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A Unique Structure of Poly(benzyldimethylvinylsilane) by Isomerization Polymerization

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ABSTRACT: The anionic polymerization of benzyldimethylvinylsilane (BDMVS) was revealed to be accompanied by the isomerization reaction, which takes place regularly, once per two vinyl addition reactions. In the polymerizations of BDMVS, all polymers that were obtained both in the absence and presence of *N,N,N′,N′*-tetramethylethylenediamine, both at 40 °C and at 60 °C, had the same spectra of IR, ^{1}H NMR, and ^{13}C NMR. The analyses of ^{1}H NMR and ^{13}C NMR certified the strictly regular isomerization. Owing to this isomerization, the polymer has a unique structure where silicon atoms are incorporated both in the backbone and in the pendant groups. This structure was supported by a decomposition experiment of the polymer. The six-membered ring structure, where the silylmethine anion of a propagating end and a benzylic proton in a penultimate unit exist adjacently, is considered to contribute to the isomerization, in collaboration with the high acidity of the benzylic protons.

Introduction

Anionic polymerizations of vinylsilanes were first reported by Nametkin et al. in 1963.[1] As for benzyldimethylvinylsilane[2] (BDMVS), the anionic polymerization was reported by them in 1969.[3] In their paper[3] and subsequent patents,[4] it was reported that the polymers obtained from BDMVS as well as other vinylsilanes had the structure that was given by the ordinary vinyl polymerization.

On the other hand, we have recently found an isomerization reaction in the polymerization of trimethylvinylsilane[5] by *n*-butyllithium in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA).[6] Though the mechanism of the isomerization has not been clarified perfectly, the addition of TMEDA to the polymerization system undoubtedly causes an incorporation of silicon atoms into the main chain. This isomerization, which is always accompanied with a change in physical properties of the polymer, is observed not only for the polymerization of trimethylvinylsilane but also for that of other vinylsilanes.[7] The isomerization is supposed to take place via proton transfer from a silylmethyl group to the silylmethine anion of a propagating end, and the transfer is explained in terms of the stability of a silylmethine anion and a silylmethylene anion. In the case of BDMVS, the acidity of benzylic protons, which is expected to be much higher than that of silylmethyl protons, results in high susceptibility to the abstraction by a silylmethine anion. This nature of the benzylic protons prompted us to study the anionic polymerization of BDMVS in the presence or absence of TMEDA. We now report a unique polymer structure that is obtained by the polymerization of BDMVS via a regular chain transfer to the benzylic methylene in a penultimate unit.

Experimental Section

Materials. All chemicals except BDMVS were purchased from commercial sources. Cyclohexane was distilled from sodium. TMEDA was distilled from CaH_2 and then distilled over a sodium mirror. Tetrahydrofuran (THF) was distilled from successive CaH_2, potassium, and a sodium–benzophenone complex. Commercially available *sec*-butyllithium (*sec*-BuLi) in hexane was used after filtration and solvent substitution. Benzyl bromide, dimethylvinylchlorosilane, and benzaldehyde were distilled under reduced pressure. Dry diethyl ether, magnesium for Grignard reaction, trimethylchlorosilane, and CH_2Cl_2 were used without further purification.

Benzyldimethylvinylsilane (BDMVS). A solution of 58 g (0.34 mol) of benzyl bromide in 75 mL of dry diethyl ether was added dropwise during 1 h to 9.5 g (0.39 mol) of magnesium turnings in 75 mL of refluxing diethyl ether under nitrogen atmosphere. After it was stirred for an additional 1 h at room temperature, the supernatant solution was transferred under nitrogen atmosphere to a three-necked flask equipped with a mechanical stirring rod, an addition funnel, and a reflux condenser. A solution of 36.5 g (0.30 mol) of dimethylvinylchlorosilane in 120 mL of diethyl ether was added dropwise during 30 min through the addition funnel at 0 °C with stirring. The reaction mixture was allowed to stand overnight at room temperature, and then aqueous HCl was added to it. The ether layer was washed with aqueous $NaHCO_3$ and with water. After the solution was dried over Na_2CO_3, the ether of the solution was evaporated and the residue was distilled to give 27.1 g (0.15 mol, 51%) of BDMVS [bp 63.5–65.5 °C (5 mmHg) (lit.[3] bp 80 °C (7 mmHg))]: ^{1}H NMR ($CDCl_3$) δ 7.05–7.35 (5 H, m, Ar), 5.97–6.32 (2 H, m, $CH_2{=}$), 5.73 (1 H, dd, $={CH}-$), 2.20 (2 H, s, benzyl), 0.10 (6 H, s, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ 139.8 (Ar C-1), 138.2 ($={CH}-$), 132.1 ($CH_2{=}$), 128.2 and 128.1 (Ar C-3 and C-4), 124.0 (Ar C-2), 25.8 (benzyl), −3.7 ($SiCH_3$). The monomer was distilled from CaH_2 and then from *sec*-BuLi prior to the polymerization.

Polymerization of BDMVS. The polymerizations were carried out by *sec*-BuLi in cyclohexane under high vacuum conditions using breakable seal techniques. The initial concentrations of the reagents were as follows: [BDMVS] = 1.0 mol/L, [*sec*-BuLi] = 2×10^{-2} mol/L, [TMEDA] = 0 or 2×10^{-2} mol/L. After the quenching by methanol, the reaction mixture was concentrated by evaporation. Then the residue was dissolved in benzene and washed with aqueous HCl. Freeze-drying of the benzene solution gave a sticky polymer.

Decomposition of the Polymer. Decomposition of poly(benzyldimethylvinylsilane) (PBDMVS) was carried out under nitrogen atmosphere according to the literature.[8,9] A solution of 890 mg of PBDMVS (corresponding to 5.05 mmol of BDMVS) in 30 mL of hexane was stirred with coarse CaH_2 powder overnight in vacuo. After removal of CaH_2 by filtration, the hexane was distilled off and 12 mL of THF was added. Nitrogen was introduced to this solution, and then 8.5 mmol of freshly distilled benzaldehyde was added. To this mixture was added dropwise at room temperature a THF solution (20 mL) of 7.9 mmol of anhydrous tetrabutylammonium fluoride (TBAF), which was prepared from TBAF·$3H_2O$ by the procedure of Bartoli et al.[9] After the addition of TBAF, the reaction mixture was maintained at room temperature for 30 min with stirring and refluxed for 10 h, followed by additions of 4.0 g (37 mmol) of trimethylchlo-

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Table I
Polymerization of BDMVS[a]

time, days	temp, °C	yield, %	$\bar{M}_n/10^3$ calcd[b]	$\bar{M}_n/10^3$ obsd[c]	$\bar{M}_w/\bar{M}_n$[c]
In the Absence of TMEDA					
2	40	68	6.0	4.1	1.10
2	40	92	8.1	5.8	1.11
7	60	98	8.7	6.3	1.12
In the Presence of TMEDA[d]					
2	40	30	2.7	1.9	1.18
7	40	61	5.5	4.3	1.14
7	60	100	8.9	6.2	1.14

[a] Solvent, cyclohexane; [BDMVS] = 1.0 mol/L; [*sec*-BuLi] = 2×10^{-2} mol/L. [b] Calculated from the monomer to initiator ratio and the percent yield. [c] Determined by GPC. [d] [TMEDA] = [*sec*-BuLi].

rosilane and of 840 mg (47 mmol) of distilled water to it. The mixture was subjected to evaporation, and the residue was resolved in 50 mL of CH_2Cl_2, washed with water, with saturated aqueous $NaHCO_3$, and with water again, and dried over Na_2SO_4. Removal of CH_2Cl_2 by a vacuum pump at 50 °C gave 1.44 g of brown liquid.

Characterization of the Polymers. Number-average molecular weights ($\bar{M}_n$) and molecular weight distributions ($\bar{M}_w/\bar{M}_n$, MWD) were determined by gel permeation chromatography (GPC) data obtained in THF using Toyo Soda HLC-802UR with G2000H (250 Å, 60 cm) and G3000H (1500 Å, 60 cm) columns or using Toyo Soda HLC-802A with two GMH (1500–1×10^7-Å mixture, 60 cm) columns. These data were calibrated with polystyrene standards ($M_{GPC} = 1.0 \times 10^3$–$6.8 \times 10^6$). ^{1}H NMR spectra were taken with a Varian XL-200 spectrometer operating at 200 MHz in the Fourier transform mode. Chloroform-d_1 containing 3% CH_2Cl_2 as an internal reference (5.34 ppm) was used for the solvent. ^{13}C NMR spectra were obtained with the same spectrometer operating at 50.3 MHz in the Fourier transform mode. Chloroform-d_1 containing 1% tetramethylsilane as an internal standard was used for the solvent.

Results

Anionic polymerization of BDMVS was carried out in the presence or absence of TMEDA. Whether in the presence or absence of TMEDA, a sticky polymer was obtained. The physical appearance of the polymer resembled that of poly(trimethylvinylsilane) (PTMVS) obtained in the presence of TMEDA rather than that of PTMVS obtained in the absence of TMEDA. Reaction conditions and the results are shown in Table I. $\bar{M}_n$ of PBDMVS increased linearly with the yield. The values of MWD were less than 1.2 in all runs. The addition of TMEDA to the polymerization system lowered the polymerization rate, but no obvious effect was observed on the linearity of $\bar{M}_n$ and on $\bar{M}_w/\bar{M}_n$. The change in the polymerization rate would be caused by the steric hindrance between the bulky substituent of the monomer and the TMEDA-coordinated lithium cation of the living end.

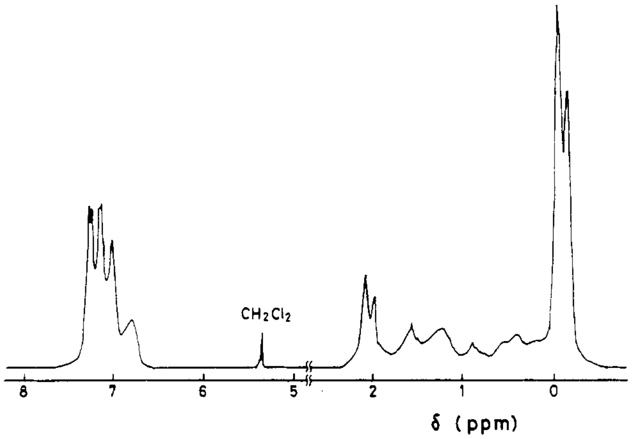


Figure 1. ^{1}H NMR spectrum of PBDMVS in $CDCl_3$. Dichloromethane was used for the internal standard.

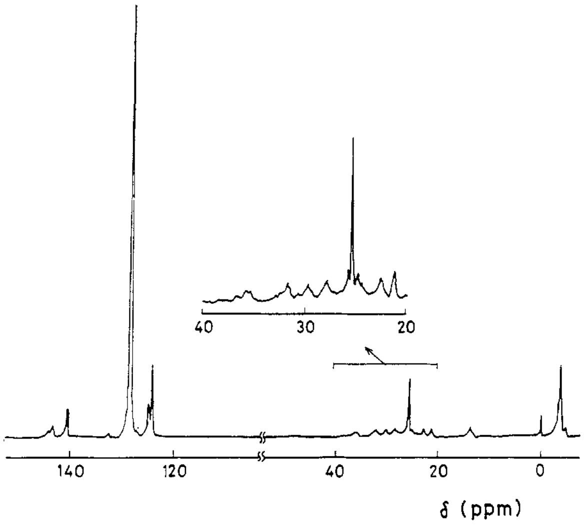


Figure 2. ^{13}C NMR spectrum of PBDMVS in $CDCl_3$. Tetramethylsilane was used for the internal standard.

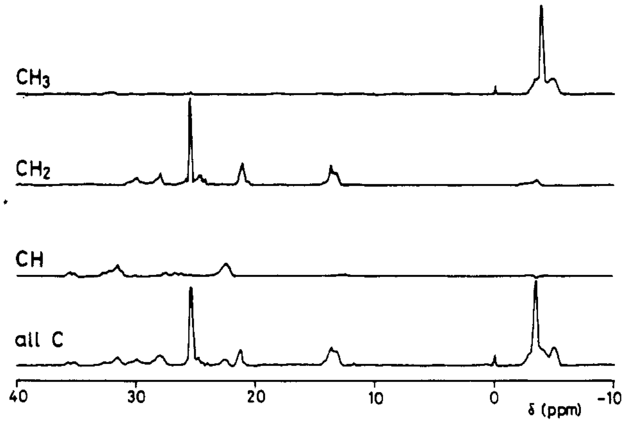


Figure 3. High-field region of ^{13}C DEPT spectra of PBDMVS in $CDCl_3$.

All PBDMVS's obtained under various conditions gave the same spectra of IR, ^{1}H NMR, and ^{13}C NMR. In the ^{1}H NMR spectrum of PBDMVS (Figure 1), six groups of signals appeared at −0.2–0.2 (12 H), 0.3–0.7 (2 H), 0.8–1.0 (1 H), 1.1–1.7 (4 H), 1.9–2.2 (3 H), and 6.7–7.3 ppm (10 H). Each group was assigned to silylmethyl, silylmethylene, silylmethine, methylene, silylbenzylic and silylbenzylidene, and aromatic protons, respectively.[10] Figure 2 shows the ^{13}C NMR spectrum of PBDMVS. Each group of the peaks was assigned as follows: −4.9–3.1 (silylmethyl), 13.7 (silylmethylene), 21.1–35.7 (silylmethine, methylene, silylbenzylic, and silylbenzylidene), 123.9 and 124.3 (Ar C-2), 128.0 (Ar C-3 and C-4), 140.1–142.9 ppm (Ar C-1). More detailed assignments were carried out for the peaks from 21.1 to 35.7 ppm by distortionless enhancement by polarization transfer[11] (DEPT, Figure 3) and selective decoupling methods (Figure 4). DEPT spectra indicate that the peaks at 21.2, 25.4, 27.9, and 29.7 ppm are CH_2 signals and that those at 22.6, 31.7, and 35.6 ppm are CH signals. The peak at 22.6 ppm is revealed to be a silylmethine carbon signal from the selective decoupling spectrum with the silylmethine proton at 0.9 ppm in the ^{1}H NMR spectrum (Figure 4A). In a similar manner, the peaks at 21.2, 27.9, and 29.7 ppm can be assigned as methylene carbons (Figure 4B,C). The CH_2 signal at 25.4 ppm and

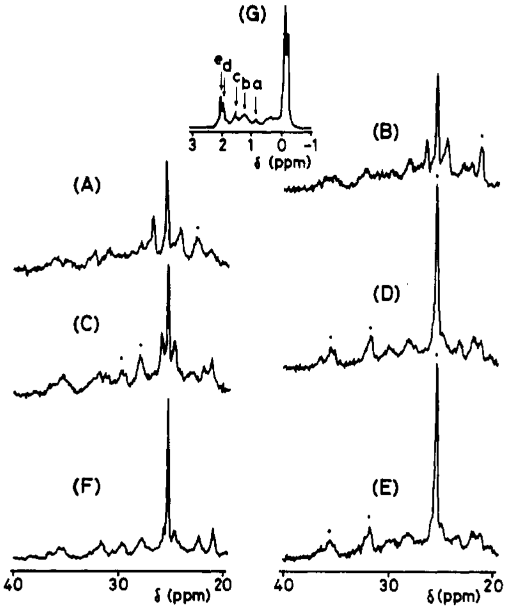


Figure 4. ^{13}C NMR spectra of PBDMVS in $CDCl_3$; decoupled with (F) all protons, (A) signal a, (B) signal b, (C) signal c, (D) signal d, (E) signal e in ^1H NMR spectrum (G), respectively. Dotted peaks were found decoupling.

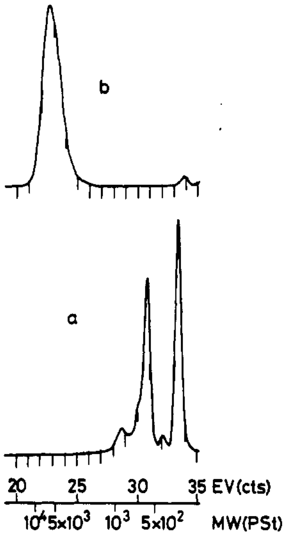


Figure 5. GPC traces of (a) decomposition product of PBDMVS and (b) PBDMVS before the decomposition.

the CH signals at 31.7 and 35.6 ppm should be assigned to silylbenzylic and silylbenzylidene carbons, respectively (Figure 4D,E).

As an alternative method for confirming the structure of PBDMVS, the decomposition of PBDMVS was carried out as described in the Experimental Section. The molecular weight (MW) of the decomposition product of PBDMVS, whose $\bar{M}_n$ was 5.8 × 10^3 originally, was determined by GPC (Figure 5). Its trace showed no high MW peaks. The peak at 30.7 count corresponds to MW ~ 480. The minor peak at 28.6 count corresponds to MW ~ 850.

In the ^1H NMR spectrum of the decomposition product (Figure 6), neither silylbenzylic nor silylbenzylidene signals can be seen. Several new peaks appeared, instead, at 1.0, around 2.3, 2.5, 3.1, around 4.8, and 5.0 ppm.

Discussion

All PBDMVS's, which were obtained under various polymerization conditions such as different temperatures and the presence or absence of TMEDA, provided the same spectra of IR, ^1H NMR, and ^{13}C NMR, respectively. The invariance of the spectra suggests the existence of a certain regularity in the polymer structure. The ^1H NMR spectrum indicates that the structure of PBDMVS differs from what would be obtained if the polymerization proceeded without isomerization. The obtained spectrum showed silylmethyl (12 H), silylmethylene (2 H), silylmethine (1 H), methylene (4 H), benzylic and benzylidene (3 H), and aromatic (10 H) signals, though the spectrum of the imaginary polymer, which should have been formed without the isomerization, must show the different signals (12 H, none, 2 H, 4 H, 4 H, 10 H, respectively). The existence of the silylmethylene carbon signal in the ^{13}C NMR spectrum similarly indicates that the isomerization has occurred.

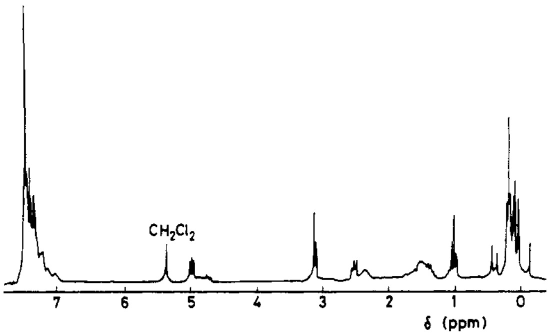
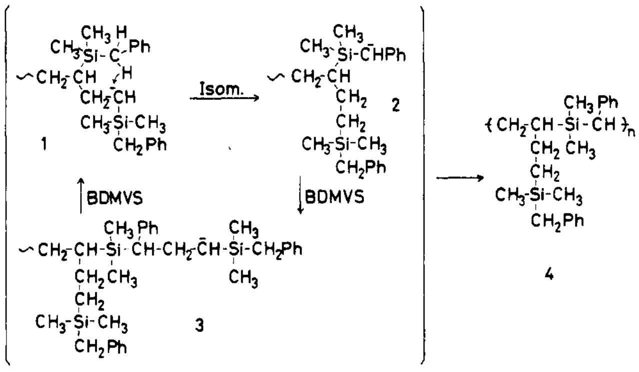


Figure 6. ^1H NMR spectrum of the decomposition product of PBDMVS in $CDCl_3$. Dichloromethane was used for the internal standard.

Scheme I



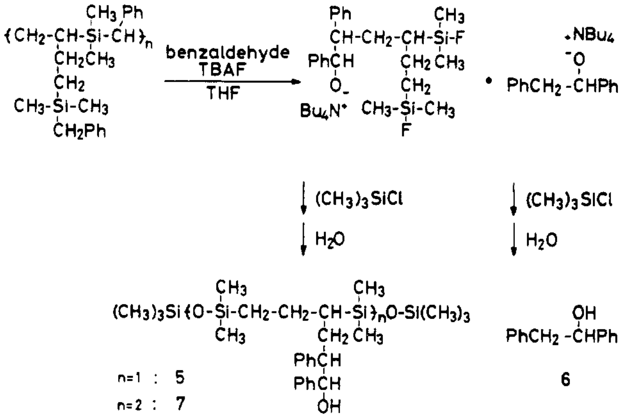
For the polymerization reaction, which is consistent with the experimental results, Scheme I is proposed. After the addition of the monomer to a silylmethine anion, the newly formed silylmethine anion (1) abstracts a silylbenzylic proton in the penultimate monomer unit. To the resulting silylbenzylidene anion (2), the addition of the next monomer takes place. Though a silylmethine anion is regenerated (3), it cannot isomerize to a silylbenzylidene anion, owing to the difference in the structure of the penultimate monomer unit from that described above. Repetition of these two alternating propagation reactions affords the polymer structure (4), which consists of two kinds of monomer units: one forms the backbone and the other exists as a pendant group. This structure is in accord with ^1H NMR data described above. The peak ranging from 1.9 to 2.2 ppm in Figure 1 can be divided into two peaks at 1.98 ppm (1 H) and at 2.08 ppm (2 H), and they are explicable as the silylbenzylidene proton and the silylbenzylic protons, respectively.

The polymer structure (4) is also supported by ^{13}C NMR data. Two signals of Ar C-2 carbons at 123.9 and 124.3 ppm indicate that two kinds of C-2 carbons exist in the polymer. The sharp signal at the higher magnetic field corresponds to the C-2 carbons in the pendant group, whereas the less sharp signal at the lower magnetic field corresponds to the C-2 carbons in the benzene ring directly attached to the main chain. Ar C-1 carbons also exhibited two kinds of signals at 140.2 and 142.9 ppm. The sharp peak at 140.2 ppm corresponds to the C-1 carbon in the pendant group, and the broad peak at 142.9 ppm corresponds to the C-1 carbon directly attached to the main chain. The latter peak showed a splitting that was induced by the asymmetry in the main chain. In the region of silylmethyl carbon signals, there seemed to be three peaks. One locates at −4.7 ppm. Another is the sharp peak at −3.7 ppm. The other peak is present at −3.3 ppm as a shoulder of the sharp peak. The peak at −3.7 ppm corresponds to the silylmethyl carbons in the pendant group because the sharpness of this peak indicates a high mobility of these methyl groups. The other peaks are considered to correspond to the methyl carbons directly attached to the silicon atom in the main chain. Two signals of this carbon would reflect the asymmetry of the adjacent carbon atoms. The sharp peak at 25.4 ppm was found to arise from a silylbenzylic carbon by DEPT and the selective decoupling. On the other hand, two broad peaks at 31.7 and 35.6 ppm were assigned similarly to a silylbenzylidene carbon. The only one sharp signal of the silylbenzylic carbon indicates that the environment of the silylbenzyl group is uniform and that its mobility is high. The methylene peak at 21.2 ppm is considered to be the methylene in the pendant group since it is relatively sharp. Other methylene signals at 27.9 and 29.7 ppm can be assigned to be the methylene in the main chain.

The reaction of PBDMVS with benzaldehyde in the presence of TBAF causes the cleavage of the bond between a benzylic carbon and a silicon atom. If the benzylic carbons in PBDMVS existed only as pendants of the main chain, the decomposition product had to contain a still high MW fraction though it was lower than the original polymer. The result shown in Figure 5 is against such a structure. The reaction is shown in Scheme II. The peak at 30.7 count in the GPC trace would be depending on 1,2-diphenyl-4,6-bis[(trimethylsiloxy)dimethylsilyl]-1-hexanol (**5**, MW = 546). The peak based on 1,2-diphenylethanol (**6**) can be seen at 33.3 count. The minor peak at 28.6 count corresponds to the dimerized byproduct (**7**, MW = 930). The new peaks in the ^{1}H NMR of the product can be assigned as follows: 1.0 (silylmethylene in **5**), around 2.3 (OH), 2.5 ($CH_2CH(Ph)CH(Ph)$-OH in **5**), 3.1 (CH_2 in **6**), around 4.8 (−*C**H***(Ph)OH in **5**), 5.0 ppm (−*CH*OHPh in **6**). These experimental results support the polymerization scheme proposed in this article.

The isomerization reaction takes place once per two addition reactions because of not only high acidity of benzylic protons but also steric effect. The silylmethine anion of a propagating end of which penultimate unit was not isomerized can abstract a silylbenzylic proton through a six-membered ring. This abstraction can occur only intramolecularly, because $\bar{M}_n$ increases linearly with the yield and MWD shows no obvious increase with the yield. The absence of the intermolecular chain transfer implies that the formation of the six-membered ring plays a very important role in the chain-transfer reaction.

Scheme II



In conclusion, the polymer obtained in the anionic polymerization of BDMVS has been revealed to have such a unique structure that silicon atoms are incorporated both in the backbone and in the pendant group with strict regularity. The six-membered ring structure, in collaboration with the high acidity of the benzylic protons, contributes to the isomerization, which occurs even in the absence of TMEDA. Similar isomerization reactions would occur more or less for other vinylsilanes.

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