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Kinetic Studies of the Solution Polymerization of Trioxane Catalyzed by $BF_3 \cdot O(C_2H_5)_2$. VI. The Catalytic Mechanism of Boron Trifluoride Coordination Complexes in Ethylene Dichloride

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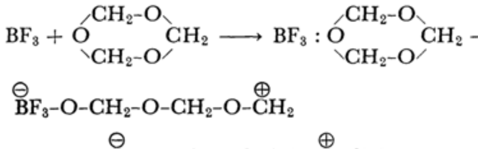
The initiation mechanism in the cationic polymerization of trioxane by the BF_3 coordination complex catalyst was studied in ethylene dichloride at 30°C. The coordination complexes of BF_3 with diethyl ether (Et_2O), ethyl alcohol (EtOH) and acetic acid (AcOH) were used as catalysts. Under similar conditions, the rates of polymerization decreased in the order: $BF_3 \cdot EtOH > BF_3 \cdot AcOH > BF_3 \cdot Et_2O$, whereas the molecular weights of the polymers decreased in the order: $BF_3 \cdot Et_2O > BF_3 \cdot EtOH \simeq BF_3 \cdot AcOH$. The molecular weight of the polymer formed was unaffected by the addition of the same compound as the donor molecule in the BF_3 coordination complex. However, on the addition of EtOH to the polymerization system catalyzed by $BF_3 \cdot Et_2O$, the rate of polymerization increased and the molecular weight of the polymer decreased. On the other hand, the addition of Et_2O to the system catalyzed by $BF_3 \cdot EtOH$ decreased the rate of polymerization and increased the molecular weight of the polymer formed. The order of catalytic reactivity and the effect of the additive support the idea that the initiation reaction is not an interaction of the BF_3 molecule with trioxane but an addition of the cation produced from the BF_3 coordination complex to the trioxane molecule.

It has been reported that the polymerization of trioxane catalyzed by boron trifluoride (BF_3) is initiated by a direct interaction of BF_3 with trioxane without a cocatalyst such as water, and that it proceeds through a zwitter-ion or by a free-ion mechanism,1) as is shown in Eq. 1. According to this scheme, the true initiating species of trioxane polymerization catalyzed by BF_3 coordination complexes may be the BF_3 derived from the BF_3 coordination complex molecule, rather than the actual BF_3 coordination complex molecule itself. On the other hand, as reported in a previous paper,2) it has been found that water is necessary as a cocatalyst to initiate the polymerization by $BF_3 \cdot O(C_2H_5)_2$ in *n*-hexane. This fact suggests that an initiation mechanism through the formation of a BF_3-trioxane coordination complex does not apply in *n*-hexane.


(1)

In this paper, the catalytic mechanism involving BF_3 coordination complexes in the solution polymerization of trioxane will be discussed. In addition, the effect of some additives on the polymerization has been investigated in order to clarify the initiation mechanism. As a result, it is concluded that the BF_3 coordination complex itself participates in the initiation of trioxane polymerization; that is, trioxane is attacked by a cationic species produced directly by the ionization of the BF_3 coordination complex.

Experimental

The procedures of the polymerization, the measurement of the viscosity number, and the method of purifying trioxane, ethylene dichloride and $BF_3 \cdot O(C_2H_5)_2$ were the same as those described in previous papers.2,3) The coordination complexes of BF_3 with two molecules of ethyl alcohol and acetic acid were purified by distilling, in a vacuum, commercial materials (b. p., $BF_3(C_2H_5OH)_2$: 77.5—78°C/11—12 mmHg, $BF_3(CH_3CO_2H)_2$: 78—79°C/18—22 mmHg). The density of these catalysts was measured approximately by the usual piconometer technique at 20°C; $BF_3(C_2H_5OH)_2$: 1.18_1 (lit.,4) 1.164, $BF_3 \cdot C_2H_5OH$; 1.272), $BF_3(CH_3CO_2H)_2$: 1.37_6 (lit.,4) 1.342, $BF_3 \cdot CH_3CO_2H$; 1.496). Although precise measurement was very difficult due to the hygroscopic character of these compounds, these values show that these catalysts can approximately be treated

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1) V. Jaacks and W. Kern, *J. Polymer Sci.*, **48**, 391 (1962).

2) T. Higashimura, T. Miki and S. Okamura, This Bulletin, **38**, 2067 (1965).

3) T. Higashimura, T. Miki and S. Okamura, ibid., **39**, 25 (1966).

4) N. N. Greenwood, *Quant. Rev.*, **8**, 1 (1954); G. A. Olah, D. R. Martin and J. M. Canon, "Friedel-Crafts and Related Reactions," Vol. I, Ed by G. A. Olah, Interscience Publishers, John Wiley & Sons, Inc., New York (1963), Chap. 4, 6, 8.

as the coordination complexes of BF_3 with two donor molecules.

Results

The Effect of the Nature of the Donor Molecule in the BF_3 Coordination Complex Catalyst on the Polymerization Reaction.—Ethyl ether (Et_2O), ethyl alcohol (EtOH) and acetic acid (AcOH) were selected as donor molecules, and the coordination complexes of BF_3 with these compounds were used as catalysts. It was found by preliminary experiments that, in the case of the $BF_3(EtOH)_2$ and $BF_3(AcOH)_2$ catalysts, the order of reaction with respect to the catalyst was smaller than one, and that the molecular weights of the polymers formed decreased with an increase in the catalyst concentration, as was shown in the case of the $BF_3{\cdot}Et_2O$ catalyst.[2,3)]

Figure 1 shows the effect of the donor molecule

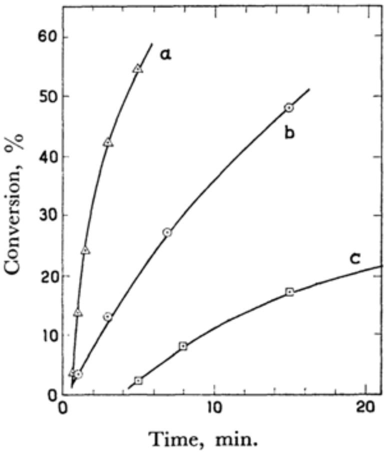

Fig. 1. Effect of the kind of the donor molecule in the BF_3 coordination complex catalyst on the rate of polymerization in ethylene dichloride at 30°C.
($[M]_0$; 3.3 mole/l., $[H_2O]$; 2—3 mmole/l., Catalyst (mmole/l.); a(△): $BF_3(EtOH)_2$ (10.0), b(○): $BF_3(AcOH)_2$ (9.8) and c(□): $BF_3{\cdot}Et_2O$ (10.0))

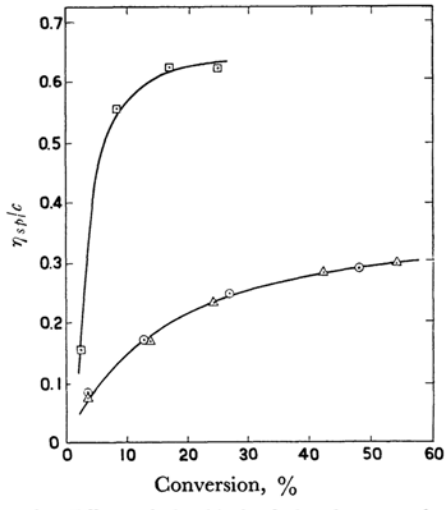

Fig. 2. Effect of the kind of the donor molecule in the BF_3 coordination complex catalyst on the molecular weight of the polymer formed in ethylene dichloride at 30°C.
($[M]_0$; 3.3 mole/l., $[H_2O]$; 2—3 mmole/l., Catalyst (mmole/l.); a(△): $BF_3(EtOH)_2$ (10.0), b(○): $BF_3(AcOH)_2$ (9.8) and c(□): $BF_3{\cdot}Et_2O$ (10.0))

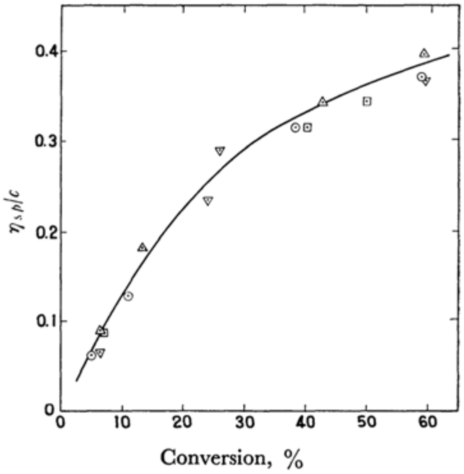

Fig. 3. Effect of the concentration of added EtOH on the molecular weight of the polymer formed by $BF_3(EtOH)_2$ in ethylene dichloride at 30°C.
($[M]_0$; 3.3 mole/l., $[H_2O]$; 3 mmole/l., $[BF_3(EtOH)_2]$; 10.0 mmole/l., [EtOH]; (△): 0, (○): 2.2, (▽): 4.4 and (□): 8.8 mmole/l.)

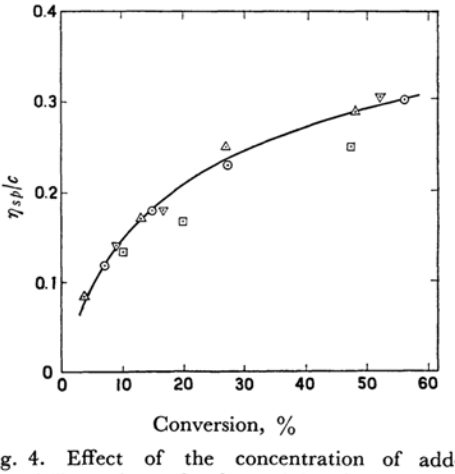

Fig. 4. Effect of the concentration of added AcOH on the molecular weight of the polymer formed by $BF_3(AcOH)_2$ in ethylene dichloride at 30°C.
($[M]_0$; 3.3 mole/l., $[H_2O]$; 3 mmole/l., $[BF_3(AcOH)_2]$; 9.8 mmole/l., [AcOH]; (△): 0, (○): 2.5, (▽): 4.9 and (□): 9.9 mmole/l.)

on the polymerization rate, while Fig. 2 shows its effect on the molecular weight of the polymer formed under similar conditions. In all cases, the molecular weights of the polymer formed increased with an increase in the polymer yield. This fact may be explained in terms of a larger initiation rate than the propagation rate and no termination reaction, as has been shown in a previous paper³⁾ and in another report.⁵⁾

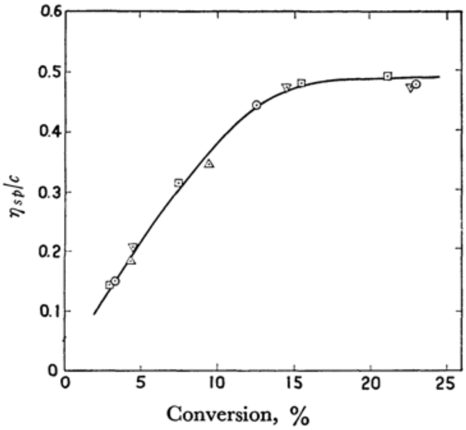

Fig. 5. Effect of the concentration of added Et_2O on the molecular weight of the polymer formed by $BF_3\cdot Et_2O$ in ethylene dichloride at 30°C. ($[M]_0$; 3.3 mole/l., $[H_2O]$; 7 mmole/l., $[BF_3\cdot Et_2O]$; 10 mmole/l., $[Et_2O]$; (○): 0, (△): 1.9, (□): 5.0 and (▽): 10 mmole/l.)

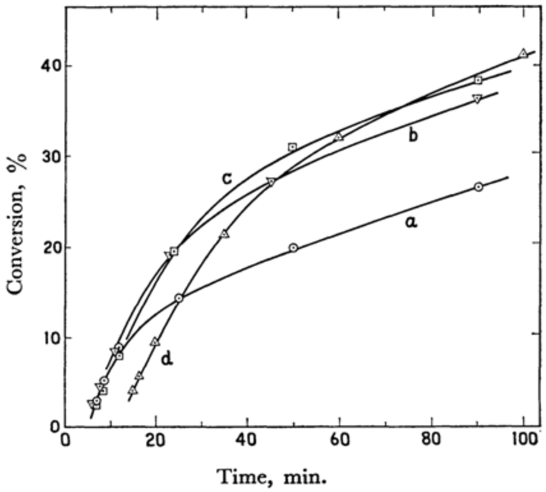

Fig. 6. Effect of the concentration of added EtOH on the rate of polymerization catalyzed by $BF_3\cdot Et_2O$ in ethylene dichloride at 30°C. ($[M]_0$; 3.3 mole/l., $[H_2O]$; 2 mmole/l., $[BF_3\cdot Et_2O]$; 10.0 mmole/l., [EtOH]; a(○): 0, b(▽): 2.5, c(□): 4.9 and d(△): 9.9 mmole/l.)

As is clear from Fig. 1, the polymerization rates decrease in the order:

$$BF_3(EtOH)_2 > BF_3(AcOH)_2 > BF_3\cdot Et_2O.$$

As may be seen in Fig. 2, the molecular weights of the polymers obtained at a fixed polymer yield decrease in the order:

$$BF_3\cdot Et_2O > BF_3(EtOH)_2 \simeq BF_3(AcOH)_2.$$

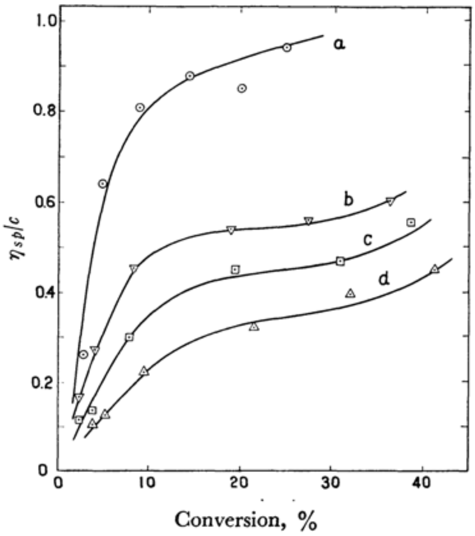

Fig. 7. Effect of the concentration of added EtOH on the molecular weight of the polymer formed by $BF_3\cdot Et_2O$ in ethylene dichloride at 30°C. ($[M]_0$; 3.3 mole/l., $[H_2O]$; 2 mmole/l., $[BF_3\cdot Et_2O]$; 10.0 mmole/l., [EtOH]; a(○): 0, b(▽): 2.5, c(□): 4.9 and d(△): 9.9 mole/l.)

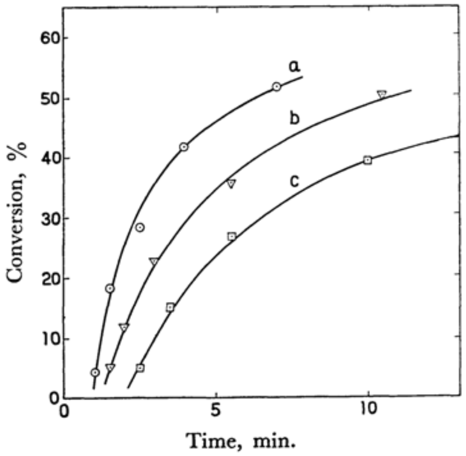

Fig. 8. Effect of the concentration of added Et_2O on the rate of polymerization catalyzed by $BF_3(EtOH)_2$ in ethylene dichloride at 30°C. ($[M]_0$; 3.3 mole/l., $[H_2O]$; 1.8 mmole/l., $BF_3(EtOH)_2$; 7.3 mmole/l., $[Et_2O]$; a(○): 0, b(▽): 2.0, and c(□): 5.0 mmole/l.)

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5) T. Kagiya, M. Hatta and K. Fukui, *Chem. High Polymers, Japan,* **20**, 730, 737 (1963).

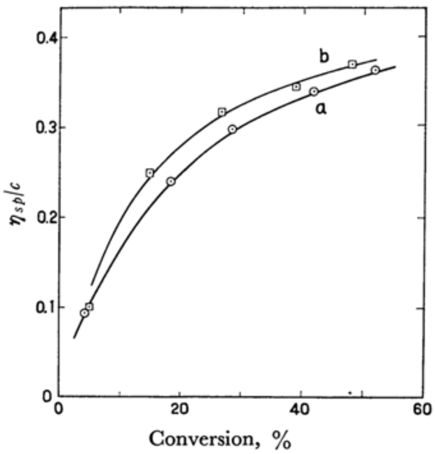


Fig. 9. Effect of the concentration of added Et_2O on the molecular weight of the polymer formed by $BF_3(EtOH)_2$ in ethylene dichloride at 30°C.
($[M]_0$; 3.3 mole/l., $[H_2O]$; 1.8 mmole/l., $[BF_3(EtOH)_2]$; 7.3 mmole/l., $[Et_2O]$; a(○): 0 and b(□): 5.0 mmole/l.)

The Effect of Additives on the Polymerization.—Figures 3, 4, and 5 show the effect of the additive (X), when this is the same as the donor molecule in the $BF_3{\cdot}X$ coordination complex, on the molecular weight of the polymer formed by $BF_3{\cdot}X$. The X is EtOH in Fig. 3, AcOH in Fig. 4, and Et_2O in Fig. 5.

Figure 6 shows the effect of added EtOH on the rate of polymerization catalyzed by $BF_3{\cdot}Et_2O$, while Fig. 7 shows its effect on the molecular weight of the polymer formed by $BF_3{\cdot}Et_2O$.

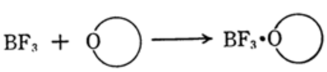
Figure 8 shows the effect of added Et_2O on the rate of polymerization catalyzed by $BF_3(EtOH)_2$, while Fig. 9 shows its effect on the molecular weight of the polymer formed in the reaction.

Discussion

In vinyl polymerization catalyzed by Lewis acids, there are many cases in which a cocatalyst is necessary.⁶⁾ In the trioxane polymerization catalyzed by BF_3, however, no necessity for a cocatalyst has been suggested.¹⁾ In this case, the boron trifluoride - trioxane coordination complex should be formed if the polymerization is to occur according to Eq. 1. Then the ring of this complex opens and the polymerization proceeds either through a free-ion or zwitter-ion mechanism.

According to this suggestion, the following mechanisms may be proposed for the trioxane polymerization catalyzed by BF_3 coordination complexes, where X is a donor molecule:

$$BF_3{\cdot}X \rightleftharpoons BF_3 + X \tag{2}$$


(2′)

or


(3)

In either case, the rate of polymerization will be controlled by the concentration of the BF_3-trioxane coordination complex formed. Consequently, the variation in the concentration of this complex with the character of the donor molecule will now be discussed.

According to Eqs. 2 and 3, it may be considered that the BF_3-trioxane coordination complex is more easily produced when the strength of the BF_3-donor bond is weaker. The BF_3-donor bond energy is considered to be larger when the ionization potential of the donor molecule is small.⁷⁾ The ionization potential decreases in the order⁸⁾:

$$AcOH > EtOH > Et_2O.$$

Therefore, the BF_3-donor bond energy will decrease in the order:

$$BF_3{\cdot}Et_2O > BF_3(EtOH)_2 > BF_3(AcOH)_2.$$

The BF_3-donor bond energy of the 1 : 2 complexes used in this paper is considered to be in the same order as that of the corresponding 1 : 1 complexes, since the 1 : 2 complexes are formed by an additional donor-acceptor interaction of the second molecule, not with BF_3, but with the proton of the donor molecule in the corresponding 1 : 1 complex.⁴⁾ Therefore, it might be expected that the rates of polymerization catalyzed by these complexes decrease in the order:

$$BF_3(AcOH)_2 > BF_3(EtOH)_2 > BF_3{\cdot}Et_2O.$$

This order, however, does not agree with the experimental results.

According to Eq. 2 or 3 the structure of the growing chain end is considered to be always the same, independent of the kind of donor molecule in the BF_3 coordination complex. As the rate of polymerization catalyzed by $BF_3(EtOH)_2$ is, as Fig. 1 shows, larger than that catalyzed by BF_3-$(AcOH)_2$, the concentration of the BF_3-trioxane coordination complex formed by the $BF_3(EtOH)_2$ catalyst is considered to be larger than that formed by the $BF_3(AcOH)_2$ catalyst. Therefore, the molecular weight of the polymer formed by the former ought to be smaller than that formed by

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6) A. G. Evans, D. Holden, P. H. Plesch, M. Polanyi, H. A. Skinner and M. A. Weinberger, *Nature,* **158,** 94 (1946); and their studies of this series. "The Chemistry of Cationic Polymerizations," Ed. by P. H. Plesch, Pergamon Press, London (1963).

7) H. A. Skinner "Cationic Polymerization and Related Complexes", Ed. by P. H. Plesch, W. Heffer & Sons Ltd., Cambridge (1953), p. 28.

8) J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.,* **20,** 1021 (1952).

the latter, at the same polymer yield. This speculation does not agree with the experimental result, either.

However, for the purposes of the above speculation, it is necessary to assume that the free AcOH or EtOH resulting from the exchange reaction does not act as a transfer agent. In fact, as is shown in Figs. 3 and 4, AcOH and EtOH do not act as transfer agents to any significant degree when these additives are employed at lower concentrations than that of the corresponding catalyst.

In view of the above-mentioned facts, the mechanism of the initiation reaction for trioxane polymerization according to Eqs. 2 and 3 must be rejected. Indeed, the exchange reaction according to Eqs. 2 and 3 might occur to produce the BF_3-trioxane coordination complex, but this complex does not seem to play an essential part in the polymerization reaction.

Another mechanism for the initiation reaction of trioxane polymerization must also be taken into account. The vinyl polymerization catalyzed by $BF_3 \cdot X$ coordination complexes is considered to be initiated by the attack of the alkyl cation, resulting from an ionization of the $BF_3 \cdot X$ coordination complex, on the monomer, and to proceed through an ion-pair mechanism, as is shown in Eq. 4:⁹⁾

$$BF_3 \cdot X \rightleftarrows BF_3Y^{\ominus}R^{\oplus}$$

$$BF_3Y^{\ominus}R^{\oplus} + M \longrightarrow R\text{-}M^{\oplus} \cdots BF_3Y^{\ominus} \qquad (4)$$

$R^{\oplus}$: a proton or alkyl cation

We believe that this idea may also be adopted in the trioxane polymerization on the grounds of the following considerations.

The rate of polymerization catalyzed by $BF_3(EtOH)_2$ is, as Fig. 1 shows, larger than that catalyzed by $BF_3(AcOH)_2$. However, the molecular weights of the polymers obtained at the same polymer yield in both systems are nearly equal. The latter fact means that the numbers of the polymer molecules produced in both polymerization systems under similar conditions are equal; that is, the concentrations of the initiating species, or of the growing chains, are equal in both systems. This speculation is supported by the fact that the addition of a small amount of an additive (X) to the $BF_3 \cdot X_2$ catalyst does not affect the molecular weight of the resultant polymer. As the initiating species is a proton solvated by the corresponding donor molecule in both cases, the difference in the polymerization rate between both catalysts can probably be ascribed to that of the rate of propagation reaction. This implies that there is a difference in the structure of the growing chain end or in the gegen ion between the two polymerization systems, as is suggested in the usual vinyl polymerization. Therefore, it may be concluded that, in the trioxane polymerization, the $BF_3 \cdot X$ coordination complex is partially ionized in a polar solvent, and that the resulting cation attacks the monomer.

The rate of polymerization catalyzed by $BF_3(EtOH)_2$ is, as is shown in Fig. 1, much larger than catalyzed by $BF_3 \cdot Et_2O$. The initiating species is considered to be a proton solvated by ethyl alcohol (or an ethoxonium ion) in the $BF_3(EtOH)_2$ catalyst, and an ethyl cation in $BF_3 \cdot Et_2O$, while the gegen ion is considered to be the same in both catalysts according to Eq. 4. This supposition has been confirmed in the polymerization of styrene catalyzed by these similar catalysts.¹⁰⁾ Therefore, the differences between the two catalysts in the rate of polymerization and in the molecular weight of the polymers may be due to the initiation step. As the degree of ionic dissociation of molten $BF_3(EtOH)_2$ is about sixty times larger than that of molten $BF_3 \cdot Et_2O$,¹¹⁾ it may be anticipated that the former will also be ionized more easily than the latter in ethylene dichloride. Therefore, the larger rate of polymerization and the lower molecular weight of the polymer in $BF_3(EtOH)_2$ than in $BF_3 \cdot Et_2O$ are probably caused by the higher concentration of the initiating species in $BF_3(EtOH)_2$ than in $BF_3 \cdot Et_2O$. Also, the difference in the rate of polymerization between the two catalysts may be partly ascribed to a difference in the reactivity of the initiating species; that is, to the difference in reactivity between a proton (solvated by ethyl alcohol) and an ethyl cation.

Thus, the mechanism for the function of the BF_3 coordination complex according to Eq. 4 can explain the experimental results. As has been shown in a previous paper,²⁾ $BF_3 \cdot Et_2O$ cannot initiate the polymerization of trioxane without a cocatalyst such as water in a non-polar solvent. It may probably be concluded that, on the basis of such a mechanism, the polymerization of trioxane catalyzed by BF_3 does not occur without a cocatalyst.

In the trioxane polymerization catalyzed by $BF_3 \cdot Et_2O$, the polymer yield in a given period of time increased upon the addition of a small amount of water in ethylene dichloride.²⁾ In this work the effect of EtOH on the trioxane polymerization catalyzed by $BF_3 \cdot Et_2O$ was also studied. As is clear from Figs. 6 and 7, the addition of EtOH increases the polymer yield in a given period of time and decreases the molecular weight of the polymer formed. This result indicates that, besides the occurrence of the usual transfer reaction of a growing chain to EtOH, it can be supposed that the exchange reaction, as is shown in Eq. 5,

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9) e. g., J. P. Kennedy, *J. Polymer Sci.*, **38**, 263 (1959).

10) S. Aoki and M. Imoto, *Makromol. Chem.*, **65**, 243 (1963).

11) N. N. Greenwood and R. L. Martin, *J. Chem. Soc.*, **1953**, 1427 (1953).

takes place upon the addition of $BF_3 \cdot Et_2O$ to a monomer solution containing a small amount of EtOH. Such an exchange reaction with respect to BF_3 has been observed by NMR spectroscopy.[12]

$$BF_3 \cdot Et_2O + EtOH \rightleftharpoons BF_3 \cdot EtOH (\text{or } BF_3(EtOH)_2) + Et_2O \quad (5)$$

The increase in the polymerization rate upon the addition of a small amount of EtOH is probably due to the simultaneous occurrence of the polymerization catalyzed by $BF_3(EtOH)_2$, which has a much larger ability to produce the initiating species than does $BF_3 \cdot Et_2O$.

According to this speculation, the addition of Et_2O to the polymerization system catalyzed by $BF_3(EtOH)_2$ ought to lead to the following reaction (Eq. 6); the polymerization may then proceed through two kinds of catalyst.

$$BF_3(EtOH)_2 + Et_2O \rightleftharpoons BF_3 \cdot Et_2O + 2EtOH \quad (6)$$

As the concentration of $BF_3(EtOH)_2$ decreases upon the equilibrium of Eq. 6, and as the $BF_3 \cdot Et_2O$ catalyst has only a small tendency to form the initiating species, the total concentration of the initiating species will decrease in comparison with the case without the additive. Consequently, the rate of polymerization will decrease and the molecular weight of the polymer will increase, since the molecular weight of the formed polymer increases with the decrease in the catalyst concentration, as has been reported in a previous paper.[3] The experimental results support this speculation, as is shown in Figs. 8 and 9. That is, the rate of polymerization decreases and the molecular weight of the polymer increases upon the addition of Et_2O to the trioxane-$BF_3(EtOH)_2$ system. The increase in the molecular weight was not caused by an experimental error in the viscosity measurement. In fact, the molecular weight of the polymer was decreased by the addition of AcOH instead of Et_2O under the same conditions.[13]

If the additive acts only as a transfer agent, it should only decrease the molecular weight of the polymer formed. However, in the present paper, the additive caused an increase in the polymerization rate or in the molecular weight of the polymer formed, depending on the particular system examined. These facts mean that the additive participates in the initiation of the polymerization reaction. Therefore, it may concluded that the polymerization reaction of trioxane occurs according to Eq. 4, not according to Eqs. 2 and 3.

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[12] R. A. Craig and R. E. Richards, *Trans. Faraday Soc.*, **59**, 1962 (1963); A. C. Rutenberg, A. A. Palko and J. S. Drury, *J. Am. Chem. Soc.*, **85**, 2702 (1963).

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