

Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. II. Properties of Copolymer Obtained by Beaker-Scale Copolymerization

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Synopsis

In order to elucidate the copolymerization mechanism, the properties of the copolymer obtained by the iodine-initiated copolymerization of the tetraoxane-1,3-dioxolane-methylal system have been studied using gas chromatography, microscopy, scanning electron microscopy, differential scanning calorimetry, and gel permeation chromatography. From the behavior of the thermal stability and gas chromatography of the reaction mixture, it was found that reactivity of 1,3-dioxolane with active center is larger than that of tetraoxane, i.e., more than 90% 1,3-dioxolane is consumed at an early stage of the polymerization. The results obtained by microscopy, DSC, and GPC of the copolymer suggested that the copolymerization proceeds from the surface to the center of the tetraoxane crystal as if it were a core model. It was also suggested that the heterogeneity in copolymer properties can be explained not only by heterogeneous dispersion of 1,3-dioxolane in tetraoxane crystal, but also by the difference of reactivity of 1,3-dioxolane with the active center.

INTRODUCTION

Much is known about, and many patents have been granted for, the preparation of thermally stable poly(oxyethylene). One of them is the copolymerization of tetraoxane with 1,3-dioxolane.¹

In a previous paper,² we have reported that the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal gives easily poly(oxyethylene) with excellent thermal stability in a high polymer yield. In this system, 1,3-dioxolane reacts as a comonomer to elevate a thermal stability of poly(oxyethylene), and methylal reacts as a chain transfer reagent to control the molecular weight of the polymer. Further, the polymerization rate is largely affected by 1,3-dioxolane concentration and polymerization temperature. We have discussed the copolymerization mechanism to suggest that the characteristics of the solid-state copolymerization can be explained by a heterogeneous dispersion of iodine, 1,3-dioxolane, and methylal in the tetraoxane crystal.

In the present paper, thermal stability and intrinsic viscosity of the copolymer obtained by the iodine-initiated, solid-state copolymerization of tetraoxane with

1,3-dioxolane in the presence of methylal have been measured. Further, microscopy, scanning electron microscopy, differential scanning calorimetry, and gel permeation chromatography of the copolymer have been done in detail. The purpose of this paper is to give support for the copolymerization mechanism proposed in the previous paper.²

EXPERIMENTAL

Purification of materials used in this work and polymerization procedure were described in detail in the previous paper.²

Measurements of molecular weight and thermal stability of the copolymer were the same as mentioned in the previous paper.² In order to determine consumption rates of polymeric materials in this system, the polymerization reaction was stopped by quenching the sample in liquid nitrogen, and a certain amount of toluene was added to the reaction mixture. Subsequently, the residual polymeric materials were extracted with toluene at room temperature, and the extract was analyzed by gas chromatography. Microscopic observations of the copolymer were carried out using a microscope (Olympus Co. Ltd., Model FHA-531) and a scanning electron microscope (Japan Electron Optics Laboratory Co. Ltd., Model JSM-U3).

Samples for the microscopy and the scanning electron microscopy were prepared as follows. A polymer particle (size ca. $1 \times 1 \times 1$ mm) was briefly washed with acetone and sliced as thin as possible by a knife. The slice of the polymer was washed again with acetone, dried under vacuum, and observed under microscope. For scanning electron microscopy, the slice of the copolymer was coated with a thin layer of carbon film. Differential scanning calorimetry of the copolymer has been described in detail in the previous paper.² Molecular weight distribution of the copolymer was determined using gel permeation chromatography (Waters Associates GPC, Model 200). Gel permeation chromatography of poly(oxyethylene) has been described previously in detail.³

RESULTS AND DISCUSSION

It has been found previously that, in the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal, 1,3-dioxolane and methylal react as a comonomer and a chain transfer reagent, respectively, and affect the thermal stability and the molecular weight of the copolymer.² It has also been found that the initial rate of the copolymerization increases with increasing 1,3-dioxolane concentration, and yield-time plots in the range of 1–5% 1,3-dioxolane give curves which are divided into two stages of copolymerization by a nick point.

Figure 1 shows polymerization time dependence of thermal stability of the copolymer obtained at various 1,3-dioxolane concentrations. At higher 1,3-dioxolane concentration, e.g., in the range of 5–7.5% 1,3-dioxolane, the thermal stability of the copolymer was high and nearly constant regardless of polymerization time. At lower 1,3-dioxolane concentration, such as 0.3–1.0%, however, the thermal stability decreased with increasing polymerization time.

Figures 2 and 3 show polymerization time dependences of the yield, thermal stability, and intrinsic viscosity of the copolymer obtained under the following

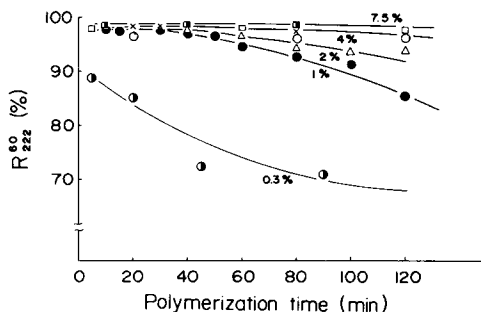


Fig. 1. Effect of 1,3-dioxolane concentration on the thermal stability of copolymer: iodine, 30 ppm; methylal, 0.15%; polymerization temperature, 105°C.

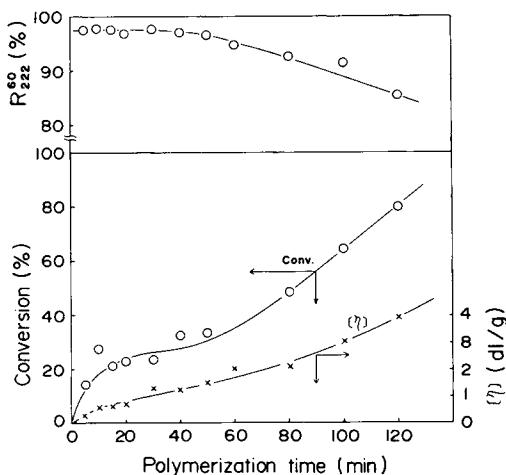


Fig. 2. Copolymerization of tetraoxane-1,3-dioxolane-methylal system: iodine, 30 ppm; 1,3-dioxolane, 1.0%; methylal, 0.15%; polymerization temperature, 105°C.

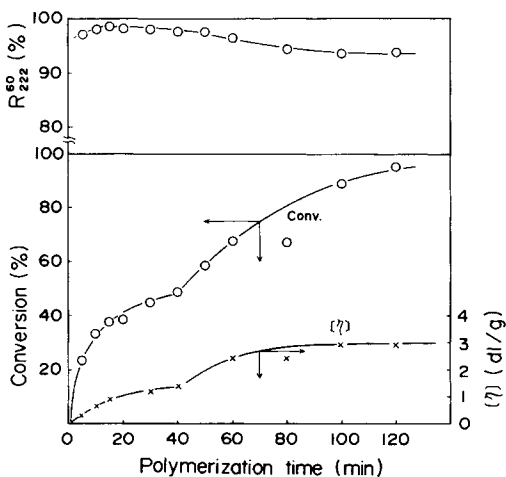


Fig. 3. Copolymerization of tetraoxane-1,3-dioxolane-methylal system: iodine, 30 ppm; 1,3-dioxolane, 2.0%; methylal, 0.15%; polymerization temperature, 105°C.

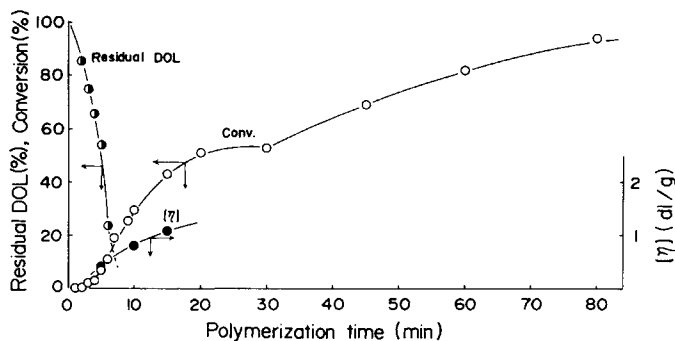


Fig. 4. Consumption of 1,3-dioxolane in copolymerization of tetraoxane with 1,3-dioxolane: iodine, 30 ppm; 1,3-dioxolane, 3.0%; methylal, 0.15%; polymerization temperature, 105°C.

conditions; 1,3-dioxolane concentration, 1% (in Fig. 2) and 2% (in Fig. 3); methylal, 0.15%; iodine, 30 ppm; polymerization temperature, 105°C. Under these conditions, as mentioned previously, plots of polymer yield as a function of polymerization time give a typical curve with a knick characteristic for this system. The time dependence of the copolymer yield has been discussed previously with relation to 1,3-dioxolane concentration and polymerization temperature.²

As shown in Figures 2 and 3, it can be seen that, while thermal stability is high and approximately constant in the early stage of copolymerization, in the later stage it decreases gradually as the polymerization time increases. Especially when 1,3-dioxolane concentration was lower (e.g., Fig. 2), thermal stability of the copolymer decreased remarkably in the later stage. Polymerization time at which the thermal stability of the copolymer begins to decrease was nearly the same as obtained a knick on the polymer yield–time curve. On the other hand, intrinsic viscosity of the copolymer increased with increasing polymerization time, and shapes of the intrinsic viscosity–polymerization time curves were similar to those of the polymer yield–time curves.

In this system, 1,3-dioxolane and methylal were found to be rapidly consumed in the early stage of polymerization by gas chromatography of the reaction mixture. The residual amount of 1,3-dioxolane in the reaction mixture are shown in Figure 4. In the copolymerization of tetraoxane, over 90% of initial content of 1,3-dioxolane was consumed during the early stage of copolymerization (within 10 min). Therefore, the composition of copolymer formed in the early stage of copolymerization may be considerably different from that formed in the later stage, i.e., the content of 1,3-dioxolane in the copolymer decreases steeply as the polymerization time increases. The copolymerization reaction during the early stage before the knick point of the yield–time curve takes place at relatively high 1,3-dioxolane and methylal concentrations. The thermal stability of the copolymer formed in this stage was, therefore, very high and the molecular weight was relatively low, although the latter increased gradually with increasing polymer yield. On the other hand, the copolymerization reaction in the later stage takes place at lower concentration of 1,3-dioxolane and methylal because of their rapid consumption in the early stage of copolymerization. In the later stage, therefore, the thermal stability of the copolymer decreased gradually and the molecular weight increased remarkably with increasing copolymer yield. These results, as well as those in the previous paper,² suggest that the copoly-

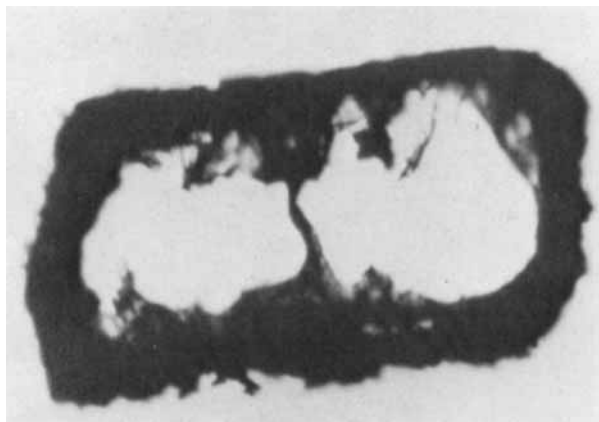


Fig. 5 Microscopic sectional view (150 \times) of copolymer particle obtained at 5 min (conversion, 23%).

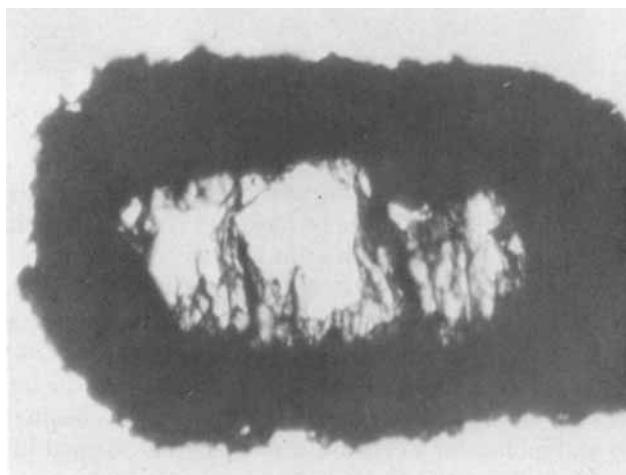


Fig. 6. Microscopic sectional view (150 \times) of copolymer particle obtained at 60 min (conversion, 67%).

merization of tetraoxane with 1,3-dioxolane is characterized by heterogeneous dispersion of 1,3-dioxolane and methylal in the tetraoxane monomer crystal.

Figures 5 and 6 show microscopic sectional view of the copolymer particles which were polymerized under the following conditions; 1,3-dioxolane, 2%; methylal, 0.15%; iodine, 30 ppm; polymerization, 5 min (Fig. 5) and 60 min (Fig. 6) at 105°C, respectively. A dark part in the photograph shows the copolymer crystal formed. A blank part surrounded with a dark part corresponds to unpolymerized monomer phase. The copolymer yields of the samples were 23% (Fig. 5) and 67% (Fig. 6), and they were obtained at the early and at the later stage of the copolymerization, respectively. Figure 5 indicates that the formation of the copolymer predominates on the surface region of tetraoxane crystal and no copolymer forms in the central region. As shown in Figure 6, it can be seen that the copolymerization proceeds in the direction of the center of the tetraoxane crystal as polymerization time increases. These results indicate that in the

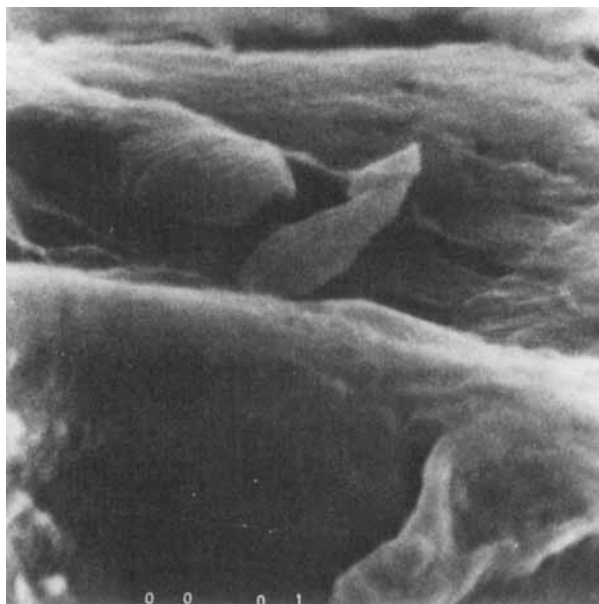


Fig. 7. Scanning electron micrograph ($10^4\times$) of copolymer (conversion, 67%) on the surface of the particle.

solid-state copolymerization of tetraoxane, 1,3-dioxolane, methylal, and iodine are dispersed heterogeneously in the tetraoxane crystal, i.e., their concentrations are higher in the surface region than in the central region of the tetraoxane crystal. In other words, the solid-state copolymerization proceeds mainly on the surface of the tetraoxane crystal in the early stage and subsequently occurs in the central region. Consequently, it can be concluded that the copolymerization reaction proceeds from the surface to the center of the tetraoxane crystal and is approximated by a core model. Further, it can be suggested that the composition and molecular weight of the copolymer formed in the early stage are considerably different from those formed in the later stage of the copolymerization.

In order to observe the microstructure of the copolymer crystal, scanning electron-microscopic photographs of cross sections of the copolymer particle were taken and shown in Figures 7, 8, and 9. The sample was the same copolymer particle as used in Figure 6. Photographs show copolymer crystals formed in the surface region (Fig. 7), in the central region (Fig. 9), and in the intermediate region between surface and center of the copolymer particle (Fig. 8), respectively. As seen in Figure 7, it is very hard to judge the direction of crystal axes of the copolymer in the surface region of the copolymer particle. This result suggests that the copolymerization occurs in a phase where the tetraoxane crystal melts or under conditions similar to partial melting, because of high concentration of 1,3-dioxolane and methylal added.

At the intermediate region (Fig. 8), a fibril-like copolymer was obviously formed, although the crystal axis of the copolymer was not orientated. The disorder of the copolymer crystal in this region was much less than that in the surface region of the particle. On the other hand, a fibril-like copolymer of which the crystal axis is well orientated was observed in the central region of the particle. This suggests that in this region, the copolymerization proceeds along the crystal

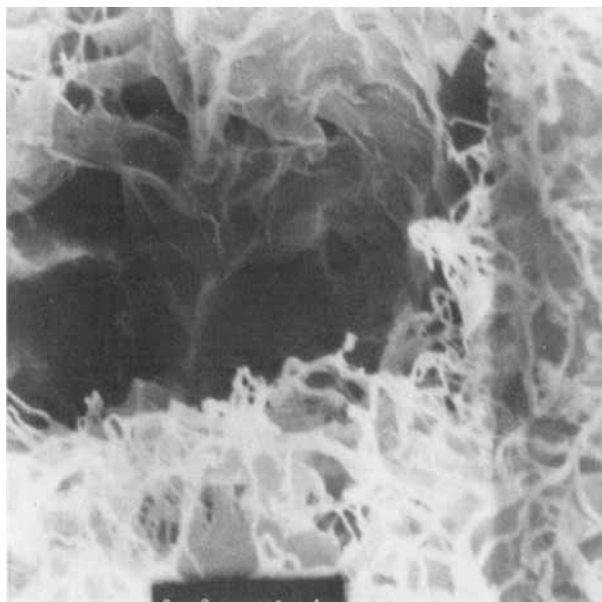


Fig. 8. Scanning electron micrograph ($10^4\times$) of copolymer (conversion, 67%) in the intermediate region between surface and center of the particle.

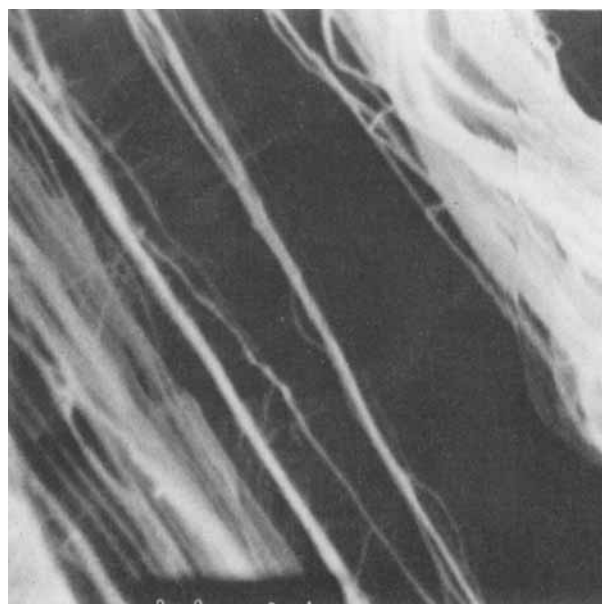


Fig. 9. Scanning electron micrograph ($10^4\times$) of copolymer (conversion, 67%) in the center of the particle.

axis of tetraoxane. This also indicates that only a small amount of 1,3-dioxolane and methylal added disperses in the central region of the tetraoxane crystal and that the tetraoxane crystal is scarcely disarranged by them.

As mentioned above, in the solid-state copolymerization of tetraoxane, the copolymerization occurs in heterogeneous dispersion of 1,3-dioxolane and

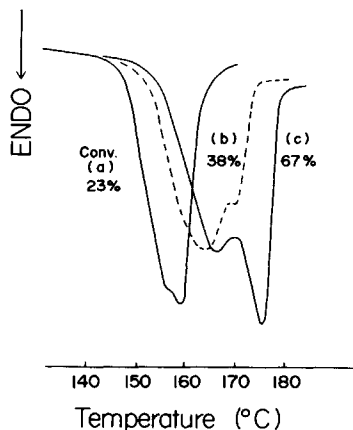


Fig. 10. DSC thermograms of copolymer: iodine, 30 ppm; 1,3-dioxolane, 2.0%; methylal, 0.15%; polymerization temperature, 105°C.

methylal in the tetraoxane crystal. This heterogeneity might influence not only the copolymerization rate, but also the composition and the molecular weight distribution of the copolymer. Although these influences, as shown in Figures 1, 2, and 3, can be seen on the time dependence of the thermal stability and the intrinsic viscosity of the copolymer, in order to study these influences in detail, differential scanning calorimetry (DSC) and gel permeation chromatography (GPC) of the copolymer were carried out.

Figure 10 shows DSC thermograms of the copolymer which were obtained under the same conditions as shown in Figure 3. The copolymer yield (and polymerization time) of the samples were (a) 23% (5 min); (b) 38% (20 min); (c) 67% (60 min), respectively. Samples (a) and (b) were obtained in the early stage of the copolymerization (before the knick in the time–yield curve) and sample (c), in the later stage (after the knick). The DSC thermogram of the copolymer obtained in the early stage, as shown in (a), is characterized by a narrow, single peak at a relatively low temperature. As the polymerization time increases, as shown in (b), the DSC thermogram becomes a broader melting curve with a side peak at a higher temperature, and the main melting peak shifts to a higher temperature. Further, as shown in (c), the DSC thermogram of the copolymer obtained in later stages is characterized by two peaks shifted to higher temperature, and the higher one becomes remarkably larger than the lower.

In general, it should be noted that the first-scan melting endotherm of a crystalline copolymer is a reflection of the copolymer composition as well as the crystal structure of a copolymer, such as a lamellar structure and an extended one. It was reported that in the case of poly(oxymethylene), the melting point of the polymer obtained by radiation-induced, solid-state polymerization of trioxane or tetraoxane is much higher than that obtained by liquid-state polymerization, because the former has an extended crystal structure (mp over 180°C), the latter a lamellar crystal structure (mp ca. 175°C).⁴ It is also well known that the melting point of oxymethylene copolymer decreases with increasing comonomer content in the copolymer main chain.^{5,6}

Therefore, on the basis of both DSC (Fig. 10) and scanning electron microscopy (Figs. 7, 8, and 9) of the copolymer, the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane can be explained as follows. In the early stage of copolymerization, reaction occurs mainly in the region where 1,3-diox-

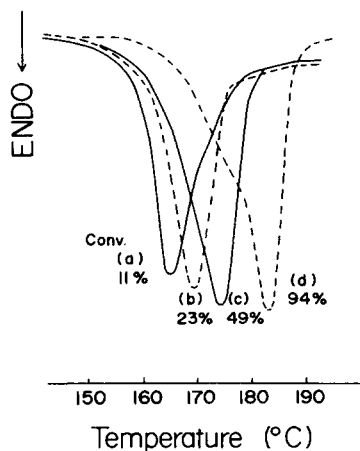


Fig. 11. DSC thermograms of copolymer: iodine, 30 ppm; 1,3-dioxolane, 0.3%; methylal, 0.017%; polymerization temperature, 105°C.

olane concentration is higher. 1,3-Dioxolane content in the copolymer formed during this stage is so high that its melting point is relatively low [Fig. 10(a)] and its crystal structure is disordered (Fig. 7). As the copolymerization proceeds, the 1,3-dioxolane content of the copolymer becomes lower so that the peak in DSC thermogram [Fig. 10(b)] shifts to a higher temperature and the copolymer has a fibril-like crystal. The appearance of a side peak, as seen in Figure 10(b), indicates that the copolymer with very small 1,3-dioxolane content and with a high crystallinity begins to form.

Upon further progress of copolymerization, i.e., in the later stage of copolymerization, copolymerization occurs at a very lower 1,3-dioxolane concentration or under the condition which can be almost approximated by a homopolymerization. The copolymer formed in this stage has a higher melting point [Fig. 10(c)] and a well-orientated crystal structure (Fig. 9), because the tetraoxane crystal is scarcely disordered by 1,3-dioxolane and other reactants. On the other hand, Figure 11 shows DSC thermograms of the copolymer obtained at 1,3-dioxolane and methylal concentrations of 0.3% and 0.017%, respectively, and under other conditions the same as Figure 10. The copolymer yield (and copolymerization time) of the samples were (a) 11.2% (30 min); (b) 23.0% (60 min); (c) 49.3% (90 min); and (d) 94.5% (180 min), respectively. At 1,3-dioxolane concentration of 0.3%, all DSC thermograms were single peaks regardless of the copolymerization time. The peak temperature for Figure 11(a) was 165°C and, as copolymerization time increased, the peak shifted gradually to higher temperature and then reached 182°C for the sample of Figure 11(d). This result indicates that 1,3-dioxolane content in the copolymer varies continuously as copolymerization time increases.

Comparing Figure 11 with Figure 10, it is impossible to explain the double peak for the copolymer obtained at 2% 1,3-dioxolane concentration only on the basis of the diffusion of 1,3-dioxolane in the tetraoxane crystal. For the double peak of the DSC thermogram, the following explanation may be reasonable. Although in order to disperse 1,3-dioxolane, methylal, and iodine, the reaction mixture was allowed to stand overnight after the ingredients were added, they may concentrate in the surface region more than in the central region of the tetraoxane crystal. So, when the reaction mixture is heated to copolymerization tempera-

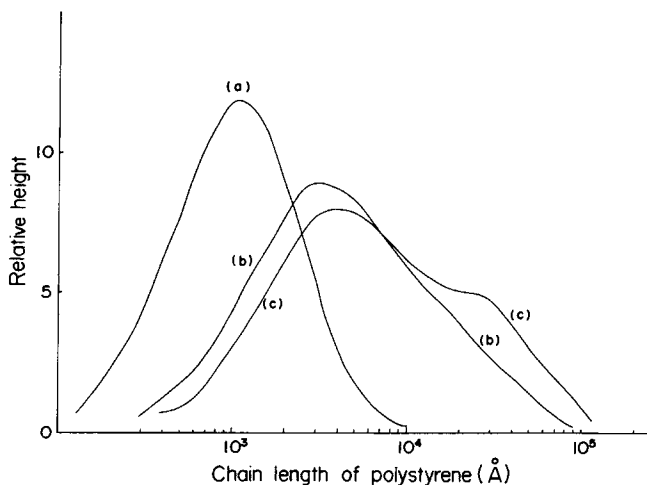


Fig. 12. GPC curves of copolymer: iodine, 30 ppm; 1,3-dioxolane, 2.0%; methylal, 0.15%; polymerization temperature, 105°C; (a) conversion, 23%; $[\eta]$, 0.3 dl/g; (b) conversion, 38%; $[\eta]$, 1.0 dl/g; (c) conversion, 67%; $[\eta]$, 2.4 dl/g.

ture, copolymerization occurs predominantly in the surface region of the tetraoxane crystal (because of large dependence of copolymerization rate on 1,3-dioxolane concentration, i.e., the higher the 1,3-dioxolane concentration, the larger the copolymerization rate). On the other hand, since 1,3-dioxolane hardly disperses in the central region of tetraoxane crystal on standing, copolymerization proceeds gradually with a diffusion of 1,3-dioxolane from the surface region or outside of the monomer crystal. Therefore, the copolymer obtained in the later stage, such as in Figure 10(c), has a DSC thermogram characterized by a double peak. At an especially low concentration of 1,3-dioxolane, such as 0.3%, the localization of 1,3-dioxolane and others may not be present and copolymer composition changes continuously as the copolymerization time increases.

Molecular weight distribution of the copolymer was measured by gel permeation chromatography and is shown in Figure 12. The sample copolymers of Figure 12(a), (b), and (c) correspond to those of Figure 10(a), (b), and (c), respectively. The copolymer formed in the early stage of copolymerization [Fig. 12(a)] gave a narrow GPC curve with a peak at a relatively low molecular weight. The GPC curve shifted to larger molecular weight and became broader as the copolymerization time increased [Fig. 12(b)]. The copolymer obtained in the later stage [Fig. 12(c)], has a considerably wide molecular weight distribution with a discernible shoulder at the larger molecular weight side. Although the tendency of the time dependence of the molecular weight distribution agreed very closely with that of the DSC thermogram, the former relates to the molecular weight of the copolymer, which is influenced by methylal, and the latter is mainly dependent on the composition and the crystal structure of the copolymer, which is influenced by 1,3-dioxolane. Consequently, it can be reasonably considered that in the solid-state copolymerization of tetraoxane, the dispersions of 1,3-dioxolane and methylal in tetraoxane monomer crystal are considerably heterogeneous.

The reason why the large molecular weight copolymer forms in the later stage of copolymerization may be considered as follows. In the later stage of copoly-

merization, as mentioned for the DSC thermograms, the copolymerization occurs mainly in the central part of the monomer crystal after methylal is almost consumed. Moreover, tetraoxane monomer crystal in the central region is scarcely disordered by 1,3-dioxolane, methylal, and iodine. Trofimova et al.⁷ studied the solid-state polymerization of trioxane using monomer crystal obtained by various purification methods and found that the higher the crystallinity of monomer, the higher the polymerization rate and the larger the molecular weight of the polymer. It was also reported that in solid-state polymerization of trioxane, a defect or a disorder in monomer crystal lowers the molecular weight of polymer.⁸ The effects of monomer crystal on molecular weight of the polymer, as mentioned above, might be similar to those in the solid-state copolymerization of tetraoxane initiated by iodine.

In summary, in the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane, the copolymerization time dependences of thermal stability, intrinsic viscosity, thermal behavior, and molecular weight distribution of the copolymer have been studied in detail. Microscopic observation of the copolymer has been done using the usual microscope and a scanning electron microscope. It was found that, in this system, copolymerization proceeds from the surface to the center of the monomer crystal as if it were a core model, and that composition and molecular weight of the copolymer vary with copolymerization time. Microscopy of the copolymer indicated that there are copolymers having various crystallinities and they are heterogeneously distributed in the copolymer particle. It was suggested that the heterogeneity in copolymer properties can be explained not only by the difference of reactivity of the reactants with the active center, but also by heterogeneous dispersion of 1,3-dioxolane and methylal in the monomer crystal.

The results and discussion mentioned above appear to support our idea for the mechanism of copolymerization of tetraoxane with 1,3-dioxolane in the presence methylal in the previous paper.²

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