	22	1790	2000	2830	19	23

[a] See Scheme 1.
[b] Calculated from the amounts of BuLi and consumed D_3.

formation of $MeO(SiMe_2O)_3SiMe_2Vi$ upon the addition of methanol was confirmed by GC-MS.
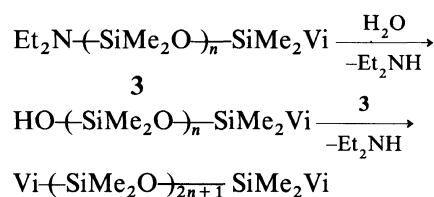
The conversion of the amine into the corresponding lithium amide can be regarded as quantitative because no formation of siloxane species with a butylsilyl group was observed, i.e., no unreacted BuLi remained when D_3 was added to the reaction mixture.

Polymer Synthesis. Three kinds of aminosilyl-functional PDMS were prepared. Their molecular weights and degrees of polymerization as determined by GPC and NMR are listed in Table I.

Each of the polymers showed a narrow molecular weight distribution, typical of the non-equilibrium polymerization of D_3. The molecular weights relative to standard PDMS samples are in good agreement with the theoretical values as calculated from the amounts of consumed D_3 and loaded BuLi. The NMR data of the polymers are consistent with the expected structures based on comparison with those of **1**. Figure 1 shows the ^{29}Si NMR spectrum of **3** as a typical example.

When **3** (without solvent) was exposed to ambient moisture for 24 h, its M_n as determined by GPC increased from 2680 to 4470 and the molecular weight distribution did not change significantly (from 1.20 to 1.25). This indicates that **3** underwent hydrolysis to form a silanol species which subsequently condensed with the available aminosilyl groups (Scheme 2). Since terminal silanol groups attached to a polymeric siloxane species are very stable towards self-

condensation at room temperature,[6] the increase in molecular weight strongly suggests the occurrence of condensation between aminosilyl groups and silanol groups. The fact that the M_n after hydrolysis (4470) is less than double to the original value (2680) implies that there were residual terminal silanol groups. The well-retained molecular weight distribution can be regarded as evidence that each polymer molecule of **3** had exactly one aminosilyl group at the initiation end.

$$Et_2N\text{--}(SiMe_2O\text{--})_n\text{--}SiMe_2Vi \xrightarrow[-Et_2NH]{H_2O}$$

3

$$HO\text{--}(SiMe_2O\text{--})_n\text{--}SiMe_2Vi \xrightarrow[-Et_2NH]{3}$$

$$Vi\text{--}(SiMe_2O\text{--})_{2n+1}SiMe_2Vi$$

Scheme 2

Amidosilyl-Functional PDMS

Model Compound. Since the starting chlorotetrasiloxane had an unambiguous structure and the transsilylation reaction is known to be straightforward, it is quite reasonable to assume that the product has structure **6**. The assignments for the ^{29}Si NMR signals had to be made using methoxylation due to the lack of literature data. The assignments are listed in the EXPERIMENTAL section. It was not possible to obtain satisfactory GC/MS data for this compound, probably because of its high reactivity with the coating material of the GC column.
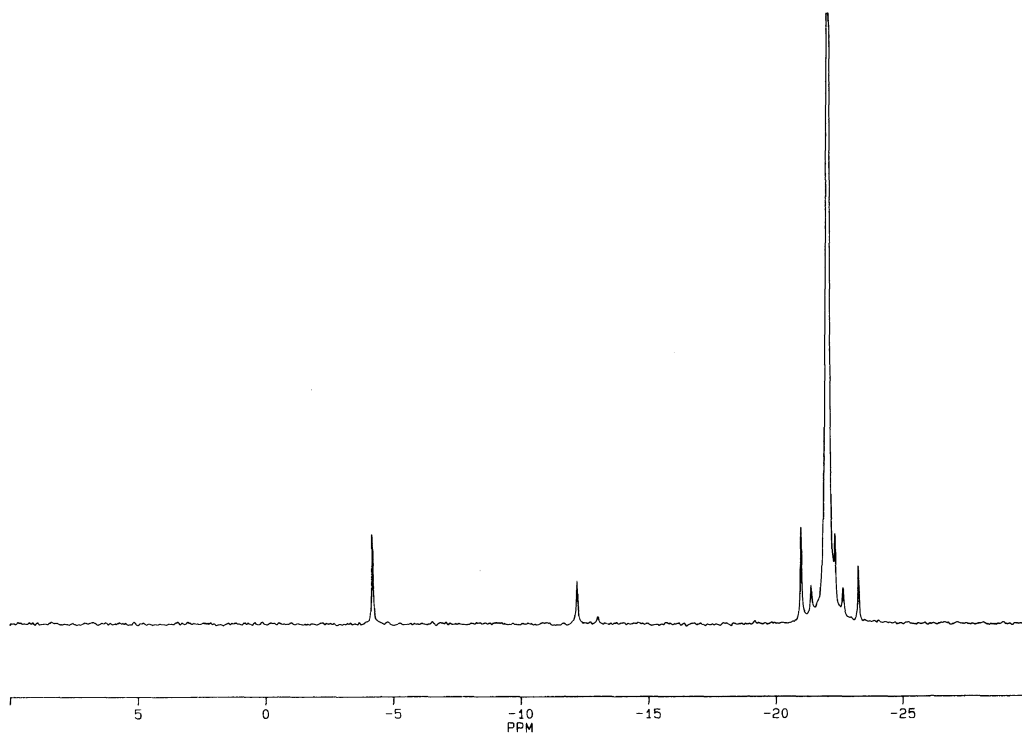
Polymer Synthesis. PDMS containing a

Figure 1. ⁹Si NMR spectrum of amino-functional PDMS **3**.
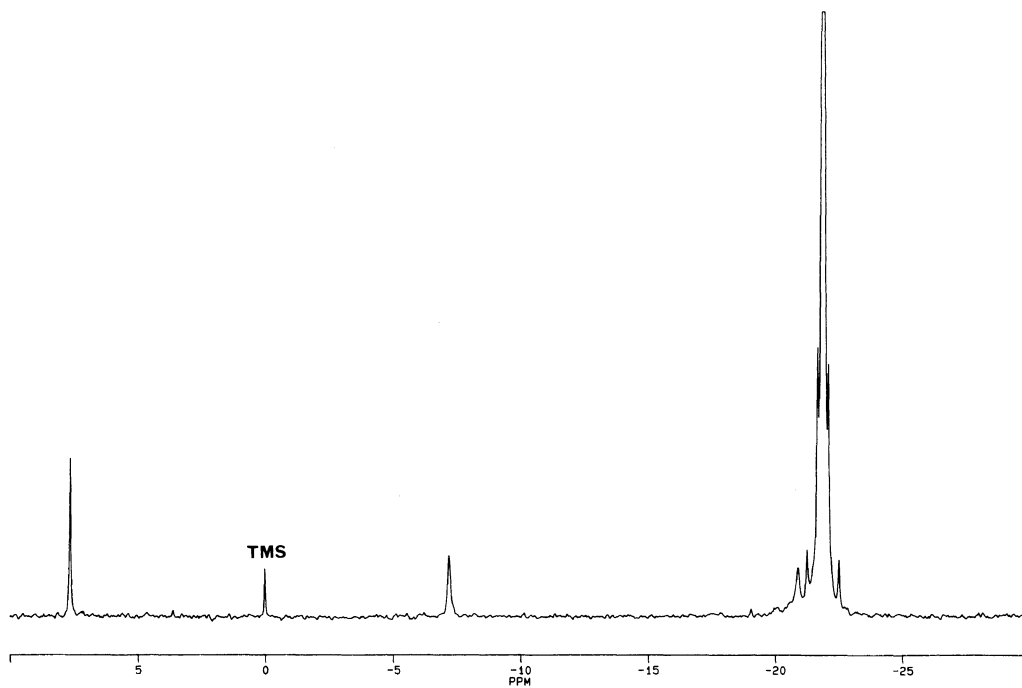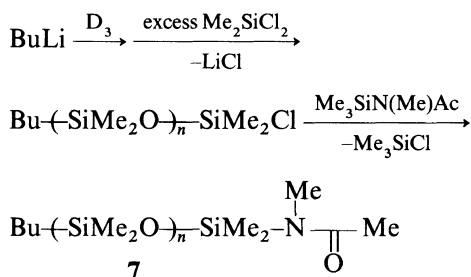

Figure 2. ²⁹Si NMR spectrum of amido-functional PDMS **7**.

chlorosilyl group at one end and a butylsilyl group at the other was prepared from BuLi, D_3, and dichlorodimethylsilane using the usual non-equilibrium polymerization technique. The chloro-functional polymer thus obtained underwent transsilylation with N-methyl-N-trimethylsilylacetamide to give the desired amido-functional PDMS (7) as illustrated in Scheme 3.

$$BuLi \xrightarrow{D_3} \xrightarrow[-LiCl]{excess\ Me_2SiCl_2}$$

$$Bu\text{-}(SiMe_2O)_n\text{-}SiMe_2Cl \xrightarrow[-Me_3SiCl]{Me_3SiN(Me)Ac}$$

$$\underset{7}{Bu\text{-}(SiMe_2O)_n\text{-}SiMe_2\text{-}N} \overset{Me}{\underset{O}{\|}} Me$$

Scheme 3

The polymer, according to GPC analysis after methoxylation, had a M_n of 2120 and M_w of 2610. The former is very close to the theoretical value of 2150. ^{29}Si and ^{1}H NMR spectroscopic data are consistent with those of the model compound. The ^{29}Si NMR spectrum is shown in Figure 3.

When 7 was exposed to the ambient moisture for 24 h, its M_n as determined by GPC increased from 2120 to 4150. The GPC traces before and after the exposure to moisture are presented in Figure 3. As in the case of the amino-functional PDMS, the molecular weight distribution did not change significantly, indicating that 7 had
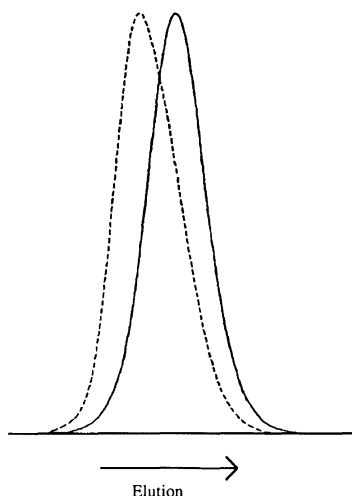

Figure 3. GPC traces of **7**: Solid line, before hydrolysis; Dotted line, after hydrolysis (ambient moisture, 24 h).

a well defined molecular structure.

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