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Kinetic Studies of the Solution Polymerization of Trioxane Catalyzed by $BF_3 \cdot O(C_2H_5)_2$. II. The Effect of Catalyst and Water Concentrations of the Molecular Weight of the Polymer

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In the solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$, the dependence of the molecular weight of the polymer formed on the polymerization conditions has been studied. In general, the molecular weight of the polymer formed increases in the course of polymerization, keeps a constant value over a certain range of conversion, and then again incerases remarkably. The molecular weight of the polymers formed decrease with an increase in the catalyst and water concentrations. This phenomenon can be explained qualitatively on the assumptions that the rate of the propagation reaction is smaller than that of the initiation reaction and that the chain breaking occurs through the reaction with water, which is consumed as the polymerization proceeds. This is equal to the assumption that the chain carrier is an oxonium ion in the cationic polymerization of trioxane.

It is neccessary for a study of the characteristics of the polymerization of the cyclic compound to know the molecular weight of the produced polymer as well as the rate of polymerization. None of the papers on the solution polymerization of trioxane has, however, dealt with the relation between the polymerization conditions and the molecular weight of the produced polymer, This relation has been discussed only in connection with the polymerization of molten trioxane.(1,2)

The effect of the concentrations of $BF_3 \cdot O(C_2H_5)_2$ and of water on the rate of polymerization in various solvents was described in previous paper.(3) For the present paper, the molecular weight of the polymer obtained in the previous paper was measured, and its dependence on the concentrations of catalyst and water was studied. The exact relationship between the solution viscosity and the molecular weight for polyoxymethylene has not yet been obtained, so we used the viscosity number instead of the molecular weight of the produced polymer.

The peculiar phenomenon was found that the molecular weight of the produced polymer increased as the polymerization proceeded but decreased as the catalyst concentration increased; no such phenomenon has been found in the cationic polymerization of vinyl monomers.

Experimental

After the polymer obtained in the previous paper(3) had been throughly dried, viscosity number (η_{sp}/C; C=0.6 g./100 ml. solution) was measured in a *p*-chlorophenol solution including 2% α-pinene at 60°C. The polymer was dissoved in *p*-chlorophenol under nitrogen gas by heating it at 120°C for 2—4 min. Under such conditions, it was not clear whether the polymer was decomposed or not during dissolution. The decomposition of the polymer during dissolution was, however, inferred to be negligible since the reproducibility of the measurements of the same sample within 5 min. of heating was very good and since the value of η_{sp}/C varied regularly with the polymerization conditions.

Results

The Effect of the Catslyst Concentration and the Conversion.—The effects of both the

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1) M. Kučera and E. Spousta, *Makromol. Chem.*, **76**, 183 (1964).

2) M, Kučera and E. Spousta, ibid., **76**, 190 (1964).

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

catalyst concentration and the conversion on the molecular weight of the resulting polymer in various solvents were studied. The polymerization conditions were the same as those in the corresponding figures in the previous paper.[3)]

The results for the polymers obtained in benzene and ethylene dichloride are shown in Figs. 1 and 2. The molecular weight of both polymers increased with the conversion. Moreover, the molecular weight is the smaller at larger catalyst concentrations.

Although the catalyst concentration did not affect the rate of polymerization at a high-monomer concentration (3.3 mol./l.) in nitrobenzene, the

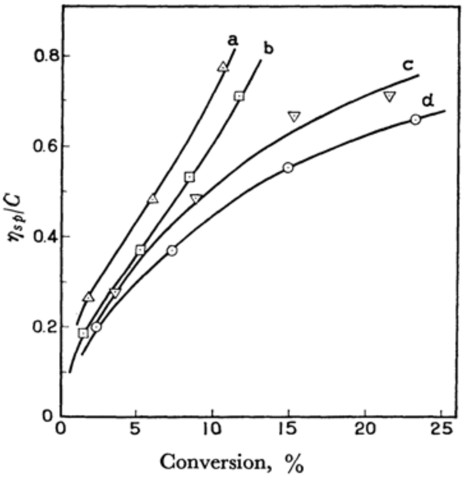


Fig. 1. Effect of catalyst concentration on the molecular weight of resultant polymers in benzene solution at 30°C.
$[M]_0$; 3.3 mol./l., $[H_2O]$; 2.5 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; a(△): 5, b(☐): 10, c(▽): 20 and d(○): 30 mmol./l.

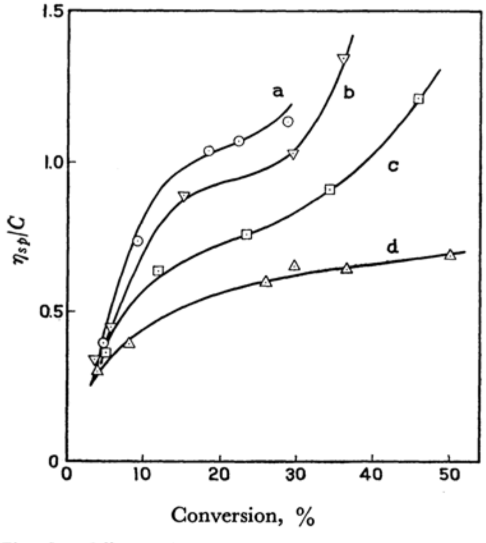


Fig. 2. Effect of catalyst concentration on the molecular weight of resultant polymers in ethylene chloride solution at 30°C.
$[M]_0$; 3.3 mol./l., $[H_2O]$; 2.9 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; a(○): 2.5, b(▽); 5, c(☐): 10 and d(△): 20 mmol./l.

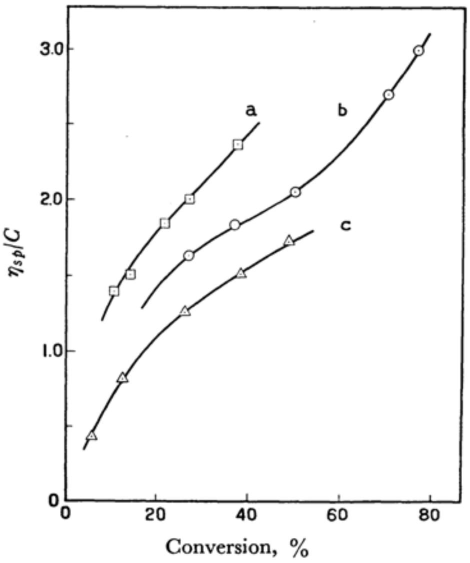


Fig. 3. Effect of catalyst concentration on the molecular weight of resultant polymers in nitrobenzene solution at 30°C.
$[M]_0$; 3.3 mol./l., $[H_2O]$; 1.8 mmol./l., $[BF_3 \cdot O(C_2H_5)_2]$; a(☐): 0.5, b(○): 1.0 and c(△): 2.5 mmol./.

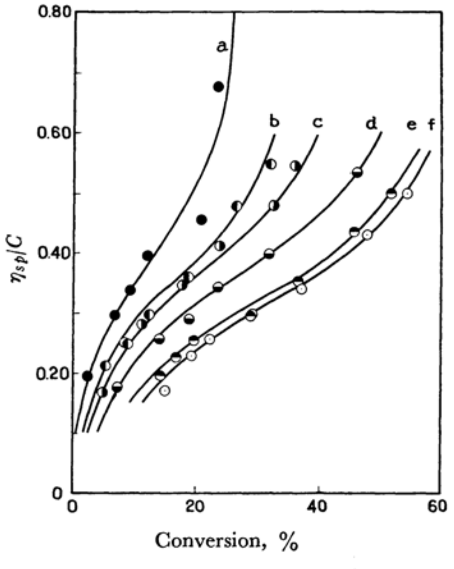


Fig. 4. Effect of water concentration on the molecular weight of resultant polymers in *n*-hexane at 30°C.
$[M]_0$; 0.37 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 9.4 mmol./l., $[H_2O]$; a(●): 0.4, b(◐): 0.9, c(◑): 1.1, d(◒): 1.7, e(◓): 2.2 and f(○): 3.4 mmol./l.

molecular weight of the produced polymers decreased regularly with an increase in the catalyst concentration and increased remarkably with the conversion, as is shown in Fig. 3. A similar behavior was found in the nitroethane solvent.

The Effect of the Water Concentration—The addition of water also decreased the molecular weight of the produced polymer. The results in *n*-hexane and ethylene dichloride are shown in Figs. 4 and 5, respectively. A similar result was obtained in benzene. In these solvents a small amount of water accelerates the polymerization, but an excessive addition of water decreases the rate. In all these solvents, it may be noted that the molecular weight decreases monotonously with the increase of water, but not with the conversion. In ethylene dichloride, for examlpe, the rate of the increase in molecular weight is remarkably raised at certain conversions.

In nitrobenzene the relation between the molecular weight and the water concentration was also curious. As is shown in Fig 6, when the monomer concentration was equal to 3.3 mol./l., a small amount of water did not affect the molecular weight. However, when the monomer concentration was low, the molecular weight was decreased

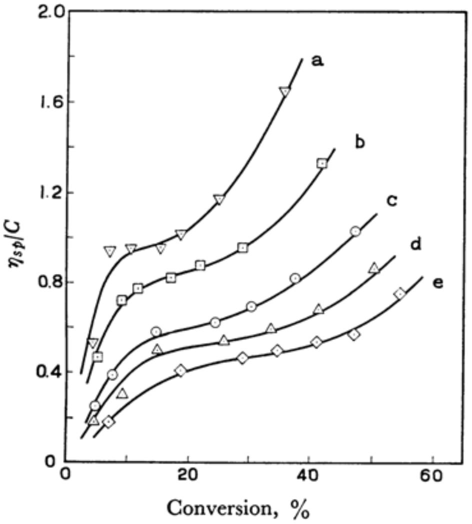
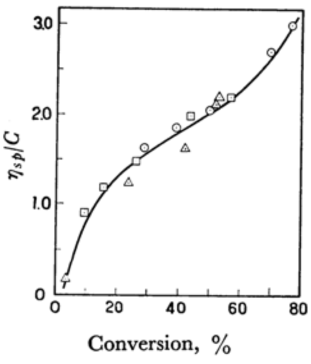


Fig. 5. Effect of water concentration on the molecular weight of resultant polymers in ethylene dichloride at 30°C.
$[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 10 mmol./l., $[H_2O]$; a(▽): 0.3, b(□): 1.6, c(○): 3.7, d(△): 5.9 and e(◇): 10.8 mmol./l.



Fih. 6. Effect of water concentration on the molecular weight of resultant polymers in nitrobenzene at 30°C.
$[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 1.0 mmol./l., $[H_2O]$; ○: 1.8, △: 4.7 and □: 8.3 mmol./l.

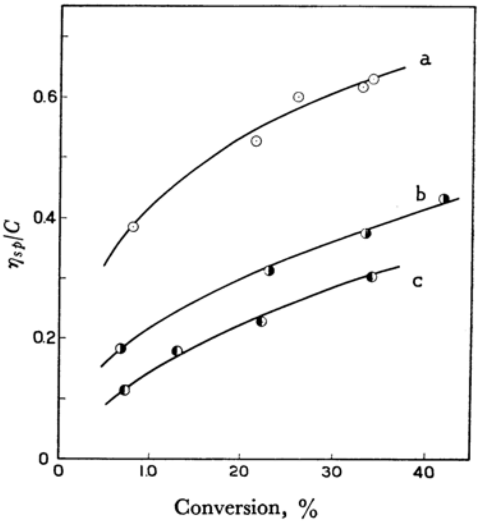


Fig. 7. Effect of methanol concentration on the molecular weight of resultant polymers in ethylene dichloride at 30°C.
$[M]_0$: 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 20 mmol./l., $[H_2O]$; 2.7 mmol./l., $[CH_3OH]$; a(○): 0, b(◑): 10.0 and c(◐): 20.0 mmol./l.

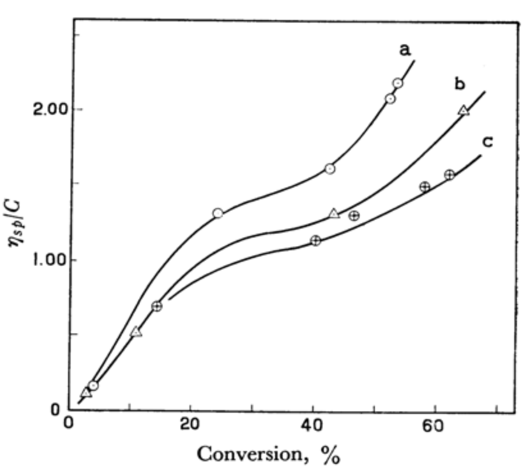


Fig. 8. Effect of methanol concentration on the molecular weight of resultant polymers in nitrobenzene at 30°C.
$[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 1.0 mmol./l., $[H_2O]$; 4.7 mmol./l., $[CH_3OH]$; a(○): 0, b(△): 2.5 and c(⊕): 5.0 mmol./l.

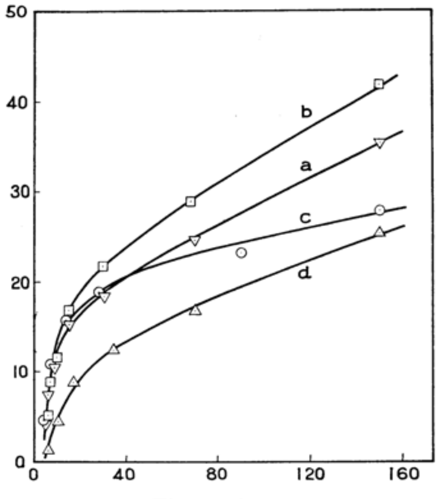


Fig. 9. Comparison between the rate of polymerization in ethylene dichloride and that in methylene chloride at 30°C.
$[M]_0$; 3.3 mol./l., $[BF_3 \cdot O(C_2H_5)_2]$; 10 mmol./l.,
a(▽); $(CH_2Cl)_2$ solvent, $[H_2O]$: 0.3 mmol./l.,
b(□); $(CH_2Cl)_2$ solvent, $[H_2O]$: 1.6 mmol./l.,
c(○); $(CH_2Cl)_2$ and CH_2Cl_2 mixed solvent (equal volume), $[H_2O]$: 0.9 mmol./l.,
d(△); CH_2Cl_2 solvent, $[H_2O]$: 0.9 mmol./l.

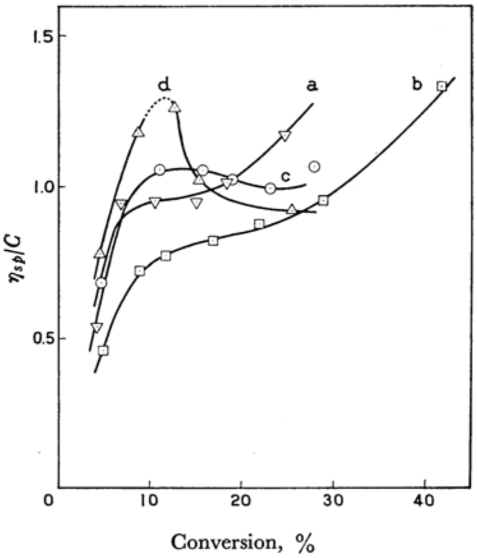


Fig. 10. Comparison between molecular weight of polymer obtained in ethylene chloride and that in methylene chloride at 30°C. Polymerization condition and notes of courves are the same as in Fig. 9.

by an increase in the water concentration. As the relation between the conversion and the molecular weight at a low-monomer concentration was extraordinary, this matter will be discussed in the next paper.[4]

The Effect of the Addition of Methanol.—The effect of added methanol in ethylene dichloride and nitrobenzene was also studied. As is shown in Figs. 7 and 8, the molecular weight of the polymer decreased with an increase in the concentration of methanol. At a fixed conversion, the rate of the decrease in molecular weight by the addition of methanol in ethylene dichloride was larger than that in nitrobenzene.

Abnormality in Methylene Chloride.—It has been reported that, in the case of the polymerization of trioxane by iron(III) chloride in cyclohexane, the molecular weight of the produced polymer decreased with an increase in the conversion.[5] In our results on the solution polymerization of trioxane, however, the molecular weight of the polymer increased in the course of polymerization. Therefore, we have studied whether the molecular weight of the resultant polymers decreased or not with an increase in the conversion in a $BF_3 \cdot O(C_2H_5)_2$-methylene chloride which is considered to act as a transfer agent.

As is shown in Fig. 9, the rate of the polymerization of trioxane in methylene chloride was smaller than that in ethylene dichloride, but there was no essential difference in the behavior between two solvents. The molecular weight of the produced polymer in methylene chloride, however, was found to exhibit the characteristic behavior as is shown in Fig. 10. In methylene chloride the molecular weight of the polymer increased in the course of polymerization at the initial stage of polymerization, reached a maximum at a certain conversion, and then decreased.

Discussion

Generally in the cationic polymerization of vinyl monomers, the molecular weight of the produced polymers is independent of the catalyst concentration and the conversion. However, in the solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$, the molecular weight of the polymers formed increases in the course of polymerization but decreases with an increase in the catalyst and water concentrations.

The change in the molecular weight in the course of the polymerization of trioxane can be characterized as follows. The molecular weight increases monotonously up to 10—20% conversion; the rate of its increase decreases in the middle stage of the polymerization, and then again increases rapidly at a high conversion. As may be seen from Figs. 4 and 5, the range in which the molecular weight did not increase with the conversion was influenced by the quantity of water. In order

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[4] T. Higashimura, T. Miki and S. Okamura, ibid., **39**, 31 (1966).
[5] V. Jaacks and W. Kern, *Makromol. Chem.*, **62**, 1 (1963).

to clarify the reaction mechanism, we shall first try to explain the relation between the change in molecular weight and the conversion.

Other instances where the moleculat weight of the polymers formed increases in the course of polymerization have been found in the cationic polymerization of such cyclic ethers as ethylene oxide and 1, 3-dioxolane,[6,7] and in the anionic polymerization of the cyclic monomers and vinyl monomers. These results have been summarized[8] and explained by the concept of "successive" polymerization[9] by Kagiya et al.

As for trioxane, this phenomenon was recognized in the cationic polymerization in the molten state.[1] It has been regarded as being caused by the polymerization's proceeding step by step through a living end and by the impurities which act as chain breakers being consumed in the course of polymerization. This suggestion involved the two points that the molecular weight of the polymers formed was independent of the catalyst concentration and that the molecular weight at 0% conversion was not equal to zero.

These proposals[1,8,9] could explain many things, but not the complicated behavior of the solution polymerization of trioxane found in this paper. To explain the observed change in molecular weight, then, the following three elementary reactions are assumed for the solution polymerization of trioxane:

Initiation reaction $$M + C \xrightarrow{k_i} M_1^* \tag{1}$$

Propagation reaction $$M_r^* + M \xrightarrow{k_p} M_{r+1}^* \tag{2}$$

Transfer reaction $$M_r^* + X_{tr} \xrightarrow{k_{tr}} P_n + X'_{tr} \tag{3}$$

Where M, C, and X_{tr} denote a monomer, a catalyst and a chain-transfer reagent like water respectively. If X_{tr} is water, X'_{tr} implies a proton. Consequently, X_{tr} is consumed during the polymerization according to reaction 3. It may be inferred that, in the cationic polymerization of trioxane, the transfer reactions to monomer and solvents used in this paper scarcely ever occur.

According to Kagiya et al.[9] the phenomenon of the molecular weight of the polymers formed increasing in the course of polymerization is found only when the rate of the initiation reaction is larger than those of the propagation and the transfer reaction. In such a system the average degree of polymerization ($\bar{P}$) corresponding to the elementary reactions 1—3 is shown by Eq. 4[9]:

$$\bar{P} = \frac{[M]_0 - [M]}{\alpha[C]_0 + k_{tr}\int[M^*][X_{tr}]dt} \tag{4}$$

where α is a constant which denotes the mole concentration of active center produced per mole of catalyst and where the suffix 0 denotes the initial concentration. If X_{tr} is not consumed during the polymerization (e. g., if $[X_{tr}]$ is a constant), Eq. 5 is obtained by substituting Eq. 2 into Eq. 4:

$$\bar{P} = \frac{[M]_0 - [M]}{\alpha[C]_0 + (k_{tr}/k_p)[X_{tr}]_0 \ln([M]_0/[M])} \tag{5}$$

Equation 5, as derived by Kagiya et al., implies that the degree of polymerization increases with the conversion to the limited value and that after that it again decreases. This behavior is shown schematically in curve c in Fig. 11. This does not agree with our experimental results.

As is shown in Eq. 3, X_{tr} decreases in the course of polymerization. In such a case, the relation between $[X_{tr}]$ and $[M]$ has already been indicated, as is shown in Eq. 6[1]:

$$[X_{tr}] = [X_{tr}]_0([M]/[M]_0)^{k_{tr}/k_p} \tag{6}$$

Equation 7 is obtained by putting Eqs. 2 and 6 into Eq. 4 and integrating;

$$\bar{P} = \frac{[M]_0 - [M]}{\alpha[C]_0 + [X_{tr}]_0\{1 - ([M]/[M]_0)^a\}} \tag{7}$$

$$= \frac{[M]_0 x}{\alpha[C]_0 + [X_{tr}]_0\{1 - (1-x)^a\}} \tag{7'}$$

where $a = k_{tr}/k_p$ and where x denotes the fractional conversion. This is equal to the equation obtained by Kučera[1] except for the first term of the denominator.

In our experiments, η_{sp}/C was measured, but not the molecular weight. There was also the added complexity that the polymer formed precipitated from the reaction system during the polymerization. Therefore, the experimental results will be compared qualitatively.

If the transfer reaction (Eq. 3) does not occur, the second term of the denominator in Eq. 7′ may be omitted and $\bar{P}$ increases in proportion to the conversion. This is shown by line a in Fig. 11. If $\bar{P}$, as proposed by Kučera,[1] depends on only the transfer reaction, $\bar{P}$ is indicated by curve b in Fig. 11. If the transfer reagent (X_{tr}) is not consumed during the polymerization, $\bar{P}$ is indicated by Eq. 5 and its change will obey curve c in Fig. 11. These lines do not agree with our experimental results. When a in Eq. 7′ is smaller than 1, $\bar{P}$ indicates curve d. However, the rapid increase in the molecular weight at a high conversion cannot be explained. On the other hand, when a is larger than 1, curve e is obtained and the shape of the curve agrees qualitatively with the experimental data. According to this result, it is recognized that, as the water is consumed during the initial

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

[7] T. Kagiya, M. Hatta, T. Shimizu and K. Fukui, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 1890 (1963).

[8] T. Kagiya, M. Hatta and K. Fukui, *Chem. High Polymers Japan* (*Kobunshi Kagaku*), **20**, 737 (1963).

[9] T. Kagiya, M. Hatta and K. Fukui, ibid., **20**, 730 (1963).

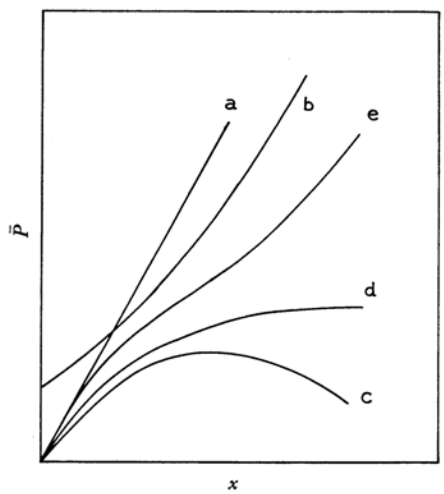


Fig. 11. Schematic diagram of the relationship between the degree of polymerization ($\bar{P}$) and the fractional conversion (x).

stages of polymerization, such a η_{sp}/C-conversion curve is observed. Also, the rate of the transfer reaction may be fairly fast, because k_{tr}/k_p is larger than unity. However, another reason can be given for this phenomenon. Polymer transfer reactions have been reported in the cationic polymerization of trioxane[10] and tetrahydrofuran[11]. Therefore, the transfer reaction of the growing chain to the dead polymer may be considered to exist in this system also.

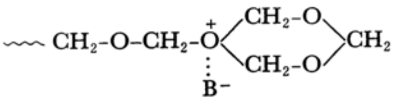
If α in Eq. 7 is independent of the catalyst concentration,[9] it is recognized that the molecular weight of the polymers decreases with the increase in the catalyst concentration. It is also clear from this equation that an increase in the transfer reagent concentration decreases the molecular weight of the polymers.

In methylene chloride the molecular weight of the polymers decreased at a high conversion. It has also been found that, in the polymerization of trioxane in cyclohexane catalyzed by iron(III) chloride the molecular weight of the polymers decreases in the course of the polymerization.[5] It is considered that these phenomena are caused by the decomposition of the resultant polymers. It is not clear, however, why the decomposition of the polymers takes place only in methylene chloride and cyclohexane.

It has been considered that, in the cationic polymerization of vinyl monomers, the rate of the propagation reaction is larger than that of the other elementary reactions. However, as has been mentioned above, Eq. 7 was derived on the assumption that the rate of the initiation reaction is larger than that of the propagation reaction. This fact is understandable assuming that the growing chain is stable in the cationic polymerization of trioxane. If the active chain end produced from trioxane has the structure shown in Eq. 8, however, this chain end is more unstable than that of vinyl monomers, and the reactivity of the former should be larger than that of the latter;

$$\sim\!\sim\!\sim CH_2\text{-}O\text{-}\overset{+}{C}H_2\cdots B^- \tag{8}$$

Nevertheless, the rate of the propagation reaction was smaller than that of the other elementary reaction, according to our results. This may be because the chain carrier is stabilized in a shape of the oxonium ion shown in Eq. 9, as is considered to be the case in the cationic polymerization of many cyclic ethers.



$$\sim\!\sim\!\sim CH_2\text{-}O\text{-}CH_2\text{-}\underset{\substack{\vdots\\ B^-}}{\overset{+}{O}}\begin{matrix}\diagup CH_2\text{-}O\diagdown\\ \diagdown CH_2\text{-}O\diagup\end{matrix}CH_2 \tag{9}$$

Even if the polymerization reaction would proceed through the oxonium ion, there are many cases in which the molecular weight of the polymers formed does not increase in the course of polymerization.[12,13] However, in a system in which the molecular weight of the polymers increases rapidly with the conversion, it may be reasonable to consider the chain carrier to be a stable oxonium ion.

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[10] K. Weissermel, E. Fischer, K. Gutweiler and H. D. Hermann, *Kunststoffe*, **54**, 410 (1964).

[11] A. Rosenberg, E. B. Lyudvig, A. R. Gantmakher and S. S. Medvedev, *Visokomol. Soed.*, **7**, 188 (1965).

[12] J. B. Rose, *J. Chem. Soc.*, **1956**, 542.

[13] I. Penczek and S. Penczek, *Makromol. Chem.*, **67**, 203 (1963).