Lamellar Structure in Poly(tetraoxane) Obtained by the Radiation-Induced Polymerization in the Solid State

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(Received November 18, 1975)

ABSTRACT: In the small-angle X-ray scattering (SAXS) patterns of poly(tetraoxane), two discrete scatterings in the meridional direction are observed: one spot-like weak scattering corresponding to a long spacing of about 100 Å, and the other to that of about 500 Å.

The annealing effects on the long spacing of about 100 Å and on the melting behavior of polytetraoxane have been investigated and compared with those of the melt-crystallized poly(oxymethylene) (lamellar crystal).

It is concluded that polytetraoxane obtained by the postpolymerization contains lamellar-type crystallites which exist between the fibrillar bundles of the extended chain crystallite, since the annealing effect in the 100 Å spacing shows the characteristics of the lamellar crystal.

KEY WORDS Poly(tetraoxane) / 100-Å Long Spacing / Annealing Effect / Small-Angle X-Ray Scattering / Melting Behavior / Thickening / Preferential Orientation / Lamellae /

In a previous paper¹ the melting behavior of the poly(tetraoxane) obtained by radiation-induced polymerization in the solid state was investigated; it was found that the profile of a broad double melting endotherm was related mainly to the polymer yield. The molecular weight of the polymer, as well as the polymer yield, was affected by the atmosphere during the postpolymerization.² It was also suggested¹ that polymer crystals with a high melting point were formed at an early stage of the polymerization, and at a later stage, polymer crystals of a slightly different kind might be produced, and thus the melting endotherm would become broad with a inseparable double peak. In the preceding paper,³ the annealing effect under nitrogen atmosphere showed clearly that the fine structure which gave an endotherm at a lower temperature on the heating curve of the as-polymerized poly-

(tetraoxane) was different from the melt-crystallized sample, since the rearrangement of the polymer chains in as-polymerized poly(tetraoxane) took place by annealing even above T_s , the starting temperature of the melting, while the melt-crystallized sample showed no rearrangement of the crystal, but only melted, by the annealing above T_s .

The existence of the long period of *ca.* 100 Å in poly(tetraoxane) polymerized at 100°C has been demonstrated by small-angle X-ray scattering (SAXS) photographs and electron micrographs⁴ without any detailed description. Several intensity maxima in SAXS of poly(tetraoxane) postpolymerized at above 90°C were observed by us;³ here two intensity maxima were clearly observed, corresponding to the long spacings of *ca.* 100 Å and *ca.* 500 Å.

In this paper, the structure of the as-polymerized poly(tetraoxane), especially the long spacing of *ca.* 100 Å, is investigated from the annealing effects on the sample, using X-ray

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scattering methods and thermal analysis.

EXPERIMENTAL

Tetraoxane crystal (*ca.* 1 mm × 10 mm) was prepared by sublimation under reduced pressure, and heated at 105°C for 1 hr before irradiation to remove the residual strain in the monomer crystal. The preirradiated (10^5 R at 25°C in air) samples were postpolymerized in a solid state at 105°C for 6 hr in air. Poly(tetraoxane) thus prepared, which has a polymer yield of 48%, appeared to keep the same needle like shape as the monomer crystal.

Poly(oxymethylene diacetate) (acetylated poly(trioxane)⁵) was compared with poly(tetraoxane) in annealing effect. The samples were annealed under a nitrogen atmosphere in an apparatus which was used also for the study of melting behavior. After annealing for a given time at a desired temperature, the sample was cooled to about 100°C at a rate of 64°C/min.

The apparatus for the X-ray scattering was a Rigaku Denki RU-3 rotating anode X-ray unit operated at 40 kV, 80 mA. The monochromatic $\text{CuK}\alpha$ radiation was directed normal to the *c*-axis of the needle-like poly(tetraoxane) crystal. The wide-angle X-ray scattering (WAXS) patterns were obtained photographically with a flat

plate camera for the sample without rotation.

The small-angle X-ray scattering (SAXS) patterns were obtained also photographically with a pin-hole collimation system (0.5 mm ϕ and 0.3 mm ϕ); the specimen-to-film distance was 350 mm. The intensity of the SAXS patterns was measured with a microdensitometer to determine the maximum position along the meridional direction.

The apparatus for the measurement of the melting behavior of polymers was a differential scanning calorimeter (DSC-1B, Perkin-Elmer) with a small amount of the sample (*ca.* 1 mg). The heating rate was 16°C/min; the instrument was calibrated with indium.

RESULTS AND DISCUSSION

Figure 1 shows the SAXS patterns of as-polymerized poly(tetraoxane) (A), the annealed (B–G), and the melt-crystallized (H). The annealing conditions and the results are summarized in Table I.

In SAXS of the as-polymerized (A), the diffuse equatorial scattering is observed, indicating the existence of the microvoids between fibrils.⁶ The two discrete scatterings in the meridional direction (indicated by half-arrows) are also observed. One is of weak spot-like

Figure 1. Small-angle X-ray scattering patterns of poly(tetraoxane) obtained by the radiation-induced postpolymerization in the solid state: A, as-polymerized; annealed B, at 140°C for 30 min; C, 150°C, 30 min; D, 168°C, 10 min; E, D annealed at 171.5°C for 15 min; F, E annealed at 176°C for 12 min; G, 181°C, 2 min; H, 195°C for 1 min (melt-crystallized); intensities are not comparable.

Table I. The annealing conditions of poly(tetraoxane) and the results

Sample no.	Annealing condition		Result			Note
	Temp, °C	Time, min	Long spacing l , Å	melting		
				T_{s1} , °C	T_{s2} , °C	
1	—(Original)		95	171	179	A in Figures 1, 2, & 3
2	120	30	96	171	180	
3	130	30	98	172	179	
4	140	30	98	172	180	
5	150	30	110	173	179	
6	155	30	122	172	180	
7	160	30	135	173	179	
8	162	30	133	172	180	
9	165	30	146	174	180	
10	(165 168)	30) & 10	155	174	—	
11	168	10	165	174	180	D in Figures 1, & 3
12	(168 171.5	10) & 15	220	178	181	E in Figures 1, & 3
13	175	10	180, & 270	166	182	
14	(168 (171.5 176	10) & 15) & 12	240	180	183	F in Figures 1, & 3
15	179	6	—	169	185	
16	181	2	190, & 280	169	185	G in Figures 1, & 3, & Figure 2C
17	195 (melt-crystallized)	1	190	170	—	H in Figures 1, & 3, & Figure 2D
			Figure 5	Figure 3		

scattering corresponding to the Bragg spacing of about 100 Å (100-Å scattering), and the other to that of about 500 Å (500-Å scattering).

In the annealing at 140°C (B), the 100-Å scattering remains unaltered, while the intensity maximum of the 500-Å scattering shifts to the center. In the annealing above 150°C (C—F), both of the maxima shift to the center, and the 500-Å scattering goes under the beam trap. The SAXS pattern of the sample annealed at 181°C (G) is quite different from the others: namely, the equatorial scattering is very faint, indicating the diminution of the microvoids, and the weak scattering (indicated by half-arrows) equivalent to the Bragg spacing (190 Å) of the melt-crystallized (a faint ring-like scattering (H)) is also observed, besides the intense scattering corresponding to 280 Å.

Figure 2 shows WAXS patterns of the as-poly-

merized poly(tetraoxane) (A), the annealed (B and C), and the melt-crystallized (D). The WAXS pattern of the as-polymerized (A) shows a highly preferential orientation of the polymer chain along the c -axis. The WAXS pattern of the as-polymerized (A) shows no twin reflection, since the polymerization temperature of the sample (A) is 105°C, while in the samples polymerized at below 90°C, the twin reflection is observed clearly. Chatani, *et al.*⁷ reported that the twin reflection (the extra reflection, when compared with the usual fiber WAXS patterns, due to the twin crystal oriented perpendicular to the main crystal) was observed in the sample polymerized at 62°C, but not in the sample at 100°C. The present result agrees with their findings. The patterns of the annealed samples (B and C) are similar to that of the as-polymerized, though the sample annealed at

Figure 2. Wide-angle X-ray scattering patterns of poly(tetraoxane): A, as-polymerized; annealed B, at 160°C for 30 min; C, 181°C, 2 min; D, 195°C for 1 min (melt-crystallized).

181°C (C) shows the double melting endotherm in the heating curve, as described later. On the other hand, the pattern of the melt-crystallized (D) shows no preferential orientation of the polymer chains.

An amorphous halo inside the crystal reflection (100) is detected if one inspects closely the WAXS photographs of all samples.

Melting Behavior of the Annealed Samples

Figure 3 shows the heating curves of the as-polymerized poly(tetraoxane) (A), the annealed (B–G), and the melt-crystallized (H). The samples (B–D and G) are annealed directly at the desired temperature, and E and F are annealed stepwise, since, as mentioned in the preceding paper,³ the annealing at the temperature

Figure 3. Heating curves of poly(tetraoxane) obtained by the radiation-induced postpolymerization (in air) in the solid state. Heating rate: 16°C/min; sample weight, 1.0 ± 0.1 mg; A, as-polymerized; annealed B, at 130°C for 30 min; C, 155°C, 30 min; D, 168°C, 10 min; E, D annealed at 171.5°C for 15 min; F, E annealed at 176°C for 12 min; G, 181°C, 2 min; H, 195°C, 1 min (melt-crystallized).

below the starting temperature of the melting (T_s) of the sample causes the rearrangement of the polymer chains, while above T_s the melting occurs during annealing.

Poly(tetraoxane) shows the double melting endotherms in the heating curve, so the starting temperature of the melting endotherm at the lower temperature denotes T_{s1} , and that at the higher temperature T_{s2} , as shown in Figure 3. T_{s1} of the as-polymerized (A) is 171°C, therefore the annealing temperature of 168°C is below T_{s1} of the sample A; then a sharp melting endotherm can be obtained in the heating

Figure 4. Effect of annealing on the starting temperature of the melting (T_s), which is calculated from melting endotherms such as are shown in Figure 3.

curve, as shown in Figure 3 D. The annealing at 171.5°C (above T_{s1} of the sample A, but below T_{s1} of the sample D), therefore, causes the rearrangement of the polymer chains to give a sharp melting endotherm (E) when the sample D is used as the starting material. The situation is the same in the case of the sample F, obtained by annealing the sample E at 176°C.

The annealing of the sample A at the temperature (181°C) above T_{s1} causes the partial melting to show a double melting endotherm (G) in the heating curve. The endotherm at the lower temperature is similar to that of the melt-crystallized (H).

The change of the melting profile in the heating curve caused by the annealing is represented by T_{s1} and T_{s2} , as shown in Figure 4, where the weight loss during annealing is less than 5%, even at the temperature of 181°C. T_{s1} becomes higher in the annealing above 160°C, while T_{s2} increases above 170°C. These changes of T_{s1} and T_{s2} in the annealing are quite similar to that reported in the previous paper,¹ though T_{s2} in this paper is higher. This difference may be attributed to the polymer preparation conditions. In the previous paper,¹ poly(tetraoxane) was prepared *in vacuo* in the form of a powder with the polymer yield of 27%, while in this paper, the needle-like crystalline sample has been obtained in air with the polymer yield of 48%. The plots of T_s below 170°C in Figure 4 are of the crystal formed from the partial melt on cooling, and the mark at the annealing temperature 195°C is of the melt-crystallized sample.

Annealing Effect on the 100-Å Scattering

Figure 5 shows the relationship between the annealing temperatures and the long spacings of the 100-Å scattering. The long spacing of the 100-Å scattering stays constant in the annealing below 140°C, while it increases in the annealing above 150°C, and abruptly above 165°C. The long spacing of the melt-crystallized is about 190 Å.

In the samples annealed directly at 175°C (Table I no. 13) and 181°C (Table I no. 16), two intensity maxima are observed. One long spacing at a higher angle corresponds to that of the melt-crystallized mentioned above, and the other at a lower angle to the developed 100-Å spacing. But the sample annealed below T_s of the starting material, even at 176°C, (Table I no. 14) gives only one long spacing (240 Å) of the developed 100-Å spacing.

The increase of the 100-Å spacing occurs in the annealing above 150°C, which is about 10°C lower than the temperature from which T_{s1} increases by annealing. That is, the increase of the 100-Å spacing takes place before the occurrence of the rearrangement of the polymer chains in the melting behavior, indicating a very small enthalpy change in the annealing below 160°C. However, the fine texture with the 100-Å spacing relates to the structure giving the melting endotherm at the lower temperature in the heating curve, because the increase of T_{s1} corresponds to the increase of the long spacing.

Figure 5. Relationship between annealing temperatures and long spacings of about 100 Å in an original sample (○), and the melt-crystallized (●).

Annealing Effect of the Melt-Crystallized Poly(oxy-methylene diacetate)

The thickening of a lamellar crystal by the annealing was investigated in the samples of the melt-crystallized poly(oxymethylene). Figure 6 shows the SAXS patterns of the melt-crystallized poly(oxymethylene) (A) and the annealed (B–E). The faint ring-like scattering of the original sample becomes smaller in diameter in annealing, indicating the increase of the lamellar thickness. The WAXS patterns also show ring-like scatterings to indicate that there is no preferential orientation, though the figures are eliminated.

Figure 7a shows the relationship between the long spacings of the melt-crystallized samples and the annealing temperatures. The long spacing of the melt-crystallized increases with the annealing temperature above 150°C. A similar increase of the long spacing was reported in the cases of poly(oxymethylene)^{8a} and its copolymer⁹ during the annealing, and also in the case of Delrin⁸ with the increase of the recrystallization temperature.

The values of the long spacings in each sample differ depending on the history of the polymer preparation, and hence the onset of the long spacing increase in annealing also differs within a few degrees.

Figure 7b shows that T_s of the melt-crystallized shifts to a higher temperature in the annealing above 150°C.

Figures 7a and b show that when the long spacing increases by annealing, T_s of the annealed sample also increases. The rearrangement of the polymer chains of the melt-crystallized in the annealing causes the increase of both melting point and long spacing. In other words, the thickening of the lamellar crystal occurs if the annealing is performed at a temperature above 150°C, but below T_s of the starting sample.³

In conclusion, it has been confirmed that the characteristics of the lamellar crystal are the increase of the long spacing and the increase of the starting temperature of the melting by annealing under the conditions mentioned above.

Lamellar Structure in Poly(tetraoxane)

Figure 6. Small-angle X-ray scattering patterns of the melt-crystallized poly(oxyethylene), the acetylated poly(trioxane): A, melt-crystallized; annealed B, at 156°C for 30 min; C, 165°C, 20 min; D, 168°C 20 min; E, D annealed at 172°C for 10 min, intensities are not comparable.

Comparison of the Annealing Effect on the 100-Å Spacing in Poly(tetraoxane) with that on the Long Spacing in the Melt-Crystallized Poly(oxyethylene)

Figure 8 shows the relative increases Δl of the 100-Å spacing of poly(tetraoxane) and that

of the long spacing of the melt-crystallized poly(oxyethylene), from the original values. The increments of the long spacing from the original in both samples indicate similar thickenings of lamellae in annealing above 150°C. Similar results were reported by increasing the

Figure 7. Relationships between annealing temperatures and long spacings of the melt-crystallized poly(oxymethylene) (a), and starting temperature of the melting (T_s) (b).

Figure 8. Relative increase of long spacing (Δl) from the original value in the annealing, calculated from Figure 5 (○, poly(tetraoxane)) and Figure 7 (●, melt-crystallized poly(oxymethylene)).

Figure 9. Relationship between starting temperature of the melting at the lower temperature (T_{s1}) and the reciprocal of the long spacing: ○, poly(tetraoxane); ●, melt-crystallized poly(oxymethylene).

recrystallization temperature for Delrin,⁸ and by increasing the annealing temperature for Celcon,^{9a} and trioxane—dioxolane copolymer^{9b} with different dioxolane contents.

Figure 9 shows the relationship between T_{s1} and the reciprocal of the long spacing in both samples. The line were evaluated by the least square method. Provided T_{s1} behaves as T_m , it is related to the long spacing by

$$T_m = T_m^\circ (1 - 2\sigma_e/l \cdot \Delta H_m)$$

where T_m is the melting point of the sample, T_m° the equilibrium melting point, l the long spacing, σ_e the end-surface free energy, and ΔH_m the enthalpy of melting.¹⁰

The linear relation between T_s and $1/l$ is observed as shown in Figure 9. T_p° , the extrapolated peak temperature T_p of an endotherm to the sample weight 0 mg for the melt-crystallized poly(oxymethylene), has been applied to the equation instead of T_s ; a quite similar result is obtained.

The similarity of the equilibrium melting temperature, 185°C is observed in both samples, as shown in Figure 9; this indicates a similar packing of the polymer chains between the 100-Å spacings in poly(tetraoxane) and lamellae in the melt-crystallized poly(oxymethylene). The melting point must be equivalent in both samples at the extreme condition (infinite lamellar length), provided the native structure is of the same type, since the melting point (T_m) is thermodynamically defined as $T_m = \Delta H_m/\Delta S_m$, where ΔH_m and ΔS_m are, respectively, the enthalpy and entropy of melting. The 185°C of the equilibrium melting temperature is not so far from the values reported for poly(oxymethylenes) in several papers.¹¹

From these results, it is concluded that the fine texture having a long spacing of about 100-Å in the as-polymerized poly(tetraoxane) without the sub-crystal is of lamellar type, since it shows a quite similar annealing effect with that of the melt crystallized: *i.e.*, the lamellar crystal.

The slope of the straight line in Figure 9 is greater in the melt-crystallized than in poly-tetraoxane. The slope represents the ratio of the end-surface free energy (σ_e) of the lamellae to the enthalpy of melting (ΔH_m). The difference

of the slopes suggests a difference of the lamellar stacking in the samples, that is, the lamellar crystallites in the as-polymerized poly(tetraoxane) situate between fibrillar bundles of the extended chain crystal with a preferential orientation, while those in the melt-crystallized aggregate in the form of spherulites.

Fischer, *et al.*,⁴ reported that crystallization of poly(tetraoxane) at 100°C took place with folding using only their findings of a clear striation structure in the electron micrographs and a long spacing in a small-angle X-ray diagram.

The following data may support our suggestion: (1) The electron micrographs of poly(tetraoxane) postpolymerized in this work showed only fibrils, just like those of poly(trioxane). (2) The heating curve of the sample as-polymerized shows an inseparable double endotherm, as shown in Figure 3A, which is quite different from that of the sample annealed at 181°C (Figure 3G). (3) The rearrangement of the polymer chains takes place in annealing even above T_{s1} , as demonstrated elsewhere.^{1,3}

CONCLUSION

The long spacing corresponding to 100 Å in the poly(tetraoxane) without the sub-crystal increases in annealing at the temperatures above 150°C, and also the starting temperature of the melting (T_{s1}) increases so as to indicate the rearrangement of polymer chains during annealing. This annealing effect is a characteristic of the lamellar crystal (the melt-crystallized). Then the fine texture having a long spacing about 100 Å is of the lamellar type, and this lamellar crystal gives the melting endotherm at a lower

temperature in the heating curve. In other words, poly(tetraoxane) obtained by the radiation-induced polymerization in the solid state contains the lamellar crystals between fibrillar bundles of the extended chain crystals.

The details of the melting endotherm at the higher temperature and the structure with *ca.* 500-Å long spacing will be reported soon.

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