

SHORT COMMUNICATIONS

Anionic Polymerization of Vinylsilanes I. Novel Isomerization in the Anionic Polymerization of Trimethylvinylsilane

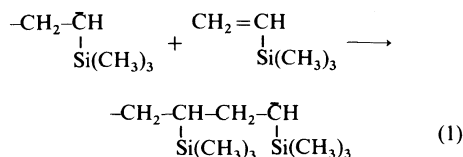
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Since Nametkin and his co-workers reported the anionic polymerization of trimethylvinylsilane (TMVS) and other vinylsilanes,¹ several studies have been done in this field. Nametkin *et al.* revealed that the polymerization of TMVS was a living polymerization although a slow termination² and a chain transfer to the monomer at high temperature³ occurred. The propagation reaction has been described to proceed via the addition of an α -methine anion to a β -carbon of a vinyl group (Scheme 1).



This report demonstrates another propagation reaction occurring in the polymerization of TMVS.

EXPERIMENTAL

Materials

All chemicals were purchased from commercial sources. Hexane was distilled from sodium. TMVS and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled

from calcium hydride. Commercially available *n*-butyllithium (*n*-BuLi) in hexane was used after filtration.

Polymerization of TMVS

Polymerizations were carried out under high vacuum conditions using the breakable seal technique. An initiator solution was introduced into a reactor, then TMEDA solution was added to it followed by the addition of TMVS solution. The reaction mixture was allowed to stand for 48 h at room temperature and quenched by methanol. The resulting polymer was purified by the following method. The reaction mixture was poured into a large amount of methanol to precipitate the polymer. A white powder was filtered, washed, and dried. When the precipitation was not successful, the reaction mixture was washed with aqueous HCl and evaporated. Freeze-drying of a benzene solution of the residue gave a viscous liquid.

Characterization of the Polymers

Number average molecular weights (\bar{M}_n) were determined mainly by vapor pressure osmometry (VPO) using a Hitachi Perkin-Elmer 115 osmometer. Molecular weight distributions (\bar{M}_w/\bar{M}_n , MWD) were calculated from gel per-

meation chromatography (GPC) data obtained in tetrahydrofuran (THF) 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. ^1H NMR spectra were taken with a Varian XL-200 spectrometer at 200 MHz in the Fourier transform mode. Chloroform- d_1 was used as the NMR solvent.

RESULTS AND DISCUSSION

The polymerization data of TMVS are shown in Table I. When TMEDA was not added to the reaction mixture, similar results to the previous studies^{1,2,4} were obtained. At a low TMVS/*n*-BuLi ratio, the MWD of the polymer was shown to be nearly monodisperse. However, it became broader as the TMVS/*n*-BuLi ratio increased, indicating that a slow termination reaction accompanied the propagation reaction. In the presence of TMEDA the same relationship between the MWD and TMVS/*n*-BuLi ratio was obtained.

The physical properties of the polymer obtained in the presence of TMEDA were considerably different from those made in the absence of TMEDA. The latter was a white powder, whereas the former was a highly viscous liquid despite nearly the same molec-

ular weight.

To confirm the microstructures of the polymer obtained ^1H NMR measurements were carried out. Typical spectra are shown in Figure 1. When TMEDA was not used for the

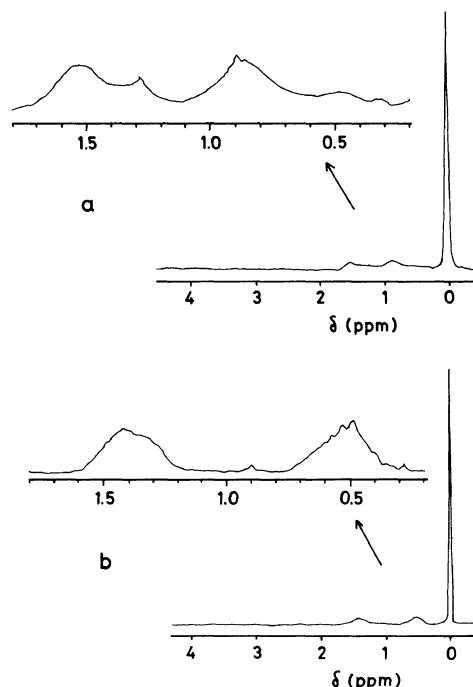


Figure 1. ^1H NMR spectra of poly(trimethylvinylsilane). a) $[\text{TMVS}]/[n\text{-BuLi}] = 52$, $\bar{M}_n = 6.8 \times 10^3$, polymerized without TMEDA; b) $[\text{TMVS}]/[n\text{-BuLi}] = 52$, $\bar{M}_n = 3.9 \times 10^3$, polymerized with TMEDA.

Table I. Polymerization of trimethylvinylsilane^a

TMVS	<i>n</i> -BuLi	TMEDA	[TMVS]	Yield	\bar{M}_n^b	\bar{M}_w^c	Content of the isomerized structure/%
mol l^{-1}	mmol l^{-1}	mmol l^{-1}	[<i>n</i> -BuLi]	%	$\times 10^{-3}$	\bar{M}_n	
0.952	58.3	—	16	50	2.4	1.22	8
1.05	20.3	—	52	94	6.8	1.39	7
5.11	5.15	—	992	95 ^d	33.5 ^c	1.95	14
0.509	28.7	24.1	18	92	1.7	1.10	71
0.743	14.3	14.8	52	67	3.9	1.35	87
3.76	4.43	4.64	850	61 ^d	9.4 ^c	1.83	100

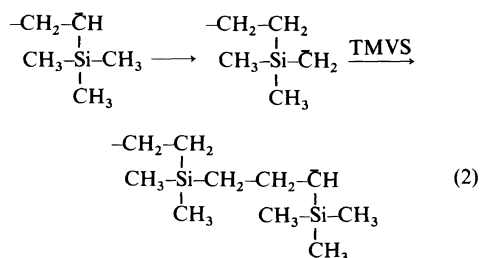
^a Polymerization time, 48 h; temp, r.t.; solvent, *n*-hexane.

^b Determined by VPO.

^c Determined by GPC.

^d Polymerization temp, 60°C.

polymerization the ^1H NMR spectrum of the resulting polymer contained mainly three kinds of signals (Figure 1a); $\delta=0.0$ ppm (silylmethyl), 0.9 ppm (silylmethine), and 1.2—1.7 ppm (methylene not attached to a silicon atom). The polymer obtained in the presence of TMEDA exhibited chiefly three peaks (Figure 1b); $\delta=0.0$ ppm, 0.5 ppm (silylmethylene) and 1.2—1.6 ppm. In these assignments propyltrimethylsilane and (2-methyl)ethyltrimethylsilane were used as references. The spectrum shown in Figure 1a corresponds to the structure which can be obtained *via* an ordinary vinyl polymerization, and this means that the propagation reaction is an addition of an α -methine anion to a β -carbon of vinyl group (Scheme 1). It is clear that the spectrum shown in Figure 1b differs from that of Figure 1a. The silylmethine signal at 0.9 ppm disappeared in Figure 1b, while the silylmethylene signal at 0.5 ppm appeared. These differences in the spectra suggest that the polymerization of TMVS in the presence of TMEDA proceeds by another propagation mechanism. The authors propose Scheme 2 as a novel propagation reaction of TMVS. At



first the initially formed α -methine anion isomerizes to an α -methylene anion which is considered to be more stable than the former anion. Then it attacks a β -carbon of TMVS. By this isomerization polymerization can be explained both disappearance of silylmethine and appearance of silylmethylene. Although the similar mechanism of the isomerization in the cationic polymerization of branched α -olefins is known by Kennedy *et al.*,⁵ for the typical anionic polymerization, the isomeriza-

tion polymerization of TMVS is first reported here.

It was found that the ^1H NMR spectrum of PTMVS prepared without TMEDA even contained a peak in the silylmethylene region ($\delta=0.5$ ppm), though it was much less amount than that of PTMVS obtained in the presence of TMEDA. The contents of the isomerized structure in both polymers prepared with and without TMEDA could be evaluated from the ratios of the peak areas of these signals. The fraction of the isomerization calculated are summarized in Table I.

It is concluded that in the presence of TMEDA, the anionic polymerization of TMVS mainly proceeds by the isomerization shown in Scheme 2. Even in the absence of TMEDA, around 10% of the propagation reaction proceeded by the isomerization. Although the papers published do not suggest an isomerization mechanism at all, this study revealed that the anionic polymerization of trialkylvinylsilane may consist of two kinds of the propagation reactions. As the isomerization reaction does not occur so frequently without TMEDA, previous workers may not have been able to detect it. The change in physical property from the white solid of the low isomerized PTMVS (mp, 224—234°C) to the viscous liquid of the mostly isomerized polymer suggests that most of silyl groups join the main chain of the polymer by the isomerization mechanism, since it is known that polysiloxanes are also oily or pasty even at a high molecular weight. The role of TMEDA in the isomerization reaction is considered to make proton transfer easy through coordination with the lithium cation. It is known that a similar metalation of a silylmethyl group is caused by *n*-BuLi/TMEDA.⁶

It is also worth noting that the polymerization procedure of trimethylvinylsilane with *n*-BuLi/TMEDA may become important as a method for preparing polymer containing silicon atoms in a main chain such as polycarbosilane.

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