

Anionic polymerization of vinylsilanes VII

Effects of *N,N,N',N'*-tetramethylethylenediamine on the polymerization of tetravinylsilane

Yasuhiro Suga, Yukiko Itoh, Jun-ichi Oku*, Mikio Takaki

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

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Summary

The anionic polymerization of tetravinylsilane (TeVS) was carried out in the presence and absence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). Without TMEDA, the polymerization proceeded extremely slowly and the polymer yield was still low even after an extended polymerization time. When TMEDA was added to the system, the polymerization was remarkably accelerated and gelation was suppressed. Such polymerization behavior of TeVS is closely similar to that of methyltrivinylsilane under similar conditions. The effects of TMEDA are explained by its coordination to the propagating end that increases the selectivity in the reaction of the propagating end with vinyl groups.

Introduction

We have studied the anionic cyclopolymerization of multivinylsilanes, namely dimethyldivinylsilane (DMDVS), methyltrivinylsilane (MTVS), and bis(dimethylvinylsilyl)methane (BVSM) (1-3). The addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the polymerization system of multivinylsilanes causes various interesting effects. For example, the anionic polymerization of BVSM hardly proceeds without TMEDA, while that with *n*-butyllithium (*n*-BuLi)/TMEDA affords the polymer having six-membered ring structure as a repeating cyclic unit through cyclopolymerization (1).

The polymerization of MTVS with *sec*-butyllithium (*s*-BuLi) is remarkably accelerated by the addition of TMEDA to the polymerization system. The fraction of the remaining vinyl groups in the polymer obtained in the presence of TMEDA is much higher than that obtained without TMEDA. The number-average molecular weights (M_n) of the polymers obtained with *s*-BuLi/TMEDA at low polymer yields are close to the values calculated from the monomer-to-initiator ratios and the polymer yields on the assumption that no cross-linking reaction occurred. Their molecular weight distributions (MWD) are fairly narrow. Such polymerization behavior indicates that the addition of TMEDA to the polymerization system suppresses the reaction between the propagating ends and vinyl groups in other polymer chains by increasing the selectivity in the reactions of propagating ends (2). Similar effects of TMEDA were observed in the polymerization of DMDVS (3). These polymers were found containing monocyclic and bicyclic rings in their backbones.

* Corresponding author

On the other hand, when TMEDA is added to the polymerization system of monovinylsilanes such as trimethylvinylsilane, the isomerization of the propagating end from silylmethine anion to silylmethylene anion takes place (4-6). The resulting silylmethylene anion is more stable than the silylmethine anion, and hence its addition to various types of vinyl groups could be more selective. The effects of TMEDA on the polymerization of MTVS can be explained by the isomerization of the propagating end and/or the change in the reactivity of the propagating silylmethine anion itself caused by the coordination of TMEDA to the lithium cation (2).

In the current paper, we report the anionic polymerization of tetravinylsilane (TeVS), which has no silylmethyl group responsible for the isomerization. Thus far the anionic polymerization of TeVS has not been reported.

Experimental

Materials

TeVS (Shin-Etsu Silicon Chemicals) was distilled over CaH_2 immediately before the polymerization. *s*-BuLi, TMEDA, and hexane were purified according to the conventional method for anionic polymerization (5). Other chemicals were purchased from commercial sources and used without further purification.

Polymerization of TeVS

Polymerizations were carried out in hexane at -10°C or 40°C under high vacuum conditions using breakable seal techniques. The initial concentrations of the reagents were as follows: [TeVS] ~ 0.25 mol/L, [*s*-BuLi] ~ 5.0 mmol/L, [TMEDA] ~ 0 or 5.0 mmol/L. Detailed polymerization procedure and the treatment of the resulting polymer were previously described (2,4).

Measurements

Both M_n and MWD (M_w/M_n) of the polymer were determined by gel permeation chromatography 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. ^1H and ^{13}C NMR spectra were taken with a Varian XL-200 spectrometer operated at 200 MHz and 50 MHz, respectively, in the Fourier transform mode. For the measurement of ^1H NMR spectrum, chloroform- d_1 containing dichloromethane as the internal reference (5.34 ppm) was used for the solvent. For the measurement of ^{13}C NMR spectrum, chloroform- d_1 was used for the solvent and the internal reference (77.6 ppm).

Results and discussion

Typical results of the anionic polymerization of TeVS are shown in Table 1. Polymers were white powder except when only oligomer was obtained. Although the polymerization proceeded extremely slowly without TMEDA at -10°C and gave only oligomer, completely soluble polymers were obtained in good yields in all the polymerizations with TMEDA at -10°C . In contrast to the polymerizations at -10°C , those at 40°C both in the presence and absence of TMEDA were accompanied by the formation of benzene-insoluble parts, which were also insoluble in any other solvent, when the

Table 1. Anionic polymerization of tetravinylsilane^a

temp (°C)	time (h)	yield ^b (%)	$M_n \times 10^{-3}$		M_w/M_n^d	vinyl ^e (%)
			calcd ^c	obsd ^d		
In the absence of TMEDA						
-10	6	3	0.23	1.6	2.25	35
-10	24	4	0.24	2.0	2.66	37
-10	168	6	0.37	5.5	11.6	46
40	3	8	0.52	7.2	10.2	48
40	6	10	0.67	10.5	Broad	57
40	24	17(8)	1.2	-	-	-
In the presence of TMEDA ^f						
-10	6	25	1.7	2.3	1.59	68
-10	24	42	2.8	3.4	2.90	70
-10	48	41	2.8	3.7	3.14	68
40	1	37	2.5	4.8	8.68	60
40	3	56(39)	3.7	-	-	-

^a Solvent, hexane; [TeVS] ~ 0.25 mol/L; [*s*-BuLi] = 5 × 10⁻³ mol/L. ^b Benzene-insoluble parts are shown in the parentheses. ^c Calculated from the monomer-to-initiator ratio and the percent polymer yield. ^d Determined by gel permeation chromatography. ^e Fraction of the remaining 2nd, 3rd, and 4th vinyl groups in the polymer determined by ¹H NMR measurement. ^f [TMEDA] = [*s*-BuLi].

polymerization proceeded to some extent. However, the addition of TMEDA suppressed gelation obviously at 40°C: a completely soluble polymer was obtained with TMEDA even at the 37% polymer yield, whereas gel formation was observed without TMEDA at as low a polymer yield as 17%.

The M_n 's of the polymers obtained without TMEDA were much higher than those calculated from the monomer-to-initiator ratios and the percent polymer yields. However, the M_n 's of the polymers obtained in the presence of TMEDA were not very different from the calculated values despite the high polymer yields. The MWD's of the resulting polymers, which broadened with the increase in the polymer yield, were far narrower for the polymers obtained in the presence of TMEDA than those obtained in the absence of TMEDA, considering the polymer yields.

Figure 1 shows ¹H NMR spectrum of poly(TeVS) obtained in the presence of TMEDA. The broad peak around 2 ppm in the spectrum is assigned to some protons in silicon-containing ring structure, and corresponding peaks were also observed in the spectra of poly(MTVS) and poly(DMDVS) (2,3). Consequently, the propagation of TeVS is accompanied by the formation of cyclized units, as with the polymerizations of MTVS and DMDVS. The fraction of the remaining second, third, and fourth vinyl groups in the polymer is calculated from the peak areas of these vinyl signals, from 5.6 ppm to 6.4 ppm, and of all signals. Further assignment of the signals between 0.5 ppm and 2.4 ppm will be discussed afterward.

The fractions of the remaining vinyl groups in the polymers obtained with TMEDA at -10°C (around 70%) are much higher than those in the polymers obtained without TMEDA (35-46%). With regard to the M_n 's of the resulting polymers and the fractions of the

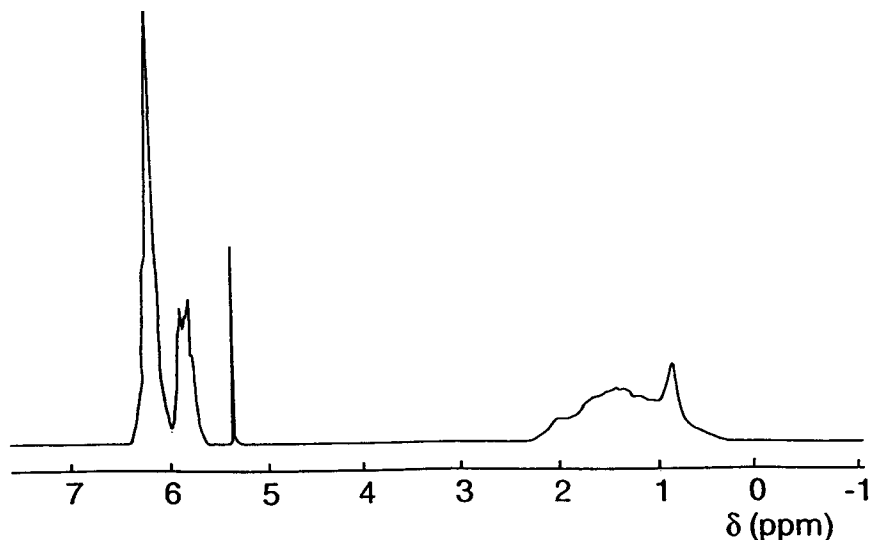
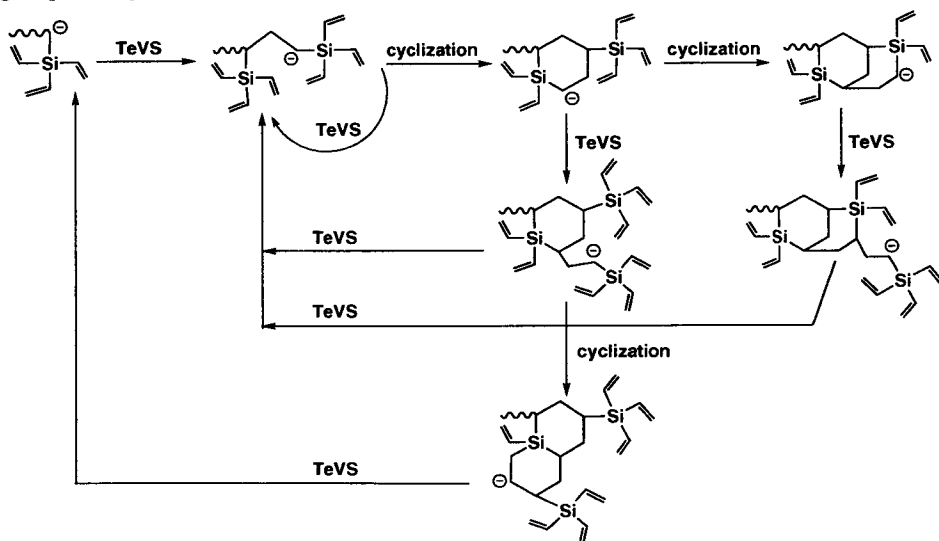


Figure 1. ^1H NMR spectrum of poly(TeVS) obtained with TMEDA ($M_n = 1600$; fraction of the remaining vinyl groups, 67 %) in CDCl_3 . CH_2Cl_2 was used as an internal standard.

remaining vinyl groups, the polymerization behavior of TeVS is similar to that of MTVS. As described in the previous paper (2), this suggests that the polymer obtained without TMEDA contains more of complicated ring structures and cross-linking parts than that obtained with TMEDA.

On the analogy of the cyclopolymerization mode of MTVS (2), a possible scheme for that of TeVS in the presence of TMEDA is illustrated below. In this scheme, monocyclic and bicyclic rings are shown. Though the formation of more complicated ring structure would be possible, it cannot often take place, considering that the fraction of the remaining vinyl groups is high.



In the ^1H NMR spectrum of poly(TeVS) obtained in the presence of TMEDA shown in Figure 1, many peaks overlap each other in the range of 0.5 ppm to 2.4 ppm. However, in this region locate the signals of all protons except the vinyl protons in the polymer that is obtained according to the scheme. The broad peak from 0.5 ppm to 0.8 ppm, which is a slightly higher field than 0.9 ppm of silylmethine protons in linear polymer chains (4), is assigned to the silylmethine protons in the silicon-containing six-membered ring by reference to the spectrum of poly(BVSM) (1). The sharp peak at 0.9 ppm is a signal of methyl groups of the initiator fragment. Silylmethine protons not in the silicon-containing ring, if any, will overlap with this peak. Methylene protons not constituting the silicon-containing ring exhibit signals around 1.3 ppm like methylene protons in linear alkanes. The broad peak around 2 ppm is assigned to methylene protons in the silicon-containing rings as described in the previous part. However, if this peak is assumed to correspond to all the ring methylene protons, the area of this peak is too small. Since the methylene protons in the six-membered ring whose conformation is fixed consist of two different protons, namely an equatorial proton and an axial proton, this peak is assigned to the equatorial proton, which is expected to have a resonance at a lower field. The signal of the axial proton would exist around 1.6 ppm, overlapping with that of the methylene protons in the linear polymer chain. Unfortunately, the chemical shifts of the bicyclic ring protons cannot be accurately estimated owing to the lack of appropriate model compounds, and hence the assignment is considered to be carried out similarly to the monocyclic ring. On the basis of these assignments, the frequency of the cyclization shown in the scheme is roughly estimated. The ratio of the peak area of the equatorial ring methylene protons to that of the other methylene protons (the axial ring methylene protons and the methylene protons in the linear chains) indicates that the cyclization occurs more than once but less than twice per two addition reactions. The fraction of the remaining vinyl groups in this polymer, 67%, is consistent with this frequency.

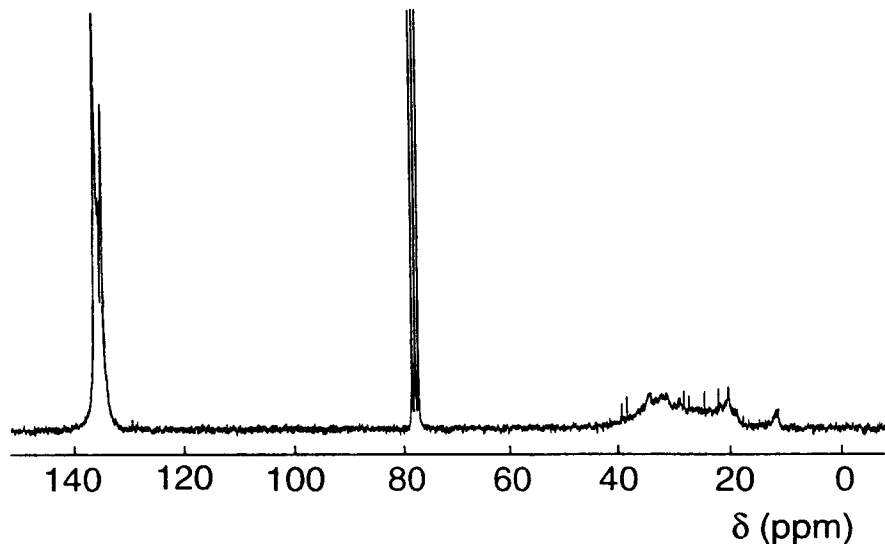


Figure 2. ^{13}C NMR spectrum of poly(TeVS) obtained with TMEDA ($M_n = 1800$; fraction of the remaining vinyl groups, 69 %) in CDCl_3 . CDCl_3 was used as an internal standard.

Figure 2 shows the ^{13}C NMR spectrum of poly(TeVS) obtained in the presence of TMEDA. Vinyl carbons and methyl carbons of the initiator fragment appear at 134 - 136 ppm and 12.1 ppm, respectively. However, all other carbon signals locate between 18 ppm and 40 ppm, broadened and overlapping each other, then these signals cannot be assigned. The broadening and overlapping are attributable to a similarity in the chemical shifts of silylmethine carbons (7) and methylene carbons and to a variety of environment of these carbons. The measurement of 40 MHz ^{29}Si NMR of the same polymer afforded only one broad peak at -17 ppm from external tetramethylsilane.

Figure 3 shows the relationships between the polymerization time and the polymer yield in the anionic polymerization of TeVS, together with those in the polymerization of MTVS under similar conditions. The polymerization of both monomers hardly proceeded without TMEDA at -10°C , on the other hand it was remarkably accelerated by the addition of TMEDA. The extremely low polymer yields even for the prolonged polymerization time in the absence of TMEDA can result from a low reactivity of the oligomer anion and/or the occurrence of some termination reaction. Additional experiments on the polymerization of MTVS revealed that the low polymer yields are due not to the termination reaction principally but to incorporation of the propagating end into crowded surroundings (2). The effect of TMEDA on the polymer yield was explained by the increase in the selectivity of the propagating end anion toward the propagation against the cross-linking, which prevents steric hindrance around the propagating end. This would be also the case for the polymerization of TeVS.

In the case of MTVS, two factors were offered as the cause of the increase in the selectivity toward the propagation: one is the isomerization of the propagating end from silylmethine anion to silylmethylene anion, and the other is the change in the reactivity of the propagating silylmethine anion caused by the coordination of TMEDA to the lithium cation.

However, in the polymerization of TeVS, the former factor is excluded because TeVS molecules have no silylmethyl groups subject to the proton abstraction. Since the polymerization behavior of TeVS including the effects of TMEDA is closely similar to that of MTVS, the increase in the selectivity toward the propagation against cross-linking reaction is explained by the change in the reactivity of the propagating end for both polymerizations.

The propagating ends in the absence of TMEDA are supposed to exist in equilibrium of associated form and dissociated one (8, 9), and only the latter, minor species, is involved in the propagation. In the presence of TMEDA, the propagating ends exist as 1:1

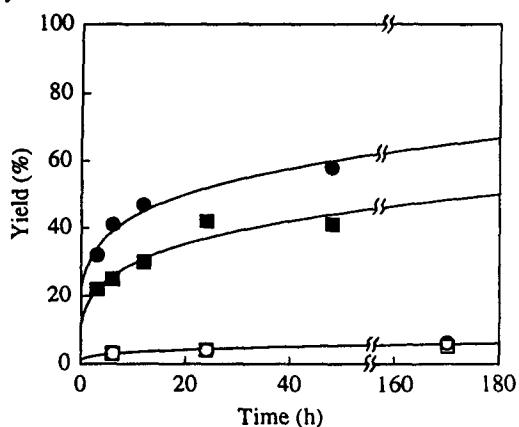


Figure 3. Polymerization of TeVS (this work) and MTVS (previous work (2)) with *s*-BuLi at -10°C in hexane. Polymerization conditions: [vinyl] = 1 mol/L, [Monomer]/[*s*-BuLi] = 50. TeVS, in the presence of TMEDA (■); TeVS, in the absence of TMEDA (□); MTVS, in the presence of TMEDA (●); MTVS, in the absence of TMEDA (○).

complexes (10). Compared with the propagating end complexed with TMEDA, the dissociated one is highly reactive (11). The more reactive propagating ends without TMEDA would attack various types of vinyl groups, i.e. vinyl groups in monomers and polymer chains, with less selectivity, which causes hard access of a monomer molecule to the propagating end anion incorporated into crowded surroundings. On the other hand, the propagating ends coordinated by TMEDA with relatively low reactivity are kept free from steric hindrance owing to the higher selectivity in vinyl addition and hence accessible to the monomers.

In summary, it has been revealed that TMEDA accelerates the polymerization of TeVS and suppresses gelation during the polymerization. The fraction of the remaining vinyl groups in the polymer obtained with TMEDA is much higher than that in the polymer obtained without TMEDA. These effects of TMEDA were also observed on the polymerization of MTVS. It is concluded that they result from the increased selectivity in vinyl addition of the propagating end due to the lowered reactivity.

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