

Small-Angle X-Ray Scattering of Poly(tetraoxane) Obtained by the Radiation-Induced Solid-State Polymerization

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ABSTRACT: Intensities of small-angle X-ray scattering of a poly(tetraoxane) system, on both the direction of the equator and that of the meridian, increase by reducing the amount of unreacted tetraoxane, indicating the formation of voids.

A broad scattering maximum in the meridian besides a spot-like scattering corresponding to 100-Å spacing was observed in a polymer prepared at 105°C. The broad maximum shifts to a low angle by annealing the sample below 140°C, *i.e.*, at a temperature range which has no influence on the polymer chain aggregation. The shift is associated with the sublimation of the unreacted monomer or the thermal decomposition of low-molecular-weight polymer. These materials are held in voids formed periodically on the fibrillar polymer crystal.

The fibrillar structure of poly(tetraoxane) seems to be an extended polymer chain aggregation with a periodic void appearance, *i.e.*, a stacking of crystallites along the *c*-axis, while a lamellar crystal corresponding to 100-Å spacing situates between these fibrils.

KEY WORDS Poly(tetraoxane) / Small-Angle X-Ray Scattering /
Annealing / Fibrillar Structure / Periodic Voids / Melting Behavior /
Weight Loss /

In a preceding paper,¹ we reported that two discrete scatterings were observed in the meridional direction of small-angle X-ray scattering (SAXS) patterns of poly(tetraoxane) (PT_EOX) postpolymerized at 105°C, not showing twinned structures; one was a weak spot-like scattering corresponding to the Bragg spacing of about 100 Å (100 Å-scattering), and the other corresponding to about 500 Å (500 Å-scattering). In the equatorial directions of a SAXS pattern, only continuous scattering was observed, indicating the existence of micro-voids between fibrils.² It was clarified¹ that the 100 Å-scattering is due to lamellar crystallites having a thickness of *ca.* 100 Å, situated between fibrillar bundles of extended chain crystallites (main crystal).

The 500 Å-scattering reflects another fluctuation of an electron density along the fibrillar direction due to the extended chain crystallites.

In this paper, the origin of the 500 Å-scattering is investigated in detail by SAXS and the melting behavior of PT_EOX.

EXPERIMENTAL

A single tetraoxane crystal prepared by sublimation under reduced pressure was post-polymerized at a certain temperature in the solid state. The polymer yield was determined gravimetrically after washing the sample with acetone and drying it under reduced pressure for 24 h at room temperature.

The annealing of PT_EOX was performed in a glass ampule at temperature below 140°C. In annealing at temperatures below 140°C, no increase in the long spacing of the 100 Å-scattering was observed nor was any effect of oxygen observed in either weight loss or melting behavior.¹

The apparatus for the X-ray scattering measurements was the Rigaku Denki RU-3L rotating anode X-ray unit. The SAXS patterns were obtained photographically with a pin-hole collimation ($0.5\text{ mm}\phi$ and $0.3\text{ mm}\phi$), and the SAXS intensity curves were recorded by a step-scan method with a Kratky U-slit ($20\ \mu\text{m}$, 0.1 mm and 0.05 mm). The scattering intensity was uncertain at angle (2θ) below $2'$ because of the

strong incident beam. The intensity at angles over $2'$ has been corrected for air scattering.

The apparatus for measuring the melting behavior of $\text{PT}_{\text{E}}\text{OX}$ was a differential scanning calorimeter (DSC-1B, Perkin-Elmer) with a small amount of the sample (*ca.* 1 mg). The measurements were performed at a heating rate of $16^\circ\text{C min}^{-1}$ under a nitrogen stream. The experimental details have been described elsewhere.¹

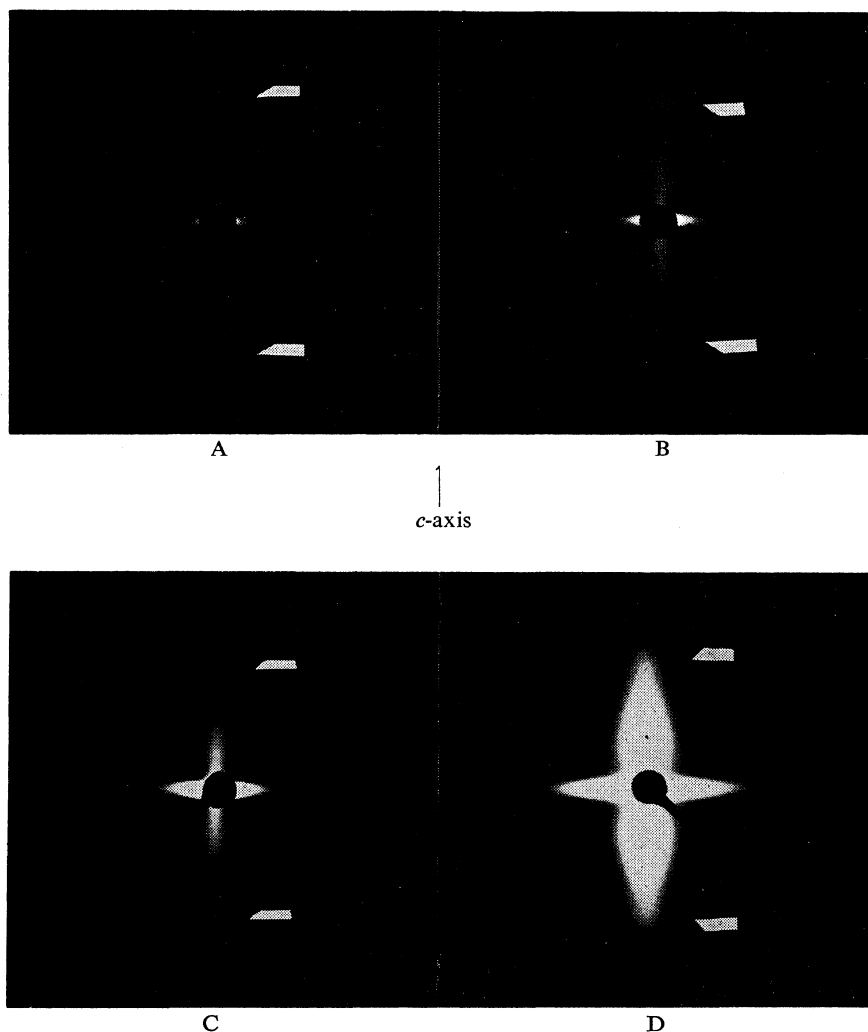


Figure 1. Small-angle X-ray scattering patterns of poly(tetraoxane) post-polymerized at 105°C for 15 min after the preirradiation of 0.1 MR in air, polymer yield is 26%: (A), just after polymerization (before the extraction of unreacted monomers; (B), after the sublimation of unreacted monomer at 80°C for 3 h; (C), after the sublimation for 5 h; and (D), after the sublimation for 24 h (almost polymer alone). Half-arrows indicate spot-like scattering corresponding to 100\AA -spacing.

RESULTS AND DISCUSSION

Figure 1 shows the SAXS patterns for various types of PT_EOX systems; (A), the system includes unreacted monomeric tetraoxane just after polymerization; (B), the system A is heated at 80°C for 3 h to sublime unreacted monomer; (C), the system A is heated for 5 h; and (D), the system A is heated for 24 h. The sample was washed with acetone and dried to give a polymer yield of 26%. In the sample A, faint scatterings are observed in both directions of the equator and the meridian. A spot-like scattering in the meridian indicated by half-arrows is from the lamellar crystal with a Bragg spacing of *ca.* 100 Å as mentioned already.¹

The scattering intensities of both directions increase with the sublimation time (B, C, and D), indicating an increase in the electron density fluctuation by a reduction of the residual monomer. The equatorial scattering was due to the needle-shaped voids between the fibrils,² but the mechanism for the meridional scattering corresponding to the 500 Å-scattering has not been clarified yet. Therefore, the intensity curve at angles lower than 25' in the meridional di-

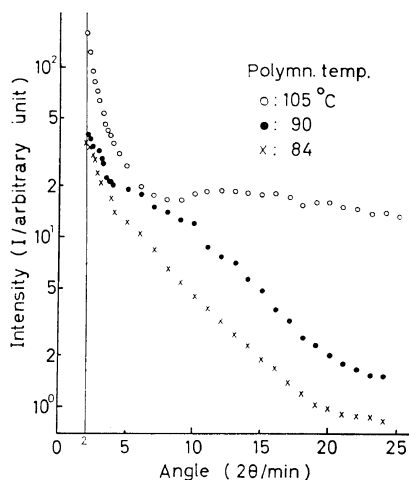


Figure 2. Small-angle X-ray scattering (meridian) curves of the sample prepared at several different temperatures: preirradiation, 1 MR; polymerization, for 1 h at 105°C, for 14 h at 90°C and for 25 h at 84°C in air (*ca.* 30-% yield in each case). Intensities are not comparable because of difference in sample size.

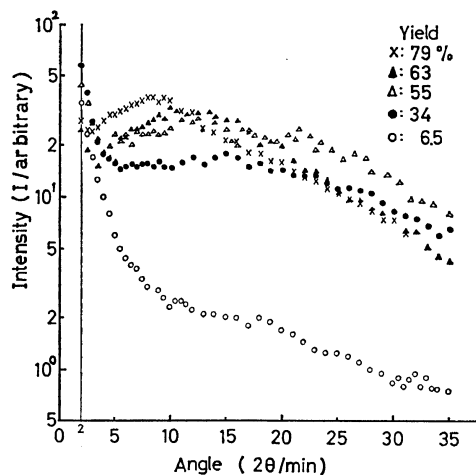


Figure 3. Small-angle X-ray scattering patterns of the samples with various polymer yields: polymerization at 105°C for a given time after the preirradiation of 1.0 MR in air. Polymer yields are indicated in the figure.

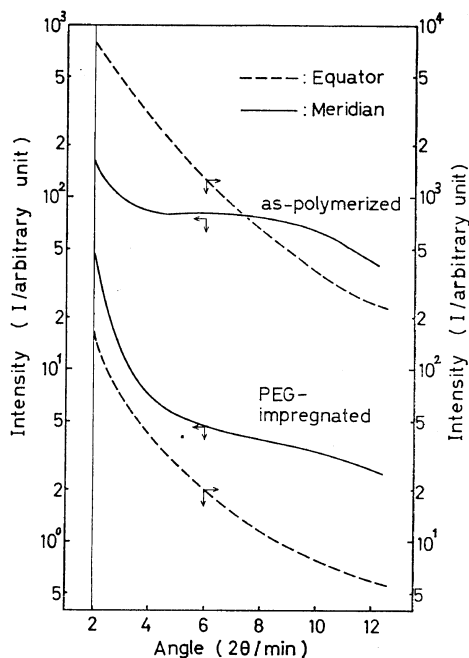


Figure 4. Effect of impregnation of poly(ethylene glycol) on the small angle X-ray scattering curves on equator and meridian of the sample polymerized at 105°C for 1 h (polymer yield, 40%) after the preirradiation of 1 MR in nitrogen atmosphere.

rection was investigated using a Kratky U-slit camera.

Figure 2 shows the SAXS curves on the meridian of the $PT_{1.0}OX$ obtained by the post-polymerization at various temperatures with a poly-

mer yield of about 30% in each case. A broad scattering peak was observed at about $13'$ (500 \AA -scattering) in the sample prepared at 105°C , but a shoulder at about $10'$ in the samples at 90° and 84°C . The intensity curve of $PT_{1.0}OX$ pre-

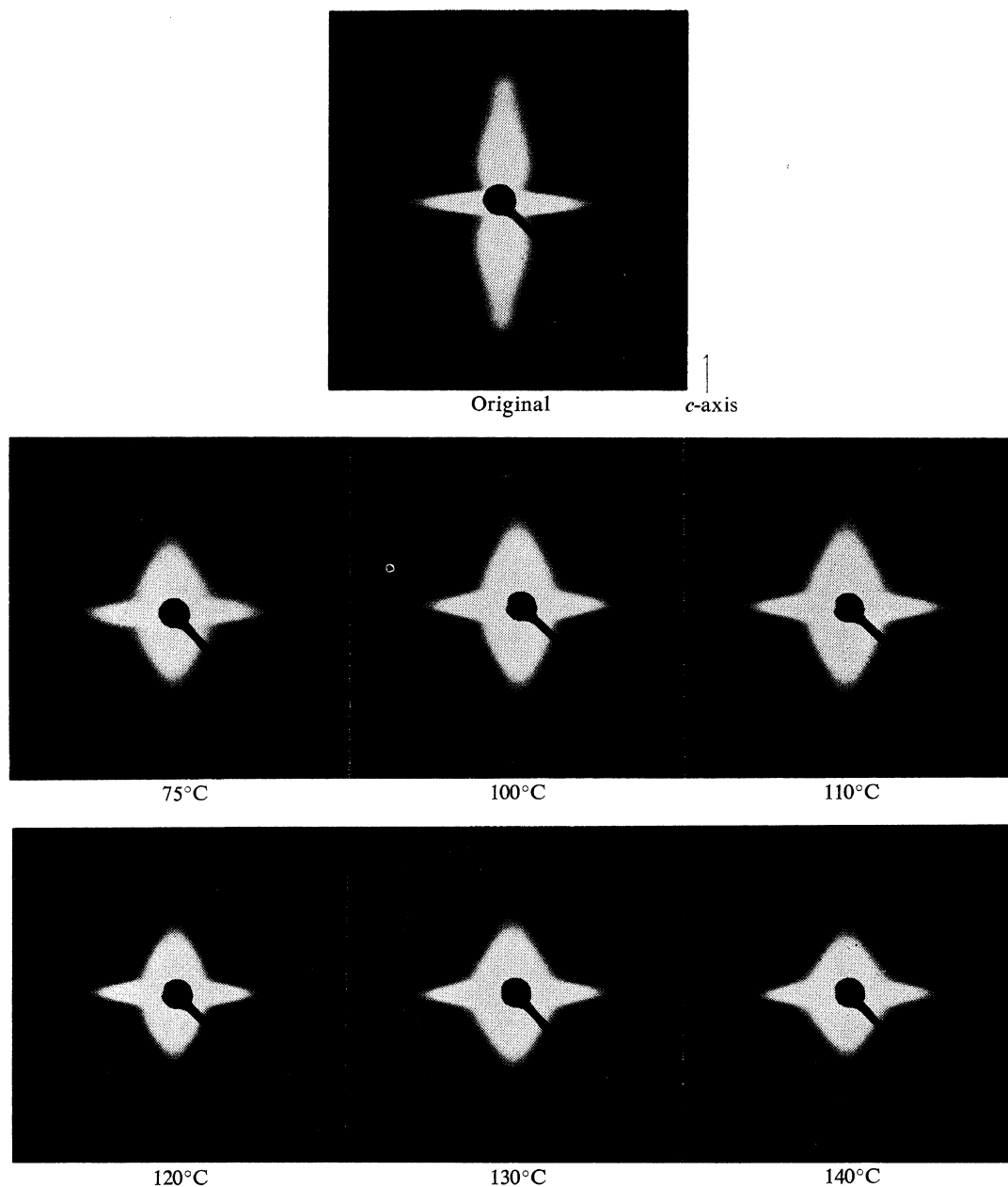


Figure 5. Small-angle X-ray scattering patterns of the sample annealed at various temperatures for 30 min except at 75°C for 8 days: polymerized at 105°C 1 h in air (yield 40%) after 1 MR irradiation. The annealing temperatures are indicated in the figure.

pared at $70^{\circ}C$ (polymer yield of about 10%) is similar to that at $84^{\circ}C$, indicating a rapid decrease in the intensity with the scattering angle.

The effect of the polymer yield on the broad peak (500 Å-scattering) is examined in the sample prepared at $105^{\circ}C$. Figure 3 shows the SAXS curves of $PT_{E}OX$ with various polymer yields. Since the size and weight of the sample cannot be made equal for each sample, the intensities of SAXS cannot be compared. When the polymer yield is low, the scattering maximum at about $13'$ or a higher angle can hardly be observed, and as the yield increases, the maximum becomes clearer and the peak position shifts to a lower angle size.

Figure 4 shows the reduction of the SAXS intensity by impregnation of poly(ethylene glycol) (PEG) in the directions of both the equator and the meridian. A similar result has been obtained with a sample impregnated with silicone oil. A great decrease in the SAXS intensity by impregnation suggests that the scatterings are caused by voids formed during the polymerization crystallization.

While investigating the annealing effect on spot-like scattering (100 Å-scattering) in the meridional direction, it was found that an increase of the 100 Å-scattering occurred only at temperatures above $140^{\circ}C$, but that the maximum of the broad 500 Å-scattering shifted to a lower angle by annealing a sample below $140^{\circ}C$.¹

Figure 5 shows the SAXS patterns of $PT_{E}OX$ (40% yield) as-polymerized, annealed for 30 min at various temperatures and annealed for 8 days at $75^{\circ}C$. The annealing at $75^{\circ}C$ for 100 h brought about no change in the SAXS patterns, but after 200 h a change was observed in the scattering patterns, as well as after 30 min in the temperature range between $100^{\circ}C$ and $140^{\circ}C$. On annealing $PT_{E}OX$, a ring-like scattering pattern was noticed around the beam trap, suggesting the existence of unoriented voids.

The melting behaviors of the same samples as in Figure 5 are shown in Figure 6. The endothermic profile of the original $PT_{E}OX$ changes so that the two peaks become a little clear by annealing, but, the total area under the double peak stays constant. This indicates that the aggregations of the polymer chains are affected little during annealing.

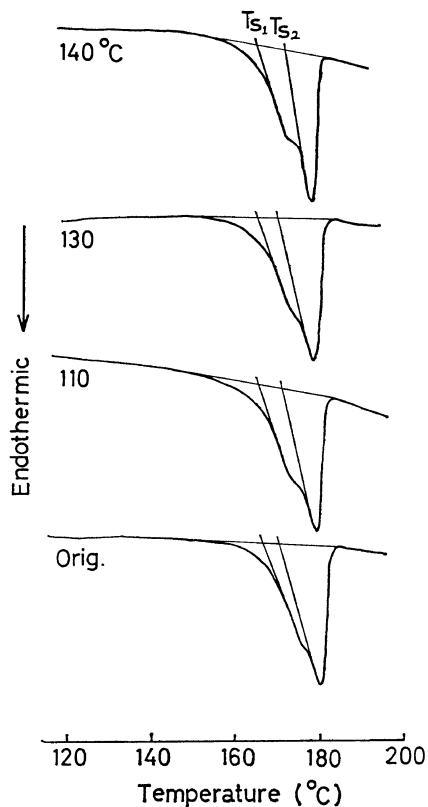


Figure 6. Heating curves of the samples annealed (the same sample used in Figure 5): heating rate, $16^{\circ}C/min$; sample weight used, 1.00 ± 0.5 mg.

Table I. Weight loss during the annealing at various temperatures

Annealing temperature, $^{\circ}C$	Weight loss, %
75	5
100	7
110	10
120	8
130	10
140	15

Table I summarizes the weight loss of the sample during annealing. The loss increases by raising the annealing temperature, and a maximum loss of 15% occurs in the sample annealed at $140^{\circ}C$. If such an amount of weight loss is due to the thermal decomposition of high-molecular-weight polymers, the profiles of the melting endotherm as well as the scattering behavior

must be influenced seriously. Thus, the weight loss during annealing is caused by the sublimation of unreacted monomers and/or by the decomposition of low-molecular-weight polymers.

The voids formed during polymerization retain unreacted monomers and/or low-molecular-weight polymers, which are easily removed by annealing because of the high vapor pressure of the monomers and the thermal instability of low-molecular-weight polymers at elevated temperatures. These findings suggest us that the fibrillar crystal, or the extended chain crystal, must be composed of stacking crystallites.

Figure 7 shows the meridional SAXS intensity curves for PT_EOX (the same sample used in Figure 5). The original sample shows a very broad intensity maximum at about 13° , the position of which shifts to a low angle side by annealing the sample. This indicates an increase in the spacing of the void appearance by annealing PT_EOX .

Figure 8 shows the SAXS curves of PT_EOX obtained at $105^\circ C$ in vacuum. The profile of the SAXS intensity curve of the original changes similarly to that of the sample post-polymerized in air (Figure 7) during annealing, indicating no special effect of oxygen on the 500 Å-scattering. The length of the crystallites men-

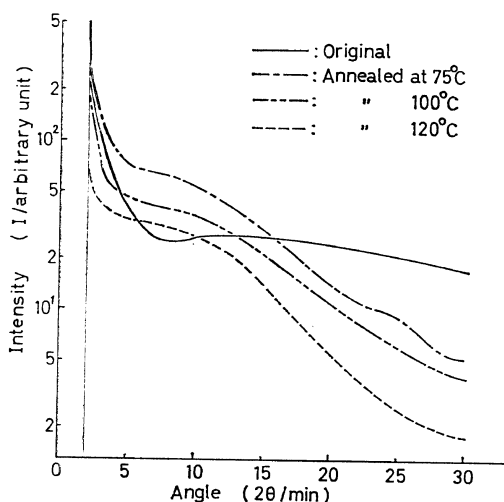


Figure 7. Small-angle X-ray scattering curves of the sample annealed (the sample used in Figure 5). The annealing temperatures are indicated in the figure.

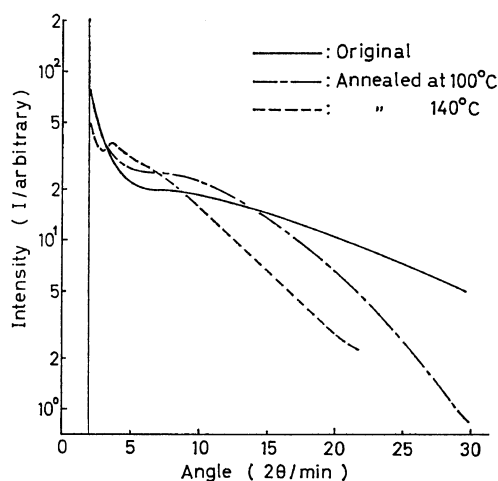


Figure 8. Small-angle X-ray scattering curves of the sample prepared in vacuum: polymerization at $105^\circ C$ for 1 h after 1 MR preirradiation in vacuum (polymer yield, 36%).

tioned above, therefore, does not reflect the molecular weight of the polymers, since the post-polymerization of PT_EOX in air gives a polymer with a lower molecular weight than that in vacuum³. The periodic appearance of voids on the polymer fibrils prepared both in air and in vacuum is a characteristic of the PT_EOX texture, having to do mainly with the difference in unit cell dimensions⁴ of both the crystals of monomeric T_EOX and PT_EOX .

CONCLUSIONS

The texture of PT_EOX post-polymerized at a temperature below $80^\circ C$ is different from that of PT_EOX prepared above $80^\circ C$. The SAXS patterns of the sample obtained at $105^\circ C$, which has no twinned structure, have a broad maximum besides a spot-like scattering due to a lamellar crystal with a *ca.* 100-Å spacing¹ on the meridian, and a diffuse scattering on the equator. Both scatterings are caused by voids; the former broad maximum is the scattering from the voids arranged periodically on a fibrillar crystal and the latter from those between the fibrils.

The voids are filled with unreacted monomers and/or low-molecular-weight polymers in the polymerization, and the monomers in the needle-

shaped voids between fibrils can be easily washed off with acetone, but materials situated between the crystallite ends in the fibrils are occluded rather tightly and are hard to wash off with acetone. The broad SAXS intensity maximum in the meridional direction is affected by the materials in the voids. The annealing reduces these materials by the sublimation of unreacted monomers and/or by the thermal decomposition of low-molecular-weight polymers to emphasize the periodic appearance of voids.

The characteristics of the voids in PT_EOX must be related to the polymerization mechanism in the solid state, and this can be clarified

by quantitative analysis of X-ray diffraction behavior.

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