On the small-angle X-ray scattering of rigid-rod polymer fibres

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Small-angle X-ray scattering was carried out on as-spun and heat-treated poly(*p*-phenylene benzobisoxazole) (PBO) fibre. While as-spun PBO fibre exhibits only an equatorial streak, generally attributed to elongated voids or fibrils, the heat-treated fibre shows in addition a radial four-point pattern. The long period and radial spacing of this pattern are 28 and 15 nm, respectively. The spacings do not vary with heat-treatment temperature. As the angle defined by the plane normal to the fibre axis and the X-ray beam is increased from 0° to 30° to 60°, the four-point pattern gradually changes to a two-point pattern. The measured long period in the tilted fibre is a projection of that in the untilted fibre. Various possible morphological models are discussed.

(Keywords: PBO fibre; small-angle X-ray scattering; rigid-rod polymers)

INTRODUCTION

Poly(*p*-phenylene benzobisoxazole) (PBO) was first synthesized in the late 1970s. Synthesis, processing and properties of PBO and other ordered polymeric fibres are well documented in the published literature[1-3]. Over the last decade significant developmental efforts have focused on the processing of PBO fibres. PBO molecules have high molecular rigidity, as evidence by a Mark–Houwink–Sakurada exponent of 1.8 and a persistence length of at least 50 nm. The onset of degradation in PBO is about 650°C in air and 700°C in an inert atmosphere. Experimental PBO fibres with tensile modulus of 350 GPa have been reported, which is 51% of the theoretical tensile modulus[4]. PBO fibres are dry-jet wet spun at about 80–120°C from anisotropic solutions containing about 15 wt% polymer in polyphosphoric acid. The intrinsic viscosity of the polymer solution used for fibre spinning is 25–30 dl g^{-1} (ref. 5) or a viscosity-average molecular weight of about 25000–30000 g mol^{-1}. Fibre is usually coagulated in water at room temperature, though other coagulants have been used. The coagulated fibre is washed to remove residual acid, dried and heat-treated at 500–700°C in N_2 for 30–120 s under tension. The results of wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have been published previously[1,3,6-9]. That a four-point small-angle X-ray scattering (SAXS) pattern may be obtained from the PBO fibre after heat treatment was first reported in 1984[10] and later confirmed[11,12]. The object of the present communication is to report some additional observations concerning the SAXS pattern and to suggest a morphological basis for the existence of a radial four-point pattern.

EXPERIMENTAL

The fibres used in this study were obtained as multifilament tows. The tows were heat-treated under stress in N_2 at 600–710°C. The heat-treatment temperature and the mechanical properties of the fibres are reported in *Table 1*[13]. Fibres heat-treated at 710°C were rather brittle and their mechanical properties are not reported. Small-angle X-ray scattering was conducted on well aligned fibre bundles at the Cornell High Energy Synchrotron Source (CHESS) on the A-1 beam line using pinhole collimation 200 μm in diameter and a sample-to-film distance of 76 cm[14]. The X-ray wavelength was 0.15 nm. An exposure time of 15 min was sufficient for Kodak DEF or AA films. Characteristic spacings in the fibres were determined using a Joyce–Loebl Scandig III microdensitometer by tracing radial and meridional scans from the negative.

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RESULTS

The SAXS of as-spun and heat-treated PBO fibres are shown in *Figures 1* and *2*. The SAXS pattern of the as-spun fibre has only an equatorial streak, which is generally attributed to the presence of voids[15] or crystals[14] elongated along the fibre axis.

In addition to the central streak, SAXS from the heat-treated PBO fibre has a four-point pattern that smears towards the origin. Distinct maxima are observed in the meridional traces and a shoulder in the intensity is observed in radial scans. An example of a microdensitometer meridional trace is shown in *Figure 3*.

The radial (d_1) and meridional (d_2) spacings in real space, as defined in reciprocal space as d'_1 and d'_2 in *Figure 2*, were calculated, and the results are shown in *Table 2*. The characteristic angle, ϕ, is 58–60° in both real and reciprocal space. The long-period spacing, d_2, does not change with heat-treatment temperature. The radial spacing appears to increase slightly with heat-treatment temperature; however, the measurement accuracy does not allow for meaningful quantification of the change. Therefore, further confirmation of d_1 increasing with heat-treatment temperature is needed. On the other hand, the long period seems to be a function of only the solution source and does not vary with processing or post-processing treatment for a given fibre batch. Specifically, other PBO fibres have been characterized by a long period of 23 nm[1], rather than the 28 nm reported here. The long period in PBO does not change with coagulation conditions, though the relative intensity of the four-point pattern and the equatorial streak changes considerably. Under fast coagulation conditions, such as in water at 90°C, the four-point pattern in PBO almost disappears[1]. The long period in PBO also does not change with tension, although the long period intensity appears to decrease when measurements were carried out up to about 0.8% strain. SAXS was also conducted on fibres boiled in water for 6 h, after which time the water uptake was about 0.4%. Again, the intensity of the four-point pattern decreased, but the long period was invariant.

In order to obtain yet more structural information, the fibre was tilted towards the X-ray beam in the plane defined by the fibre and the X-ray beam. The scattering patterns of the fibre tilted 30° and 60° from vertical

Table 1 PBO fibre properties[13]

Heat-treatment temperature (°C)	Tensile modulus (GPa)	Strength (GPa)	Crystal modulus by X-rays (GPa)
As-spun	166	4.6	387
600	318	4.9	477
665	290	3.0	433
710	–	–	–

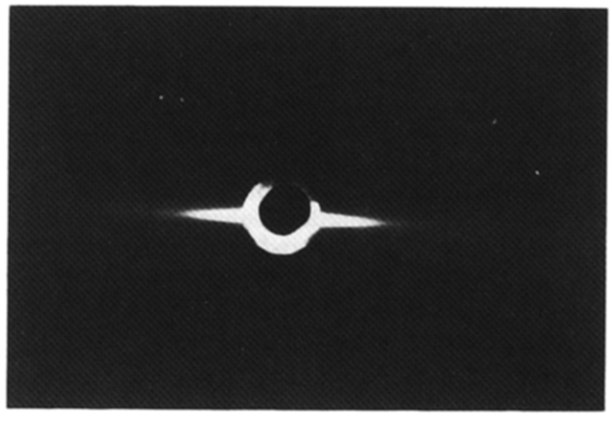

Figure 1 Small-angle X-ray scattering of as-spun PBO fibre

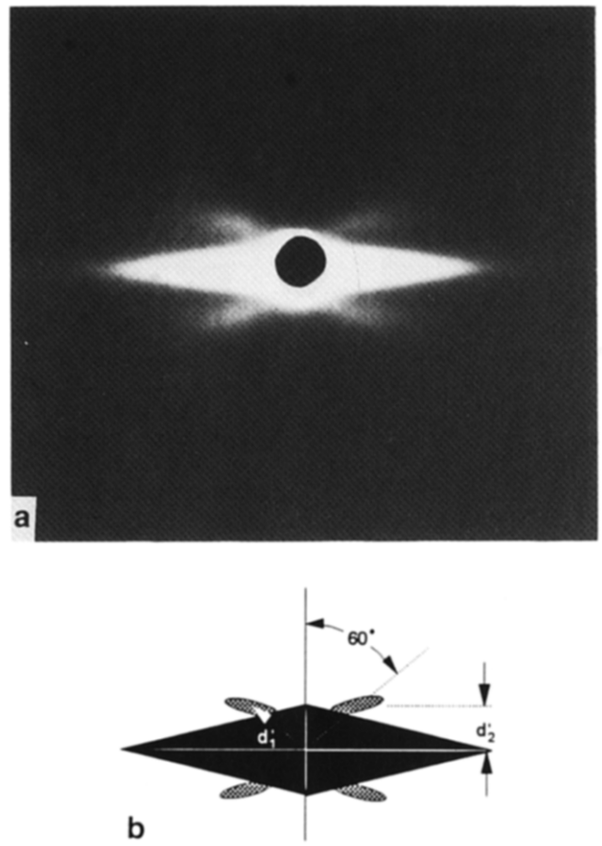

Figure 2 Small-angle X-ray scattering of 600°C heat-treated PBO fibre

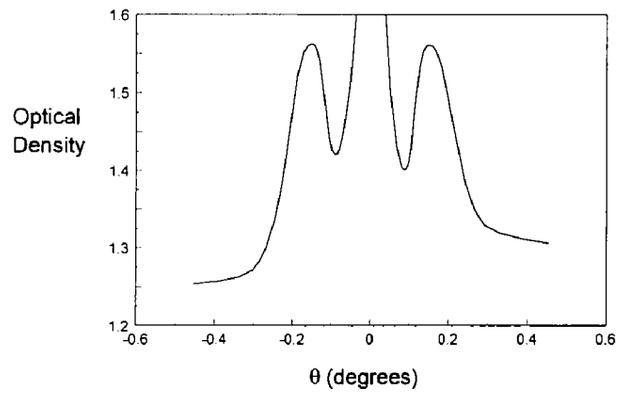

Figure 3 Meridional scan through four-point pattern of PBO heat-treated at 700°C showing central streak and two of the four points

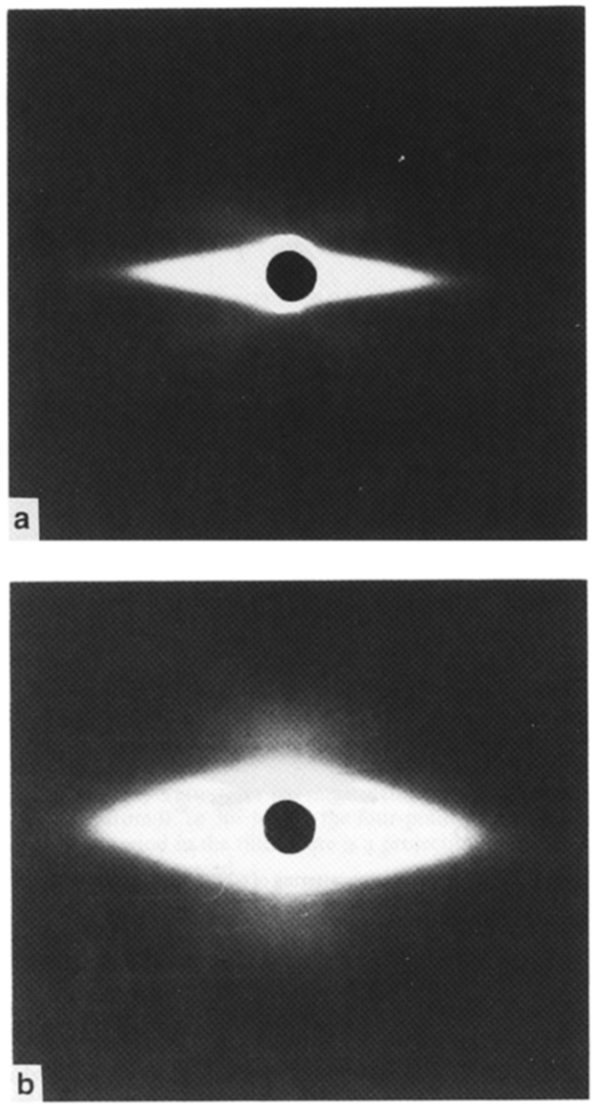

Figure 4 Small-angle X-ray scattering of 600 C heat-treated PBO fibre tilted towards the beam (a) 30 and (b) 60 from vertical (X-ray beam horizontal)

Table 2 Effect of heat-treatment temperature on PBO SAXS parameters

Temperature (C)	d_1 (nm)	d_2 (nm)
600	15.5	28.0
665	16.0	29.0
710	16.5	28.0

towards the horizontal X-ray beam are shown in *Figure 4*, and the parameters measured from these scans are given in *Table 3*. The radial spacing does not change with tilting; however, the pattern changes from four points to two points. The long period of the tilted fibre is a projection of the untilted fibre long period, as seen by comparing columns 3 and 4 in *Table 3*. The angular intensity dispersion or line breadth is greater in the tilted fibre than in the untilted fibre. In addition, on tilting to

Table 3 Change in SAXS parameters of PBO fibre heat-treated at 600 C with fibre tilt

Tilt angle, ψ (deg)	d_1 (nm)	d_2 (nm)	$d_2(0)\cos\psi$ (nm)
0	15.5	28.0	28.0
30	16.0	24.5	24.2
60	15.0	15.0	14.0

60 the contribution from the fibrils, voids, or both increases, causing the central streak to broaden significantly.

Other polymer films and fibres show four-point SAXS patterns. Poly(2,5-benzoxazole) (ABPBO), which is a semi-rigid polymer, exhibits a readily discernible four-point pattern from heat-treated fibre[12]. On the other hand, such a pattern is not observed in heat-treated poly(*p*-phenylene benzobisthiazole) (PBZT) fibre; however, four very weak streaks that form an X through the origin have been observed[11]. A weak four-streak radial pattern is also observed in poly(*p*-phenylene terephthalamide) (PPTA; Kevlar™ 149)[14]. These results suggest that the observation of a four-point radial pattern with X streaking is not unique to PBO, but is characteristic of other highly oriented polymers.

DISCUSSION

Four-point and two-point SAXS patterns were first reported in flexible-chain polymeric fibres over four decades ago in nylon-6,10 and polyethylene[16,17]. Since then, such patterns have been obtained in many flexible-chain polymeric fibres and one- and two-dimensionally extruded films[18-31]; however, few, if any of the four-point patterns show radial streaking. In the case of flexible-chain polymers, SAXS patterns are explained on the basis of electron-density differences between the crystalline and non-crystalline regions. The long period, then, is the sum of the thickness of crystalline and non-crystalline regions. Significant modelling and optical diffraction work has been done to explain the scattering patterns[32-38]. The results of the modelling show that the four-point radial pattern can be obtained from using either (1) an inclined lamellar fibril model or (2) a microparacrystalline model. In either case there may or may not be lateral correlation among fibrils or crystallites. According to the computer modelling work done by Vonk[34], a four-point radial pattern may be obtained without correlation among microcrystals when the fibril diameter divided by the long period is greater than 1.0 and preferably at least as large as 2.0. According to Gerasimov[35,36], a four-point pattern with radial streaking may be obtained from an inclined fibril model containing rectangular microcrystallites with correlation when either the ordered or disordered regions become vanishingly thin. According to Asherov and Ginzburg[37], a rhombohedrally shaped pseudo-crystal can give rise to a four- or six-point SAXS pattern, the details of the intensity distribution depends on morphological details.

The most common explanation for the observation of a two- or four-point pattern is that periodic density fluctuations associated with crystalline and non-crystalline regions are present along the length of a fibre. Either without modification or perhaps with extended heat

treatment, chemical etching, or staining, a SAXS pattern in oriented fibres is observable. For example, highly drawn acrylic fibres show no SAXS pattern other than the central equatorial streak until the fibre is partially oxidized or infused with metal salts to enhance density differences among structurally heterogeneous regions within the fibre[25].

The four-point pattern arises when the higher- and lower-density regions are oriented at an angle to the fibre axis or, as Vonk suggests[34], when the crystals become narrow and randomly correlated. Crystals may appear tilted from the fibre axis because of growth conditions or as a result of shear between crystalline and non-crystalline regions. The physical model shown in *Figure 5a*, which is along the lines of the mathematical models proposed by Asherov and Ginzburg[37], is consistent with the SAXS pattern observed from the heat-treated PBO fibre. A value of $d_1 \sin \phi = 13.2$ nm can be taken as the upper limit of the crystal breadth, which presumably cannot exceed the fibril diameter. This value, 13.2 nm, is slightly larger than those of the fibril diameter, 7 nm, calculated from SAXS[39] and crystal width measured using selected-area electron diffraction, which range from 1.6 to 9.0 nm[1].

The two-phase model as described for flexible-chain polymers is not perceived to apply directly to rigid-rod polymers, which are often modelled as containing two-dimensionally and three-dimensionally ordered region. A possible explanation for the observation of a four-point pattern in rigid chains must be due to electron-density differences between regions of different order that are periodically spaced along fibrils. The concept of density and other morphological differences between regions of different orders is an extension of the two-phase crystalline and non-crystalline model and is not unique to rigid-rod polymers. The structure of acrylic fibres is best envisioned as consisting of two-dimensionally ordered and oriented amorphous regions[40]. As already mentioned, two- and four-point SAXS patterns have been observed on oriented acrylic fibres and the four-point pattern does show weak X streaking as well. What we need to explain is the origin of the tilt in PBO and other polymers and the reasons for the radial streaking.

Before addressing this issue, let us direct our attention towards understanding why the four-point pattern is more distinct in PBO than in other rigid-rod polymers. We suggest that the difference in density between the two- and three-dimensionally ordered regions in PBO is sufficiently great that the pattern has reasonable intensity. The density of a PBO crystal has been estimated to be about 1.66 g cm^{-3}, whereas that of the fibre is about 1.58 g cm^{-3}. PPTA in the form of Kevlar 149, on the other hand, has a fibre density of 1.47 g cm^{-3} and a crystal density of 1.50 g cm^{-3} (ref. 41). PBZT has so little three-dimensionally ordered material that the SAXS intensity is insufficient to allow for a four-point pattern.

In flexible-chain polymers the four-point pattern usually evolves from the two-point pattern when the polymer is appropriately plastically deformed. The four-point pattern may revert to a two-point pattern upon annealing[29,34]. Hence, the four-point pattern reflects a deformation-induced morphology, suggesting that the morphology reflected by the two-point pattern is thermodynamically more stable than that corresponding to the four-point pattern. In PBO and other lyotropic

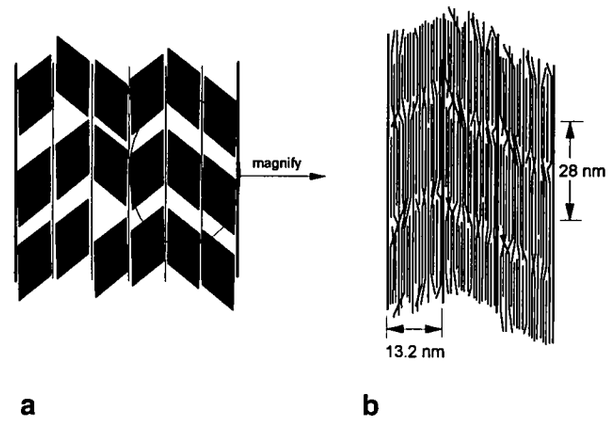

Figure 5 Morphology that accounts for four-point SAXS pattern: (a) block model; (b) molecular model

polymeric fibres, on the other hand, annealing enhances differences between phases and perhaps promotes three-dimensional crystal growth. This suggests that the morphology associated with the four-point pattern is thermodynamically favourable. Perhaps crystal growth and perfection in fibres of rigid-rod polymers occurs so as to produce crystal boundaries other than parallel and normal to the fibre axis, as illustrated in *Figure 5b*. Hence, the interface between three-dimensional and two-dimensional materials is at an angle to the fibre axis, so that the crystallites actually take shape of rhombohedra. Since the (3 0 2) reflection is strong in both wide-angle X-ray scattering and electron diffraction and it makes an angle of 58° with the fibre axis, since chains are axially shifted $c/4$ relative to one another, Martin and Thomas[42,43] proposed that interfaces between regions of different order are actually (3 0 2) planes, caused by twist defects that segregate to form 'grain boundaries'. Chevrons have been observed on occasion in dark-field imaging of PBO[8], as have rhombohedral crystallites in slow-coagulated films of PPTA[44].

Lamellar surfaces at 60° to the fibre axis have 15% more surface area than do surfaces at 90° to the fibre axis. Thus, rhombohedral shapes might be expected to lead to a higher total energy; however, perhaps (3 0 2) surfaces have a lower energy per unit area than do (0 0 1) surfaces, more than compensating for the higher area. In addition, perhaps surfaces at 60° are capable of providing less strain energy to the system. In any event, similar growth patterns that gave rise to pyramidal crystals, for example, were recognized in the 1960s for a variety of polymers[45].

The model as presented in *Figure 5* agrees with the coarse and fine structure on the SAXS diagrams. The two-point pattern that develops from the four-point pattern upon tilting is due to lamellar stacking, which is seen by the X-ray beam when the fibre is tilted 60° from the vertical. The equality between d_2 and $d_2(0°) \cos \psi$ in *Table 3* is due to the X-ray beam responding to the lamellar structure in both cases. The relatively weak intensity of the two- and four-point patterns is due both to the small differences in density between ordered regions and to the fact that only a small amount of material in the fibre is oriented properly for the two- or four-point pattern. Streaking of the four points towards the centre is also consistent with the model proposed.

Small-angle scattering data cannot be used to develop a unique model; rather, it can be used only to ascertain that a proposed model is consistent with experimental data. Thus, other models need to be considered. Vonk convincingly showed that a four-point radial pattern can develop with or without correlation among fibrils in a lamellar structure when the microcrystallites are narrow[34]. While Vonk's model is quite appealing, it does not seem to fit the data in this case. The model of Gerasimov *et al.*[35,36] can also be used to generate the observed four-point pattern; however, it seems unlikely for physical reasons to expect three-dimensionally or two-dimensionally ordered regions to be infinitely thin, and if they were, the polymer would not give a SAXS pattern. We realize, however, that these and other results based on computer simulation or optical masking may be sensitive to the extent of disorder in the polymer.

CONCLUSIONS

Small-angle X-ray scattering experiments have been conducted on a number of fibres of rigid-rod polymers. The results show that all the fibres are characterized by a strong central equatorial streak indicative of a fibrillar structure with needle-shaped voids. In addition, heat-treated PBO fibre shows a clear four-point pattern that streaks towards the origin and many of the other lyotropic fibres show a very weak four-point radial or X streak pattern. The presence of the four-point pattern requires and is indicative of significant periodic density fluctuations along the fibre. In some fibres the small density differences between the regions or the amount of three-dimensionally ordered material is insufficient to allow the observation of a strong two- or four-point pattern. Tilting of PBO fibre towards the beam causes the four-point pattern to become a two-point pattern. A model is presented in which crystal interfaces are inclined to the fibre axis, giving the crystals a rhombohedral shape. The model is consistent with the SAXS pattern, the changes in the pattern with fibre tilting and other known morphological features of the fibres.

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