Synthesis of Sequence-Ordered Polysilane by Anionic Ring-Opening Polymerization of Phenylnonamethylcyclopentasilane[1]

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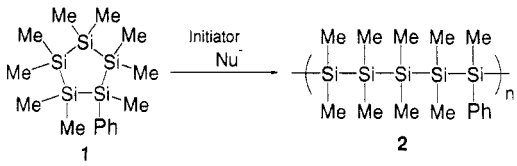
Polysilanes are attracting considerable attention due to their unique characteristics.[2] They have been prepared usually by means of the Kipping method, i.e., the reductive polycondensation of dichlorosilanes with Na metal. This method is facile, but there are some defects. Notably, it is quite unsatisfactory in terms of structure control, which is essential to the further development of polysilane chemistry. Thus new synthetic methods are under active exploration.[3-6] The anionic polymerization of masked disilenes has provided a useful method to prepare some poly(disilanylene)s whose units are ordered well in two sequences.[5] As the first example of the ring-opening polymerization of a cyclic oligosilane, the anionic polymerization of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane has also opened a new approach to polysilane synthesis.[6]

In the meantime, we have been interested in the polymerization chemistry of active silicon species which are generated by Si–Si bond scission. We started to study the ring-opening polymerization of the simplest cyclic monomers having one Si–Si bond and found some new polymerizations of 1,2-disilacycloalkanes.[7] These results have prompted us to study ring-opening polymerization of an advanced ring system that is fully constructed of Si–Si bonds, i.e., cyclic oligosilanes. Our strategy is to introduce a substituent(s), which might stabilize a propagating end, to the cyclopolysilane ring in order to induce selective ring cleavage. Accordingly, it was expected that the product polysilane would have an ordered sequence. In addition, there are potentials that the stereoregularity of substituents might be achieved as well as the control of the molecular weight and of the terminal group. Herein, we report the anionic ring-opening polymerization of phenylnonamethylcyclopentasilane (**1**).[8] The single phenyl substituent introduced on the ring has successfully led the polymerization to produce a new sequence-ordered polysilane, i.e., poly(phenylnonamethylpentasilanylene) (**2**; Scheme 1).

Tetrabutylammonium fluoride and silyl potassium were effective initiators for the polymerization (Table 1).[9] The strong affinity of fluoride anion to silicon promoted the generation of silyl anion in the initiation with the former initiator. Whereas this metal-free silyl anion conducted the polymerization without any additives, the latter initiator required the use of HMPA or 18-crown-6, which solvates the potassium cation and raises the reactivity of the silyl anion. In either case, the polymer was produced in THF or DME at −20 to −78 °C. A brief procedure is as follows. An initiator solution was added to a cold monomer solution with or without the additive under Ar. The yellowish polymer precipitated with the progress of the reaction which was monitored by gas chromatography. The almost complete conversion of the monomer was followed by the addition of an anion quencher such as methyl iodide and chlorosilane. Afterward, the reaction mixture was gradually warmed to room temperature. During this period, the pale-yellow color due to the silyl anion disappeared and the polymer had dissolved. The reaction mixture was then poured into methanol to precipitate a white powdery polymer, which was collected and dried in vacuo.

Scheme 1



1 **2**

Temperature control was significantly important for successful polymerization. Higher reaction temperatures made the reaction faster but the polymer yield lower. The reaction at room temperature gave no polymer but mainly five- and six-membered cyclic oligosilanes (**3–6**; Scheme 2). It is noteworthy that warming the reaction mixture to room temperature without the addition of the anion quencher similarly produced no polymer but **3–6**. These findings are ascribable to a back-biting reaction; a silyl anion of the propagating end successively attacked the Si–Si bond of its own polymer chain to produce the stable cyclic oligosilanes. While, at −78 °C, the silyl anion stabilized with a phenyl substituent is specifically generated to give rise to production of the sequence-ordered polymer, the predominancy of the stabilized silyl anion over a nonstabilized one is completely broken at room temperature. Consequently, at room temperature, nonselective cleavage of the monomer ring and/or intermolecular random attack by the silyl anion to the polymer chain take(s) place to disorder the polymer chain sequence, and the subsequent back-biting reaction results in the formation of **3–6**. In other words, cyclic oligosilanes **3–6** are thermodynamically more stable than linear polysilane **2**, which is a kinetic product.

We explored polymerization conditions which should produce a living polymer, as this is favorable for macromolecular designs. In the polymerization initiated with tetrabutylammonium fluoride or silyl potassium with HMPA, the degrees of polymerization (DP) of the product polymers were not in proportion to the feed ratio of the monomer to the initiator (runs 1–9 in Table 1). However, dimethylphenylsilyl potassium with 18-crown-6 provided a livinglike nature to some extent. In contrast with the silyl potassium with HMPA (run 9), this system yielded a comparable oligomer (run 10). The propagating end was quenched by chlorodimethyl-(2-ferrocenylethyl)silane[10] and was subjected to end-group analysis. The DP value evaluated by ^{1}H NMR spectroscopy was 11.6 on the basis of the relative signal intensity of the ferrocenyl group to the polymer unit. On the other hand, the M_n value measured by VPO was 4700, which was equivalent to 12.2 for the DP value. Although these two values are a little larger than the theoretical one (=10), their good agreement indicates that it is possible to prepare the terminal-defined oligomer by use of this system. A two-step feed experiment (run 11) also suggested that the propagating end had somewhat of a living character; the monomer that was fed again after the consumption of the first fed monomer was consumed to yield the polymer whose GPC profile was unimodal and shifted to the higher molecular weight

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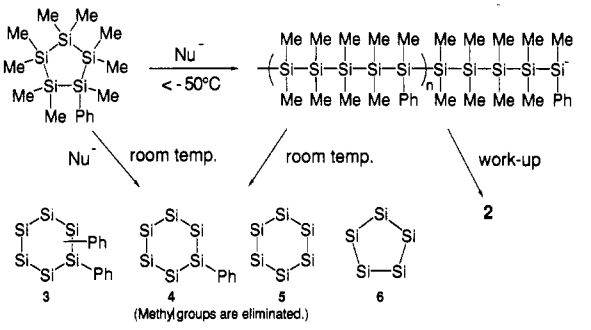
Table 1. Anionic Ring-Opening Polymerization of Phenylnonamethylcyclopentasilane (1)

run	initiator (mol %)	solvent	additive[a]	temp, °C	time, h	yield,[b] %	M_n[c]	M_w/M_n[c]
1	Bu_4NF (2)	THF	none	−20	1.5	17	3100	1.67
2	Bu_4NF (2)	THF	none	−78	24	82	8000 (6900)[d]	1.76
3	Bu_4NF (2)	DME	none	−50	3	74	7000	1.76
4	Me_3SiK (2)	THF	HMPA	−20	1	3	3900	1.62
5	Me_3SiK (2)	THF	HMPA	−50	2	68	17000	1.26
6	Me_3SiK (2)	DME	HMPA	−50	5	35	2000	1.26
7	Me_2PhSiK (2)	THF	none	−78	27	0		
8	Me_2PhSiK (2)	THF	HMPA	−78	17	81	58000	1.78
9	Me_2PhSiK (20)	THF	HMPA	−78	6	79	25000	1.69
10[e]	Me_2PhSiK (10)	THF	18-crown-6	−78	1	83	7400 (4700)[d]	1.28
11[f]	Me_2PhSiK (5)	THF	18-crown-6	−78	2 + 5	80	26000 (10900)[d]	1.48

[a] HMPA: 5% (v/v) for the solvent. 18-crown-6: the equimolar amount to Me_2PhSiK. [b] A MeOH-insoluble portion. [c] These values were estimated by use of GPC (PSt standard, eluent $CHCl_3$). M_n values shown in the parentheses were measured by VPO ($CHCl_3$, 40 °C). [d] Degree of polymerization evaluated from M_n (VPO) = 19 (run 2), 12 (run 10), and 31 (run 11). [e] The reaction was terminated by the addition of chlorodimethyl(2-ferrocenylethyl)silane [f] Two-step feed: after the consumption of the first fed monomer (2 h), the same amount of 1 was fed again (totally, [I]/[M] = 0.05, the reaction time = 7 h).

Scheme 2



region. However, the DP value of this polymer was 31 (M_n(VPO) = 10 900), which was larger than the theoretical value (=20), and besides the molecular weight distribution was somewhat broad (M_w/M_n = 1.48). It appears that the deposition of the product polymer during the polymerization increases the difficulty in conducting a living system. It is worth mentioning that silyl cuprate, which, we found, conducted the living polymerization of the phenyl-substituted 1,2-disilacyclopentane,[7c,7d] did not initiate the polymerization of 1.

The sequence-ordered structure of product polymer **2** was disclosed by NMR spectroscopies. Figure 1 shows ^{29}Si, ^1H, and ^{13}C NMR spectra.[11] The ^{29}Si NMR spectrum strongly suggests the ordered structure through showing three clear signals. In the ^1H and ^{13}C NMR spectra, however, there appear signal splittings caused by tacticity (vide infra). In order to assign the signals, 2D ^1H–^{29}Si and ^1H–^{13}C correlated NMR spectra were employed. Figure 2 shows the 2D ^1H–^{29}Si correlated NMR spectrum, which effectively reveals Si–Si connectivities.[12] The chemical shift values of signals Si-1 and H-1 allow the assignment of these signals to the silicon having the phenyl group and the protons of the methyl group connected to this silicon, respectively. Actually, there is a strong cross-peak between these signals. Although signal H-1 shows no other cross-peaks that should have revealed the connectivity of the Si-1 silicon, other signals reveal the connectivities. The two signals of H-2 show a very strong cross-peak to signal Si-2 along with two weaker ones to signals Si-1 and Si-3. So, it is concluded that signals H-2 are ascribed to the protons of the methyl groups connecting directly to the Si-2 silicons, which connect to the Si-1 and Si-3 silicons. Considered likewise, the appearance of cross-peaks given by signals grouped as H-3 is in good agreement with these assignments; all of these four ^1H peaks are assigned to the protons of the methyl groups connecting to the Si-3 silicons because the strong cross-peaks to signal Si-3 appear together with the very weak ones to Si-2. Now, the ^{13}C

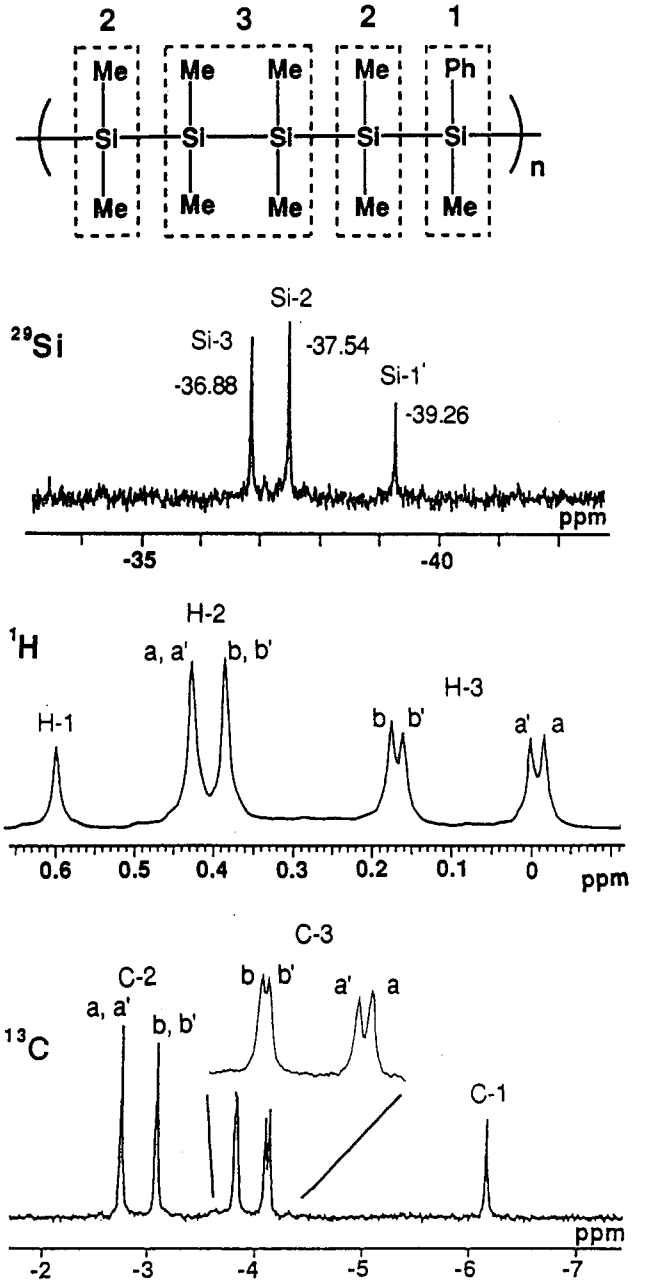


Figure 1. ^{29}Si (^1H gate decoupling), ^1H, and ^{13}C (^1H complete decoupling) NMR spectra of polysilane **2** (in C_6D_6).[11] As for the ^1H and ^{13}C NMR spectra, the high field regions including signals ascribed to the methyl groups are shown.

NMR signals are easily assigned through the 2D ^1H–^{13}C correlated NMR spectrum.

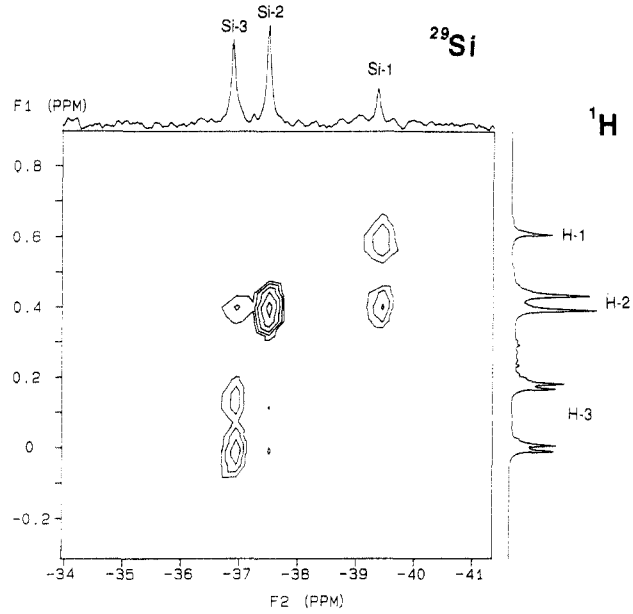


Figure 2. 2D ^{1}H–^{29}Si correlated NMR spectra of polysilane **2** (in C_6D_6).

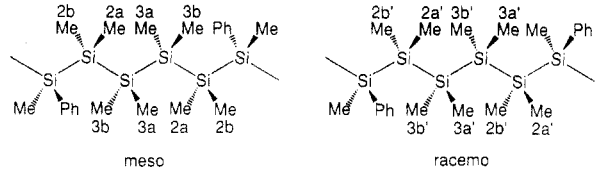


Figure 3. ζ-Diad structures of polysilane **2**.

Although the NMR signals have been assigned as mentioned above, we have to consider ζ-tacticity to explain the finely splitting signals in the ^{1}H and ^{13}C NMR spectra (Figure 1). There are two and double two peaks for the H-2 and H-3 methyl protons, respectively, and the corresponding carbons present similar signal splittings. Figure 3 shows two structures based on the ζ-diad (meso and racemo). In both of these structures, the geminal methyl groups are not identical due to the spatial position relative to two phenyl groups. Thus there exist totally four kinds of methyl groups for each pair (2a, 2b, 2a′, and 2b′ and 3a, 3b, 3a′, and 3b′). Accordingly, it is reasonable that four ^{1}H and ^{13}C NMR peaks are observed for the methyl groups labeled as 3. As for those labeled as 2, however, there appear only two peaks. It is because the influence of the distant phenyl group located six bonds away is so weak that the NMR instrument employed (400 MHz for ^{1}H) is unable to distinguish 2a from 2a′ and 2b from 2b′. Considering two subjects, i.e., shielding and deshielding effects of a phenyl group in NMR spectroscopy and the most stable conformation (trans–trans) of the polymer chain, allows the tentative assignment of these fine peaks as shown in Figure 1. Since these split peaks have almost equal intensities, it is indicated that product polysilane **2** has an atactic structure (meso:racemo = 1:1). Theoretically, the H-1 and C-1 signals should have also split in terms of triad but do not. The phenyl groups of the adjacent units are located too far away to exert a magnetic influence on the methyl group labeled as 1. There appeared to be no signal splittings in the ^{29}Si NMR spectrum unlike the ^{1}H and ^{13}C NMR spectra. This is ascribable to the lower sensitivity of the ^{29}Si resonance and/or to a smaller influence of the phenyl side groups on the silicons forming the polymer main chain. All of the polymers produced without the back-biting reaction (wide supra) showed the same spectroscopic data.

As well as the sequence order, the tacticity definitely plays an important role on polysilanes' character like that of vinyl polymers. Although we tried to bring stereoregularity to the anionic polymerization of **1** by employing other additives and initiators, all polymers produced were atactic. Palladium-catalyzed polymerization, which yielded high polymer from 1,2-disilacyclopentane,[7b,7c] was also investigated under various conditions, but monomer **1** was recovered without reaction. The study was extended to the anionic polymerization of other related cyclopentasilanes, which had a 4-(trifluoromethyl)phenyl (**7**), pentafluorophenyl (**8**), trimethylsilyl (**9**), or ethoxy (**10**) group in place of the phenyl one of **1**. While **7** was polymerized with the initiator of Me_3SiK (2 mol %) in THF containing HMPA at −78 °C for 24 h to give the corresponding atactic polymer (M_n(GPC) = 12 800, M_w/M_n = 1.92, yield = 57%), the anionic polymerizations of **8**–**10** resulted in the production of complex mixtures of unisolable oligomeric materials.[13] However, further studies according to this strategy are ongoing.

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References and Notes

(1) This work was preliminarily presented in parts at: (a) The 62nd Annual Autumn Meeting of The Chemical Society of Japan, Sapporo, Japan, Sept 1991. Kotani, J.; Suzuki, M.; Saegusa, T. *Prepr. II* **1992**, 901. (b) The 41st Annual Meeting of The Society of Polymer Science, Japan, Yokohama, Japan, May 1992. Kotani, J.; Suzuki, M.; Saegusa, T. *Polym. Prepr. Jpn.* **1992**, *41*, 334; *Engl. Ed.* **1992**, *41*, E112. (c) The 4th SPSJ International Polymer Conference, Yokohama, Japan, Nov 1992. Suzuki, M.; Kotani, J.; Saegusa, T. *Prepr.* **1992**, 396. (d) Suzuki, M. In *Mukikobunshi 1*; Kajiwara, M., Murakami, K., Eds.; Sangyo Tosho: Tokyo, 1992; pp 5–16.

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(8) Monomer **1** was prepared according to a modified literature method: Ishikawa, M.; Kumada, M. *Synth. React. Inorg. Met.-Org. Chem.* **1971**, *1*, 229.

(9) *n*-BuLi also acted as initiator to produce **2**, but this reaction was not reproducible. It is assumed that a trace of a contaminant sensitively affected the reaction. KF and KHF_2 with 18-crown-6 required room temperature for the initiation so that the reaction produced no polymer but cyclic oligosilanes (see text).

(10) This compound was prepared by hydrosilation of vinylferrocene with chlorodimethylsilane.

(11) ^{29}Si NMR (C_6D_6) δ −39.26, −37.54, −36.88; ^{1}H NMR (C_6D_6, residual protons of C_6D_6 = δ 7.15) δ −0.017 (3H), 0.000 (3H), 0.159 (3H), 0.174 (3H), 0.384 (6H), 0.425 (6H), 0.599 (3H), 7.12–7.20 (m, 3H), 7.49 (d, J = 6.5 Hz, 2H); ^{13}C NMR (C_6D_6, carbons of C_6D_6 = δ 128.0) δ −6.18, −4.15, −4.11, −3.85, −3.83, −3.10, −2.76, 134.81, 138.45 (two more peaks due to phenyl carbons were hidden by strong peaks of C_6D_6).

(12) The following papers deal with examples and measurement parameters of 2D ^{1}H–^{29}Si correlated NMR spectra: (a) Maxka, J.; Huang, L.-M.; West, R. *Organometallics* **1991**, *10*, 656. (b) Babu, G. N.; Newmark, R. A. *Macromolecules* **1991**, *24*, 4503. A clue for the analysis is that there appears a relatively weaker cross-peak due to vicinal H–Si correlation (through three bonds) together with a stronger one due to geminal H–Si correlation (through two bonds). The relative intensity of a cross-peak depends on an H–Si coupling constant as well as on the numbers of these nuclei.

(13) This was probably due to the bond scission of Si–C_6F_5 or Si–OEt in the cases of **8** and **10**. The trimethylsilyl group of **9** was probably so weak to stabilize the silyl anion that the backbiting reaction so frequently occurred as to give no polymer.