

Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. III. Study on Larger-Scale Copolymerization

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Synopsis

The iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal has been studied using 15 l kneader-type reactor. Effects of the addition method of the 1,3-dioxolane-methylal solution on the copolymerization has been mainly discussed. The copolymerization rate, intrinsic viscosity, and thermal stability of the copolymer were found to be largely dependent on the addition method of the 1,3-dioxolane-methylal solution, i.e., if the solution is added all at once, properties of the copolymer are different at the early stage than at the later stage of the copolymerization, while on successive addition of the solution, the copolymer properties become almost constant irrespective of the polymerization time. Therefore, it was suggested that 1,3-dioxolane and methylal can easily diffuse through the copolymer layer formed on the surface of the tetraoxane particle and reacts with an active center as copolymerization proceeds.

INTRODUCTION

In the previous paper,^{1,2} the authors have studied in detail the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal. They found that (1) in this copolymerization, oxymethylene copolymer of excellent thermal stability is very easily obtained in a high polymer yield; (2) 1,3-dioxolane reacts as a comonomer to elevate thermal stability of the copolymer, and methylal acts as a strong chain transfer reagent to control molecular weight of the copolymer; (3) composition and molecular weight of the copolymer vary largely with increasing the copolymerization time, as reactivities of 1,3-dioxolane and methylal with an active center are much higher than that of tetraoxane and dispersion of them in tetraoxane crystal is heterogeneous; (4) the copolymerization proceeds from the surface to the center of the tetraoxane crystal as if it were a core model.

The authors believe that this copolymerization system is worthy of further study for the manufacture of poly(oxymethylene). The main purpose of this paper is to make clear the effects of the addition methods, i.e., how to add 1,3-dioxolane, methylal, and iodine to tetraoxane crystal on the copolymerization when a relatively large-scale reactor (15 l kneader-type reactor) is used. Further,

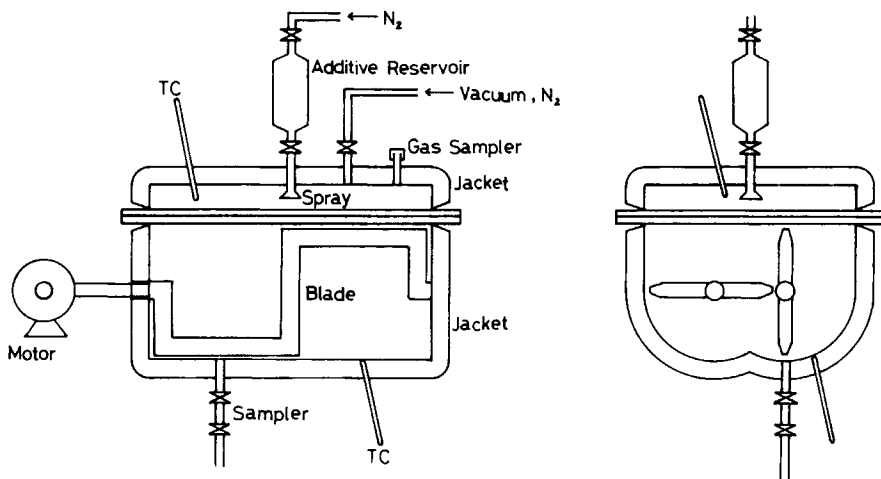


Fig. 1. Schematic drawing of polymerization reactor: TC, thermocouple.

when 1,3-dioxolane and methylal were fractionally added to tetraoxane monomer, the influences of 1,3-dioxolane, methylal, and iodine and of the polymerization temperature on this copolymerization were investigated.

EXPERIMENTAL

Commercial tetraoxane (Mitsuiotsu Chemical Co. Ltd.) was purified by sublimation under reduced pressure of about 5–8 mm Hg at a constant temperature of 80°C. The amounts of various impurities in the purified tetraoxane were reported previously.¹ Before polymerization, the purified tetraoxane was crushed into granules smaller than 18 mesh (1 × 1 × 1 mm). The purification methods of 1,3-dioxolane, methylal, and iodine have been described in detail in the previous paper.¹

The copolymerization was carried out using the kneader-type reactor (15 l) whose schematic drawing is shown in Figure 1. A solution which consists of 1,3-dioxolane, methylal, and iodine was added to tetraoxane through a spray nozzle in which the solution was pressurized by nitrogen gas. Only when the solution was continuously added, a quantitative volume pump connected directly to the spray nozzle was used. In order to pursue a time dependence of this copolymerization, a small amount of the reaction mixture was sampled at appropriate time intervals from a sampling nozzle equipped at the bottom of the reactor. The reaction mixture was kept at a constant polymerization temperature by controlling the temperatures of the jackets.

The purified tetraoxane (4 kg) was put into the reactor. The atmosphere of air in the reactor was replaced by nitrogen gas. Then, tetraoxane in the reactor was heated to polymerization temperature under stirring. The necessary amounts of the solution consisting of 1,3-dioxolane, methylal, and iodine and which was prepared just before use were sprayed through the nozzle into the reactor to initiate the copolymerization. In this paper, concentrations of 1,3-dioxolane and methylal were calculated by percentage of their milliliter-per-gram content of tetraoxane and denoted in an abbreviate form by %. Iodine was denoted by ppm based on the amount of tetraoxane.

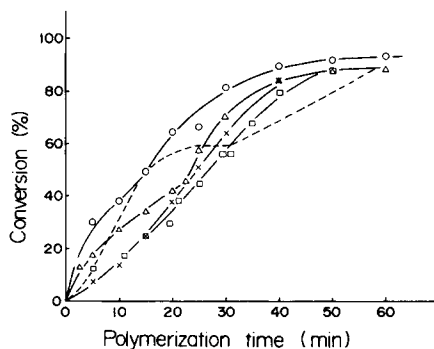


Fig. 2. Effect of addition methods of 1,3-dioxolane-methylal solution on conversion curve: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.25%; polymerization temperature, 105°C; (O) one-addition copolymerization; (Δ) two-addition; (X) four-addition; (□) continuous addition; (- - -) beaker-scale experiment.

In this study, the copolymerization experiments were classified by the addition method of 1,3-dioxolane and methylal to tetraoxane as follows:

1. One-addition copolymerization: 1,3-dioxolane-methylal solution which dissolved iodine was added all at once to tetraoxane previously heated to the polymerization temperature.

2. Two-addition copolymerization: Iodine was dissolved in one half of the total amount of 1,3-dioxolane-methylal solution, and the solution thus obtained was sprayed onto tetraoxane to initiate the copolymerization. The residual one-half of the 1,3-dioxolane-methylal solution was added to the reaction mixture at a polymerization time of 20 min.

3. Four-addition copolymerization: After iodine was dissolved in two fifths of the total amount of the 1,3-dioxolane-methylal solution, this solution was sprayed into the reactor to initiate the copolymerization. Subsequently, each one-third of the residual 1,3-dioxolane-methylal solution was successively added to the reaction mixture at 10-min intervals (i.e., at a polymerization time of 10, 20, and 30 min).

4. Continuous-addition copolymerization: Iodine was dissolved in 10 ml of the 1,3-dioxolane-methylal solution. This solution was sprayed onto tetraoxane to start the copolymerization reaction. Immediately, two thirds of the residual amounts of the solution were continuously added with a constant speed into the reactor in the first 10 min. Subsequently, one-third of that was continuously added in the next 15 min.

The reaction mixture was washed with a water-acetone solution containing 2 wt % sodium thiosulfate to remove residual reactants and other soluble products which may be formed during the copolymerization. The copolymer was dried under vacuum to determine copolymer yield gravimetrically.

Intrinsic viscosity, thermal stability, and melting point of the copolymer were determined by the same method as mentioned in the previous paper.¹

RESULTS AND DISCUSSION

Copolymer yield-polymerization time curves obtained at a constant temperature (105°C) and at various addition methods of 1,3-dioxolane-methylal solution are shown in Figure 2 in comparison with that (dashed line) obtained by a

beaker-scale copolymerization (reported in a previous paper¹). As shown in this figure, an initial rate of the one-addition copolymerization was larger than those of the other copolymerization methods. The copolymerization rate, however, decreased with increasing polymerization time without any knick observed for the yield-time curve obtained by the beaker-scale copolymerization.

The copolymerization rate of the two-addition copolymerization increased steeply at the polymerization time of 22.5 min to give a knick on the yield-time curve because of the second addition of 1,3-dioxolane-methylal solution. Further, initial rates of the four-addition and the continuous-addition copolymerizations were smaller than those of the one- and two-addition copolymerizations, although the copolymer yield of these copolymerizations increased linearly with increasing polymerization time. From the yield-time curves, it is suggested that the fewer the addition number of 1,3-dioxolane-methylal solution (i.e., the more the amount of 1,3-dioxolane-methylal solution added at the first time), the larger the initial rate of the copolymerization and the decrease of the copolymerization rate in the later stage of the copolymerization. However, the polymerization time when copolymer yield reaches the saturation value was nearly constant regardless the addition method of 1,3-dioxolane-methylal solution.

The difference on the yield-time curve between beaker-scale and the one-addition copolymerization (i.e., with and without a knick on the curves) could be explained as follows. In the previous paper,¹ it was suggested that 1,3-dioxolane and methylal are almost consumed in the early stage of the copolymerization because of the large reactivities of 1,3-dioxolane and methylal with an active center. Although in the beaker-scale copolymerization the reaction mixture was allowed to stand overnight before copolymerization, it was reasonably considered that the tetraoxane crystal can be approximately divided into two parts, i.e., one is the surface region in which relatively large amounts of 1,3-dioxolane and methylal are dispersed, and the other is the center region of the tetraoxane crystal in which 1,3-dioxolane and methylal are scarcely dispersed before copolymerization and they diffuse from the outside as copolymerization proceeds. Therefore, it was concluded that the yield-time curve has a knick because of the remarkable difference in copolymerization rate attributed to the concentrations of 1,3-dioxolane and methylal in these regions of tetraoxane crystal. On the other hand, in the one-addition copolymerization, 1,3-dioxolane and methylal were rapidly consumed in the early stage of the copolymerization (their consumption rates were measured by gas chromatography and will be reported in detail in a subsequent paper). However, as the copolymerization reaction takes place simultaneously with the addition of 1,3-dioxolane and methylal, 1,3-dioxolane and methylal disperse as the copolymerization proceeds, so that their concentrations in the tetraoxane particle vary continuously from the surface to the center. Therefore, it is considered that the yield-time curve does not have a knick.

On the contrary, it could be explained that in the two-addition copolymerization, the acceleration of the copolymerization observed immediately after the second addition of 1,3-dioxolane-methylal solution can be attributed to an increment in initiation reaction due to the second addition. As mentioned in the previous paper, Watanabe et al.³ found that in iodine-initiated, solid-state polymerization of tetraoxane, the polymerization rate is accelerated by a small amount of solvent, such as benzene, 1,4-dioxane, and methanol, and also found

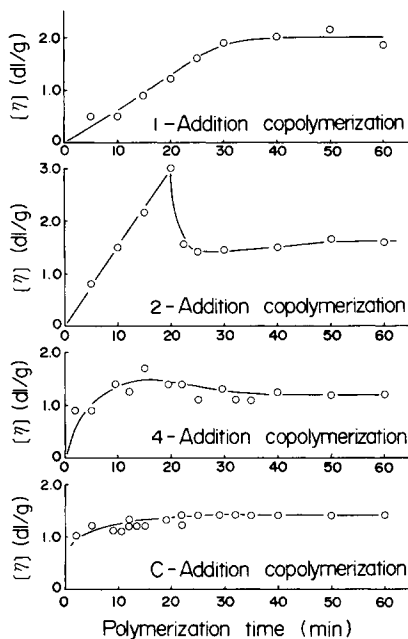


Fig. 3. Effect of addition methods of 1,3-dioxolane-methylal solution on intrinsic viscosity of copolymer: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.25%; polymerization temperature, 105°C.

that the higher the solubility of tetraoxane in the solvent, the higher the initial rate of polymerization. And they concluded that in the solid-state polymerization of tetraoxane, iodine initiates more easily in the presence than in the absence of solvent. In the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal, since 1,3-dioxolane and methylal act not only as a solvent of tetraoxane, but also a comonomer and a chain transfer reagent, respectively, the reaction mechanism in this system is more complicated than that found by Watanabe et al. In the four-addition and the continuous-addition copolymerization, 1,3-dioxolane and methylal were gradually consumed during the copolymerization, since they were added successively and continuously in the course of polymerization.

Therefore, it is suggested that, in the four-addition and the continuous-addition copolymerization, actual concentrations of 1,3-dioxolane and methylal in the reactor are approximately constant regardless of the polymerization time. The time dependences of the copolymerization rate were nearly constant so that the yield-time curves became approximately straight. Further, as the copolymerization reaction proceeds from the surface of tetraoxane particle to the center, it might be considered that 1,3-dioxolane and methylal diffuse easily into central region of monomer particle through the copolymer formed at the surface region in the early stage of the copolymerization.

Figure 3 shows the polymerization time dependence of the intrinsic viscosity of the copolymer obtained in the one-, the two-, the four-, and the continuous-addition copolymerizations. Intrinsic viscosity of the copolymer obtained by the one-addition copolymerization increased monotonously with increasing polymerization time. In the two-addition copolymerization, the intrinsic vis-

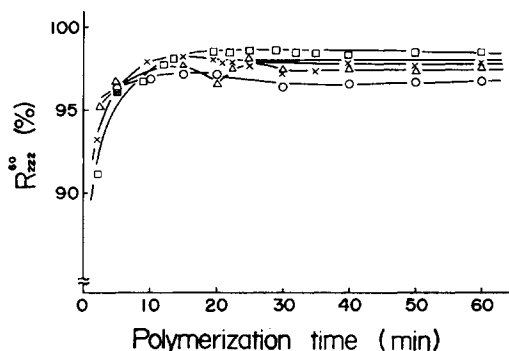


Fig. 4. Effect of addition methods of 1,3-dioxolane-methylal solution on thermal stability of copolymer: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.25%; polymerization temperature, 105°C; (O) one-addition copolymerization; (Δ) two-addition; (\times) four-addition; (\square) continuous addition.

cosity of the copolymer increased during first 20 min and fell suddenly right after the second addition of 1,3-dioxolane-methylal solution, and then became approximately constant. The sudden fall in the intrinsic viscosity can be attributed to the rapid increase in chain transfer reaction and in initiation reaction due to the second addition of 1,3-dioxolane-methylal solution, since, as mentioned previously, methylal reacts as a strong chain transfer reagent and 1,3-dioxolane accelerates initiation reaction in this system. Moreover, the gel permeation chromatography of the copolymer suggested that scission of the poly(oxymethylene) main chain may occur by the second addition of 1,3-dioxolane-methylal solution. A more detail study on gel permeation chromatography of the copolymer will be reported in a subsequent paper. On the other hand, the intrinsic viscosities of the copolymer obtained by the four-addition and the continuous-addition copolymerization scarcely varied to give a nearly constant value after a polymerization time of 10 min.

Figure 4 shows the polymerization time dependence of the thermal stability, R_{222}^{60} , of the copolymer. In the early stage of the copolymerization, i.e., within a polymerization time of 5 min, R_{222}^{60} values of the copolymer obtained by the four- and the continuous-addition copolymerization were lower than those found for the one-addition copolymerization. After polymerization time of ca. 10 min, R_{222}^{60} values of the copolymer for the four- and the continuous-addition copolymerization, on the contrary, became higher and, particularly in the continuous copolymerization, reached a constant value of over 98% regardless of the polymerization time.

Figure 5 shows the dependences of R_{222}^{60} of the copolymer obtained by the one- and the four-addition copolymerization on the 1,3-dioxolane concentration. R_{222}^{60} values of the copolymer for the one-addition copolymerization increased with increasing 1,3-dioxolane concentration. At the lower 1,3-dioxolane concentration, e.g., at 2% 1,3-dioxolane, R_{222}^{60} values were lower after a polymerization time of 30 min. In the four-addition copolymerization, however, R_{222}^{60} values of the copolymer gave approximately similar curves irrespective of 1,3-dioxolane concentration. In the two-addition copolymerization, as seen in Figures 3 and 4, the characteristic changes in intrinsic viscosity and R_{222}^{60} values due to the second addition of 1,3-dioxolane-methylal solution suggest that the added

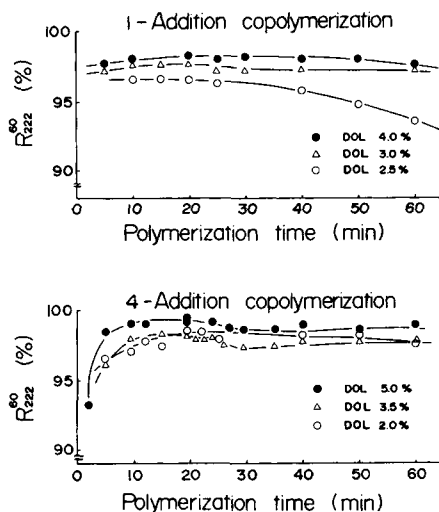


Fig. 5. Effect of 1,3-dioxolane concentration on thermal stability of copolymer: iodine, 30 ppm; methylal, 0.25%; polymerization temperature, 105°C.

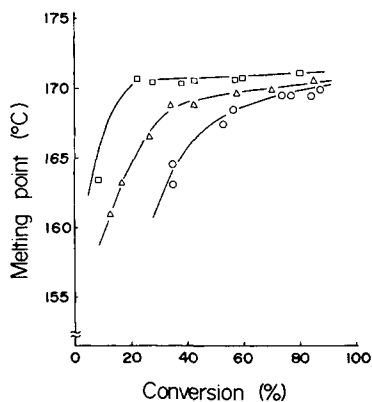


Fig. 6. Relationship between melting point and yield of copolymer at various addition methods of 1,3-dioxolane-methylal solution: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.25%; polymerization temperature, 105°C; (○) one-addition copolymerization; (△) two-addition, (□) four-addition.

1,3-dioxolane and methylal diffuse easily through the copolymer layer formed before the second addition and react with active center. Further, when 1,3-dioxolane and methylal were added in proportion to their consumption rate, e.g., in the four- and the continuous-addition copolymerization, the copolymers thus obtained had constant intrinsic viscosity and R_{222}^{60} values regardless polymerization time. This result also supports the suggestion mentioned above.

In order to clarify further the effects of the addition method of 1,3-dioxolane-methylal solution on the copolymerization of tetraoxane, the melting point of the copolymer was determined by differential scanning calorimetry. For the one-, the two-, and the four-addition copolymerizations, the melting point of the copolymer as a function of copolymer yield is shown in Figure 6. It can be seen that, for the one-addition copolymerization, the content of 1,3-dioxolane in the

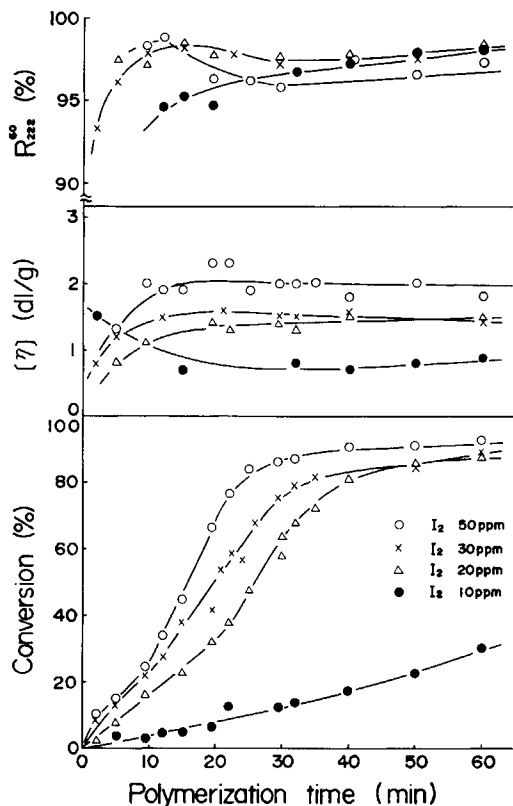


Fig. 7. Effect of iodine concentration on four-addition copolymerization: 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C.

copolymer is larger in the early stage of the copolymerization and decreases gradually with progress of the copolymerization, since the melting point increased with the copolymer yield. In the four-addition, however, the melting point of the copolymer was nearly constant about 171°C irrespective of the copolymer yield, except a lower copolymer yield (less than 20%). This result suggests that the content of 1,3-dioxolane in the copolymer obtained in this system is approximately constant.

From the results mentioned above, we can conclude the following: In the one- and the two-addition copolymerization, the molecular weight and the content of 1,3-dioxolane of the copolymer are considerably different between at the early stage and at the later stage of the copolymerization. In contrast, in the four- and the continuous-addition copolymerization, they are approximately constant. Measurements of differential scanning calorimetry, gel permeation chromatography, and high-resolution NMR of the copolymer obtained in this system have been carried out and will be reported in detail in a subsequent paper.

In order to study further this copolymerization system, the four-addition copolymerization has been investigated in detail. The polymerization time dependences of yield, intrinsic viscosity, and thermal stability of the copolymer obtained in the range of 10 to 50 ppm I_2 are shown in Figure 7. It is known that the molecular weight of polymer obtained in a solution polymerization decreases

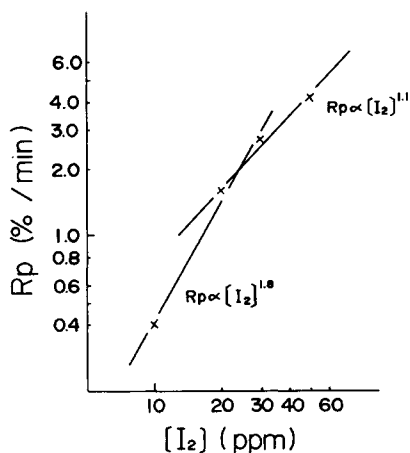


Fig. 8. Relationship between polymerization rate and iodine concentration; experimental condition is the same as in Fig. 7.

with increasing concentration of initiator. On the contrary, in this copolymerization system, intrinsic viscosity of the copolymer was found to increase with increasing the concentration of iodine. It is considered that the intrinsic viscosity of the copolymer becomes larger at a higher iodine concentration because copolymerization rate at a higher iodine concentration is so high that apparent concentration of methylal becomes relatively lower. It may also be suggested that diffusion of methylal in tetraoxane is lower than the copolymerization rate at a higher concentration of iodine. R_{222}^{60} of the copolymer obtained at 50 ppm I_2 decreased in the polymerization time range of 15 to 25 min. This finding can be explained in the same manner as above, i.e., the apparent concentration of 1,3-dioxolane in the neighborhood of the active center becomes lower on account of rapid increase in the polymerization rate at a polymerization time of ca. 12 min.

The logarithmic plot of the copolymerization rate obtained in Figure 7 against iodine concentration is shown in Figure 8. In this copolymerization system, the experimental values, such as copolymer yield, intrinsic viscosity, and thermal stability, obtained especially at the early stage of copolymerization may scatter because of heterogeneous dispersion of 1,3-dioxolane, methylal, and iodine in the reactor and of a temporary drop in the polymerization temperature due to the addition of 1,3-dioxolane-methylal solution. Therefore, the copolymerization rates plotted in Figure 8 were determined in the polymerization time ranging from 10 to 20 min. The plots in Figure 8 can be regarded as a straight line the slope of which is 1.1 in the range of 20 to 50 ppm I_2 , although a plot at 10 ppm I_2 deviated from this line. It is well known that in a solution polymerization initiated by cationic initiator, the initial rate of polymerization is proportional to the first order of initiator concentration.^{4,5} In the beaker-scale study on the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane, as described in the previous paper,¹ the initial rate of the copolymerization was found to be proportional to the first order of iodine concentration. Therefore, it is reasonably concluded that in the four-addition copolymerization, the rate of the copolymerization is proportional to the first order of iodine con-

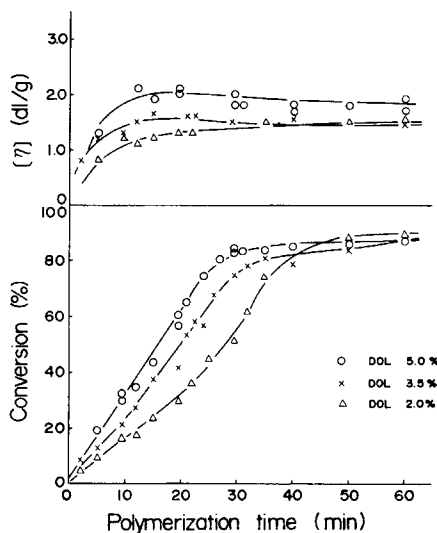


Fig. 9. Effect of 1,3-dioxolane concentration on yield and intrinsic viscosity of copolymer in four-addition copolymerization: iodine, 30 ppm; methylal, 0.15%; polymerization temperature, 107°C.

centration, within experimental error. On the other hand, the deviation of R_p at 10 ppm I_2 from this relationship may be explained as follows. A small part of iodine may remain in the space of the reactor (15 l). This amount of iodine may be negligible if the total amount of iodine added to polymerization system is large enough. However, when the total amount of it is rather small, iodine which does not take part in the polymerization should be taken into consideration. Although the exact amount of iodine which remains in the space of the reactor cannot be estimated, the lower concentration of iodine, such as 10 ppm, may correspond to the latter case. Therefore, the apparent rate of copolymerization at 10 ppm I_2 became extremely low.

Figure 9 shows the time dependences of yield and intrinsic viscosity of the copolymer obtained at various 1,3-dioxolane concentrations. In the four-addition copolymerization, the copolymerization rate increased with increasing 1,3-dioxolane concentration in a similar manner to that found for the beaker-scale copolymerization; and at 2% 1,3-dioxolane, the copolymerization rate was obviously accelerated after the third and last addition of 1,3-dioxolane-methylal solution. Further, in the time dependence of the intrinsic viscosity of the copolymer, it was found that the higher the 1,3-dioxolane concentration, the higher the intrinsic viscosity of the copolymer. This finding can be explained in the same manner as was done for the relationship between intrinsic viscosity and iodine concentration. That is, the apparent concentration of methylal in the vicinity of an active center becomes lower with increasing copolymerization rate which becomes higher in proportional to 1,3-dioxolane concentration.

Figure 10 shows the logarithmic plot of the copolymerization rate determined for Figure 9 as a function of 1,3-dioxolane concentration. In this case, 1,3-dioxolane concentration was determined from the sum of amounts of the first and the second addition (i.e., $\frac{2}{5}$ of the total amount of 1,3-dioxolane), and the copolymerization rate was obtained in the polymerization time ranging from 10

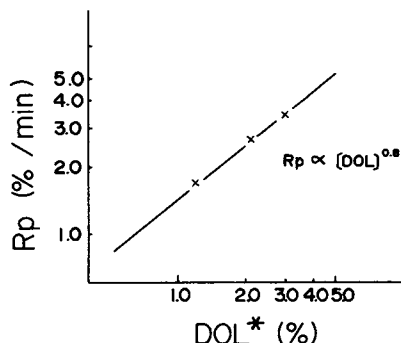


Fig. 10. Relationship between polymerization rate and 1,3-dioxolane concentration; experimental condition is the same as in Fig. 9. * 1,3-Dioxolane concentration plotted here presents the sum of amounts of the first and second addition (i.e., $\frac{2}{3}$ of the total amount of 1,3-dioxolane).

to 20 min. This plot gave a relation of $R_p \propto [\text{DOL}]^{0.8}$ which agrees with that found for the beaker-scale experiment.

The time dependences of yield, intrinsic viscosity, and thermal stability of the copolymer obtained at various methylal concentration are shown in Figure 11. In this copolymerization system, methylal reacts as a chain transfer reagent to influence not only molecular weight but also thermal stability of the copolymer. The copolymer has methoxyl endgroups due to the reaction of methylal. Although it was reported that the thermal stability of oxymethylene polymer with methoxyl endgroups is much higher than that of oxymethylene polymer with hydroxyl endgroups,⁶ the dependence of thermal stability of the copolymer on the methylal concentration, as shown in Figure 11, was hardly observed. It is, therefore, considered that the contribution of methylal to the thermal stability of the copolymer is negligibly small when 1,3-dioxolane concentration is considerably high as compared with methylal concentration. However, intrinsic viscosity of the copolymer obtained by the four-addition copolymerization decreased with increasing methylal concentration. As shown in Figure 11, the time dependence of intrinsic viscosity of the copolymer obtained in the presence of methylal became approximately constant after a polymerization time of 10 min.

In the absence of methylal, intrinsic viscosity of the copolymer was extremely higher than those of the copolymer obtained in the presence of methylal and increased remarkably with polymerization time. However, the intrinsic viscosity of the copolymer dropped slightly by the second addition of 1,3-dioxolane. This result may be attributed to a discernible increase in the initiation reaction rate by the second addition of 1,3-dioxolane. The intrinsic viscosity of the copolymer obtained after polymerization time of 15 min could not be measured because it was too difficult to dissolve the copolymer in *p*-chlorophenol. This difficulty may be caused by the very high molecular weight of the copolymer. The increase of copolymerization rate with increasing methylal concentration, as shown in Figure 11, can be explained in analogy with the copolymerization rate-1,3-dioxolane concentration relation mentioned above.

The log-log plot for methylal concentration and intrinsic viscosity of the copolymer obtained at the saturation yield is shown in Figure 12. This plot gave

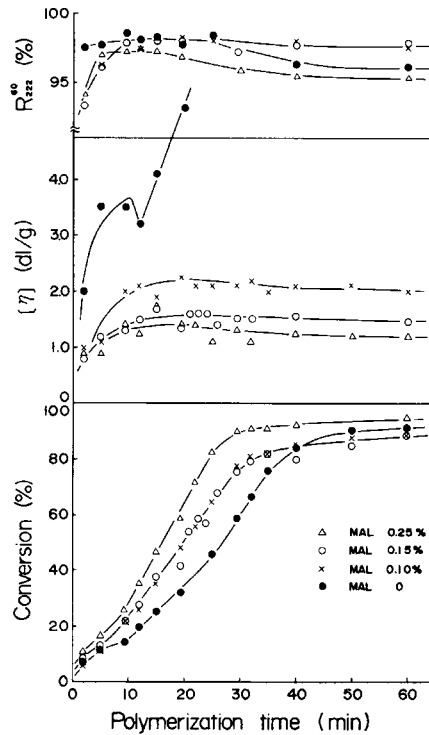


Fig. 11. Effect of methylal concentration on four-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; polymerization temperature, 107°C.

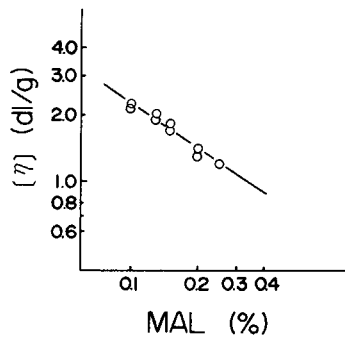


Fig. 12. Effect of methylal concentration on intrinsic viscosity of copolymer at a saturation yield in four-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; polymerization, 60 min at 107°C.

a straight line (i.e., $[\eta] \propto [\text{MAL}]$), which was almost the same as obtained for the beaker-scale experiment.

Figure 13 shows the temperature dependence of the four-addition copolymerization. Since, as mentioned above, apparent concentrations of 1,3-dioxolane and methylal seem to decrease with the copolymerization rate, the higher the polymerization temperature, the higher the intrinsic viscosity of the copolymer. However, as seen in Figure 13, the thermal stabilities of the copolymer obtained at 105° and 107°C were not different from each other. It is suggested that

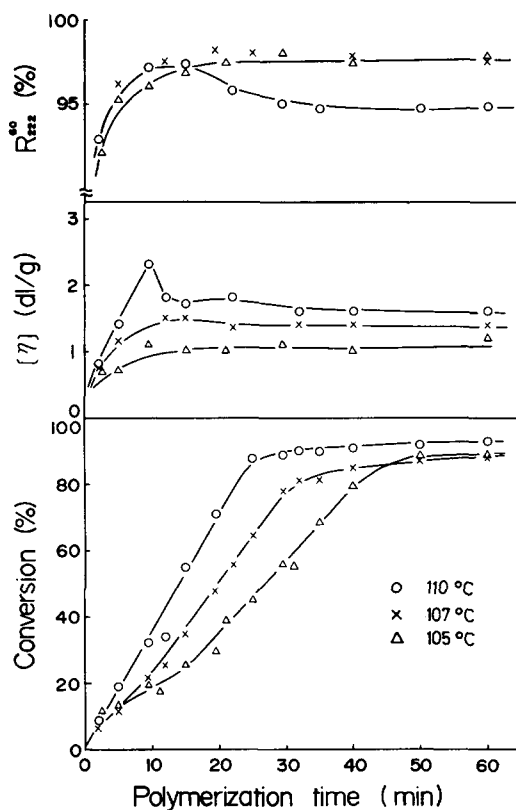


Fig. 13. Effect of polymerization temperature on four-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%.

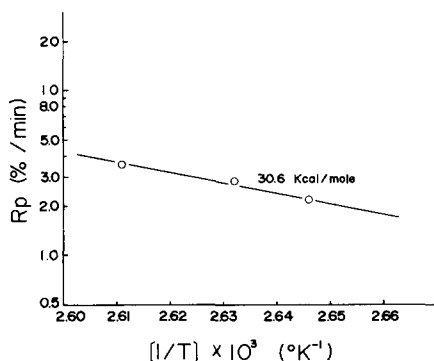


Fig. 14. Arrhenius plot of polymerization rate obtained in Fig. 13.

thermal stability of the copolymer is scarcely influenced by the copolymerization rate if 1,3-dioxolane concentration is high enough (such as 3.5%). On the other hand, intrinsic viscosity and thermal stability of the copolymer obtained at 110°C became lower after reaching maximum values. This finding indicates that the copolymer degrades at a higher temperature.

Figure 14 shows Arrhenius plots of the copolymerization rate obtained from Figure 13. The apparent activation energy in this system was given as 30.6

kcal/mole. This value agreed very closely with that obtained in the beaker-scale copolymerization at 2% 1,3-dioxolane concentration. This agreement seems to be reasonable because in the four-addition copolymerization, the actual 1,3-dioxolane concentration is nearly equal to 2% before a polymerization time of 20 min (before the third addition), and the copolymerization rates were determined by the yield-time curve in the range of 10–20 min of polymerization time.

Summarizing these results and the discussion we found the following: (1) By using 15 l kneader-type reactor, oxymethylene copolymer with an excellent thermal stability was obtained in high polymer yield in the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal. (2) The relations between the addition method of 1,3-dioxolane-methylal solution and the polymerization time dependence of this system on various factors were made clear. The copolymerization rate, intrinsic viscosity, and thermal stability of the copolymer were found to be largely dependent on the addition method of the 1,3-dioxolane-methylal solution. (3) It was suggested that 1,3-dioxolane and methylal can easily diffuse through the copolymer layer formed on the surface of monomer particles and react with an active center as copolymerization proceeds. (4) It was also indicated that in the four-addition copolymerization the dependences of copolymerization rate, intrinsic viscosity, and thermal stability of the copolymer on polymerization temperature and on 1,3-dioxolane and methylal concentrations are similar to those found for the beaker-scale experiment of this system.

In a subsequent paper, we will discuss further this 15 l kneader-scale copolymerization system on the basis of the characterization of the copolymer using DSC, GPC, and NMR in order to elucidate the mechanism of the copolymerization.

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