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Mechanism of the Anionic Cyclopolymerization of Bis(dimethylvinylsilyl)methane

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ABSTRACT: The driving force of the complete cyclization in the anionic cyclopolymerization of bis(dimethylvinylsilyl)methane with *n*-BuLi/TMEDA in hexane is clarified with resonance Raman and ^{1}H NMR measurements. Vinyl groups coordinating to the lithium cation are detected in both measurements of the polymerization mixture at −70 °C, and they, at least some part of them, are shown to be the vinyl groups in uncyclized end units. Disappearance of these species from the resonance Raman spectrum at −20 °C indicates that the cyclization proceeds fast and is accelerated by the coordination of the second vinyl group in the uncyclized end unit. This is the first case that the interaction between the vinyl group in an uncyclized end unit and the counterion was found in ionic cyclopolymerization.

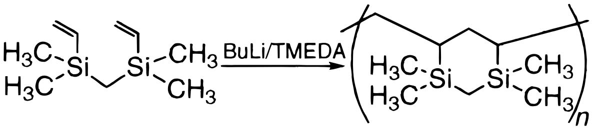
Introduction

Since Butler and Ingley reported the formation of water-soluble polymers from quaternary diallylammonium salts in 1951,[1] cyclopolymerization has been studied by many researchers.[2] In general, the activation energy for intramolecular cyclization is higher than that for intermolecular propagation.[3] However, despite the disadvantage in the activation energy, various nonconjugated 1,6-heptadienes undergo cyclopolymerization in high cyclization efficiencies to form five- and/or six-membered rings as repeating cyclic units. To account for the high cyclization efficiency, many kinetic studies have been made on the cyclopolymerization of dienes.

Butler and co-workers investigated kinetically the radical cyclopolymerization of substituted 1,6-heptadienes and methacrylic anhydride.[4] They concluded that a much higher collision frequency factor for the cyclization step than that for the intermolecular propagation step leads to the cyclopolymerization. Guaita et al. determined two activation entropies in the radical cyclopolymerization of methacrylic anhydride, considering that a loss of rotational degrees of freedom decreases entropy in the cyclization step and that a loss of translational degrees of freedom governs an entropy decrease in the intermolecular propagation.[5] Their experimental results and semiempirical calculation indicated that smaller entropy decrease in the cyclization step is responsible for the cyclopolymerization.

Although many 1,6-heptadienes undergo cyclopolymerization, complete cyclization is not easily attained because cyclization reaction competes with intermolecular propagation. To increase the cyclization efficiency, two approaches can be utilized. One is the suppression of the intermolecular propagation before cyclization. For example, the lower the monomer concentration is, the higher the cyclization efficiency. The other is the acceleration of the intramolecular cyclization. As one of the latter approaches, Kakiuchi et al. introduced bulky *N*-alkyl substituents into *N*-allylacrylamide.[6] The cyclization efficiency in the radical polymerization of *N*-alkyl-*N*-allylacrylamide increased with the chain length of the *N*-alkyl substituent. Their interpretation of the effect of the *N*-alkyl substituent is that the longer alkyl group facilitates more favorable conformation of the acryloyl radical for cyclization. Tsuda and Mathias found that a favorable conformation for cyclization can be also realized by hydrogen bonding.[7] They investigated the radical cyclopolymerization of ether dimers of α-(hydroxymethyl)acrylic acid and its alkyl esters. The ether dimer of the acid was found to show an unexpectedly high cyclization efficiency, and this was attributed to the intramolecular hydrogen bonding between acid groups.

Scheme 1



We have studied the anionic cyclopolymerization of multivinylsilanes, the compounds having two or more silylvinyl groups per molecule.[8−11] The polymerization of methyltrivinylsilane and tetravinylsilane proceeds only in the presence of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and the resulting polymers contain monocyclic and bicyclic ring structures.[9] Bis(dimethylvinylsilyl)methane (BVSM) undergoes anionic cyclopolymerization with *n*-butyllithium (*n*-BuLi) at −10 °C in hexane in the presence of TMEDA in 100% cyclization efficiency (Scheme 1).[10] Unlike the cases of radical cyclopolymerization of 1,6-heptadienes, the resulting polymer contains only six-membered, 1,3-disilacyclohexane rings as repeating cyclic units. Though the polymerization is accompanied by a termination reaction with low frequency, the molecular weight distribution of the polymer is rather narrow.[11] The number-average molecular weight (M_n) is in accord with the calculated value for the polymer without cross-linking structure. In the absence of TMEDA, the polymerization of BVSM with *n*-BuLi gives only oligomers in low yields.

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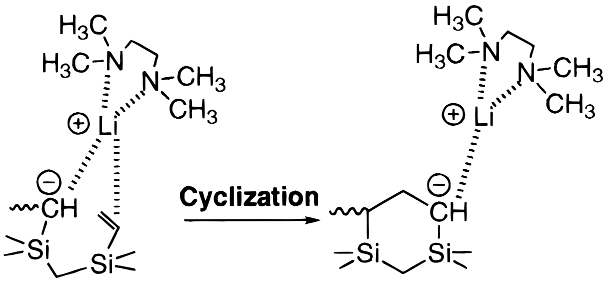
Scheme 2



In the present paper, we reveal the mechanism of anionic polymerization of BVSM with *n*-BuLi/TMEDA that leads to the quantitative cyclization.

Results and Discussion

As described in Introduction, the cyclopolymerization of BVSM with *n*-BuLi in hexane proceeds only in the presence of TMEDA.[10,11] The cyclization efficiency is 100% when the polymerization is carried out at −10 °C with the following initial concentrations of the reagents: [BVSM] = 0.1 mol/L, [*n*-BuLi] = [TMEDA] = 2 × 10^{-3} mol/L. The repeating cyclic unit is exclusively the 1,3-disilacyclohexane ring. The addition of TMEDA prevents the propagating ends from incorporation into crowded surroundings through the inhibition of cross-linking. Nevertheless, it is not clear why the cross-linking does not occur in the presence of TMEDA. Since the oligomer obtained without TMEDA has a cross-linked structure, complete cyclization with *n*-BuLi/TMEDA should be considered in connection with the existence of TMEDA.

A kinetic study on the anionic oligomerization of ethylene with *n*-BuLi/TMEDA revealed the coordination of the monomer to lithium.[12] Assuming similar coordination of the vinyl group in the polymerization of BVSM, the second vinyl group of the uncyclized end monomer unit locates in the neighborhood of the propagating end anion, and the cyclization will be accelerated (Scheme 2). This idea is examined by spectroscopic measurements of the propagating end in the polymerization of BVSM with *n*-BuLi/TMEDA in hexane.

Resonance Raman spectra of the polymerization mixtures and the monomer were measured. First, the measurements were carried out for three samples at −70 °C. One is a 0.12 mol/L solution of BVSM in hexane (a). Another sample is a polymerization mixture where the polymerization has not been completed (b). This polymerization was carried out under the following conditions: [BVSM] (initial monomer concentration) = 0.1 mol/L; [M]/[I] (initial monomer-to-initiator ratio) = 15; temperature, −78 °C; time, 10 h. The other sample is a polymerization mixture where the polymerization has been completed, in other words, after the consumption of whole monomer, but not terminated (c). The polymerization was carried out at −78 °C for 5 days and then at −10 °C for 70 days ([BVSM] = 0.1 mol/L, [M]/[I] = 30). Figure 1 shows resonance Raman spectra of these samples in the 1500−1800 cm^{-1} region. The intense band at 1594 cm^{-1} is assigned to the C=C stretching vibration (ν(C=C)) of the vinyl groups in BVSM by spectrum a. Spectrum b shows a weaker Raman band at 1584 cm^{-1}, 10 cm^{-1} lower than ν(C=C) band of the monomer. It is known that ν(C=C) bands of carbon−carbon double bonds shift to lower wavenumbers by their electron delocalization; accordingly, the band at 1584 cm^{-1} can be assigned to the ν(C=C) band of the vinyl group that coordinates to the lithium cation. Similar coordination of a vinyl group to a lithium cation has already been reported for but-3-enyllithium.[13] Spectrum c exhibits no ν(C=C) band at 1594 or 1584 cm^{-1}, and hence the band at 1584 cm^{-1} is assignable to the vinyl group in the propagating end in the course of the polymerization. The smaller shift to the lower wavenumber, 10 cm^{-1}, than in the case of but-3-enyllithium (23 cm^{-1}) is a reasonable value, considering that the coordination of TMEDA to the lithium cation weakens the interaction between the vinyl group and the lithium cation.

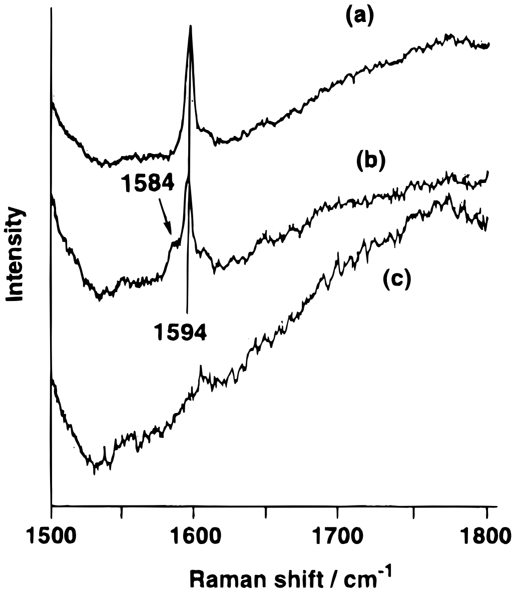


Figure 1. Resonance Raman spectra of (a) BVSM in hexane, (b) a polymerization mixture in the course of the polymerization, and (c) a polymerization mixture where the polymerization has been completed but not terminated. All spectra were obtained at −70 °C. Polymerization conditions are described in the text.

Figure 2 shows the temperature dependence of the resonance Raman spectrum of the polymerization mixture in the course of the polymerization. The polymerization was carried out under the same conditions as the sample in Figure 1b. The Raman band at 1584 cm^{-1} weakened with the increase in the temperature of the measurement from −70 (a) to −40 °C (b). In the spectrum measured at −20 °C (c), this band disappeared. These results suggest that the vinyl group coordinating to the lithium cation adds to the propagating end anion too fast to detect this vinyl group by the measurement of the resonance Raman spectrum at −20 °C.

The polymerization mixtures were also analyzed by ^{1}H NMR measurement at −70 °C. Figure 3 shows ^{1}H NMR spectra of BVSM in hexane (a) and polymerization mixtures (b, c). The polymerization was carried out under the following conditions: [BVSM] = 0.1 mol/L; [M]/[I] = 10; at −78 °C for 24 h (b) or at −78 °C for 8 days and then at −10 °C for 14 days (c). The polymerization has not been completed in the sample of spectrum b, and whole monomer was consumed but the polymerization has not been terminated in the sample of spectrum c. Other than the vinyl signals of BVSM, broad peaks at 5.71, 5.95, and 6.24 ppm, slightly lower magnetic field than each vinyl proton in BVSM, appeared in spectrum b. After the consumption of a whole

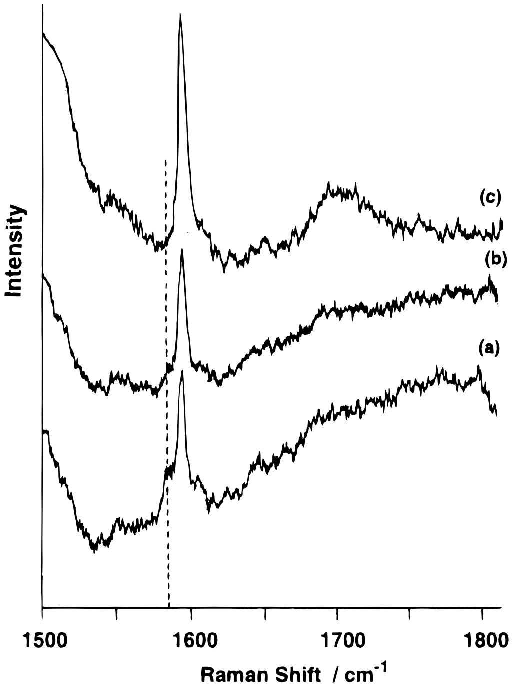


Figure 2. Resonance Raman spectra of the polymerization mixture in the course of the polymerization measured at (a) −70, (b) −40, and (c) −20 °C. The polymerization conditions are given in the text.

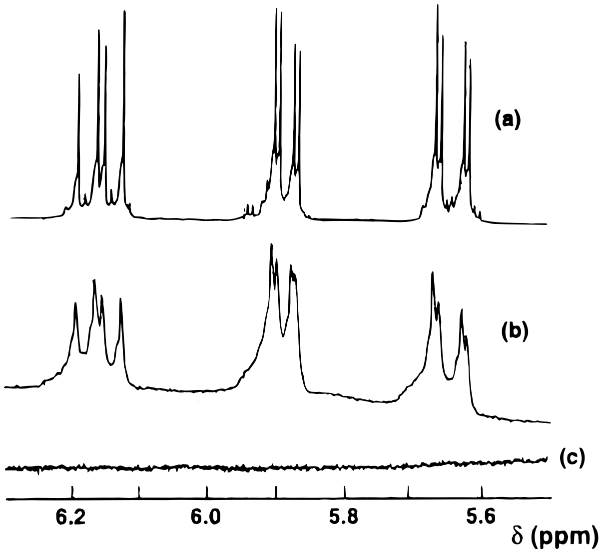


Figure 3. Partial 500 MHz ^{1}H NMR spectra at −70 °C of (a) BVSM in hexane, (b) a polymerization mixture in the course of the polymerization, and (c) a polymerization mixture where the polymerization has been completed but not terminated. An internal CD_3OD capillary was used for locking, and the methylene signal of the solvent, hexane, was used for the internal reference (1.30 ppm). Polymerization conditions are described in the text.

monomer, these broad peaks and the vinyl signals of BVSM disappeared. These observations reveal that the broad peaks are assignable to the vinyl group in the propagating end. The downfield shifts from the vinyl signals of BVSM can be explained by the deshielding through the decrease in π-electron density on the vinyl group, which indicates that the vinyl group coordinates to the lithium cation. The results of both resonance Raman and ^{1}H NMR measurements support the existence of the coordination of the vinyl group to the lithium cation.

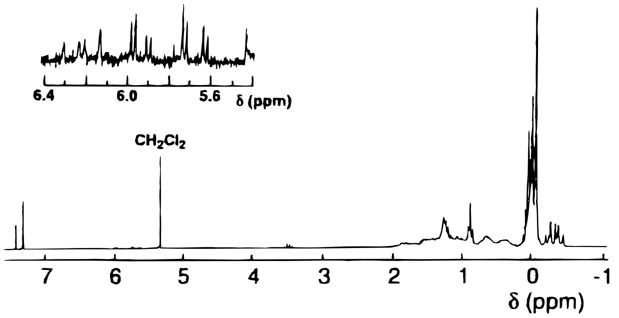
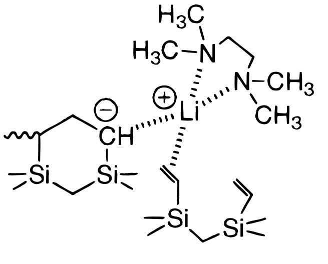


Figure 4. The 200 MHz ^{1}H NMR spectrum in $CDCl_3$ of poly(BVSM) obtained by terminating the polymerization at −78 °C. CH_2Cl_2 was used as an internal reference. Polymerization conditions are described in the text.

Since BVSM is a nonconjugated diene, it is hard to decide from the spectra whether the coordinating vinyl group is that of the monomer (**1**) or the uncyclized end unit (**2**). To determine which type of coordinating vinyl group was observed in the resonance Raman and ^{1}H NMR spectra, the ^{1}H NMR spectrum was taken for the polymer obtained by quenching at −78 °C the polymerization mixture that had exhibited the ν(C=C) band of the coordinating vinyl group in the resonance Raman spectrum. The polymerization conditions were as follows: [BVSM] = 0.1 mol/L; [M]/[I] = 10; temperature, −78 °C; time, 5 days. Methanol was used for the quenching, and M_n of the polymer was 1.4 × 10^3 (yield 35%). If the coordinating species is **1**, the resulting polymer cannot contain a vinyl group. If **2** is the coordinating species observed, a vinyl group should be attached to the chain end of the resulting polymer. In the ^{1}H NMR spectrum of the quenched polymer shown in Figure 4, vinyl signals were apparently observed. Figure 5 is the ^{1}H NMR spectrum of the polymer obtained by quenching at −10 °C the polymerization mixture similar to that used for the polymer of Figure 4. The polymerization conditions were as follows: [BVSM] = 0.1 mol/L; [M]/[I] = 10; temperature, −78 °C; time, 7 days. Methanol was used for the quenching, and M_n of the polymer was 1.7 × 10^3 (yield 45%). In contrast to the spectrum in Figure 4, no vinyl signal was shown in Figure 5. In collaboration with the results obtained in Figure 4, the absence of the vinyl group in the polymer quenched at −10 °C, at which temperature no coordination was detected by the resonance Raman spectrum, confirmed that the coordinating vinyl groups observed in the resonance Raman spectrum at −70 °C are the second vinyl groups of the uncyclized chain end units (**2**), though it cannot be asserted that all the coordinating species are **2**.



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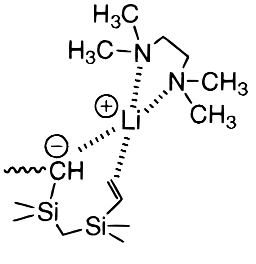

2

In this study, the coordination of the vinyl group was detected in the polymerization at −78 °C. However, the

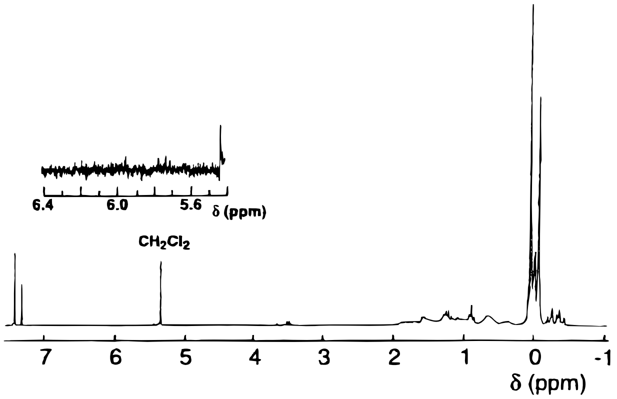

Figure 5. The 200 MHz ^1H NMR spectrum in $CDCl_3$ of poly(BVSM) obtained by terminating the polymerization at −10 °C. CH_2Cl_2 was used as an internal reference. Polymerization conditions are described in the text.

^1H NMR spectrum in Figure 5 is the same as that of the polymer obtained in the polymerization at −10 °C[10] except for the relative intensities of end unit signals, and consequently the mechanism of the polymerization at −78 °C would be the same as that at −10 °C. The intensity of the Raman band of the coordinating vinyl groups diminished with the increase in the temperature of the measurement and disappeared at −20 °C as shown in Figure 2. This dependence of the resonance Raman spectrum on the temperature of the measurement indicates that the intramolecular cyclization is too fast on the time scale of resonance Raman measurement at −20 °C. The acceleration of the intramolecular cyclization, which leads to high cyclization efficiency, is explained by the electronic effect of the coordination of the second vinyl group to the lithium cation. Electron donation from the vinyl group to the lithium cation facilitates the nucleophilic addition of the end anion to the coordinating vinyl group. Coordinating to the lithium counterion, the second vinyl group is fixed in the neighborhood of the propagating end anion. Thus, the steric factor would also accelerate the intramolecular cyclization. The coordination of the second vinyl group to the lithium cation is therefore a key factor for the complete cyclization.

Conclusion

In the cyclopolymerization of BVSM with *n*-BuLi/TMEDA, the coordination of vinyl groups to the lithium cations was characterized by resonance Raman and ^1H NMR measurements at −70 °C. The coordinating vinyl groups were found to be those in uncyclized end units, though it cannot be asserted that all the coordinating species are so. The coordination of the second vinyl group in the uncyclized end unit to the lithium cation is considered to accelerate the intramolecular cyclization, which leads to the complete cyclization. The present paper first reported the interaction between the vinyl group in the uncyclized end unit and the counterion in ionic cyclopolymerization.

Experimental Section

Materials. *n*-BuLi (Wako Pure Chemical, 1.6 mol/L solution in hexane), TMEDA (Nakalai Tesque), and hexane were purified according to the conventional method for the anionic polymerization as described in a previous paper.[11] BVSM was prepared and purified as already reported.[11] Sodium naphthalenide in tetrahydrofuran (THF) used in the preparation of NMR samples was prepared according to the conventional method for the anionic syntheses. All other chemicals were purchased from commercial sources and used as received.

Polymerization of BVSM. All polymerizations were carried out in hexane with *n*-BuLi in the presence of an equimolar amount of TMEDA to *n*-BuLi under high-vacuum conditions using breakable seal techniques. Detailed polymerization procedures and the purification of the resulting polymers were previously described.[11]

Measurements of Resonance Raman Spectra. All resonance Raman spectra were measured with a Chromex 250IS equipped with an EG&G Instrument model 1530-CUV detector, which were made with excitation at 406.7 nm from a Kr ion laser (Spectra Physics model 2016). Power at the samples was kept at 12−16 mW. Calibrations were performed for each measurement by using known Raman lines of indene. All the samples were prepared under vacuum. For the preparation of the sample of the polymerization mixture, a sample tube was attached to a Pyrex round-bottomed flask. After the polymerization mixture was prepared in the flask under vacuum, a required amount of that was introduced to the sample tube, and then it was sealed.

Measurements of ^1H NMR Spectra. ^1H NMR spectra shown in Figure 3 were recorded at −70 °C in hexane on a JEOL Lambda-500 spectrometer operated at 500 MHz in the Fourier transform mode. An internal CD_3OD capillary was used for locking. The methylene signal of the solvent, hexane, was used for the internal reference (1.30 ppm). The spectra of the polymerization mixtures (Figure 3b,c) were measured under vacuum, and the samples were prepared in the following way. An NMR sample tube (5 mm o.d.) was attached to a Pyrex vessel. Before the polymerization, the inside of the vessel and the sample tube were rinsed with a solution of sodium naphthalenide in THF. After the washing was sealed off, the solutions of *n*-BuLi, TMEDA, and BVSM were introduced to the vessel through breakable seals. A required amount of the polymerization mixture was transferred to the sample tube, and then it was sealed. ^1H NMR spectra shown in Figures 4 and 5 were recorded at 20 °C on a Varian Gemini-200 spectrometer operated at 200 MHz in the Fourier transform mode. $CDCl_3$ containing CH_2Cl_2 as an internal reference (5.34 ppm) was used for the solvent.

Determination of Molecular Weights. For the estimation of M_n of the polymers, gel permeation chromatography was performed at 40 °C on a Toyo Soda HLC-802A with TSKgel G1000H (30 cm), G2000H (60 cm), and G3000H (60 cm) columns connected in series. The instrument was equipped with a refractive index detector and a UV detector. THF was used as an eluent at a flow rate of 1.0 mL/min. The data were calibrated with polystyrene standards.[14]

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(14) The relationship between M_n estimated by gel permeation chromatography ($M_{n,GPC}$) and M_n determined by vapor pressure osmometry ($M_{n,VPO}$) was already reported in ref 11: the ratio of $M_{n,GPC}$ to $M_{n,VPO}$ was approximately constant (1.23−1.29). In the text, $M_{n,GPC}$ was adopted.

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