Anionic Ring Opening Polymerization of Octamethyltetrasilacyclopentane[1]

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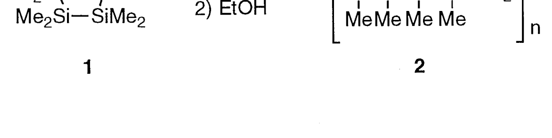
Poly(1,1,2,2,3,3,4,4-octamethyltetrasilanylenemethylene) of a highly regulated structure was synthesized by anionic ring opening polymerization of octamethyltetrasilacyclopentane. In this polymerization process, α-silyl carbanions play an important role. In this polymer, delocalization in the ground state is much important in the σ-conjugation between the tetrasilanylene units *via* the methylene units.

Polysilanes,[1] a relatively new class of polymers, have attracted considerable interest in the last decade. Although the main chain of the polysilanes comprises saturated σ-bonds, electrons are highly delocalized through the silicon backbone. As a result of the σ-conjugation, the polysilanes exhibit an intense absorption in an ultraviolet region, while the polyalkanes exhibit no absorption in such a region. The unique photophysical and photochemical properties of the polysilanes have been explained in terms of a simplified segment model;[2] the polysilane chain is a collection of certain short length segments of 10-20 silicon atoms with different length and photoexcitation energies. Then the characteristic nature of the polysilanes must be explained in terms of the interaction among the segments. It is therefore of interest to investigate the conjugation among the segments of the polysilanes. Especially, studies are highly desired on heterocatenates with polysilane chains at least longer than tetrasilane chains separated by a methylene, since the tetrasilane is a minimum unit as the polysilane with every possible conformations around the central silicon-silicon bond.

In this paper, we report an anionic ring opening polymerization of octamethyltetrasilacyclopentane (**1**) to structurally highly regulated poly(1,1,2,2,3,3,4,4-octamethyltetrasilanylenemethylene) (**2**).[3] The polymer consists of tetrasilanylene units linked with methylene units and should be a good model for the segment model proposed for polysilanes and σ-conjugation in heterocatenated structure.

Octamethyltetrasilacyclopentane (**1**) was prepared in 68% yield by coupling of bis(2-chloro-1,1,2,2-tetramethyldisilanyl)methane with lithium.[4] The ring compound **1** was readily polymerized with anionic initiators (Eq. 1).[5] Table 1 shows typical examples of the anionic ring opening polymerization of **1**. The polymerization in THF with a catalytic amount of HMPA at -78 ℃ proceeded smoothly, the polymer **2** being obtained in 64% yield (run 1). Although the polymerization proceeded at -48 ℃ (54 % yield), the molecular weight of the obtained polymer was relatively low (run 2). The polymerization also proceeded with phenyllithium as an initiator and the polymer **2** was obtained in good yield (run 3).



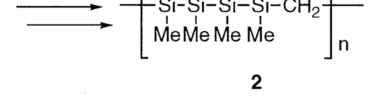
(1)

Table 1. Polymerization of 1,1,2,2,3,3,4,4-octamethyltetrasilacyclopentane **1**

Run	Initiator (eq.)	Solvent[a]	Temp. /°C	Time /h	Yield /%	$\overline{Mn}$[b] (×10^4)	$\overline{Mw}/\overline{Mn}$
1	BuLi (0.2)	THF/ HMPA	-78	9	64	2.4	1.6
2	BuLi (0.3)	THF/ HMPA	-48	8	54	1.5	1.7
3	PhLi (0.3)	THF/ HMPA	-78	8	80	2.1	1.7

[a] HMPA: 2 % (v./v.) for the solvent. [b] Estimated with polystyrene standards.

The sequence ordered structure of the polymer was estimated by NMR analyses.[6] Figure 1 shows the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the polymer. In the ^{1}H and ^{13}C NMR spectra, there are only three signals. These signals are assigned to the methylene, the methyl groups of the $-CH_2-\underline{SiMe_2}-SiMe_2-$ unit adjacent to the methylene (unit A), and the $-CH_2-SiMe_2-\underline{SiMe_2}-$ unit (unit B), respectively. Thus the ^{1}H and ^{13}C NMR spectra are consistent with those for **2** in the heterocatenated structure with highly regulated structure. This conclusion is further supported by ^{29}Si NMR spectrum; the ^{29}Si NMR spectrum of **2** shows only two sharp signals assignable to those of unit A and B. These results indicate that the anionic ring opening polymerization process itself must be highly regioselective.



Scheme 1.

Scheme 1 shows the possible reaction mechanism of **1**. The anionic polymerization of **1** proceeds at first by nucleophilic attack at the silicon atom adjacent to the methylene. The ring opening results in relief of the ring strain and the formation of a primary carbanion adjacent to the silyl groups. Next, the carbanion attacks the silicon atom adjacent to the methylene of another monomer.

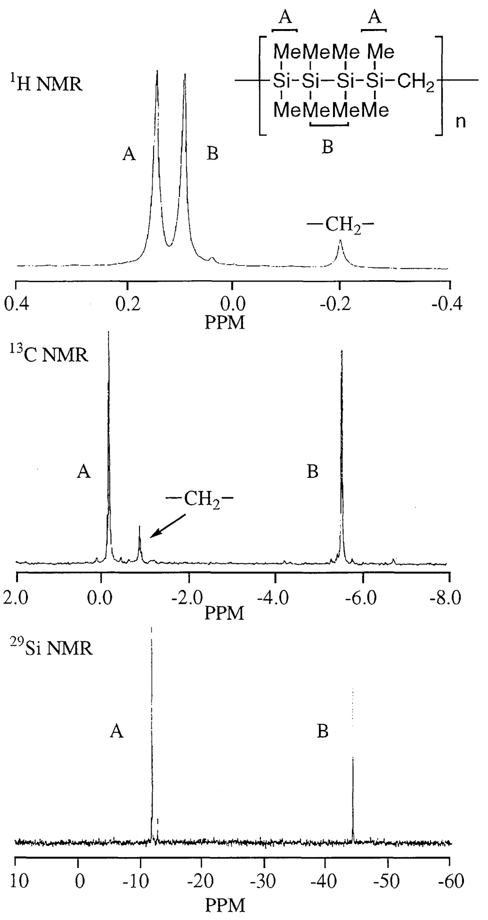


Figure 1. ^{1}H, ^{13}C, and ^{29}Si NMR spectra of **2** in CDCl$_3$.

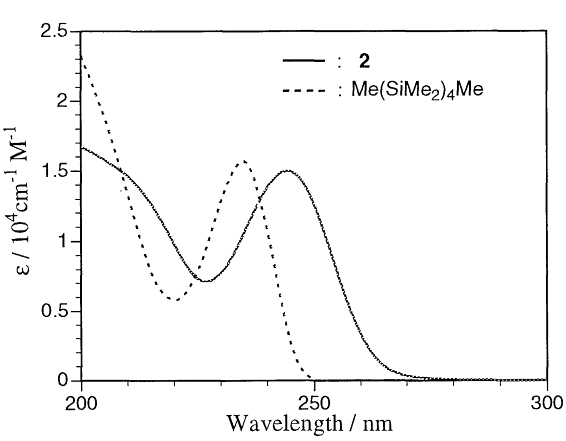


Figure 2. UV absorption spectra of **2** and decamethyltetrasilane in hexane.

It is well documented that such α-silyl carbanions could be stabilized by σ*-π conjugation.[7] The polymerization proceeds further in this manner.

Figure 2 shows the UV absorption spectra of **2** compared with decamethyltetrasilane in hexane at room temperature. While the absorption intensity of **2** was almost equal to that of decamethyltetrasilane, the absorption maximum of **2** (245 nm) exhibited a 10 nm bathochromic shift in contrast with that of decamethyltetrasilane (235 nm). This bathochromic shift must be originated in the σ-conjugation between the tetrasilanylene units *via* the methylene units. It is interesting to note that the fluorescence spectra of the polymer in 3-methylpentane at 77 K [8] is almost identical to that of decamethyltetrasilane assignable to the self-trapped state.[9] These results indicate that the stabilization by σ-conjugation in the excited state is rather small. Thus the delocalization in the ground state is much important in the σ-conjugation between the tetrasilanylene units *via* the methylene units in this polymer.

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References and Notes

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3 Preliminary results were presented at the 43rd Symposium on Organometallic Chemistry, Osaka, Japan, T. Sanji, H. Hanao, and H. Sakurai, PA 121 (1996). Very recently, an NTT group reported that the syntheses and properties of poly(1,1,2,2,3,3,4,4-octamethyltetrasilanylenemethylene) and related polymers by sodium coupling method: a) H. Isaka, H. Taramae, M. Fujiki, and N. Matsumoto, *Macromolecules*, **28**, 4733 (1995); b) H. Isaka, *Macromolecules*, **30**, 344 (1997).

4 Spectral data for **1**: colorless crystals; mp 36 °C; bp 55 °C / 0.01 mmHg; ^{1}H NMR (CDCl$_3$, 300 MHz) δ -0.22 (s, 2H), 0.08 (s, 12H), 0.12 (s, 12H); ^{13}C NMR (CDCl$_3$, 75.4 MHz) δ -6.65, -0.44, 3.87; ^{29}Si NMR (CDCl$_3$, 59 MHz) δ -46.53, -10.29; GC-MS (70 eV) m/z (rel. intensity) 246 (M$^+$, 100), 231 (15.3).

5 In a 50 ml two-necked flask, equipped with a magnetic stirring bar, a rubber septum, and a three-way stopcock, were placed **1** (960 mg, 3.9 mmol), THF (5 ml), and HMPA (0.1 ml) under dry argon. A hexane solution of n-butyllithium (0.78 mmol) was added to the solution at -78 °C. The mixture was stirring at -78 °C for 9 h, a few drops of ethanol were added to the mixture. After removal of the solvent, the residual mass was dissolved in benzene and polymer was precipitated by pouring the solution into methanol. The second cycle of dissolving-precipitation followed by freeze-drying gave polymer as a white powder (610 mg, 64 %).

6 E. A. Williams, in " The Chemistry of Organic Silicon Compounds" , ed by S. Patai and Z. Rappoport, John Willey & Sons, Chichester, England (1989), Part 1, Chap. 8.

7 a) L. F. Cason and H. G. Brooks, *J. Am. Chem. Soc.*, **74**, 4582 (1952); b) A. R. Bassindale and P. G. Taylor, in "The Chemistry of Organic Silicon Compounds", ed by S. Patai and Z. Rappoport, John Willey & Sons, Chichester, England (1989), Part 2, Chap. 14.

8 A broad emission was observed for the polymer **2** around at 340 nm in 3-methylpentane at 77 K with a strong Stokes shift (11,000 cm^{-1}).

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