Anionic Polymerization of Vinylsilanes II. Mechanism of Isomerization in the Polymerization of Trimethylvinylsilane with Butyllithium-*N,N,N',N'*-tetramethylethylenediamine

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ABSTRACT: The isomerization reaction in the anionic polymerization of trimethylvinylsilane (TMVS) with butyllithium (*n*-BuLi) in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was investigated. An equimolar amount of TMEDA with *n*-BuLi was found to be necessary and enough for the quantitative isomerization. The isomerization reaction was revealed to take place only intramolecularly. From the spin-lattice relaxation time measurements of the polymer obtained in the isomerization polymerization of TMVS, it was found out that the abstraction of a silylmethyl proton from an end unit and the abstraction from a penultimate unit are both possible.

KEY WORDS Anionic Polymerization / Isomerization Polymerization / Trimethylvinylsilane / *N,N,N',N'*-Tetramethylethylenediamine / ¹H NMR / Relaxation Time / Proton Abstraction / Penultimate Unit / End Unit /

Since the anionic polymerization of vinylsilanes was reported by Nametkin and his co-workers in 1963,¹ several studies have been done on this polymerization.²⁻⁶ In the first paper it was reported that trimethylvinylsilane (TMVS) and other vinylsilanes were polymerized by alkylolithium in heptane. They revealed that the polymerization of TMVS was accompanied by a slow termination² and that a chain transfer to the monomer occurred at high temperature.³ These side reactions were also studied in detail using model reactions.⁴ The termination reaction in the presence of ethers was investigated by Rickle as well.⁵ From the results, he determined the optimum polymerization conditions to obtain a diblock copolymer poly(styrene-*b*-trimethylvinylsilane).⁶

We have recently reported that an isomerization reaction occurs in the polymerization of TMVS with butyllithium (*n*-BuLi) and that it is enhanced by the addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the

polymerization system.⁷ This isomerization was found to be the abstraction of a silylmethyl proton by the silylmethine anion in the propagating end. As a result, an isomerized unit, $-\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2-$, is incorporated in the polymer structure. The incorporation of the silicon atoms in the main chain causes a drastic change in the physical appearance of the polymer from a white powder to a viscous liquid.

The isomerization manner in the anionic polymerization of benzyldimethylvinylsilane (BDMVS) has been elucidated in detail.⁸ In the polymerization of BDMVS, the proton abstraction takes place regularly once per two addition reactions from the silybenzylic group in the penultimate monomer unit, whether in the presence or absence of TMEDA. On the other hand, in the case of TMVS, the isomerization manner are not the same as that in the polymerization of BDMVS, because all the monomer units can isomerize in the case

of TMVS whereas only half of the monomer units isomerize in the case of BDMVS.

In the present work, we study the mechanism of the isomerization reaction in the polymerization of TMVS in detail.

EXPERIMENTAL

Materials

All chemicals were purchased from commercial sources. Hexane was distilled from sodium-benzophenone. *n*-BuLi in hexane was used after filtration. TMEDA was distilled over CaH₂ and then over sodium mirror. TMVS was distilled over CaH₂ and then from *n*-BuLi.

Poly(trimethylvinylsilane) (PTMVS; number average molecular weight ($\bar{M}_n$), 7.8×10^3 ; molecular weight distribution ($\bar{M}_w/\bar{M}_n$), 1.33; content of the isomerized units (CIU), 6%) used as an additive to the polymerization system was purified in benzene under a high vacuum condition as follows. Into the mixture of CaH₂ and 1.6 g of PTMVS, about 20 ml of benzene was distilled from CaH₂ on a vacuum line. Stirred overnight at room temperature, the solution was filtered. The filtrate was freeze-dried, then hexane was added to the residue. After subdivided properly, a necessary amount of the solution was placed in a polymerization apparatus, then hexane was removed *in vacuo*.

Polymerization of TMVS

Polymerizations were carried out in hexane at room temperature or 60°C for 48 h or 72 h. Detailed polymerization procedures were previously described.⁷

CIU was calculated from the ratio of the peak areas of silylmethine signal at 0.9 ppm and silylmethylene signal at 0.5 ppm in the ¹H NMR of PTMVS as previously described.⁷

Measurements

$\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were determined from gel permeation chromatography (GPC) data obtained in tetrahydrofuran using Toyo Soda

HLC-802UR with G2000H and G3000H columns or using Toyo Soda HLC-802A with two GMH columns. These data were calibrated with polystyrene standards. $\bar{M}_n$ determined from GPC was found to be 10% higher than the true value from vapor pressure osmometry measurements.

¹H NMR spectra were recorded on a Varian XL-200 spectrometer at 200 MHz in the Fourier transform mode with a spectral width of 2600 Hz, 15600 points in the time domain, and an acquisition time of 3 s. Relaxation data were obtained by the inversion recovery method^{9,10} using 180°- τ -90° pulse sequence and a repetition between the pulse trains of 8 s, varying the τ value in the range of 7.81×10^{-3} –4.0 s. Spin-lattice relaxation times (T_1) were determined by using the program with which XL-200 was equipped. For the determination of the content of the isomerized units, chloroform-*d*₁ containing 3% CH₂Cl₂ was used as a solvent. For the measurements of T_1 's of the silylmethyl signals, benzene-*d*₆ containing 1% tetramethylsilane was used as a solvent.

RESULTS AND DISCUSSION

The polymerization results of TMVS at 60°C under various ratios of TMEDA to *n*-BuLi are shown in Table I. In the absence of TMEDA, CIU of the resulting polymer was 14%. This value increased with increasing TMEDA/*n*-BuLi ratio and reached 100% at the ratio of 1.0. At the TMEDA/*n*-BuLi ratio over 1.0, CIU of the polymer was constantly 100%. The physical appearance of the polymer changed successively from a white powder to a viscous liquid with the increase in CIU. Accordingly, the relationship between the TMEDA/*n*-BuLi ratio and CIU can be explained on one-to-one complex formation between a lithium cation and a TMEDA molecule. A silylmethine anion abstracts a silylmethyl proton only to a little extent when the counterion is free from TMEDA. Once a TMEDA molecule coor-

Table I. Polymerization of trimethylvinylsilane^a

[TMVS] mol l ⁻¹	[TMVS] [<i>n</i> -BuLi]	[TMEDA] [<i>n</i> -BuLi]	Time h	Yield %	$\bar{M}_n^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n^b$	CIU %
5.11	992	0	48	95	33.5	1.95	14
5.64	823	0.25	48	64	15.1	1.82	35
5.63	818	0.51	48	36	10.5	1.72	55
5.23	826	0.74	48	42	10.9	1.74	60
3.76	849	0.95	48	61	9.4	1.83	100
5.61	798	2.6	72	57	7.9	1.83	100
5.54	805	5.0	72	60	8.0	1.79	100
5.50	808	10.1	72	92	7.6	2.19	100

^a Polymerization temp, 60°C; solvent, hexane.^b Determined by GPC.

dinates with a lithium cation, the silylmethine anion is forced to abstract a silylmethyl proton. When the TMEDA/*n*-BuLi ratio lies between 0 and 1, some lithium cations are free from TMEDA and the others form complexes with TMEDA in one-to-one ratio, which results in an intermediate CIU. When the TMEDA/*n*-BuLi ratio is over 1.0, all lithium cations exist as the complexes with TMEDA. This leads to a quantitative isomerization.

Eberhardt and Butte¹¹ demonstrated that *n*-BuLi was coordinated with an equimolar amount of TMEDA to form the complex which could transmetalate aromatic hydrocarbons. The complex was also found to be capable of converting methylsilanes to the corresponding silylmethyl lithium compounds.¹² These results are closely correlated to our polymerization results described above.

When the TMEDA/*n*-BuLi ratio increased from 0 to 1, $\bar{M}_n$ of the polymer lowered apparently. This decrease in $\bar{M}_n$ is attributable to the chain transfer reaction to the monomer, which was observed in the polymerization at temperatures above 80°C even in the absence of TMEDA.³ The chain transfer reaction caused by the addition of TMEDA will be discussed in a forthcoming paper.

To determine whether the proton abstraction occurs only as an intramolecular reaction or both as intra- and intermolecular reactions,

Figure 1. GPC profiles of poly(trimethylvinylsilane)'s: (a), used as an additive in the polymerization of trimethylvinylsilane; (b), obtained in the polymerization in the presence of (a).

polymerization of TMVS was carried out in the presence of a PTMVS. The reaction conditions were as follows: [TMVS] = 2.07 mol l⁻¹ (TMVS, 1.06 g); [*n*-BuLi] = [TMEDA] = 0.066 mol l⁻¹; [TMVS]/[*n*-BuLi] = 31.2; PTMVS, 350 mg; reaction temperature, room temperature; time, 48 h. The polymer obtained was a viscous liquid (1.13 g, 73%). Its overall CIU was 55%.

Figure 1 shows the GPC profiles of the PTMVS used as an additive (precursor) and the polymer obtained above. The latter profile exhibits two peaks. The lower molecular weight peak can be assigned to the newly formed

PTMVS of which $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ are 2.8×10^3 and 1.17, respectively. The other peak coincides with that of the precursor in position and shape. The peak area is smaller than expected, but it is just due to the loss in the course of the purification of the precursor. If the isomerization could occur intermolecularly, $\bar{M}_n$ of the precursor had shown a shift to higher molecular weight region owing to the propagation from the silylmethylene anion formed in the precursor. The GPC profiles indicate that the isomerization proceeds by only an intramolecular proton abstraction.

Although the isomerization was proved to be the intramolecular reaction, it is not clear which proton of the polymer molecule is subject to the abstraction. The possible protons subject to the abstraction are the methyl protons of the propagating end unit and the penultimate unit, considering the fact that intermolecular abstraction does not take place. To clarify how the abstraction occurs, ^1H NMR measurements were carried out on PTMVS which was obtained in the presence of TMEDA. The $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and CIU of the PTMVS were 7.6×10^3 , 2.19, 100%, respectively. Silylmethyl signal showed a slight splitting in CDCl_3 , CCl_4 , cyclohexane, and benzene. Since the most remarkable splitting was observed in benzene among these solvents, ^1H NMR spectrum measurement in C_6D_6 was examined in more detail.

The ^1H NMR spectrum and an expanded spectrum of silylmethyl region are shown in Figure 2 along with those of PTMVS obtained in the absence of TMEDA. In the silylmethyl region two discrete peaks can be seen at 0.129 ppm (**A**) and 0.192 ppm (**B**). Furthermore, an additional peak can be seen at 0.209 ppm (**C**) as a shoulder. Chemical shifts for all these peaks are different from that of trimethylsilyl groups (0.267 ppm) in PTMVS obtained in the absence of TMEDA. The environments of these silylmethyl groups were investigated by means of T_1 measurement. The T_1 value of **A** was 1.179 ± 0.026 s, whereas those

Figure 2. 200 MHz ^1H NMR spectra of poly(trimethylvinylsilane): (a) obtained in the presence of TMEDA; (b) obtained in the absence of TMEDA.

Scheme 1.

of **B** and **C** were 0.546 ± 0.022 s and 0.467 ± 0.028 s, respectively. The slower relaxation means that the methyl groups of the peak **A** are located apart from the main chain. The methyl groups of the peaks **B** and **C**, on the contrary, are considered to be directly attached to the silicon atoms in the main chain. From the chemical shifts of these three peaks and the assignments described above, the peak **A** at the higher magnetic field appears to correspond to $(\text{CH}_3)_3\text{Si}$ - in pendant groups and the peaks **B** and **C** at the lower magnetic fields are considered to correspond to $(\text{CH}_3)_2\text{Si}=\text{}$ and/ or $\text{CH}_3\text{Si}\equiv$ in the main chain.

These assignments are consistent with the polymer structure which is formed by the two types of proton abstractions from the end unit and from the penultimate unit (Scheme 1). All monomer units are isomerized because 100%

CIU is attainable. At first the initially formed silylmethine anion (**1**) abstracts a silylmethyl proton within the end unit. Then the resulting silylmethylene anion (**2**) attacks the monomer. The silylmethine anion formed again (**3**) abstracts a silylmethyl proton from either the end unit or the penultimate unit. When the silylmethyl proton in the end unit is abstracted, the resulting silylmethylene anion (**4**) adds the monomer to regenerate **3**. When the proton abstraction from the penultimate unit occurred, the silylmethylene anion formed (**5**) adds the monomer, but the resulting silylmethine anion (**6**) has a different structure from **3**. This anion tends to abstract the silylmethyl proton of the end unit to form **2**.

The peak A in Figure 2 is attributed to the silylmethyl protons in the pendant groups $-(\text{CH}_2)_3\text{Si}(\text{CH}_3)_3$ which appeared through the proton abstraction from the penultimate unit. The peak C would be assigned to $\text{CH}_3\text{Si}\equiv$ at the branching point which was also formed by the abstraction from the penultimate unit. The peak B is assigned to $(\text{CH}_3)_2\text{Si}=\text{}$ in the main chain which was brought about by the two successive proton abstractions within the end units.

In the polymerization of BDMVS, the addition of TMEDA is not necessary for the isomerization and the proton abstraction takes place only from the penultimate unit through six-membered ring.⁸ In the case of TMVS, the isomerization is enhanced by addition of TMEDA and the proton abstraction within the end unit is also possible. These differences in the isomerization behavior would result from the difference in the bulkiness of substituents on the silicon atom.

CONCLUSIONS

An equimolar amount of TMEDA with *n*-BuLi is necessary and enough for the quantitative isomerization. The isomerization in the polymerization of TMVS is an intramolecular reaction. A silylmethyl proton in the end unit is abstracted by the silylmethine anion. The abstraction from the penultimate unit also takes place.

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