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Kinetic Studies of the Solution Polymerization of Trioxane Catalyzed by $BF_3 \cdot O(C_2H_5)_2$. IV. The Change in the Formaldehyde Concentration during Polymerization

By Tetsuro MIKI, Toshinobu HIGASHIMURA and Seizo OKAMURA

Department of Polymer Chemistry, Kyoto University, Sakyo-ku, Kyoto

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In the solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ and boron fluoride, the dependence of the yield of CH_2O produced in the induction period on the polymerization conditions has been studied at 30°C. In the case of the $BF_3 \cdot O(C_2H_5)_2$ catalyst, the formation of CH_2O has been recognized in *n*-hexane just after the addition of the catalyst while no induction period of the polymerization was seen. In polar solvents, both the formation of CH_2O and the polymerization were retarded as the water concentration increased. In these systems the concentration of the CH_2O formed changed with time, and no equilibrium or stationary concentration was recognized. In the case of the boron fluoride catalyst, an increase in the water concentration remarkably increased the induction period, also. For either catalyst the induction period was not decreased by the addition of CH_2O to the polymerization system in advance of the catalyst addition. Therefore, it has been deduced that, in the polymerization system catalyzed by $BF_3 \cdot O(C_2H_5)_2$, the polymerization and depolymerization reaction took place simultaneously and that the induction period was caused by water, which inhibits the formation of high polymers.

In the solution polymerization of trioxane by an acidic catalyst, an induction period and the formation of formaldehyde (CH_2O) have been recognized under certain conditions. Kern et al.[1] considered that, during the initial stage of polymerization, a certain concentration of CH_2O was obtained by the depolymerization of CH_2O from the active centers. Monomeric CH_2O must be present in an equilibrium concentration before the polymerization of trioxane can take place; they regarded the induction period as the time during which such a concentration of CH_2O was obtained. Thereafter, kinetic studies of the induction period of the polymerization were carried out by Kučera[2] and by Rakova.[3] While they have agreed that

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

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

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

the free CH_2O produced at the initial stages of polymerization reacts rapidly with the catalyst to form the active centers, they differed on the relationship to the yield of CH_2O during polymerization. Moreover, since they worked under different polymerization conditions, it is impossible to apply their results to our system.

For the present paper, the yield of CH_2O produced during the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ was measured under the same conditions as in the previous papers. For comparison, the polymerization catalyzed by boron fluoride was also carried out. Considering the relation between the induction period and the yield of CH_2O, it may be deduced that the induction period is caused mainly by water in the reaction system.

Experimental

The procedures of the polymerization except for the stopping of the reaction, and of the purification of the materials were the same as in the previous paper.[4] Commercial boron fluoride (Matheson Co., Inc., boron fluride content: 99.5%) was used without purification. In the case of the addition of CH_2O to the polymerization system, the necessary quantity of the formaldehyde solution was prepared by the thermal decomposition of polyoxymethylene at 250—300°C under nitrogen.

The concentration of CH_2O was determined by the sodium sulfite method.[5]

For the measurement of the concentration of CH_2O produced in the polymerization system, the polymerization at a fixed time was stopped by adding a certain quantity of a 1 M sodium sulfite aqueous solution, in which the free sodium hydroxide had previously been neutralized, using thymolphthalein (0.1% alcohol soln.) as an indicator. When necessary, the polymers were separated and CH_2O was measured immediately after the polymerization was stopped. As this solution showed a blue color if CH_2O had been produced, it was quickly titrated by 1/20 N hydrogen chloride until its color disappeared. As the catalyst present in the polymerization system acts as an acid, sodium hydroxide corresponding to the initial catalyst concentration was added before the titration.

Results

The Formation of CH_2O in the Polymerization System Catalyzed by $BF_3 \cdot O(C_2H_5)_2$.—In the polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ in various solvents, the relation between the reaction time and the yields of polymer and CH_2O was studied. Here "polymer" is defined as that polyoxymethylene which was insoluble in methanol, and the CH_2O formed means all those CH_2O units which could be measured by the method described in the Experimantal section.

In *n*-hexane, as Fig. 1 shows, the polymerization took place without any induction period. The formation of CH_2O could be detected immediately after the addition of the catalyst (within 6 sec.), and the concentration of CH_2O was almost constant up to a 10% conversion. These results did not change even if the concentrations of catalyst and water were changed.

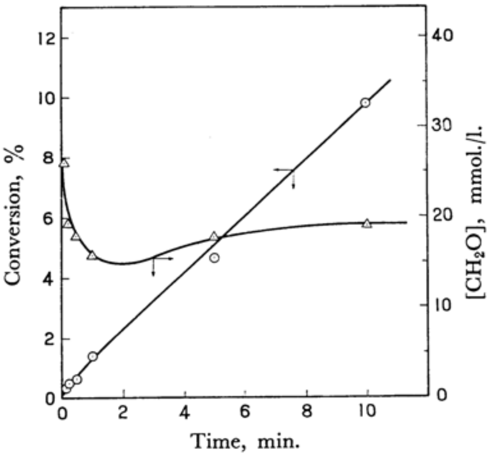

Fig. 1. Relationship between conversion and the concentration of produced CH_2O during polymerization in *n*-hexane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ at 30°C.
$[M]_0$; 0.35 mol./l., [C]; 2.0 mmol./l., $[H_2O]$; 0.8 mmol./l.

In ethylene dichloride, as is shown in Fig. 2, an increase in the water concentration increased both the initial rate of polymerization and the induction period. At a low concentration

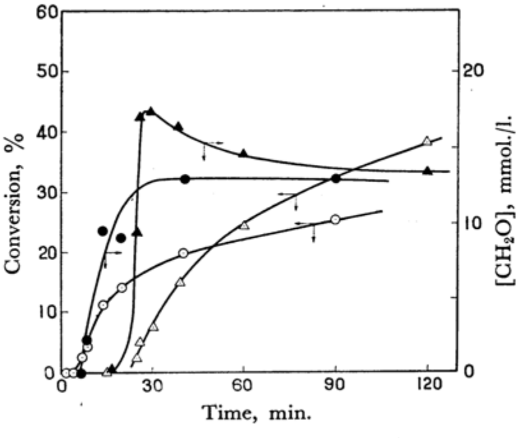

Fig. 2. Effect of water on the rate of polymerization and the concentration of produced CH_2O during polymerization in ethylene dichloride catalyzed by $BF_3 \cdot O(C_2H_5)_2$ at 30°C.
$[M]_0$; 3.3 mol./l., [C]; 10 mmol./l., $[H_2O]$; ○ and ●: 2.3, △ and ▲: 9.8 mmol./l.

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

[5] J. Frederic Walker, "Formaldehyde," Reinhold Publishing Corporation, New York (1953), Chap. 18.

of water the induction period for the formation of CH_2O was short (CH_2O was found just after the production of polymer), while at a high concentration of water the induction period for the formation of CH_2O was long; here the formation of CH_2O and the polymerization occurred simultaneously.

In nitrobenzene we studied two systems, in one of which the concentration of water was low and, in the other, extremely high. In the former system, as Fig. 3 shows, both the polymer and CH_2O were produced less than one minute after the addition of the catalyst. The maximum concentration of CH_2O was about 15 mmol./l., as in ethylene dichloride. The concentration of the CH_2O formed tended to decrease during the course of the polymerization. However, in a system containing much water, a large quantity of CH_2O was produced during the induction period, the concentration of the CH_2O decreased just before polymerization occurred, and no CH_2O was found in the system after the polymerization had taken place. So far as Fig. 3 is concerned, no equilibrium concentration of CH_2O was observed.

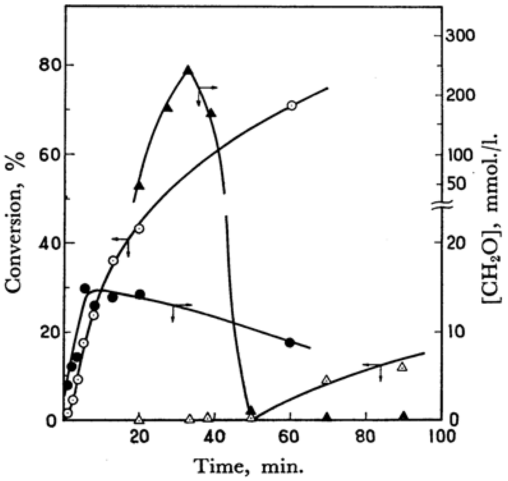

Fig. 3. Effect of water on the rate of polymerization and the concentration of produced CH_2O during polymerization in nitrobenzene catalyzed by $BF_3 \cdot O(C_2H_5)_2$ at 30°C.
$[M]_0$; 1.1 mol./l., [C]; 10 mmol./l., $[H_2O]$; ○ and ●: 2.2, △ and ▲: 18.6 mmol./l.

The Effect of CH_2O Added to the Polymerization System Catalyzed by $BF_3 \cdot O(C_2H_5)_2$.—The effect of the added CH_2O was studied in ethylene dichloride, using $BF_3 \cdot O(C_2H_5)_2$ as a catalyst. When CH_2O was present, the polymerization system became turbid immediately after the addition of the catalyst and the polymerization of trioxane seemed to occur. Nevertheless, the yield of polymers did not increase during a given period, and the true induction period was not changed by the addition of CH_2O, as Fig. 4 shows. These facts indicate that the added CH_2O was polymerized upon the addition of the catalyst, thus giving the observed turbidity. It apparently did not participate in the induction period of the polymerization of trioxane. Increasing the amount of CH_2O added did, however, increase the rate of the polymerization of trioxane and, as Fig. 5 shows, decrease the molecular weight of the resulting polymer. This same tendency was also caused by the increase

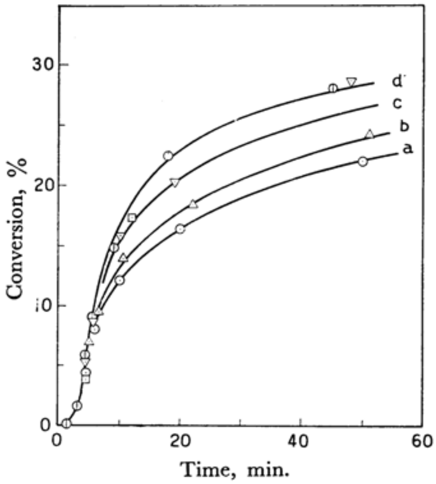

Fig. 4. Effect of addition of CH_2O on the rate of polymerization in ethylene dichloride catalyzed by $BF_3 \cdot O(C_2H_5)_2$ at 30°C. (The exact curve for *e* could not be determined.)
$[M]_0$; 3.3 mol./l., [C]; 10 mmol./l., $[H_2O]$; 1.7 mmol./l., $[CH_2O]$; a(○): 0, b(△): 14, c(▽): 28, d(⦶): 58 and e(□): 93 mmol./l.

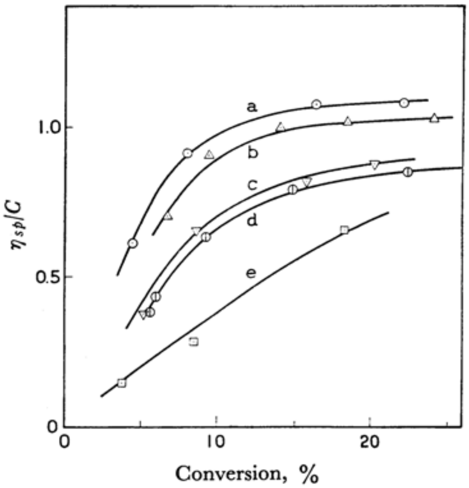

Fig. 5. Effect of addition of CH_2O on the molecular weight of resultant polymers in ethylene dichloride catalyzed by $BF_3 \cdot O(C_2H_5)_2$ at 30°C. Polymerization conditions are the same as in Fig. 4.

in the catalyst concentration.

The Formation of CH_2O in the Polymerization System Catalyzed by Boron Fluoride.—As the CH_2O formation in the polymerization system catalyzed by BF_3, which had been reported earlier,1) differed from that of the $BF_3 \cdot O(C_2H_5)_2$ catalyst reported in this paper, we again studied the former polymerization system. The effect of the water concentration was studied in ethylene dichloride at a fixed catalyst concentration. As Fig. 6 shows, an increase in the water concentration increased the rate of polymerization and the induction period. When the water concentration was larger than that of the catalyst, the time-conversion curve assumed a typical S-shape, as in the results obtained by Kern et al.1) in methylene chloride. The saturated yield of the polymer was found to be independent of the water concentration in the case of the BF_3 catalyst. Figure 7 shows that, although the molecular weight of the resulting polymers increased with the conversion (as in $BF_3 \cdot O(C_2H_5)_2$ catalysis), the water concentrations used did not affect the molecular weight of the polymers.

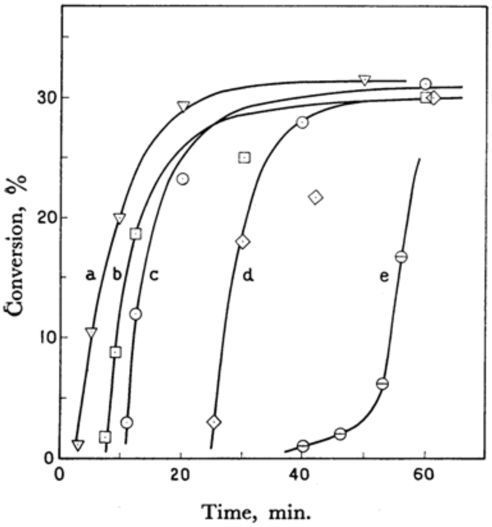

Fig. 6. Effect of water on the rate of polymerization in ethylene dichloride catalyzed by BF_3 at 30°C.
$[M]_0$; 4.4 mol./l., [C]; 3.8 mmol./l., $[H_2O]$; a(▽): 2.7, b(□): 3.6, c(○): 4.0, d(◇): 4.5 and e(⊖): 5.5 mmol./l.

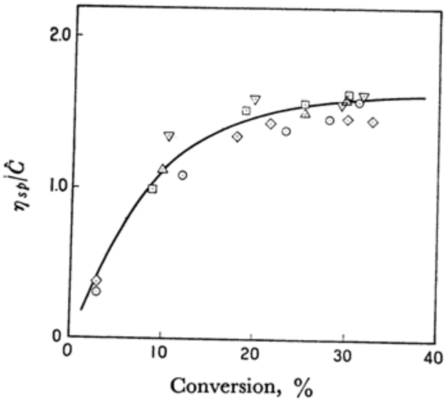

Fig. 7. Effect of water on the molecular weight of resultant polymers in ethylene dichloride catalyzed by BF_3 at 30°C.
$[M]_0$; 4.4 mol./l., [C]; 3.8 mmol./l., $[H_2O]$; ▽: 2.7, △: 3.4, □: 3.6, ○: 4.0 and ◇: 4.5 mmol./l.

In the same system the change in the concentration of CH_2O produced during the induction period of the polymerization was also measured. As Fig. 8 shows, CH_2O was produced during the induction period. When the concentration of CH_2O seemed to reach a maximum, the polymerization of trioxane took place. Thereafter, the concentration of CH_2O suddenly decreased. Here no equilibrium concentration of CH_2O was found, either. The change in the CH_2O concentration was so sudden both before and after the polymerization that the measurement of the maximum concentration of CH_2O was very difficult.

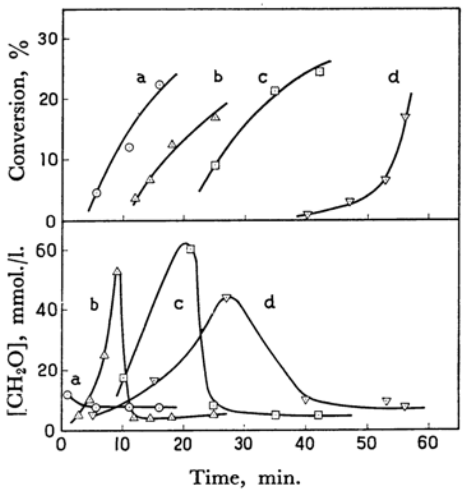

Fig. 8. Effect of water on the rate of polymerization and the concentration of produced CH_2O during polymerization in ethylene dichloride catalyzed by BF_3 at 30°C.
$[M]_0$; 4.4 mol./l., $[BF_3]$; a(○) and d(▽): 3.5 mmol./l., b(△) and c(□): 3.0 mmol./l., $[H_2O]$; a(○): 2.4, b(△): 2.2, c(□) 4.8 and d(▽): 5.5 mmol./l.

The Effect of the CH_2O Added to the Polymerization System Catalyzed by Boron Fluoride. — The effect of the added CH_2O on the polymerization reaction was studied in ethylene dichloride, as in the case of the $BF_3 \cdot O(C_2H_5)_2$ catalyst. Similarly to the case of the $BF_3 \cdot O(C_2H_5)_2$ catalyst, when CH_2O was present the reaction system became turbid just after the addition of the catalyst, but the quantity of polymers was fairly small and did not increase during the settled period. As Fig. 9 shows, a small amount of the added CH_2O did not greatly affect the rate of polymerization and did not decrease the induction period. It was impossible to conclude that these results were caused only by the added CH_2O because of the possibilities that water came into the solvent during the preparation of the CH_2O solution by our method and that CH_2O reacted with water in the polymerization system.

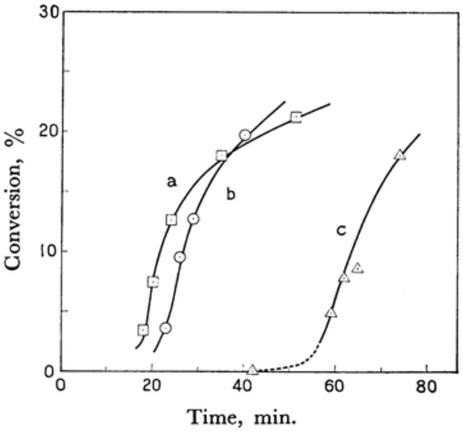

Fig. 9. Effect of addition of CH_2O on the rate of polymerization in ethylene dichloride catalyzed by BF_3 at 30°C.
$[M]_0$; 4.4 mol./l., $[BF_3]$; 2.5 mmol./l., $[H_2O]$; 2.0 mmol./l., $[CH_2O]$; a(□): 0, b(○): 25 and c(△): 71 mmol./l.

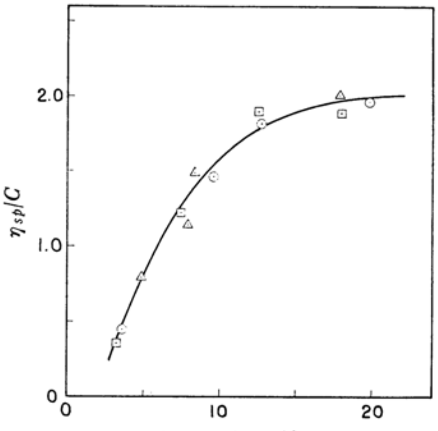

Fig. 10. Effect of addition of CH_2O on the molecular weight of resultant polymers in ethylene dichloride catalyzed by BF_3 at 30°C. (Polymerization conditions are the same as in Fig. 9.)

The molecular weight of the resulting polymers was not affected by the added CH_2O, as Fig. 10. shows. While in the case of the $BF_3 \cdot O(C_2H_5)_2$ catalyst the addition of water and CH_2O decreased the molecular weight of the polymers, in the case of the BF_3 catalyst the addition of water and CH_2O did not affect the molecular weight of the polymers.

Discussion

In the cationic solution-polymerization of trioxane, the induction period of the polymerization and the formation of CH_2O during the polymerization have often been recognized. In Table I we have summarized our experimental results on the induction period. Here the relation between the induction period and the concentrations of the catalyst and of the monomer was too complicated to be explained quantitatively, as was the relation between the polymerization rate and the concentrations of the catalyst and of the monomer.

In *n*-hexane, no induction period of the polymerization was observed. This agrees with Rakova's result³⁾ in a non-polar solvent wherein the formation of CH_2O was recognized immediately after the addition of a catalyst. This is probably due to the facile depolymerization of the unsolvated growing-chain end.

On the other hand, our results in polar solvents showed that the factor which most greatly influences the induction period of the polymerization seemed to be the concentration of water. This relation was considered to hold not only in the case of the $BF_3 \cdot O(C_2H_5)_2$ catalyst, but also in the case of the boron fluoride catalyst, as Fig. 6 shows. In the latter case, when the water concentration was about 1.5 times larger than that of the boron fluoride catalyst, a very long induction period was observed and the time-conversion curve assumed a typical S-shape. In earlier papers, this view has not been dealt with at all.

Kern et al.¹⁾ have indicated that, in the polymerization of trioxane catalyzed by boron fluoride, the active chains were depolymerized, thus liberating free, monomeric CH_2O, whose concentration reached a certain value (i. e., the equilibrium concentration) before the polymerization reaction took place. This conception has been supported by

TABLE I. SUMMARY OF THE RELATIONSHIP BETWEEN INDUCTION PERIOD (t_i) AND REACTION CONDITIONS

Solvent	$n\text{-}C_6H_{14}$	C_6H_6	$(CH_2Cl)_2$	$C_2H_5NO_2$	$C_2H_5NO_2$
$[BF_3 \cdot O(C_2H_5)_2]$	None	$t_i \propto 1/[C]^{0.6}$	$t_i \propto 1/[C]^{1.0}$	$t_i \propto 1/[C]^{1.7}$	$t_i \propto 1/[C]^{2.0}$
[Trioxane]	—	—	$t_i \propto 1/[M]^{1.3}$	—	$t_i \propto 1/[M]^{a*}$
$[H_2O]$	None	—	$[H_2O]\uparrow\ t_i\uparrow$	—	$[H_2O]\uparrow\ t_i\uparrow$

* *a* was a very large number, but the value could not be settled.

Kučera in the cationic polymerization of molten trioxane.[2]

In our results concerning the $BF_3 \cdot O(C_2H_5)_2$ catalyst, as long as the water content in the reaction system was not very large, the polymerization reaction and the formation of CH_2O took place simultaneously; we did not observe that the polymerization reaction occurred only when a certain concentration of CH_2O is present. As the change in the induction period was not observed when CH_2O had been added to the polymerization system, the conception of Kern et al.[1] can not be applied to the polymerization catalyzed by $BF_3 \cdot O(C_2H_5)_2$.

Rakova et al.[3] dealt quantitatively with the induction period in the solution-polymerization of trioxane. Considering that, in their results, the stationary concentration of CH_2O varied with the polymerization conditions, and also considering that in our results no stationary or equilibrium concentration was clearly recognized, it is doubtful whether the equilibrium concentration of CH_2O is present.

The behavior of a system containing a large amount of water should be considered, also. In general, an increase in the water concentration increased the induction period during which a high concentration of CH_2O was attained. We have defined "polymer" as the methanol-insoluble polyoxymethylene. Therefore, it seems that the polymerization does not occur if only the methanol-soluble oligomer is formed. Besides, it is well known[6] that, in water, this oligomer decomposes into CH_2O, the decomposition being facilitated by an acid or a base. As the determination of the CH_2O concentration was carried out by using a sodium sulfite aqueous solution, the free monomeric CH_2O could not be distinguished from the CH_2O unit which was decomposed from the oligomer. As water might act as a transfer agent or as an inhibitor and much more oligomer would be produced in the presence of much water, a large quantity of CH_2O might be measured experimentally during the induction period. The decrease in the concentration of CH_2O in the course of polymerization was probably due to the growth of these oligomers to high polymers. Without exact knowledge of the concentration of the free monomeric CH_2O in the polymerization system, however, it will be difficult to discuss the induction period in detail. At any rate, it is clear that the induction period is caused by water, which inhibits the formation of high polymers.

Such aspects of the polymerization catalyzed by $BF_3 \cdot O(C_2H_5)_2$ as the effect of water differed from those of the polymerization catalyzed by boron fluoride; it must be established by future studies whether a consistent mechanism can be applied to both systems.

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[6] J. Löbering, *Ber.*, **69**, 1884 (1936).