Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. V. Studies on Molecular Weight Distribution of Copolymer

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Synopsis

The iodine-initiated, solid-state copolymerization of the tetraoxane–1,3-dioxolane–methylal system has been studied by measuring the molecular weight distribution of the copolymer. The molecular weight distribution of the copolymer is found to be strongly dependent on the addition method of the 1,3-dioxolane–methylal solution to tetraoxane. The copolymer obtained by the one-addition copolymerization has a molecular weight distribution curve that shows a very broad distribution, with a discernible shoulder; and the copolymer obtained by the continuous-addition copolymerization has a very sharp curve. Particle size of the copolymer also influences the molecular weight distribution. For the one-addition copolymerization, the larger the particle size of the copolymer, the broader the molecular weight distribution. For the continuous-addition copolymerization, however, the molecular weight distribution is nearly constant regardless of particle size. The dependence of the molecular weight distribution on the polymerization time and the concentrations of iodine, 1,3-dioxolane, and methylal is discussed in detail. These results suggest that this copolymerization system is characterized by a reaction that proceeds from the surface to the center of the tetraoxane crystals.

INTRODUCTION

The iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal has been studied not only on a beaker scale but also on a larger scale using a kneader-type reactor. In this copolymerization system the authors have found the following: (1) Oxymethylene copolymer with excellent thermal stability is easily obtained in a high polymer yield. (2) 1,3-Dioxolane and methylal react as comonomer and chain transfer reagent to influence mainly the thermal stability and the molecular weight of the copolymer, respectively. (3) Reactivities of 1,3-dioxolane and methylal with an active center are higher than that of tetraoxane, i.e., 1,3-dioxolane and methylal are consumed in an early stage of the copolymerization. (4) Polymerization reaction proceeds from the surface of the tetraoxane crystal to the center. (5) Polymerization time dependences of intrinsic viscosity and thermal stability of the copolymer are strongly influenced by the addition method of the 1,3-dioxolane–methylal solution to the tetraoxane monomer.

It has also been found that the composition and molecular weight of the copolymer formed in the early stage of copolymerization are considerably different from those formed in the later stage except when 1,3-dioxolane and methylal are

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added successively to the reaction system as the copolymerization proceeds. In the latter case, the thermal stability and intrinsic viscosity of the copolymer have been found to be nearly constant regardless of polymerization time. Consequently, in previous papers[1-4] it has been suggested that the composition and the molecular weight distribution of the copolymer are largely dependent not only on the amounts of 1,3-dioxolane and methylal but also on the addition method of the 1,3-dioxolane–methylal solution to the polymeric system.

In the present paper, in order to study the relationship between the molecular weight distribution of the copolymer and the addition amount and method of the 1,3-dioxolane–methylal solution, gel permeation chromatography of the copolymer was carried out. The characteristics of the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal were further discussed on the basis of the results.

It is well known that poly(oxymethylene) is easily decomposed by heating or by acids and that there is no good solvent in which poly(oxymethylene) can be easily dissolved at a relatively low temperature. These reasons complicate the gel permeation chromatography of poly(oxymethylene). In fact, no paper on the subject had been reported before we established a procedure for gel permeation chromatography of poly(oxymethylene) and reported it in this journal.[5]

EXPERIMENTAL

The copolymer samples were obtained by the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal by using a kneader-type reactor. The copolymerization procedures were described in detail in the previous paper.[3] The copolymerization methods were classified according to the addition method of 1,3-dioxolane and methylal to tetraoxane as follows:

1. One-addition copolymerization: 1,3-dioxolane–methylal solution with 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 onto tetraoxane 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 times 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 constant speed onto tetraoxane in the first 10 min. Subsequently, one third of this was continuously added in the next 15 min.

Unless otherwise noted, the samples used in this paper were obtained under

the following conditions: 1,3-dioxolane, 3.5%; methylal, 0.15%; iodine, 30 ppm; polymerization temperature, 107°C.

The GPC samples were obtained by repeated conical quartering, except when determing the effects of polymer particle size on the molecular weight distribution. In the latter case, the copolymer samples were sieved to obtain the following fractions: (a) smaller than 120 mesh (< 0.125 mm), (b) 120–70 mesh (0.125–0.210 mm), (c) 70–30 mesh (0.210–0.595 mm), (d) 30–18 mesh (0.595–1.000 mm).

The conditions of GPC measurement on poly(oxymethylene) were previously described in detail.[5] The calibration work in GPC measurement was carried out by using the narrow molecular weight distribution polystyrene standards, since it is impossible to obtain commercial poly(oxymethylene) standards whose molecular weight distributions are known. In this work, the molecular weight of poly(oxymethylene) was represented by the chain length of polystyrene.

RESULTS AND DISCUSSION

In a previous paper[3] it has been suggested that in this copolymerization system the molecular weight distribution of copolymer varies according to the addition method of the 1,3-dioxolane–methylal solution to tetraoxane. Figure 1 shows the gel permeation chromatograms of the copolymer obtained at the saturation yield by various addition methods of the solution. The copolymer obtained by the one-addition copolymerization has a considerably wide molecular weight distribution with a discernible shoulder at the higher molecular weight side. Each copolymers obtained by the two-, four-, and continuous-addition copolymerizations possesses a narrow distribution curve with a single peak.

The $\overline{M}_w/\overline{M}_n$ value, which indicates a broadness of the molecular weight distribution, and the intrinsic viscosity of the copolymer are listed in Table I. The $\overline{M}_w/\overline{M}_n$ value cannot be determined for a wide distribution curve with a shoulder, such as the distribution curve of the copolymer obtained by the one-addition
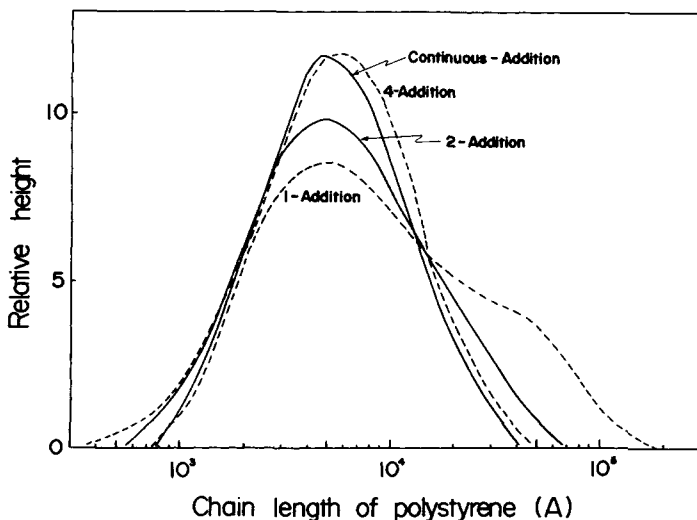

Fig. 1. Effect of addition method of 1,3-dioxolane–methylal solution on GPC curve: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C.

TABLE I
$\overline{M}_w/\overline{M}_n$ and $[\eta]$ of Copolymer Obtained by Various Addition Methods

Addition method of 1,3-dioxolane–methylal solution	$\overline{M}_w/\overline{M}_n$	$[\eta]$, dl/g
One-addition	—[a]	2.8
Two-addition	3.12	1.5
Four-addition	1.97	1.6
Continuous-addition	1.80	1.4

[a] Molecular weight distribution was very broad, so that $\overline{M}_w/\overline{M}_n$ could not be calculated.

copolymerization. As shown in Table I, the $\overline{M}_w/\overline{M}_n$ value decreases with increasing addition number of the 1,3-dioxolane–methylal solution. It is concluded that the molecular weight distribution of the copolymer is strongly dependent upon the addition method of the solution.

In order to make clear their relationships, polymerization time dependence on the molecular weight distribution of the copolymer obtained by the various addition methods was measured. Figure 2 shows the molecular weight distribution change for the one-addition copolymerization. At the early stage of the copolymerization, the copolymer has a very narrow molecular weight distribution. As polymerization proceeds, the copolymer possesses a wide distribution, with tailing at the higher molecular weight side. At the later stage, finally, the copolymer has a considerably wide distribution, with an appreciable shoulder at the higher molecular weight side. The peak of the molecular weight distribution curve is shifted to the higher molecular weight side with increasing polymerization time. As shown in the previous paper,[3] in the one-addition copolymerization the intrinsic viscosity of the copolymer increases monotonously with increasing polymerization time. For the one-addition copolymerization it is concluded that the lower molecular weight copolymer is formed in the early stage of the copolymerization and the higher molecular weight copolymer, in the later
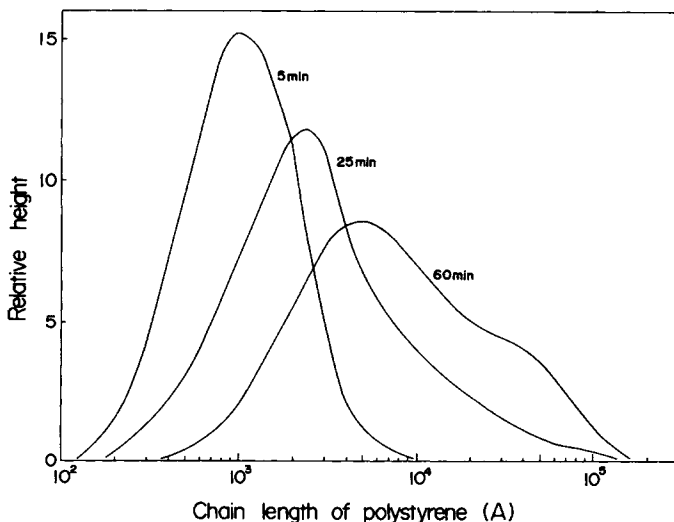

Fig. 2. Effect of polymerization time on GPC curve of copolymer obtained by one-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C.

stage because of a rapid consumption of methylal, which has a higher reactivity with an active center.

Figures 3 and 4 show the polymerization time dependence of the molecular weight distribution of the copolymer obtained in the two-addition copolymerization. The former shows the distribution curves of the copolymers obtained in the polymerization time up to 20 min (i.e., before the second addition of the 1,3-dioxolane–methylal solution); the latter shows those obtained in the polymerization time ranging from 20 to 60 min. The time dependence of the molecular weight distribution curve in Figure 3 is similar to that found for the one-addition copolymerization. In both Figures 2 and 3, the copolymer obtained at the early stage of the copolymerization has a very narrow molecular weight distribution curve, with a peak situated in the lower molecular weight side. As
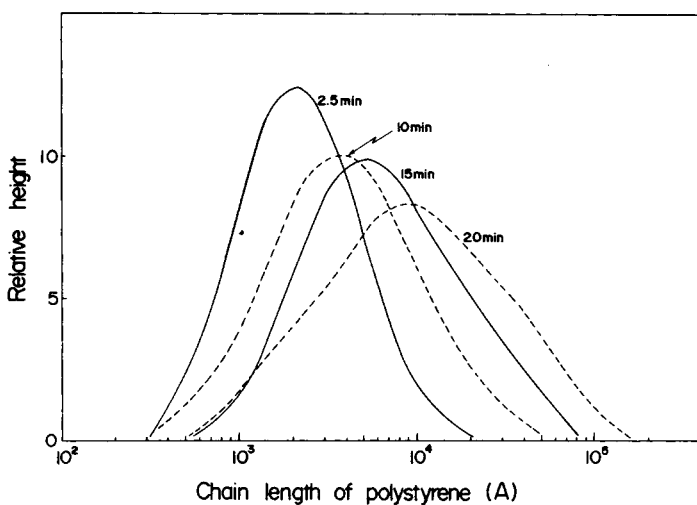
Fig. 3. Effect of polymerization time on GPC curve of copolymer obtained by two-addition copolymerization. Other polymerization conditions same as in Fig. 2.
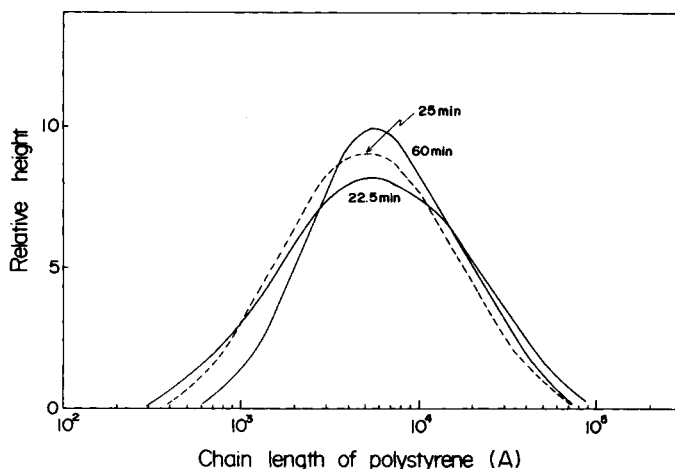
Fig. 4. Effect of polymerization time on GPC curve of copolymer obtained by two-addition copolymerization. Other polymerization conditions same as in Fig. 2.

polymerization proceeds, the copolymer possesses a wider distribution, with a peak shifted to the higher molecular weight side. On the other hand, after the second addition of the 1,3-dioxolane–methylal solution (see Fig. 4), the distribution curve becomes narrower with increasing polymerization time, and its peak scarcely shifts.

As mentioned in the previous paper,[3] the intrinsic viscosity of the copolymer obtained in the two-addition copolymerization is steeply lowered by the second addition of the 1,3-dioxolane–methylal solution, and it has been concluded that this sudden fall in the intrinsic viscosity is caused by a rapid increase in very low molecular weight copolymer due to an increase in chain transfer and initiation reactions. As can be seen from the comparison of the distribution curves before and after the second addition of the 1,3-dioxolane–methylal solution, the distribution curve is shifted to the lower molecular weight side, i.e., the lower molecular weight copolymer increases on the second addition of the solution. The molecular weight distribution of the copolymer obtained at 20 min is wider than that at 22.5 min, and the discernible shoulder of the former is not perceived in the latter. The increase in the polymer yield between before and after the second addition of the solution is only 3.3%. Therefore, the variation of the molecular weight distribution of the copolymer obtained before and after the second addition is probably caused not only by a rapid increase in very low molecular weight copolymer but also by a scission of the copolymer.main chain. A scission of the main chain may occur by an attack of cation formed in the polymerization process. For example, it may be considered that the copolymer chain is attacked by $CH_3OCH_2^+$, which is produced as follows:

$$CH_3OCH_2OCH_3 + Cat^+ \longrightarrow CH_3O^-Cat^+ + CH_3OCH_2^+$$
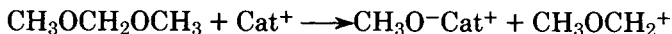
However, it is beyond this paper to discuss these problems in further detail, and studies in this region will be continued in our laboratory.

The polymerization time dependence of the molecular weight distribution of the copolymer obtained in the four- and continuous-addition copolymerizations are shown in Figures 5 and 6, respectively. The $\overline{M}_w/\overline{M}_n$ values determined for them are also listed in Tables II and III. In both copolymerizations, $\overline{M}_w/\overline{M}_n$ values of the copolymer slightly decrease and the distribution curves become slightly narrower as the polymerization time increases. In addition, the shift in the peak in the distribution curves is far less than those found for the one- and two-addition copolymerizations. These results indicate that in the four- and continuous-addition copolymerizations the molecular weight distribution of the copolymer is nearly constant in the entire stage of the copolymerization.

The copolymer obtained at a saturation yield in the one-addition copolymerization was sieved and measured by gel permeation chromatography for particle size. The results are shown in Figure 7. The copolymer of smaller particle size (smaller than 120 mesh) has a considerably narrow molecular weight distribution, with a single peak at the higher molecular weight side, and the copolymer of middle particle size (120–70 mesh) possesses a wide molecular weight distribution, with a discernible shoulder at the higher molecular weight side. Further, the copolymer of large size (30–18 mesh) has a wider bimodal molecular weight distribution. As indicated before with regard to the polymerization time dependence of the molecular weight distribution of the copolymer obtained in
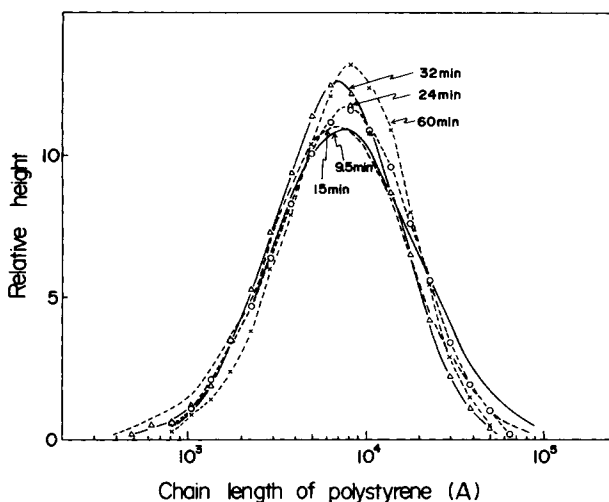
Fig. 5. Effect of polymerization time on GPC curve of copolymer obtained by four-addition copolymerization. Other polymerization condition same as in Fig. 2.
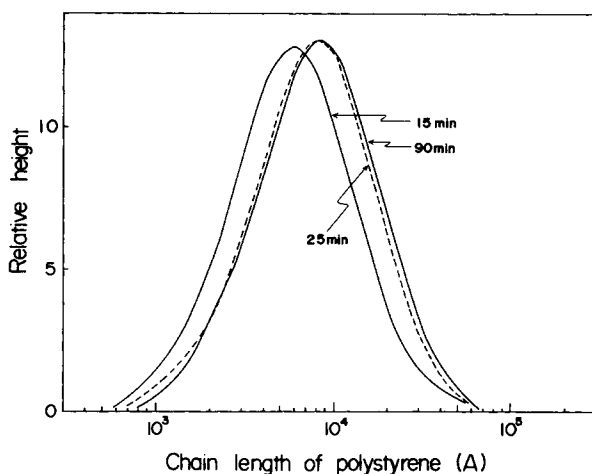

Fig. 6. Effect of polymerization time on GPC curve of copolymer obtained by continuous-addition copolymerization. Other polymerization conditions same as in Fig. 2.

the one-addition copolymerization (Fig. 2), copolymer with a lower molecular weight is formed at the early stage of the copolymerization, and copolymer with a higher molecular weight, at the later stage. Therefore, it can be reasonably concluded that the smaller copolymer particle mainly consists of copolymer formed in the early stage, and the larger one consists of both the copolymers formed in the early and later stages of the copolymerization. In other words, the smaller the tetraoxane particle size, the earlier the polymerization is completed; i.e., in this system the copolymerization proceeds from the surface to the center of tetraoxane particle, as if it were a core model.

In the continuous-addition copolymerization, the molecular weight distribution of the copolymer having various particle sizes are shown in Figure 8. All the copolymers are found to have a narrow molecular weight distribution, with

TABLE II
$\overline{M}_w/\overline{M}_n$ and [η] of Copolymer Obtained by Four-Addition Copolymerization

Polymerization time, min	Polymer yield, %	$\overline{M}_w/\overline{M}_n$	[η], dl/g
9.5	21.7	2.29	1.3
15	37.7	2.41	1.7
24	56.8	2.01	1.6
32	79.0	2.05	1.5
60	85.8	1.97	1.6

TABLE III
$\overline{M}_w/\overline{M}_n$ and [η] of Copolymer Obtained by Continuous-Addition Copolymerization

Polymerization time, min	Polymer yield, %	$\overline{M}_w/\overline{M}_n$	[η], dl/g
15	49.9	2.01	1.2
25	87.2	1.97	1.5
55	92.1	1.82	1.5
90	97.2	1.80	1.4

a single peak at nearly constant molecular weight, regardless the copolymer particle size. In the four- and continuous-addition copolymerizations, as mentioned above, the molecular weight distribution scarcely varies in the course of the polymerization. It should be mentioned that concentrations of 1,3-dioxolane and methylal in the reaction mixture are nearly constant, regardless of polymerization time. Therefore, copolymer with approximately constant molecular weight is formed in the entire stage of the copolymerization. This finding indicates that methylal diffuses easily through the copolymer layer formed at the early stage to react with an active site at the center of the monomer particle.

In the four-addition copolymerization, the relationships between the molecular
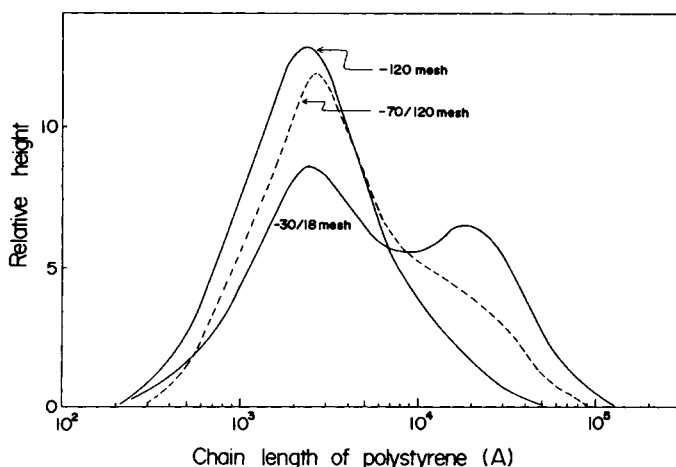

Fig. 7. Effect of particle size on GPC curve of copolymer obtained by one-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C.
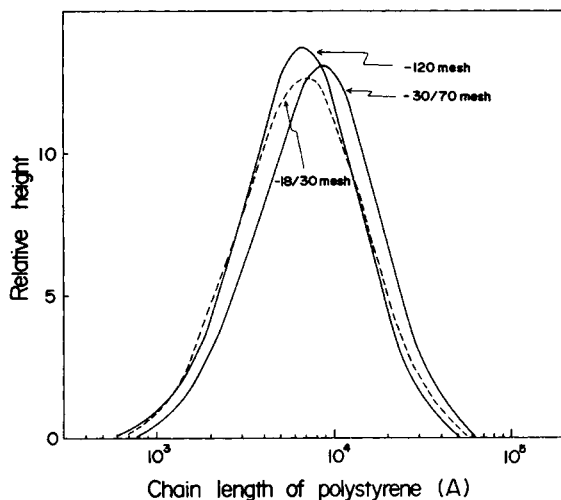
Fig. 8. Effect of particle size on GPC curve of copolymer obtained by continuous-addition co-polymerization. Other polymerization conditions same as in Fig. 7.

weight distribution of the copolymer and methylal, 1,3-dioxolane, and iodine concentrations are shown in Figures 9, 10, and 11, respectively. In the methylal concentration ranging from 0.10% to 0.25%, the molecular weight distribution curve of the copolymer is shifted to the lower molecular weight side and becomes narrower with increasing methylal concentration. The narrowing of the curves is also confirmed by the slight reduction in $\overline{M}_w/\overline{M}_n$ value, as listed in Table IV. On the other hand, it may be considered that the influence of 1,3-dioxolane and iodine concentrations on molecular weight distribution of the copolymer is much smaller than that of methylal, as 1,3-dioxolane and iodine react as comonomer and initiator, respectively. However, as found in a previous paper,[3] the intrinsic viscosity of the copolymer obtained at constant methylal concentration increases with increasing copolymerization rate, because the apparent concentration of
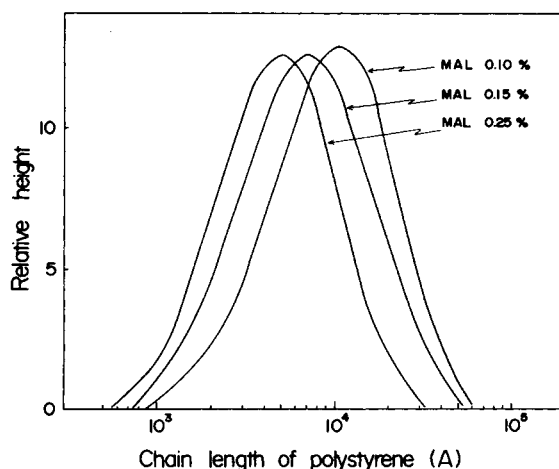

Fig. 9. Effect of methylal concentration on GPC curve of copolymer obtained by four-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; polymerization temperature, 107°C.
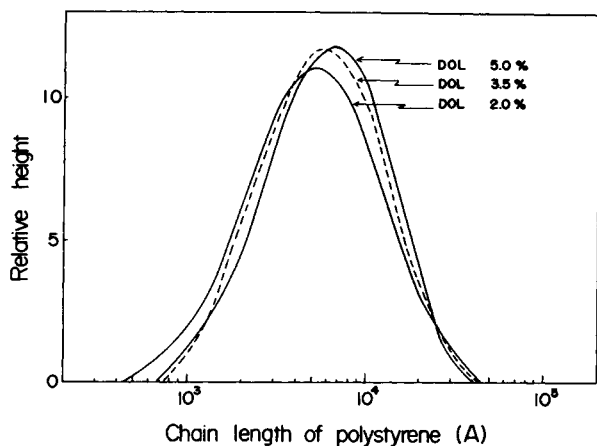
Fig. 10. Effect of 1,3-dioxolane concentration on GPC curve of copolymer obtained by four-addition copolymerization: iodine, 30 ppm; methylal, 0.15%; polymerization temperature, 107°C.
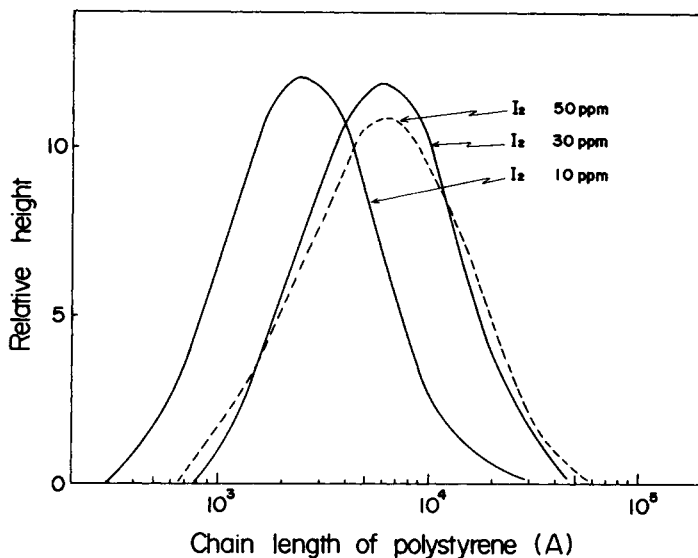
Fig. 11. Effect of iodine concentration on GPC curve of copolymer obtained by four-addition copolymerization: 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C.

methylal in the vicinity of an active center decreases with increasing copolymerization rate. Therefore, the increase in the copolymerization rate due to a higher concentration of 1,3-dioxolane and iodine results in the formation of higher molecular weight copolymer, i.e., in a slight shift of the molecular weight distribution curve to the higher molecular weight side, as seen in Figures 10 and 11. This effect is striking in the case of the copolymerization at 10 ppm I_2 (Fig. 11). In this system, as mentioned previously,[3] the copolymerization rate is especially low and deviates from the first-order relationship between the copolymerization rate and the iodine concentration which is obtained in the range of 20–50 ppm I_2.

The results and discussion above can be summarized as follows. To further

TABLE IV

$\overline{M}_w/\overline{M}_n$ and $[\eta]$ of Copolymer Obtained by Four-Addition Copolymerization

	$\overline{M}_w/\overline{M}_n$	$[\eta]$, dl/g
Amount of methylal, %[a]		
0.10	2.05	2.2
0.15	1.86	1.6
0.25	1.80	1.2
Amount of 1,3-dioxolane, %[b]		
2.0	2.05	1.6
3.5	1.86	1.6
5.0	1.93	1.8
Amount of iodine, ppm[c]		
10	1.93	1.0
30	1.86	1.6
50	2.34	1.8

[a] Iodine, 30 ppm; 1,3-dioxolane, 3.5%.
[b] Iodine, 30 ppm; methylal, 0.15%.
[c] 1,3-Dioxolane, 3.5%; methylal, 0.15%.

elucidate the characteristic of the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal, by using a kneader-type reactor, the molecular weight distribution of the copolymer was measured by gel permeation chromatography. It was found that the molecular weight distribution of the copolymer is strongly dependent upon the addition method of the 1,3-dioxolane–methylal solution to tetraoxane. The copolymer obtained by the one-addition copolymerization has a very wide molecular weight distribution curve, with a discernible shoulder, and the copolymer obtained by the continuous-addition copolymerization has a curve of a more narrow distribution.

The molecular weight distribution of the copolymer is largely influenced by the particle size of the copolymer. For the one-addition copolymerization, the larger the particle size of the copolymer, the wider the molecular weight distribution. The distribution of the copolymer obtained by the continuous-addition copolymerization is nearly constant, regardless of particle size. These results indicate clearly that the copolymerization reaction proceeds from the surface to the center of tetraoxane particle and that methylal can easily diffuse the copolymer layer during the polymerization.

The dependence of the molecular weight distribution of the copolymer on the polymerization time and the concentrations of methylal, iodine, and 1,3-dioxolane has been discussed in detail. These results and the discussion also support the mechanism of this copolymerization system proposed in several previous papers.[1–4]

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