Wide-Angle X-Ray Scattering of Poly(tetroxocane) Obtained by Radiation-Induced Polymerization in the Solid State

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ABSTRACT: X-Ray scattering profiles of 009 and 0018 reflections of poly(tetroxocane) prepared by radiation-induced polymerization were investigated. It was confirmed that two types of crystallites coexisted in the polymers obtained by post-polymerization above 80°C: lamellar type crystallites with a longitudinal dimension of 100 Å and fibrillar crystals 250 Å in crystallite size. The lamellar crystallites were less distorted than the fibrillar ones. Only fibrillar crystallites were found in samples polymerized below 80°C.

KEY WORDS Poly(tetroxocane) / Wide-Angle X-Ray Scattering / Crystallite Size / Distortion Parameter / Lamellar Fibrils / Melting Behavior /

In a preceding paper,¹ the fibrillar structure of a poly(tetroxocane) (PT_EOX) sample prepared by the radiation-induced post-polymerization of tetroxocane above 80°C was investigated by small-angle X-ray scattering (SAXS) and thermal analysis. A broad discrete reflection corresponding to a Bragg spacing of about 500 Å was observed on the meridian in addition to the reflection associated with a long spacing of 100 Å. It was ascertained that the former reflection was due to the density difference between void and fibrillar crystals stacked alternately in the direction of the *c*-axis, while the latter was due to the lamellar crystals probably situated between the fibrillar ones.²

In this paper, wide-angle X-ray scattering (WAXS) of PT_EOX is investigated in order to clarify the lamellar and fibrillar structures of PT_EOX polymerized at various temperatures.

EXPERIMENTAL

A single-crystal of tetroxocane prepared by sub-

limation under reduced pressure was irradiated by γ -ray and subjected to post-polymerization in the solid state at various temperatures. The polymer yield was determined gravimetrically after washing the sample with acetone. Polymerization conditions and yields are summarized in Table I.

X-ray was generated by a Rigaku denki 100 PL Rotating anode X-ray unit operated at 40 kV and 80 mA. Ni-filtered Cu- K_{α} radiation was used. The line profiles of the 009 and 0018 reflections of PT_EOX were measured by a step-scanning method with a fixed time of 80 or 400 s in the symmetrical transmission mode. SAXS patterns were obtained with a pin-hole collimation (0.5 and 0.3 mm in diameter).

The instrumental broadening of WAXS profiles was corrected using a single crystal of tetroxocane having the same dimensions as the reference. The experimental procedure is described in detail in ref 2.

Table I. Polymerization conditions for tetroxane and polymer yields

Sample notation	Polymerization condition ^a		Polymer yield
	Temp	Time	
	°C	h	%
PT _E OX-62	62	25	12
PT _E OX-81	81	25	25
PT _E OX-105	105	6	80

^a T_EOX was preirradiated. 10 kGy at room temperature.

LINE-BROADENING ANALYSIS

A corrected diffraction profile can be expressed by the convolution product³ of the crystallite-size profile I_s and the lattice-distortion profile I_d ($I = I_s * I_d$). The Fourier transform (FT) method gives the most reliable value for the 'number-average' crystallite size ($\bar{D}_n$) and the mean-square lattice distortion ($\bar{L}_t^2$) over the distance of t .

According to the integral breadth (IB) method⁴ based on the paracrystalline theory the IB of the 001 reflection (ΔS_l) of the Cauchy type is given by

$$\Delta S_l = 1/D_w + (\pi g s_l)^2 / \bar{c} \quad (1)$$

where $\bar{D}_w$ denotes the 'weight-average' crystallite size along the chain axis, $\bar{c}$ the averaged c -dimension, g the longitudinal distortion parameter, and $s_l = 2 \sin \theta_l / \lambda$. Among the 001 reflections of PT_EOX only two reflections 009 and 0018 can be used, since the 0027 reflection is too weak. In the IB method, additional distortions due, for example, to lattice strains in the chain direction are neglected. In the present work, however, this method was used because of its simplicity. The experimental value of ΔS_l and s_l^2 for the 009 and 0018 reflections were substituted into eq 1 to evaluate g and $\bar{D}_w$.

RESULTS AND DISCUSSION

As previously reported,¹ the SAXS patterns of the PT_EOX samples obtained by post-polymerization at 55°C and 62°C (referred to as PT_EOX -55 and -62) showed only a sharp continuous equatorial scattering, while PT_EOX-81 and -105 showed two discrete meridional scatterings, a weak spot-like reflection at a Bragg spacing of about 100 Å and a broad

reflection at about 500 Å. It was suggested that the sharp continuous equatorial scattering is associated with microvoids contained between polymer fibrils.⁵ These microvoids were found in the PT_EOX samples polymerized at any temperature. Hence, it was concluded that the PT_EOX samples prepared below 80°C consisted of fibrillar crystallites, while the PT_EOX samples prepared above 80°C consisted of fibrillar crystallites arranged along the c -axis with lamellar crystals between them.² The variation in morphology with polymerization temperature may be attributed to the temperature dependence of the motional freedom of the molecules in the PT_EOX crystal.⁶ The formation of a lamellar structure above 80°C may be related to the vigorous molecular motion in the monomer crystal occurring in the liquid state.

The WAXS profiles of PT_EOX-81 and -105 are illustrated by the solid lines in Figure 1. The 009 profiles of both samples are asymmetric with long tails on the lower-angle side. These profiles are broader than that of PT_EOX-62 shown by open circles in Figure 1. The 0018 profiles of PT_EOX-81 and -105 (solid line) are somewhat symmetric but very broad, indicating that they consist of, at least, two components.

Both the 009 and 0018 profiles were decomposed into two components shown in Figure 1, where the sharp profile of PT_EOX-62 (open circles) has been subtracted from the observed profiles of PT_EOX-81 and -105 (solid line), leaving a rather symmetric component with the peak at a lower-angle side (filled circles).

The distance between the two separated peaks in the 0018 profile for both samples is twice as large as that in the 009 profile, indicating that the same value of s_l can be obtained from each reflection. For PT_EOX-105, the area under the higher-angle component (open circles) is smaller than that under the lower-angle component (filled circles), whereas for PT_EOX-81, the reverse is this case. Thus it may be considered that in the PT_EOX-105 sample the amount of lamellar crystallites is larger than that of fibrillar crystallites, and the reverse is so for the PT_EOX-81 sample.

The existence of two types of crystallites was ascertained from melting behavior. As shown in Figure 2, the extremely sharp endothermic peaks in the heating curves of PT_EOX-55 and -62 indicate that only fibrillar crystallites exist in these samples,

Figure 1. Profiles of 009 and 0018 reflections of PT_EOX-62 (open circles), and -81 and -105 (both solid lines). The profiles of PT_EOX-81 and -105 indicate the superposition of two different profiles.

Figure 2. Heating curves of poly(tetroxocane) PT_EOX-55, -62, -81, and -105. Heating rate, 16°C min⁻¹; sample weight, 1.0 ± 0.2 mg.

while the broad endotherm with a shoulder observed in the cases of PT_EOX-81 and -105 can be decomposed into the two endothermic peaks shown

Table II. Weight-average crystal size ($\bar{D}_w$) and distortion parameters (g) in PT_EOX prepared at various temperatures

Samples No.	$\bar{D}_w$	g
	Å	%
PT _E OX-62	250	2.4
PT _E OX-81	250	2.4
	100	1.0
PT _E OX-105	250	2.4
	100	0.7

by the dotted lines. These results support the conclusion that PT_EOX prepared at a temperature above 80°C contains low-melting lamellar crystals and high-melting fibrillar crystals.

It is very likely that the lamellar crystals give the lower-angle component (filled circles in Figure 1) in the X-ray diffraction profiles, and the fibrillar crystals, the higher angle component (open circles in Figure 1).

Table II gives the sizes ($\bar{D}_w$) and the distortion parameters (g) along the chain axis for the two types of crystallites in the samples PT_EOX-62, 81, and -105. The crystal sizes of 250 Å and 100 Å are associated with the fibrillar and lamellar crystals, respectively. The distortion parameter of the fibrillar crystallites is about 3 times as large as that of the

Figure 3. Profiles of 009 and 0018 reflections of PT_EOX-81 and -105 original (solid lines) annealed at 160 and 170°C (broken lines), respectively.

Table III. Relative difference in lattice constants ($\Delta c/c$) in PT_EOX-62, -81, and -105 from $c = 17.29 \text{ \AA}$ 009 and $17.32 \text{ \AA}$ 0018 of poly(trioxane)

Specimen	$\Delta c/c$	
	%	
	009	0018
PT _E OX-62, Fibrils	-0.12	-0.29
PT _E OX-81, Fibrils	-0.12	-0.29
	0.75	0.52
PT _E OX-105, Fibrils	-0.12	-0.29
	0.75	0.40

lamellar crystallite for both PT_EOX-81 and -105. It should be noticed that the small g value (0.7%) for the lamellar crystallites is comparable to those for the poly(trioxane) (PTOX) or melt crystallized POM samples.⁷

The values of the lattice constant c for various PT_EOX samples was evaluated from the 009 and 0018 reflections, and the relative deviations ($\Delta c/c$) from $c = 17.29 \text{ \AA}$ (009) and $17.31 \text{ \AA}$ (0018) for PTOX are summarized in Table III. The fibrillar crystals of PT_EOX give negative values of $\Delta c/c$, indicating contraction in the longitudinal direction, whereas the lamellar crystals give positive values of $\Delta c/c$, indicating expansion of the lattice.

When polymerization and crystallization of

PT_EOX proceed simultaneously, the molecular chains in the fibrillar crystals may incur a strong compression in a vertical direction, and the lamellar crystallites may be formed under less stressful conditions than the fibrillar crystals in PT_EOX.

It was reported⁸ that annealing below the melting temperature gave rise to a sharp endothermic peak in the heating curve and an increase in the long spacing. In this study, the effect of annealing on the WAXS profile was examined. The 009 and 0018 reflections of the PT_EOX-81 and -105 samples before and after annealing are shown in Figure 3. On annealing, the profiles become more symmetrical and sharper, and the peaks shift to the lower-angle side.

The values of $\bar{D}_w$ and g for the annealed PT_EOX-105 samples (170°C for 2 h in air) were estimated to be $250 \text{ \AA}$ and 1.2%, respectively. This g value is much smaller than those of the fibrillar crystals in the corresponding as-polymerized sample (Table II). These annealed samples showed characteristics similar to the main crystals in PTOX.⁹

The relative difference ($\Delta c/c$) of the annealed samples was also estimated. The PT_EOX-105 sample annealed at 170°C (above the melting point of the sample) for 2 h showed $\Delta c/c$ value comparable to the lamellar crystals in the as-polymerized sample in Table III. This indicates that the fibrillar crystallites were converted to the lamellar crystallites by annealing at 170°C. On the other hand, $\Delta c/c$ of the PT_EOX-81 sample annealed at 160°C (below the melting point) for 30 min was 0.29% for

both 009 and 0018 reflections, this value falls intermediate between of those for fibrillar and lamellar crystallites in the unannealed sample in Table III. Such an expansion of the *c*-dimension may be caused by relaxation of the distortion due to the rearrangement of the molecules in the fibrillar crystallites during annealing. In fact, lamellar-type crystals with a long-spacing of 250 Å appeared by annealing.² However, these two components could not be separated from the WAXS profiles.

These findings suggest that the fibrillar crystallites in PT_EOX are longitudinally compressed by the stress field appearing in the monomer matrix during polymerization.

CONCLUSION

The WAXS of PT_EOX post-polymerized at temperatures above 80°C showed asymmetric scattering profiles of 009 and 0018 reflections, indicating the superposition of two components associated with fibrillar and lamellar-type crystallites. The weight-average crystal sizes and the distortion parameters along the chain axis were evaluated for these two components. The crystal size of the lamellar crystallites is comparable to a long period about 100 Å obtained from the SAXS measurement and that of the fibrillar crystallites to a long period of about 500 Å. The WAXS of PT_EOX post-polymerized at a

temperature below 80°C showed symmetric profiles, indicating the existence of only fibrillar crystals. These results were consistent with the melting behavior of the original samples and the annealing effect on the WAXS reflections.

The fibrillar crystallites in PT_EOX appear to be longitudinally compressed by the stress field generated in the monomer matrix during the polymerization process.

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