

## Anionic Polymerization of Vinylsilanes VI. Effects of *N,N,N',N'*-Tetramethylethylenediamine on the Polymerization of Methyltrivinylsilane

Jun-ichi OKU, Masako TAKAHASHI, Yukiko ITOH,  
Kenji SHIRAISHI, and Mikiyo TAKAKI

*Department of Applied Chemistry, Nagoya Institute of Technology,  
Gokiso-cho, Showa-ku, Nagoya 466, Japan*

(Received June 15, 1993)

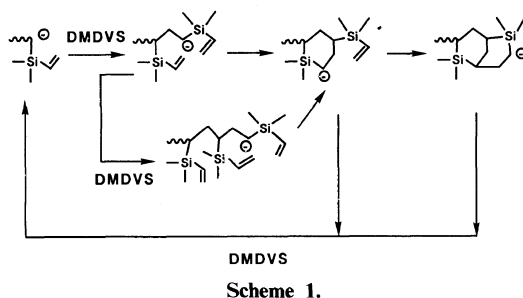
**ABSTRACT:** Anionic polymerization of methyltrivinylsilane was conducted in the presence and absence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). In the polymerization, cyclopolymerization always took place similarly to the polymerization of dimethyldivinylsilane. In the absence of TMEDA at  $-10^{\circ}\text{C}$ , the polymerization proceeded extremely slowly and only 5% polymer was obtained even after 168 h. In the presence of TMEDA, on the other hand, the remarkable acceleration of the polymerization and the suppression of gelation were observed. The fraction of the remaining second and third vinyl groups in the polymer was much higher for the polymer obtained in the presence of TMEDA. These effects of TMEDA were explained by the change in the reactivity of the propagating ends, that is, the increase in the selectivity in the addition of propagating ends to vinyl groups.

**KEY WORDS** Anionic Polymerization / Cyclopolymerization / *N,N,N',N'*-Tetramethylethylenediamine / Methyltrivinylsilane / Selectivity /

We have studied the anionic polymerization of vinylsilanes, especially with respect to an isomerization of the propagating end in the course of the polymerization. The isomerization, observed in the polymerization of trimethylvinylsilane with *n*-butyllithium or *s*-butyllithium (*s*-BuLi) in hexane, takes place through the intramolecular abstraction of a silylmethyl proton by the propagating end anion, and its frequency is remarkably increased by the addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the polymerization system.<sup>1-3</sup> Similar isomerization was observed in the polymerization of dimethylphenylvinylsilane with *s*-BuLi/TMEDA.<sup>4</sup> Interestingly, in the case of benzyldimethylvinylsilane the proton abstraction occurs quite regularly from the benzylic methylene in the penultimate monomer unit even in the absence of TMEDA.<sup>5</sup> In the polymeriza-

tions of allylvinylsilanes similar intramolecular abstraction also takes place from the allylic methylene in the absence of TMEDA.<sup>6</sup>

By contrast to the polymerizations of monovinylsilanes, our study on the polymerization of dimethyldivinylsilane (DMDVS)<sup>7</sup> revealed that monocyclic and bicyclic rings are formed in the course of polymerization both in the presence and absence of TMEDA (shown in Scheme 1), mainly based on low contents



of remaining vinyl groups in the polymers and the good agreement between calculated and observed molecular weights at low polymer yields. More importantly, the addition of TMEDA was found to suppress cross-linking reaction.

We now report the anionic polymerization behavior of another multivinylsilane, methyltrivinylsilane (MTVS), particularly remarkable effects of the addition of TMEDA on the polymerization.

## EXPERIMENTAL

### Materials

MTVS (Shin-Etsu Silicon Chemicals) was distilled over  $\text{CaH}_2$ . *s*-BuLi, TMEDA, and hexane were purified according to the conventional method for the anionic polymerization.<sup>2,5</sup>

### Polymerization of MTVS

Polymerizations were carried out in hexane at  $-10^\circ\text{C}$  or  $40^\circ\text{C}$  under high vacuum conditions using breakable seal techniques. The initial concentrations of the reagents were as follows:  $[\text{MTVS}] \sim 0.33 \text{ mol l}^{-1}$ ,  $[\textit{s}\text{-BuLi}] \sim 6.6 \text{ mmol l}^{-1}$ ,  $[\text{TMEDA}] \sim 0$  or  $6.6 \text{ mmol l}^{-1}$ . Detailed polymerization procedure was previously described.<sup>1</sup> After the reaction mixture was quenched by methanol, it was concentrated by evaporation. Then the residue was dissolved in benzene and the solution was washed with aqueous HCl. When a benzene-insoluble part was present, it was separated by filtration and dried. Freeze-drying of the benzene solution gave white powder except when only oligomer was obtained.

### Measurements

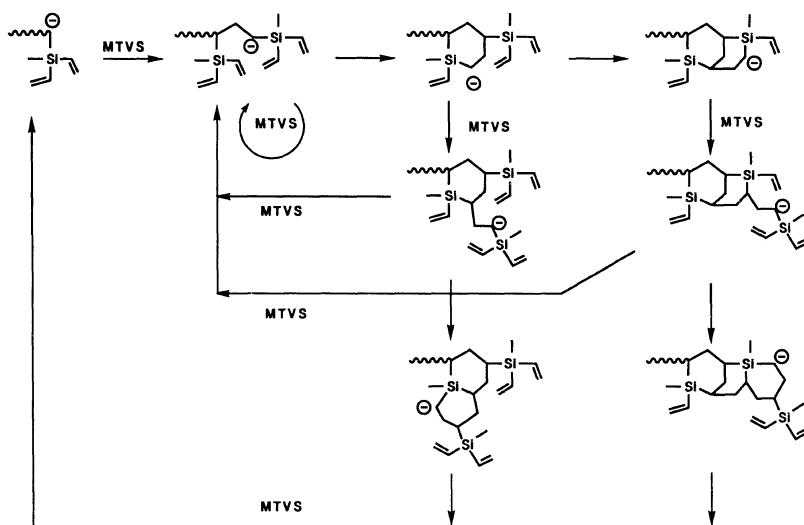
Number-average molecular weights ( $\bar{M}_n$ ) and molecular weight distributions ( $\text{MWD}/\bar{M}_w/\bar{M}_n$ ) were determined by gel permeation chromatography (GPC) using Toyo Soda HLC-802UR equipped with G2000H and G3000H columns or using Toyo Soda

HLC-802A with two GMH columns. Tetrahydrofuran was used as an eluent. The chromatograms were calibrated with polystyrene standards. For two polymers,  $\bar{M}_n$ 's were also determined by vapor pressure osmometry (VPO) to compare with those determined by GPC. VPO measurements were carried out in benzene solution at  $40^\circ\text{C}$  using a Corona 117 molecular weight apparatus.  $^1\text{H}$  NMR spectra were taken with a Varian XL-200 spectrometer operated at 200 MHz in the Fourier transform mode. Chloroform- $d_1$  containing dichloromethane as an internal reference (5.34 ppm) was used for the solvent.

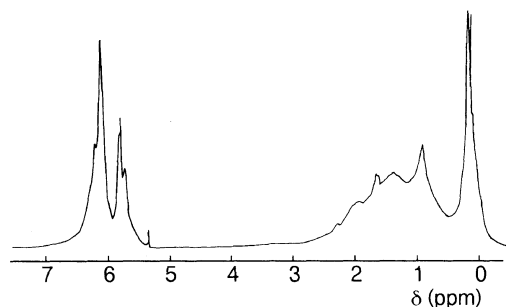
## RESULTS AND DISCUSSION

Polymerizations of MTVS always yielded white powdery polymers with and without TMEDA except for the case in which oligomer was obtained. Considering that the polymerization of DMDVS affords white powdery polymer in both the absence and presence of TMEDA<sup>7</sup> and that monovinylsilanes polymerize to give viscous polymers in the presence of TMEDA,<sup>1,4</sup> cyclopolymerization similar to that of DMDVS is suggested to take place in the polymerization of MTVS. The possible cyclopolymerization mode of MTVS, where various types of complicated rings can be formed, is illustrated in Scheme 2.

Figure 1 shows the  $^1\text{H}$  NMR spectrum of the polymer obtained in the polymerization at  $40^\circ\text{C}$  for 1 h with TMEDA. The intense peak around 0.2 ppm and two groups of signals between 5.5 and 6.5 ppm are assigned to silylmethyl protons and vinyl protons, respectively. Signals of all other protons locate in the broad peaks from 0.5 to 2.5 ppm. All polymers obtained in this study exhibited similar spectra except for the relative intensities of the vinyl signals and of the signals corresponding to methyl protons of initiator fragments at 0.9 ppm. The fraction of the remaining second and third vinyl groups in the polymer was calculated from the peak areas of the vinyl



Scheme 2.



**Figure 1.**  $^1\text{H}$  NMR spectrum in  $\text{CDCl}_3$  of poly(MTVS) obtained in the polymerization at  $40^\circ\text{C}$  for 1 h with TMEDA.  $\text{CH}_2\text{Cl}_2$  was used as an internal reference.

signals and of all signals, and it will be discussed afterward. The difference in the relative intensity of the methyl proton signal results from the difference in the polymer yield.

The broad peak around 2 ppm is also observed in the spectrum of poly(DMDVS). In this region, 1,1-dimethyl-1-silacycloalkanes having alkyl substituent(s) at  $\alpha$ -position(s) of Si atom, such as 1,1,2-trimethyl- and 1,1,2,6-tetramethyl-1-silacyclohexane, have resonance,<sup>8</sup> however, neither trialkylvinylsilanes nor poly-(trialkylvinylsilane)s show any peak. Consequently, the broad peaks around 2 ppm in the spectra of poly(MTVS) and poly(DMDVS)

are assigned to some protons in ring structure. The ratio of the peak area of the silylmethyl protons to those of all the protons is somewhat less than the expected value. This deviation is explicable with the isomerization reaction of the propagating end similar to that observed in the polymerization of trimethylvinylsilane,<sup>1,2</sup> however the content of the isomerized units cannot be determined accurately owing to the broadness of the peaks of silylmethine and silylmethylene protons.

Typical polymerization results are shown in Table I. In the absence of TMEDA the polymer yield did not increase to high extent at  $-10^\circ\text{C}$  even after a long polymerization time, whereas the polymerization in the presence of TMEDA at  $-10^\circ\text{C}$  afforded a soluble polymer in 32% yield for 3 h. When the polymerization in the absence of TMEDA was carried out at  $40^\circ\text{C}$ , benzene-insoluble polymer was obtained in 44% yield for 48 h. As would be expected, the polymerization in the presence of TMEDA at  $40^\circ\text{C}$  proceeded much faster. Although benzene-insoluble part was present in the resulting polymer for the polymerization longer than 3 h, completely soluble polymer was also obtained in 46% yield for 1 h. Benzene-insoluble

**Table I.** Anionic polymerization of methyltrivinylsilane (MTVS)<sup>a</sup>

Temp °C	Time h	Yield <sup>b</sup> %	$\bar{M}_n \times 10^{-3}$		$\bar{M}_w/\bar{M}_n^d$	Vinyl <sup>e</sup> %
			Calcd <sup>c</sup>	Obsd <sup>d</sup>		
In the absence of TMEDA						
-10	6	3	0.19	Oligomer	—	—
-10	24	4	0.25	1.1	1.64	33
-10	168	5	0.29	2.0	2.39	34
40	3	8	0.48	4.5	2.89	36
40	6	12	0.75	9.5	6.56	50
40	24	21 (19)	1.3	—	—	—
40	48	44 (43)	2.7	—	—	—
In the presence of TMEDA <sup>f</sup>						
-10	3	32	2.0	3.6	1.66	62
-10	6	41	2.5	5.6	2.39	64
-10	12	47	2.9	7.1	3.23	63
-10	48	58	3.6	15.4	Broad	64
40	1	46	2.9	6.5	Broad	58
40	3	55 ( 3)	3.4	—	—	—
40	12	84 (79)	5.2	—	—	—

<sup>a</sup> Solvent, hexane; [MTVS]  $\sim 0.33 \text{ mol l}^{-1}$ ; [*s*-BuLi]  $\sim 6.6 \text{ mmol l}^{-1}$ .

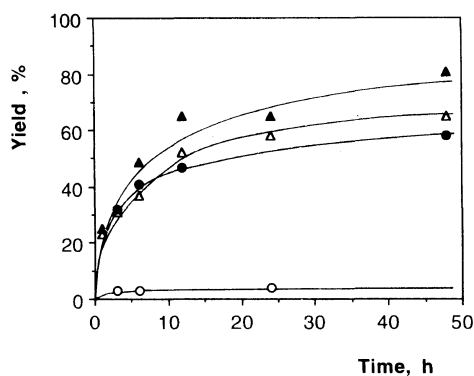
<sup>b</sup> Insoluble parts are shown in the parentheses.

<sup>c</sup> Calculated from the monomer-to-initiator ratio and the polymer yield on the assumption that no cross-linking reaction takes place.

<sup>d</sup> Determined by GPC.

<sup>e</sup> Fraction of the remaining 2nd and 3rd vinyl groups in the polymer calculated from the peak areas of the vinyl signals and of all signals in the <sup>1</sup>H NMR spectrum. 100% means two vinyl groups per monomer unit are found in the polymer.

<sup>f</sup> [TMEDA] = [*s*-BuLi].



**Figure 2.** Anionic polymerization of MTVS (this work) and DMDVS (previous work<sup>7</sup>). Polymerization conditions: [Vinyl]  $\sim 1 \text{ mol l}^{-1}$ , [Monomer]/[*s*-BuLi]  $\sim 50$ , at  $-10^\circ\text{C}$ , in hexane. MTVS, in the absence of TMEDA ( $\circ$ ); MTVS, in the presence of TMEDA ( $\bullet$ ); DMDVS, in the absence of TMEDA ( $\Delta$ ); DMDVS, in the presence of TMEDA ( $\blacktriangle$ ).

parts were also insoluble in other solvents such as hexane and tetrahydrofuran, and hence it is considered to be highly cross-linked material.

Figure 2 shows the relationships between the polymerization time and the polymer yield in the polymerization of MTVS at  $-10^\circ\text{C}$  in both the absence and presence of TMEDA, together with those in the polymerization of DMDVS under similar conditions.<sup>7</sup> As can be seen, the addition of TMEDA remarkably accelerates the polymerization of either monomer, and the extent is larger in the polymerization of MTVS. On the other hand, the polymerization of MTVS without TMEDA at  $-10^\circ\text{C}$  hardly proceeded. This can result from a low reactivity of the propagating oligomer anion and/or the occurrence of some termination reaction. In order to examine whether the termination re-

action plays a major role in the low polymerizability of MTVS, the following experiments were carried out.

After the polymerization of MTVS at  $-10^{\circ}\text{C}$  for 24 h in the absence of TMEDA, the polymerization temperature was raised to  $40^{\circ}\text{C}$  or equimolar amount of TMEDA to the initiator was added to the polymerization mixture, then the polymerizations were continued for an additional 24 h at  $40^{\circ}\text{C}$  and  $-10^{\circ}\text{C}$ , respectively. In the polymerization at the elevated temperature, a benzene-insoluble polymer was obtained in 31% yield. The polymerization after the addition of TMEDA gave a polymer, which included a little amount of insoluble part, in 39% yield. Since the initiator had been completely consumed at the end of the first stage,<sup>3</sup> these results strongly indicated that the termination reaction is not the principal cause of the low polymer yield at  $-10^{\circ}\text{C}$  in the absence of TMEDA even after a long polymerization time.

As shown in Table I, the  $\bar{M}_n$ 's of the resulting polymers are much higher than those calculated from the monomer-to-initiator ratios and the polymer yields on the assumption that no cross-linking reaction took place. Though the ratio of the observed  $\bar{M}_n$  to the calculated value increases with the increase in the polymer yield, it is not very high for the polymer obtained in the presence of TMEDA despite high polymer yield. Similar tendencies are observed in MWD's, *i.e.*, MWD broadens with the increase in the polymer yield, and it is not very broad for the polymer obtained in the presence of TMEDA at  $-10^{\circ}\text{C}$  at rather high polymer yield (32% or 41%). To evaluate  $\bar{M}_n$  values determined by GPC, VPO measurements were carried out for two polymers (both not shown in Table I). For a polymer obtained without TMEDA at  $-10^{\circ}\text{C}$ ,  $1.9 \times 10^{-3}$  was determined by VPO against  $2.9 \times 10^{-3}$  by GPC. A polymer given with TMEDA at  $-10^{\circ}\text{C}$  had an  $\bar{M}_n$  value of  $6.4 \times 10^{-3}$  by VPO against that of  $9.5 \times 10^{-3}$  by GPC. These results indicate that about 50% larger  $\bar{M}_n$  values are given by GPC than VPO.

The most characteristic difference between the polymers obtained in the absence and the presence of TMEDA lies in the fractions of the remaining second and third vinyl groups. When the polymerization was carried out at  $-10^{\circ}\text{C}$  in the absence of TMEDA, 33–34% of the second and third vinyl groups remain in the resulting polymer, whereas 62–64% vinyl contents are observed in the polymer obtained in the presence of TMEDA. This difference in the fraction of the remaining vinyl groups suggests that the polymer obtained in the absence of TMEDA contains more of complicated ring structures, such as bicyclic ring.

As described in the preceding parts, the addition of TMEDA exhibits the remarkable effects on the polymerization of MTVS. These effects are explicable based on the change in the reactivity of the propagating ends. Increase in the selectivity toward the propagation against the cross-linking by the addition of TMEDA results in the polymer with relatively low  $\bar{M}_n$  in comparison with that obtained without TMEDA considering the polymer yields. Narrower MWD can be accounted for similarly. These effects of TMEDA on  $\bar{M}_n$  and MWD directly correspond to the suppression of gelation. The difference in the fraction of the remaining vinyl groups, though such a difference was not clearly observed in the polymerization of DMDVS,<sup>9</sup> can be explained in terms of the change in the selectivity toward the propagation against the cyclization. Less cyclization and less cross-linking, which lead to larger fraction of the remaining vinyl groups, prevent incorporation of the propagating end into crowded surroundings, and hence the polymerization is accelerated by the addition of TMEDA. These ideas are corroborated by extremely low polymer yield at  $-10^{\circ}\text{C}$  in the absence of TMEDA, which is attributable to hard access of a monomer molecule to the propagating end, and high polymer yield after raising the polymerization temperature or adding TMEDA.

The increase in the selectivity toward the

propagation could be attributed to two factors. One is the isomerization of the propagating end from silylmethine anion to silylmethylene anion, which is observed in the polymerization of monovinylsilanes in the presence of TMEDA. When the isomerization has occurred, the cyclization that forms six-membered ring becomes impossible. In addition, the resulting silylmethylene anion is more stable, and hence its addition to various types of vinyl groups could be highly selective. The vinyl groups in the monomer are more susceptible to the addition of the propagating end than those in the polymers, accordingly the propagation becomes more favorable. The other factor is a decrease in the reactivity of the actual propagating end. In the absence of TMEDA, the propagating end is supposed to exist in equilibrium of associated form and dissociated one, similarly to those in the polymerization of vinyl monomers in non-polar media.<sup>10</sup> This equilibrium lies far to the associated form, however only the dissociated species is involved in the propagation. In the presence of an equimolar amount of TMEDA, the propagating end exists as 1:1 complex.<sup>11</sup> It is known that the reactivity of the complexed propagating end in the presence of TMEDA is lower than that of the dissociated species in the absence of TMEDA.<sup>12</sup> Therefore the selectivity in the addition of propagating ends to vinyl groups comes to high in the presence of TMEDA. Though it is not sure at the present stage which factor is significant, the characteristic effects of TMEDA are undoubtedly caused by the increase in the selectivity in the addition of propagating ends.

Soluble poly(MTVS) with high content of reactive vinylsilyl groups can be obtained in the presence of TMEDA in considerable yield, and thereby a variety of novel graft and star polymers have become available.

*Acknowledgment.* This work was partially supported by a Grant-in-Aid for Scientific Research (No. 04650827) from the Ministry of Education, Science, and Culture of Japan.

## REFERENCES AND NOTES

1. R. Asami, J. Oku, M. Takeuchi, K. Nakamura, and M. Takaki, *Polym. J.*, **20**, 699 (1988).
2. J. Oku, T. Hasegawa, K. Nakamura, M. Takeuchi, M. Takaki, and R. Asami, *Polym. J.*, **23**, 195 (1991).
3. J. Oku, T. Hasegawa, T. Takeuchi, and M. Takaki, *Polym. J.*, **23**, 1377 (1991).
4. J. Oku, T. Hasegawa, Y. Kubota, M. Takaki, and R. Asami, *Polym. Bull.*, **28**, 505 (1992).
5. J. Oku, T. Hasegawa, T. Kawakita, Y. Kondo, and M. Takaki, *Macromolecules*, **24**, 1253 (1991).
6. S. G. Durgar'yan, V. S. Khotimskii, Yu. V. Barskov, and I. B. Shevaldina, U.S.S.R. SU 1460063, 1989; J. Oku, M. Takeuchi, A. Saito, and R. Asami, *Polym. J.*, **24**, 1409 (1992).
7. J. Oku, T. Hasegawa, and M. Takaki, "Chemistry and Technology of Silicon and Tin," V. G. Kumar Das, S. W. Ng, and M. Gielen, Ed., Oxford University Press, Oxford, 1992, p 440. Since there are many serious misprints, the erratum slip that was issued afterward should be referred to. For example, the title of the paper "Copolymerization of dimethyldivynylsilane" should be corrected to "Cyclopolymerization of dimethyldivynylsilane".
8. J. V. Swisher and H.-H. Chen, *J. Organometal. Chem.*, **69**, 83 (1974); B. T. Nguyen and F. K. Cartledge, *J. Org. Chem.*, **51**, 2206 (1986).
9. In the polymerization of DMDVS under similar conditions ( $[DMDVS] \sim 0.3 \text{ mol l}^{-1}$ ,  $[s\text{-BuLi}] \sim 6 \text{ mmol l}^{-1}$ ,  $[TMEDA] \sim 0 \text{ or } 6 \text{ mmol l}^{-1}$ , at  $-10^\circ\text{C}$ , in hexane), the fraction of the remaining second vinyl groups was around 30% regardless of the TMEDA addition.<sup>7</sup> Though the present results cannot be compared directly with the data on DMDVS, they indicate that the addition of TMEDA hinders especially the reaction of the third vinyl group in MTVS.
10. D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960); M. Morton, E. E. Bostick, R. A. Livigni, and L. J. Fetters, *J. Polym. Sci., A*, **1**, 1735 (1963).
11. G. G. Eberhardt and W. A. Butte, *J. Org. Chem.*, **29**, 2928 (1964).
12. S. Dumas, J. Sledz, and F. Schué, *ACS Symp. Ser.*, **166**, 463 (1981).