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A Cationic Polymerization of Formaldehyde in Liquid Carbon Dioxide. V. Reaction Mechanism[*1]

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The present work was carried out in order to elucidate the reaction mechanism in the polymerization of formaldehyde in liquid carbon dioxide. Methylene glycol methylether acetate with a structure similar to that of methylene glycol monocarboxylate, which was assumed to be an initiator, exhibited a catalytic activity. On the other hand, methyl acetate terminated the polymerization. Moreover, the resulting polymer, which was terminated by the addition of methyl-$^2H_3$-acetate, contained deuterium originating from the terminator used. On the basis of these experimental results, a reaction mechanism of the elementary processes is discussed.

In our previous papers[1,2] it has been disclosed that formaldehyde, prepared by the thermal decomposition of α-polyoxymethylene, followed by no additional purification, is polymerized by a carboxylic acid catalyst in a liquid carbon dioxide solution to produce a high-molecular-weight polyoxymethylene, and that the polymerization is a cationic mechanism and belongs to a type of stationary successive polymerization with rapid initiation and no termination. Acetic anhydride added to the reaction system in advance of the polymerization reaction acetylates the endgroups of the polymer chain by means of heating the resulting polymer after the polymerization.[3] On the other hand, acetic anhydride added to a reaction system in which the polymerization was initiated by acetic acid terminates the propagation; the rate of termination was proportional to the square of the concentration of the growing polymer chain.[4]

The present paper will describe a study which was carried out in order to elucidate the role of acetic anhydride in the termination reaction and in order to discuss, in detail, the mechanism of the elementary processes in the polymerization.

Experimental

Procedure and Materials. The formaldehyde monomer was prepared and the experimental procedure of polymerization was carried out in the manner described in a previous paper.[1] The monomer concentration in each polymerization experiment was 60 wt% in liquid carbon dioxide solution, while the loading density was 10 g/30 m*l*.

In order to remove the contained acetic acid, acetic anhydride was purified by using the reaction with carbodiimide previously described.[3] The acetic acid content in the acetic anhydride thus prepared was less than 0.1 wt%.

Commercially-available methyl acetate and methyl formate were purified by distillation before use. Isoamyl acetate was prepared by the reaction of isoamyl alcohol with acetic acid in the presence of concentrated sulfuric acid, and was purified by distilltion under reduced pressure. Methylene glycol methylether acetate was synthesized by the reaction of potassium acetate with monochloromethyl ether[5] and was purified by distillation (bp 117—118°C). Methyl-$^2H_3$-acetate was prepared by the reaction of pure tetradeuteromethanol with acetic acid in the presence of sulfuric acid, and it was purified by distillation.

Analytical Procedures. The deuterium content in the polymer was determined by quantifying the concentration of deuterium in hydrogen gas which had been prepared from the polymer as follows.[6] The polymer was placed in a combustion tube packed with palladium

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

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

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

4) H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *ibid.*, **41**, 1672 (1968).

5) L. Schreiner, *Ann.*, **197**, 8 (1879).

6) J. Graff and D. Rittenberg, *Anal. Chem.*, **24**, 878 (1952).

black and was decomposed by heating under a stream of oxygen; it was thus converted into water and carbon dioxide. The water produced was frozen out in a trap at −78°C. After evacuating the system to eliminate the carbon dioxide, the evaporated water was reduced to hydrogen gas by placing it in contact with metallic zinc heated at 400°C. The hydrogen, which was collected by the use of Toepler pump, was then analyzed by a mass spectrometer (Hitachi, Model RMU-5B).

The acetyl and hydroxyl groups of the polymer were quantified by means of a study of the infrared spectrum of the polymer film, as has already been described.[3]

Methyl acetate, acetic anhydride, and other substances were quantified by using a Perkin-Elmer Model 154D gas chromatograph equipped with a Golay column and a flame-ionization detector. The operating temperature was 80°C, and the flow rate of nitrogen as the carrier gas was 0.97 m*l*/min.

Results and Discussion

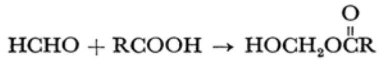
Endgroups of the Polymer Which Results from the Polymerization Initiated by An Acetic Acid Catalyst. When we studied the infrared spectrum of the polymer produced by the acetic-acid-initiated polymerization in a liquid carbon dioxide solution, an acetyl group was found in the polymer chain. Acetyl group in the polymer resulting from the polymerizations initiated by acetic acid both in the presence and in the absence of acetic anhydride, was quantified. The results are shown in Table 1. Here, the degree of acetylation is defined as the molar ratio of the acetyl group to the total endgroup, as has been described in a previous paper.[3] It was found that the degree of acetylation was independent of the polymer yield and the degree of polymerization in the polymerizations, both in the presence and in the absence of acetic anhydride. This fact indicates that the acetyl group in the polymer originates from acetic acid as the initiator.

Table 1. Acetyl group at chain end of the resulting polymer

Acetic anhydride mol%/monomer	Reaction time min	Polymer yield wt%	$\bar{P}_n$	Degree of acetylation mol%
5	10	15.1	780	18
5	30	28.9	1100	12
5	60	37.2	1280	14
—	10	17.1	970	25
—	30	54.4	1750	23
—	60	70.7	2200	22

acetic acid/monomer molar ratio, 1×10^{-3}; reaction temp., 30°C

Initiation by Methylene Glycol Methylether Acetate. It has been disclosed that carboxylic acid initiates the polymerization of formaldehyde in a liquid carbon dioxide solution.[1,2] The initiator of the present polymerization was assumed to be methylene glycol monocarboxylate, produced by the following reaction between the monomer and carboxylic acid;



$$\mathrm{HCHO + RCOOH \rightarrow HOCH_2O\overset{O}{\overset{\|}{C}}R} \qquad (1)$$

In order to verify this assumption, the catalytic activity of methylene glycol methylether acetate, $\mathrm{CH_3OCH_2O\overset{O}{\overset{\|}{C}}CH_3}$, which has a structure similar to that of the supposed initiator, was studied in the polymerization in the absence of acetic anhydride. The effects of isoamyl acetate and methyl formate on the polymerization were also investigated for the sake of comparison. The results are shown in Table 2. Only methylene glycol methylether acetate exhibited a catalytic effect.

Table 2. Effect of esters on the polymerization[a)]

Ester	Polymer yield wt%	$\bar{P}_n$	N_p[b)] mol/$l\times10^2$
EA[c)]	63.7	680	21
EA	42.6[d)]	3400	2.8
Isoamyl acetate	7.1	370	5.5
Methyl formate	5.4	400	3.0
none	5.8	410	3.1

a) ester/monomer molar ratio, 1×10^{-3}; reaction temp., 30°C; reaction time, 10 min.
b) number of moles of polymer chain, which is defined as a ratio of the polymer yield (mol)/the degree of polymerization.
c) methylene glycol methylether acetate
d) ester/monomer molar ratio, 1×10^{-4}

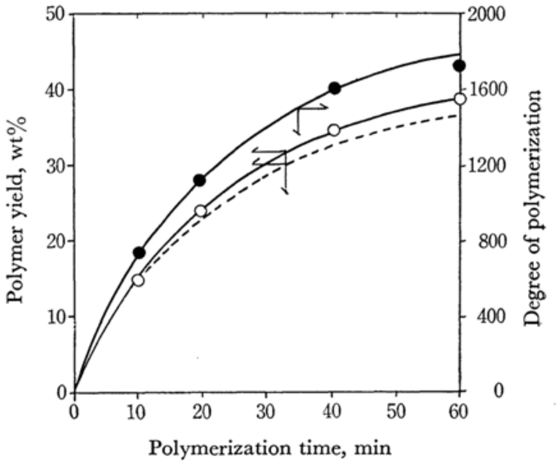


Fig. 1. Effect of methylene glycol methylether acetate on the polymerization in the presence of acetic anhydride; catalyst/monomer molar ratio, 1×10^{-3}; acetic anhydride/monomer molar ratio, 0.05; temp., 30°C; broken line, by acetic acid (quoted from the previous paper[2]).

Figure 1 shows the reaction time *versus* the polymer yield and the degree of polymerization in the polymerization which was initiated with methylene glycol methylether acetate in the presence of acetic anhydride. In the figure this polymerization is compared with the polymerization initiated by acetic acid. The results show that methylene glycol methylether acetate has almost the same catalytic activity as does acetic acid.

Formation of Methyl Acetate and the Influence of Methyl Acetate on the Polymerization. It has been already found that the termination reaction occurs only in the polymerization which is initiated with acetic acid in the presence of acetic anhydride, and that the rate of termination is proportional to the square of the concentration of the active initiating species.[4] On the other hand, the polymerization initiated with dichloroacetic acid is not terminated even in the presence of acetic anhydride.[4] Accordingly, it may be inferred that acetic acid plays an important part in the formation of a terminator. We also assumed that the methanol present in formaldehyde was another reactant in the reaction.

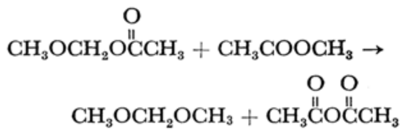
TABLE 3. EFFECT OF ACETIC ANHYDRIDE ON THE REACTION OF CARBOXYLIC ACIDS WITH METHANOL AT ROOM TEMPERATURE

Reactant, molar ratio				Reaction time	Yield of ester
acid		CH_3OH	$(CH_3CO)_2O$	min	mol%/acid
AA,	1	1	—	60	0 as MA
AA,	1	1	10	15	67 as MA
AA,	1	1	10	30	80 as MA
FA,	1	1	10	30	4.5 as MF
FA,	1	1	10	60	7.1 as MF
DCAA,	1	1	10	60	0 as MCA

AA, acetic acid; FA, formic acid; DCAA, dichloroacetic acid; MA, methyl acetate; MF, methyl formate; MCA, methyl dichloroacetate

In order to ascertain the above-mentioned assumptions, the influence of acetic anhydride on the esterification reaction of carboxylic acid and methanol was studied; the results are shown in Table 3. In the reaction of acetic acid with methanol, methyl acetate was not formed even after 60 min in the absence of acetic anhydride, whereas most of the acetic acid changed into methyl acetate within 30 min in the presence of acetic anhydride. The results indicate that the formation of methyl acetate is quite slow in a system in which acetic acid is absent. On the other hand, even in a reaction system in which acetic anhydride is present, formic and dichloroacetic acids, which have a stronger acidity than acetic acid, produced only a small quantity of esters. Based on the assumption that methyl acetate acts as a terminator, the above experimental results explain the extraordinary fact that the termination reaction occurred only in the polymerization initiated by acetic acid in the presence of acetic anhydride.

The reaction of methyl acetate with methylene glycol methylether acetate, which has a structure similar to that of the growing polymer chain, was studied in order to ascertain the termination reaction in which methyl acetate attacks the active chain end of the growing polymer. The results, shown in Table 4, indicate that methyl acetate reacted with methylene glycol methylether acetate to produce methylal and acetic anhydride in the following manner;



$$CH_3OCH_2O\overset{O}{\overset{\|}{C}}CH_3 + CH_3COOCH_3 \rightarrow CH_3OCH_2OCH_3 + CH_3\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{C}}CH_3 \qquad (2)$$

Methyl formate also produced methylal, but its yield was smaller than in the case of methyl acetate. These results support the assumption that methyl acetate terminates the propagation by means of reacting with the growing polymer chain to give a stable methoxy endgroup.

As is shown in Table 5, the addition of methyl acetate to the polymerization, which was carried out in the absence of acetic anhydride, caused the same extent of decrease in the rate of polymerization as in the polymerization which was carried out in the presence of acetic anhydride without methyl acetate, but it did not decrease the number

TABLE 4. REACTION OF ESTERS WITH METHYLENE GLYCOL METHYLETHER ACETATE AT ROOM TEMPERATURE

Reactant, molar ratio			Reaction time, min	Yield, mol%	
MGMA	Methyl acetate	Methyl formate		Methylal	Anhydride
1	1	—	30	4.5	0.21 as AH
1	1	—	100	6.2	0.65 as AH
1	1	—	200	7.8	0.68 as AH
1	—	1	180	2.1	? as MAH

MGMA, methylene glycol methylether acetate; AH, acetic anhydride; MAH, mixed anhydride of acetic and formic acids

Table 5. Effect of methyl acetate on the polymerization at 30°C

Additives, mol%/monomer			Reaction time, min	Conversion wt%	$\bar{P}_n$
CH_3COOH	$(CH_3CO)_2O$	CH_3COOCH_3			
0.1	5	—	30	25.3	980
0.1	5	—	60	36.6	1380
0.1	—	1.0	30	27.2	1260
0.1	—	1.0	60	38.0	1480
0.1	—	—	30	48.9	1730
0.1	—	—	60	53.1	1950

of moles in the resulting polymer chain. These facts lead to the conclusion that methyl acetate affects the polymerization as a terminator.

In order to confirm the terminating effect of methyl acetate, the origin of the endgroup of the polymer chain was studied by analyzing the deuterium content in the polymer which resulted from the polymerization terminated by methyl-$^2H_3$-acetate. When the amount of the deuterated methyl acetate was increased, the deuterium content increased, but both the polymer yield and the degree of polymerization decreased, as is shown in Table 6. Consequently, it was concluded that a part of the polymer chain was ended with the deuterated methyl group. This fact means that the carboxylate anion, which is a counter anion of the growing polymer chain, was replaced with a methoxy group of methyl acetate because of the termination by methyl acetate.

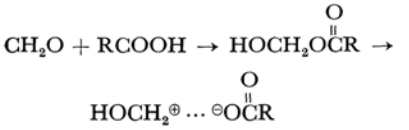
Table 6. Effect of methyl-D_3-acetate on the polymerization[a)] and deuterium content in the resulting polymer

CH_3COOCD_3 mol%	Conversion wt%	$\bar{P}_n$	D_2/H_2 atomic %
—	48.9	1730	0.015
0.9	9.7	640	0.034
7.2	5.3	470	0.091

a) acetic acid/monomer molar ratio, 1×10^{-3}; temperature, 30°C. time, 30 min.

Mechanism of Polymerization. It has already been disclosed in the previous works of the present series[1–3)] that formaldehyde is polymerized by a carboxylic acid initiator in liquid carbon dioxide solution to produce a high-molecular-weight polyoxymethylene and that the catalytic activity of carboxylic acid increases with an enhancement of the acidity of the acid used. The methanol and water present in the monomer have a chain transfer effect, but the rate of chain transfer is smaller than that of initiation or of propagation. In the polymerization which is initiated with acetic acid in the presence of acetic anhydride, acetic anhydride accelerates the formation of methyl acetate from acetic acid and methanol, and the methyl acetate thus formed attacks the active chain end of the growing polymer to terminate the propagation. Therefore, the following cationic mechanism of the polymerization in a liquid carbon dioxide solution may be presented:

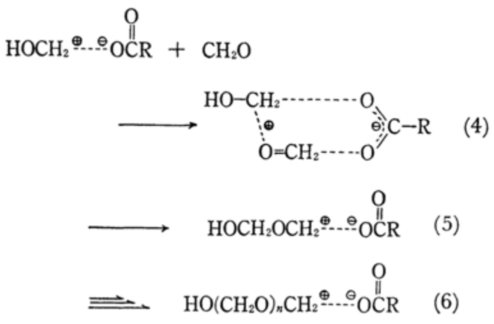
Initiation: In view of the fact that methylene glycol methylether acetate showed the same catalytic activity as acetic acid, it was considered that the intiator of polymerization was methylene glycol monocarboxylate, which was formed by the loose addition reaction of formaldehyde and carboxylic acid.



$$CH_2O + RCOOH \rightarrow HOCH_2O\overset{\overset{\displaystyle O}{\|}}{C}R \rightarrow HOCH_2{}^{\oplus}\cdots{}^{\ominus}O\overset{\overset{\displaystyle O}{\|}}{C}R \qquad (3)$$

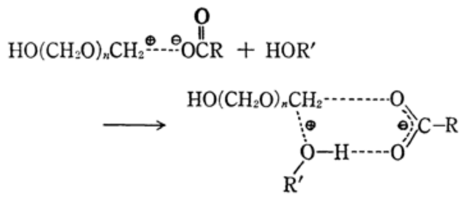
The ion pair formed by the dissociation of the addition compound is the initiating species. It has been reported that the rapid initiation takes place in this polymerization.[2,4)] Accordingly, the dissociation of methylene glycol monocarboxylate rapidly reaches equilibrium.

Propagation: The propagation proceeds by forming a co-ordinated compound from the monomer and the initiating species as follows:



The carboxylic acid with a larger dissociation constant gave the faster rate of propagation.[2,4)] Therefore, the stability of the counter anion affects the rate of propagation.

Chain Transfer: The chain transfer reaction by methanol or water is illustrated by the following scheme:



$$\mathrm{HO(CH_2O)_nCH_2^{\oplus}\cdots{}^{\ominus}O\overset{\overset{O}{\|}}{C}R + HOR'} \longrightarrow \quad (7)$$

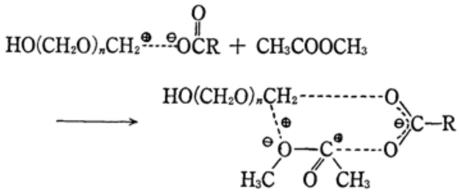
$$\longrightarrow \mathrm{HO(CH_2O)_nCH_2OR' + RCOOH} \quad (8)$$

Here, R′ is the hydrogen atom or the methyl group. It has been experimentally confirmed that the rate of chain transfer caused by water or methanol is comparatively small. This fact is probably attributable to the depression in the activity of the chain transfer agent because of the solvation of liquid carbon dioxide to water and methanol, which are basic. The retardation effect of carbon dioxide on the chain transfer may be the chief reason for the high-molecular-weight polymer being produced by the cationic polymerization process at room temperature, even though the crude monomer prepared by the thermal decomposition of α-polyoxymethylene, and not additionally purified, is used as the starting material.

Termination: As has been mentioned above, the esterification of methanol and acetic acid to produce methyl acetate is remarkably accelerated in the presence of acetic anhydride. Moreover, the addition of methyl acetate terminates the propagation, with the result that the polymer produced contains methoxy endgroup originating from methyl acetate. These facts lead to the following scheme for the termination, which, extraordinarily, takes place only in the polymerization initiated with acetic acid in the presence of acetic anhydride:

Summary. In concluding the present series, the following summary of the characteristics of the polymerization of formaldehyde in liquid carbon dioxide and the succeeding stabilization process may be given.

$$\mathrm{CH_3COOH + CH_3OH \xrightarrow{(CH_3CO)_2O} CH_3COOCH_3 + H_2O} \quad (9)$$



$$\mathrm{HO(CH_2O)_nCH_2^{\oplus}\cdots{}^{\ominus}O\overset{\overset{O}{\|}}{C}R + CH_3COOCH_3} \longrightarrow \quad (10)$$

$$\longrightarrow \mathrm{HO(CH_2O)_nCH_2OCH_3 + (CH_3CO)_2O} \quad (11)$$

(1) The not-extremely-purified monomer, which is prepared by the thermal decomposition of α-polyoxymethylene without additional purification, can be used as the starting material to produce a high-molecular-weight polymer.

(2) The polymerization initiated by carboxylic acid proceeds by a cationic mechanism.

(3) The polymerization belongs to a successive polymerization with rapid initiation. The chain transfer caused by water or methanol present in the monomer is slower than the other elementary reactions. The rate of propagation and the number of moles of the resulting polymer chain increase with an enhancement of the acidity of the acid used as a catalyst. The termination reaction is, in general, negligible except for the polymerization to be described below.

(4) Methyl acetate, which is formed from acetic acid and methanol because of the catalytic effect of acetic anhydride, terminates the propagation only in the polymerization initiated by acetic acid in the presence of acetic anhydride.

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