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Cationic Polymerization of Formaldehyde in Liquid Carbon Dioxide. IV. A Kinetic Study of the Polymerization in the Presence of Acetic Anhydride[*1]

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The influence of acetic anhydride on the polymerization of formaldehyde, which was carried out by means of initiation with an acidic catalyst in liquid carbon dioxode, was studied at 20 to 40°C. Acetic anhydride decreased the polymer yield and the degree of polymerization of the polymer resulting from the polymerization with acetic acid. Moreover, the over-all rate of polymerization with acetic acid in the presence of acetic anhydride deviated from a first-order equation with respect to the monomer concentration. On the other hand, the polymerization which was initiated by dichloroacetic acid was not affected by the presence of acetic anhydride. On the basis of a kinetical consideration, it can be said that the termination which was proportional to the square of the concentration of the initiating species was caused by the presence of acetic anhydride in the polymerization with acetic acid. The rate constants and the activation energies of the elementary processes were estimated, and a rate equation satisfying the experimental results was presented.

As has been described in previous papers,[1,2] the present authors have already disclosed that formaldehyde monomer which is prepared by the thermal decomposition of α-polyoxymethylene without additional purification polymerizes in liquid carbon dioxide both with and without a carboxylic acid catalyst to give a polymer with a high molecular weight, and that this polymerization follows a cationic mechanism and belongs to a type of successive polymerization with rapid initiation and no termination.

It has also been reported by the present authors[3] that acetic anhydride, which has already been added to the reaction system at the beginning of polymerization, acetylates the endgroups of polyoxymethylene by heating the resulting polymer after discharging the unreacted monomer and carbon dioxide at the end of the polymerization.

The purpose of the present work is to determine quantitatively the effects of acetic anhydride on the elementary steps of the polymerization of formaldehyde in liquid carbon dioxide.

Experimental

The methods of preparing the monomer and the additives, such as acetic acid, and mono-, di- and trichloroacetic acids, and the experimental procedure for the polymerization were the same as have previously been described.[1,2] Acetic anhydride was carefully prepared to remove acetic acid, as has also previously been reported.[3] The acetic anhydride used contained less than 0.1 wt% acetic acid.

The concentration of formaldehyde in the monomer solution was 60 wt%, and the loading density, which was represented as a ratio of the amount of solution fed in to the volume of the reaction vessel used, was 10 g/30 m*l*.

Results and Discussion

Influence of the Addition of Acetic Anhydride on Polymerization with Various Acids. The influence of acetic anhydride on the polymerizations initiated by acetic and dichloroacetic acids studies, as is shown in Table 1. In polymerization with dichloroacetic acid, acetic anhydride had no effects on the polymerization. On the other hand, added acetic anhydride decreased both the polymer yield and the degree of polymerization of the resulting polymer in polymerization with acetic acid.

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1) Part I: H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *J. Polymer Sci., A-1*, **6**, 425 (1968).

2) Part II: H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *ibid., A-1*, **6**, 435 (1968).

3) H. Yokota, M. Kondo, T. Kagiya and K. Dukui, This Bulletin, **41**, 1668 (1968).

Table 1. Influence of the addition of acetic anhydride on the polymerization with various acids

Acid	Acetic anhydride	Polymer yield g	Polymer yield wt%	$\overline{P}_n$
Acetic acid	presence	1.734	28.9	1100
Acetic acid	absence	3.265	54.4	1750
Dichloroacetic acid	presence	4.032	67.2	1750
Dichloroacetic acid	absence	4.052	67.5	1800

monomer solution, 10 g ; $[M]_0=20$ mol/*l* ; $[CH_3COOH] = 0.02$ mol/*l* ; $[(CH_3CO)_2O] = 1.0$ mol/*l* ; temperature, 30°C ; time, 30 min ; reaction vessel, 30 m*l*.

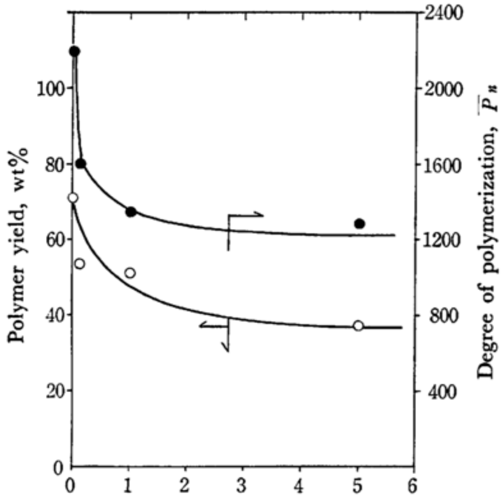

Fig. 1. Effect of acetic anhydride on the polymerization initiated by acetic acid.

Monomer solution, 10 g ; $[M]_0 = 20$ mol/*l* ; $[CH_3COOH]=0.02$ mol/*l* ; temperature, 30°C ; time, 10 min ; reaction vessel, 30 m*l*.

In order to determine the effect of acetic anhydride, the influence of the amount of acetic anhydride on the polymerization with acetic acid was examined. As Fig. 1 shows, both the polymer yield and the degree of polymerization of the resulting polymer decreased rapidly with an increase in the concentration of acetic anhydride. Moreover, the number of moles of the polymer chain, which was calculated as a ratio of the polymer yield to the degree of polymerization, was almost constant. Because the amount of acetic anhydride added was less than 5 mol% that of the monomer, the results suggest that the decrease in the polymer yield with an increase in the concentration of acetic anhydride is not due to the decrease in the amount of the initiating species or of the monomer concentration, but to the increase in the termination reaction.

Influence of the Addition of Stronger Acids on Polymerization in the Presence of Acetic Anhydride. On polymerization in the absence of acetic anhydride, it has been established[1)] that the polymer yield, the number of moles of the polymer chain, and the degree of polymerization of the resulting polymer all increase as the acidity of the acid used is increased. Analogously, the effects of acetic acid and mono-, di-, and tri-chloroacetic acids on polymerization in the presence of acetic anhydride were studied.

Table 2. Influence of various acidic catalyst on the polymerization in the presence of acetic anhydride

Catalyst	pK_a	Polymer yield g	Polymer yield wt%	$\overline{P}_n$	N_p mol ×10^5
Trichloroacetic acid	0.66	3.253	54.2	1200	9.0
Dichloroacetic acid	1.25	2.441	39.0	950	8.2
Monochloroacetic acid	2.87	1.512	25.2	900	5.6
Acetic acid	4.75	0.715	11.9	520	4.5

The experimental condition was the same as described in Table 1, except that the reaction time was 10 min.

The results are presented in Table 2. Here, pK_a and N_p represent the logarithmic value of the dissociation constant of the acid measured in water at 25°C, and the number of moles of the polymer chain (represented as a ratio of the polymer yield to the degree of polymerization), respectively. Results similar to those in the absence of acetic anhydride described previously[1)] were obtained in the polymer yield, the degree of polymerization, and the number of moles of the polymer chain.

Using the results listed in Table 2, the logarithmic ratios of the polymer yield (log Y_0/Y) and of the number of moles of the polymer chain (log N_{p_0}/N_p) are plotted against the relative acidity of the catalyst (ΔpK_a) in Fig. 2. Here, Y_0/Y and N_{p_0}/N_p are calculated as the ratio of the polymer yield by trichloroacetic acid to that by another acid, and a similar ratio of the number of moles of the polymer chain, respectively, and ΔpK_a is the difference between the pK_a values of trichloroacetic acid and another acid. It was found that (log Y_0/Y) and (log N_{p_0}/N_p) were proportional to ΔpK_a, and that the ratio of the slopes of these straight lines was about 2. This value was just the same as that calculated in the polymerization in the absence of acetic anhydride which was previously reported.[1)] In addition, the degree of polymerization of the resulting polymer also increased proportionally with a decrease in the pK_a value of the acid used. These results agree well with the behavior in the polymerization without acetic anhydride. Hence, it seems that the mechanisms of the initiation and propagation are the same whether acetic anhydride is present or not.

Polymerization with Dichloroacetic Acid. The finding that acetic anhydride did not affect the polymerization with dichloroacetic acid, a stronger acid than acetic acid, was quantitatively confirmed, as Fig. 3 shows. For comparison, the previously-reported date obtained in the polymerization without acetic anhydride[2] are also shown in the same figure.

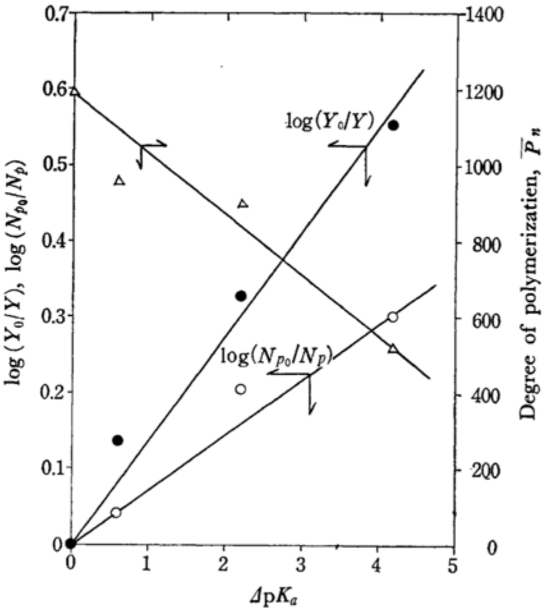

Fig. 2. Effect of acidity on the polymerization in the presence of acetic anhydride.

Monomer solution, 10 g ; $[M]_0=20$ mol/l ; [acid] $=0.02$ mol/l ; $[(CH_3CO)_2O]=1.0$ mol/l ; temperature, 30°C ; time, 10 min ; reaction vessel, 30 ml ; ●, $\log(Y_0/Y)$; ○, $\log(N_{p_0}/N_p)$; △, degree of polymerization.

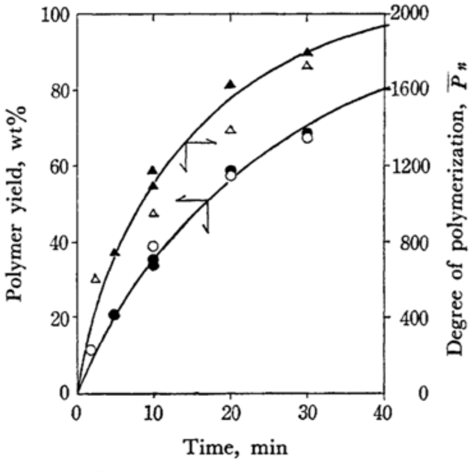

Fig. 3. Effect of the reaction time on the polymerization initiated by dichloroacetic acid.

Monomer solution, 10 g ; $[M]_0 = 20$ mol/l ; $[CHCl_2COOH]=0.02$ mol/l; temperature, 30°C; reaction vessel, 30 ml ; ○, △, in the presence of acetic anhydride of 1.0 mol/l ; ●, ▲, in the absence of acetic anhydride.

The behavior of the polymerization in this case was the same as that without acetic anhydride. It was, therefore, concluded that the polymerization by an acid stronger than acetic acid is not affected by acetic anhydride, and that the rate of polymerization follows a first-order equation with respect to the monomer concentration. Accordingly, the polymerization belongs to a type of successive polymerization with rapid initiation and no termination.

Polymerization with Acetic Acid. As has already been reported, the termination was apparently negligible in the polymerization in the absence of acetic anhydride, and also in the polymerization in the presence of acetic anhydride initiated by a stronger acid, such as dichloroacetic acid. On the other hand, termination was assumed in the polymerization with acetic acid in the presence of acetic anhydride, as has been described above. To determine quantitatively the effect of acetic anhydride on the polymerization with acetic acid, the influence of the reaction time and the temperature on the polymerization was also studied, as is shown in Table 3.

TABLE 3. EFFECT OF THE REACTION TIME AND TEMPERATURE ON THE POLYMERIZATION WITH ACETIC ACID IN THE PRESENCE OF ACETIC ANHYDRIDE

Time min	Polymer yield		$\overline{P}_n$
	g	wt%	
	Temperature, 20°C		
5	0.137	2.3	440
5	0.224	3.7	340
15	0.391	6.5	660
15	0.426	7.1	530
30	0.589	9.8	1000
30	0.756	12.6	1100
60	1.025	17.1	1600
60	0.934	15.6	1200
	Temperature, 30°C		
2	0.247	4.1	380
5	0.773	12.9	970
10	0.907	15.1	780
10	0.715	11.9	520
20	1.172	19.5	1050
30	1.734	28.9	1100
60	2.231	37.2	1300
	Temperature, 40°C		
2	0.977	16.3	320
5	1.483	24.7	820
10	2.186	36.4	1000
30	3.275	54.6	1200

Experimental conditions were the same as those in Table 1, except temperature and time.

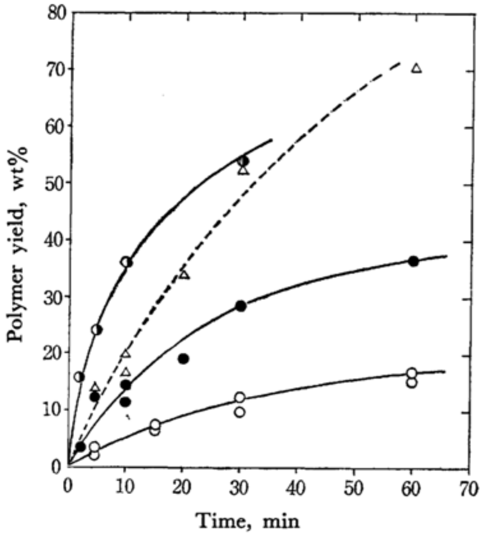

Fig. 4. Influence of reaction time and temperature on the rate of the polymerization in the presence of acetic anhydride.

Monomer solution, 10 g ; $[M]_0 = 20$ mol/l ; $[CH_3COOH]=0.02$ mol/l ; $[(CH_3CO)_2O]=1.0$ mol/l; reaction vessel, 30 ml; ○, 20°C; ●, 30°C; ◑, 40°C ; △, 30°C without acetic anhydride.

Figure 4 is the plot of the polymer yield against the reaction time at each temperature, using the data listed in Table 3. The results[2)] of the polymerization which was carried out at 30°C with acetic acid in the absence of acetic anhydride are also shown for the sake of comparison. The rate of polymerization in the early stages was almost the same as that without acetic anhydride. Two characteristics of the behavior of the polymerization with acetic anhydride were that the rate in the later stages decreased rapidly with the reaction time and that the polymer yield tended to reach a saturated value.

In Fig. 5, the degree of polymerization of the resulting polymer is plotted against the polymer yield, using the data listed in Table 3. It was found that the degree of polymerization increased with the polymer in the same way as in the polymerization without acetic anhydride. This indicates that the rate of chain transfer in this case is also considerably smaller than that of propagation.

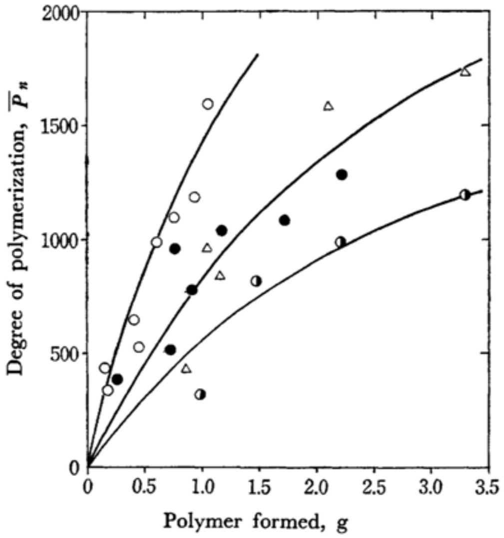

Fig. 5. Degree of polymerization *versus* polymer yield.

Reaction condition are the same as in Fig. 4.
with acetic anhydride : ○, 20°C ; ●, 30°C ; ◑, 40°C
without acetic anhydride : △, 30°C

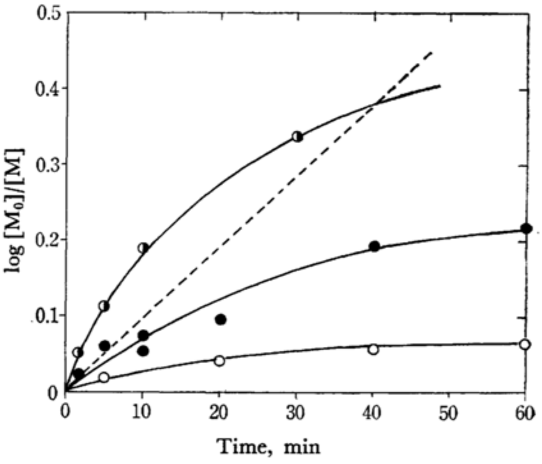

Fig. 6. Deviation of the polymerization rate from a first-order rate equation.

○, 20°C ; ●, 30°C ; ◑, 40°C ; Broken line is the same as in Fig. 4.

Deviation from a First-order Rate Equation. In the polymerization with acetic acid in the presence of acetic anhydride, the rate of polymerization decreased rapidly with the progress of the polymerization, as has been described above. The following kinetical treatments of the polymerization were focused on the elucidation of this behavior.

As Fig. 6 shows, the over-all rate of polymerization, which was calculated by using the data in Table 3, deviated from the first-order equation with respect to the monomer concentration. The deviation from the first-order rate equation is a peculiarity observed only in the polymerization initiated by acetic acid in the presence of acetic anhydride. This characteristic fact let to the assumption that the decrease in the rate of polymerization may be attributed to a termination reaction between the growing polymer chain and a component which was originally present in the reaction system or which was produced as a by-product.

Kinetics in the Polymerization with Acetic Acid in the Presence of Acetic Anhydride. *Elementary Processes.* It may be concluded, in view of the characteristic behavior described above, that polymerization initiated with acetic acid in the presence of acetic anhydride belongs to the type of non-stationary successive polymerization, with rapid initiation.

In almost the same manner as in the polymerization without acetic anhydride, using the graphical method proposed by Kagiya *et al.*,[4] the elementary processes were postulated to be as follows:

Initiation:

$$\mathrm{C} + \mathrm{M} \xrightarrow{k_i} \mathrm{P}^*, \qquad R_i = \text{rapid} \tag{1}$$

$$\int R_i \mathrm{d}t = [\mathrm{P}^*]_0 \tag{2}$$

Propagation:

$$\mathrm{P}^* + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_n^*, \quad R_p = k_p[\mathrm{P}^*][\mathrm{M}] \tag{3}$$

$$\int R_p \mathrm{d}t = [\mathrm{M_p}] \tag{4}$$

Chain Transfer:

$$\mathrm{P}_n^* + \mathrm{Y} \xrightarrow{k_{tr}} \mathrm{P}_n + \mathrm{Y}^*, \; R_{tr} = k_{tr}[\mathrm{P}^*][\mathrm{Y}] \tag{5}$$

$$\int R_{tr} \mathrm{d}t = \frac{k_{tr}[\mathrm{Y}]}{k_p} \int \frac{R_p}{[\mathrm{M}]} \mathrm{d}t \tag{6}$$

Here R_i, R_p and R_{tr} are the rates of initiation, propagation, and chain transfer; k_p and k_{tr} are the rate constants of propagation and chain transfer; and $[\mathrm{P}^*]_0$, $[\mathrm{P}^*]$, $[\mathrm{M}]$, $[\mathrm{M_p}]$, and $[\mathrm{Y}]$ are the concentrations of the initiating species, the propagating species, the monomer, the polymerized monomer, and the chain transfer agent respectively.

Termination:

$$\mathrm{P}_n^* + \mathrm{Z} \xrightarrow{k_d} \mathrm{P}_n, \qquad R_d = k_d[\mathrm{P}^*][\mathrm{Z}] \tag{7}$$

where R_d, k_d, and [Z] are the rate of termination, the rate constant of termination, and the concentration of the terminator respectively. The experimental results could not be interpreted successfully on the assumption that [Z] in Eq. (7) is constant during the course of polymerization. Hence, it was assumed that the concentration of the terminator is proportional to that of the growing polymer chain; then the following equation was derived from Eq. (7).

$$R_d = k_d'[\mathrm{P}^*]^2 \tag{8}$$

Accordingly, the integration of R_d gives the following equation when Eq. (3) is substituted into Eq. (8):

$$\int R_d \mathrm{d}t = \frac{k_d'}{k_p^2} \int \frac{R_p^2}{[\mathrm{M}]^2} \mathrm{d}t \tag{9}$$

Estimation of the Concentration of the Initiating Species and the Rate Constant of Chain Transfer. Because there is no termination caused by recombination between the growing polymer chains, the following equation for the degree of polymerization is given, in the same manner as has been reported in a previous paper[1]:

$$\frac{1}{\overline{P}_n} = \frac{\int R_i \mathrm{d}t}{\int R_p \mathrm{d}t} + \frac{\int R_{tr} \mathrm{d}t}{\int R_p \mathrm{d}t} \tag{10}$$

By substituting Eqs (2), (4), and (6) into Eq. (10), we derive:

$$\frac{[\mathrm{M}_p]}{\overline{P}_n \int \frac{R_p}{[\mathrm{M}]} \mathrm{d}t} = \frac{[\mathrm{P}^*]_0}{\int \frac{R_p}{[\mathrm{M}]} \mathrm{d}t} + \frac{k_{tr}[\mathrm{Y}]}{k_p} \tag{11}$$

Here, $[\mathrm{M_p}]$, $\overline{P}_n$, R_p, and [M] are graphically determined by using the values in Figs. 4 and 5; of these, R_p was estimated from the tangent of the curve in Fig. 4. The estimated values are listed in Table 4. Here, the value of $\int \frac{R_p}{[\mathrm{M}]} \mathrm{d}t$ was calculated by a graphical integration.

In order to evaluate graphically the values of $[\mathrm{P}^*]_0$ and $k_{tr}[\mathrm{Y}]/k_p$, the relation between the values of $\frac{[\mathrm{M_p}]}{\overline{P}_n \int \frac{R_p}{[\mathrm{M}]} \mathrm{d}t}$ and $\frac{1}{\int \frac{R_p}{[\mathrm{M}]} \mathrm{d}t}$ was plotted; it is shown in Fig. 7. The existence of linear relations in the same figure proves the validity of the assumption that the polymerization is rapidly initiated and that the reaction of chain transfer is quite slow.

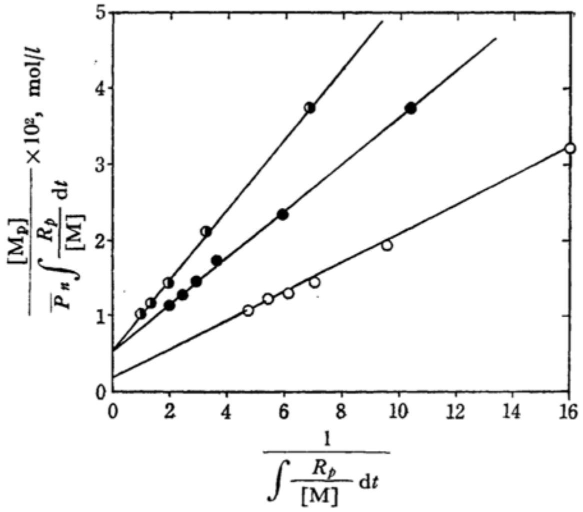

Fig. 7. Estimation of the concentration of initiating species and the rate constants of chain transfer.
○, 20°C ; ●, 30°C ; ◑, 40°C.

The $k_{tr}[\mathrm{Y}]/k_p$ ratio, as shown in Table 5, was evaluated from all the intercepts on the ordinate, while the concentration of the initiator, $[\mathrm{P}^*]_0$, was evaluated from the slopes of all the lines in

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[4] T. Kagiya, M. Izu and K. Fukui, This Bulletin, **40**, 1045 (1967).

TABLE 4. CALCULATED VALUES IN THE POLYMERIZATION WITH ACETIC ACID IN THE PRESENCE OF ACETIC ANHYDRIDE

Time min	$[M_p]$ mol/l	[M] mol/l	R_p mol/l min	$\overline{P}_n$	$\dfrac{1}{\int \frac{R_p}{[M]} dt}$	$\dfrac{[M_p]}{\overline{P}_n \int \frac{R_p}{[M]} dt}$ mol/l × 10^{-2}	$\dfrac{R_p}{[M] \int \frac{R_p^2}{[M]^2} dt}$	$\dfrac{[P^*]_0}{\int \frac{R_p^2}{[M]^2} dt}$ mol·min/l
Temperature, 20°C								
5	0.54	19.5	1.17	300	28.7	5.17	43.9	7.32
10	1.04	19.0	0.96	530	16.0	3.14	13.0	4.46
20	1.64	18.4	0.71	820	9.35	1.87	6.64	2.94
30	2.14	17.9	0.58	1050	6.98	1.42	4.44	2.43
40	2.56	17.4	0.45	1200	5.88	1.26	3.35	2.20
50	2.96	17.1	0.38	1330	5.18	1.15	2.66	2.04
60	3.16	16.8	0.33	1400	4.69	1.06	2.25	1.94
Temperature, 30°C								
5	1.72	18.3	2.89	470	10.2	3.78	8.83	1.82
10	2.96	17.0	2.09	750	5.82	2.31	4.88	1.17
20	4.56	15.5	1.32	970	3.59	1.70	2.26	0.853
30	5.66	14.3	0.93	1120	2.81	1.42	1.49	0.737
40	6.16	13.8	0.73	1180	2.39	1.25	1.11	0.675
50	7.10	12.9	0.57	1290	2.14	1.17	0.89	0.644
60	7.68	12.3	0.49	1340	1.96	1.12	0.78	0.622
Temperature, 40°C								
2	2.44	17.6	2.34	430	6.57	18.7	6.80	0.545
5	4.90	15.1	1.49	750	3.08	10.0	2.90	0.305
10	7.34	12.7	0.88	980	1.85	6.93	1.40	0.218
15	8.90	11.1	0.58	1100	1.45	5.87	0.995	0.187
20	9.96	10.0	0.43	1150	1.23	5.34	0.752	0.174
25	10.8	9.08	0.33	1180	1.10	5.05	0.605	0.166
30	11.5	8.55	0.27	1200	1.01	4.82	0.500	0.158

TABLE 5. CONCENTRATION OF INITIATING SPECIES AND RATE CONSTANTS OF ELEMENTARY REACTION IN THE POLYMERIZATION INITIATED BY ACETIC ACID

Temp. °C	$[P^*]_0$ mol/l × 10^{-3}	k_p l/mol min	$k_{tr}[Y]$ min^{-1} × 10^{-2}	$k_{tr}[Y]/k_p$ mol/l × 10^{-3}	k_d l/mol min
		In the presence of acetic anhydride			
20	1.7	4.0	1.0	2.5	22
30	3.2	7.1	3.6	5.0	25
40	5.0	15.0	6.7	4.5	30
		In the absence of acetic anhyride			
30	3.4	6.5	2.1	3.2	0

Fig. 7. The previously reported values²⁾ for the rate constants of the elementary processes are also listed in Table 5 for convenience in comparing the two polymerizations, initiated by acetic acid in the presence and absence of acetic anhydride.

Estimation of the Rate Constants of Propagation and Termination. The concentration of the growing polymer chain [P*] can be expressed by the following equation:

$$[P^*] = \int R_t dt - \int R_d dt \tag{12}$$

By substituting Eqs. (2), (3), (4), and (9) into Eq. (12), it follows that:

$$\frac{R_p}{[M]\int \frac{R_p^2}{[M]^2} dt} = \frac{k_p [P^*]_0}{\int \frac{R_p^2}{[M]^2} dt} - \frac{k_d'}{k_p} \tag{13}$$

The values of $\dfrac{R_p}{[M]\int \frac{R_p^2}{[M]^2} dt}$ and $\dfrac{[P^*]_0}{\int \frac{R_p^2}{[M]^2} dt}$, which were calculated in a way similar to that described above, are also listed in Table 4. The relation

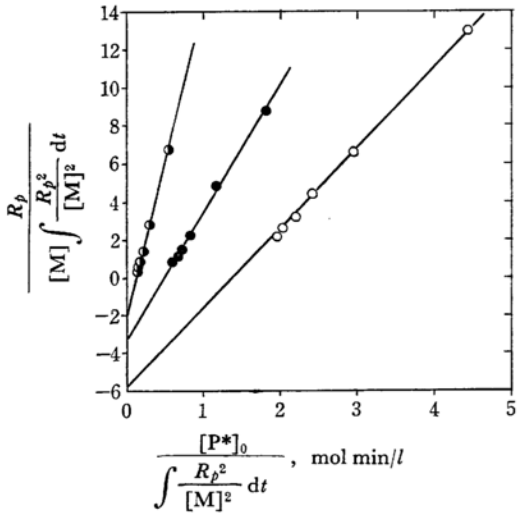

Fig. 8. Estimation of the rate constants of propagation and termination.

○, 20°C ; ●, 30°C ; ◑, 40°C.

between the two values is plotted in Fig. 8. A distinct linear relation exists between them at each temperature. This fact indicates that the rate of termination is proportional to the square of the concentration of the growing polymer chain. The rate constants of propagation and termination were then estimated in the manner described above; they are listed in Table 5. Using the values of k_p, the $k_{tr}[Y]$ values were also estimated.

Over-all Rate Equation. It was concluded from the above considerations that the termination apparently ocurred according to a second-order equation with respect to the concentration of active species. Consequently, the concentration of the growing polymer chain may be represented as follows by integrating Equation 8:

$$[P^*] = [P^*]_0\left\{\frac{1}{1+[P^*]_0k_dt}\right\} \tag{14}$$

The rate of polymerization can, therefore, be expressed by the following equation by introducing Equation 14 into Eq. (3):

$$R_p = -\frac{\mathrm{d}[M]}{\mathrm{d}t} = k_p[M][P^*]_0\left\{\frac{1}{1+[P^*]_0k_dt}\right\} \tag{15}$$

Hence;

$$\ln\frac{[M]_0}{[M]} = \frac{k_p}{k_d}\ln\{1+[P^*]_0k_dt\} \tag{16}$$

Figure 9 shows a plot of the logarithmic values of $[M]_0/[M]$, a plot which has been calculated by using the data in Table 3, against the value of $\log\{1+[P^*]_0k_dt\}$, which was calculated by using the values of $[P^*]_0$ and k_d shown in Table 5. The linear relation observed proves the validity of Eq. (16).

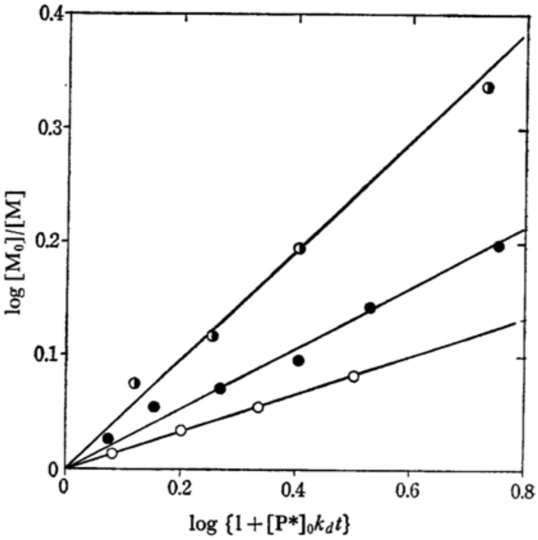

Fig. 9. Coincidence of the rate equation with the experimental results.

○, 20°C ; ●, 30°C ; ◑, 40°C

In conclusion, the over-all rate of polymerization is proportional to the monomer concentration, and rate of termination is proportional to the square of the concentration of the intiating species.

Activation Energies of Each Elementary Process. By using the Arrhenius plot of the rate constants listed in Table 5, the activation energies for each elementary process were calculated to be as follows; 9.4, 12, 15 and 2.2 kcal/mol for initiation, propagation, chain transfer, and termination respectively. The activation energies in each process were larger in the polymerization with acetic anhydride than in that without acetic anhydride.

Comparison between the Kinetic Features of Polymerization both with and without Acetic Anhydride. The above-mentioned considerations and a previous paper[2)] established that the polymerizations of formaldehyde in liquid carbon dioxide which were initiated by acetic acid in both the presence and absence of acetic anhydride were of the successive-polymerization type with a rapid initiation. The concentration of active species and the rate constant of propagation in the polymerization with acetic anhydride were almost the same as those in the polymerization without acetic anhydride at 30°C. Moreover, a small contribution of chain transfer was observed in both cases.

While the polymerization without acetic anhydride was a stationary successive polymerization, the polymerization with acetic anhydride was of the non-stationary successive polymerization type. The reaction of termination in the latter polymerization was attributable to the reaction of the growing polymer chain with a compound which was originally present in the reaction system or which was produced as a by-product during the polymerization.

The increase in the rate constant upon the addition of acetic anhydride, which was observed in spite of the increase in the activation energy, may ascribed to the considerable increase in the entropy caused by the addition of acetic anhydride, and hence the decrease in the free energy as a whole.

The mechanism of the polymerization will be reported in a subsequent paper.