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The Copolymerization of 2-Chloroacrylaldehyde with Styrene[1]

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The copolymerization of α-chloroacrolein (M_1) with styrene (M_2) has been investigated. An alternating copolymer was obtained without an initiator in dimethyl sulfoxide at 60°C. The formation of a charge-transfer complex between the respective monomers was observed by the continuous-variation method, and it was found that this complex plays an important role in the polymerization. Meanwhile, in the case of the BF_3OEt_2-catalyzed system, it was observed that the polymerization temperature strongly affected the copolymerizability and the structure of the copolymer.

In the course of our research on the polymerization of acrolein and its derivatives,[2–4] the copolymerization of α-chloroacrolein (CAL) with styrene (St) was investigated. Our work on the copolymerization CAL with pyridazinone derivatives[5] has already been reported.

Recently, Elias *et al.*[6] investigated the radical polymerizations of CAL, α-chloroacrolein diacetate, and α-chloroacrolein dimethyl acetal, and also reported the radical copolymerizations of CAL with St and vinyl chloride. It was also indicated by these workers that α-chloroacrolein dimethyl acetal formed a 1:2 complex with boron trifluoride etherate at −60°C *via* the acetal oxygen atoms, which then gave oligomers at 25° to 30°C through cationic mechanism. However, this work did not contain any data on the cationic copolymerization.

In the present paper, we intend to discuss the formation and the polymerization of the 1: 1 charge transfer complex due to some donor-acceptor-type interaction between CAL and St both in the absence of and in the presence of boron trifluoride etherate.

Experimental

Materials. The CAL was synthesized from acrolein according to Moureu's method[7] and purified by vacuum distillation (bp 29°C/17 mmHg, d_{25} 1.193, n_D^{25} 1.458).

The St was purified by distillation under a vacuum before use. The boron trifluoride etherate was purified by distillation in the usual manner.

Copolymerization Procedure. The copolymerization was carried out under the dry nitrogen atmosphere in a glass ampoule. Given amounts of the monomer and the solvent were placed in an ampoule, a catalyst solution was added at required temperature, and the ampoule was sealed. After the reaction, the resulting mixture was poured into a large amount of methanol to precipitate the copolymer.

Characterization of the Copolymer. The composition of the copolymer was determined by elemental analysis. The nuclear magnetic resonance (NMR) spectra of the copolymer were measured in carbon tetrachloride with a HITACHI R-20 spectrometer. The infrared(IR) spectra reported in this paper were taken with a YANAGIMOTO LSG-25 infrared spectrometer. The X-ray diffraction spectra of the copolymer were obtained by using nickel-filtered Cu*Kα* radiation with a RIGAKU DENKI geiger flex. The viscosity measurements were carried out with an Ostwald viscometer using toluene as the solvent and at 25°C. The number-average molecular weight of the copolymer was determined by vapour-pressure osmometry using benzene as a solvent at 40.5°C with HITACHI PERKIN ELMER MODEL 105 apparatus. The continuous-variation method[8] applied to the CAL-St system was carried out in dimethyl sulfoxide or toluene using a quartz cell with a path length of 10 mm and at room temperature.

Results and Discussion

Copolymerization without a Catalyst. The results of the copolymerization of CAL with St in the absence of a catalyst are summarized in Table 1. The copolymer obtained was a white powder, soluble in toluene, pyridine, and tetrahydrofuran, and insoluble in methanol and diethyl ether. Figure 1 shows that the maximum values of both the copolymerization rate and the limiting viscosity number of the copolymer were observed at the CAL mole fraction with a monomer-feed com-

TABLE 1. COPOLYMERIZATION OF CAL(M_1) WITH St(M_2) WITHOUT INITIATOR IN DIMETHYL SULFOXIDE AT 60°C, $[M_1]+[M_2]=4$ mol/*l*

M_1 (mol%)	Time (hr)	Conversion (%)	m_1 (mol%)	$[\eta]^{25°C}_{benzene}$
0	10	0.93	0	0.28
10	10	3.59	44.73	0.29
20	10	4.79	46.86	0.36
30	10	7.29	48.04	0.38
40	5	4.28	50.70	0.40
50	4	4.04	52.03	0.44
60	5	4.10	54.41	0.37
70	8	3.49	58.26	0.29
80	10	5.39	63.08	0.20
90	10	3.57	70.38	0.12
100	10	1.26	100	0.08

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[1] Polymerization of Acrolein and Its Derivatives. VII.

[2] N. Yamashita, H. Sumitomo, and T. Maeshima, *Kogyo Kagaku Zasshi*, **71**, 1723 (1968).

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[6] H. G. Elias and W. Nengweiler, *Makromol. Chem.*, **113**, 115 (1968).

[7] C. Moureu, *Ann. Chim.*, **15**, 158 (1921).

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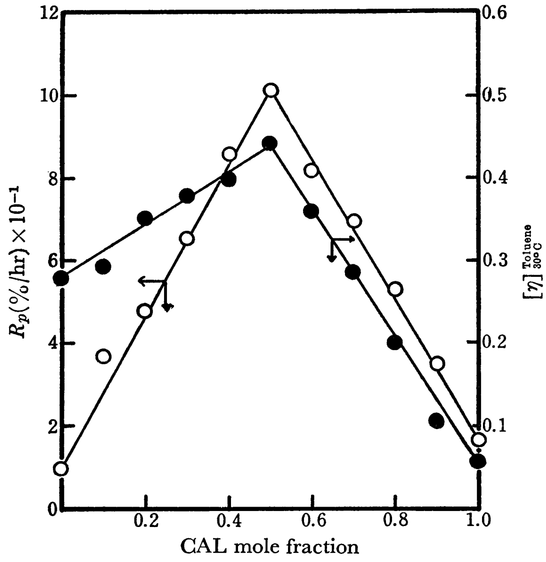

Fig. 1. Copolymerization rate and limiting viscosity numbers for copolymerization of α-chloroacrolein (CAL) with styrene (St) without initiator.

position of 0.5, indicating that there may be some interaction between CAL and St. Meanwhile, the initial copolymerization rate was proportional to the 1.88 order of the monomer concentration, suggesting that the initiation takes place as a result of the interaction between the two monomers.[9] In order to estimate the over-all activation energy for the copolymerization of CAL with St, the polymerization was carried out at 60, 70, and 80°C in the monomer-feed composition of 0.5. Plots of the logarithm of the copolymerization rate against the reciprocal of the absolute temperature gave a linear relation, and from its slope the activation energy was given as 11.37 kcal/mol. This value of the activation energy is much lower than that obtained for usual radical polymerization. The Fineman-Ross plot gave monomer reactivity ratios of $r_1=0.18$ and $r_2=0.06$ for the non-catalyzed copolymerization of CAL (M_1) with St (M_2). These values of r_1 and r_2 are less than those for the radical copolymerization reported by Elias ($r_1=0.18$, $r_2=0.078$).[6]

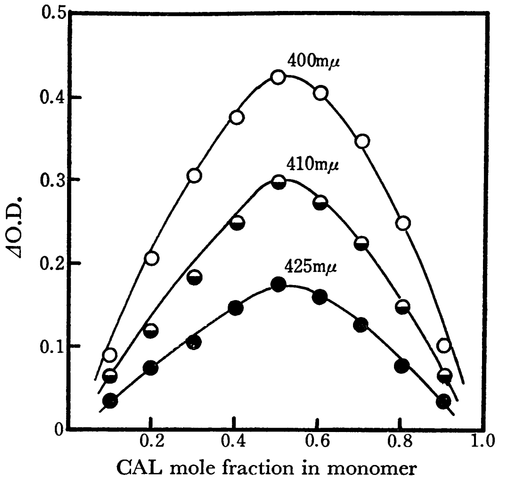

Fig. 2. Continuous variation method in CAL and St system. [CAL]+[St]=0.1 mol/l in DMSO at room temperature

All these results indicate that this copolymerization might take place through a charge-transfer complex. This theory is critically supported by the fact that electronic spectra obtained by means of the continuous variation method gave a maximum value in the optical density when an eouimolar mixture was employed (Fig. 2).

Copolymerization in the Presence of Boron Trifluoride Etherate. CAL was copolymerized with St, using boron trifluoride etherate as the catalyst and toluene as the solvent, at −78, 0, 30, and 60°C.

The results of the copolymerization at −78°C are as shown in Table 2. The copolymer obtained as a white powder had a molecular weight in the range of 2300—2800 and was soluble in most organic solvents, such as acetone, carbon tetrachloride, benzene, tetrahydrofuran, and dimethylformamide. Figure 3 shows that an in-

TABLE 2. COPOLYMERIZATION OF CAL(M_1) WITH St(M_2) BY BF_3OEt_2 IN TOLUENE AT −78°C, [M]=2 mol/l, [BF_3OEt_2]=1 mol%/monomer

M_1 (mol%)	Time (hr)	Conversion (%)	m_1 (mol%)	Molecular weight ($\bar{M}_n$)
0	0.5	15.23	0	2880
10	0.5	10.62	5.01	2800
20	0.5	7.05	10.37	2730
30	1	8.78	15.89	2690
40	1	3.69	23.75	2620
50	1	1.58	30.87	2570
60	10	4.67	43.32	2490
70	50	4.89	58.13	2450
80	50	1.18	77.31	2410
90	50	0.11	88.41	2380
100	100	—	—	—

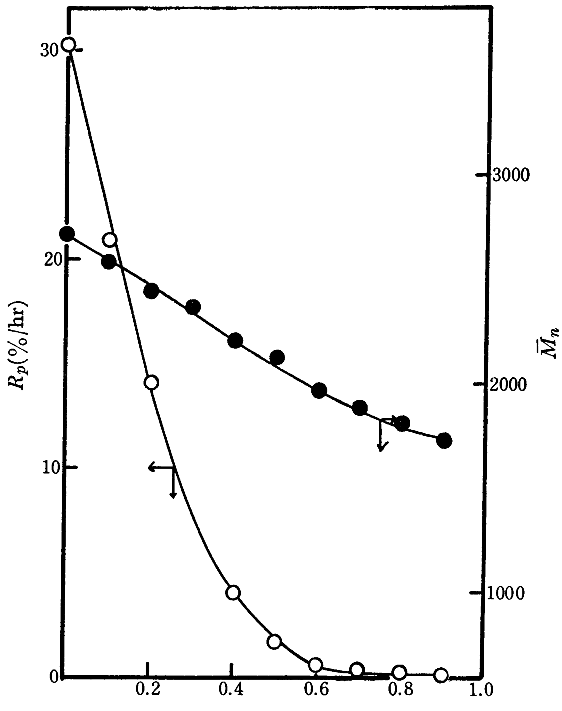

Fig. 3. Copolymerization rates and molecular weights for copolymerization of CAL with St by BF_3OEt_2.
[M]=2 mol/l, [BF_3OEt_2]=1 mol%/monomer in toluene at −78°C

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[9] A. D. Jenkins, *J. Polymer Sci.*, **29**, 245 (1958).

crease the CAL mole fraction of the monomer-feed composition clearly decreases both the copolymerization rate and the number-average molecular weight of the copolymer. These facts are well in accord with the reluctance of CAL to homopolymerize in the presence of BF_3OEt_2.

A colour change from colourless to reddish-brown during polymerization in this system was observed in every case except at −78°C, and the colour became darker with an increase in the time and the temperature. This appearance of the colour at room temperature was recorded by electronic absorption spectra at suitable time intervals; the results are shown in Fig. 4. The A spectrum, obtained without a catalyst, had a shoulder at 400 mμ, while, the B spectra, obtained when BF_3OEt_2 was added, showed a new peak at 486 mμ, the intensity of which tended to be enhanced as time passed. Moreover, it was found that the continuous-variation method gave a maximum peak for the CAL-St ratio of 1 : 1 (Fig. 5). However, the optical density in this case was quite large as compared to that of the CAL-St system. These observations imply that the strong appearance of a colour in the presence of BF_3-OEt_2 might be caused by the formation of a coordina-

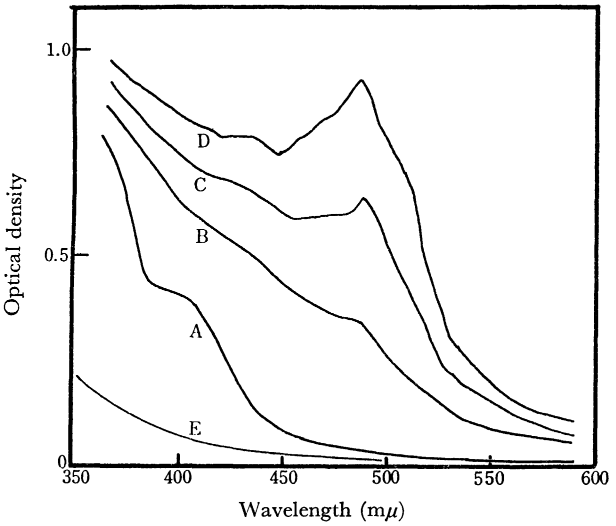

Fig. 4. Electronic absorption spectra.
A: CAL–St system 60 min
B: CAL–St–BF_3OEt_2 system 20 min
C: CAL–St–BF_3OEt_2 system 60 min
D: CAL–St–BF_3OEt_2 system 120 min
E: Copolymer from CAL–St–BF_3OEt_2 system

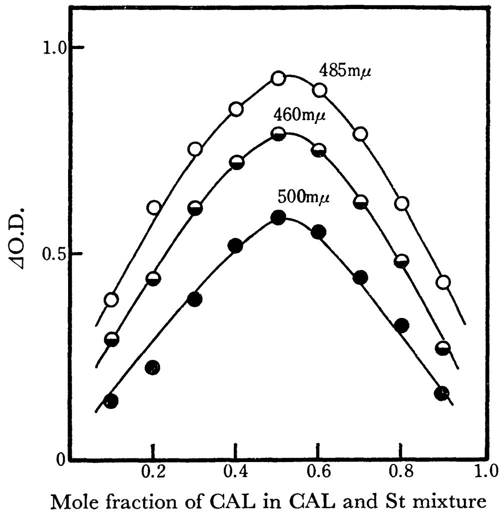

Fig. 5. Continuous variation method in CAL–St–BF_3OEt_2 system.
[CAL] + [St] = 0.1 mol/l in toluene,
[BF_3OEt_2] = 1 mol%/monomer at room temperature

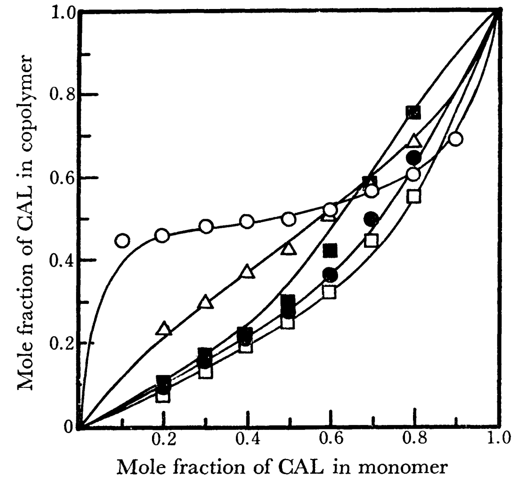

Fig. 6. Composition of copolymer in CAL(M_1)–St(M_2) system.
-○- Non-catalyzed system at 60°C
-△- BF_3OEt_2 system at 60°C
-■- BF_3OEt_2 system at 30°C
-●- BF_3OEt_2 system at 0°C
-□- BF_3OEt_2 system at −78°C

Table 3. Monomer reactivity ratios of copolymerization of CAL(M_1) with St(M_2) by BF_3OEt_2 at various temperature

Temperature (°C)	r_1	r_2	$r_1 \cdot r_2$
−78	0.9	2.8	2.52
0	0.5	2.8	1.40
30	0.4	2.8	1.12
60	0.4	0.7	0.28
60[a]	0.18	0.06	0.11

a) Without catalyst.

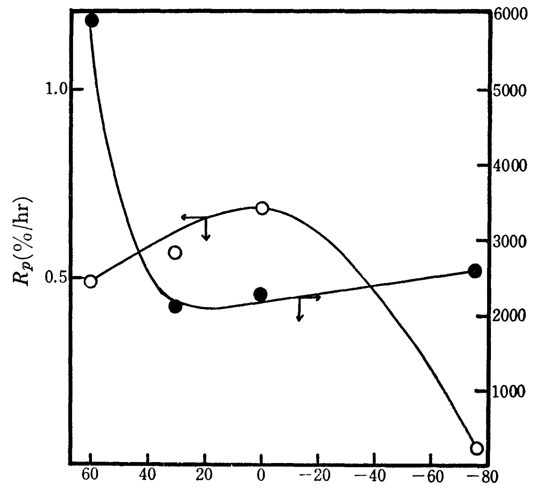

Fig. 7. Correlation between copolymerization rates or molecular weights and temperature.

tion bond between BF_3OEt_2 and the aldehyde group of CAL, this would decrease the electron density of its vinyl group, and, hence, the charge-transfer complex would be intensified. A few investigations have shown that such an interaction appeared in the reaction of a carbonyl compound with an inorganic metallic compound.[10-13] It is noted that the peak due to the complex disappeared when water or alcohol was added to the system.

Figure 6 shows monomer-copolymer composition curves obtained at various temperatures, and Table 3 tabulates the monomer-reactivity ratios obtained from the Fineman Ross plots. One of the most interesting manifestations in Table 3 is the fact that the value of $r_1 \cdot r_2$ gradually decreased with a rise in the polymerization temperature. This observation suggests that a radical polymerization through the charge-transfer complex takes place in some portion at higher temperatures. The same phenomenon has been observed by Sumitomo *et al.*[14] in the formation of the charge-transfer complex between α-cyanomethyl acrolein and zinc chloride, whose copolymerization with styrene gave an alternating copolymer.

It is interesting to note that the copolymerization rate reached its maximum value at about 0°C (Fig. 7). It is also indicated in Fig. 7 that the molecular weight of the copolymer decreased with a rise in the temperature, but increased after reaching a minimum value at about 30°C. This also suggests that a change in the temperature caused a different type of polymerization process to occur as has been described above.

Structure of the Copolymer. The IR, NMR, and X-ray diffraction spectra of the copolymer obtained with a CAL mole fraction of 0.5 in the monomer-feed composition are shown in Figs. 8, 9, and 10 respectively. The spectra of the copolymer obtained from a non-catalyzed system are marked A, whereas those obtained from a catalyzed system at 60, 30, 0, and −78°C are marked B, C, D, and E respectively.

The IR spectra, remarkably, contained the characteristic peaks of both CAL and St. A and B were

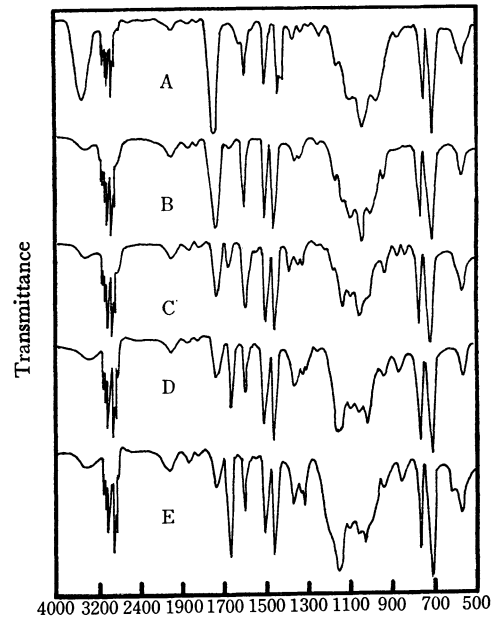

Fig. 8. Infrared spectra of copolymers obtained in CAL mole fraction of 0.5 (KBr disk).
A: Non-catalyzed system at 60°C
B: BF_3OEt_2 system at 60°C
C: BF_3OEt_2 system at 30°C
D: BF_3OEt_2 system at 0°C
E: BF_3OEt_2 system at −78°C

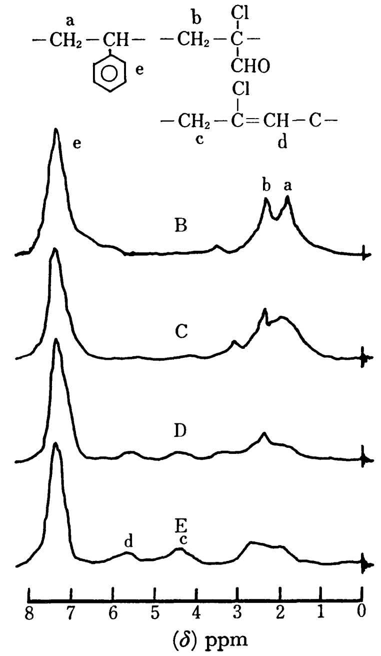

Fig. 9. NMR spectra of copolymers obtained using BF_3OEt_2 at various temperature (solvent DMSO-d_6).
Symbols are same as in Fig. 8.

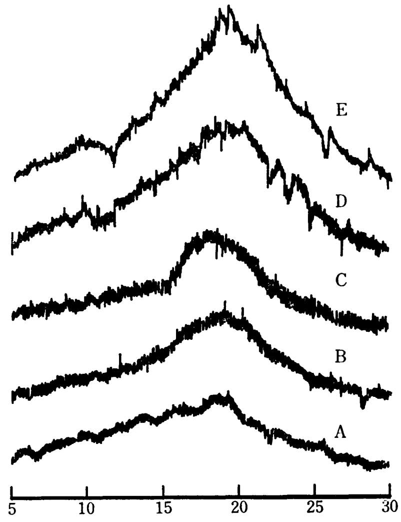

Fig. 10. X-Ray diffraction spectra of copolymers (CuK_α, Ni filter).
Symbols are same as in Fig. 8.

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[11] V. A. Kabanov and P. K. Medelskaya, *Vysokomol. Soyed.*, **2**, 165 (1960).

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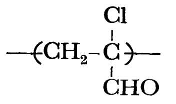
[14] I. Takemura and H. Sumitomo, 19th Annual Meeting at the Society of Polymer Science of Japan.

found to contain very similar absorption peaks. However, in the spectra obtained from a BF_3OEt_2-catalyzed system, namely, B, C, D, and E, the intensities of the peaks due to the C=O of the aldehyde groups decreased as the temperature decreased. On the other hand, the decrease in the temperature was found to increase the intensities of the peaks at 1670 cm^{-1} due to C=C and those at 1170 cm^{-1} due to the C–O of C=C–O in the order of B, C, D, and E.

This fact is in good agreement with the results of the NMR spectra. The peak at 4.2 and 5.7 ppm in the D and E spectra might be caused by the methylene proton signals, c and d respectively, as Fig. 9 shows.

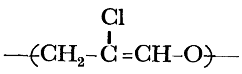
In the X-ray diffraction spectra (Fig. 10), the intensities of the peaks were found to decrease in the order of B, C, D, and E. However the A and B spectra had similar peaks.

All these results lead to the conclusion that the BF_3OEt_2-catalyzed system gave a crystalline copolymer with Structure II at lower temperatures, while a noncrystalline polymer with Structure I was obtained at higher temperatures. This may be explained by taking account of the stability of the terminal CAL cation with the counter anion, as is indicated below.



$$-\!(\mathrm{CH_2}-\overset{\mathrm{Cl}}{\underset{\mathrm{CHO}}{\mathrm{C}}})\!-$$

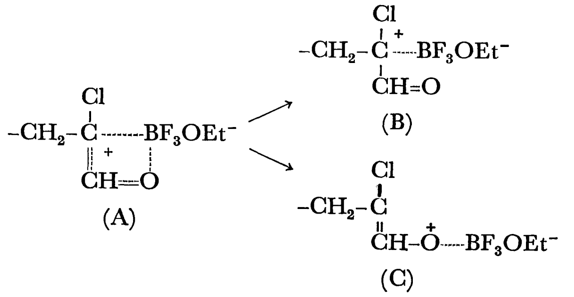
(I)



$$-\!(\mathrm{CH_2}-\overset{\mathrm{Cl}}{\mathrm{C}}=\mathrm{CH}-\mathrm{O})\!-$$

(II)

Thus, when the polymerization occurs *via* the polymer cation A, the higher the temperature, the easier it will be for the reaction to proceed *via* vinyl polymerization, B, than *via* carbonyl Polymerization, C, the carbonyl cation may be destabilized at higher temperatures.[15]



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[15] G. Ham, "Vinyl Polymerization," Vol. I, Marcel Dekker, N. Y. (1967), p. 427.