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Formation of layer-like voids in irradiated polytrioxane

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The formation of voids and defects is investigated by X-ray diffraction methods, by weight loss measurement and by electron microscopy, for an irradiated polytrioxane (PTOX) obtained by the γ-ray-induced polymerization of trioxane in the solid state. The main reasons for the formation of the layer-like voids are transverse decomposition at a selective point accessible to the radiation in the micro-fibrils, and the subsequent extensible depolymerization which may occur from the unstable chain end with increase of the radiation dose. The analysis of the SAXS curve for the irradiated PTOX, according to Tsvankin's method gives reasonable results for the void structure, where the reduction of the sub-crystal fraction and also the weight loss of the sample by irradiation are taken into account.

1. Introduction

The effects of radiation on polyoxymethylene (POM) have been studied extensively in the past. Fischer and Langbein [1] reported detailed product analyses for polyoxymethylene diacetate (Delrin 500) irradiated with 1 MeV electrons *in vacuo*. The yield of chemically changed units is in good agreement with a cryoscopic estimate obtained from the depression of the melting point for samples irradiated *in vacuo* [2], and in air [3].

When irradiated by γ-rays *in vacuo* or air, POM predominantly degraded though evidence for some crosslinking was also found [1]. Torikai [4] found that main-chain scission occurred to form thermally stable polymers. It has also been reported that the intensity of the discrete small-angle X-ray scattering (SAXS) decreases with a radiation dose of less than 10 MR [5]. This seems to be related to a decrease in molecular weight, which facilitates the recrystallization of the fractured chains.

Although the changes of the physical properties of POM subjected to radiation have been studied in some detail, there is little information about radiation effects on the supermolecular texture in the POM crystals. So far there has been only one study [6] on the structural changes caused by radiation with electrons in solution-grown single crystals of POM, and it was reported that no appreciable enlargement of the lattice constants and lattice distortions took place in the case of POM in contrast to polyethylene, in which the crosslinking between adjacent chains within the lattice was produced as a result of irradition.

In the previous paper [7], the radiation effect on the melting behaviour of polytrioxane was, studied, since the X-ray scattering behaviour is kept constant in the range below 1 MR of the exposure dose. The main purpose of the present investigation is to discover how the fine structure of the polymer is affected by γ-irradiation ($>$ 1 MR). The effects of radiation on polytrioxane (PTOX) obtained by the γ-induced polymerization of trioxane in the solid state are of considerable interest, since PTOX is composed of highly oriented extended-chain molecules without so-called chain-folds and possess a high degree of perfection. It has been shown, however, that PTOX is not so perfect as a single crystal and has a complicated fine structure. Colson and Reneker [8] found three distinguishable morphologies of PTOX crystals which they called Z-crystals, W-crystals and T-twin crystals. Wegner, Fischer and Munoz-Escalone [9] proposed a kinked model of PTOX microfibril, in which main- and sub-crystallites are linked. With this in mind, we undertook an X-ray investigation of the structural changes occuring in PTOX when exposed to γ-irradiation in air, especially at doses exceeding 10 MR.

2. Experimental

Trioxane (TOX) crystals were sublimed under reduced pressure and recrystallized into a long needle-like form. Such single crystals were annealed at 50° C for 2 h in order to increase their perfection. After γ-irradiation of 1 MR at room temperature, the sample was polymerized in air at 50° C for 26 h in a glass ampule. A bundle of PTOX fibrils, with a polymer yield of about 80%, was obtained after unreacted monomer was removed with methanol. The PTOX sample thus prepared was placed in an open glass ampoule, and exposed to up to 100 MR of γ-radiation from a ^{60}Co source at dose rates of 0.2 to 2.0 MR h^{-1} The temperature inside the irradiation cavity seems to have been about 25° C, although the sample temperature was not measured during irradiation. The weight loss during the irradiation was determined gravimetrically after more than 200 h removal from the source, since post-irradiation changes in the sample weight were almost completed at 200 h [2].

Small-angle X-ray scattering (SAXS) patterns were recorded photographically with a small-angle vacuum camera with a pin-hole type collimating system (0.5 and 0.3 mm diameter) and a specimen-to-film distance of 280 mm. The intensity of SAXS was measured by the diffraction method using a Kratky U-slit collimation (50 μm) and a scintillation detector. The half-width of the primary beam 1.7′ and the upper resolution limit of the instrument was more than 2000 Å.

Photographs of the wide-angle X-ray scattering (WAXS) were taken with a cylindrical camera

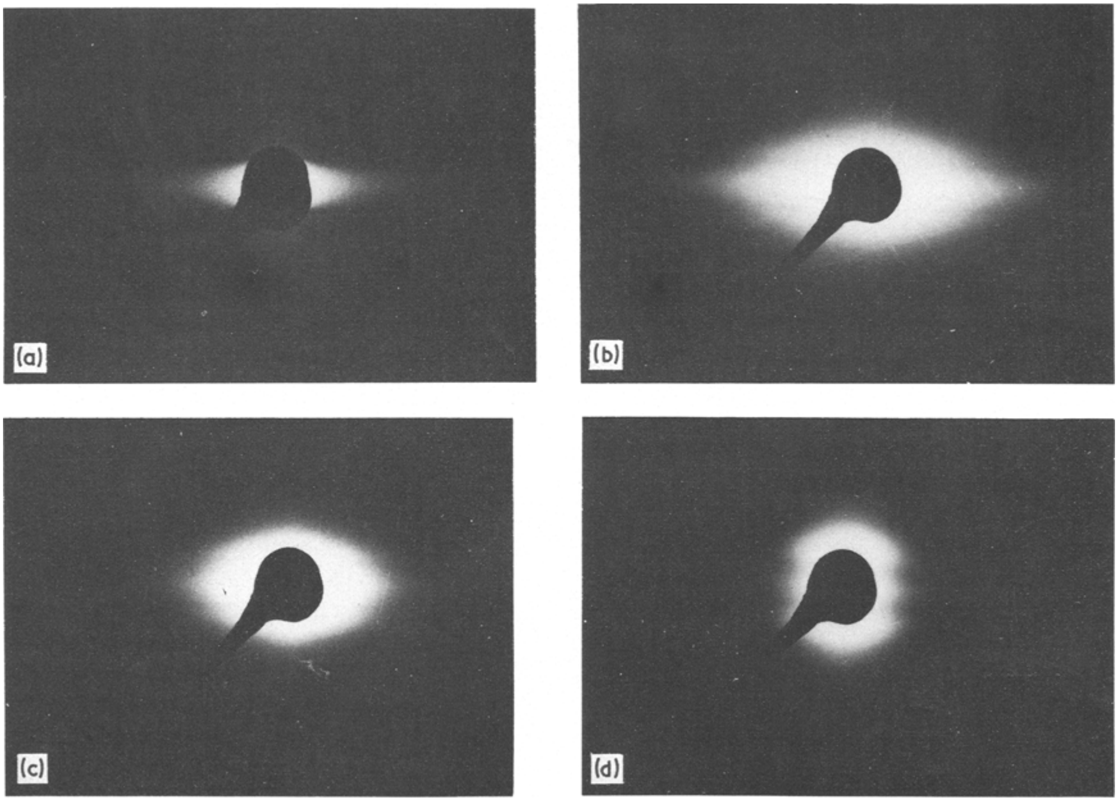

Figure 1 Small-angle X-ray scattering patterns obtained from polytrioxane irradiated with various doses at room temperature; dose rate: 0.2 MR h^{-1} (a) unirradiated, (b) Irradiated 30 Mr, (c) 50 MR, and (d) 100 MR, intensities of X-ray diffraction are not comparable.

57 mm in diameter using a 1 mm diameter collimator. All the experiments were carried out with nickel-fitted Cu*Kα*-radiation on Rigaku Denki Model D-3F and Model RU-3 X-ray units.

Electron micrographs of PTOX as-polymerized and irradiated were observed with a JEM-7 electron microscope by a direct replication technique.

3. Results and discussion

3.1. SAXS

Fig. 1 shows the SAXS patterns for PTOX unirradiated, or as-polymerized (a), and irradiated with various doses up to 100 MR, (b to d). Above 100 MR, the material became brittle and was no longer entirely sutiable for X-ray measurement. The long axis of a bundle-like specimen is parallel to the meridian of the SAXS patterns shown in Fig. 1.

Diffuse scattering is observed in all of these patterns, but is strongly anisotropic around the primary beam, that is, the diffuse scatterings are more extended along the equatorial direction than along the meridional. The scattering along the equator for as-polymerized PTOX is similar to that reported previously by others [10–13]. This scattering is due to micro-voids stretching along the fibre axis and lying between microfibrils in a polymer crystal [14]. On the other hand, the diffuse scattering along the meridian in PTOX as-polymerized is very weak, even in the vicinity of the primary beam, and no discrete scattering is observed. Over 30 MR, however, a striated reflection can be seen on the meridian.

As shown in Fig. 1 (b, c and d), not only does the maximum of the discrete scattering shift toward a higher angle, but also the shape of the reflection, i.e. the length along the layer line and the width of the reflection, change with increasing irradiation. Concurrent changes in the scattering intensity distribution, not clearly seen in the photographs, can be seen in the intensity curves obtained awith a Kratky U-slit collimation as shown in Fig. 2. This figure shows how the meridional diffraction peak shifts to a higher angle and increases in intensity as the exposure dose increases, and how the meridional diffuse (continuous) scattering increases at the same time. It is also worthwhile to note that the peak intensity shown in Fig. 2 is more than ten times larger than those in the meridional discrete discrete scattering due to the lamellar structure in the drawn sample of the melt-crystallized POM.

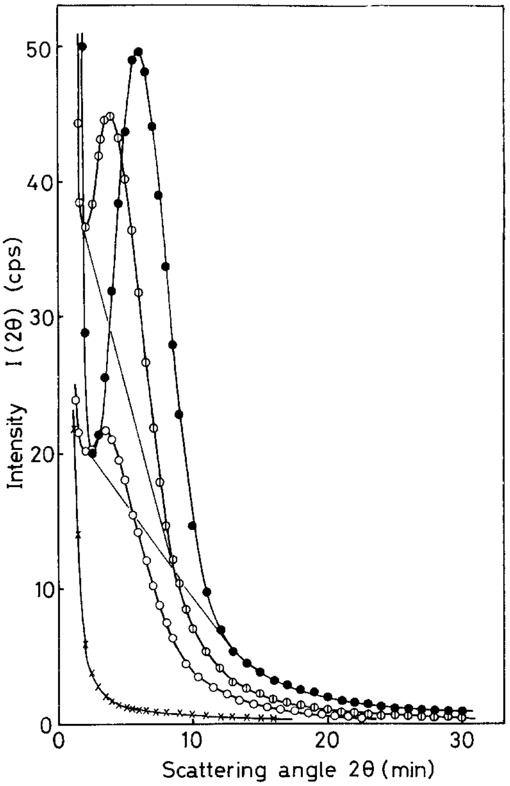

Figure 2 Effect of irradiation on the small-angle X-ray scattering intensity curve of polytrioxane (meridional direction) using a Kratky U-slit camera: X as-polymerized, o irradiated 30 MR, ⦶ 50 MR, and ● 100 MR.

In constrast with γ-irradiation, the heat treatment at 179° C in air (open ampoule) gave only a small increase in scattering intensity on the meridian as reported before [12]. The annealing in the sealed ampule with nitrogen gas also did not give the intensity peak associated with the long period which was reported by Amano *et al.* [11] and by us [12].

3.2. WAXS

As can be seen in Fig. 3, a comparison of the wide angle X-ray scattering (WAXS) patterns of the unirradiated PTOX with that of the irradiated shows that even after γ-irradiation up to 100 MR, no trace of an amorphous halo is detected inside of the (1 0 0) reflection; it seems to dissappear completely. As the irradiation increases, spots due to crystal reflections fade but show no change in the orientation of micro-fibril. The intensity of twin-reflections from the sub-crystal decreases

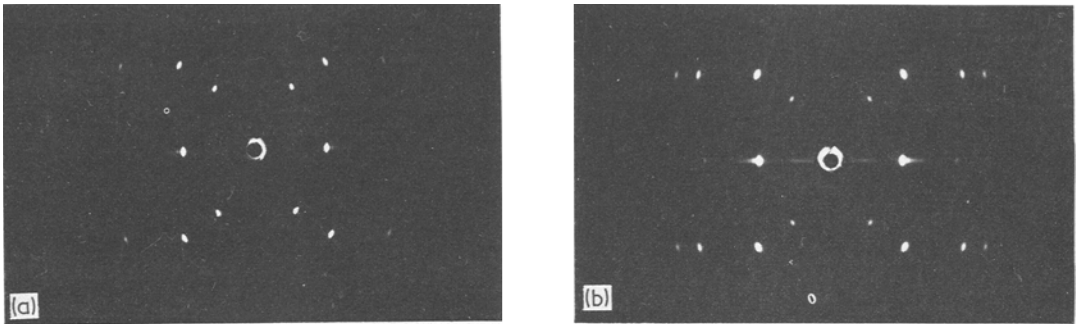

Figure 3 Rotation photographs of polytrioxane (rotation axis is a needle axis of specimen); dose rate 0.2 MR h^{-1} (a) unirradiated, (b) irradiated 100 MR.

more rapidly than that from the main-crystal with increasing exposure dose, but total disappearance of the twins is not observed.

The (1 0 0) reflection and the (0 0 5) reflection peaks were observed in WAXS diagram, indicating the existence of large amounts of unoriented micro-crystals and conformational disorder [15].

The fraction of sub-crystals with the twinned structure was calculated from the intensity ratio of the main- and sub-(1 0 0) reflections after the correction for Lorentz factor was made, and also the amorphous content and the amounts of randomly oriented crystallites were calculate. These results are shown in Table I. The fraction of the sub-crystal in the unirradiated sample of polymer yield of 80% was 40%, which is equivalent to the value (45%) reported by Carazzolo *et al.* [16] who did not report yield. The fraction amount of the sub-crystals increases with decreasing polymer yield [17].

The reductions in fractional amounts of main- and sub-crystals, amorphous content, and randomly oriented crystals during irradiation (including post-irradiation). The reductions of the sub-crystal are more extensive than the main, except after γ-irradiation up to 100 MR, in which they are almost the same. The amorphous was reduced completely, and unoriented micro-crystals greatly after irradiation of 50 MR.

3.3. Weight loss

A loss of sample weight took place as a result of γ-irradiation in air (and in nitrogen gas). The values for various exposure dose are given in Table I. Preliminary measurements of melting behaviour for the PTOX γ-irradiated more than 10 MR showed the depression of the melting point as reported already [2, 3], and broadening of the endothermic peak over 30 MR [15], associating with vigorous radiolysis.

3.4. Electron micrographs

Fig. 4 shows the electron micrographs of PTOX irradiated with 70 or 100 MR. The micro-fibrils of PTOX change into a mosaic-like stack of crystallites with the irradiation, and the larger the exposure dose, the more uniform the stacking observable. These patterns indicate the formation of the layer-like voids perpendicular to the *c*-axis of fibrillar crystals with a period of about 1000 Å.

3.5. Analysis of the observed SAXS curve

3.5.1. Layer-like voids

The maxima in the SAXS patterns shown in Fig. 1 and 2 are characteristic to a super-lattice structure of one-dimensional heterogeneity in electron density and are regarded as evidence of the existence of a "long period". In drawn semi-crystalline

TABLE I Fractional amounts of main-crystals, sub-crystals, amorphous contents and randomly oriented crystals, and reductions in fractional amounts of them and weight loss of poly (trioxane) irradiated in air at room temperature.

Exposure dose (MR)	Reduction in fractional amounts (%)				Weight loss (%)
	main-crystal	sub-crystal	amorphous	randomly oriented crystal	
0 (as-polymerized)	0 (initially 51%)	0 (initially 40%)	0 (initially 4%)	0 (initially 5%)	0
30	0 (51)	20 (32)	100 (0)	60 (2)	20 ± 5
50	7 (47)	20 (32)	100 (0)	80 (1)	30 ± 5
100	25 (38)	25 (30)	100 (0)	100 (0)	50 ± 5

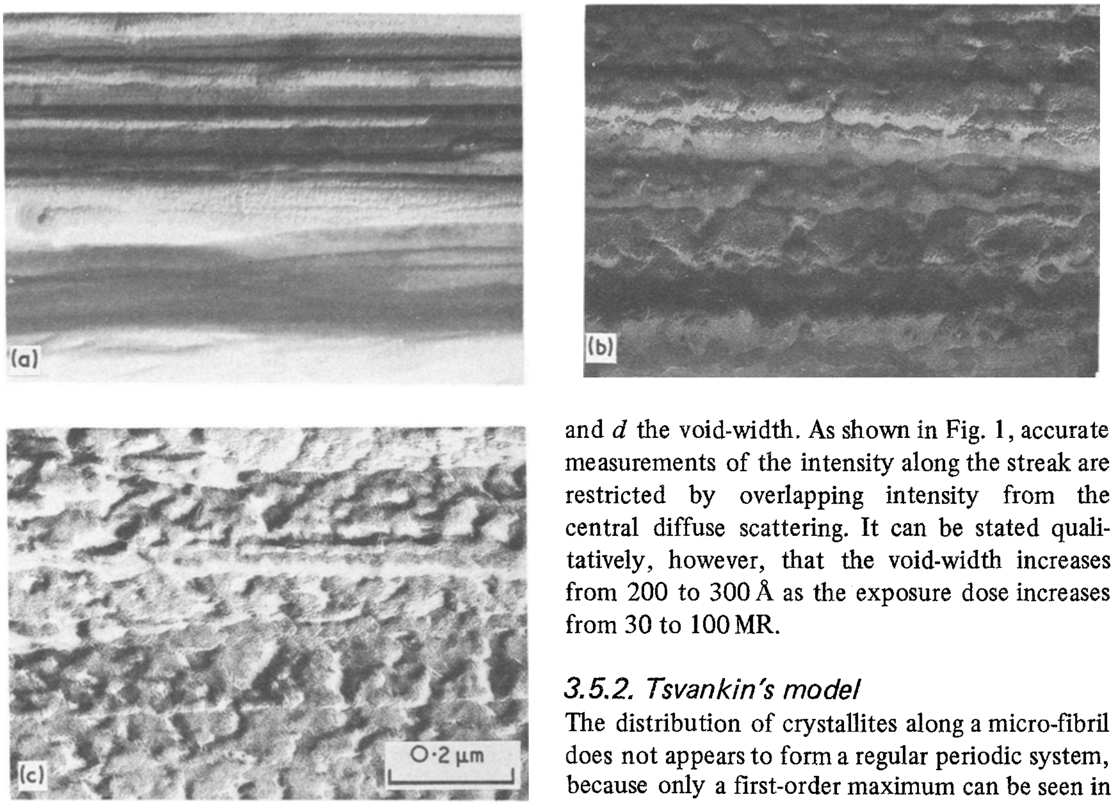

Figure 4 Electron micrographs of the free surface of polytrioxane crystal as-polymerized and irradiated 70 or 100 MR.

polymers, this maximum is observed most distinctly on the meridian of the SAXS and is considered to be due to the alternating layers of dense crystalline and less dense amorphous regions. In PTOX, as-polymerized amorphous regions are quite small. The present investigations of the γ-irradiated PTOX also show no evidence of the amorphous halo detectable on the WAXS patterns mentioned above.

Therefore, it is suspected that the meridional layer reflection in the above-mentioned SAXS is evidence of porosity caused by layer-like voids formed normal to the long axis of the fibrillar bundle. These voids may be associated with the weight loss of the irradiated polymer. The horizontal width of the meridional reflection can be used to evaluate the transverse dimensions of layer-like voids with the Scherrers'equation

$$\Delta\psi_{1/2} \simeq 0.9\lambda/d \qquad (1)$$

where $\Delta\psi_{1/2}$ is the angular half-width of the streak, λ the wave lenght of the X-ray radiation and d the void-width. As shown in Fig. 1, accurate measurements of the intensity along the streak are restricted by overlapping intensity from the central diffuse scattering. It can be stated qualitatively, however, that the void-width increases from 200 to 300 Å as the exposure dose increases from 30 to 100 MR.

3.5.2. Tsvankin's model

The distribution of crystallites along a micro-fibril does not appears to form a regular periodic system, because only a first-order maximum can be seen in the intensity curve. The first order diffraction peaks allow the estimation of the Bragg spacing. The apparent long periods, L, thus calculated for the irradiated samples are given in Table II. The true long period, D, can be calculated form the SAXS curve according to the Tsvankin's [18, 19] and Blundell's [20] analyses. Recently, Crist [21] critically reviewed the various proposed models of a paracrystalline one-dimentional superlattice. In the Tsvankin's theory, we assume the following model of the irradiated micro-fibril: (1) Zones of different density (crystal and void zones) form a superlattice which is responsible for the long period. (2) The crystallite lengths c are uniformly distributed with the mean lenght $\bar{c}$ and

TABLE II The positions and widths of the maxima on the SAXS curves for PTOX irradiated with various doses.

Parameter	Exposure Dose (MR)		
	30	50	100
Observed Long Period L(Å)	1500	1300	900
Half Width $\theta_{\frac{1}{2}}$($\times 10^{-4}$ Å^{-1})		5.78	7.66
Width Parameter $q(= L\theta_{\frac{1}{2}})$		0.75	0.69

the dispersion about the mean value by σ_c. (3) The electron density as a function of distance in the fibre axis direction Z is

$$p(z)\begin{cases} = 0 \text{ for } z < c & \text{(2a)} \\ = \dfrac{1}{\bar{v}} \exp\left[-(z-c)/\bar{v}\right] \quad \text{for } z \geqslant c & \text{(2b)} \end{cases}$$

Here $\bar{v}$ is the mean value of the void length between the crystallites so that $D = \bar{z} = \bar{c} + \bar{v}$ represents the true periodicity of the super-lattice.

3.5.3. Analysis by Tsvankin's method

The background intensity of diffuse scattering must be taken into account. If the electron density is distributed irregularly, the intensity of the diffuse scattering falls monotonically with the scattering angle. Fig. 2 shows that after irradiation the longitudinal distribution of density becomes less regular. It is not clear at present whether or not the diffuse scattering and the diffraction peak arise in the same heterogeneous regions.

For simplicity, the diffraction maximum was separated from the background fairly arbitrarily, as shown in Fig. 2, and then the experimental curves were analysed with respect to the position and widths of the maxima to compute the mean crystallite and void lengths.

The experimental half-widths of the maximum, Δ_e were corrected by subtracting the influence of broadening of the primary beam as follows:

$$\theta^2_{\frac{1}{2}} = \Delta_e^2 - \Delta_p^2, \quad (3)$$

where Δ_p is the primary beam half-width, 1.7′ in the present case. The values of the corrected half-width of the maximum $\theta_{1/2}$, in units of $2 \sin \theta/\lambda$ and the width parameter, $q = L\theta^{1/2}$, for the irradiated PTOX are given in Table II.

Difficulties with this simple approach are that *a priori* knowledge of the following parameters is required: the dispersion of crystallite lengths, σ_c; the crystallite packing density along the fibre axis (or the linear crystallinity), $\rho_1 = \bar{c}/d$; and the one-dimensional variation in electron density at each crystal-void boundary, ϵ. Tsvankin [18] noted that the shape of the scattering curve was relatively insensitive to the value of ϵ chosen. The large values of the parameter q, which are 0.75 and 0.69 for the samples irradiated 50 and 100 MR as shown in Table II, respectively, indicated less regularity in the periodicity. From these values of the parameter q, the true long period D, the mean crystallite length $\bar{c}$ and the linear crystallinity of the linear weight loss, $\chi_1 = 1 - \rho_1$, can be estimated, once a suitable value is assigned to the parameter $\sigma_c/\bar{c}$ which characterizes the dispersion of crystallites about the mean value. When the broadness of the first maximum and the fact that no second order was observed are taken into account, the parameter $\sigma_c/\bar{c}$ cannot be assumed to be small. According to Buchanan's results [22] (see Table I of [22]), D, $\bar{c}$ and χ_1 were obtained for the values of $\sigma_c/\bar{c}$ in the range of 0.2 to 0.5, when $\epsilon = 0.2$, as shown in Table III.

The losses of mass and sub-crystal content caused by γ-irradiation enable us to estimate the value of $\sigma_c/\bar{c}$, assuming that the irradiation produces the electron density distribution described in Equation 2.

For 50 MR, $\sigma_c/\bar{c}$ probably takes a value between 0.4 and 0.5, since the weight loss is about 30% as shown in Table I. So that the true long period of 1200 to 1300 Å and the crystallite length 800 to 1000 Å are determined. For 100 MR, $\sigma_c/\bar{c}$ seems to be about 0.2, so the true long period ~1000 Å and the crystallite length ~600 Å are obtained.

The mean crystallite length as well as lattice distortion is also obtained by the method of X-ray line broadening analysis based on the paracrystalline theory.

TABLE III Analysis of SAXS data for PTOX irradiated 50 and 100 MR.

$\sigma_c/\bar{c}$	50 MR Long Period D (Å)	50 MR Crystallite Length, $\bar{c}$ (Å)	50 MR Weight Loss, χ_1 (%)	100 MR Long Period D (Å)	100 MR Crystallite Length $\bar{c}$ (Å)	100 MR Weight Loss χ_1 (%)
0.2	1560	790	50	1050	560	47
0.3	1310	690	48	960	530	45
0.4	1270	770	39	870	540	38
0.5	1170	1020	13	710	640	10

TABLE IV Crystallite length of PTOX parellel and perpendicular to the chain axis.

	Parallel to *c*-axis (Å)	Perpendicular to *c*-axis (Å)
As-polymerized		
(Main)	500	300
(Sub)	200	400
Irradiated		
100 MR (Main)	350	250

The mean crystallite lengths in both parallel and perpendicular directions to the chain axis are estimated by using the intrinsic integral breadth of the (0 0 9) and (0 0 1 8) reflections and of the four reflections from the (1 0 0) to (4 0 0).

Table IV shows the values of the main- and sub-crystallite of PTOX as-polymerized and on the main of the irradiated 100 MR, since the WAXS intensity of the sub was very weak.

A mean repeated period of a stacking unit along the fibre axis can be the sum of the longitudinal length of the main (500 Å) and the lateral length of the sub (400 Å), that is, about 900 Å. The decrease of the *c*-axis dimension of the main from 500 Å to 350 Å, and the perpendicular dimension from 300 to 250 Å after the irradiation of 100 MR corresponds to the reduction of the weight loss of about 50%.

On considering the bulk weight loss of ~ 50% shown in Table I, the loss of the mass of the sub must be in the same order.

The reductions in fractional amounts of the main and sub in the as-polymerized during irradiation is in the order of 25% of the original main- and sub-crystallite from Table I. The layer-like voids as well as local defects are formed by the γ-irradiation in PTOX crystals, suggesting the periodical (~ 1000 Å) characteristics of the fibrillar crystal of PTOX. For example, the existence of a selective region where is acccessible to the radiolysis is assumed along the *c*-axis of PTOX crystals.

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