

# Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. I. Fundamental Study on Beaker-Scale Copolymerization

ISAO ISHIGAKI, YUHEI WATANABE, YOSUKE MORITA, KIYOSHI TAKADA, and AKIHIKO ITO, *Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment, Takasaki, Gunma, Japan*

## Synopsis

The iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal has been studied on a beaker scale. It was found that tetraoxane can be easily copolymerized with 1,3-dioxolane by a small amount of iodine as initiator and gives oxymethylene copolymer with excellent thermal stability in a high yield. The copolymerization was largely influenced by the concentrations of iodine, 1,3-dioxolane, and methylal, i.e., the polymerization rate increased with increase not only in iodine but also in 1,3-dioxolane, and the thermal stability and the molecular weight of the copolymer were mainly affected by 1,3-dioxolane and methylal concentration, respectively.

## INTRODUCTION

Poly(oxymethylene), the polymer of formaldehyde, is useful for engineering plastics due to its excellent mechanical properties, such as tensile strength, impact resistance, abrasion resistance, etc. Delrin and Celcon, manufactured by du Pont and Celanese, respectively, have been commercially available.

Poly(oxymethylene) is prepared by polymerizing monomeric formaldehyde and its cyclic oligomers, such as trioxane (trimer) and tetraoxane (tetramer). In general, formaldehyde is polymerized by ionic initiator in a liquid phase using appropriate solvent. The cyclic oligomers are polymerized not only in the liquid phase but also in the solid state by ionic initiator. They are also polymerized by ionizing radiation in the solid state. As is well known, it is too difficult to obtain a high molecular weight poly(oxymethylene) in the liquid phase unless monomer and solvent are rigorously purified. In the solid-state polymerization, however, a high molecular weight poly(oxymethylene) can be easily prepared even if monomers are not so carefully purified.<sup>1</sup>

It is well known that oxymethylene homopolymer is easily decomposed by heating, alkalis, and acids to form formaldehyde. Therefore, when poly(oxymethylene) is utilized as engineering plastics, it is indispensable to depress such a decomposition of polymer. Further, in order to give excellent mechanical

properties and moldability to polymer, it is also necessary for poly(oxymethylene) to have appropriately controlled molecular weight, as well as excellent thermal stability. Two methods are known for depression of the decomposition: one is the end-capping method<sup>2</sup> in which the unstable polymer chain end, the hydroxyl group, is substituted with a stable endgroup, such as acyl or ether groups; and the other is the copolymerization method<sup>3</sup> using comonomer with a molecular structure different from that of the monomer, whereby small amounts of the thermally stable units such as ethylene oxide ( $-\text{C}-\text{C}-\text{O}-$ ) are introduced into the poly(oxymethylene) chain. In the former, i.e., the end-capping method, the unstable chain end is usually acetylated with acetic anhydride. Delrin may be produced by this method. Celcon, the copolymer of trioxane and ethylene oxide, may be made by the latter method.

For the end-capping method, two processes are required: one is the polymerization process and the other, the stabilization process in which the molecular weight of polymer decreases. Therefore, high molecular weight poly(oxymethylene) must be obtained before its stabilization. On the other hand, if thermally stable and appropriately high molecular weight polymer is obtained by copolymerization, the copolymerization method seems to be advantageous compared with the end-capping method. Although trioxane and tetraoxane can easily copolymerize with 1,3-dioxolane or ethylene oxide in the liquid phase, it is too difficult, as mentioned above, to obtain the high molecular weight polymer without careful purification of monomers and solvent. In order to obtain the thermally stable, high molecular weight poly(oxymethylene), solid-state copolymerization of cyclic oligomers looks more promising from the viewpoint of monomer purification and the process.

Rösinger et al.<sup>4</sup> studied the solid-state copolymerization of trioxane with various cyclic ethers and formals by using  $\gamma$  radiation from a  $^{60}\text{Co}$  source and found that the unstable part of polymer is markedly reduced with increasing concentration of these comonomers. However, they obtained polymer of low molecular weight, probably due to the radiolysis of the polymer formed, since they used the in-source polymerization technique.

Sakamoto et al.,<sup>5</sup> studying the radiation-induced postpolymerization of trioxane with 1,3-dioxolane in the solid state, found that the thermal stability of the polymer is somewhat improved. Ishigaki et al.<sup>6</sup> also studied the solid-state copolymerization of trioxane with 1,3-dioxolane using postpolymerization technique and found that trioxane can be easily copolymerized to give a copolymer having high molecular weight and excellent thermal stability only when monomers are carefully purified in a rigorously dry, high-vacuum system. However, in both papers,<sup>5,6</sup> they found that the yield and molecular weight of the copolymer are decreased with increasing concentration of 1,3-dioxolane.

We have found that tetraoxane can be easily copolymerized with 1,3-dioxolane by a trace amount of  $\text{I}_2$  as an initiator in the solid state to give in a high-yield oxymethylene copolymer having excellent thermal stability and high molecular weight. Moreover, it has been also found that the molecular weight of copolymer can be arbitrarily controlled by addition of methylal as a chain transfer reagent to this system. We have investigated in detail this copolymerization system not only on a beaker scale but also on a relatively large scale (using a 15 l-kneader-type reactor) and elucidated the effects of various factors on this copolymerization, the reaction mechanism, the mechanical properties, etc.

The various interesting results obtained on this copolymerization system will be successively reported in several papers. In this paper, the results in the beaker-scale copolymerization will be discussed in detail.

## EXPERIMENTAL

### Materials

Commercial tetraoxane (Mitsuitoatsu Co. Ltd.) was purified by sublimation under reduced pressure of about 5–8 mm Hg at a constant temperature of 80°C. Water and formaldehyde, and methanol and trioxane, contained in the tetraoxane thus purified, were analyzed by Karl Fisher titration, colorimetric determination with phenyl hydrazine, and gas chromatography, respectively. The amounts of these impurities were less than 200 ppm of water, 10 ppm of formaldehyde, 10 ppm of methanol, and 200 ppm of trioxane. Before polymerization, the purified tetraoxane was crushed into granules in the range of 65–200 mesh. 1,3-Dioxolane was kept over sodium metal for a few weeks and then distilled over new sodium metal under a nitrogen stream. Methylal was kept over calcium chloride for a couple of days and refluxed over sodium metal for 6 hr and then distilled. Gas chromatography of the 1,3-dioxolane and methylal thus purified showed that no detectable amount of impurities (under ca. 1 ppm) is present. Iodine was purified by sublimation in the usual way.

### Apparatus and Procedure

To the necessary amount of a solution which consisted of 1,3-dioxolane, methylal, and iodine and which was prepared just before use was added 2 g of the purified tetraoxane into a glass ampoule (inner diameter 16 mm), and then the glass ampoule was sealed off at Dry-Ice temperature. In this paper, the concentrations of 1,3-dioxolane and methylal were calculated by percentage of their milliliter per gram of tetraoxane and denoted in an abbreviated form by %. Iodine was denoted by ppm based on the amount of tetraoxane. In order to disperse 1,3-dioxolane, methylal, and iodine homogeneously into the tetraoxane, the sample was left in the dark for ca. 24 hr at room temperature and then polymerized in a thermostated bath. The reaction mixture in the ampoule was poured into the acetone–water solution (1:1 by volume) containing 2 wt % sodium thiosulfate for neutralization of residual iodine. Subsequently, the reaction mixture was washed with water and hot acetone to remove residual reactants and other soluble products which may be formed during the polymerization, and the polymer was dried under vacuum for ca. 24 hr at room temperature. The polymer yield was determined gravimetrically.

The solution viscosity of the polymer was measured at 60°C in *p*-chlorophenol containing 2%  $\alpha$ -pinene after the polymer sample was dissolved at 115°C within 15 min. The molecular weight of the sample was calculated by using the equation<sup>7</sup>

$$[\eta] = 5.43 \times 10^{-4} \bar{M}_n^{0.66}$$

The thermal stability of the polymer was measured by weight loss measurement under a stream of nitrogen at 222°C using a thermobalance, and the result

was quoted as  $R_{222}^{60}$  value, i.e., percentage of the residual weight after 60 min of heating at 222°C.

A Perkin-Elmer differential scanning calorimeter, Model DSC-1, was used to determine the melting point of the polymer. Measurement was carried out under a nitrogen stream flowing through the sample holder assembly. A sample of 3 mg polymer was used, and the scanning rate was 16°C/min. In order to minimize the effect of crystal structure of the polymer, the peak point of the DSC curve in the second scan was measured as a melting point of the polymer. A first scan was done up to 222°C to avoid appreciable thermal decomposition of the sample, and then the temperature was lowered to 50°C, recrystallizing the specimen from its melt; and finally, a second scan was made through the melting range to obtain the DSC curve.

## RESULTS AND DISCUSSION

In the radiation-induced, solid-state copolymerizations of trioxane and tetraoxane with 1,3-dioxolane, it was found that the copolymerization rate becomes low compared with their homopolymerization rate. In the present study, however, it was found that the higher the 1,3-dioxolane concentration, the higher the initial rate in the solid-state copolymerization of tetraoxane initiated by iodine. Figure 1 shows the effects of 1,3-dioxolane concentration on the polymer yield-time curve under the following conditions: methylal, 0.15%; iodine, 30 ppm; polymerization temperature, 105°C. As 1,3-dioxolane concentration increased, the initial rate of the copolymerization and a polymerization time at which the polymer yield leveled off decreased. Further, the shape of the yield-time curve varied complicatedly with change in 1,3-dioxolane concentration. That is, at low concentration of 1,3-dioxolane (e.g., 0.3%), the curve was approximately straight, and curves with a knick were obtained at a higher concentration of 1,3-dioxolane (e.g., 1.0–5.0%), and then a smooth curve was obtained at further higher concentration (e.g., 7.5%). Particularly, this copolymerization of tetraoxane is characterized by curves with a knick as compared with those obtained in homopolymerization. This characteristic will be discussed later with the temperature dependence of this copolymerization.

A logarithmic plot of the initial rate as a function of 1,3-dioxolane concentration gave a straight line as shown in Figure 2. Watanabe et al.<sup>8</sup> studied the

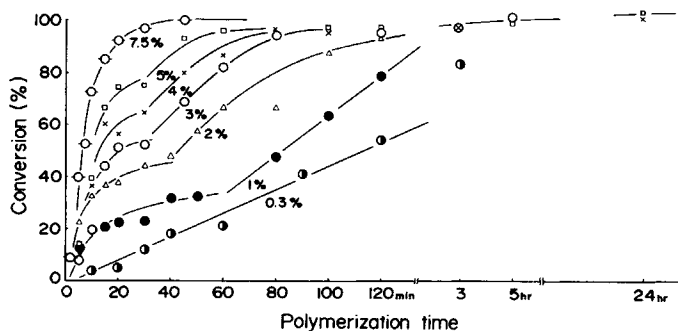


Fig. 1. Effect of 1,3-dioxolane concentration on polymer yield-time curves: iodine, 30 ppm; methylal, 0.15%; polymerization temperature, 105°C.

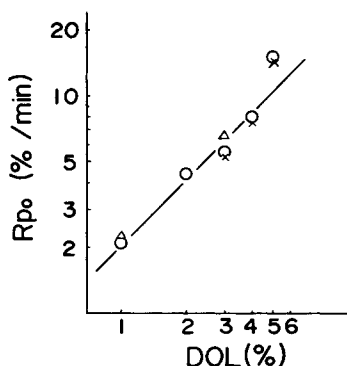


Fig. 2. Relationship between initial polymerization rate and 1,3-dioxolane concentration: iodine, 30 ppm; polymerization temperature, 105°C; methylal, (X) 0.20%, (O) 0.15%, ( $\Delta$ ) 0.10%.

effects of the addition of various solvents, such as benzene, nitrobenzene, 1,4-dioxane, methanol, etc. (in the range of 0.1–5% contents) on the solid-state polymerization of tetraoxane initiated by iodine and found that the larger the amount of solvent added, the higher the initial rate of polymerization, and also found that the logarithmic plot of the initial polymerization rate as a function of the amount of solvent gave a straight line the slope of which varies with the kind of solvent. They concluded that the initial rate of the polymerization increases with increasing solubility of tetraoxane in the solvent in the present study. The 1,3-dioxolane concentration dependence of the initial polymerization rate is compatible with their results. However, it should be considered that 1,3-dioxolane can undergo homopolymerization in the liquid phase with iodine as an initiator. Therefore, the mechanism of this copolymerization may be more complicated than that of polymerization of tetraoxane in the presence of an inert solvent, since 1,3-dioxolane affects both the initiation and the propagation reaction.

Figure 3 shows the relationship between 1,3-dioxolane concentration and thermal stability of the copolymer at a saturated yield under the condition in Figure 1. In general, in the copolymerization of tetraoxane with 1,3-dioxolane as well as that of trioxane with 1,3-dioxolane or ethylene oxide, the thermal stability of the copolymer is considered as one of the most reliable indications

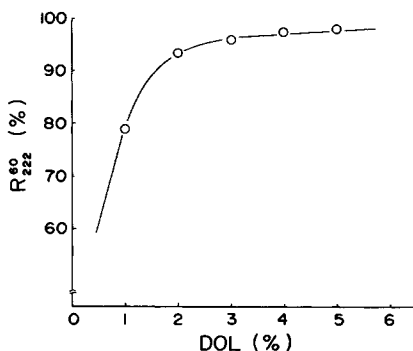


Fig. 3. Effect of 1,3-dioxolane concentration on thermal stability of copolymer obtained at a saturation yield: iodine, 30 ppm; methylal, 0.15%; polymerization temperature, 105°C.

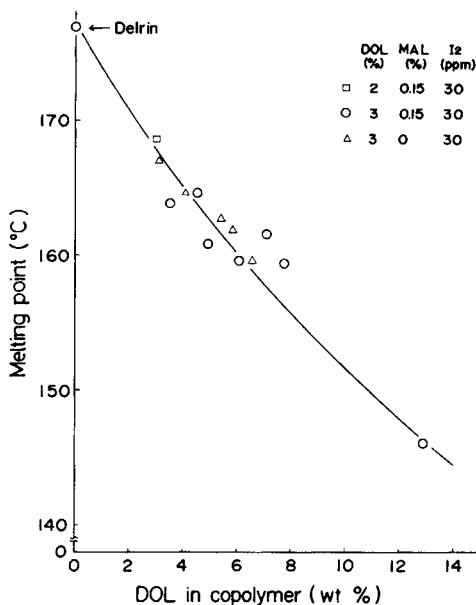


Fig. 4. Relationship between melting point and 1,3-dioxolane content in copolymer: polymerization temperature, 105°C.

to confirm whether tetraoxane copolymerizes with 1,3-dioxolane or not. While the thermal stability ( $R_{222}^{80}$ ) of the homopolymer obtained (by the polymerization of tetraoxane) in the absence of 1,3-dioxolane was less than 30%, the polymer obtained in the presence of 1,3-dioxolane is characterized by excellent thermal stability; and, particularly, the thermal stability of the polymer obtained at a concentration of over 3% 1,3-dioxolane was higher than 95%.

These results indicate clearly that tetraoxane copolymerizes with 1,3-dioxolane by iodine in the solid state to give a copolymer with excellent thermal stability. As mentioned above, 1,3-dioxolane may be polymerized by iodine. In order to examine it, the reaction mixture was extracted by hot acetone, and it was found

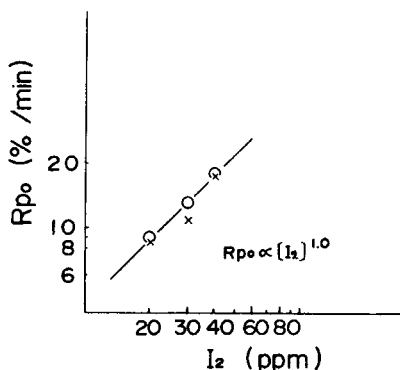


Fig. 5. Relationship between initial polymerization rate and iodine concentration: 1,3-dioxolane, 4.0%; polymerization temperature, 105°C; methylal, (O) 0.15%, (X) 0.10%.

that there was no change in the sample weight before and after the extraction and that any oligomer or polymer of 1,3-dioxolane were not detected in the extract. This result indicates that 1,3-dioxolane does not homopolymerize in this system. On the other hand, the melting point of the copolymer is another evidence of the copolymerization of tetraoxane with 1,3-dioxolane.

Figure 4 shows the relationship between the melting point of the copolymer and 1,3-dioxolane unit content in the copolymer. As shown later in another paper, it was found that the sum of the residual 1,3-dioxolane measured by gas chromatography and of 1,3-dioxolane incorporated into the copolymer chain, as determined by NMR spectroscopy, agreed very closely with the amount of 1,3-dioxolane added. Therefore, by subtracting the residual amount of 1,3-dioxolane from the added amount, it is possible to calculate the content of 1,3-dioxolane in the copolymer. As seen in Figure 4, the plot of the melting point as a function of the 1,3-dioxolane content in the copolymer gave a smooth curve, regardless of the original amounts of 1,3-dioxolane and methylal added in the polymerization system.

It is well known that the melting point of poly(oxymethylene) decreases with increasing the content of ethylene oxide units in the oxymethylene main chain.<sup>9,10</sup> It is also known that the melting point of poly(oxymethylene) with acetyl or methoxyl chain ends is as high as that of the homopolymers (ca. 178°C.)<sup>11</sup> As shown in Figure 4, all the melting points of the copolymer obtained in this study were lower than that of commercial Delrin, which is homopolymer of formaldehyde having acetyl endgroups. These results are consistent with that reported by Park,<sup>10</sup> who gave the relationship between the melting points and the ethylene oxide contents of the copolymer.

The molecular weight of the polymer should be considered one of the factors which influence the melting point of the polymer. However, it is known that the melting point of poly(oxymethylene) is scarcely influenced by the molecular weight if it is high enough ( $M_n \geq 1000$ ).<sup>11</sup> In this system, as discussed later, the molecular weight of the copolymer can be controlled by the amount of methylal added, since methylal reacts as a chain transfer reagent (i.e., the molecular weight of the copolymer decreases with increasing methylal concentration). The melting point of the copolymer was independent of methylal concentration (compare (O) and ( $\Delta$ ) in Fig. 4). Therefore, it can be concluded that the decrease in the melting point of the copolymer is mainly attributable to the incorporation of ethylene oxide units into the poly(oxymethylene) chain.

Figure 5 shows the dependence of the initial rate of the copolymerization on the amount of iodine as an initiator under the following conditions; 1,3-dioxolane, 4%; methylal, 0.15%; polymerization temperature, 105°C. The logarithmic plot of initial rate as a function of iodine concentration gave a straight line the slope of which is approximately 1.0 in the range of 20 to 40 ppm  $I_2$ . The initial rate is directly proportional to the iodine concentration. The  $I_2$  initiates the cationic polymerization of trioxane, vinylcarbazole, and various vinyl ethers in the liquid or solid state. Their mechanisms of initiation, however, are hardly elucidated in detail. Although the definite initiation mechanism in this system cannot be clarified, it may be presumed that the copolymerization of tetraoxane is initiated by a cationic mechanism. The dependence of the initial rate on iodine concentration and the fact that trioxane polymerizes by a cationic mechanism support the presumption mentioned above. In addition, as discussed in another paper,

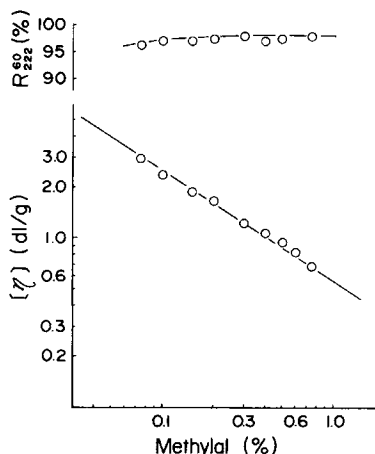


Fig. 6. Effect of methylal concentration on intrinsic viscosity and thermal stability of copolymer: iodine, 30 ppm; 1,3-dioxolane, 4.0%; polymerization temperature, 105°C.

this polymerization was perfectly inhibited by the addition of a small amount of  $\text{NH}_3$ .

As mentioned above, methylal acts as a chain transfer reagent in the copolymerization of tetraoxane. It is well known that, in the radiation-induced, solid-state polymerization of trioxane, methylal reacts as a strong chain transfer reagent to give a polymer with methoxyl endgroups ( $-\text{OCH}_3$ ) which contributes to the thermal stability of the polymer.

Figure 6 shows the relationships between methylal concentration and intrinsic viscosity and thermal stability of the copolymer obtained under the following conditions; 1,3-dioxolane, 4%; iodine, 30 ppm; polymerization temperature, 105°C. A logarithmic plot of intrinsic viscosity of the copolymer and methylal concentration gave a straight line. The intrinsic viscosity of the copolymer decreased with increasing methylal concentration. Consequently, it is considered that methylal reacts as a chain transfer reagent also in the iodine-initiated copolymerization of tetraoxane.

On the other hand, the thermal stability of the copolymer was scarcely influenced by the methylal concentration under the condition shown in Figure 6.

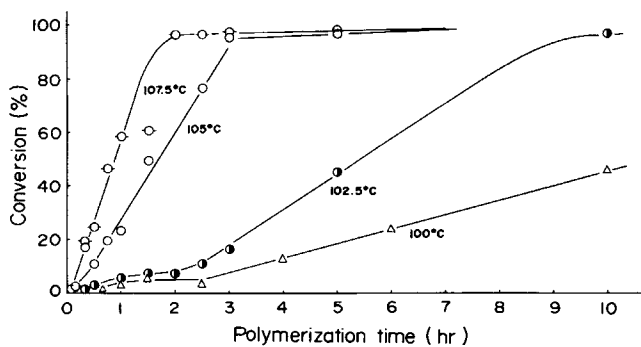


Fig. 7. Effect of polymerization temperature on polymer yield curves: iodine, 30 ppm; 1,3-dioxolane, 0.3%; methylal, 0.017%.



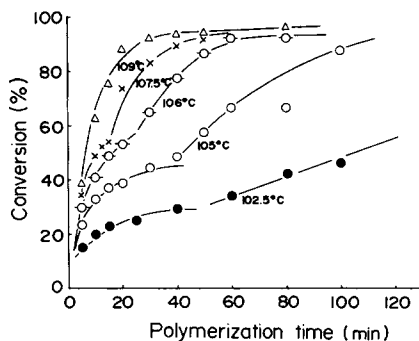


Fig. 8. Effect of polymerization temperature on polymer yield curves: iodine, 30 ppm; 1,3-dioxolane, 2.0%; methylal, 0.15%.

It is suggested that the contribution of methylal to the thermal stability is hardly recognized in the case of higher 1,3-dioxolane concentration. In the absence or at a very low concentration of 1,3-dioxolane, the effect of methylal on the thermal stability was clearly recognized. For example, the polymer having an  $R_{222}^{60}$  of 81% was obtained in the absence of 1,3-dioxolane under the following conditions; methylal, 0.5%; iodine, 30 ppm; polymerization, 60 min at 105°C. The thermal stability ( $R_{222}^{60} = 81\%$ ) is very high compared with that of polytetraoxane ( $R_{222} = 10\text{--}30\%$ ) obtained in the absence of 1,3-dioxolane and methylal. The difference in the thermal stability can be mainly attributed to the presence of methylal.

Effects of polymerization temperature on the copolymerization of tetraoxane are discussed below. Figures 7, 8, and 9 show a dependence of yield-time curves on polymerization temperature at constant methylal and iodine concentrations at 1,3-dioxolane concentrations of 0.3%, 2%, and 7.5%, respectively. The yield-time curves varied complicatedly with 1,3-dioxolane concentration, and the smaller the amount of 1,3-dioxolane, the larger the dependence of the polymerization rate on the polymerization temperature. At 0.3% 1,3-dioxolane, the yield-time relationships can be approximated by a straight line at a temperature above 105°C (before the polymer yield reaches a saturation point). However, at a relatively low temperature, such as 102.5° and 100°C, the polymer yields were very low in the early stage of copolymerization and increased remarkably

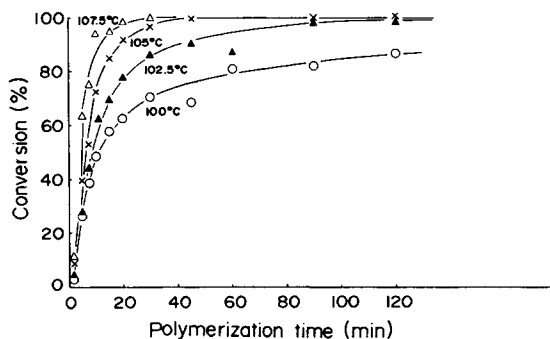


Fig. 9. Effect of polymerization temperature on polymer yield curves: iodine, 30 ppm; 1,3-dioxolane, 7.5%; methylal, 0.18%.

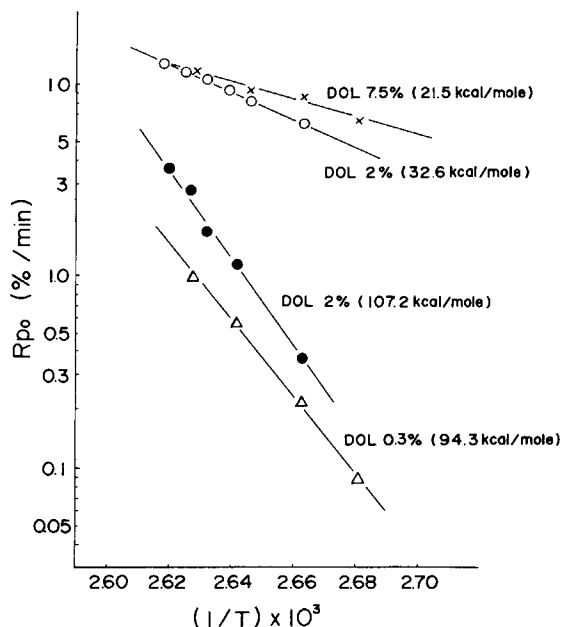


Fig. 10. Arrhenius plots of initial polymerization rate obtained in Figs. 7 ( $\Delta$ ), 8 (O), and 9 ( $\times$ ): ( $\bullet$ ) obtained at the later stage of copolymerization in Fig. 8.

after 3 hr. At 2% 1,3-dioxolane, the yield-time plots gave curves with a knick at a temperature below 107.5°C and a smooth curve without a knick at 109°C (see Fig. 8). On the other hand, at 7.5% 1,3-dioxolane, the yield-time relationships gave smooth curves with large initial rates in the entire range of polymerization temperature examined in this paper (see Fig. 9).

Figure 10 shows Arrhenius plots of initial rates of the copolymerization. Only when the concentration of 1,3-dioxolane was 0.3% and the polymerization temperatures were 100° and 102.5°C, the initial rates were determined from the maximum slope of the yield-time curves. As seen in the figure, apparent activation energies in this system decreased with increasing 1,3-dioxolane concentration. The apparent activation energies at 0.3%, 2%, and 7.5% 1,3-dioxolane were 94.3, 32.6, and 21.5 kcal/mole, respectively. The interaction between 1,3-dioxolane and iodine, e.g., the formation of their complex, may be present in this system. The larger apparent activation energy in the case of lower 1,3-dioxolane concentration may be attributed to the decrease in the contribution of the 1,3-dioxolane-iodine complex to the initiation reaction.

Watanabe et al.<sup>12</sup> found that an apparent activation energy is very large in the solid-state polymerization of tetraoxane initiated by iodine. It is, however, impossible to discuss the apparent activation energy of this copolymerization in detail, for there are only a few papers on a solid-state polymerization of tetraoxane. Miyama et al.<sup>13</sup> and Berlin et al.<sup>14</sup> studied a solid-state polymerization of trioxane initiated by iodine and obtained values of 29 and 74 kcal/mole as its apparent activation energy, respectively. Okamura et al.<sup>1,15</sup> also reported that, in a solid-state polymerization of trioxane initiated by  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$  and  $\text{SnCl}_4\text{-CCl}_3\text{COOH}$ , which are typical cationic initiators, the apparent activation energies were 8.6 and 15.8 kcal/mole, respectively. From these results, it is

suggested that the apparent activation energy of trioxane polymerization is larger in the iodine initiator than in the  $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ . On the assumption that this tendency is in conformity with the copolymerization of tetraoxane, it may be considered that the apparent activation energies obtained above are reasonable as a characteristic of the copolymerization of tetraoxane initiated by iodine, although they are considerably large.

As shown in Figure 8, the rate of copolymerization at the 2% 1,3-dioxolane suddenly changed to give a knick on the yield-time curves. (Similar yield-time curves with a knick were obtained in the range of 1% to 5% 1,3-dioxolane at a constant polymerization temperature of  $105^\circ\text{C}$ , as seen in Figure 1.) It may be considered that there are two stages, i.e., the early and the later stages of the copolymerization, before and after the knick. Slopes of tangent to the yield-time curves at the knick point could be taken as the initial rate of the later stage of copolymerization, and their Arrhenius plots are shown in Figure 10.

The apparent activation energy of the later stage of the copolymerization was ca. 107 kcal/mole, which was very close to that obtained at 0.3% 1,3-dioxolane (94 kcal/mole). As discussed on Figure 1, it was shown that the initial rates of the copolymerization are largely affected by 1,3-dioxolane concentration, i.e., increased with decreasing concentration. Therefore, it is suggested that the copolymerization reaction in the later stage at 2% 1,3-dioxolane proceeds under a condition corresponding to a lower 1,3-dioxolane concentration. As described in a subsequent paper, it was found that the residual 1,3-dioxolane concentration in the reaction mixture falls rapidly in the early stage of this copolymerization. Consequently, it is reasonable to conclude that the copolymerization of tetraoxane at 2% 1,3-dioxolane proceeds under a higher 1,3-dioxolane concentration in the early stage and under a lower concentration in the later stage.

As explained in the experimental part of this paper, the 1,3-dioxolane-methylal solution containing iodine was added to the purified tetraoxane which was ground to a fine, powdery granule, and the ampoule containing them was left overnight at room temperature before polymerization. During this standing, 1,3-dioxolane, methylal, and iodine may be considered to disperse homogeneously to the tetraoxane granules. However, it is still doubtful if they disperse homogeneously into the central part of tetraoxane crystal. As reported in a subsequent paper, studies on the microscopy and scanning electron microscopy of the copolymer suggest that there are differences in 1,3-dioxolane and methylal concentration between the surface and the central part of tetraoxane crystal, i.e., their concentrations are lower in the center than on the surface of the tetraoxane crystal. As mentioned above, since the copolymerization rate increased with increasing 1,3-dioxolane concentration, it is larger on the surface than in the center of the tetraoxane crystal. Consequently, it can be concluded that the copolymerization of tetraoxane proceeds apparently from the surface to the center of the tetraoxane crystal (it may be approximated by a core model). According to the difference of 1,3-dioxolane and methylal concentrations between the surface and the center of the tetraoxane crystal, it can be explained why the yield-time curves were divided into two stages in the 1,3-dioxolane concentration ranging from 1% to 5%.

Summarizing these results and the discussion, we find (1) in the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane, tetraoxane can be easily copolymerized to give a copolymer with an excellent thermal sta-

bility in a high yield. (2) Methylal reacts as a chain transfer reagent to control the molecular weight of the copolymer. (3) The copolymerization rate of tetraoxane depends largely upon iodine and 1,3-dioxolane concentrations. (4) In addition, it is reasonably suggested that, in the case of a relatively low concentration of 1,3-dioxolane (e.g., 2%), the copolymerization consists of two stages, i.e., an early and a later stage, at which the copolymerization reaction occurs mainly on the surface part of the tetraoxane crystal and in its central part, respectively. Therefore, it may be expected that the copolymer has various heterogeneities in its physical properties.

In a subsequent paper, we shall discuss further this copolymerization on the basis of gas chromatography of the reaction mixture, differential scanning calorimetry, gel permeation chromatography, and scanning electron microscopy of the copolymer.

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