

Anionic Ring-Opening Polymerization of 1,2,2-Trimethyl-1-phenyl-1,2-disilacyclopentane

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ABSTRACT: The anionic ring-opening polymerization of 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane took place in THF at 0 ~ -78°C. The initiators were ⁿBu₄NF, PhMe₂SiK, and (PhMe₂Si)₂Cu(CN)Li₂. When PhMe₂SiK was used, the addition of HMPA was required for the polymerization. The polymerization initiated with (PhMe₂Si)₂Cu(CN)Li₂ showed a living character to some extent. The product polymers contained not only a head-to-tail structure but also head-to-head and tail-to-tail structures, whose amounts were dependent on the initiator: 4% (ⁿBu₄NF), 30% (PhMe₂SiK), and 12% ((PhMe₂Si)₂Cu(CN)Li₂). These values reflect the efficiency of the phenyl group to stabilize the silyl anion that is the propagating end.

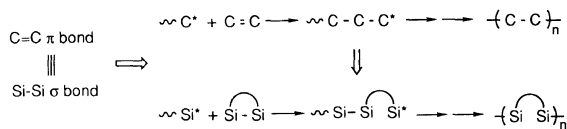
KEY WORDS Anionic Polymerization / Ring-Opening Polymerization / Disilacyclopentane / Silicon-Containing Polymer / Silyl Cuprate /

It is of much interest that an Si–Si σ bond has analogous character and reactivity with a C=C π bond, e.g., σ – σ or σ – π conjugation, coordination to transition metals, and C–T complex formation.¹ This analogy, linking with the fact that polymerization of a C=C π bond is the biggest and most basic field in polymerization chemistry, prompted us to study polymerization participated with an Si–Si σ bond. It is inevitably designed as ring-opening polymerization that proceeds through scission-recombination of Si–Si σ bonds (Scheme 1). The propagating end is accordingly a silicon active species, as is interestingly compared with the ordinary vinyl polymerization conducted by a carbon active species.

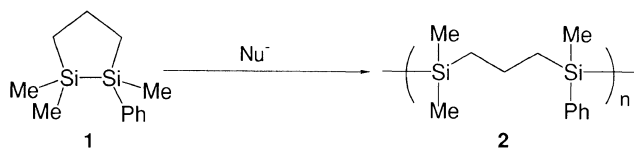
In this context, we have already found the anionic ring-opening polymerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane and -hexane.² It is then interesting to investigate a substituent effect on this polymerization. We here describe the anionic ring-opening polymerization of 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane (**1**) (Scheme 2). A phenyl group is capable of conjugating with an Si–Si bond and stabilizing a silyl anion that

is the propagating end, however, weakly as compared with these effects on a C=C π bond and a carbon anion.¹ By introducing a phenyl group on a silicon atom, we recently succeeded in regio-selective ring scission of cyclopentasilane leading to the production of the sequence ordered polysilane by way of anionic ring-opening polymerization.³ This paper presents further information on the substituent effects of the phenyl group, discussing the anionic ring-opening polymerization of **1**. In addition, a higher ordered silylcuprate is introduced as a new initiator.

Before mentioning the results, we have to refer to the related studies. Polymerizations of cyclic carbosilanes such as silacyclobutane and 1,3-disilacyclobutane were found more than thirty years ago. Recently, increasing interest in Si-containing polymers as new materials has promoted reinvestigation of this field, including studies about several new types of monomers.^{4,5} There thus appeared polymerizations of cyclic systems containing an Si–Si bond(s): the thermal or AlCl₃-catalyzed polymerization of benzo-1,2-disilacyclobutene,⁶ the anionic polymerization of 1,2,3,4-tetramethyl-1,2,3,4-tetra-phenylcyclooctasilane,⁷ the anionic polymerizations of 1-phenyl-7,8-disilabicyclo[2.2.2]octa-2,5-dienes,⁸ and the anionic, thermal, or radical polymerizations of 1,2,5,6-tetrasilacycloocta-3,7-dienes.⁹ The former two include the scission-recombination process of the Si–Si bond. The second polymerization, published during our study, apparently propagates by the reaction of an Si–Si bond with a silyl anion. From a larger viewpoint on the basis of the above-mentioned conception, we have advanced our studies. It should be mentioned that palladium-catalyzed copolymerizations of cyclopolysilanes and cyclic disilanes with *p*-quinones were recently reported.¹⁰



Scheme 1



Scheme 2

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EXPERIMENTAL

Diethyl ether and tetrahydrofuran (THF) were dried over Na and freshly distilled under Ar before use. Hexane and toluene were dried over Na, distilled, and stored under N₂. hexamethylphosphoramide (HMPA) and acetonitrile dried over CaH₂ were distilled under Ar and stored over molecular sieves 3A (Merck). Other commercially available reagents were used without further purification unless otherwise noted.

GPC analysis was carried out by use of Shodex[®] K-803 and K-802 (Showa Denko) as the column and CHCl₃ as the eluent. The GPC calibration curves were made on the basis of polystyrene standards. VPO measurement was carried out in CHCl₃ at 40°C.

NMR measurement on the course of monomer synthesis was performed using HITACHI R-600 (60 MHz for ¹H) and R-900 (90 MHz for ¹H) spectrometers. NMR spectra of the polymers were recorded on a JOEL JMX-JX-400 spectrometer (400 MHz for ¹H).

Monomer Synthesis

The monomer, 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane (**1**), was prepared according to the following three steps under N₂ (Scheme 3).

(1) To a solution of dichloro(methyl)(phenyl)silane (10 g, 52 mmol) in diethyl ether (50 ml) was slowly added allylmagnesium chloride¹¹ (0.48 M in diethyl ether, 109 ml, 52 mmol) at -78°C over 1 h. After stirring for 2 h, the reaction mixture was allowed to warm to ambient temperature. MgCl₂ precipitated was filtered off under N₂ and the filtrate was concentrated under reduced pressure. The residue was distilled to give allyl(chloro)-(methyl)(phenyl)silane (7.8 g, 76%): bp 56–57°C/1.2 mmHg; ¹H NMR (CDCl₃) δ 0.57 (s, 3H), 1.78 (dd, *J* = 7.6 Hz, *J* = 12.0 Hz, 2H), 4.45–5.05 (m, 2H), 5.21–6.05 (m, 1H), 6.87–7.81 (m, 5H).

(2) To a solution of chloro(dimethyl)silane (7.0 g, 75 mmol) in toluene (100 ml) containing a catalytic amount of H₂PtCl₆·6H₂O was added allyl(chloro)-(methyl)(phenyl)silane (10 g, 51 mmol) over 30 min. The addition should be controlled because moderate heat evolution was observed after an induction period (a few minutes). After the exothermic reaction ceased, the reaction mixture was heated to reflux for 30 min. The solvent was then excluded under reduced pressure and the residue was distilled to give 2,6-dichloro-6-methyl-2-phenyl-2,6-disilaheptane (12.5 g, 84%): bp 105–110°C/0.5 mmHg; ¹H NMR (CDCl₃) δ 0.23 (s, 6H), 0.57 (s, 3H), 0.68–1.85 (m, 6H), 7.06–7.74 (m, 5H).

(3) Lithium metal (0.65 g, 95 mg atom) (lithium oxide on the surface should be excluded as much as possible) was cut into small pieces and simultaneously dropped into THF (120 ml). To the mixture cooled to 0°C was slowly added 2,6-dichloro-6-methyl-2-phenyl-2,6-disilaheptane (13.0 g, 45 mmol) in THF (15 ml) over 1 h with vigorous stir. After 2.5 h at 0°C, THF was evaporat-

ed from the reaction mixture under reduced pressure. Hexane (100 ml) was added to the residue and the precipitated material was filtrated off under N₂. To the filtrate was added a diethyl ether solution of methyl lithium (1.0 M, 28 ml, 28 mmol) at 0°C. After disappearance of the siloxane (by-product) was confirmed by gas chromatography (after 2 h), excess of iodomethane was added to neutralize the mixture; when the siloxane still remained, methyl lithium was added and the reaction was continued. The precipitate, lithium iodide, was filtrated off under N₂, and the filtrate was subjected to the distillation under reduced pressure to give 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane (3.2 g, 31%): bp 72–75°C/0.8 mmHg (lit.¹²: 105°C/2.5 mmHg); ¹H NMR (CDCl₃) δ 0.12 (s, 3H), 0.21 (s, 3H), 0.40 (s, 3H), 0.65–1.12 (m, 4H), 1.64–2.01 (m, 2H), 7.31–7.62 (m, 5H); ¹³C NMR (CDCl₃) δ -4.38, -3.00, -2.65, 18.87, 19.91, 23.72, 127.48, 128.17, 134.07, 138.89.

Polymerization with ⁿBu₄NF

According to the literature,¹³ commercially available ⁿBu₄NF hydrate was azeotropically dried twice with benzene-acetonitrile (3 : 1, v/v) under reduced pressure and kept *in vacuo* for 12 h. THF was then added to the residue. The concentration of ⁿBu₄NF was determined by relative weight content.

To **1** (220 mg, 1 mmol) in THF (1 ml) was added THF solution of ⁿBu₄NF (0.02 mmol) under Ar at the temperature shown in Table I. The conversion of **1** was monitored by gas chromatography. After **1** was almost consumed, excess MeI (50 μl) for the initiator was added to the reaction mixture. Pouring this mixture into MeOH precipitated the paste-like polymer: ¹H NMR (CD₂Cl₂, Figure 1) δ -0.02 (s, 6H), 0.24 (s, 3H), 0.61 (t, *J* = 8.2 Hz, 2H), 0.84 (t, *J* = 7.9 Hz, 2H), 1.29 (m, 2H), 7.26 (m, 3H), 7.35 (m, 2H); ¹³C NMR (CD₂Cl₂, Figure 2) δ -5.74, -5.73, -3.43, -3.41, 19.06, 19.07, 20.18, 20.52, 128.09, 128.58, 134.46, 139.28; ²⁹Si NMR (CDCl₃, ppm, Figure 3) -20.80, -18.57; *Anal. Calcd*: C 65.38, H 9.14, Found: C 64.46, H 9.16: a little error in the C content is assumably due to ceramization.

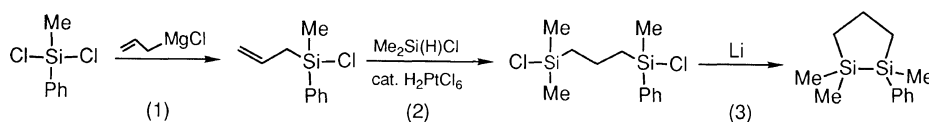
Polymerization with PhMe₂SiK

A THF solution of PhMe₂SiK was prepared as follows. To potassium metal (150 mg, 3.84 mg atom) in THF (5 ml) was added 1,1,2,2-tetramethyl-1,2-diphenyldisilane (500 mg, 1.85 mmol). The mixture was stirred for 5 h at room temperature under Ar. The concentration of PhMe₂SiK, evaluated by titration with 0.01 M HCl aq, was 0.600 mmol g⁻¹ solution.

The procedure for the polymerization of **1** using PhMe₂SiK was the same as that using ⁿBu₄NF with the exception that HMPA (50 μl) was added to the reaction media.

Polymerization with (PhMe₂Si)₂Cu(CN)Li₂

According to the literature,¹⁴ (PhMe₂Si)₂Cu(CN)Li₂



Scheme 3

was prepared just before use by reaction of PhMe_2SiLi with a homogenous solution of CuCN with LiCl in THF. The preparation of PhMe_2SiLi was carried out in a similar way to that of PhMe_2SiK . Stirring 1,1,2,2-tetramethyl-1,2-diphenyldisilane (1.35 g, 5 mmol) with lithium metal (70 mg, 10 mg atom) in THF (25 ml) at -10°C for 36 h produced a THF solution of PhMe_2SiLi whose concentration was 0.417 mmol g^{-1} solution. CuCN purchased from Mitsuwa Chemicals was azeotropically dried with toluene under reduced pressure three times, and LiCl was dried over a flame *in vacuo*. CuCN was mixed with 2 eq of LiCl in THF to give a homogenous solution. The concentration was evaluated by relative weight content.

The polymerization of **1** was carried out under Ar at the temperature shown in Table II. The THF solutions of $\text{CuCN} \cdot 2\text{LiCl}$ (0.2 mmol) and PhMe_2SiLi (0.4 mmol) were mixed in THF (10 ml) containing *n*-decane (1 mmol) as the internal standard for gas chromatographical analysis. After 1 h, **1** (10 mmol) was added to the reaction mixture, and conversion was monitored. The addition of MeI (200 μl) was followed by gradually warming the mixture to ambient temperature. The precipitate obtained by pouring the reaction mixture into MeOH was resolved in CH_2Cl_2 . The solution was washed with dil NH_3 aq to extract copper and dried over MgSO_4 . Evaporating CH_2Cl_2 under reduced pressure gave the pure polymer.

RESULTS AND DISCUSSION

Monomer Synthesis

The monomer, 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane (**1**), was synthesized in 1964.¹² However, we applied the method for the preparation of 1,1,2,2-tetramethyl-1,2-disilacyclopentane (**3**)² to prepare **1** (Scheme 3). In the final step, however, HMPA whose addition was required for the production of **3** was unnecessary for **1**. This agrees with the fact that dimethylphenylsilyl lithium is generated in THF without HMPA but trimethylsilyl lithium is not.¹ As generally observed in a coupling reaction of chlorosilane with alkali metal, monomer **1** produced in the final step was also contaminated with the siloxane, *i.e.*, 2,6,6-trimethyl-2-phenyl-1-oxa-2,6-disilacyclohexane, whose chromatographical separation was difficult. Washing with cold concd H_2SO_4 is usually effective to eliminate siloxane.¹⁵ But this method was not applicable because **1** was easily decomposed by concd H_2SO_4 . We thus explored a good method to eliminate the contaminant and successfully found treatment with methyl lithium in hexane-ether to be effective to liberate **1** from the contamination with the siloxane.

Polymerization

Initiators such as ${}^n\text{Bu}_4\text{NF}$, PhMe_2SiK , and $(\text{PhMe}_2\text{-Si})_2\text{Cu}(\text{CN})\text{Li}_2$ were used for the anionic ring-opening polymerization of **1**. The results are discussed comparatively about each initiator in the following sections.

Initiated with ${}^n\text{Bu}_4\text{NF}$

Owing to the Si-affinity of fluoride anion, ${}^n\text{Bu}_4\text{NF}$ is capable of initiating the polymerization of **1** by the

Table I. Anionic ring-opening polymerization of 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane (**1**)

Run	Initiator ^a	Solvent	Temp	Time	Yield ^b	M_n^c	M_w/M_n^c
			$^\circ\text{C}$	h	%		
1	${}^n\text{Bu}_4\text{NF}$	THF	0	4	72	6400	2.09
2	${}^n\text{Bu}_4\text{NF}$	THF	-50	1	97	9300	2.17
3	PhMe_2SiK	THF/HMPA ^d	0	4.5	78	6000	1.91
4	PhMe_2SiK	THF/HMPA ^d	-40	6	91	19000	2.22

^a 2 mol% for **1**. ^b Conversion of **1** > 90%, yield = wt% of a MeOH -insoluble part. ^c Estimated by GPC (PSt standard: eluent, CHCl_3). ^d THF-HMPA = 20:1 (v/v).

reaction with the Si-Si bond to generate the metal-free silyl anion. The polymerization smoothly took place in THF (runs 1 and 2 in Table I) in contrast with the polymerization of **3** requiring the addition of HMPA.² It is evident that this difference arises from the anion stabilization effect of the phenyl group. The reaction mixtures of both of these two runs showed two elution peaks on the GPC charts; they were ascribable to the polymer and the oligomer, respectively. This finding indicates that the polymerization under above conditions includes some side reactions such as back-biting and chain-transfer. The polymer was isolated by the precipitation into MeOH .

The structure of the product polymer was investigated in detail by NMR spectroscopy. Figures 1, 2, and 3 respectively shows the ${}^1\text{H}$, ${}^{13}\text{C}$, and ${}^{29}\text{Si}$ NMR spectra of the polymer produced at 0°C (run 1). These spectra suggest the fairly regular structure of the polymer shown as **2**. The ${}^{29}\text{Si}$ NMR spectrum (Figure 3), showing two peaks except for a trace of peaks, informs that two kinds of silicon atoms almost exclusively construct the polymer; these peaks were easily assigned on the basis of the chemical shift values (a trace of an irregular structure is discussed in the next section). The peak assignment in the ${}^1\text{H}$ NMR spectrum (Figure 1) was confirmed by the ${}^1\text{H}$ NOESY 2D NMR spectrum. Then, the peaks in the ${}^{13}\text{C}$ NMR spectrum (Figure 2) have been assigned with the aid of ${}^1\text{H}$ - ${}^{13}\text{C}$ COSY 2D NMR spectrum. It is noted that there are observed clearly separate two peaks for the carbons E and very close two peaks for the carbons A and B respectively. The two methyl carbons labeled E are essentially different in NMR spectroscopy due to the vicinal substituents so that the above observation is reasonable for the carbons E. As for the carbons A and B, ζ -tacticity has to be considered to explain the peak separation. Theoretically, the carbon A should have shown three peaks due to triad. It seems that they are not completely discriminated from each other. On the other hand, it is reasonable that the diad causes the peak for the carbon B to separate into two.

Initiated with PhMe_2SiK

When PhMe_2SiK was used as the initiator, the addition of a small amount of HMPA (THF : HMPA = 20 : 1, v/v) was required for the polymerization of **1** (runs 3 and 4 in Table I). The effect of HMPA is to activate the silyl anion by coordination to potassium cation. In contrast with the polymerization initiated with ${}^n\text{Bu}_4\text{NF}$, GPC analysis of these reaction mixtures showed no noticeable

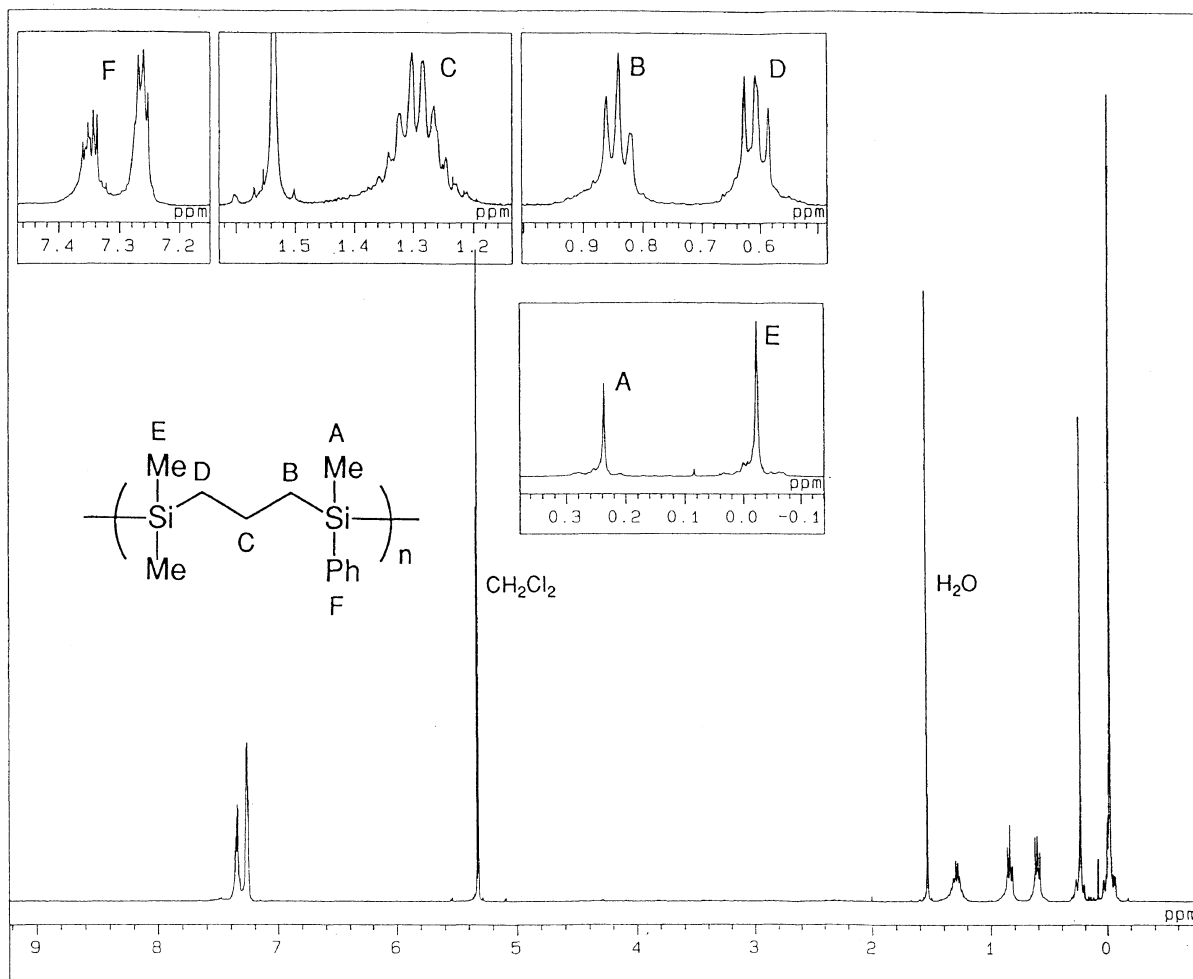
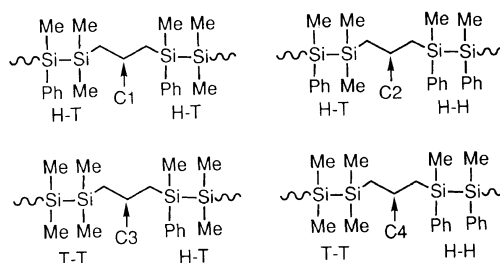


Figure 1. ^1H NMR spectrum (in CD_2Cl_2) of the polymer produced with $t\text{Bu}_4\text{NF}$ (run 1 in Table I).

peak due to the oligomer. This means that the back-biting reaction hardly occurred during the polymerization. The higher molecular weight polymer was obtained at the lower reaction temperature that suppressed the chain-transfer reaction, but its molecular weight distribution was still over 2.

The product polymers showed very different NMR spectra from that produced with $t\text{Bu}_4\text{NF}$. The NMR spectra of the polymer produced at -40°C (run 4) was analyzed in detail. In the ^{29}Si NMR spectrum (Figure 4), there were observed two pairs of the bigger and the smaller peaks. This chart informs that the polymer consists of not only the H-T (head to tail) but also the H-H and T-T connections. A couple of the smaller peaks at -18.75 and -21.17 ppm are assignable to the silicons of the T-T and H-H connections, respectively. The proportion of the H-H (T-T) to the H-T connection was easily calculated to be H-T : H-H(T-T) = 0.70 : 0.15 on the basis of the integral ratio of the corresponding peaks.

The ^1H and ^{13}C NMR spectra are rather complicated (Figures 5 and 6). The clue to analyze the structure is obtained only from the peaks due to the carbon C in the ^{13}C NMR spectra. It is noticed on the expanded chart of the corresponding part that there are observed two smaller peaks having equal intensity on the both sides of one bigger peak. All of them are assignable to the carbon C. As shown in Scheme 4, there are four



Scheme 4

kinds of the carbon C due to the H-T connectivities. Considering the environment around the carbon C, the three peaks are reasonably assigned as follows; the central peak is due to not only the carbon C1 but also the carbon C4, and the other two are due to the carbons C2 and C3. Thus, from the integral ratio ($=0.410$) of one of the latter peaks to the former, the relative content ($=X$) of the H-H (T-T) connection can be calculated according to the equation: $2X(1-2X)/\{X^2+(1-2X)^2\}=0.410$. As the result, the evaluated value of the ratio H-T : H-H(T-T) ($=(1-2X):X$) was 0.70 : 0.15, the same as that calculated on the basis of the data in the ^{29}Si NMR spectrum. When careful attention is paid again to the same part of the ^{13}C NMR spectrum of the polymer produced with Bu_4NF (Figure 2), two tiny peaks are noticed to imply the existence of a trace amount of the H-H and T-T structures. The ratio H-T : H-H(T-T) was

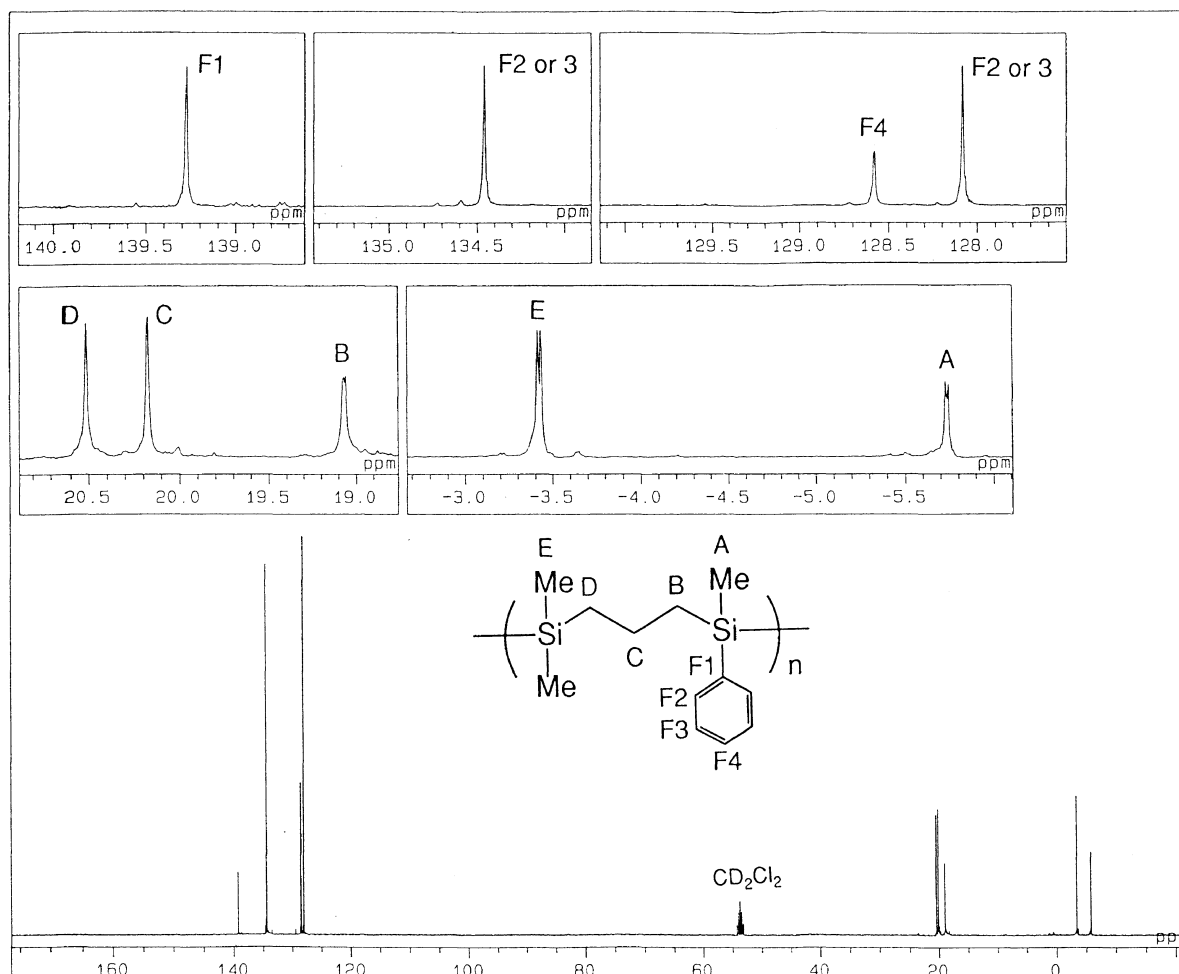


Figure 2. ^{13}C NMR spectrum (^1H complete decoupling, in CD_2Cl_2) of the polymer produced with $^t\text{Bu}_4\text{NF}$ (run 1 in Table I).

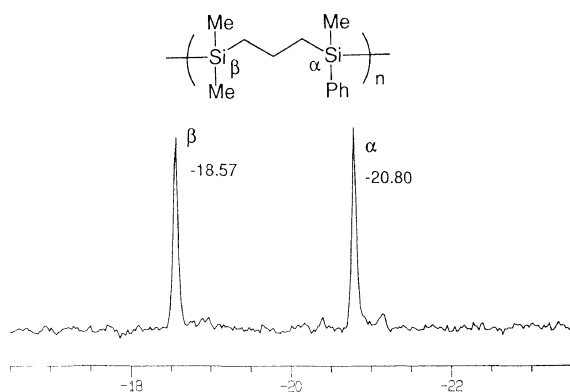


Figure 3. ^{29}Si NMR spectrum (^1H gate decoupling, in CDCl_3) of the polymer produced with $^t\text{Bu}_4\text{NF}$ (run 1 in Table I).

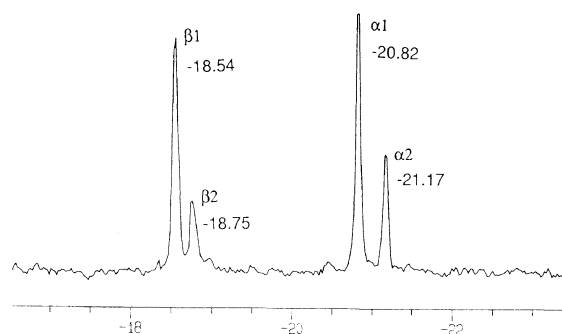
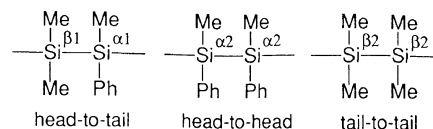


Figure 4. ^{29}Si NMR spectrum (^1H gate decoupling, in CDCl_3) of the polymer produced with Me_3SiK (run 4 in Table I).

calculated as 0.96:0.02.

Formation of the H-H and T-T structures means that not only the alkyl(methyl)(phenyl)silyl anion but also the alkyl(dimethyl)silyl anion is generated as the propagating end. Although the silyl anion is certainly stabilized by the introduction of phenyl in place of methyl on the silicon atom, its efficiency is dependent on a solvent, an additive, and a counter cation. When the silyl anion coupled with potassium cation is compared with a non-metallic silyl anion generated with $^t\text{Bu}_4\text{NF}$, the former is in a more stable state than the latter.

Accordingly, it seems that the stabilization effect of the phenyl group is less efficient in the case of the former. This may be a reasonable explanation for the observation that the polymer produced with PhMe_2SiK contained more H-H and T-T structures.

Initiated with $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$

Although cuprate is usually derived from RLi or RMgX , the reaction feature of the former is much

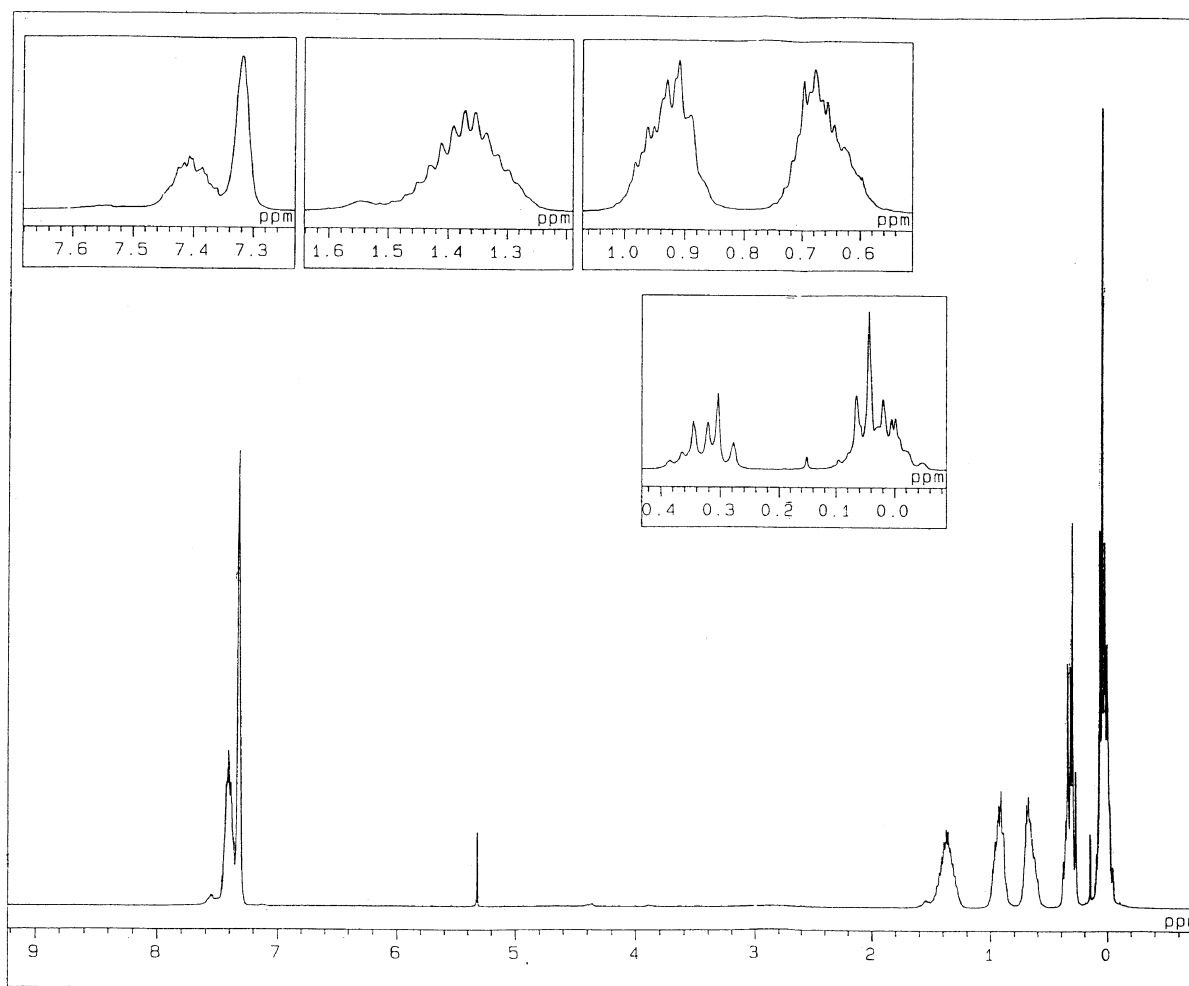


Figure 5. ^1H NMR spectrum (in CD_2Cl_2) of the polymer produced with Me_2PhSiK (run 4 in Table I).

different from that of the latter reagents. Thus there have been some investigations using cuprate to initiate vinyl polymerization.¹⁶ Here we made use of silyl cuprate, *i.e.*, $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$, for the polymerization of **1**. As was prompted by our preliminary report,¹⁷ $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ was very recently used as the initiator for the polymerization of cyclotetrasilane.¹⁸ Table II shows the results of the polymerization of **1** by use of $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$. The polymerization took place at $0 \sim -78^\circ\text{C}$ in THF without HMPA to produce the polymer quantitatively based on the conversion. It should be discussed first that the initiator in run 1 showed very different character from those in other runs. The initiator was freshly prepared just before charging the monomer. The initiator solution prepared at 0°C was deep purple while that prepared below -40°C was red. It is known that the THF solution of $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ is red,¹⁴ so that it seems that the initiator prepared at 0°C is not actually $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$. Interestingly, the product polymer in run 1 had a much higher molecular weight and narrower molecular weight distribution than in other runs, though the polymerization took a longer time. This polymerization was, however, poorly reproducible; the molecular weight of the product polymer varied from 18000 to 35000, and often the polymerization stopped before completion or did not proceed. These observations indicate that a small amount of active

Table II. Anionic ring-opening polymerization of 1,2,2-trimethyl-1-phenyl-1,2-disilacyclopentane (**1**) initiated with $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2^a$ in THF

Run	Temp ^b	Time	Conv. ^c	M_n		M_w/M_n^d
	$^\circ\text{C}$			h	%	
1	0	21	— ^f	30000	—	1.09
2	0 ^g	1.1	91	5800	5000	1.49
3	-40	1.0	91	7000	5000	1.18
4	-50	0.3	51	4200 (4000 ^h)	2800	1.19
5	-50	1.2	88	6600 (6400 ^h)	4800	1.21
6	-78	5.5	77	5900	4200	1.18
7	-78	18	94	7500	5200	1.23

^a 2 mol% of **1**. ^b Cuprate was also prepared at this temperature except for run 2. ^c Determined by gas chromatography. Polymer yield was quantitative based on the conversion. ^d Estimated by GPC (PSt standard, eluent: CHCl_3) unless otherwise noted. ^e $\{([\text{I}] \times \text{conv.}/100)/(2 \times [\text{cuprate}])\} \times (\text{MW of } \mathbf{1})$. ^f Although the conversion was not determined, the polymer yield was 98%. ^g Using the cuprate prepared at -40°C (see the text). ^h Determined by VPO (CHCl_3 , 40°C).

species, unidentified, was inconstantly generated at 0°C . On the other hand, run 2, where the monomer was charged to the cuprate prepared at -40°C and the mixture was immediately warmed to 0°C , gave com-

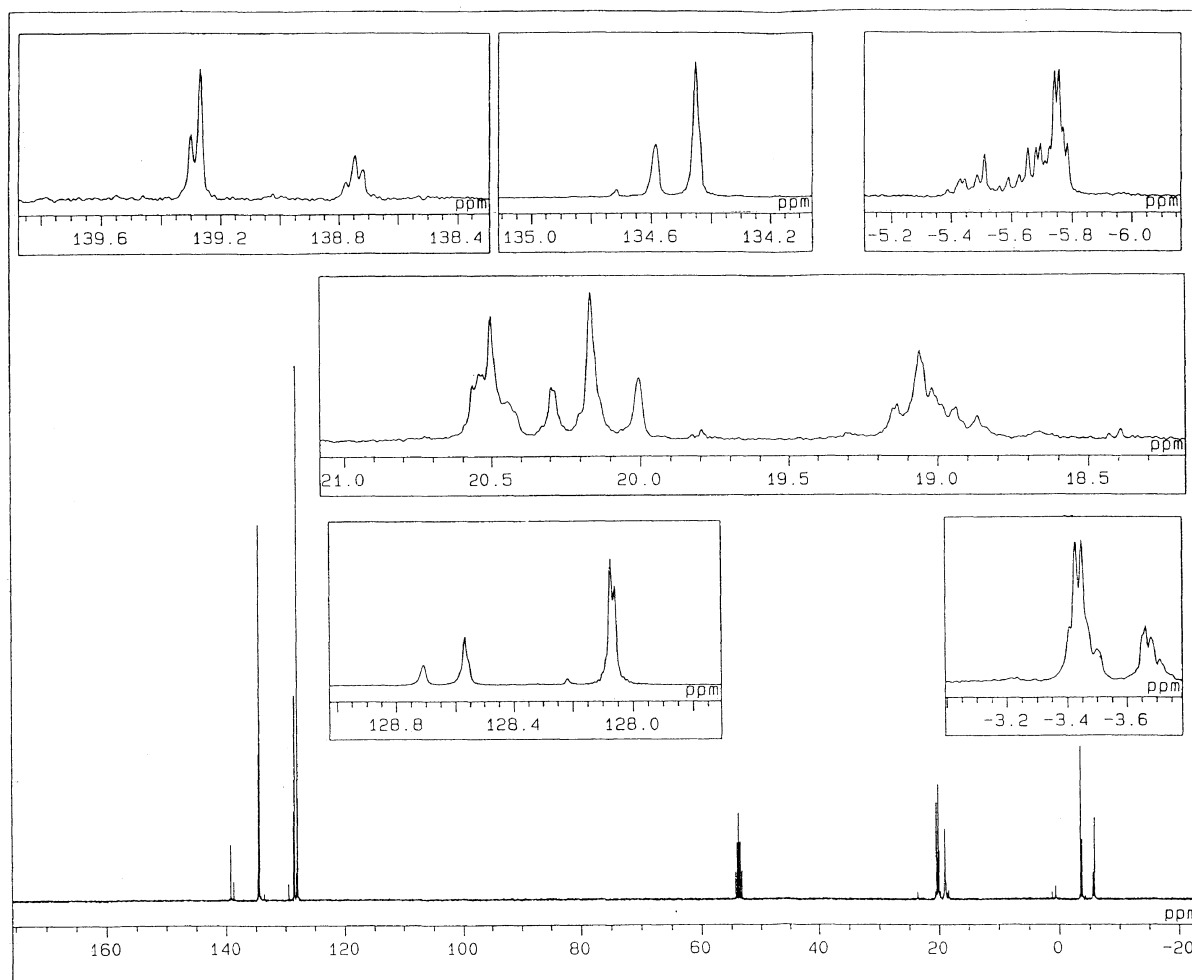


Figure 6. ^{13}C NMR spectrum (^1H complete decoupling, in CD_2Cl_2) of the polymer produced with Me_2PhSiK (run 4 in Table I).

parable results for runs 3–7. In these runs, the molecular weight of the product polymer almost linearly increased with the conversion of the monomer and was always about 1.4 times the values calculated from the conversion together with the feed ratio of the monomer to the initiator, which is bifunctional. Additionally, the values of the molecular weight distribution were constantly about 1.2. These observations mean that the polymerization has a living character to some extent but the silyl anion added dose not completely work to initiate the polymerization. It is assumed that $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ is not quantitatively formed, as is actually shown in the literature.¹⁴ In contrast with $^t\text{Bu}_4\text{NF}$ and PhMe_2SiK , however, $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ induced the quantitative conversion of the monomer to the polymer having the narrower molecular weight distribution. These behaviors of the polymerization initiated with $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ is owing to the high covalency of an Si–Cu bond (electronegativity: Si = 1.8 and Cu = 1.9). The polymerization may propagate *via* anionic coordination mechanism or one-electron transfer process.

Analysis of the polymer structure by NMR spectroscopy indicated that the polymer contained a small amount of the H–H and T–T connections. As discussed in the former section, the contents of them were evaluated from the peaks due to the carbon C in the ^{13}C NMR

spectrum: H–T : H–H(T–T) = 0.92 : 0.04 (run 1) and = 0.88 : 0.06 (run 5). The high covalency of the Si–Cu bond is assumed to reduce the anion stabilization effect of the phenyl group and cause contamination of the H–H and T–T structures in the product polymer.

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