BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 39 41—46 (1966)

Kinetic Studies of the Solution Polymerization of Trioxane Catalyzed by $BF_3 \cdot O(C_2H_5)_2$. V. The Effect of the Solvent and of the Polymerization Temperature

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(Received April 5, 1965)

The effect of the polarity of solvents in the solution polymerization of trioxane catalyzed by $BF_3 \cdot O(C_2H_5)_2$ has been studied. While the molecular weight of the resulting polymer is almost independent of the kind of solvent, the rate of polymerization in a polar solvent is large at a high initial monomer concentration. At a low monomer concentration, however, the rate of polymerization in a non-polar solvent is larger than that in a polar solvent. This fact can probably be explained by observing that, at the low monomer concentration, the initiation species produced from the catalyst is solvated by the solvent molecule rather than by trioxane because of the small basicity of trioxane. The activation energies of the over-all polymerization rate as determined in ethylene dichloride, nitroethane and nitrobenzene are all about 16 kcal./mol. The decrease in the molecular weight of the resulting polymers caused by raising the temperature is very small.

In the cationic polymerization of vinyl monomers, the dielectric constant of the reaction system remarkably affects the rate of polymerization and the molecular weight of the resultant polymers. It is well known that in the polymerization of styrene, the rate of polymerization increases with the dielectric constant.[1] However, the relation between the molecular weight of the polymers and the dielectric constant varies with the kind of solvent. While in the cationic polymerization of the styrene and its derivatives the molecular weight of the resultant polymers increases with the dielectric constant,[1,2] a reverse relation is shown in the polymerization of isobutene[3] and of vinyl ethers.[4] This may be ascribed mainly to the difference between the mechanisms of the monomer transfer reactions.

If, in the cationic polymerization of trioxane, an ionic active species is produced by the interaction between the neutral molecules, as in the cationic polymerization of vinyl monomers, it is to be expected that the increase in the dielectric constant of the reaction system will increases the rate of polymerization.

In the present paper we will try to clarify the effect of the polarity of solvents in the ring-opening polymerization. Therefore, the findings on solvent variation will be summarized from the previous papers in this series and then the temperature dependence in several solvents will be studied. It will be found that the effect of a sovlent in the cationic polymerization of trioxane is not always the same as in the polymerization of vinyl monomers.

Experimental

The procedures of the polymerization and of the purification of the materials were the same as in the previous papers.[5]

Results

The Effect of the Solvent.—As the kinetic orders of the monomer and catalyst to the polymerization rate are changed by the kind of solvent, it was impossible to compare the polymerization rates in various solvents exactly. Figure 1, therefore, compares the polymerization rates in various solvents on the condition that the concentrations of the reagents were selected to be as equal as possible. From this result it can be seen that, at a high monomer concentration (3.3 mol./l.), the polymerization rate increases with the dielectric constant. Nitrobenzene is also found to be a very useful solvent, one in which high polymers can be obtained at high yields.

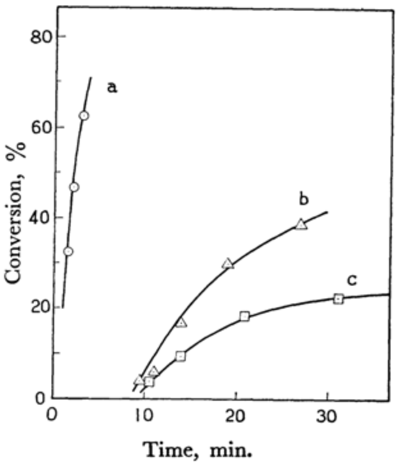

Fig. 1. Effect of a kind of solvents on the rate of polymerization at 30°C.
[M]$_0$; 3.3 mol./l., [C]; 2.5 mmol./l., Solvent; a(○); nitrobenzene ([H_2O]: 3.6 mmol./l.), b(△): nitroethane (2.7) and c(□): ethylene dichloride (2.9)

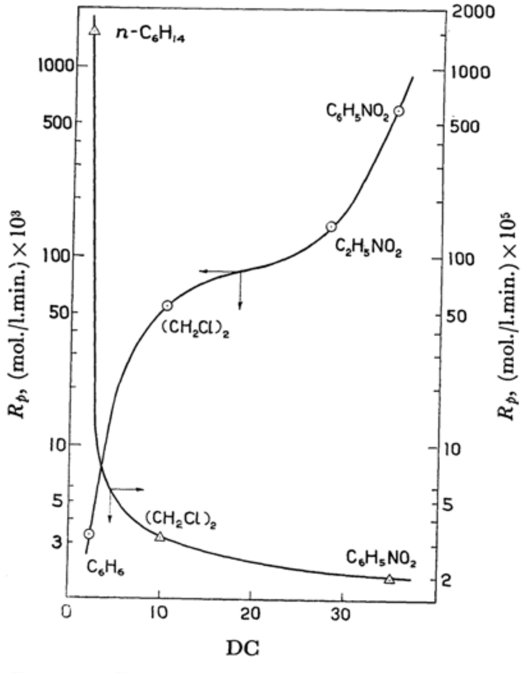

Fig. 2. Effect of a kind of solvents on the initial rate at low and high monomer concentrations at 30°C.
[H_2O]; 2-3 mmol./l., [M]$_0$; ○: 3.3 and △: 0.4 mol./l., [C]$_0$; ○: 2.5 and △: 10 mmol./l.

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[1] D. C. Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949); J. George and H. Wechsler, *J. Polymer Sci.*, **6**, 725 (1951); T. Higashimura, and S. Okamura, *Chem. High Polymers Japan* (*Kobunshi Kagaku*), **13**, 338 (1956).

[2] E. g., Y. Sakurada, T. Higashimura and S. Okamura, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zassi*), **61**, 1640 (1958); Y. Imanishi, S. Matsushita, T. Higashimura and S. Okamura, *Makromol. Chem.*, **70**, 68 (1964).

[3] Y. Imanishi, T. Higashimura and S. Okamura, *Chem. High Polymers Japan* (*Kobunshi Kagaku*), **18**, 333 (1961).

[4] Y. Imanishi, H. Nakayama, T. Higashimura and S. Okamura, ibid., **19**, 154, 565 (1962).

[5] T. Higashimura, T. Miki and S. Okamura, This Bulletin, **38**, 2067 (1965); **39**, 25 (1966).

As *n*-hexane did not have a large solubility of trioxane, the rate of polymerization in *n*-hexane was compared with the rates in polar solvents at only a low monomer concentration. In this case, as the experimental data were not obtained at a very low monomer concentration in the polar solvents, the extrapolated values were used as the rates in the polar solvents. Figure 2 shows the resultant relation between the dielectric constant of the solvent and the rate of polymerization. At a high monomer concentration, as Fig. 1 shows, the rate of polymerization in a polar solvent was larger than that in a non-polar solvent, but the reverse tendency was found at the low monomer concentration. Although it may be difficult to compare these data quantitatively because some of them are extrapolated, this tendency seems to be correct qualitatively.

On the other hand, Fig. 3 shows the molecular weight of the polymers which should be produced under the conditions corresponding to those in Fig. 2. Here the molecular weight was compared at a low conversion (10%). It can be said that the molecular weight of the resultant polymers is independent of the kind of solvent if the other conditions are equal.

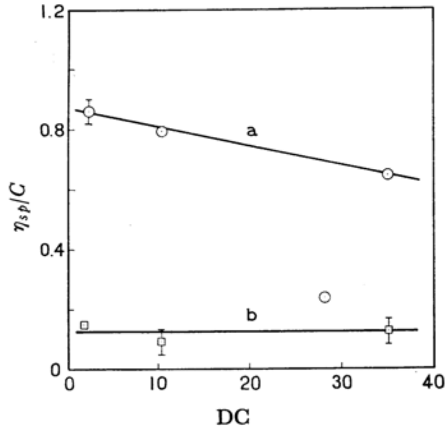

Fig. 3. Effect of a kind of solvents on the molecular weight of resultant polymers at conversion 10%.
Polymerization conditions are the same as in Fig. 2. $[M]_0$; a(○): 3.3 and b(□): 0.4 mol./l.

The Effect of the Polymerization Temperature.—In the polymerization of trioxane at a high monomer concentration, the increase in the polarity of the solvent remarkably increased the rate of polymerization. Therefore, the dependence of the polymerization reaction on the reaction temperature was studied in various solvents.

Figures 4, 5 and 6 show the time-conversion curves at various temperatures in ethylene dichloride, nitroethane and nitrobenzene respectively. The increaes in the reaction temperature increase the rate of polymerization and decreased the induction period of the polymerization. Except for the polymerization at a low temperature, the reaction order of the monomer as determined from the course of polymerization, as described in the previous paper,[6] was independent of the reaction temperature.

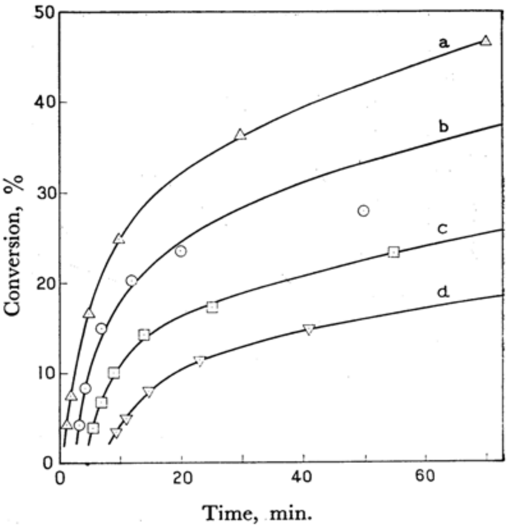

Fig. 4. Effect of temperature on the rate of polymerization in ethylene dichloride.
$[M]_0$; 3.3 mml./l., [C]; 5.0 mmol./l., $[H_2O]$; 2.5 mml./l., Polymerization temp. ; a(△): 46.0, b(○): 38.5, c(□): 30.0 and d(▽): 23.0°C

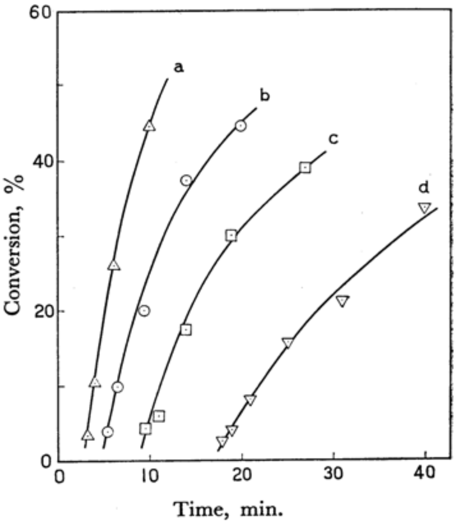

Fig. 5. Effect of temperature on the rate of polymerization in nitroethane.
$[M]_0$; 3.3 mol./l., [C], 2.5 mmol./l., $[H_2O]$; 2.7 mmol./l., Polymerization temp.; a(△): 45.0, b(○): 38.0, c(□): 30.0 and d(▽): 23.0°C

The activation energy determined from the initial

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[6] T. Higashimura, T. Miki and S. Okamura, ibid., **39**, 31 (1966).

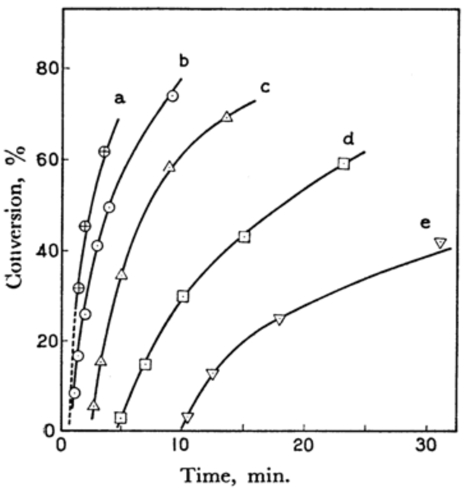


Fig. 6. Effect of temperature on the rate of polymerization in nitrobenzene.
$[M]_0$; 3.3 mol./l., [C]; 2.5 mmol./l., $[H_2O]$; 3.6 mmol./l., Polymerization temp.; a(⊕): 30.0, b(○): 23.0, c(△): 15.0, d(□): 8.0 and e(▽): 3.0°C

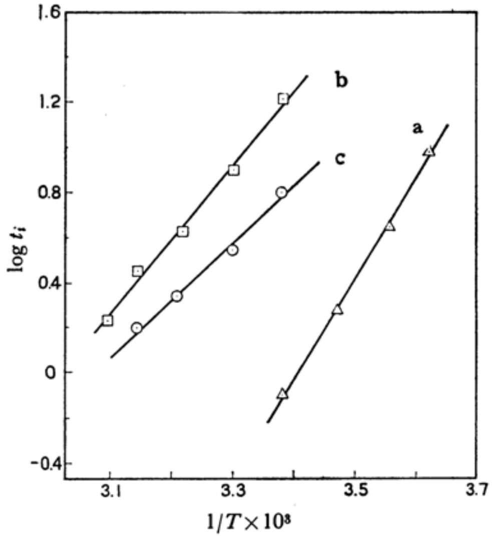


Fig. 8. Arrhenius plot of the induction period in various solvents.
Calculated from Figs. 4—6. Solvent; a(△): nitrobenzene, b(□): nitroethane and c(○): ethylene dichloride

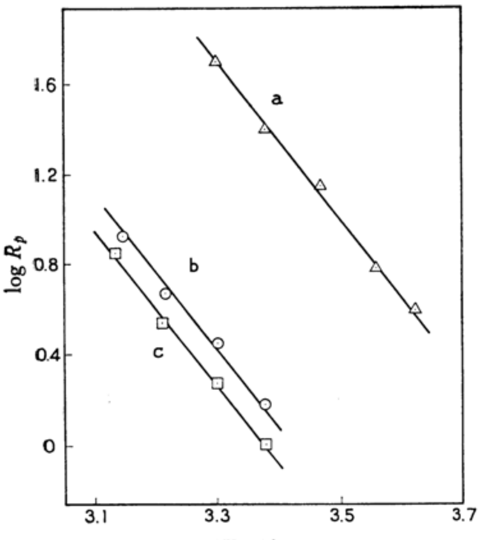


Fig. 7. Arrhenius plot of the initial rate in various solvents.
Calculated from Figs. 4—6. Solvent; a(△): nitrobenzene, b(○): nitroethane and c(□): ethylene dichloride

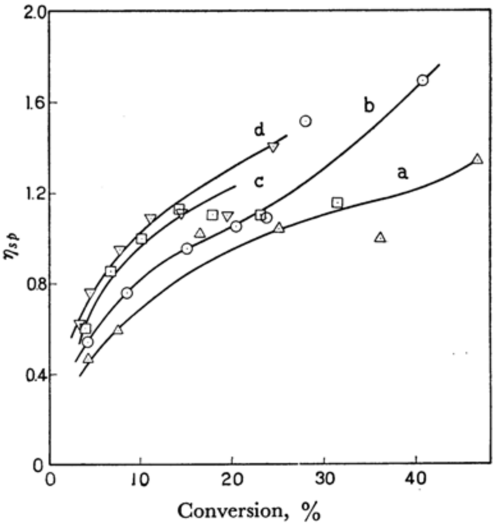


Fig. 9. Effect of temperature on the molecular weight of resultant polymers in ethylene dichloride.
Polymerization conditions are the same as in Fig. 4. Temp.; a(△): 46.0, b(○): 38.5, c(□): 30.0 and d(▽): 23.0°C

rate of these curves was about 16 kcal./mol., as is shown in Fig. 7, in each solvent,

By plotting the logarithms of the induction period against the reciprocal of temperature, the linear correlation was obtained in all the solvents, as Fig. 8 shows. The activation energy with respect to the induction period, as determined from the slope of each line in Fig. 8, was smaller the smaller the dielectric constant of the solvent.

The polymerization temperature also affected the molecular weight of the resultant polymers. Figures 9, 10 and 11 show the relations between the conversion and the molecular weights of the polymers obtained in Figs. 4, 5 and 6 respectively. An increase in the polymerization temperature decreased the molecular weight of the resultant

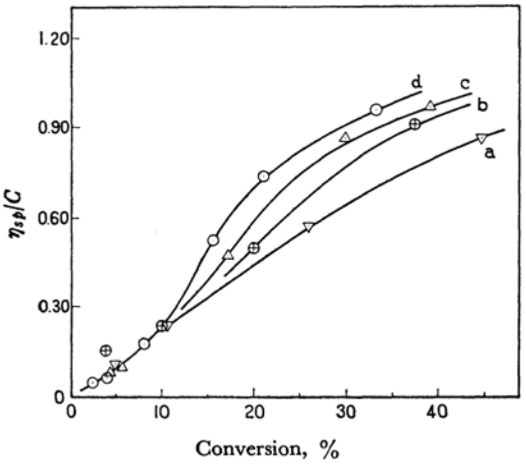


Fig. 10. Effect to temperature on the molecular weight of resultant polymers in nitroethane. Polymerization conditions are the same as in Fig. 5. Temp.; a(▽): 45.0, b(⊕): 38.0, c(△): 30.0 and d(○): 23.0°C

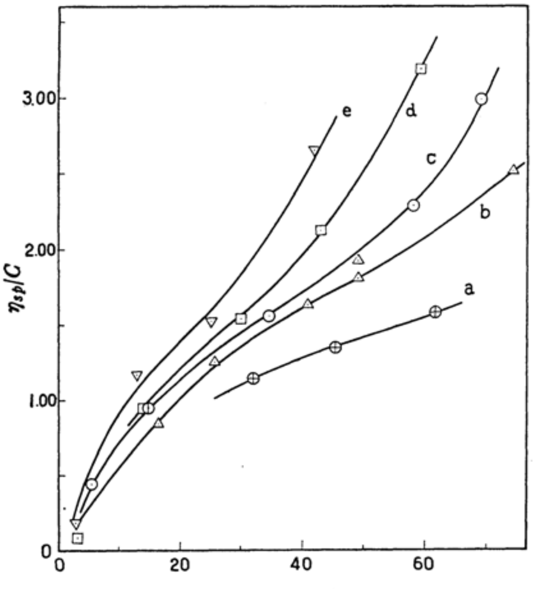


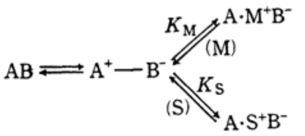
Fig. 11. Effect of temperature on the molecular weight of resultant polymers in nitrobenzene. Polymerization conditions are the same as in Fig. 6. Temp.; a(⊕): 30.0, b(△): 23.0, c(○): 15.0, d(□): 8.0 and e(▽): 3.0°C

polymers. This tendency has also been found in the polymerization of trioxane in toluene, a non-polar solvent.7)

Discussion

One of the most remarkable characteristics of the solution polymerization of trioxane is the effect of the polarity of the solvent on the polymerization rate. At a high monomer concentration, an increase in the dielectric constant of the solvent increased the rate of polymerization, as in vinyl polymerization. On the other hand, at a low monomer concentration, an increase in the dielectric constant decreased the rate of polymerization. As the molecular weight of the polymers produced did not greatly depend on the dielectric constant of the solvent, the change in the polymerization rate with the kind of solvent is probably caused by the initiation reaction.

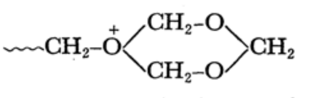
In general, an increase in the dielectric constant of a solvent ought to facilitate a reaction in which the neutral catalyst molecule itself dissociates to produce an ionic species. Therefore, the behavior observed at the high monomer concentration is probably normal. The unusual behavior observed at the low monomer concentration suggests that some reactions which decrease the polymerization rate are present. This postulate is also supported by the large kinetic order of the initial monomer concentration in a polar solvent.6) It may be considered that the catalyst (AB) dissociates to the ion-pairs ($A^+—B^-$), and that they then are stabilized by solvation with monomer (M) or solvent molecules (S), as is shown in Eq. 1. The solvation of ion-pairs with a monomer implies the



$$\mathrm{AB} \rightleftharpoons \mathrm{A^{+}—B^{-}} \begin{array}{l} \xrightleftharpoons[\mathrm{(M)}]{K_{\mathrm{M}}} \mathrm{A\cdot M^{+}B^{-}} \\ \xrightleftharpoons[\mathrm{(S)}]{K_{\mathrm{S}}} \mathrm{A\cdot S^{+}B^{-}} \end{array} \qquad (1)$$

occurrence of the initiation reaction. As A^+ will be solvated mainly with monomers at a high monomer concentration, the rate-determining step in the initiation reaction is possibly the process in which AB dissociates. In this case, the dissociation constant, K_1, increases with the dielectric constant, and the active centers (AM^+) are rapidly formed as the dielectric constant of the system increases.

At a low monomer concentration the formation of the active centers is in competition with the reaction in which A^+ is solvated with solvent molecules. It has been reported that the trioxane molecule has no great complex-forming ability with the carbonium ion indicated in Eq. 2, i. e., the basicity of trioxane is not very large.8) In



(2)

fact, in the copolymerization of 3, 3-bis(chloromethyl)oxethane (BCMO) with trioxane, the copolymer was not obtained, was obtained only the

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7) T. Higashimura, M. Tomikawa and S. Okamura, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 712 (1962).

8) S. Iwatsuki, M. Okada, Y. Yamashita and Y. Ishii, ibid., **67**, 1236 (1964).

homopolymer of BCMO.⁽⁹⁾ Therefore, it may be expected that, in a polar solvent, K_S will be larger than K_M and that the active center will be produced with difficulty at a low monomer concentration because A^+ will be solvated with the solvent and so become inert. It has been reported that nitro compounds act strongly as transfer agents in the cationic polymerization of styrene.⁽¹⁰⁾ This is one instance in which a polar solvent may stabilize a carbonium ion. On the other hand, in a non-polar solvent such as *n*-hexane, A^+ is not stabilized by solvation with a solvent, but by solvation with a monomer. Such a consideration can explain qualitatively the dependence of the polymeriz ation rate onthe dielectric constant of the solvent.

If the relation indicated in Eq. 1 is valid, the large kinetic order of the initial monomer concentration in the polar solvent is understandable. That is, in the polar solvent, a decrease in the initial monomer concentration implies an increase in the solvent molecule (S), which so stabilizes A^+ that the active centers are not produced. Consequently, a decrease in the initial monomer concentration rapidly decreases the rate of polymerization.

Although the meaning of the induction period is not clear, it must be related to the time during which a certain amount of the active center is produced. It is also clear that the formation of the active centers is hindered by water. This may be explained by the idea which has been described above, the idea that the temperature coefficient is smaller, the smaller the dielectric constant of the solvent. That is, the destruction of the ionic active-center by a water molecule should be easier in a non-polar solvent than in a polar solvent.

The activation energy of the initial rate of polymerization in a polar solvent was independent of the kind of solvent. Although no detailed discussion can be carried out becuase of the obscurity of the elementary reactions in each solvent, it may be inferred that the reaction mechanisms in these halogenated and nitronized solvents is not graetly different. The activation energy in benzene, a non-polar solvent, was reported by Rakova et al.⁽¹¹⁾ to be 12 kcal./mol.; this value was estimated by a method different from ours.

The activation energy for the decomposition of polyoxymethylene catalyzed by acids has been reported to be about 19 kcal./mol.⁽¹²⁾ Since the molecular weight of polymers decreased slightly as the reaction temperature was raised in our work, it is clear that the decomposition of the polymers during polymerization did not greatly affect the molecular weight.

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9) T. Higashimura, Y. Kitagawa and S. Okamura, unpublished data.

10) D. H. Jenkinson and D. C. Pepper, *Proc. Roy. Soc.*, **A263** 82 (1961).

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

12) J. Mejzlik, *Macromol. Chem.*, **59**, 184 (1963).