Communications to the Editor

Cross-Linking Reaction in the Polymerization of Trimethylvinylsilane

Jun-ichi Oku,* Kenji Shiraishi, Shigeru Sago, and Mikio Takaki

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

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Since trimethylvinylsilane (TMVS) and some other vinylsilanes were found to be susceptible to the anionic polymerization with alkyllithium,[1] the nature of this polymerization has been well investigated. According to the studies by Nametkin and his co-workers, the polymerization of TMVS is accompanied by side reactions: (1) elimination of LiH from the propagating end, which forms a C=C double bond at the polymer end;[2,3] (2) formation of a branch by addition of a propagating polymer chain to the double bond formed by reaction 1;[2,4] and (3) chain transfer to the monomer at elevated temperature.[2,5]

We have found an isomerization reaction in the polymerization of vinylsilanes.[6] In the polymerization of TMVS by butyllithium, the isomerization, which results from abstraction of a silylmethyl proton by the silylmethine anion of the propagating end, is remarkably accelerated by addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the polymerization system. In this case, the isomerization was found to take place intramolecularly both from the penultimate unit and within the end unit.[7] On the other hand, in the polymerization of benzyldimethylvinylsilane, the proton abstraction takes place regularly once per two addition reactions from the silylbenzylic group in the penultimate monomer unit, whether in the presence or absence of TMEDA.[8]

We report here effects of another type of amine on the polymerization of TMVS, which results in the formation of insoluble polymer.

The polymerization was carried out with *sec*-butyllithium (*s*-BuLi)/triethylamine (TEA) in hexane at −10 °C under vacuum using break-seal techniques. The initial concentrations of the reagents were as follows: [TMVS] = 1 mol/L, [*s*-BuLi] = 2×10^{-2} mol/L. The polymerization and the workup of the reaction mixture were carried out according to the previously outlined procedure,[6] except that whole reaction mixture was treated by freeze-drying altogether though they contained insoluble polymer. The resulting polymer was separated into a benzene-soluble part and a benzene-insoluble part by filtration. Content of the isomerized units (CIU), which is the ratio of the monomer units having the isomerized structure to all monomer units, was calculated for the soluble part from the peak areas of the silylmethylene signal and of the silylmethine signal in the ^{1}H NMR spectrum of the polymer by the previously described method.[9]

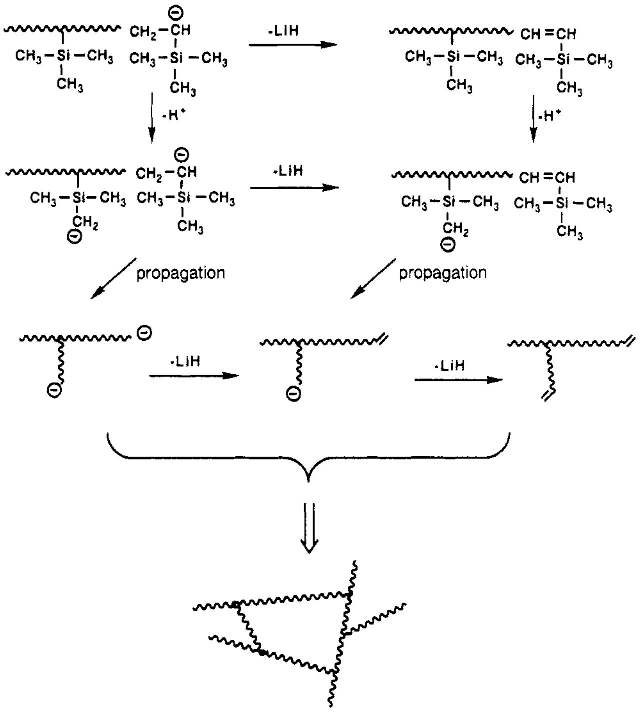
The polymerization results are shown in Table I. In all cases swollen gels appeared in the reaction mixture. Their volume increased with the reaction time, and the whole mixtures were eventually incorporated in the gels. The addition of TEA accelerates the polymerization appreciably.[10] The polymerization rate increases with an increase in the ratio of TEA to the initiator. A benzene-insoluble part, which is also insoluble in tetrahydrofuran, hexane, and other solvents, exists in the resulting polymer in every case and increases with the yield. Benzene-soluble parts mainly consisted of low molecular weight polymers whose molecular weights were (1–3) × 10^3. The formation of the insoluble polymer indicates the presence of some cross-linking reaction. CIU's are almost constant at 13–16%, which are lower than those of the polymer obtained in the presence of TMEDA (40–60%) but higher than those obtained in the absence of the additives (around 10%).[9]

Table I
Polymerization of TMVS with *s*-BuLi/TEA[a]

[TEA]/[*s*-BuLi]	time, h	yield, %	insol,[b] %	CIU,[c] %
1	1	14	*d*	13
1	6	28	*d*	14
1	168	89	55	15
2	1	18	trace	13
2	3	32	trace	14
2	6	46	*d*	14
2	12	54	8	16
2	48	87	25	*d*
2	168	97	40	*d*
20	1	43	*d*	13
20	3	69	20	13
20	6	76	22	15

[a] Solvent, hexane; temp, −10 °C; [TMVS] = 1 mol/L; [*s*-BuLi] = 2×10^{-2} mol/L. [b] Benzene-insoluble part. [c] Content of isomerized units calculated from ^{1}H NMR spectrum. [d] Not measured.

Scheme I



In the polymerization of TMVS with BuLi/TMEDA, the proton abstraction takes place from the silylmethyl

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group intramolecularly and the resulting polymer is completely soluble in benzene.[6,7] The cross-linking in the polymerization with *s*-BuLi/TEA should therefore be attributed to some reaction other than those present in the polymerization with *s*-BuLi/TMEDA. For the polymerization of TMVS with *s*-BuLi/TEA, we propose Scheme I which includes *intermolecular* proton abstraction, on the basis of the presence of the cross-linking.

Among these reactions, the elimination of LiH and the addition of a propagating chain to the double bond in the polymer are known for the polymerization at elevated temperature in the absence of the additives.[2-4] The existence of the isomerized units in the soluble part reveals that the proton abstraction does occur though less frequently than in the case of *s*-BuLi/TMEDA. The intermolecular proton abstraction, the existence of which differentiates the polymerization with *s*-BuLi/TEA from that with *s*-BuLi/TMEDA, is essential for the cross-linking. The increase in the proportion of the insoluble part with the polymer yield is explicable by the existence of such a cross-linking reaction.[11] It is speculated that the difference in the proton abstraction mode would be caused by the difference in the coordination state of amine to the lithium cation.

TMEDA normally forms a 1:1 complex with lithium cation in hydrocarbon medium; on the other hand, the coordination of TEA is influenced by equilibrium.[12] If a lithium cation forms a 1:2 complex with TEA, its structure and therefore its behavior would resemble those of the Li/TMEDA complex. Polymerization with *s*-BuLi/TEA, however, suggests that some complex other than a 1:2 complex, e.g., a 1:1 complex, plays an important part in this polymerization because of the existence of the intermolecular proton abstraction. In the case of TEA, the silylmethine anion whose counterion forms a 1:1 complex with TEA is more accessible than that in the case of TMEDA because the counterion of the silylmethine anion in the case of TMEDA forms the complex that corresponds to the more crowded 1:2 complex of lithium cation with TEA. Hence, the silylmethyl proton of the other polymer chain can be abstracted in the case of TEA.

The increase in the polymerization rate with an increase in the ratio of TEA to the initiator could be attributed to two factors. One is the change in the polarity of the medium. The other is the shift in the coordination equilibrium. The equilibrium between the uncomplexed species and a 1:1 complex, though the complex between TEA and lithium cation is not well-defined, shifts to the complex with the addition of TEA. The propagating end whose counterion is in the 1:1 complex adds to the monomer more easily than the propagating end with uncomplexed and aggregated counterion owing to the steric effect. The formation of a 1:2 complex has little influence on the polymerization rate because of its sterically hindered structure, as predicted by the minor effect of the addition of TMEDA on the polymerization rate.[9] A much higher activity of the 1:1 complex in the propagation explains the constancy of CIU regardless of the ratio of TEA to *s*-BuLi.

Further studies on the effect of various amines on the polymerization of TMVS are in progress.

References and Notes

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(10) The polymer yields in the absence of TEA are 1% at 1 h, 6% at 6 h, 22% at 48 h, and 56% at 168 h when the other polymerization conditions are the same. See ref 9.

(11) This cross-linking reaction cannot be discussed in quite the same way as that in the polymerization of divinyl monomers because the cross-linking reaction dealt with here consists of three reactions. However, the analogous relationship between the weight fraction of gel and the conversion is expected. Gelation in the polymerization of multifunctional monomers was treated in detail in the literature: Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 9.

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Registry No. TMVS, 754-05-2; TMVS (homopolymer), 25036-32-2; *s*-BuLi, 598-30-1; TEA, 121-44-8; TMEDA, 110-18-9.