Kinetic Studies of the Solution Polymerization of Trioxane Catalyzed by $BF_3\cdot O(C_2H_5)_2$. I. The Effect of the Catalyst and the Water Concentration on the Rate of Polymerization

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It has been considered that, in the case of the cationic polymerization of cyclic oxygen compounds such as ethylene oxide, the chain carrier (active center) is a *t*-oxonium ion rather than a carbonium ion.[1-3] The reason for this is as follows: as the carbonium ion produced from cyclic monomers is generally unstable in comparison with that of vinyl monomer, the carbonium ion is transformed to the more stable oxonium ion by solvation at the ether group of the monomer whose concentration in the reaction system is very large. It is also inferred that, because of its stability, the oxonium ion is less reactive than the carbonium ion in vinyl polymerization.

Many patents on the cationic polymerization of trioxane (TO) have been presented, but only a few papers have been published on the kinetic study

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1) H. Meerwein, E. Battenberg, H. Glod, E. Pfeil and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939); K. Hamann, *Angew. Chem.*, **63**, 231 (1951).

2) J. B. Rose, *J. Chem. Soc.*, **1956**, 546.

3) D. J. Worsfold and A. M. Eastham, *J. Am. Chem. Soc.*, **79**, 897 (1957).

of the solution polymerization of TO catalyzed by cationic catalyst.[4-6] Recently, however, reports on the nature of the induction period of the solution polymerization[7] and on the kinetics of polymerization of molten TO[8-11] have been published, the results of the latter differing from those of solution polymerization. Kern et al.[4] suggested that the active center was a zwitter ion, unlike as in the usual polymerization mechanism of vinyl monomers.

In this series of reports we will try to establish the characteristics of the cationic polymerization of cyclic monomers. As such a monomer, trioxane was selected. Up to the present, none of the published papers on the cationic polymerization of TO has dealt with the quantitative relation between the polymerization condition and the rate of polymerization or the molecular weight of the resultant polymer. Therefore, we tried to mesaure the rate of polymerization and the molecular weight of the resultant polymer under various conditions, using $BF_3 \cdot O(C_2H_5)_2$ as the catalyst because it is most often used in cationic polymerizations. Even with the limitation of a single catalyst, the polymerizations in the different kinds of solvents were very dissimilar and it was difficult to infer the reaction mechanism.

In this first report the dependence of the rate of polymerization of the concentrations of the catalyst and the water will be discussed. In a non-polar solvent, a small amount of water acts as a co-catalyst. On the other hand, in a polar solvent water does not accelerate the polymerization reaction. It will also be found that the kinetic order of the catalyst concentration to the rate of polymerization varies with the kind of solvent in a complicated manner.

Experimental

Procedures.—The polymerization was initiated by adding the catalyst solution from a syringe through a rubber stopper into a flask containing the monomer solution. Here the effects of air were not considered, and the polymerization solution was not stirred. In the course of the polymerization the polymers produced were suspended in the medium (when the water concentration was small) or precipitated (when the water concentration was large), and at longer times the whole reaction system gelled. The polymerization was stopped by adding methanol containing a small amount of ammonia to the reaction system. The resultant polymer was washed by methanol, dried in a vacuum at 40°C, and weighed. The initial rate of polymerization in this paper means the maximum rate at a range of 5—15% conversion. The induction period was determined from the intersection between the time axis and the extrapolated part of the maximum inclination of a time-conversion curve.

The water concentration in the reaction system was measured by the Karl-Fischer method. The reproducibility of the induction period and the rate of polymerization was fairly good as long as the water concentration was controlled.

Materials. — Trioxane (Celanese Co.) was twice recrylstallized in methylene chloride and stored in a desiccator over potassium hydroxide in a cool and dark place. The water content in the refined monomer was less than 0.008 wt.% (by the Karl-Fischer method), and the content of methylene chloride was less than 0.3% (by the gas chromatographic method).

The solvents were washed, dried, and distilled by the usual method; then they were refluxed and distilled on CaH_2 just before use. The water concentration was controlled by adding distilled water to a polymerizing solution.

$BF_3 \cdot O(C_2H_5)_2$ was refined by distilling commercial material.

Results

The Effects of the Catalyst Concentration.—The effects of the catalyst concentration on the induction period and the rate of polymerization were studied at fixed concentrations of monomer and water.

Here benzene was used as the non-polar solvent, ethylene dichloride as the polar solvent, and nitrobenzene as the more polar solvent. As the polymerization in each solvent was characteristic and complicated, the time-conversion curves of each solvent are shown in the figures.

Figure 1 shows the time-conversion curve in benzene. The initial rate, as is shown in Fig. 2,

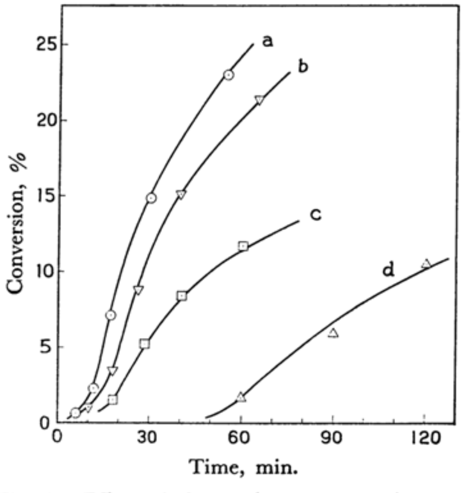

Fig. 1. Effect of the catalyst concentration on the rate of polymerization in benzene at 30°C. $[M]_0$; 3.3 mol./l., $[H_2O]$; 2.5 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; a(○): 30, b(▽): 20, c(□): 10 and d(△): 5.0 mmol./l.

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[4] W. Kern and V. Jaacks, *J. Polymer Sci.*, **48**, 399 (1960).

[5] V. Jaacks and W. Kern, *Makromol. Chem.*, **62**, 1 (1963).

[6] S. Okamura, T. Higashimura and M. Tomikawa, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 712 (1962).

[7] G. V. Rakova, L. M. Romanov and N. S. Enikolopyan, *Vysokomol. Soed.*, **6**, 2178 (1964).

[8] M. Kučara and E. Spousta, *J. Polymer Sci.*, **A2**, 3431 (1964).

[9] M. Kučera and E. Spousta, ibid., **A2**, 3443 (1964).

[10] M. Kučera and E. Spousta, *Makromol. Chem.*, **76**, 183 (1964).

[11] M. Kučera and E. Spousta, ibid., **76**, 190 (1964).

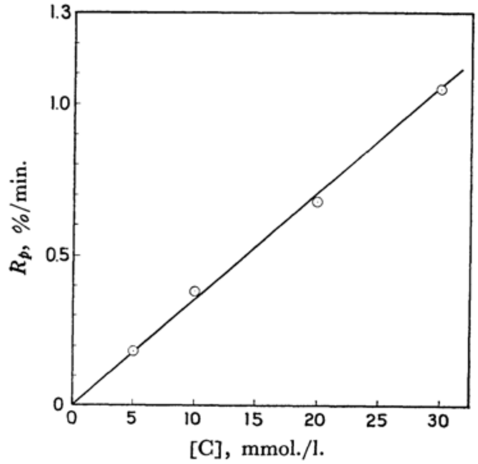

Fig. 2. Relationship between the catalyst concentration and the initial rate in benzene at 30°C. (Calculated from Fig. 1).

was proportional to the catalyst concentration. The decrease in the catalyst concentration increased the induction period. No simple relationship between the catalyst concentration and the induction period could be obtained.

Figure 3 shows the relation between the reaction time and conversion in the ethylene dichloride solvent. The initial rate was, as Fig. 4 shows, proportional to the square root of the catalyst concentration. No such phenomenon has been found in the cationic polymerization of vinyl monomers. When the catalyst concentration was more than the water concentration in the reaction system, the induction period of polymerization was less than 5 min. and was inversely proportional to the catalyst concentration, as is shown in Fig. 5.

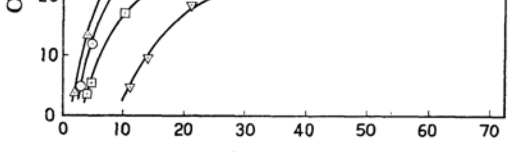

Fig. 3. Effect of the catalyst concentration on the rate of polymerization in ethylene dichloride at 30°C.

$[M]_0$; 3.3 mol./l, $[H_2O]$; 2.9 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; a(△): 20, b(○): 10, c(□): 5.0 and d(▽): 2.5 mmol./l.

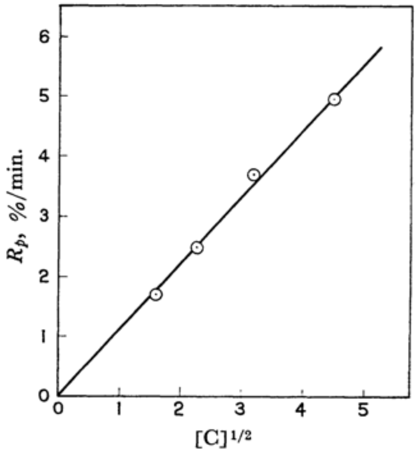

Fig. 4. Relationship between the catalyst concentration and the initial rate in ethylene dichloride at 30°C.
(Calculated from Fig. 3.)

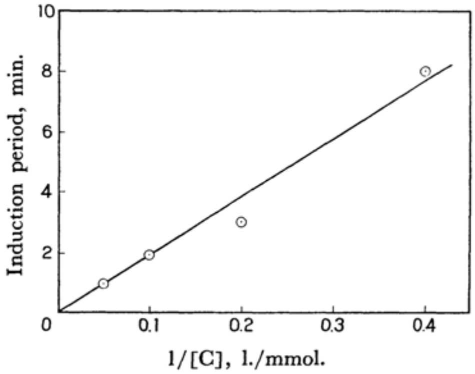

Fig. 5. Relationship between the reciprocal of the catalyst concentration and induction period in ethylene dichloride solution at 30°C.
(Calculated from Fig. 3.)

In the polymerization in nitrobenzene, the relation between the catalyst concentration and the polymerization rate was unusual. At a high monomer concentration, the polymerization reaction proceeded too fast for the rate of polymerization in nitrobenzene to be measured. Such an example is shown by the dotted line in Fig. 6. In order to ascertain the relation between the catalyst concentration and the polymerization rate, the polymerization was carried out at lower monomer concentrations. As Fig. 6 shows, the polymerization rate in nitrobenzene was almost independent of the catalyst concentration. The induction period tended to decrease with an increase in the catalyst concentration, being roughly proportional to the inverse square of the catalyst concentration.

The Effects of the Water Concentration.— At fixed concentrations of catalyst and monomer, the effects of the concentration of added water were

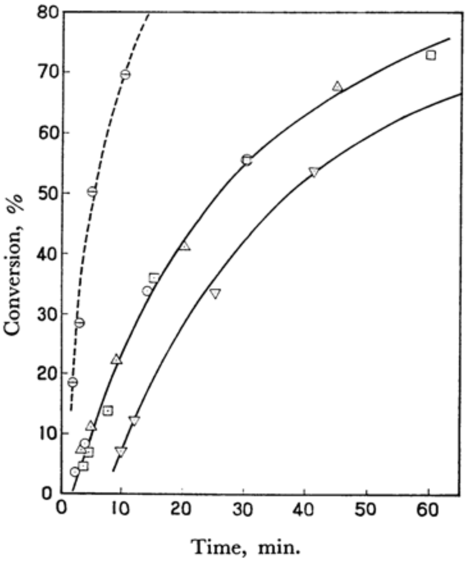

Fig. 6. Effect of the catalyst concentration on the rate of polymerization in nitrobezene at 30°C.
$[M]_0$; 1.1 mol./l., $[H_2O]$; 2.4 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; (○): 20, (△): 10, (□): 5 and (▽): 2.5 mmol./l. Dotted line (—); $[M]_0$; 3.3 mol./l., $[H_2O]$; 1.8 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 1.0 mmol./l.

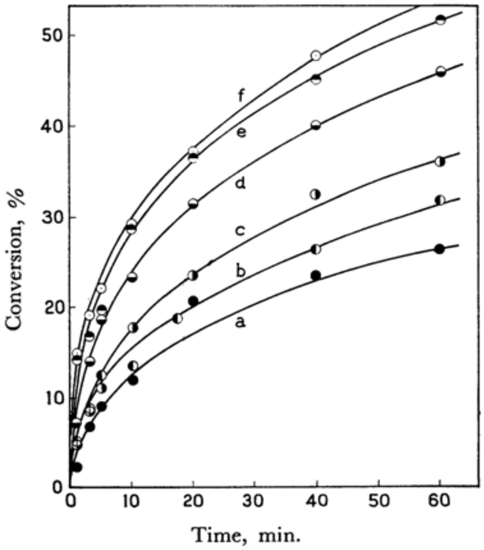

Fig. 7. Effect of the water concentration on the rate of polymerization in *n*-hexane at 30°C.
$[M]_0$; 0.37 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 9.4 mmol./l., $[H_2O]$; a(●): 0.4, b(◐): 0.9, c(◑): 1.1, d(◒): 1.7, e(◓): 2.2 and f(○): 3.4 mmol./l.

studied. Here, *n*-hexane was used as the non-polar solvent, since it could dissolve less water than benzene.

Figure 7 shows the effects of water in *n*-hexane. At this range of water concentration, the polymerization proceeded entirely without an induction period, and even a small amount of water accelerated the reaction. However, the rate of polymerization decreases if more water is added.

Similar phenomena were found for the polymerization in the benzene solvent. A small amount of water accelerated the polymerization, but the rate of polymerization decreased upon the addition of a larger amount of water.

In the ethylene dichloride solvent, as is shown in Fig. 8, the induction period increased almost proportionally to the water concentration; the initial rate of polymerization reached its maximum at $[H_2O]/[BF_3 \cdot O(C_2H_5)_2] \simeq 1/2$.

As can be seen in Fig. 8, the time-conversion curve consisted of the initial part, where the rate of polymerization was large, and the subsequent part, where the rate was small. It is interesting that the initial part lasts longer at higher water concentrations.

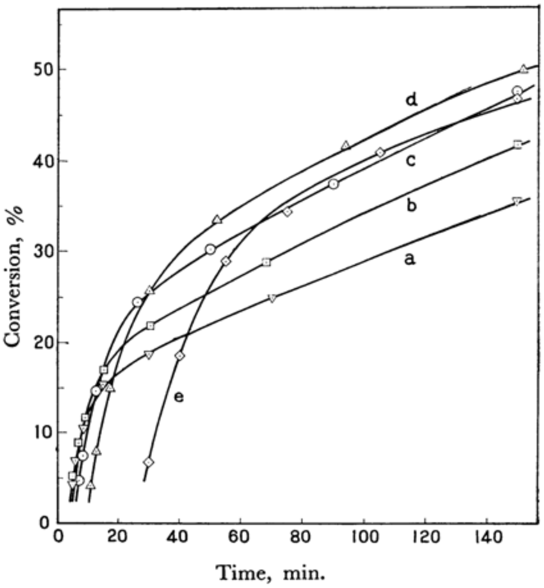

Fig. 8. Effect of the water concentration on the rate of polymerization in ethylene dichloride at 30°C.
$[M]_0$; 3.3mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 10mmol./l., $[H_2O]$; a(▽): 0.3, b(□): 1.6, c(○): 3.7, d(△): 5.9 and e(◇): 10.8 mmol./l.)

In nitrobenzene, where the water concentration was larger than that of the catalyst, the rate of polymerization was, as Fig. 9 shows, almost independent of the water concentration and only the induction period varied remarkably. On the other hand, where the water concentration was less than that of the catalyst, neither the induction period nor the rate of polymerization was affected, as is shown in Fig. 10.

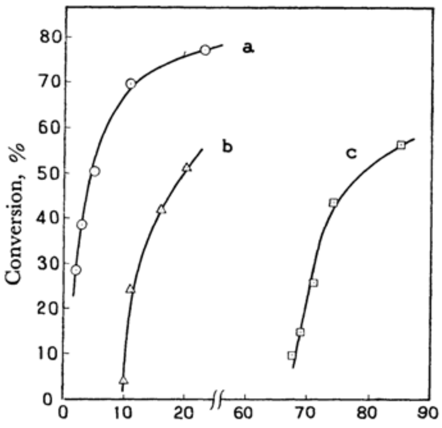

Fig. 9. Effect of the water concentration on the rate of polymerization in nitrobenzene at high concentrations of monomer and water at 30°C. $[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 1.0 mmol./l., $[H_2O]$; a(○): 1.8, b(△): 4.7 and c(□): 8.3 mmol./l.

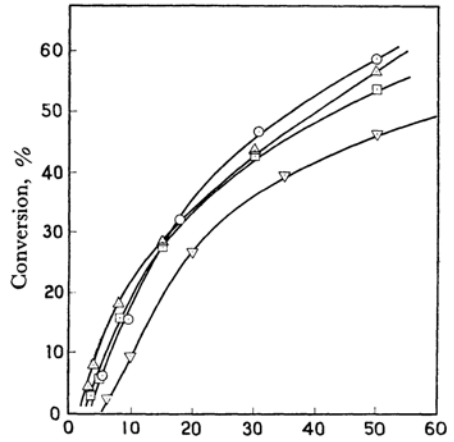

Fig. 10. Effect of the water concentration on the rate of polymerization in nitrobenzene at low concentrations of monomer and water at 30°C. $[M]_0$; 1.1 mol./l., $[BF_3 \cdot O(C_2H)_2]$; 10 mmol./l., $[H_2O]$; (△): 2.2, (□): 4.0, (○): 5.9 and (▽): 7.8 mmol./l.

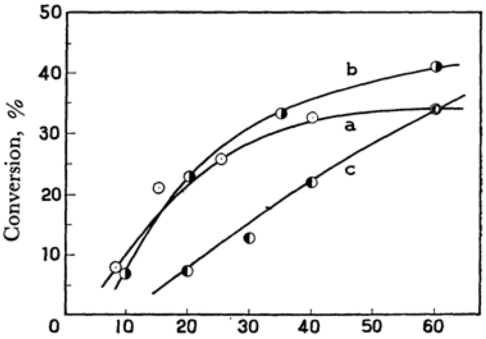

Fig. 11. Effect of the methanol concentration on the rate of polymerization in ethylene dichloride at 30°C. $[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 20 mmol./l., $[H_2O]$; 2.7 mmol./l., $[CH_3OH]$; a(○): 0, b(◑): 10 and c(◑): 20 mmol./l..

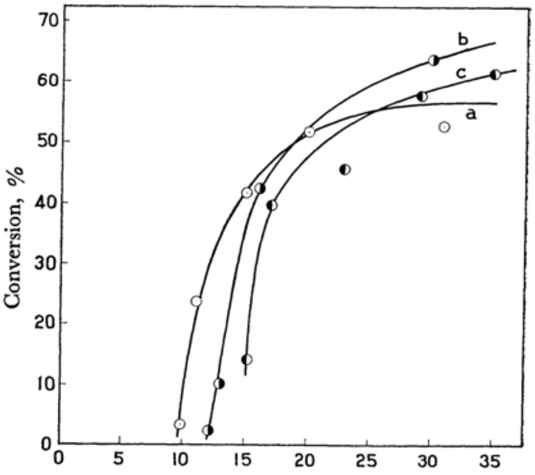

Fig. 12. Effect of the methanol concentration on the rate of polymerization in nitrobenzene at 30°C. $[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 1.0 mmol./l., $[H_2O]$; 4.7 mmol./l., $[CH_3OH]$; a(○): 0, b(◑): 2.5 and c(◐): 5.0 mmol./l.

The Effects of Added Methanol.—As has been shown above, a small amount of water did not affect the polymerization in nitrobenzene. In order to clarify this point, the effects of the addition of methanol in nitrobenzene and in ethylene dichloride were compared.

In ethylene dichloride, as Fig. 11 shows, methanol equivalent to half the amount of the catalyst accelerated the polymerization, while an amount of methanol equal to the catalyst decreased the rate of polymerization. The addition of methanol increased the induction period, as did the addition of water.

On the other hand, in nitrobenzene, as is shown in Fig. 12, even the addition of five times as much methanol to the catalyst tended to accelerate the rate, and its effect was very small, much as in the case of the addition of water.

Discussion

Table I summarizes the effects of the catalyst concentration on the rate of polymerization. In Fig. 13 the effect of the water concentration on the rate of polymerization is schematically shown.

TABLE I. SUMMARY OF THE EFFECT OF CATALYST CONCENTRATION OF THE RATE OF POLYMERIZATION (R_p) IN VARIOUS SOLVENTS AT 30°C ($[BF_3 \cdot O(C_2H_5)_2] > [H_2O]$)

Solvent	R_p
C_6H_6	$R_p \propto [C]^{1.0}$
$(CH_2Cl)_2$	$R_p \propto [C]^{0.5}$
$C_6H_5NO_2$	$R_p \propto [C]^{0}$

Figure 13 was obtained from the results of Figs. 7, 8 and 10. In a non-polar solvent such as *n*-hexane, the polymerization seems not to proceed when water is strictly excluded. Therefore, it may be concluded that water is necessary as a co-catalyst for the polymerization in a non-polar solvent. Even in this case, however, the rate of polymerization decreased when more water than a limited quantity was added. A similar tendency was found in the benzene solvent, also.

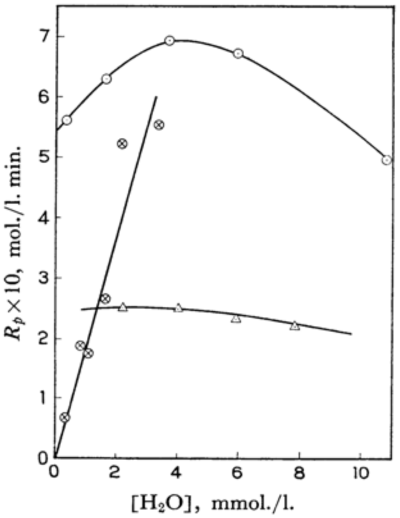

Fig. 13. Effect of the water concentration on the initial rate in various solvents at 30°C.
a(⊗); *n*-hexane solvent (from Fig. 7),
b(○); ethylene dichloride solvent (from Fig. 8),
c(△); nitrobenzene solvent (from Fig. 10)

On the other hand, in nitrobenzene the rate of polymerization was not affected by the water concentration within the range of our experiment, and water is not considered to act as a co-catalyst. In ethylene dichloride the rate of polymerization was slightly increased by a small amount of water, but the effect was very small and the polymerization seems to occur even without water.

In a polar solvent the catalyst $BF_3 \cdot O(C_2H_5)_2$, as is well known, dissociates according to Eq. 1, thus producing the ethyl cation.[12,13] The latter can initiate the polymerization of trioxane. On the contraty, in a non-polar solvent the catalyst $BF_3 \cdot O(C_2H_5)_2$ canont dissociate by itself according to Eq. 1; it needs water as a co-catalyst;

$$BF_3 \cdot O(C_2H_5)_2 \rightarrow BF_3 \cdot O(C_2H_5)^- \ (C_2H_5)^+ \quad (1)$$

$$BF_3 \cdot O(C_2H_5)_2 + H_2O \rightarrow (BF_3OH)^- \ H^+ + O(C_2H_5)_2 \quad (2)$$

as is shown in Eq. 2, to produce an ionizable species which has the ability to initiate the polymerization. In ethylene dichloride, it is inferred that the two processes (Eq. 1 and Eq. 2) took place simultaneously; and a behavior between that in *n*-hexane and that in nitrobenzene was observed. This consideration is supported by the thermodecomposition rate of the resultant polymer in each solvent, whose ends were not chemically treated and whose molecular weights (η_{sp}/c) were nearly equal. That is, the decomposition of the polymer obtained in *n*-hexane was 5 to 10 times faster than the rate of the polymer produced in nitrobenzene. The polymer obtained in ethylene dichloride had an intermediate value. The relationship between the co-catalytic effect of water and the thermodecomposition rate of the resultant polymer can be reasonably explained. The polymer produced in the presence of water as a co-catalyst, both of whose ends were –OH groups may be easily decomposed, while the polymer obtained by the initiation of the ethyl cation, one of whose ends was the ethoxyl radical, decomposes with more difficulty.

Kern et al.[4] have found that, in the cationic polymerization of trioxane by boron fluoride gas in methylene chloride, the rate of polymerization decreases with an increase in the concentration of added water; they have proposed that the polymerization of this system proceeds without a co-catalyst and that the active center is a zwitter ion. However, in the polymerization catalyzed by $BF_3 \cdot O(C_2H_5)_2$ the mechanism of the zwitter ion is considered to be impossible for the above-mentioned reasons; that is, a co-catalyst was necessary in the non-polar solvent, the thermodecomposition rate of polymers was affected by the kind of solvent, and the alkoxyl-end group was detected in the produced polymer.[14] On the other hand, it has been considered that water as a co-catalyst is necessary in the polymerization of trioxane by tin(IV) chloride.[5] The idea of the zwitter ion has also been rejected in the polymerization of 3, 3-bis-(chloromethyl)-oxetane by boron fluoride.[15] Therefore, it may be concluded that, under the conditions of our experiments, the polymerization reaction does not proceed through the zwitter ion. The above considerations also lead to the conclusion that the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ is initiated by the attack of the proton or the ethyl cation on trioxane.

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[12] J. D. Coombes and D. D. Eley, *J. Chem. Soc.*, **1957**, 3700.

[13] J. P. Kennedy, *J. Polymer Sci.*, **38**, 263 (1959).

[14] T. Miki, T. Higashimura and S. Okamura, unpublished data.

[15] I. Penczek and S. Penczek, *Makromol. Chem.*, **67**, 213 (1963).

This interpretation of the co-catalysis was confirmed by the addition of not only water but also methanol. As is shown in Fig. 11 and Fig. 12, a small amount of methanol accelerated the polymerization in ethylene dichloride but scarcely affected that in nitrobenzene.

In the case of the cationic polymerization of vinyl monomers, the rate of polymerization is generally proportional to the catalyst concentration. As Table I shows, in the polymerization of trioxane in a non-polar solvent such as benzene, the polymerization rate is proportional to the catalyst concentration. However, it is difficult to explain the experimental fact that the kinetic order of the catalyst concentration to the rate of polymerization is equal to 0.5 in ethylene dichloride and to zero in nitrobenzene. It has been found that, in the polymerization of trioxane catalyzed by tin(IV) chloride, the final yield in both polar and non-polar solvents is not dependent on the catalyst concentration when the concentration of the catalyst is larger than that of water.5) A similar result has been obtained in the polymerization of isobutene catalyzed by tin(IV) chloride16) and aluminum chloride17). In our experiment, however, $BF_3 \cdot O(C_2H_5)_2$ can cause the polymerization reaction of trioxane in nitrobenzene without water as a co-catalyst; consequently, it is impossible to explain the above-mentioned phenomena only in terms of the relation between the water and catalyst concentrations.

Rose2) has proposed, on the basis of the relation between the reaction rate and kinetic order of the concentration of the reagents, that, in the polymerization of cycloxabutane, the active center is an oxonium ion. However, in our experiment the relationship between the rate of polymerization and the catalyst concentration was very complicated; the nature of the active center can not be discussed on the basis of our kinetic results.

Summary

In the solution polymerization of TO catalyzed by $BF_3 \cdot O(C_2H_5)_2$, water acted as a co-catalyst in *n*-hexane, a non-polar solvent; in ethylene dichloride, a polar solvent, water slightly accelerated the rate of polymerization, and in nitrobenzene, a more polar solvent, water did not affect the rate at all. The kinetic order of the catalyst concentration to the polymerization rate was 1.0 in benzene, 0.5 in ethylene dichloride, and zero in nitrobenzene. The induction period was very short when water was excluded as much as possible, but it increased with an increase in the water concentration and with a decrease in the catalyst concentration.

On the basis of these results, it may be concluded that the polymerization of TO by $BF_3 \cdot O(C_2H_5)_2$ is initiated by the attack of the proton or the ethyl cation on the monomer.

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16) R. G. W. Norrish and K. E. Russell, *Trans. Faraday Soc.*, **48**, 91 (1952).

17) J. H. Beard, P. H. Plasch and P. P. Rutherford, *J. Chem. Soc.*, **1964**, 2566.