*The Cationic Polymerization of Acrolein**

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Generally speaking, the ionic polymerization of acrolein[1,3] gives soluble polymers in organic solvents and the polymers have low molecular weights and melting points. The structures of the polymers are extremely different from those of the polymers obtained by radical polymerization;[1-9] contrary to the case of radical polymerization, which proceeds through the vinyl group, in the case of ionic polymerization the carbonyl group plays a more important role in the polymerization than does the vinyl group. Schulz and Passmann[10] reported on the behavior of acrolein in ionic polymerization in their recent work on anionic polymerization. In the present paper the cationic polymerization of acrolein will be studied. The kinetics of polymerization and the influence of the polymerization temperature on the structure of polymers will be investigated.

Experimental

Material. — Commercial acrolein was distilled, dried over anhydrous cupric sulfate, and distilled again immediately before the polymerization procedure; the distillate at b. p. 52.5$\sim$53.5°C was used as the acrolein monomer.

Polymerization Procedure.—The monomer and the solvent were precooled at the desired temperature under nitrogen in a glass tube with a rubber stopper; the initiator, boron trifluoride etherate, was stirred in via the rubber stopper with an injector. The mixture was kept at the desired temperature for the desired length of time. After

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[1] R. C. Schulz, *Makromol. Chem.*, **17**, 62 (1955).

[2] R. C. Schulz and W. Kern, ibid., **18/19**, 4 (1956).

[3] R. C. Schulz, H. Fauth and W. Kern, ibid., **20**, 161 (1956).

[4] R. C. Schulz, H. Fauth and W. Kern, ibid., **21**, 227 (1956).

[5] R. C. Schulz, H. Cherdron and W. Kern, ibid., **24**, 141 (1957).

[6] R. C. Schulz, *Kunststoffe*, **48**, 257 (1958).

[7] R. C. Schulz, E. Muller and W. Kern, *Makromol. Chem.*, **30**, 39 (1959).

[8] R. C. Schulz, S. Suzuki, H. Cherdron and W. Kern, ibid., **53**, 145 (1962).

[9] R. C. Schulz, J. Kovacs and W. Kern, ibid., **54**, 140 (1962).

[10] R. C. Schulz and W. Passmann, ibid., **60**, 139 (1963).

the polymerization, the resulting mixture was added to a large excess of a water-methanol mixture (3 : 1 vol.), and then the unreacted monomer, the solvent and most of the methanol were removed by distillation under reduced pressure until the polymer was precipitated as a white powder in a transparent aqueous solution. The polymer was filtered, washed with water and dried under reduced pressure at room temperature.

The Treatment of the Polymer. — *Aldehyde Content.*—The method reported by Bryant and Smith[11] was employed. 0.5 g. of polymer was dissolved in 25 ml. of dioxane, to this solution 10 ml. of a 0.5 N hydroxylamine hydrochloride water-methanol solution and 35 ml. of a bromophenol blue ethanol solution containing pyridine were added, and the resulting mixture was warmed at 70°C for three hours. After this treatment, the mixture was titrated with a 0.5 N sodium hydroxide methanol solution. A blank was run under the same conditions without the polymer. The aldehyde content was calculated from the amount of alkali consumed.

The Determination of the Unsaturation Value.—0.5 g. of the polymer was dissolved in 90 ml. of acetic acid and was hydrogenated in the presence of 0.2 g. of platinum black under the atmospheric pressure of hydrogen and at room temperature. The carbon-carbon double bond in the polymer was calculated from the volume of hydrogen gas consumed.

Ozone Degradation.—0.5 g. of the polymer was dissolved in 250 ml. of dry chloroform, and an oxygen-ozone mixture was passed through the solution for a long enough length of time at −50°C. After ozonization, the chloroform was removed from the solution under reduced pressure at room temperature. The ozonide which remained as a white powder was cleaved by treatment with 50 ml. of 3% aqueous hydrogen peroxide at 50°C to yield a transparent solution. The solution was distilled under reduced pressure to separate the volatile organic acid from the other products. The distillate was titrated with alkali, and the acidity was calculated as formic acid. It has been demonstrated by means of paper chromatography[12] that the distillate contains only formic acid. The R_f value of hydroxamate of formic acid was 0.49 when the mixture of 1-butanol, acetic acid and water (4 : 1 : 5 v/v) was used as the development solvent.

Molecular Weight.—For the measurement of the molecular weight of polymers, the cryoscopic method in acetic acid was employed.

Results

The polymerization of acrolein in an ethyl ether solution in the presence of a boron trifluoride etherate was made. Figure 1 shows the relationship between the concentration of the initiator ([C], mol./l.) and the overall rate of polymerization (R_p), which was calculated from the slope of the time-conversion curve shown by a straight line at the early stage of polymerization (<20% of conversion). The relationship between the monomer concentration ([M], mol./l.) and R_p is shown in Fig. 2. It is confirmed by Figs. 1 and 2 that R_p is proportional to the first order of concentration of the initiator and to the second order of concentration of the monomer. From these results, the equation of the overall rate of polymerization is shown as Eq. 1:

$$R_p = K[\mathrm{C}][\mathrm{M}]^2 \qquad K\text{: constant} \qquad (1)$$

Equation 1 supports the theory that the initiation and termination reactions are bimolecular and monomolecular respectively. The temperature dependence on R_p is shown in Fig. 3. From R_p calculated from the slope

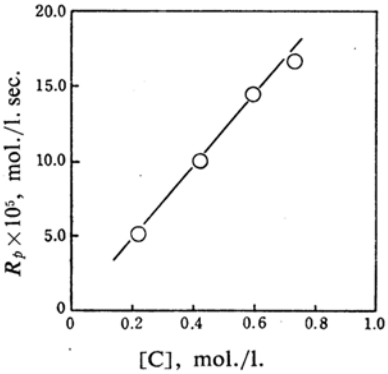

Fig. 1. Relationship between concentration of initiator and overall rate of polymerization.
Reaction temp.: 0°C
Concn. of monomer: 7.00 mol./l.
Solvent: ethyl ether

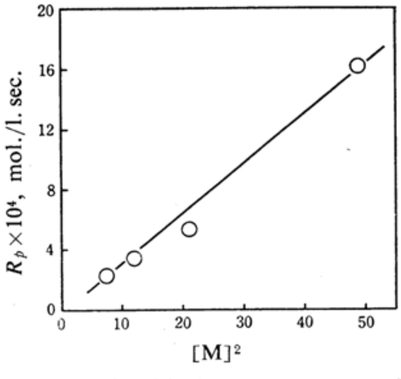

Fig. 2. Relationship between concentration of monomer and overall rate of polymerization.
Reaction temp.: 0°C
Concn. of initiator: 0.74 mol./l.
Solvent: ethyl ether

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[11] W. M. D. Bryant and D. M. Smith, *J. Am. Chem. Soc.*, 57, 57 (1935).

[12] R. J. Blook, E. L. Durrum and G. Aweig, "A Manual of Paper Chromatography and Paper Electrophoresis," Academic Press, New York (1955), p. 163.

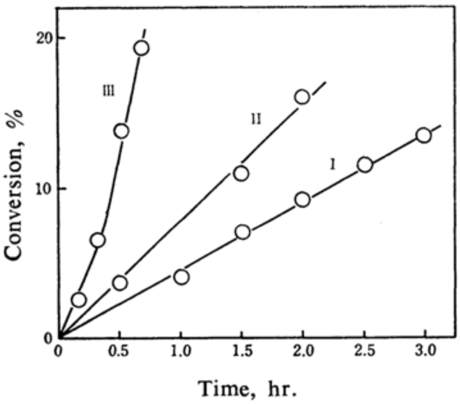


Fig. 3. Conversion curves of the polymerization of acrolein in ethyl ether solution with boron trifluoride etherate at the following temperature.
Curve I: −20°C
Curve II: 0°C
Curve III: 20°C
Concn. of monomer: 7.00 mol./l.
Concn. of initiator: 0.74 mol./l.

TABLE I. RATE CONSTANTS AT VARIOUS TEMPERATURES

Temp. °C	R_p mol./l. sec.	K
−20	9.030×10^{-5}	2.415×10^{-6}
0	1.572×10^{-4}	5.470×10^{-6}
20	2.823×10^{-4}	8.060×10^{-6}

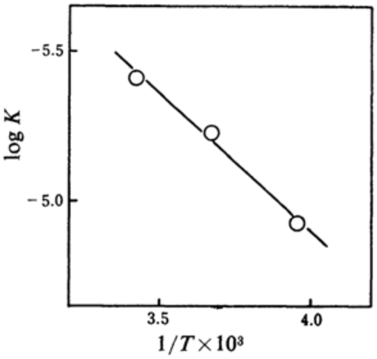


Fig. 4. Arrhenius polt of the rate constant in polymerization of acrolein by boron trifluoride etherate.

TABLE II. POLYMERIZATION BY IONIC INITIATORS

Initiator	Solvent	Temp. °C	Time hr.	Conv. %	Polymer No.
$BF_3\cdot(C_2H_5)_2O$, 2.65 mol. %d)		−78	115.0	38.1a)	I
K_2CO_3, 3.52×10^{-3} mol. %d)		20	2.0	21.3b)	II
$(C_6H_5)_3P$, 6.35×10^{-4} mol. %d)	MeOH ([M]/[S]=0.2)	5	16.7	85.0c)	III

a) The polymerization was performed as described in the polymerization procedure.
b) The polymerization was performed by the method similar to the one described by Schulz.1)
c) The polymerization was made in a round bottom flask with stirring under nitrogen, the polymerization in acetonitrile, dichloromethane and benzene solution were also made at 0∼10°C, but these polymers were not soluble in common organic solvents without warm formic acid.
d) It is shown in mol. % based on monomer used.

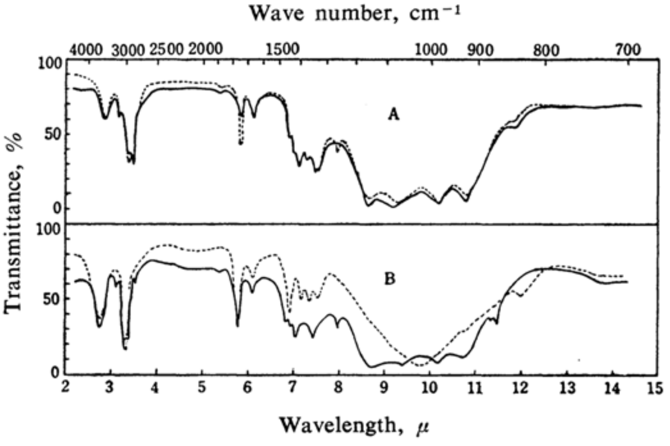
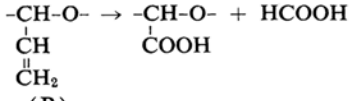


Fig. 5. Infrared spectra of polymers in KBr disk.
A: I (——) and I-7 (------)
B: II (——) and the polymer obtained by gamma-rays-initiated polymerization in bulk at −78°C (------).

of the time-conversion straight line and Eq. 1, the rate constants (K) of the polymerization reaction were calculated as is shown in Table I. 4.5 kcal./mol. was calculated as the activation energy of the reaction from the slope of the straight line of the Arrhenius plot (Fig. 4).

The bulk polymerization in the presence of boron trifluoride etherate at $-78°C$ was made, while anionic polymerizations by potassium carbonate and triphenyl phosphine were also made. These results are shown in Table II. Polymers obtained by polymerizations initiated with these cationic or anionic initiators were soluble in ethyl ether, benzene, dioxane and acetic acid, etc., but were insoluble in water and *n*-hexane. The melting points of the polymers were $65\sim70°C$.

The molecular weight of the polymer obtained by the solution polymerization with boron trifluoride etherate is given in Table III. The molecular weights of I, II and III (cf. Table II) are 643, 430 and 1270 respectively. The results of the elementary analysis of polymers are shown in Table IV. The infrared spectra of I, I-7 and II are shown in Fig. 5 (for reference, the spectrum of the polymer obtained by radical polymerization is shown in the same figure). At $1725\,cm^{-1}$, the absorption of the carbonyl group is observed. At 3080, 1645, 1410, 985 and $930\,cm^{-1}$, absorptions of the vinyl group are observed; these absorptions disappear or diminish in the spectra of hydrogenated polymers. In the spectra of II and I-7, a weak absorption of –C=C–O– is observed at $1250\,cm^{-1}$; this absorption disappears in a hydrogenated polymer. The aldehyde content and the carbon-carbon double bond in polymers were measured; these results are shown in Tables V and VI. Polymer I, which has a maximum double-bond content and a minimum aldehyde content compared with other polymers, was subjected to the ozonolysis. If the polymer has a double bond as vinyl group in a pendant of the polymer (as is shown in B), formic acid is produced as product of the ozone degradation as follows:



$$\begin{array}{lcll} -\mathrm{CH}-\mathrm{O}- & \rightarrow & -\mathrm{CH}-\mathrm{O}- & +\ \mathrm{HCOOH} \\ \ \ \mid & & \ \ \mid & \\ \ \ \mathrm{CH} & & \ \ \mathrm{COOH} & \\ \ \ \parallel & & & \\ \ \ \mathrm{CH_2} & & & \end{array}$$

(B)

TABLE III. MOLECULAR WEIGHT OF THE POLYMER OBTAINED BY ETHYL ETHER SOLUTION POLYMERIZATION WITH BORON TRIFLUORIDE ETHERATE

Monomer mol./l.	Initiator mol./l.	Temp. °C	Conv. %	M. w.	Polymer No.
7.00	0.73	−20	13.4	504	I-1
7.00	0.73	0	16.4	671	I-2
7.00	0.44	0	15.5	516	I-3
7.00	0.22	0	11.9	466	I-4
4.67	0.74	0	14.7	532	I-5
2.80	0.74	0	11.3	525	I-6
7.00	0.73	20	14.0	384	I-7

TABLE IV. RESULTS OF ELEMENTARY ANALYSES OF POLYMERS

Polymer No.	Found		Calcd. for $(C_3H_4O)_n$	
	C, %	H, %	C, %	H, %
I	63.86	7.35	64.27	7.19
I-1	62.63	7.67	64.27	7.19
I-2	62.90	7.63	64.27	7.19
I-7	60.62	7.01	64.27	7.19
II	59.59	7.52	64.27	7.19
III	58.62	7.91	64.27	7.19

TABLE V. ALDEHYDE CONTENTS OF POLYMERS

Polymer No.	Polymer g.	Consumed alkali $\times10^4$ mol.	Content of aldehyde %
I	0.1426	4.1052	16.12
I-1	0.1372	9.6746	39.50
I-2	0.1552	5.8645	21.16
I-7	0.1537	6.7442	24.57
II	0.1590	7.6239	26.85
III	0.1205	6.6600	30.80

TABLE VI. CONTENTS OF CARBON-CARBON DOUBLE BONDS IN POLYMERS

Polymer No.	Polymer g.	Consumed hydrogen ml.	Content of double bond %
I	0.5629	148.0	62.0
I-1	0.4111	67.0	43.8
I-2	0.4492	50.0	29.8
I-7	0.3952	31.0	21.1
II	0.5455	140.0	61.0
III	0.5203	75.0	34.0

On the other hand, if the polymer has a double bond in the main chain of the polymer as is shown in C, the formic ester of glycolic acid is produced as a product of the ozone degradation and this ester is saponified by the formic acid actually present in the mixture of the products, thus yielding a glycolic acid.

$$\text{-CH}_2\text{-CH=CH-O-} \rightarrow \text{O=CH-O-CH}_2\text{-COOH}$$

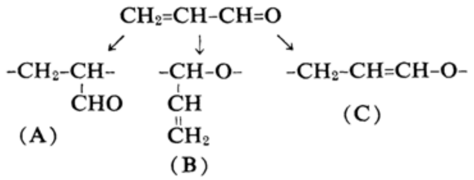
(C)

$$\rightarrow \text{HCOOH} + \text{HO-CH}_2\text{-COOH}$$

Formic acid was confirmed as the only volatile product by paper chromatography. Its acidity as determined by alkali titration was equivalent to 50% of the theoretical amount based on monomer units; this value is approximately in agreement with the degree of unsaturation as estimated by hydrogenation. In the nonvolatile product, glycolic acid was not identified by paper chromatography. It is confirmed by the above evidence that the carbon-carbon double bond belongs to vinyl group in a pendant of the polymer; this is also supported by the infrared absorption spectra of the polymer.

Discussion

Understandably, acrolein is polymerized in a different orientation under suitable conditions; the polymers thus obtained contain the following structural units in some ratios:



$$CH_2{=}CH{-}CH{=}O \rightarrow \underset{(A)}{-CH_2-\underset{CHO}{CH}-}\quad \underset{(B)}{-\underset{\underset{CH_2}{\overset{\|}{CH}}}{CH}-O-}\quad \underset{(C)}{-CH_2-CH{=}CH-O-}$$

Such behavior of acrolein is attributed to the conjugation of a carbonyl group with the vinyl group within its structure. In radical catalytic or gamma-rays-initiated polymerization, the polymers obtained belong to type A. For example, in the polymer obtained by the irradiation of gamma-rays at -78°C[13] or by redox polymerization,[5] the aldehyde content is 75～85% of the theoretical amount which is calculated as type A and the content of the carbon-carbon double bond is either not present or present in a negligibly small amount (4% in redox polymer[9]). On the other hand, in the polymer obtained by ionic polymerization, the aldehyde content is much less than that of the polymer given by radical polymerization, and the content of the carbon-carbon double bond increases. According to the recent work by Schulz[10] on anionic polymerization in the presence of sodium naphthalene, the polymer contains 70% of the theoretical amount of double bond and only 2% of the theoretical amount of the aldehyde group, and it is assumed that the polymer consists mainly of type B.

The similar behavior of acrolein upon polymerization is found in the cationic polymerization in the presence of boron trifluoride etherate. The polymer obtained at -78°C has only 16% of the aldehyde group and 60% of the carbon-carbon double bond in the side chain, findings which are supported by the infrared spectrum, the hydrogenation and the ozone degradation of the polymer, so that the polymer consists of type B in magnitude and also contains some A. On the other hand, in the infrared spectra of the polymers obtained at a higher temperature, 0 or 20°C, a weak absorption of $-C{=}C-O-$ at 1250 cm^{-1} is observed (Fig. 5), and in the polymer, the ratio of the amount of the aldehyde group to the carbon-carbon double bond is increased (Table IV). In the ionic polymerization of acrolein, the carbonyl's double bond plays an important role in the polymerization reaction, one which can be predicted from the fact that, in the acrolein molecule, the position of the maximum and minimum of π-electron density exist on the oxygen and carbon atoms of the carbonyl group respectively. This orientation of the polymerization reaction is more remarkable still at lower temperatures.

Summary

The cationic polymerization of acrolein with boron trifluoride etherate at various temperatures has been studied.

(1) The polymerization rate may be given as follows: $R_p = K[\mathrm{C}]\,[\mathrm{M}]^2$, on the basis of the polymerization in an ethyl ether solution, and the activation energy of reaction is 4.5 kcal./mol.

(2) The structure of polymers depends very much on the polymerization temperature; the polymerization at the lower temperature gives a polymer containing the larger amount of the end vinyl group as a side chain, and the smaller amount of the aldehyde group.

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[13] Y. Toi, T. Fujii and Y. Hachihama, presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963.