

Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. IV. Fractional Dissolution of Copolymer

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Synopsis

A fractional dissolution on the oxymethylene copolymer obtained by the iodine-initiated, solid-state copolymerization of the tetraoxane-1,3-dioxolane-methylal system has been carried out using a mixed solvent which consists of tetrachloroethane, phenol, and cyclohexanol. On the fractional dissolution, the oxymethylene copolymer was divided mainly into two parts: one was the copolymer containing a larger amount of ethylene oxide unit in its main chain and having lower molecular weight; the other was copolymer containing a smaller amount of ethylene oxide unit and having a higher molecular weight. It was reasonably concluded that in this copolymerization system, the reaction proceeds from the surface to the center of the tetraoxane crystal to give a divided copolymer due to the heterogeneous properties such as copolymer composition and molecular weight.

INTRODUCTION

In the previous paper,¹ it was found that oxymethylene copolymer with excellent thermal stability is obtained in the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal.

The mechanism of this copolymerization may be very complicated because in this system 1,3-dioxolane and methylal act as comonomer and chain transfer agent, respectively. In this copolymerization system, it has been also clarified that copolymerization rate and properties of copolymer, such as thermal stability and solution viscosity, are dependent on the amounts of 1,3-dioxolane and methylal, and that the copolymerization reaction proceeds from the surface to the center of the monomer particle to give two different copolymers, i.e., a copolymer with disordered crystals on the surface and a fibril-like copolymer having well-oriented crystals in the center of the particle. From these facts, it can be deduced that the copolymer containing larger amounts of ethylene oxide units in its main chain and having lower molecular weight is formed on the surface. On the other hand, the copolymer containing smaller amounts of ethylene oxide units and having a higher molecular weight is formed in the center of the monomer particle.

Further, it has been clarified that in this solid-state copolymerization, thermal stability and intrinsic viscosity of the copolymer obtained by using 15 l kneader-type reactor depend on the addition method of the 1,3-dioxolane-

methylal solution to tetraoxane preheated to the polymerization temperature. In the case of the copolymerization in which 1,3-dioxolane-methylal solution containing iodine is added all at once into the reactor, as the reactivities of 1,3-dioxolane and methylal are very high and they are consumed in the early stage of this copolymerization, composition and molecular weight of the copolymer formed on the surface of the monomer particle are different from those of copolymer formed in the center of the monomer particle.

In order to investigate the characteristics of this copolymerization, fractional dissolution of the copolymer obtained in this system was tried on the basis of the difference in dissolubility of the copolymer. In general, it is too difficult to dissolve poly(oxymethylene) in a common solvent at a relatively low temperature. It is also known that poly(oxymethylene) is easily decomposed by heating or by acids. However, oxymethylene copolymer can be dissolved slightly easier than oxymethylene homopolymer, because comonomer units contained in the oxymethylene chain disarrange crystal structure to decrease crystallinity. Further, the lower the molecular weight of polymer, the higher its dissolubility. Therefore, fractional dissolution appears to be a useful means to elucidate the characteristics of this copolymerization.

EXPERIMENTAL

Materials

Copolymer. The copolymer used for this study was prepared as follows. Tetraoxane was purified by sublimation and then crushed to granules smaller than 12 mesh (1.410 mm). The granules thus obtained were put in the reactor and heated to a polymerization temperature of 105°C. Subsequently, 1,3-dioxolane-methylal solution containing iodine was added to the reactor (1,3-dioxolane, 3.0%; methylal, 0.3%; iodine, 30 ppm). The copolymerization was carried out for 60 min at 105°C. The reaction mixture was washed with acetone-water solution (1:1 by volume) containing ca. 2% sodium thiosulfate to remove residual reactants, such as tetraoxane, 1,3-dioxolane, and iodine, and soluble products which may be formed during the copolymerization. The copolymer was filtered off and dried *in vacuo*. The copolymer thus obtained was sieved to collect the copolymer particles in the range of 16–24 mesh and used for the fractional dissolution.

Solvent. Tetrachloroethane-phenol solvent (75:25 by volume) was used as a good solvent, and cyclohexanol was used as a poor solvent. Just before use, each of the solvents was purified according to conventional methods. It was confirmed to be pure by gas chromatography. The mixed solvent, which consists of a good solvent and a poor one (50:50 by volume), was used for the fractional dissolution, and 0.5% α -pinene and 5.0% *tert*-butyl-*p*-cresol were added to the solvent as stabilizer of poly(oxymethylene).

Fractional Dissolution

After the solution containing 1 wt % copolymer was kept at 135°C for 15 min with bubbling nitrogen, the sample was separated into the dissolved and the undissolved parts by pressure filtration. Subsequently, the poor solvent (cy-

clohexanol) was added to the filtrate, followed by cooling to room temperature to precipitate the dissolved copolymer. The copolymer thus recovered was dried under reduced pressure after washing with acetone and ether, while the copolymer which remained undissolved was dried under reduced pressure, followed by addition of fresh solvent in order to prepare again the solution containing 1 wt % copolymer. The solution was heated again at 135°C for 15 min with bubbling nitrogen. Fractional dissolution was carried out by repetition of the same procedure mentioned above.

Molecular Weight Distribution

A Waters Associates gel permeation chromatograph, Model 200, was used for the determination of the molecular weight distribution of the copolymer using *N,N*-dimethylformamide as a solvent. In this paper, molecular weight of poly(oxyethylene) was represented by the chain length of polystyrene as a matter of convenience, since a calibration curve was obtained by using commercial polystyrene standards. The operation conditions for gel permeation chromatography of poly(oxyethylene) were previously reported in detail.²

Thermal Behavior

A Perkin-Elmer differential scanning calorimeter, Model DSC-1, was used to observe the thermal behavior of the copolymer. Measurements were made under a nitrogen stream flowing through the sample holder assembly. Samples of 3–4 mg copolymer were used, and the scanning rate was 16°C/min.

Thermal decomposition curves were obtained at 222°C under a nitrogen stream by using a Rigaku Denki electric thermal balance, Model RTG-1.

Copolymer Composition

NMR spectra were measured at 140–150°C in *o*-dichlorobenzene (about 5 wt % solution) with a Japan Electron Optics spectrometer, Model 4H-100, working at 100 MHz.

Viscosity and Thermal Stability

The methods for determination of solution viscosity and thermal stability of the copolymer were described in detail in the previous paper.¹ They are denoted by $[\eta]$ (intrinsic viscosity) and R_{222}^{60} (percentage of the residual weight after 60 min of heating at 222°C), respectively.

RESULTS AND DISCUSSION

Fractional Dissolution and Properties of the Copolymer Fractionated

A relationship between percentage of the dissolved copolymer and dissolution time is shown in Figure 1. The rate of dissolution seems to increase after ca. 15 min, and about 30% of the original copolymer is dissolved during the first 30 min. The rate of dissolution decreases gradually with increasing time after 30 min;

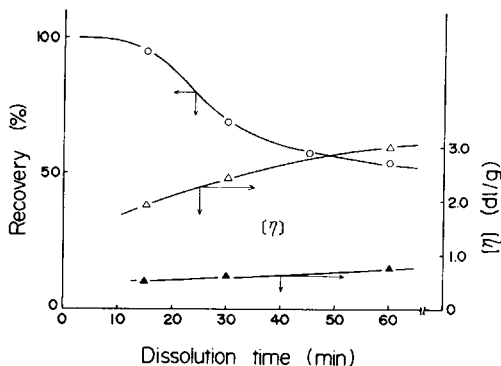


Fig. 1. Recovery of the undissolved copolymer and intrinsic viscosity of dissolved and undissolved copolymers as a function of dissolution time: (O, Δ) undissolved copolymer; (\blacktriangle) dissolved copolymer.

consequently, the percentage of the undissolved copolymer seems to become constant. Copolymer concentration of the extract obtained at the dissolution time of 30 min is ca. 0.25%. Rapid decrease in the dissolution rate after 30 min suggests that the sample consists of a copolymer different in solubility.

Intrinsic viscosity $[\eta]$, ethylene oxide unit content [E], and thermal stability R_{222}^{60} of the dissolved and the undissolved copolymers are shown in Table I. As is seen, $[\eta]$ of the dissolved copolymer is approximately constant regardless of time. The $[\eta]$ of the undissolved copolymer (1.9 dl/g) is higher than that of the dissolved one (ca. 0.75 dl/g) and increases with increasing time to reach 3.0 dl/g after 60 min. The relationship between $[\eta]$ of the undissolved copolymer and dissolution time seems to indicate that the lower the molecular weight of the copolymer, the more easily it dissolves. It can be, therefore, considered that $[\eta]$ of the undissolved copolymer becomes higher with increasing time.

As poly(oxymethylene) is scarcely dissolved in common solvents even at elevated temperature and is easily decomposed by heating, acids, and alkali, its fractionation is well known to be very difficult. According to the fractional dissolution used in this study, however, the fractionation of oxymethylene copolymer can be carried out easily with almost 100% recovery, as seen in Table

TABLE I
Fractional Dissolution

Copolymer	Recovery, %	Ethylene oxide content, mole-%	$[\eta]$, dl/g	R_{222}^{60} , %
Original copolymer	—	1.57	1.9	96.5
Dissolved for 0–15 min	4.8	—	0.5	98.8
Undissolved for 0–15 min	95.2	—	1.9	96.5
Dissolved for 15–30 min	26.2, (31.0) ^a	2.00	0.6	98.2
Undissolved for 15–30 min	69.0	1.31	2.4	96.0
Dissolved for 30–60 min	15.0, (46.0) ^a	2.00	0.75	97.7
Undissolved for 30–60 min	54.0	1.11	3.0	95.6

^a Integral value of recovery (%).

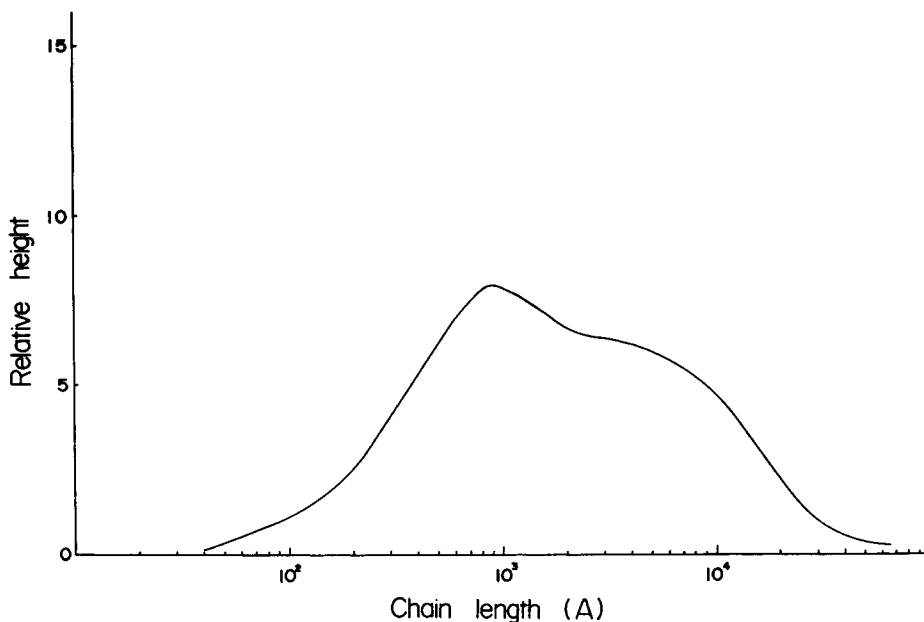


Fig. 2. GPC curve of original copolymer.

I. The composition and the thermal stability of the copolymer will be discussed later.

The molecular weight distribution of the fractionated copolymer was determined by gel permeation chromatography. Figure 2 shows the gel permeation chromatogram of the original copolymer used for the fractional dissolution. It can be seen that this copolymer has a considerably wide molecular weight distribution curve with a discernible shoulder at the larger molecular weight side. The shoulder peak and the main peak are located at ca. 5×10^3 and 8×10^2 Å, respectively. These results indicate that the original copolymer used in this study can be divided into approximately two on the basis of molecular weight, i.e., one has a smaller molecular weight and is dissolved in the solvent on fractional dissolution, and the other has a higher molecular weight and is scarcely dissolved on fractional dissolution. Figures 3 and 4 show the gel permeation chromatograms of the dissolved and the undissolved copolymers recovered by the fractional dissolution.

The gel permeation chromatogram of the dissolved copolymer recovered at 30 min, Figure 3(a), is shown to have a considerably narrow molecular weight distribution, the peak of which is located at 7.5×10^2 Å. This value agrees with that of the main peak, at the lower molecular weight side, of the original copolymer shown in Figure 2. Figure 3(b) indicates that the undissolved copolymer has a considerably wide and simple distribution of molecular weight. The value of this peak situation (5.5×10^3 Å) is approximately equal to that of the shoulder peak of the original copolymer. From Figures 3 and 4, further, both peak situations of the dissolved and the undissolved copolymers are independent of the dissolution time, although the shapes of their curves are a little different from each other. The results of the gel permeation chromatograms suggest the following: The molecular weight distribution of the copolymer obtained in this

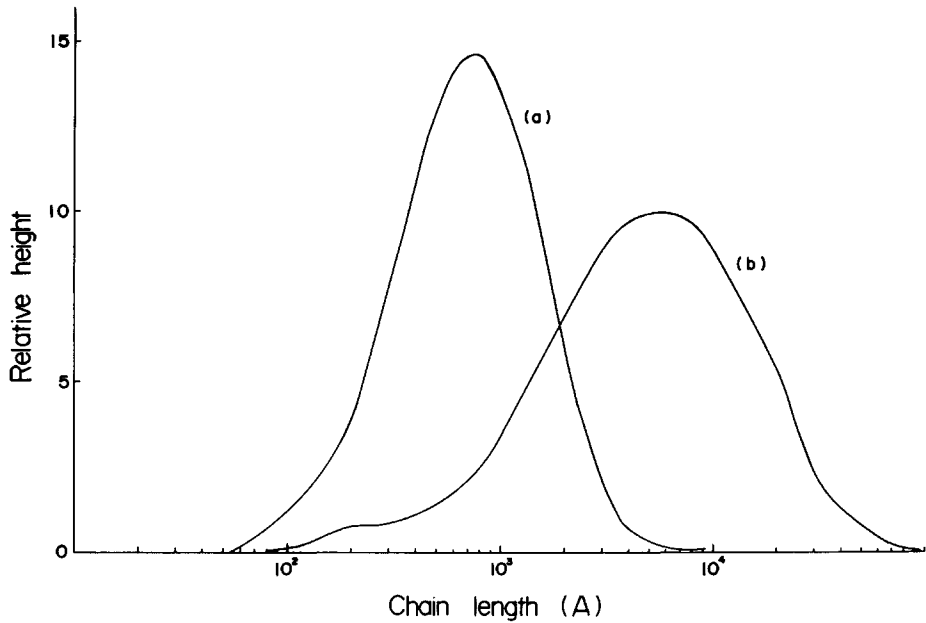


Fig. 3. GPC curves of dissolved (a) and undissolved (b) copolymer recovered at 30 min.

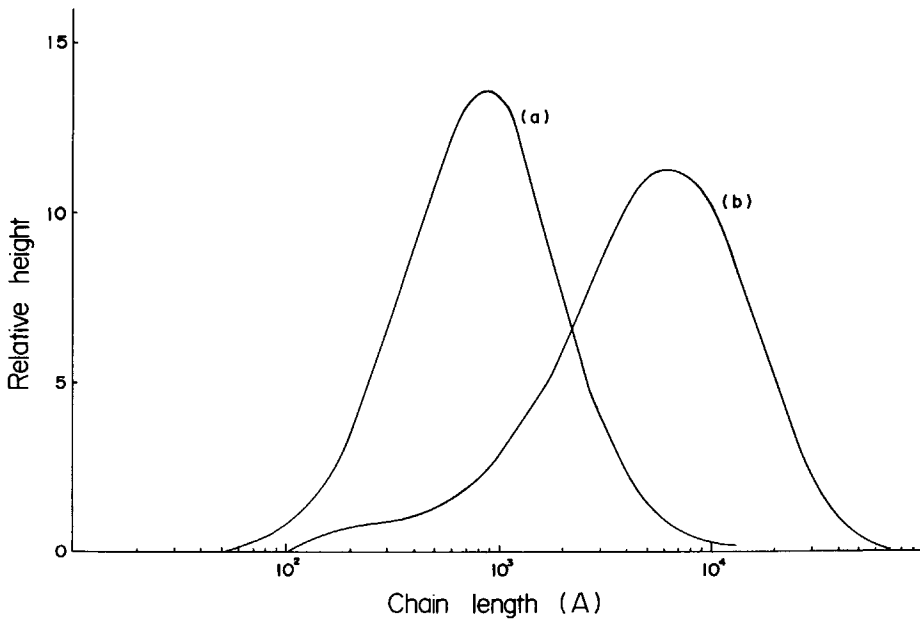


Fig. 4. GPC curves of dissolved (a) and undissolved (b) copolymer recovered at 60 min.

copolymerization system consists of two simple ones. The copolymer dissolved on fractional dissolution corresponds to the copolymer with lower molecular weight. On the other hand, the undissolved copolymer corresponds to the copolymer having the larger molecular weight.

The thermal stabilities of the dissolved and the undissolved copolymers ob-

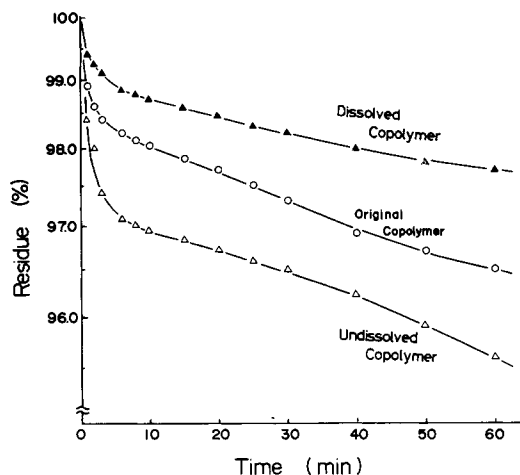


Fig. 5. Thermal decomposition curve of copolymers: decomposition, at 222°C in nitrogen stream.

tained at various dissolution times are listed in Table I, and the thermal decomposition curves are shown in Figure 5. These results indicate that the R_{222}^{60} value of the dissolved copolymer decreases with increasing dissolution time and is larger by 1–2% than that of the original copolymer, and that the R_{222}^{60} value of the undissolved copolymer, on the contrary, decreases slightly with increasing time and is smaller by ca. 1% than that of the original copolymer. Since the thermal stability of the oxymethylene copolymer obtained by the copolymerization of trioxane with 1,3-dioxolane is well known to increase with 1,3-dioxolane content in the copolymer,^{3,4} the results shown in Table I and Figure 5 suggest that the copolymer containing the larger amount of 1,3-dioxolane dissolves more easily than that having the smaller 1,3-dioxolane content. Therefore, it can be reasonably concluded that, on this fractional dissolution, the copolymer is fractionated by its dissolubility attributed to 1,3-dioxolane content as well as molecular weight.

The DSC of the undissolved copolymer was carried out to examine the copolymer composition. The DSC of the first scan for the undissolved copolymer and the original one are shown in Figure 6. The thermogram of the original copolymer has two peaks, at 163° and 172.5°C. For the undissolved copolymer, the peak at the lower temperature side becomes smaller with increasing dissolution time. On the contrary, the peak at the higher temperature side becomes larger. Further, both peaks shift to the higher temperature side as the dissolution time increases. These results suggest that the undissolved copolymer corresponds mainly to the copolymer having a peak at the higher temperature side in the original sample, even though the thermogram of the undissolved copolymer obtained at 60 min still has a discernible shoulder at the lower temperature side. Since any change in DSC thermogram of the original copolymer could not be found before and after the sample was heated at 135°C for 2 hr in the absence of solvent, the fact that the peak at the lower temperature side becomes smaller with increasing dissolution time can be explained as a result not of heating but of the preferential dissolution of the copolymer having the peak at the lower temperature side.

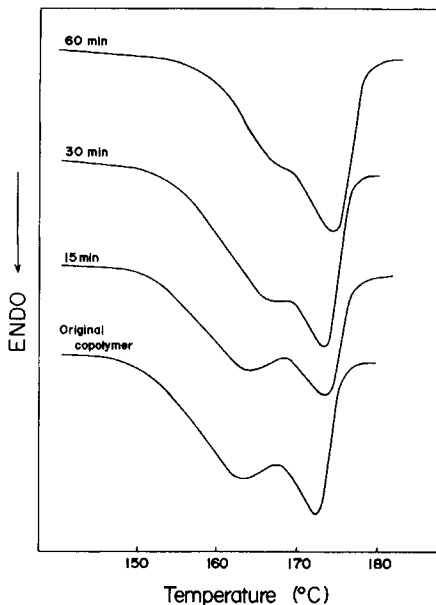


Fig. 6. DSC thermograms (first scan) of original and undissolved copolymers.

There are several reasons why the DSC thermogram of a polymer has many peaks. In the case of the oxymethylene copolymer, the reasons can be considered as follows: Marked differences in (1) the copolymer composition, (2) the crystal structure, such as extended and folding crystals,⁵ and (3) the molecular weight of the copolymer. The melting point of poly(oxymethylene) is scarcely influenced by the molecular weight if it is high enough ($M_n > 1000$).⁶ Even the lowest molecular weight of the copolymer listed in Table I is estimated to be ca. 30,000 according to the equation proposed by Kakiuchi et al.⁷ Therefore, the reasons why the original copolymer has two peaks can be mainly attributed to terms (1) and (2) described above. The original copolymer is considered to be fractionated on the basis of the difference in ethylene oxide unit content or, thereby, the distortion of the crystal structure of the copolymer. Since the copolymer having a peak at the lower temperature side has a larger amount of ethylene oxide unit, this copolymer seems to be dissolved preferentially on fractional dissolution and to be removed from the original copolymer. It is understandable that the content of the original copolymer and the dissolved copolymer recovered at 30 min are 1.57 and 2.0%, respectively, as listed in Table I.

Figure 7 shows DSC thermograms of the second run for the original and the undissolved copolymers at various dissolution times. As samples used on the second run were quenched rapidly from 200° to 50°C, all the structures are considered to be spherulites.⁵ In this case, therefore, the effect of the crystal structure on the thermal behavior can be negligible. Figure 7 indicates that the peak temperature of the undissolved copolymer shifts to the higher temperature side with increasing time. This fact supports that the copolymer containing a larger amount of ethylene oxide unit is dissolved preferentially from the original

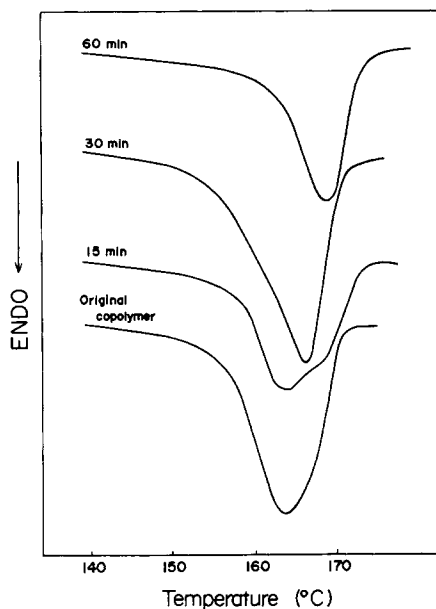


Fig. 7. DSC thermograms (second scan) of original and undissolved copolymers.

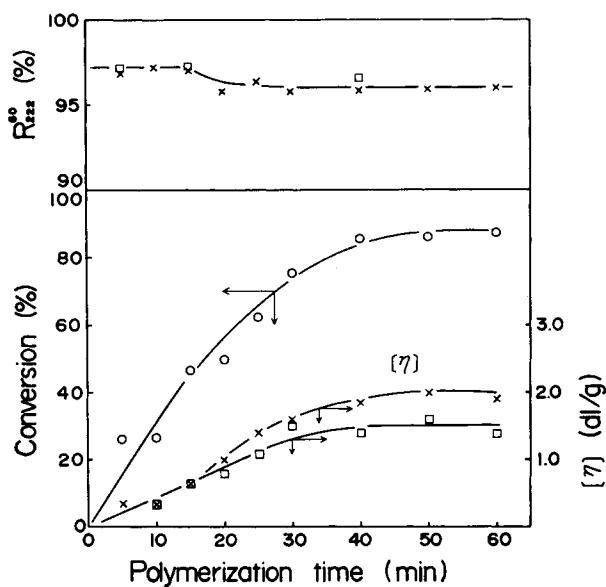


Fig. 8. Copolymerization of tetraoxane-1,3-dioxolane-methylal system: iodine, 30 ppm; 1,3-dioxolane, 3.0%; methylal, 0.35%; polymerization temperature, 105°C; (X) 24 mesh over; (□) 24 mesh under.

copolymer, hence, the content of ethylene oxide unit in the undissolved copolymer decreases with increasing time.

As discussed above, the original copolymer used in this study was found to be divided into two, i.e., the dissolved and the undissolved, on fractional dissolution. The former is the copolymer having relatively lower molecular weight and larger

content of ethylene oxide unit, and, on the other hand, the latter is the copolymer having a higher molecular weight and a smaller content of ethylene oxide unit.

In the previous paper,¹ the characteristics of the iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal were found to be as follows. (1) This copolymerization proceeds from the surface to the center of the tetraoxane particle. (2) More than 90% of 1,3-dioxolane-methylal solution is consumed during the early stage of the copolymerization, because the reactivities of 1,3-dioxolane and methylal with the active sites are higher than that of tetraoxane. (3) 1,3-Dioxolane and methylal are concentrated on the surface of the tetraoxane particle. Consequently, the copolymer formed in the surface layer is largely distorted. On the other hand, the fibril-like copolymer with well-oriented crystal axes is formed in the center of the tetraoxane particle.⁸

The results and discussion mentioned above appear to support our idea proposed for the mechanism of this copolymerization. The characteristics of this copolymerization will be clarified as discussed in the following section, not only from the results reported in previous papers,^{1,8,9} but also the results obtained by fractional dissolution.

Copolymerization Mechanism Deduced from Results of Fractional Dissolution

The copolymer used for this study was obtained at a polymerization time of 60 min under the conditions shown in Figure 8. The copolymer thus obtained was sieved into the smaller particle and the larger one by using a sieve of 24 mesh, and then $[\eta]$ and R_{222}^{60} values of each copolymer thus separated were measured. The following facts were found. As seen in Figure 8, the differences of $[\eta]$ and R_{222}^{60} between the larger copolymer particle and the smaller one develop gradually after 15 min. The copolymer yield (46%) at 15 min approximately agrees with the recovery yield of the copolymer dissolved during 60 min on fractional dissolution. Further, $[\eta]$ of the copolymer obtained in 46% polymer yield is 0.65 dl/g, which is in good agreement with 0.6 and 0.75 dl/g of the dissolved copolymers at dissolution times of 30 and 60 min, respectively (see Table I). From both the differences in $[\eta]$ and R_{222}^{60} due to the copolymer particle size and the decrease in dissolution rate after 30 min (shown in Fig. 1), it can be suggested that the copolymers formed before and after a polymerization time of 15 min differ from each other in copolymer composition and dissolubility. The differences of $[\eta]$ and R_{222}^{60} between the larger and the smaller copolymer particles suggest the following: In this system, the copolymerization proceeds from the surface to the center of the tetraoxane monomer particle. Consequently, the original copolymer is divided into two parts by fractional dissolution: one is the copolymer formed early in the surface layer, where most of the 1,3-dioxolane and methylal added are consumed, and the other is the copolymer formed in the center. This idea is also supported by the results of scanning electron microscopy.⁸

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References

1. I. Ishigaki, Y. Watanabe, Y. Morita, K. Takada, and A. Ito, *J. Appl. Polym. Sci.*, **21**, 711 (1977).
2. I. Ishigaki, Y. Morita, K. Nishimura, and A. Ito, *J. Appl. Polym. Sci.*, **18**, 1927 (1974).
3. M. Sakamoto, A. Ito, and K. Hayashi, *Kobunshi Kagaku*, **28**, 742 (1971).
4. I. Ishigaki, A. Ito, and K. Hayashi, *J. Polym. Sci. A-1*, **10**, 751 (1972).
5. B. Wunderlich, *J. Polym. Sci. A*, **2**, 3697 (1964).
6. W. H. Linton and H. H. Goodman, *J. Appl. Polym. Sci.*, **1**, 179 (1959).
7. H. Kakiuchi and W. Fukuda, *Kogyo Kagaku Zasshi*, **66**, 964 (1963).
8. Y. Morita, I. Ishigaki, Y. Watanabe, H. Okubo, and A. Ito, *J. Appl. Polym. Sci.*, **21**, 723 (1977).
9. I. Ishigaki, Y. Morita, K. Nishimura, M. Yokooji, and A. Ito, *J. Appl. Polym. Sci.*, **21**, 735 (1977).

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