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Anionic polymerization of vinylsilanes

IV. Isomerization polymerization of dimethylphenylvinylsilane

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Summary

The anionic polymerization of dimethylphenylvinylsilane with *sec*-butyllithium / *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was investigated. The polymerization proceeded up to 100 % yield and afforded the polymer having isomerized-structure units. The polymerization was accompanied by chain transfer reaction to the monomer and the polymerization rate in the presence of TMEDA was much lower than in the absence of TMEDA.

Introduction

Vinylsilanes are anionically polymerizable in hydrocarbon media (1). We found that an isomerization reaction occurred in the polymerization of trimethylvinylsilane (TMVS) with butyllithium and that it is enhanced by the addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to the polymerization system (2-4). This isomerization, which results from the intramolecular abstraction of a silylmethyl proton by the silylmethine anion in the propagating end, leads to an incorporation of silicon atoms into the main chain and a drastic change in the physical properties of the polymer. Similar proton abstraction was found to take place quite regularly from the benzylic group in the penultimate unit in the polymerization of benzyldimethylvinylsilane (BDMVS) with *sec*-butyllithium (*s*-BuLi) even in the absence of TMEDA (5).

Dimethylphenylvinylsilane (DMPVS) was also found to be anionically polymerizable (1). In the case of this monomer also we may expect the isomerization polymerization with *s*-BuLi / TMEDA, however, butyllithium-amine complex is known to transmetalate to aromatic hydrocarbons (6). If such a transmetalation occurs frequently to phenyl protons in the monomer or in the polymer, the polymerization would not proceed. Although in the polymerization of BDMVS with *s*-BuLi / TMEDA transmetalation to the benzene ring in the monomer unit was not observed even for a long reaction time (5), silylbenzylidene anion, which is a stable anion, plays a major role in this polymerization system. Hence the polymerization behavior of DMPVS with *s*-BuLi / TMEDA, where the propagating end is not so stabilized, is not necessarily the same as that of BDMVS.

We now report the polymerization results of DMPVS with *s*-BuLi in the presence or absence of TMEDA.

Experimental

Materials

DMPVS (Shin-Etsu Silicon Chemicals) was distilled over CaH_2. *s*-BuLi, TMEDA, and hexane were purified according to the conventional method for the anionic polymerization (3,5). Other chemicals were used as received.

Polymerization

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: [DMPVS] = 1.0 mol/L, [*s*-BuLi] = 2×10^{-2} mol/L, [TMEDA] = 0 or 2×10^{-2} mol/L. Detailed polymerization procedures and the treatment of the resulting polymers were previously described (2,4).

Characterization of the polymers

Number-average molecular weights (M_n) were determined by vapor pressure osmometry (VPO) and molecular weight distributions (MWD, M_w/M_n) were calculated from their gel permeation chromatography (GPC) curves by using a calibration curve with polystyrene standards. Contents of isomerized units (CIU) were calculated from the peak intensities of silylmethine protons (around 0.9 ppm) and of silylmethylene protons (around 0.6 ppm) in the ^1H NMR spectra of the polymers in a similar manner to those in the case of poly(TMVS) (4). Instruments and conditions for these measurements were the same as those previously described (4).

Results and discussion

Polymerizations of DMPVS yielded polymers in both the absence and presence of TMEDA. Poly(DMPVS)'s obtained in the presence of TMEDA varied from viscous liquid to sticky polymer depending on the molecular weight, whereas those obtained in the absence of TMEDA were white powder except for polymers having M_n's less than 3×10^3. When the polymerization was carried out in the absence of TMEDA, white polymer was observed to precipitate during the polymerization. The polymerization mixture in the presence of TMEDA turned dark red after almost all the monomer had been consumed. The polymerization results at -10 and 40 °C are shown in Table 1.

On the whole, the rate of polymerization was much higher at 40 °C than that at -10 °C. In the absence of TMEDA, the polymerization proceeded much faster than in the presence of it at each temperature. The decrease in the polymerization rate of DMPVS by the addition of TMEDA to the system, which was also observed in the case of BDMVS, is opposite to the acceleration effect of the TMEDA addition in the polymerization of TMVS (at the initial monomer concentration of 1 mol/L). Such a difference in the effect of TMEDA addition on the polymerization rate indicates that the bulkiness of the substituents at the Si atom of the monomer has significant influence on the propagation reaction. The coloration at the final stage of the polymerization in the

Table 1
Polymerization of dimethylphenylvinylsilane[a]

time	temp	yield	$M_n \times 10^{-3}$		M_w / M_n	CIU[d]
(h)	(°C)	(%)	calcd[b]	obsd[c]		(%)
In the absence of TMEDA						
1	-10	7	0.63	0.66	1.14	5
6	-10	18	1.5	2.1	1.25	5
24	-10	61	5.1	5.3	1.18	5
48	-10	79	6.6	6.3	1.41	5
1	40	78	6.5	6.0	1.14	6
3	40	90	7.4	7.7	1.21	5
6	40	97	8.0	8.0	1.25	6
In the presence of TMEDA[e]						
1	-10	5	0.46	0.41	-	19
6	-10	8	0.72	0.68	-	28
24	-10	19	1.6	1.4	1.15	44
48	-10	34	2.9	2.2	1.17	53
96	-10	57	4.7	3.7	1.12	61
168	-10	86	7.1	5.0	1.14	64
1	40	27	2.3	1.8	1.12	56
3	40	67	5.5	3.6	1.11	74
6	40	99	8.0	4.7	1.17	73

[a] Solvent, hexane; [DMPVS] = 1 mol/L; [*s*-BuLi] = 2 x 10^{-2} mol/L. [b] Calculated from the monomer to initiator ratio and the percent yield. [c] Determined by VPO. [d] Determined by ^{1}H NMR. [e] [TMEDA] = [*s*-BuLi].

presence of TMEDA is considered to be caused by the lithiation of the benzene ring of the polymer. In the polymerization system of TMVS with *s*-BuLi / TMEDA in benzene, also, such a coloration was observed in the course of the polymerization and only oligomer was obtained (7). The attainment of the polymer yield to nearly 100 % implies that the transmetalation is much slower than the propagation reaction and that therefore the polymerization is essentially little affected by the transmetalation.

Figure 1 shows the relationships of M_n and of MWD with the polymer yield at -10 °C. The polymers obtained in the absence of TMEDA had M_n's close to the calculated values, but their MWD's broadened with an increase in the yield. This polymerization behavior is similar to that of TMVS in the absence of TMEDA. Though the heterogeneity of the polymerization system would have affected the MWD, the elimination of lithium hydride from the propagating end must have caused the broadening, because GPC profile showed the tailing to the low molecular weight part. In the presence of TMEDA, M_n of the polymer deviated from the calculated value with an increase in the yield. Such a deviation was also observed for poly(TMVS) obtained in the presence of TMEDA and was attributed to the chain transfer to the monomer (4). In the polymerization of DMPVS, a similar chain transfer is considered to occur.

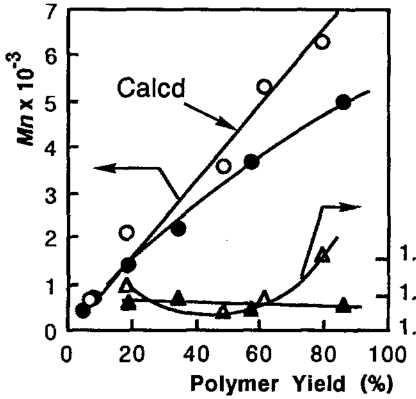


Figure 1
Relationships of M_n and of M_w/M_n with the polymer yield in the polymerization of dimethylphenylvinylsilane at -10°C: (○, △) in the absence of TMEDA; (●, ▲) in the presence of TMEDA.

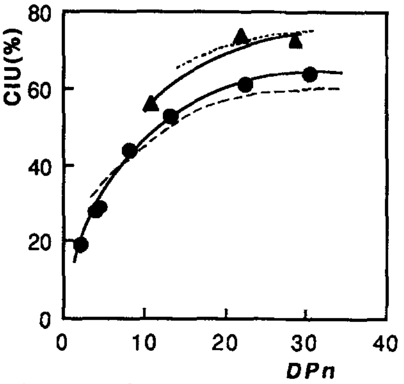
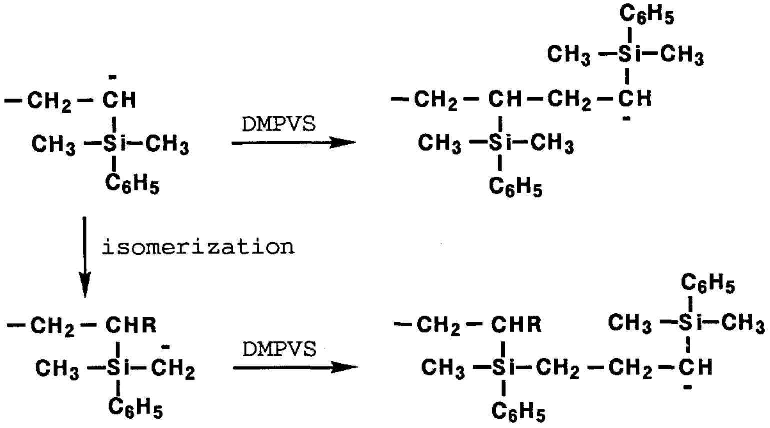


Figure 2
Relationships between degree of polymerization (DP_n) and content of isomerized units (CIU) in the polymerization of dimethylphenylvinylsilane in the presence of TMEDA: (●) at -10°C; (▲) at 40°C. Broken line (-10°C) and dotted line (40°C) are those in the polymerization of trimethylvinylsilane under similar conditions.

Figure 2 shows the relationships between degree of polymerization (DP_n) and CIU of the polymer obtained in the presence of TMEDA, together with those of poly(TMVS). These relationships closely resemble those in the polymerization of TMVS in the presence of TMEDA (4). CIU increases with an increase in DP_n. Value of CIU itself is very similar to that of poly(TMVS) having equal DP_n. Higher temperature affords higher CIU as well. These relationships are explained in a similar manner as in the case of TMVS, *i.e.*, since the isomerization is an intramolecular reaction, low monomer concentration is more favorable for it than for the propagation, and thus CIU increases with DP_n. The absence of unusually high molecular weight part also supports the intramolecular proton abstraction.

The polymerization of DMPVS proceeds much faster than that of TMVS in both the absence and presence of TMEDA (4). The isomerization, which is the competitive reaction with the propagation, in the polymerization of DMPVS, however, occurs as frequently as in the case of TMVS. This indicates that the introduction of phenyl group to the Si substituents accelerates not only the addition of propagating end to the monomer but also the intramolecular proton abstraction from a silylmethyl group by the propagating end. Higher polymerization temperature was found to be favorable for the isomerization reaction, as was observed in the case of TMVS.

In conclusion, the addition of TMEDA to the polymerization system of DMPVS has similar effects to that in the case of TMVS



R = H, $CH_2CH_2Si(CH_3)_2C_6H_5$

on the isomerization reaction. Metalation of the benzene ring occurs but to a practically negligible extent. The introduction of a phenyl group to the Si of the monomer as a substituent has the acceleration effects on both the propagation and the isomerization to a similar extent. The polymerization rate in the presence of TMEDA is lower than that in the absence of TMEDA.

References

1. Nametkin NS, Topchiev AV, Durgar'yan SG (1963) J Polym Sci, C 4: 1053
2. Asami R, Oku J, Takeuchi M, Nakamura K, Takaki M (1988) Polym J 20: 699
3. Oku J, Hasegawa T, Nakamura K, Takeuchi M, Takaki M, Asami R (1991) Polym J 23: 195
4. Oku J, Hasegawa T, Takeuchi T, Takaki M (1991) Polym J 23: 1377
5. Oku J, Hasegawa T, Kawakita T, Kondo Y, Takaki M (1991) Macromolecules 24: 1253
6. Eberhardt GG, Butte WA (1964) J Org Chem 29: 2928
7. Our unpublished results

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