

Cyclopolymerization Behavior of Bis(dimethylvinylsilyl)methane

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ABSTRACT: Anionic cyclopolymerization of bis(dimethylvinylsilyl)methane (BVSM) in hexane, which affords a polymer having six-membered rings as repeating cyclic units, is investigated. Low polymer yields in the polymerization of BVSM with *n*-butyllithium (*n*-BuLi) in the absence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) are attributed to cross-linking reactions and association of the propagating ends at -10°C and elimination of lithium hydride from the propagating end at 40°C . Polymerization with *n*-BuLi/TMEDA is accompanied, though not frequently, by the abstraction of the methylene proton interposed by two silicon atoms, which forms an inactive anion. This abstraction is caused by the propagating end in the six-membered ring. At high monomer concentration, 0.5 mol l^{-1} , cross-linking reaction is not negligible even in the presence of TMEDA. As initiators, *n*-, *s*-, *t*-BuLi are examined, and only *s*-BuLi/TMEDA is found to cause the proton abstraction from the methylene interposed by two silicon atoms. The effects of the initiator are explained by the nucleophilicity of BuLi and the steric hindrance in the abstraction. The effects of three amines on the polymerization are evaluated. TMEDA is the most suitable for the cyclopolymerization of BVSM among them.

KEY WORDS Anionic Polymerization / Cyclopolymerization / Bis(dimethylvinylsilyl)methane / *N,N,N',N'*-Tetramethylethylenediamine / Proton Abstraction / Cross-Linking /

Many attempts have been made to prepare polymers with characteristic structure, such as macrocyclics and ladder polymers. Cyclopolymerization is an effective means to obtain polymers having cyclic units in their main chains, and hence it has been studied for several decades.¹ The introduction of cyclic structure into the main chain of a linear polymer causes drastic changes in the physical properties, such as glass transition temperature and thermal stability.

We reported that bis(dimethylvinylsilyl)methane (BVSM) undergoes anionic cyclopolymerization with *n*-butyllithium (*n*-BuLi) in hexane in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (Scheme 1).² The resulting polymer contains only disilacyclohexane rings as repeating cyclic units and exhibits rather narrow molecular weight distribution (MWD). The number-average molecular weight (M_n) is in accord with the calculated value for the polymer without cross-linking structure.

Seyferth and Robison reported the cyclopolymerization of similar monomers of the type $(\text{CH}_2=\text{CHSi}(\text{CH}_3)_2\text{X})_2$ ($\text{X}=\text{O}, \text{NH}, \text{NCH}_3$) by a radical mechanism.³ In the polymers, five- and six-membered cyclic units, and possibly seven-membered cyclic and acyclic units are present. Anionic cyclopolymerization has been ever reported solely on 1,3-divinylpentamethyldisilazane ($\text{X}=\text{NCH}_3$ in the above formula) by Stober and coworkers.⁴ Although they obtained a soluble polymer by use of *n*-BuLi in the presence of triethylamine, detailed characterization of the resulting polymer was not provided. $(\text{CH}_2=\text{CH})_i\text{Si}(\text{CH}_3)_{4-i}$ ($i=2, 3, 4$) also undergoes anionic cyclopolymerization with BuLi/TMEDA.⁵⁻⁷ Six-

membered and bicyclic ring structures are formed in the main chains of the resulting polymers. Each ring consists of two monomer units, and not all vinyl groups are consumed.

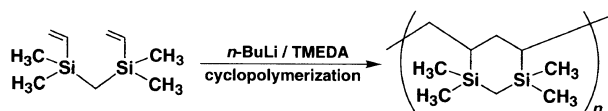
Cyclopolymerization that forms silicon-containing rings in the main chain has been studied for other various monomers. The cyclopolymerizations of diallylsilanes,⁸⁻¹⁰ dimethylsilyl silanes,⁹ allyl(3-butenyl)silanes,¹¹ bis(3-butenyl)silanes,¹¹ triallylsilanes,^{10,12} dipropargylsilanes,¹³ and dimethyldivinyloxysilane¹⁴ were carried out by radical, cationic, or coordination initiators, but anionic mechanisms could not be employed.

This paper reports the details of the anionic cyclopolymerization of BVSM, which affords the polymer with designed M_n and narrow MWD.

EXPERIMENTAL

Materials

n-BuLi (Wako Pure Chemical, 1.6 mol l^{-1} solution in hexane) was purified by filtration. *s*-BuLi (Aldrich, 1.3 mol l^{-1} solution in mixed hexanes) and *t*-BuLi (Aldrich, 1.7 mol l^{-1} solution in pentane) were used after filtration and solvent substitution *in vacuo*. Hexane was distilled from a sodium-benzophenone complex. Tetrahydrofuran (THF) used for Grignard reaction was distilled from successive CaH_2 , potassium, and a sodium-benzophenone complex. Diethyl ether was distilled over CaH_2 . Chloromethyldimethylvinylsilane and dimethylvinylchlorosilane (DMVCS) (both from Shin-Etsu Silicon Chemicals) were distilled at atmospheric pressure. TMEDA, *N,N,N',N'*-tetraethylethylenediamine (TEEDA), and triethylamine (TEA) (all from Nakalai Tesque) were distilled over CaH_2 and then over sodium mirror. Magnesium turnings for Grignard reaction (Nakalai Tesque) and other chemicals were used as received.



Scheme 1.

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Table I. Anionic polymerization of BVSM in the absence of TMEDA^a

Entry	[BVSM]	[<i>n</i> -BuLi]	Temp	Yield	$M_n \times 10^{-3}$		M_w/M_n^c
	mol l ⁻¹	mmol l ⁻¹	°C	%	Calcd ^b	GPC ^c	
1 ^d	0.10	2.0	-10	2	0.2	1.0	—
2 ^d	0.52	10	-10	2	0.2	1.3	—
3	0.10	2.0	40	8	0.7	1.8	—
4 ^d	0.50	10	40	4	0.4	2.2	—
5	0.10	3.0	40	26	1.4	2.1	1.3 ₁

^a Polymerization time, 96 h; solvent, hexane. ^b Calculated from the monomer-to-initiator ratio and percent polymer yield on the assumption that no cross-linking reaction takes place. ^c Estimated by GPC calibrated with polystyrene standards. ^d Data in ref 2.

Synthesis of BVSM

Magnesium turnings (6.5 g, 0.27 mol) and 75 ml of THF were placed in a 500 ml three-necked round-bottomed flask equipped with a reflux condenser, a dropping funnel, and a magnetic stirrer bar. A solution of chloromethyl dimethylvinylsilane (25 g, 0.18 mol) in 50 ml of THF was added dropwise during 2 h into the flask under a nitrogen atmosphere. This was initially carried out at room temperature, but the flask was cooled with an ice bath after when exothermic reaction began. After the reaction mixture was stirred for an additional 2 h at room temperature, a solution of DMVCS (21 g, 0.17 mol) in 50 ml of THF was added dropwise during 1 h at 0°C with stirring. The mixture was allowed to stand overnight at room temperature. The addition of aqueous HCl and 100 ml of diethyl ether caused phase-separation. The organic layer was washed with water, and the solvents were evaporated. The residue was distilled to give 18 g (0.11 mol) of BVSM (52–54°C/11 mmHg; lit.¹⁵ 53°C/11 mmHg) in a 60% yield. IR (neat, cm⁻¹): 3050, 3020, 2960, 2900 (C–H), 1590 (CH₂=CH), 1400, 1250 (Si–CH₃), 1050 (Si–CH₂–Si). 200 MHz ¹H NMR (CDCl₃): δ -0.08 (2H, s, SiCH₂Si), 0.13 (12H, s, SiCH₃), 5.67 (2H, dd, =CH–), 5.89–6.30 (4H, m, CH₂=). 50.3 MHz ¹³C NMR (CDCl₃): δ -0.6 (SiCH₃), 1.2 (SiCH₂Si), 130.4 (CH₂=), 141.0 (=CH–).

Polymerization of BVSM

Polymerization was carried out in hexane at -10°C or 40°C under high vacuum conditions using breakable seal techniques. Solutions of an initiator, an amine if necessary, and BVSM in hexane were introduced into a reactor with stirring in this order. After the reaction mixture was quenched by methanol, it was concentrated by evaporation. The residue was dissolved in benzene, and the solution was washed with water and freeze-dried. When a viscous oligomer was obtained, the monomer could not be completely removed and remained in the oligomer. When a white powdery polymer was obtained, it was further purified by the reprecipitation from benzene/methanol (1:9 v/v). The same work-up was done when DMVCS was used for the quenching. The polymerization was typically carried out using 330 mg (1.8 mmol) of BVSM.

Measurements

M_n and MWD (M_w/M_n) of the polymers were estimated by gel permeation chromatography (GPC) using Toyo Soda HLC-802UR equipped with G2000H and G3000H columns (60 cm each) for low molecular weight

polymers ($M_n < 7 \times 10^3$) or Toyo Soda HLC-802A with two GMH columns (60 cm each) for other polymers. Each instrument was fitted with a refractive index detector and a UV detector. THF was used as the eluent at a flow rate of 1.0 ml min⁻¹. The column temperature was maintained at 40°C. The chromatograms were calibrated with polystyrene standards. Vapor pressure osmometry (VPO) was measured in benzene solution at 40°C using a Corona 117 molecular weight apparatus. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded on a Varian XL-200 spectrometer operated at 200 MHz, 50.4 MHz, and 39.8 MHz, respectively, in the Fourier transform mode. Chloroform-*d*₁ was used as the solvent. Dichloromethane and chloroform-*d*₁ were used as internal references (5.34 ppm and 77.6 ppm) for ¹H and ¹³C NMR measurements, respectively, and tetramethylsilane was used as an external standard for ²⁹Si NMR measurement. IR spectra were recorded on a JASCO IRA-102 spectrophotometer.

RESULTS AND DISCUSSION

Polymerization of BVSM and Characterization of the Resulting Polymer

Typical polymerization results of BVSM with *n*-BuLi in the absence of TMEDA and those in the presence of TMEDA are shown in Tables I and II, respectively. In all entries in Table I, viscous liquid oligomers were obtained. VPO measurement could not be conducted owing to the remaining monomer. Their yields were very low regardless of the initial monomer concentration ([M], 0.1 mol l⁻¹ or 0.5 mol l⁻¹) and polymerization temperature (40°C or -10°C), when the initial monomer-to-initiator ratio ([M]/[I]) was 50 (entries 1–4). Such low polymer yields offer marked contrast to the polymerization results with TMEDA in Table II. Though the polymer yield without TMEDA was somewhat higher at lower [M]/[I] (entry 5), it was affected by the remaining monomer and still was much lower than with TMEDA.

Polymerization in the presence of TMEDA was carried out under conditions of [M]/[I] = 50 and [TMEDA] = [*n*-BuLi]. All polymers in Table II were obtained as white powder and entirely soluble in benzene. With either [M] (0.1 mol l⁻¹ or 0.5 mol l⁻¹) and at either temperature (40°C or -10°C), polymer yield attained 100% in 48 h. Polymerization with [M] of 0.1 mol l⁻¹ at -10°C (entries 6–9) afforded polymers whose M_n s determined by VPO were in accord with those calculated from [M]/[I] and polymer yields on the assumption that no cross-linking

Table II. Anionic polymerization of BVSM in the presence of TMEDA^a

Entry	[BVSM] mol l ⁻¹	Temp °C	Time h	Yield %	$M_n \times 10^{-3}$			M_w/M_n^c
					Calcd ^b	GPC ^c	VPO ^d	
6 ^e	0.10	-10	6	71	6.6	7.6	6.2	1.2 ₇
7 ^e	0.10	-10	12	93	8.6	11.1	8.6	1.2 ₈
8	0.10	-10	24	98	9.1	11.8	9.5	1.3 ₄
9 ^e	0.10	-10	48	100	9.3	12.4	10.1	1.2 ₈
10	0.50	-10	48	100	9.3	20.4	16.5	1.5 ₇
11	0.10	40	48	100	9.3	12.3	9.7	1.5 ₅
12	0.50	40	48	100	9.3	17.6	14.8	1.9 ₉

^a [BVSM]/[*n*-BuLi]=50; [TMEDA]=[*n*-BuLi]; solvent, hexane. ^b Calculated from the monomer-to-initiator ratio and percent polymer yield on the assumption that no cross-linking reaction takes place. ^c Estimated by GPC calibrated with polystyrene standards. ^d Determined by VPO. ^e Data in ref 2.

reaction took place. M_w/M_n s were around 1.3. Since the ratio of M_n estimated by GPC [M_n (GPC)] calibrated with polystyrene standards to that determined by VPO was approximately constant (1.23–1.29), M_n of poly(BVSM) (PBVSM) was determined by GPC measurement. The polymer structure was already examined in detail with ¹H and ¹³C NMR spectra in the previous communication,² and it was revealed that all monomer units formed exclusively six-membered rings. This was confirmed by ²⁹Si NMR measurement of PBVSM, whose M_n (GPC) is 1.8×10^4 , obtained with *n*-BuLi/TMEDA under the conditions as follows: [M]=0.1 mol l⁻¹, [M]/[I]=99, -10°C, 48 h. The spectrum shows fundamentally only one signal at 2.2 ppm, which is comparable to those of Si-3 atoms in 1,1,3,3-tetramethyl-4-trialkylsilylmethyl-1,3-disilacyclohexanes (3–4 ppm).¹⁶ The absence of signals corresponding to Si-1 and Si-3 atoms in 1,1,3,3-tetramethyl-4-trialkylsilylmethyl-5-methyl-1,3-disilacyclopentanes in the region of 12 to 15 ppm¹⁶ proves that no five-membered ring was formed.

Polymerization with [M] of 0.5 mol l⁻¹ (entry 10) and that at 40°C with either [M] (entries 11, 12) yielded the polymers with broad MWDs (>1.5). At [M]=0.5 mol l⁻¹, cross-linking reaction would have occurred, though not frequently, because M_n s of the polymers were rather higher than the calculated values.¹⁷ Side reactions in the polymerization in the presence of TMEDA will be discussed later.

Side Reaction in the Absence of TMEDA

The low polymer yields even for 96 h of the polymerization without TMEDA are attributable to various factors. To clarify the cause(s) of the low yields, the following experiments were conducted. First polymerization was carried out under the same conditions as entry 2 at -10°C for 96 h, then the equimolar amount of TMEDA to the initiator was added, and polymerization was continued for 48 h (named entry 13). Quenching by methanol followed by the purification gave a white powdery polymer in a 95% yield. The resulting polymer was entirely soluble in benzene, and exhibited an unimodal GPC trace. M_n (VPO)= 1.35×10^4 , M_n (GPC)= 1.74×10^4 (M_n (calcd)= 9.0×10^3), $M_w/M_n=1.55$. Figure 1 shows GPC traces of PBVSM obtained in entries 2 and 13. Since no oligomer fraction is found in this polymer, neither termination nor chain transfer occurred in the course of the polymerization without TMEDA at -10°C for 96 h. Marked increase in the

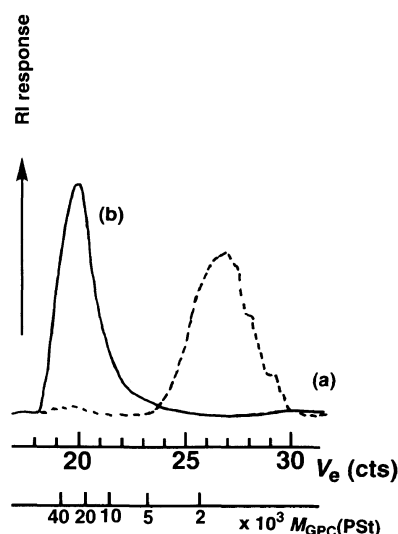


Figure 1. GPC traces of poly(BVSM)s: (a) obtained from polymerization with *n*-BuLi/TMEDA at -10°C for 96 h (entry 2); (b) obtained from polymerization first in the absence of TMEDA at -10°C for 96 h, and then in the presence of TMEDA at -10°C for 48 h (entry 13).

polymer yield from 2% to the almost quantitative yield during the additional 48 h of the polymerization with TMEDA indicates that the addition of TMEDA activates the propagating ends whose reactivities are extremely low. Such low reactivities of the propagating ends after oligomerization without TMEDA can be explained in the same manner as for polymerizations of methyltrivinylsilane⁶ and tetravinylsilane.⁷ At the oligomerization stage, cross-linking reaction¹⁸ causes the incorporation of the propagating end into crowded surroundings, which results in hard access of a monomer molecule to the propagating end. Association of the propagating ends, which is known in the polymerization of vinyl monomers in nonpolar media,¹⁹ would play an important role in this situation. The addition of TMEDA causes dissociation and makes the addition of the monomer possible, so that cyclopolymerization proceeds.

The cause of the low polymer yield without TMEDA at 40°C for 96 h was also examined. Polymerization was carried out under the same conditions as entry 5 at 40°C for 96 h. The equimolar amount of TMEDA to the initiator was added, and polymerization was continued for 48 h (named entry 14). In this case also a white powdery polymer soluble in benzene was obtained in a 33% yield. A GPC trace of the resulting polymer was

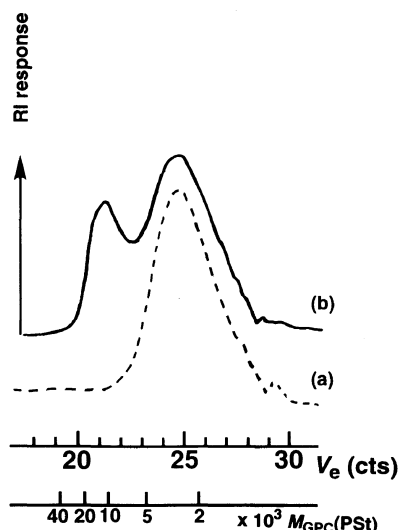


Figure 2. GPC traces of poly(BVSM)s: (a) obtained from polymerization with *n*-BuLi in the absence of TMEDA at 40°C for 96 h (entry 5); (b) obtained from polymerization with *n*-BuLi first in the absence of TMEDA at 40°C for 96 h, and then in the presence of TMEDA at -10°C for 48 h (entry 14).

bimodal, differing from that of entry 13. M_n (GPC) was 3.0×10^3 (M_n (calcd) = 1.8×10^3). Figure 2 shows GPC traces of the polymers obtained in entries 5 and 14. The lower molecular weight peak of PBVSM of entry 14 corresponds to the polymer obtained in entry 5. This peak in the GPC trace indicates that dead polymer chains were formed in the polymerization without TMEDA at 40°C by termination or chain transfer reaction. The lower polymer yield in entry 14 than that in entry 13 supports the presence of termination. A white turbidity during the polymerization without TMEDA at 40°C, which disappeared by the quenching with methanol, suggests that lithium hydride eliminated from the propagating end, as proposed as the termination reaction in the polymerization of trimethylvinylsilane.²⁰ Thus, the low yields in the polymerization of BVSM in the absence of TMEDA are attributed to the cross-linking and the association of the propagating ends at -10°C and to the elimination of lithium hydride from the propagating end at 40°C.

Side Reaction in the Presence of TMEDA

As described above, the anionic polymerization of BVSM with *n*-BuLi/TMEDA in hexane under the conditions of $[M] = 0.1 \text{ mol l}^{-1}$ and $[M]/[I] = 50$ afforded the polymers whose M_n s were in good agreement with the values calculated for polymers without cross-linking structure. ¹H and ¹³C NMR spectra revealed that all monomer units formed exclusively six-membered rings and no vinyl group remained in the polymers. MWDs were relatively narrow (around 1.3). However, some tailing could be seen in the GPC traces. The tailing can be interpreted in two ways. One is slow initiation, and the other is side reaction.

To examine whether the slow initiation was responsible for the tailing, two-stage polymerization of BVSM was performed. BVSM was first polymerized under the following conditions: $[M] = 0.10 \text{ mol l}^{-1}$, $[n\text{-BuLi}] = [\text{TMEDA}] = 10 \text{ mmol l}^{-1}$ ($[M]/[I] = 10$), -10°C, 192 h. After removal of a small amount of the reaction mixture

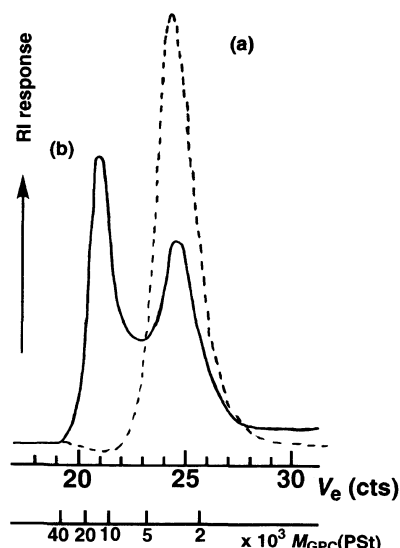
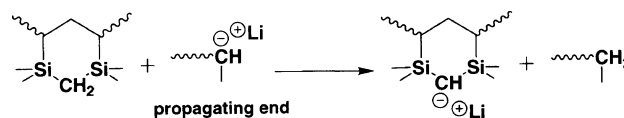


Figure 3. Two-stage polymerization of BVSM with *n*-BuLi/TMEDA at -10°C. GPC traces of poly(BVSM)s: (a) obtained from polymerization for 192 h (first stage, $[\text{BVSM}]/[n\text{-BuLi}] = 10$); (b) obtained from the second stage polymerization (entry 15, $[\text{added BVSM}]/[n\text{-BuLi}] = 7$, 72 h).

as an aliquot, 7 equivalents of BVSM to the initiator were added. The second stage polymerization was conducted at -10°C for 72 h (named entry 15). Figure 3 shows GPC curves of the prepolymer from the aliquot and polymer obtained after the two-stage polymerization. If tailing resulted from only the slow initiation, the latter polymer should still show a unimodal GPC trace. However, it clearly exhibits a bimodal peak, and hence some side reaction is the main cause of tailing.

From the possible side reactions that broaden the MWDs of the polymers, chain transfer can be excluded, because M_n s of the polymers were in good agreement with the calculated values. As the side reactions, two termination reactions are considered. One is the elimination of lithium hydride from the propagating end, which was also observed in the absence of TMEDA at 40°C. The other is the proton abstraction from -Si-CH₂-Si- methylene by the propagating end (shown in Scheme 2). The elimination of lithium hydride should form vinyl groups in the resulting polymer, but no vinyl group was detected by ¹H NMR measurement even in the polymer whose M_n (GPC) was as low as 2.3×10^3 . The absence of the vinyl group in the polymer, along with the absence of white turbidity in the polymerization system, is inconsistent with the possibility that the elimination of lithium hydride is responsible for tailing in GPC traces.

Since -Si-CH₂-Si- methylene protons are situated at the α -position of two silicon atoms, their acidity is expected to be rather high. Actually, the proton abstraction from -Si-CH₂-Si- methylene by alkylolithium/TMEDA is known for low molecular weight compounds.²¹ The resulting methine anion may be too stable to undergo propagation. To certify the existence of



Scheme 2.

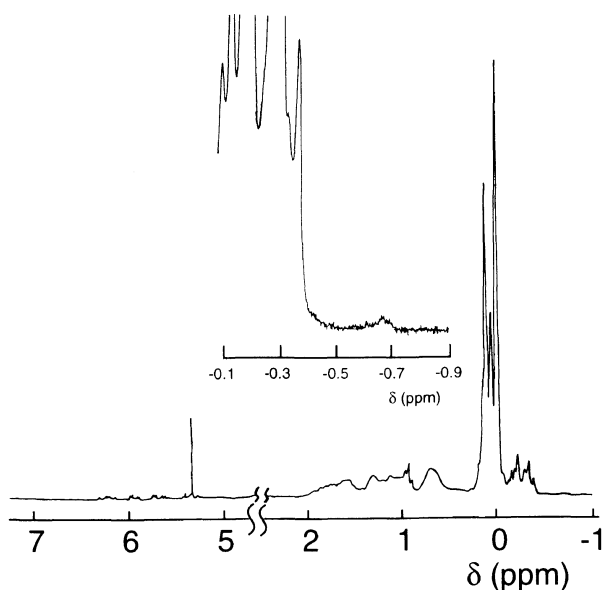


Figure 4. 200 MHz ^1H NMR spectrum of DMVCS-terminated poly(BVSM) in CDCl_3 . M_n (GPC) = 2.4×10^3 , $M_w/M_n = 1.17$.

methine anion interposed between two silicon atoms, the following experiments were carried out. After the polymerization of BVSM with *n*-BuLi/TMEDA in hexane under the conditions of $[\text{M}] = 0.1 \text{ mol l}^{-1}$ and $[\text{M}]/[\text{I}] = 10$ at -10°C for 30 days, 11 equivalents of DMVCS to the initiator in THF/hexane (1:5, v/v) were added at 0°C . M_n (GPC) and M_w/M_n of the obtained polymer were 2.4×10^3 and 1.17, respectively. ^1H NMR spectrum of the DMVCS-terminated polymer is shown in Figure 4. In addition to the signals of PBVSM quenched by methanol, vinyl signals and a small signal at -0.69 ppm were observed. Silylmethine protons surrounded by three silicon atoms exhibit signals at about -0.7 ppm ,²¹ apparently in upper field than about -0.3 ppm of methine and methylene protons interposed by two silicon atoms.²² Consequently, the methine anion interposed between two silicon atoms was proved to have formed during the polymerization. The ratio of the propagating ends that abstracted the $-\text{Si}-\text{CH}_2-\text{Si}-$ methylene protons to all propagating ends, about 20%, was determined by the intensities of the peak at -0.69 ppm and all signals in the ^1H NMR spectrum.

As the propagating end that participates in proton abstraction, two types of carbanions are considered. One is the silylmethine anion not in the six-membered ring (**1**), formed just after the addition of the monomer. If this type of propagating end abstracted the $-\text{Si}-\text{CH}_2-\text{Si}-$ methylene proton, a vinyl group should appear in the resulting polymer. However, no vinyl group was observed even in the oligomers (for example, the prepolymer of entry 15) by ^1H NMR measurement, and accordingly it is found that the anion **1** scarcely participates in the abstraction. The other carbanion is the silylmethine anion in the six-membered ring (**2**), formed by ring closure of **1**. After the monomer was completely con-

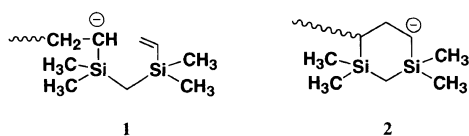


Table III. Anionic polymerization of BVSM corresponding to the first stage of two-stage polymerization^a

Entry	Time h	Yield %	$M_n \times 10^{-3}$		M_w/M_n^c
			Calcd ^b	GPC ^c	
16	3	90	1.6	1.7	1.0 ₉
17	24	96	1.8	1.8	1.1 ₁
18	168	98	1.8	1.8	1.1 ₂

^a Polymerization conditions: $[\text{BVSM}] = 0.10 \text{ mol l}^{-1}$; $[\text{TMEDA}] = [\textit{n}\text{-BuLi}] = 10 \text{ mmol l}^{-1}$; temp, -10°C ; solvent, hexane. ^b Calculated from the monomer-to-initiator ratio and percent polymer yield on the assumption that no cross-linking reaction takes place. ^c Estimated by GPC calibrated with polystyrene standards.

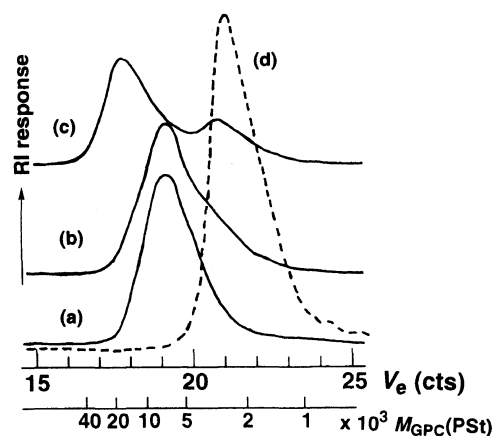


Figure 5. GPC traces of poly(BVSM)s obtained with *n*-BuLi/TMEDA at -10°C from two-stage polymerization with different intervals. Polymerization conditions of the first stage: $[\text{BVSM}] = 0.10 \text{ mol l}^{-1}$; $[\textit{n}\text{-BuLi}] = [\text{TMEDA}] = 10 \text{ mmol l}^{-1}$. Polymerization time of the first stage: (a) 3 h; (b) 24 h; (c) 168 h. Polymerization conditions of the second stage: $[\text{added BVSM}]/[\textit{n}\text{-BuLi}] = 11$; time, 72 h. GPC trace of poly(BVSM) obtained from polymerization of the first stage for 168 h (entry 18) is shown as (d).

sumed, all propagating ends should exist as anions **2**. Consequently the propagating ends will be inactivated even after the quantitative consumption of the monomer, if abstraction of the $-\text{Si}-\text{CH}_2-\text{Si}-$ methylene proton by **2** takes place. To examine the possibility of proton abstraction by **2**, two-stage polymerization experiments with different intervals were performed. First, BVSM was polymerized under the following conditions: $[\text{M}] = 0.10 \text{ mol l}^{-1}$, $[\textit{n}\text{-BuLi}] = [\text{TMEDA}] = 10 \text{ mmol l}^{-1}$ ($[\text{M}]/[\text{I}] = 10$), -10°C . After a given polymerization time (3 h, 24 h, or 168 h), 11 equivalents of BVSM to the initiator were added, and polymerization was continued for additional 72 h. All runs of the two-stage polymerization yielded the polymers quantitatively. Table III shows the results of the polymerization that correspond to the first-stage. After 3 h of polymerization, the monomer still remained in the polymerization mixture (entry 16). GPC traces of PBVSMs obtained in the two-stage polymerization are illustrated in Figure 5, together with that of entry 18 (corresponding to the polymer obtained in the first stage in approximately 100% conversion). MWD of PBVSM obtained from the two-stage polymerization with 3 h of the first stage is almost unimodal. GPC trace of PBVSM yielded in the two-stage polymerization with 24 h of the first stage has a shoulder at the lower molecular weight side. When the first stage was set at 168 h, the final

Table IV. Effects of initiator on the polymerization of BVSM^a

Entry	BuLi	[TMEDA]	Time	Yield	$M_n \times 10^{-3}$		M_w/M_n^d	f^e
		[BuLi]	h	%	Calcd ^b	VPO ^c		
1 ^f	<i>n</i> -	0	96	2	0.2	—	—	—
6 ^f	<i>n</i> -	1.0	6	71	6.6	6.2	1.2 ₇	1.0 ₆
19	<i>s</i> -	0	96	1	0.2	—	—	—
20	<i>s</i> -	1.0	6	65	6.0	7.6	1.3 ₀	0.7 ₉
21	<i>t</i> -	0	96	1	0.2	—	—	—
22	<i>t</i> -	1.0	6	64	5.9	5.7	1.2 ₈	1.0 ₃

^a [BVSM] = 0.1 mol l⁻¹; [BuLi] = 2 mmol l⁻¹; temp, -10°C; solvent, hexane. ^b Calculated from the monomer-to-initiator ratio and percent polymer yield on the assumption that no cross-linking reaction takes place. ^c Determined by VPO. ^d Estimated by GPC calibrated with polystyrene standards. ^e Initiator efficiency. ^f Data in ref 2.

Table V. Effects of amines on the polymerization of BVSM with *n*-BuLi/amine^a

Entry	Amine	[Amine]	Time	Yield	$M_n \times 10^{-3}$		M_w/M_n^c
		[<i>n</i> -BuLi]	h	%	Calcd ^b	GPC ^c	
6 ^d	TMEDA	1.0	6	71	6.6	7.6	1.2 ₇
9 ^d	TMEDA	1.0	48	100	9.3	12.4	1.2 ₈
23	TEEDA	1.0	6	4	0.4	1.0	—
24	TEEDA	1.0	168	7	0.6	1.4	—
25	TEEDA	10	6	1	0.1	1.0	—
26	TEEDA	10	168	8	0.7	1.4	—
27	TEA	1.0	6	3	0.3	0.9	—
28	TEA	1.0	24	6	0.6	0.9	—
29	TEA	20	6	10	1.0	1.9	—
30	TEA	20	168	27	2.5	5.8	1.5 ₉

^a [BVSM] = 0.1 mol l⁻¹; [*n*-BuLi] = 2 mmol l⁻¹; temp, -10°C; solvent, hexane. ^b Calculated from the monomer-to-initiator ratio and percent polymer yield on the assumption that no cross-linking reaction takes place. ^c Estimated by GPC calibrated with polystyrene standards. ^d Data in ref 2.

polymer exhibits apparently a bimodal MWD, indicating inactivation occurred as a function of the time. Since longer polymerization time results in more inactivation after the completion of the polymerization, mainly **2** causes the proton abstraction from the -Si-CH₂-Si-methylene.

When the polymerization of BVSM with *n*-BuLi/TMEDA was carried out at 40°C, MWD of the polymer was broader than that obtained at -10°C, though its M_n was in good agreement with the value calculated for the polymer without cross-linking structure (entry 11 in Table II). In this case proton abstraction would take place more frequently.

Effect of Initiator

The polymerization of BVSM was carried out using three butyllithiums, namely *n*-, *s*-, and *t*-BuLi. The results are shown in Table IV. Polymerization hardly proceeded with either BuLi in the absence of TMEDA (entries 1, 19, 21). Polymerization with *t*-BuLi/TMEDA afforded the polymer whose M_n was approximately equal to the calculated value, similarly to that with *n*-BuLi/TMEDA (entries 22, 6). M_n of the polymer obtained with *s*-BuLi/TMEDA was rather higher than the calculated value, and thus initiator efficiency was considerably low (entry 20). All these polymers obtained with BuLi/TMEDA exhibited similar ¹H NMR spectra and similar shapes of GPC traces. Since *s*-BuLi/TMEDA initiates the polymerization of trimethylvinylsilane quantitatively in hexane at -10°C,²³ the low initiator efficiency is attributable to some side reaction that wastes the ini-

tiator.

In the previous section the polymerization with *n*-BuLi/TMEDA is accompanied by the proton abstraction from the methylene interposed by two silicon atoms, though not frequently. The side reaction with *s*-BuLi/TMEDA is thus explained reasonably by similar proton abstraction. The anionic activity, nucleophilicity, of BuLi is known to be the following order,²⁴ *t*-BuLi > *s*-BuLi > *n*-BuLi. The nucleophilicity of *n*-BuLi/TMEDA is not high enough to abstract the methylene proton in -Si-CH₂-Si-, differing from that of *s*-BuLi/TMEDA. When *t*-BuLi/TMEDA is used as an initiator, the bulkiness of *t*-butyl group hinders the proton abstraction, although the nucleophilicity is high enough. Such high susceptibility of -Si-CH₂-Si- to the proton abstraction makes functionalization of PBVSM possible.²⁵

Effect of Amines

Typical polymerization results with *n*-BuLi/TEEDA and *n*-BuLi/TEA, along with those with *n*-BuLi/TMEDA, are shown in Table V. Compared with the polymerization with *n*-BuLi/TMEDA, those with *n*-BuLi/TEEDA and *n*-BuLi/TEA proceeded very slowly (entries 6, 23, 27). The resulting polymers obtained with *n*-BuLi/TEEDA and *n*-BuLi/TEA were found to contain residual vinyl groups by ¹H NMR measurement. When TEEDA was used as the additive amine, only oligomer was obtained even for a prolonged polymerization time (entry 24). Increase in the ratio of TEEDA to *n*-BuLi did not have any notable effect on the polymerization (entries 25, 26). Since the basicity of amino groups in

TEEDA is nearly equal to that in TMEDA,²⁶ the bulkiness of *N*-substituents would significantly influence the cyclization and the propagation. When an equimolar amount of TEA to *n*-BuLi was used, oligomer was obtained in a low yield (entries 27, 28). However, polymerization using a large excess of TEA gave a benzene-soluble polymer in a medium yield (entries 29, 30). The difference between M_n (GPC) and M_n (calcd) of the resulting polymers indicates that the cross-linking occurred when the initiator efficiency was quantitative. In the anionic polymerization of trimethylvinylsilane with BuLi, the addition of TEA causes marked acceleration of the polymerization and gel formation, which is considered to result from the high activity of 1:1 complex of lithium cation with TEA.²⁷ Slower polymerization of BVSM with *n*-BuLi/TEA than that with *n*-BuLi/TMEDA would result from the incorporation of the propagating end into crowded surroundings formed by the cross-linking reaction. Fast polymerization of BVSM with *n*-BuLi/TMEDA is due to the perfect cyclization.

CONCLUSIONS

Anionic cyclopolymerization of BVSM, especially side reactions, was investigated. Low polymer yields in the polymerization without TMEDA are attributed to the cross-linking reaction and association of the propagating ends at -10°C and to the elimination of lithium hydride from the propagating end at 40°C . Polymerization with TMEDA is accompanied by abstraction of the methylene proton interposed by two silicon atoms, which forms an inactive anion. This abstraction is caused by the propagating end in the six-membered ring. At high monomer concentration such as 0.5 mol l^{-1} , the cross-linking reaction is not negligible even in the presence of TMEDA. Among three butyllithiums, *s*-BuLi/TMEDA solely causes the proton abstraction from $-\text{Si}-\text{CH}_2-\text{Si}-\text{methylene}$. The effects of the initiator are explained by the nucleophilicity of BuLi and the steric hindrance in the abstraction. The effects of TMEDA, TEEDA, and TEA are examined. TMEDA is the most suitable for the cyclopolymerization of BVSM.

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