Iodine-Initiated, Solid-State Copolymerization of Tetraoxane with 1,3-Dioxolane in the Presence of Methylal. VI. Studies on Copolymer Composition

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Synopsis

In order to elucidate the mechanism of copolymerization of tetraoxane-1,3-dioxolane, the consumption rate of 1,3-dioxolane was measured by using gas chromatography, and the copolymer composition was determined by high-resolution NMR spectroscopy and differential scanning calorimetry. It was found that 1,3-dioxolane is rapidly consumed in the early stage of copolymerization if 1,3-dioxolane is added at once. The copolymer thus obtained is characterized by a heterogeneous distribution of 1,3-dioxolane in the copolymer chain. However, if 1,3-dioxolane is added continuously during the progress of the copolymerization, the distribution and content of 1,3-dioxolane in the copolymer chain was found to be very homogeneous.

INTRODUCTION

In a previous paper,[1] it was shown that, in the solid-state copolymerization of tetraoxane with 1,3-dioxolane, the molecular weight distribution of the copolymer depends largely on the addition method of methylal to the polymerization system. From the molecular weight distribution of the copolymer determined by gel permeation chromatography, it has been shown that in the one-addition copolymerization (which is described in detail in previous papers[1,2]), the distribution curve varies remarkably with increasing polymerization time to become a very broad curve having a shoulder at the higher molecular weight side. In the four- and continuous-addition copolymerizations, however, the molecular weight distribution of the copolymer is approximately constant irrespective of polymerization time. In the one-addition copolymerization, the molecular weight distribution also depends upon monomer particle size. From the results mentioned above and obtained by scanning electron microscopy of the copolymer,[3] this copolymerization has been found to proceed from the surface to the center of the monomer particle. In the one-addition copolymerization, it has also been found that the molecular weight distribution of the copolymer formed at the surface of the monomer particle differs from that formed in the center. On the other hand, in the continuous-addition copolymerization, the molecular weight distribution has been found to become constant irrespective of polymerization time and monomer particle size, because methylal diffuses through the formed copolymer layer into the center to react with active center.

The behavior of 1,3-dioxolane in this system may also be expected to be similar

to that of methylal. In this system, 1,3-dioxolane reacts with tetraoxane as a comonomer to give copolymer with excellent thermal stability.

In this paper, in order to elucidate the characteristics of this copolymerization system, the relationships between ethylene oxide unit content and experimental factors, such as addition method, particle size, and polymerization time, were obtained by NMR spectroscopy and differential scanning calorimetry of the copolymer.

EXPERIMENTAL

Copolymer used for this study was obtained by iodine-initiated, solid-state copolymerization of tetraoxane with 1,3-dioxolane in the presence of methylal by using a 15-liter kneader-type reactor. The procedure of the copolymerization and the addition methods of 1,3-dioxolane–methylal solution have been described in detail in the previous paper.[2] Unless otherwise indicated, the sample copolymers used for high-resolution NMR spectroscopy and DSC were obtained by conical quartering.

The residual 1,3-dioxolane was determined as follows. One to 2 g of the reactant was collected into a 50-ml flask containing 10 ml toluene through the sampling hole of the reactor at a given time interval. The reactant was kept in toluene for 24 hr to completely extract residual polymeric materials. The amount of 1,3-dioxolane in the extract was determined by a Perkin–Elmer gas chromatograph Model 881. The amount of 1,3-dioxolane which remains in the vapor phase in the reactor was determined by gas chromatography.

The NMR spectra of the copolymer were measured at 140–150°C in o-dichlorobenzene (about 5% solution) with a Japan Electron Optics Spectrometer Model 4H-100 working at 100 MHz. The concentration (in mole fraction) of ethylene oxide units was calculated on the basis of its ^{13}C-satellite peaks detected at both sides of the formal peak.

A Perkin–Elmer differential scanning calorimeter Model DSC-1B was used to observe the thermal behavior of the copolymer. The procedure was described in detail in the previous paper.[3]

RESULTS AND DISCUSSION

Consumption of 1,3-Dioxolane

In this copolymerization system, 1,3-dioxolane can be considered to exist as (1) one of the components of the copolymer, (2) unreacted and adsorbed in the polymeric mixture, or (3) vaporized in the reactor. Each amount can be determined by NMR spectroscopy of the copolymer for (1) and by gas chromatography of the extracts for (2) and (3).

A typical result of the material balance on 1,3-dioxolane is as follows: (1) 96.4% of 1,3-dioxolane was incorporated into a copolymer chain, (2) 1.3% of it remained unreacted in the polymeric mixture, (3) 4.0% of it remained in the vapor phase in the reactor. This result was obtained under the following polymerization conditions: 1,3-dioxolane concentration, 3.5%; methylal, 0.15%; iodine, 30 ppm; polymerization, at 105°C for 60 min. The sum, 101.7%, seems to be almost within experimental error. The amount of 1,3-dioxolane consumed by the copoly-

merization, therefore, can be estimated if the amounts of 1,3-dioxolane in (2) and (3) are determined.

Plots of the 1,3-dioxolane consumption calculated by the material balance against polymerization time are shown in Figures 1 through 4. In the one-addition copolymerization, as seen in Figure 1, about 80% of the initial amount of 1,3-dioxolane was already consumed during the early period of polymerization (within 5 min) in which the copolymer yield reached only to 30%. During polymerization time from 10 to 60 min, the amount of 1,3-dioxolane consumed was less than 10% of the initial 1,3-dioxolane, although the increment of the copolymer yield was 62.5%. This fact indicates that the composition of the copolymer formed in the early stage of polymerization is considerably different from that formed in the later stage, i.e., the content of ethylene oxide unit in the copolymer decreases steeply as the polymerization time increases.

In the two-addition copolymerization, as seen in Figure 2, both the consumption rate of 1,3-dioxolane and the copolymerization rate increase remarkably just after the second addition of the 1,3-dioxolane–methylal solution, i.e., at a polymerization time of 20 min. In this case, the copolymer yield reached
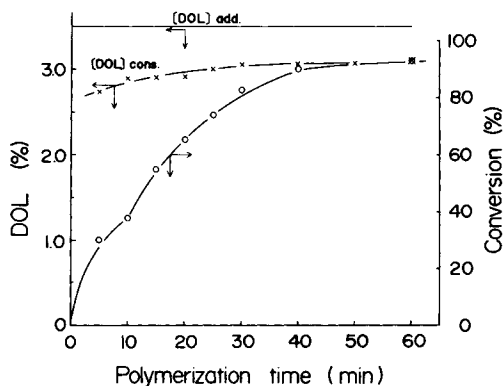

Fig. 1. 1,3-Dioxolane consumption curve in one-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C. $[DOL]_{add.}$ and $[DOL]_{cons.}$ represent the additional and consumptional amount of 1,3-dioxolane.
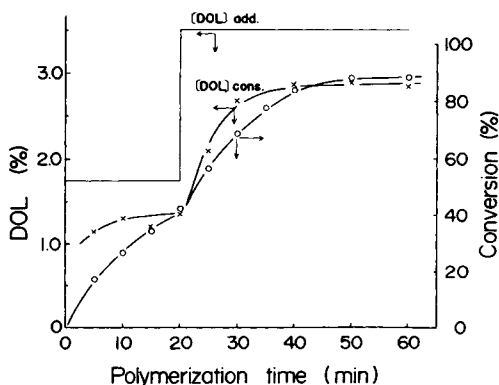

Fig. 2. 1,3-Dioxolane consumption curve in two-addition copolymerization. Other polymerization conditions same as in Fig. 1.
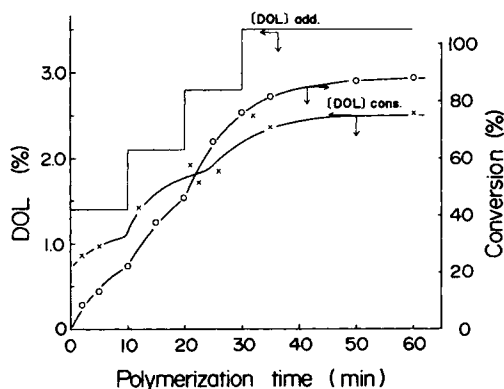
Fig. 3. 1,3-Dioxolane consumption curve in four-addition copolymerization. Other polymerization conditions same as in Fig. 1.
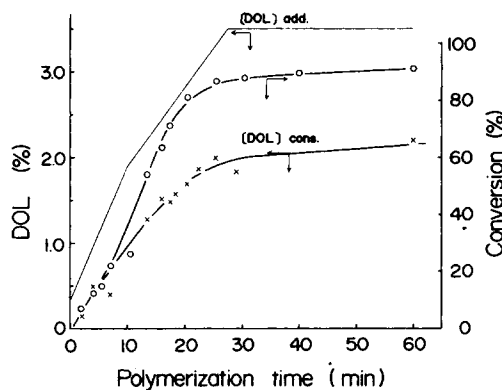

Fig. 4. 1,3-Dioxolane consumption curve in continuous-addition copolymerization. Other polymerization conditions same as in Fig. 1.

42.5% within the first 20 min, and 35% of the total amount of 1,3-dioxolane was consumed during the period.   During the copolymerization time from 20 to 60 min, the increment of the copolymer yield was 45%, and 45% of the total amount of 1,3-dioxolane was consumed.   These facts indicate that the composition of the copolymer obtained in the two-addition is more homogeneous compared with that of the copolymer obtained in the one-addition copolymerization.

In the four- and continuous-addition copolymerizations, as shown in Figures 3 and 4, the shape of the 1,3-dioxolane consumption curve is similar to that of the copolymer yield–time curve.   It can be expected that, as the number of the 1,3-dioxolane–methylal solution additions increase, the ethylene oxide unit content in the copolymer becomes constant irrespective of polymerization time, i.e., the larger the addition number of the 1,3-dioxolane–methylal solution, the more homogeneous the composition of the copolymer obtained.

Consequently, in this copolymerization, it can be concluded that if 1,3-diox- olane is added continuously as the copolymerization proceeds, the copolymer having a homogeneous distribution of ethylene oxide units in its chain can be formed irrespective of polymerization time.

NMR Spectroscopy of the Copolymer

Copolymer of tetraoxane with 1,3-dioxolane consists of formal units (—CH_2O—, denoted by F) and ethylene oxide units (—CH_2CH_2O—, denoted by E). The ethylene oxide unit content in the copolymer can be measured by high-resolution NMR. A typical NMR spectrum of the copolymer is given in Figure 5.

Relationships between the copolymer yield and the ethylene oxide unit content in the copolymer obtained in the one-, two-, four-, and continuous-addition copolymerizations are shown in Figure 6. This indicates that the copolymer having high content of ethylene oxide unit is formed in the early stage of copolymerization in the one- and two-addition copolymerizations. On the other hand, in the four-addition and especially in the continuous-addition copolymerization, the ethylene oxide unit content in the copolymer scarcely varies with increasing copolymer yield. The ethylene oxide unit content determined by NMR spectroscopy is in good agreement with that found by gas chromatography.

In Table I, the ethylene oxide unit content of the copolymers obtained at
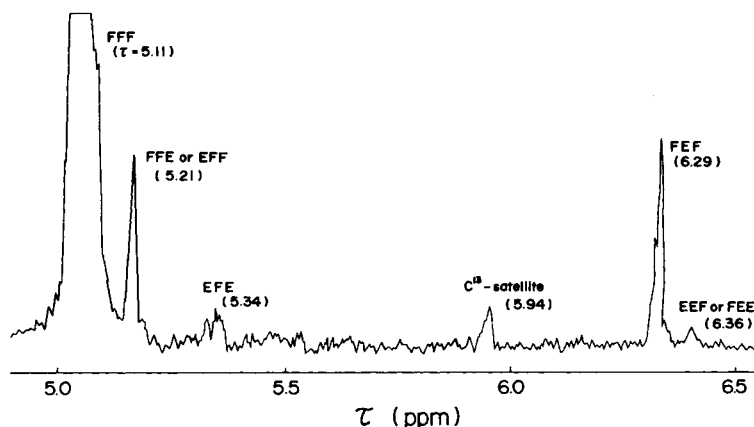

Fig. 5. NMR spectrum of copolymer obtained in four-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization, 60 min at 107°C.
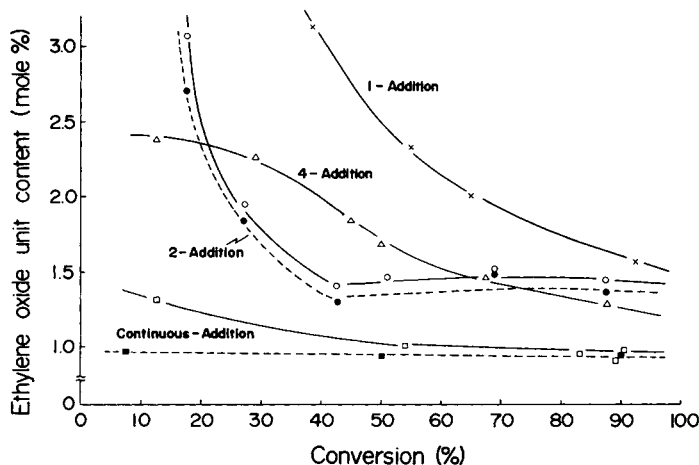

Fig. 6. Relationship between ethylene oxide unit content and yield of copolymer: (×, ○, △, □) determined by NMR spectroscopy; (●, ■) by gas chromatography.

TABLE I
Concentration of Triad Sequence[a] in Copolymer

Polymer	Amount of 1,3-dioxolane, %	Polymer yield, %	FFF, mol %	EFF, FFE, mol %	EFE, mol %	FEF, mol %	EEF, FEE, mol %	Total [E], mol %	l_E	R, %	[η], dl/g
Copolymer of one-addition[b]	3.5	92.5	96.2	2.20	—	1.51	0.054	1.56	1.1	97.0	1.7
Copolymer of two-addition	3.5	89.0	95.7	2.34	0.482	1.44	—	1.44	1.15	97.7	1.3
Copolymer of four-addition	3.5	88.0	96.7	1.98	—	1.14	0.143	1.29	1.2	97.0	1.45
Copolymer of continuous-addition	3.5	90.0	98.8	1.21	—	0.95	—	0.95	1.1	98.2	1.8
Durcon M90	—	—	95.2	2.7	—	1.2	0.9	2.1	1.4	99.4	1.4
Durcon M25	—	—	95.8	2.3	—	1.2	0.8	2.0	1.5	99.1	1.9

[a] F and E denote $-CH_2O-$ (formal unit) and $-CH_2CH_2O-$ (ethylene oxide unit), respectively.
[b] Represents number of additions of 1,3-dioxolane–methylal solution during polymerization process.

saturation polymer yield with various addition methods are listed in comparison with commercial poly(oxymethylenes) (Duracon M-90 and M-25). The [EEF] or [FEE] sequence in the tetraoxane copolymer is very small, and the number-average length of successive sequence of E, l_E, becomes approximately unity. On the other hand, Duracon, which is obtained by the liquid-state copolymerization of trioxane with ethylene oxide, has a larger [EEF] or [FEE] sequence concentration, and their l_E's are about 1.5. Consequently, it can be concluded that in the solid-state copolymerization of tetraoxane with 1,3-dioxolane, head-to-head reaction of 1,3-dioxolane scarcely occurs. Table I also shows that the larger the number of the 1,3-dioxolane–methylal solution addition, the lower the ethylene oxide unit content in the copolymer. This fact was anticipated from the determination of residual 1,3-dioxolane by gas chromatography; i.e., as seen in Figures 3 and 4, a larger part of 1,3-dioxolane added after most of tetraoxane was consumed cannot copolymerize to be incorporated into the polymer chain.

Differential Scanning Calorimetry of the Copolymer

It is well known that the melting point of the copolymer decreases with increasing the ethylene oxide unit content in the copolymer.[4] In order to obtain a relationship between thermal behavior of the copolymer and the addition method, the authors tried to measure differential scanning calorimetry of the copolymer. The differential scanning calorimetric thermograms of the first scan for the copolymer obtained in the one-addition copolymerization is shown in Figure 7(a). It can be seen that the thermograms have three peaks. They are at 155–158°C, 160–168°C, and 170–178°C and are denoted by peak 1, peak 2, and peak 3, respectively. The copolymer formed during a copolymerization time of 10 min (35% polymer yield) has two peaks (peak 1 and peak 2), and peak 2 becomes greater as the copolymerization proceeds, while peak 3 begins to appear after ca. 15 min (53% polymer yield) and becomes greater, as does peak 2. The copolymer obtained in 89% polymer yield (approximate saturation yield) at 50 min has three peaks, i.e., peak 1 (158°C), peak 2 (166°C), and peak 3 (176°C).

On the basis of these thermograms, the three peaks were separated from one another, and the products of the fraction of their endothermic peak areas, and polymer yield were plotted against the polymer yield as shown in Figure 7(b). The endothermic area of peak 1 scarcely changes irrespective of the polymer yield. This fact indicates that the copolymer giving peak 1 is formed only at the early stage of the copolymerization. On the other hand, the endothermic area of peak 3, appearing at more than 50% polymer yield, increases as well as that of peak 2. Therefore, the copolymer giving peak 2 is considered to be formed during the entire period of the copolymerization, and the copolymer giving peak 3 is formed at the later stage of the copolymerization. Plots of peak temperature against the polymer yield are given in Figure 7(c). The peak temperatures of peak 2 and peak 3 increase linearly, but that of peak 1 scarcely changes with increasing polymer yield. As discussed later, it is known that the differential scanning calorimetric thermogram of the first scan for the crystalline polymer is a reflection of copolymer composition as well as of the crystal structure. To minimize the effect of crystal structure, the differential scanning calorimetric thermogram of the second scan was measured after quenching from 220° to 50°C.
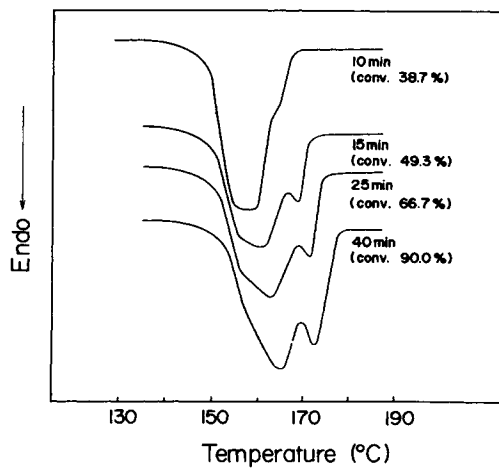
(a)
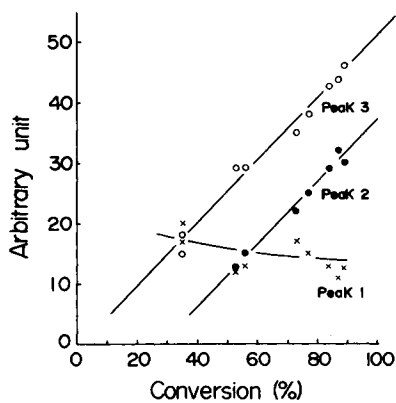
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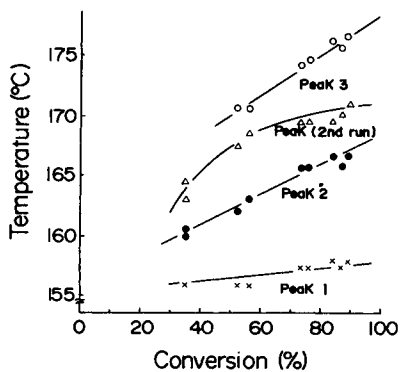
(c)

Fig. 7. Differential scanning thermogram of copolymer obtained by one-addition copolymerization: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C; (a) effect of polymerization time on DSC thermogram (first scan); (b) plots of product of endothermic area and polymer yield as function of polymer yield; (c) relationship between melting point and copolymer yield.

The differential scanning calorimetric thermogram of the second scan thus obtained was found to be a considerably narrow curve with a single peak, even if that of the first scan was characterized by three peaks. The peak temperature of the differential scanning thermogram of the second scan was plotted against polymer yield as shown in Figure 7(c). The peak temperature increases with increasing polymer yield. This indicates that, in the one-addition copolymerization, the copolymer composition changes and the average content of ethylene oxide unit in the copolymer decreases as the copolymerization proceeds.

The thermograms obtained for the two-addition copolymerization are given in Figure 8(a), and the plots of the endothermic area of each peak and the peak temperature against the polymer yield are shown in Figure 8(b) and 8(c), respectively. Although peak 1, characterized by lower temperature, can be observed only for the copolymer obtained in the earlier stage, it is very hard to recognize peak 1 in the differential scanning calorimetric thermogram of the copolymer obtained at a copolymerization time of more than 10 min. In this case, the content of the copolymer giving peak 1 seems to be very low as compared with that found for the one-addition copolymerization. As seen in Figure 8(a), the thermogram of the copolymer obtained at 10 min (26.9% polymer yield) has only two peaks, i.e., peaks 2 and 3 (the latter can be observed as a shoulder of the former). Peak 3 grows gradually and becomes higher than peak 2 by 20 min. However, as seen in Figure 8(b), both the endothermic area of peak 2 and peak 3 increase as the copolymerization proceeds. Especially, that of peak 2 increases rapidly after the second addition of 1,3-dioxolane–methylal solution (20 min). Figure 8(c) shows that the increases in peak temperatures of peaks 2 and 3 are suppressed by the second addition of the solution and their peak temperatures become constant at a more than 40% polymer yield.

Figures 9 and 10 show the thermograms of the copolymer and the relationships between peak temperature and polymer yield in the four- and continuous-addition copolymerizations, respectively. As seen in Figures 9(a) and 10(a), the differential scanning calorimetric thermograms of the first scan were found to be a very narrow curve with a single peak irrespective of polymerization time. Their peak temperatures become nearly constant at a more than 20% polymer yield and agree very closely with those obtained by the thermogram of the second scan, see Figures 9(b) and 10(b). These results suggest that in the four- and continuous-addition copolymerizations, the copolymer having not only a constant composition but also the same crystal structure can be formed during almost the entire stage of the copolymerization.

The half-width determined on the differential thermogram of the second scan are plotted as a function of polymer yield in Figure 11. It can be seen that the thermograms of the copolymer obtained in the four- and continuous-addition copolymerizations have very narrow peaks as compared with that in the one- and two-addition. This also indicates that in this copolymerization system the copolymer becomes more homogeneous as the number of additions increases.

The relationship between the ethylene oxide unit content determined by NMR spectroscopy and the melting point of the copolymer obtained at various concentration of 1,3-dioxolane in the four-addition copolymerization is shown in Figure 12. This relationship is in good agreement with that reported by Inoue.[4]
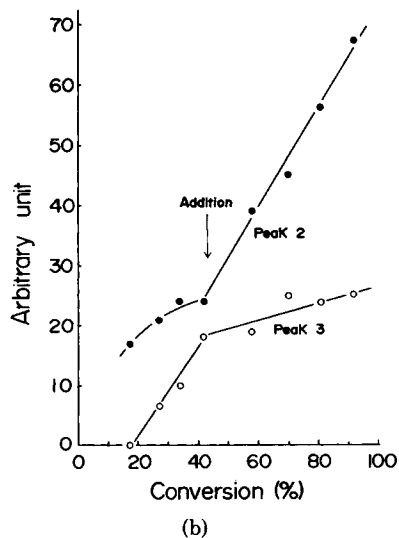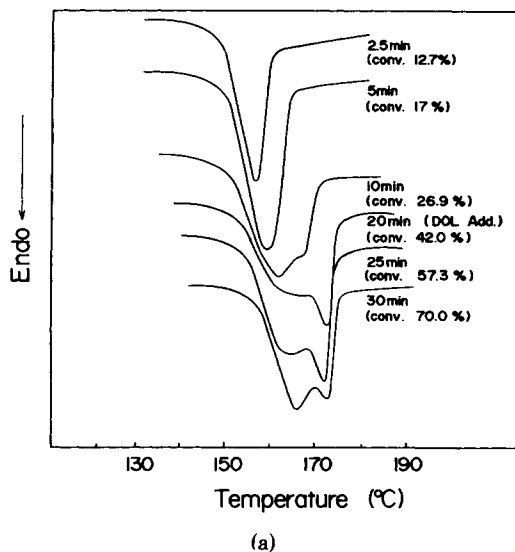
(a)

(b)

Fig. 8. Differential scanning thermogram of copolymer obtained by two-addition copolymerization. Other polymerization conditions same as in Fig. 7: (a) effect of polymerization time on DSC thermogram (first scan); (b) plots of product of endothermic area and polymer yield as function of polymer yield; (c) relationship between melting point and copolymer yield.
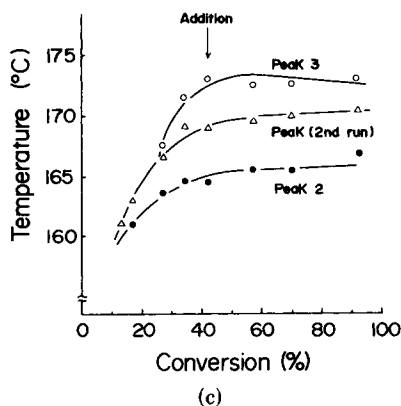
Fig. 8. (*Continued from previous page.*)

Copolymerization Mechanism

As mentioned above, the thermograms of the first scan of the copolymer obtained in the one- and two-addition copolymerizations have two or three peaks. This fact can be explained by the following reasons: (1) The melting point of oxymethylene copolymer has been found to decrease monotonously with increasing comonomer content in its main chain.[4] When the copolymer having a quite different ethylene oxide unit content is localized at the inter- or intraparticle of the differential scanning calorimetric sample, its thermogram may have a few peaks. (2) It is well known that the poly(oxymethylene) obtained in the radiation-induced polymerization of trioxane forms extended crystals, and its melting point is higher (>180°C) than that of the lamella crystal.[5] Therefore, the thermogram may have two peaks when the differential scanning calorimetric sample consists of extended and lamella crystals. (3) The thermogram of the copolymer may have a few peaks because of the great difference in the molecular weight. However, it has been known that the melting point of poly(oxymethylene) is scarcely influenced by the molecular weight if it is high enough ($\overline{M}_n > 1000$).[6] In this case, therefore, the influence of the molecular weight on the thermogram can be ignored, in as much as the molecular weight of the copolymer used in this study was more than 50,000.

As mentioned above, the reason why, in the one- and two-addition copolymerizations, the differential scanning calorimetric thermograms of the first scan consists of two or three peaks can be reasonably explained on the basis of (1) and (2) above. The sample seems to have an extremely heterogeneous distribution of ethylene oxide units or to consist of different crystal structures. Since the crystal structure of copolymer is influenced by the comonomer concentration in the copolymeric system, it is expected that the crystal structure of copolymer formed at a higher concentration of 1,3-dioxolane is lamella crystal and that formed at a lower concentration is the extended form.

In the one-addition copolymerization, as seen in Figure 1, about 80% of 1,3-dioxolane was consumed in the early stage of the copolymerization, and at the later stage the copolymerization proceeds at a very low concentration of 1,3-dioxolane. The ethylene oxide unit content of the copolymer formed at the early stage of the copolymerization is therefore expected to be very different from that of the copolymer formed at the later stage. This is supported by the NMR measurement of the copolymer as shown in Figure 6.
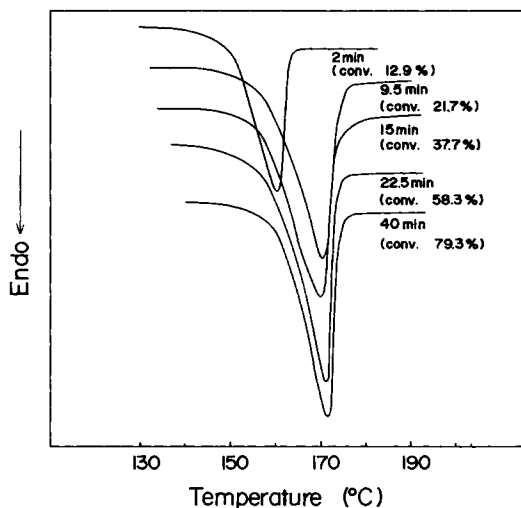
(a)
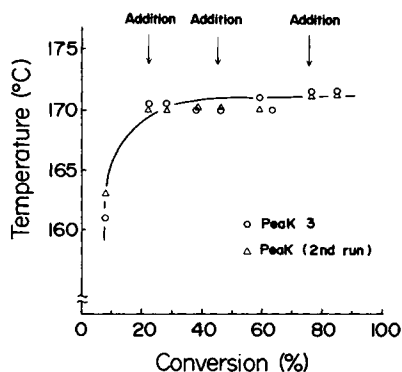
(b)

Fig. 9. Differential scanning thermogram of copolymer obtained by four-addition copolymerization. Other polymerization conditions same as in Fig. 7: (a) effect of polymerization time on DSC thermogram (first scan); (b) plots of product of endothermic area and polymer yield as function of polymer yield; (c) relationship between melting point and copolymer yield.

The copolymer giving peaks 1 and 2 in its thermograms has a high ethylene oxide unit content. Therefore, the thermogram of the copolymer obtained in the one-addition copolymerization has a few peaks. In the two-addition copolymerization, as seen in Figures 2 and 8, the consumption rate of 1,3-dioxolane increases rapidly, and peaks 2 and 3 become larger after the second addition of the 1,3-dioxolane–methylal solution. Accordingly, peaks 2 and 3 are affected by the second addition of the solution. On the other hand, in the four- and continuous-addition copolymerizations, as seen in Figures 3, 4, 9, and 10, the ratio of the consumption of 1,3-dioxolane to that of tetraoxane is approximately
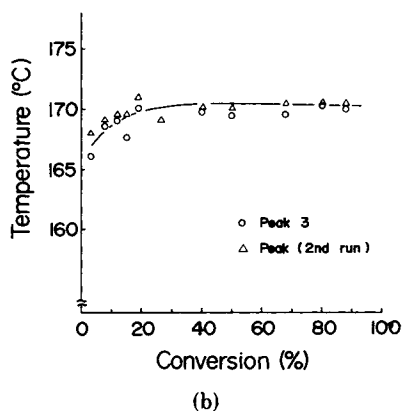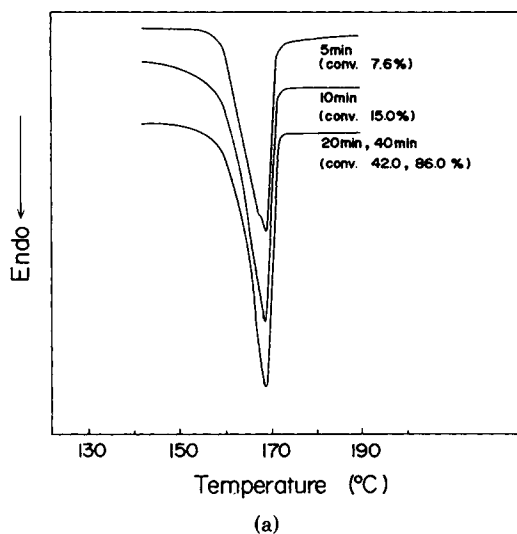
(a)

(b)

Fig. 10. Differential scanning thermogram of copolymer obtained by continuous-addition co-polymerization. Other polymerization conditions same as in Fig. 7: (a) effect of polymerization time on DSC thermogram (first scan); (b) plots of product of endothermic area and polymer yield as function of polymer yield; (c) relationship between melting point and copolymer yield.

constant in the entire course of the copolymerization, and the ethylene oxide unit distribution of the copolymer is relatively homogeneous. Consequently, the thermograms result in a narrow peak irrespective of the copolymerization time.

In the previous paper on the beaker-scale copolymerization,[3] the microscopy and scanning electron microscopy studies of the copolymer have indicated that in this copolymerization the reaction proceeds from the surface to the center of the monomer particle and that the copolymeric particle formed in this system consists of a copolymer whose crystal axis cannot be discriminated, in the surface;
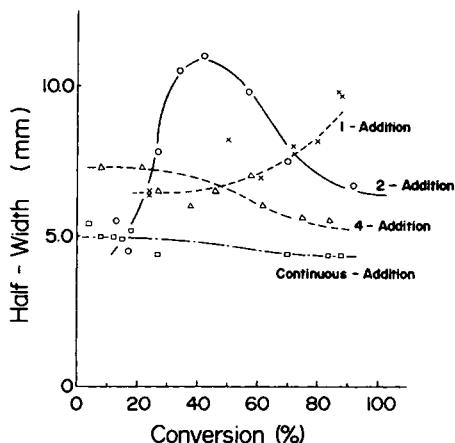
Fig. 11. Relationship between half-width of DSC thermogram (second scan) and yield of copolymer: iodine, 30 ppm; 1,3-dioxolane, 3.5%; methylal, 0.15%; polymerization temperature, 107°C.
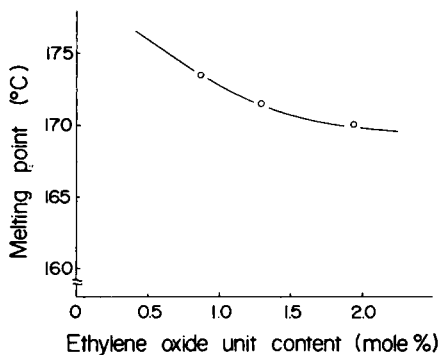

Fig. 12. Relationship between melting point and ethylene oxide unit content of copolymer obtained by four-addition copolymerization: iodine, 30 ppm; methylal, 0.15%; polymerization, 60 min at 107°C.

a fibril-like copolymer whose crystal axis is well oriented, in the center; and a fibril-like copolymer which is not oriented, in the intermediate region. In the one-addition copolymerization, therefore, it can be considered that the copolymer giving peak 1 corresponds to the one formed in the surface, the copolymer giving peak 2 corresponds to the unoriented fibril-like one in the intermediate region, and the copolymer characterized by peak 3 corresponds to the well-oriented fibril-like one in the center of the particle.

The results of fractional dissolution[7] also support the interpretation of this copolymerization mechanism. That is, the copolymer giving peak 1 or peak 2 was fractionated on fractional dissolution; on the other hand, the copolymer giving peak 3 remained undissolved. This fact indicates that the copolymer giving peak 1 or peak 2 has a poorly oriented structure and has a higher ethylene oxide unit content.

The effect of the addition method on the thermogram of the copolymer agrees with that found in the gel permeation chromatogram; the curves of both the DSC thermogram and the gel permeation chromatogram become narrower as the

number of addition increases. Especially in the continuous-addition copolymerization they have only a single peak. The similarity of the thermogram to the gel permeation chromatogram also suggests that, in this iodine-initiated, solid-state copolymerization, 1,3-dioxolane can diffuse through the polymer layer formed.

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