Small-angle X-ray scattering on fibres of heteroaromatic polymers

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(Received 9 October 1990; accepted 4 February 1991)

Fibres of the coil-like molecule poly-2,5-benzoxazole (ABPBO) as well as the rod-like molecules poly(*p*-phenylene benzobisoxazole) (PBO) and poly(*p*-phenylene benzobisthiazole) (PBT) were processed and examined by small-angle X-ray scattering (SAXS). SAXS on thermally annealed ABPBO and PBO fibres consistently showed an off-axis radial four-point intensity pattern. Molecular adjustment due to thermal annealing was believed to cause this unique fibre morphology. The distinct scattering pattern suggested a uniaxial structure of plate-like ordered regions with a tilt-angle off the fibre axis. The tilt-angle was independent of annealing temperature. This fibre morphology is in agreement with complementary evidence from numerical modelling, X-ray diffraction and selected-area electron diffraction. In contrast, SAXS on annealed PBT fibre did not show the radial four-point intensity pattern. This was attributed to the non-colinear and non-coplanar nature of the PBT backbone. For the annealed fibres, the presence of the radial four-point SAXS pattern was not a prerequisite for improvements in tensile properties.

(Keywords: heteroaromatic polymers; microstructure; fibres; thermal annealing; radial four-point SAXS pattern)

INTRODUCTION

Large-scale microstructure of materials is generally studied by microscopy (optical and electron) and small angle scattering (light, neutron and X-ray). Small-angle X-ray scattering (SAXS) has been applied to study this long-range behaviour in amorphous or semi-crystalline polymeric systems[1]. Lately, its application to high-performance polymeric fibres has been shown to be useful in correlating microstructure with mechanical properties.

For most synthetic fibres of semi-crystalline polymers, SAXS intensity generally consists of level streaks perpendicular to the fibre axis. This has been attributed to a layer structure of crystalline and amorphous components distributed along the fibre axis[2]. The polymer chains in the crystalline layer are aligned along the fibre axis, forming a lamellar phase. Other derivatives of this basic model have also been proposed. In particular, a checkerboard arrangement of alternate crystalline and amorphous components has been suggested to account for the off-axis angle of the level scattering pattern, and to accommodate the fibrillar and the transversely isotropic nature of the fibres.

Heterocyclic aromatic polymers[3-11] have been under development for their inherently superior thermo-oxidative stability and solvent resistance. Most heteroaromatic polymers do not exhibit glass transition behaviour up to degradation temperature (at above 560°C). This inherent stability prohibits the use of conventional thermal moulding or extrusion for processing these polymers. Instead, they are processed by coagulation from an acidic solution; only a few protic acids are able to dissolve these polymers. In solution, it has been observed that the polymers tend to exhibit liquid-crystalline characteristics. This greatly influences the intermolecular arrangement, and thus has a determining effect on the final morphology and properties of these heteroaromatic polymers. The coagulation scheme also induces significant dimensional and morphological changes. One of the dominant effects is the formation of voids.

This paper reports morphological findings on fibres of several heteroaromatic polymers. The investigation focused on examining fibres of a coil-like molecule, poly-2,5-benzoxazole (ABPBO), and a rod-like molecule, poly(*p*-phenylene benzobisoxazole) (PBO), by SAXS. In addition, SAXS results from fibres of another rod-like molecule, poly(*p*-phenylene benzobisthiazole) (PBT) and of a coil-rod-coil triblock copolymer with PBT as the rod component and poly-2,5(6)-benzimidazole (ABPBI) as the coil component are also discussed. Complementary evidence from numerical modelling, X-ray diffraction and selected-area electron diffraction is also included to facilitate the interpretation of the SAXS results.

ABPBO and ABPBI belong to a group of coil-like heteroaromatic polymers with the generic designation ABPBX, as illustrated in *Figure 1*, which can assume an extended-chain configuration and form a liquid-crystalline phase. PBO or PBT is one of the heteroaromatic polymers commonly called PBX, as sketched in *Figure 1*, which assume a *para*-catenated backbone. This gives a rod-like polymer. The only conformational flexibility is provided by the rotation of bonds between alternating phenylene and heterocyclic groups[12,13]. As a result of its rigidity, this type of rod-like molecule generally forms a nematic liquid-crystalline anisotropic phase having a local unidirectional order but no lateral positional order. This characteristic becomes of considerable interest, since fibres and films from these liquid-crystalline polymers

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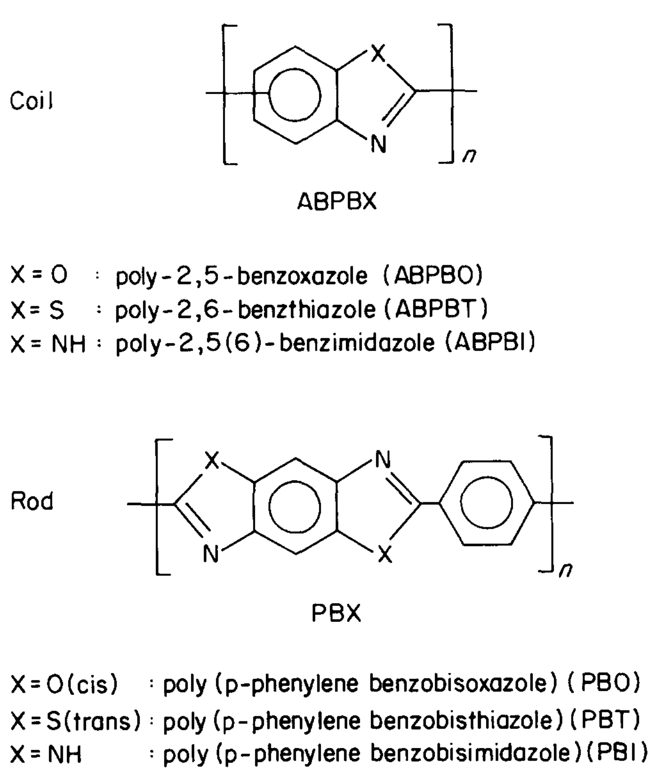

X = O : poly-2,5-benzoxazole (ABPBO)
X = S : poly-2,6-benzthiazole (ABPBT)
X = NH : poly-2,5(6)-benzimidazole (ABPBI)

X = O(cis) : poly (p-phenylene benzobisoxazole) (PBO)
X = S(trans) : poly (p-phenylene benzobisthiazole) (PBT)
X = NH : poly (p-phenylene benzobisimidazole) (PBI)

Figure 1 Chemical structures of ABPBX and PBX molecules

can have both superior mechanical properties and environmental stabilities (such as thermo-oxidative and dimensional stabilities as well as solvent resistance).

EXPERIMENTAL

Materials

ABPBO[3] and PBO[4] polymers have been synthesized by polycondensation in polyphosphoric acid (PPA). Recently, high molecular weights have been achieved for these polymers. In this study, a PBO–PPA dope with a PBO weight fraction of 9.9% and $[\eta] = 17.1$ dl g^{-1}, and an ABPBO–PPA dope with an ABPBO weight fraction of 14.2% and $[\eta] = 17.5$ dl g^{-1} were provided by J. Wolfe of SRI International, Menlo Park, CA. The intrinsic viscosity, $[\eta]$, was determined in methanesulphonic acid at 30°C.

Monofilaments of ABPBO and PBO were obtained by dry-jet wet-spinning of the polymerization mixture. The optically anisotropic liquid-crystalline dopes were heated, extruded isobarically through a spinneret at an optimized spin–draw ratio, and coagulated in distilled water at room temperature. After rinsing to remove residual acid, the fibre was air-dried at room temperature: the 'as-spun' fibre. Selected as-spun fibres were annealed in a tube furnace at 300, 415 and 510°C in a dried nitrogen atmosphere. The residence time of the fibre in the furnace was 0.5 min. A tensile strain of 0.015 ± 0.002 was maintained during the course of thermal annealing by controlling the differential speed of fibre feeding and take-up. As-spun and heat-treated fibres of PBT homopolymer[14] and ABPBI–PBT–ABPBI triblock copolymer[15] were similarly processed and studied.

Mechanical testing

Young's modulus E_t, tensile strength σ_t, and critical tensile strain at break ε_b were determined for the ABPBO and PBO fibres in accordance with ASTM test method D3379 for high-modulus filament. A single filament of the fibres was mounted on a pre-cut manila tab of 25.4 mm gauge length using sealing wax and fast-setting epoxy glue. Tensile deformation was applied by using an Instron tester with a 200 g load cell and a deformation rate of 0.5 mm min^{-1}. The diameter d_0 of each filament was determined by a split-image microscope. Because of the coagulation scheme employed here for processing the heterogeneous and anisotropic dopes, variations in fibre diameter were noted. Observations were made along several cross-sections of each specimen, and the averaged value was used for calculating tensile stress. Depending on the availability of each fibre, six to twelve specimens were tested. The results of tensile tests were corrected for compliance and then averaged.

Table 1 lists the diameter and tensile properties of the ABPBO and the PBO fibres, which indicates that the tensile modulus for a stiffer molecule, such as rod-like PBO, is higher than that of a coil-like molecule, such as ABPBO. Thermal annealing at a temperature below the degradation temperature does increase the tensile modulus significantly. These observations are also valid for fibres of PBT homopolymer[14] and of ABPBI–PBT–ABPBI triblock copolymer[15].

Small-angle X-ray scattering

To correlate fibre processing conditions with the mechanical properties, extensive X-ray scattering measurements and electron microscopy were applied to determine the morphology of the ABPBO and the PBO fibres. Details of these studies are reported in the preceding article. Here we focus on the unique results obtained from SAXS.

For SAXS measurements on the uniaxially oriented systems here, a flat-film camera with pinhole collimation and long flight path was designed and constructed. Cu K_α radiation from a Rigaku RU-300 rotating anode generator was the X-ray source. Each fibre was wound along the fibre axis to form a bundle, and the fibre bundle was attached vertically to the exit of the collimator. The convention of equatorial (horizontal) and meridional (vertical) designations applies here for the scattering patterns. The camera had a maximum sample-to-film distance of 730 mm. For the SAXS measurements, a flight path of 713 mm was used, which covered a reciprocal space of $2.29 > Q > 0.17$ nm^{-1}, where $Q = 4\pi \sin(\theta/2)/\lambda$, where λ is the wavelength and θ the scattering angle. This is equivalent to a real space distance (d) range of $2.47 < d < 44.10$ nm. This measurement range is most

Table 1 Tensile properties of fibres of heteroaromatic oxazole polymers

	d_0 (μm)	E_t (GPa)	σ_t (GPa)	ε_b (%)
ABPBO				
As-spun	33 ± 8	72	3.1	7.0
HT[a] at 300°C	43 ± 3	88	1.4	4.1
HT at 415°C	48 ± 8	96	1.9	4.0
HT at 510°C	56 ± 8	108	1.3	4.2
PBO				
As-spun	30 ± 2	87	3.1	6.6
HT at 300°C	28 ± 8	115	2.6	3.6
HT at 415°C	28 ± 8	137	2.6	3.6
HT at 510°C	27 ± 7	172	2.4	2.9

[a] Heat-treated

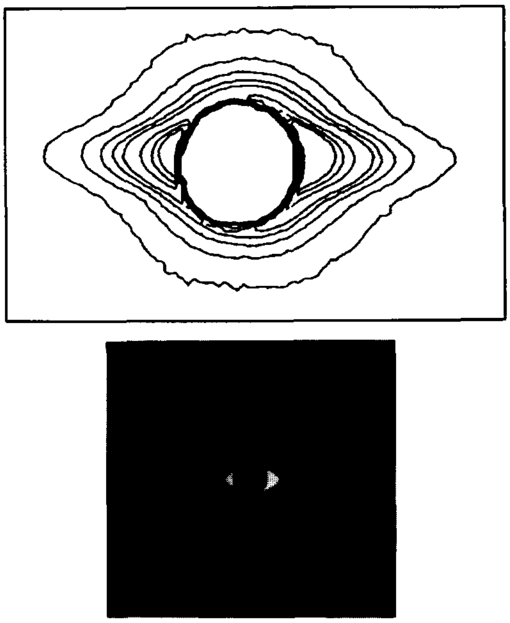

Figure 2 Contour plot of small-angle X-ray scattering intensity of ABPBO fibre annealed at 300°C

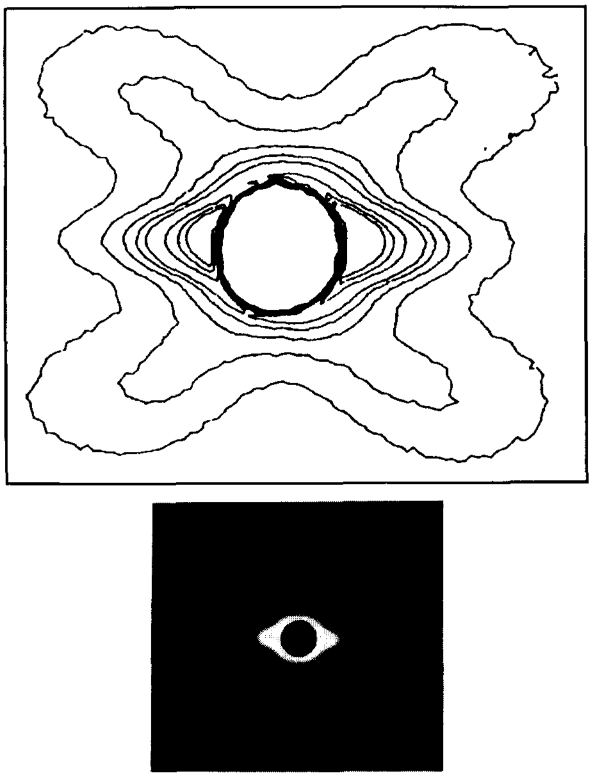

Figure 3 Contour plot of small-angle X-ray scattering intensity of ABPBO fibre annealed at 415°C

relevant to collective arrangement of crystallites as well as defects (voids), and thus to the mechanical properties of the fibres. The X-ray scattering intensities were registered on OSRAY films. The intensities were then digitized by using a Joyce Loebl SCANDIG 3 microdensitometer. The digitized intensities were processed by computer codes for generating contour plots or line scans for analyses.

RESULTS AND DISCUSSION

SAXS on various ABPBO and PBO fibres gives consistently a typical anisotropic pattern with intensity concentrated along the equatorial axis, similar to *Figure 2*. This anisotropic SAXS pattern is generally attributed to void scattering. The voids were formed as a result of a drastic volume reduction due to removal of the solvent during coagulation, and were elongated along the fibre axis through extrusion and application of spin–draw to the fibres. For ABPBO and PBO fibres thermally annealed under slight tension, as shown in *Figures 2–4*, SAXS measurements show four radial streaks emerging from the centre of the scattering pattern and becoming more pronounced with higher annealing temperatures. The radial four-point pattern from the SAXS measurements is off, as well as symmetrical to, the equatorial and the meridional axes. This SAXS pattern differs distinctly from the level four-point pattern observed for most synthetic fibres as described previously. The SAXS intensities along the equatorial and the radial directions are explored next.

Figure 5 shows equatorial line scans for the annealed ABPBO fibres. These SAXS intensities suggest that the scattering from voids (equatorial intensity) is not affected by annealing temperature. In other words, the size and the distribution of voids do not appear to be affected by the thermal annealing. However, the radial line scans given in *Figure 6* demonstrate that the radial four-point SAXS intensity increases with the annealing temperature and finally, for the ABPBO fibre annealed at 510°C, displays a distinct repeat distance of 14 nm measured along the radial direction. This is further depicted in *Figure 7* as a three-dimensional contour plot for the SAXS intensity of ABPBO fibre annealed at 510°C. The off-axis angle seems to be independent of annealing temperature for both ABPBO and PBO fibres. The off-meridional angle is about 50° and 63° for ABPBO and PBO fibres, respectively.

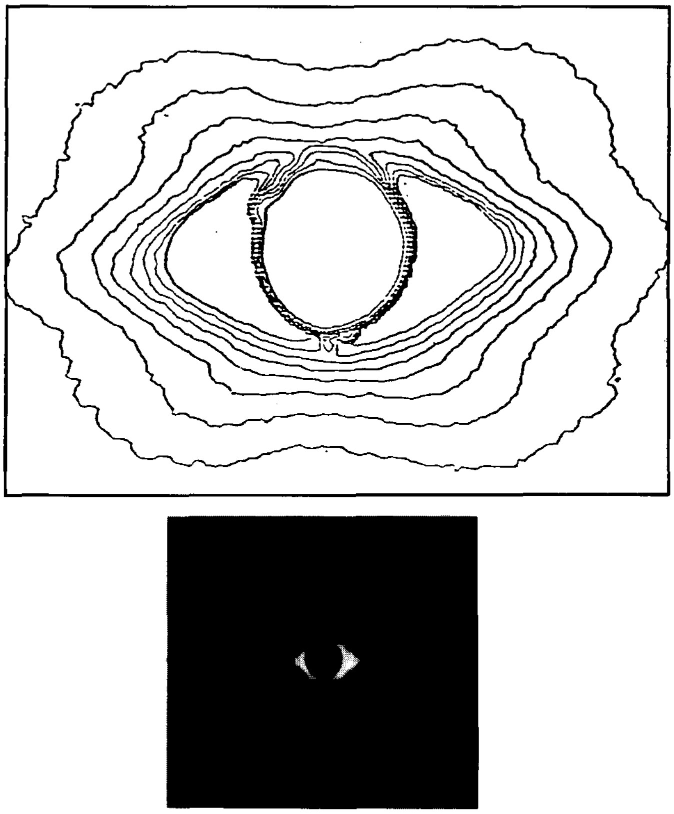

Figure 4 Contour plot of small-angle X-ray scattering intensity of PBO fibre annealed at 510°C

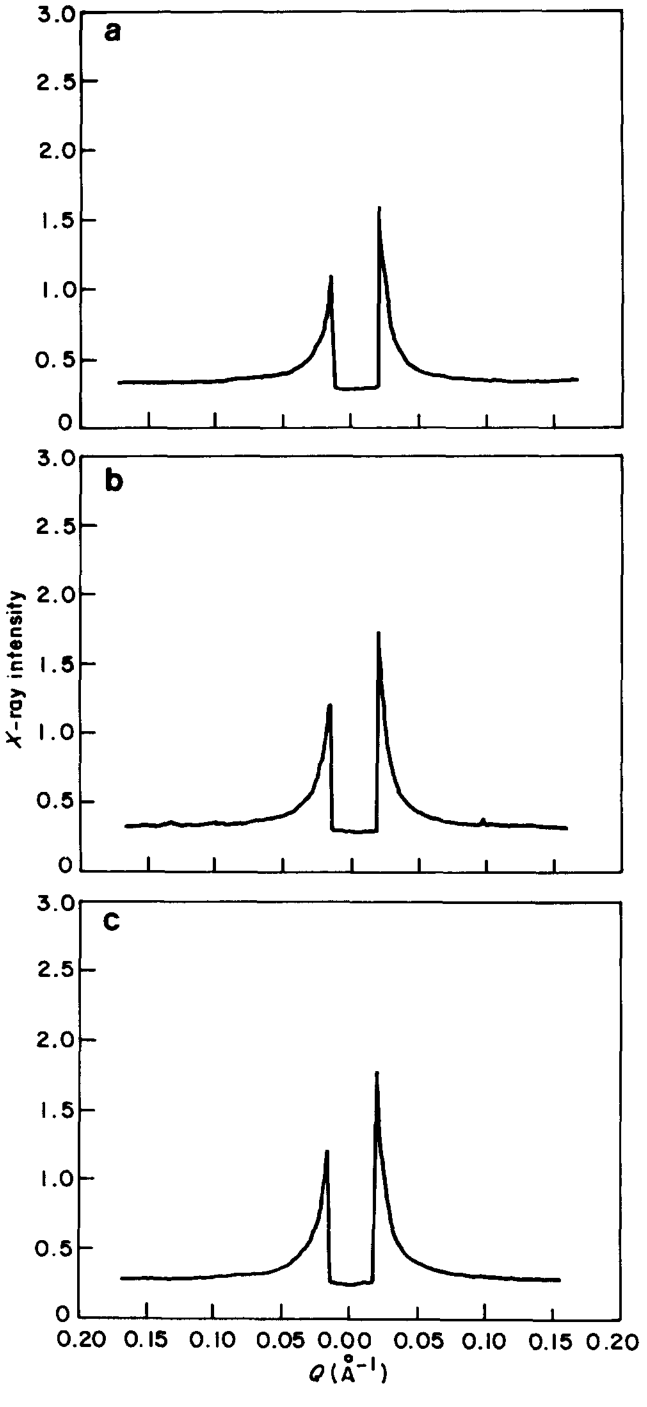

Figure 5 Equatorial line scans of small-angle X-ray scattering intensities of ABPBO fibres thermally annealed at (a) 300°C, (b) 415°C, (c) 510°C

SAXS measurements on thermally annealed PBT and ABPBI–PBT–ABPBI fibres resulted in a scattering intensity pattern similar to that of as-spun fibre of heteroaromatic polymers (cf. *Figure 2*). There was no four-point SAXS pattern over a wide range of annealing temperature. The absence of the four-point SAXS pattern becomes of great interest, since chemically PBO and PBT, or ABPBO and ABPBI, are very similar to each other and share many common physical and chemical characteristics; and the heteroaromatic polymers were fabricated into fibres by the same processing procedure. In order to understand this difference in the SAXS results, it is necessary to examine the origin of the off-axis radial four-point SAXS pattern for fibres.

Previous numerical simulations[16–19] have predicted this unique SAXS pattern for semi-crystalline unidirectional polymeric systems. The morphological interpretation given is that this off-axis radial four-point SAXS intensity is evidence of a lamellar-type crystalline phase in the fibre, with the lamellae tilting toward the fibre axis. This published model is sketched in *Figure 8*, which shows the simulated SAXS intensities together with the unit cell orientation and the semi-crystalline morphology of the unidirectional system. For semi-crystalline fibres, it demonstrates the conventional level streaks for the SAXS pattern while the polymer chains (*c*-axis) in the crystallites align along the fibre axis, *Figure 8*(*a*). As the chain orientation deviates from the fibre axis and the crystalline phase changes into a plate-like lamellar

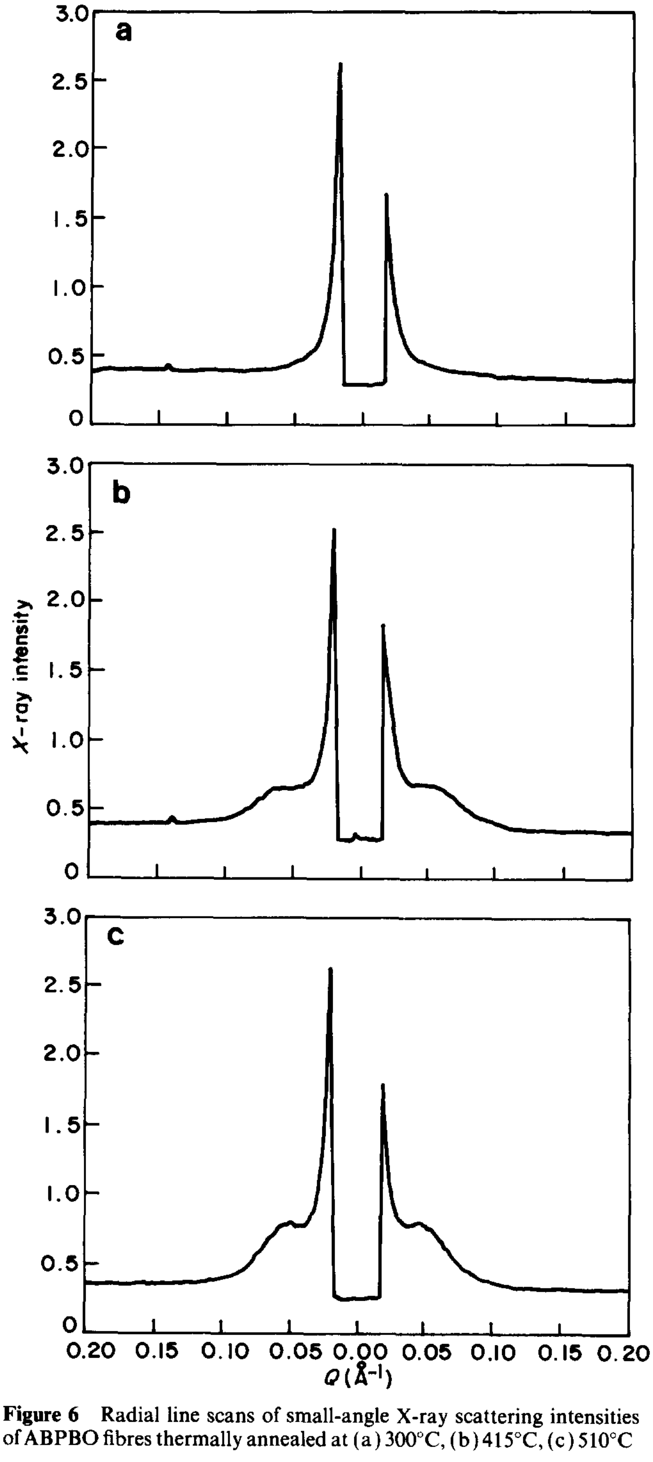

Figure 6 Radial line scans of small-angle X-ray scattering intensities of ABPBO fibres thermally annealed at (a) 300°C, (b) 415°C, (c) 510°C

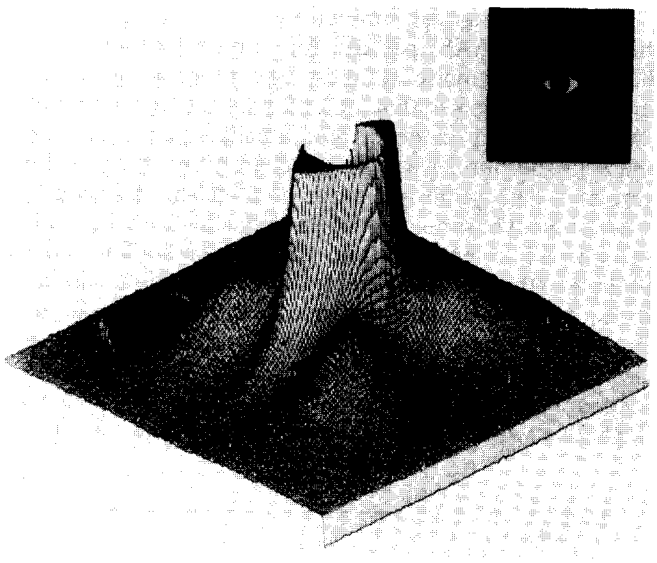

Figure 7 Three-dimensional contour plot of small-angle X-ray scattering intensity of ABPBO fibre annealed at 510°C

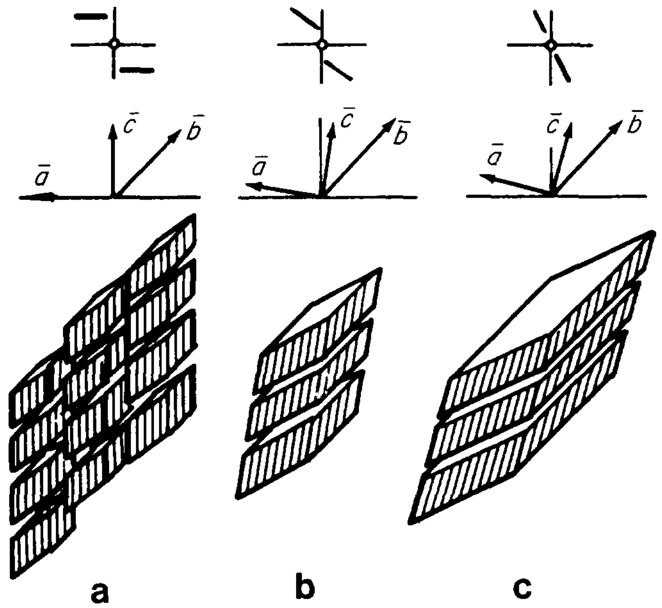

Figure 8 Numerical simulation of small-angle X-ray scattering intensities for oriented semi-crystalline polymeric systems[12]

morphology, the SAXS intensity starts to change to inclined streaks, *Figure 8(b)*. Further increase in the plate area leads to an off-axis radial two-point SAXS pattern. *Figure 8(c)*. When a bundle of fibres is studied, the fibre bundle is transversely isotropic and cylindrically symmetric. This would alter the off-axis radial SAXS intensity from a two-point pattern into a four-point pattern, as observed in annealed ABPBO and PBO fibres (but not in annealed PBT fibres).

Experimental observations of the distinct SAXS intensity were reported for oriented polyethylene[19] and polyurethane–urea elastomer[20]. It was found that when these unidirectional semi-crystalline systems were elongated to 200%, the off-axis radial four-point SAXS pattern emerged. There are two distinctions in comparison with the SAXS results for ABPBO and PBO fibres. Because the heteroaromatic polymers were spun from a nematic liquid-crystalline dope, the three-dimensional crystallinity is generally low for ABPBO fibres, even less for PBO fibres, and missing for PBT fibres, as revealed by the presence or the absence of off-axis reflections from X-ray diffraction. In addition to the absence of significant crystalline phases, the tensile elongation applied to annealed ABPBO and PBO (PBT) fibres was about 1.5%, which is smaller by a factor of 132 than that applied to the oriented polyethylene[19] and polyurethane–urea[20] systems. This distinguishes the SAXS four-point pattern of the ABPBO and PBO fibres: it arose not through high tensile deformation but by thermal annealing.

Thermal annealing generally enhances the crystallinity of materials. For semi-crystalline polymers, thermal annealing is known to raise the crystallinity through increases in lamellar thickness and area size. For heteroaromatic polymers, such as ABPBO and PBO, the as-spun fibres generally have low crystallinity. However, enhancement of the crystallinity of these fibres through thermal annealing was revealed by X-ray diffraction. Selected-area electron diffraction was applied to estimate the crystallite size for two sets of as-spun and heat-treated ABPBO and PBO fibres. The electron microscopic sampling results are listed in *Table 2*, which quantitatively confirms that (1) the crystallites are small and (2) the crystallinity can be enhanced by thermal annealing; the decrease in crystallite axial/trans. ratio suggests that a plate-like crystalline phase indeed developed in annealed ABPBO and PBO fibres. This agrees with the result of

Table 2 Fibre crystallite size determined by selected-area electron diffraction

	Range (nm)		Median (nm)		Mean (nm)		
	Axial	Trans.	Axial	Trans.	Axial	Trans.	Axial/trans. ratio
ABPBO							
61683 N1[a]	1.5–2.0	1.5–2.5	1.6	1.6	1.6	1.6	1.00
61683NHT2[b]	1.0–5.0	1.0–7.5	2.5	3.0	2.3	3.3	0.70
31883 ASC[a]	1.0–5.5	1.0–6.0	2.0	2.5	2.2	2.7	0.81
31883NHTC[b]	2.0–9.5	2.0–9.5	4.0	5.5	4.0	5.4	0.74
PBO							
42083 N1[a]	2.0–5.0	1.5–7.0	3.0	3.5	2.9	3.3	0.88
42083NHT1[b]	2.5–9.5	3.0–19	4.0	7.5	4.3	7.8	0.55
41983 N2[a]	2.5–9.5	1.5–13	5.5	5.0	5.2	5.4	0.96
41983NHT2[b]	2.5–17	4.0–24	4.5	9.0	5.7	10.6	0.54

[a] As-spun
[b] Heat-treated

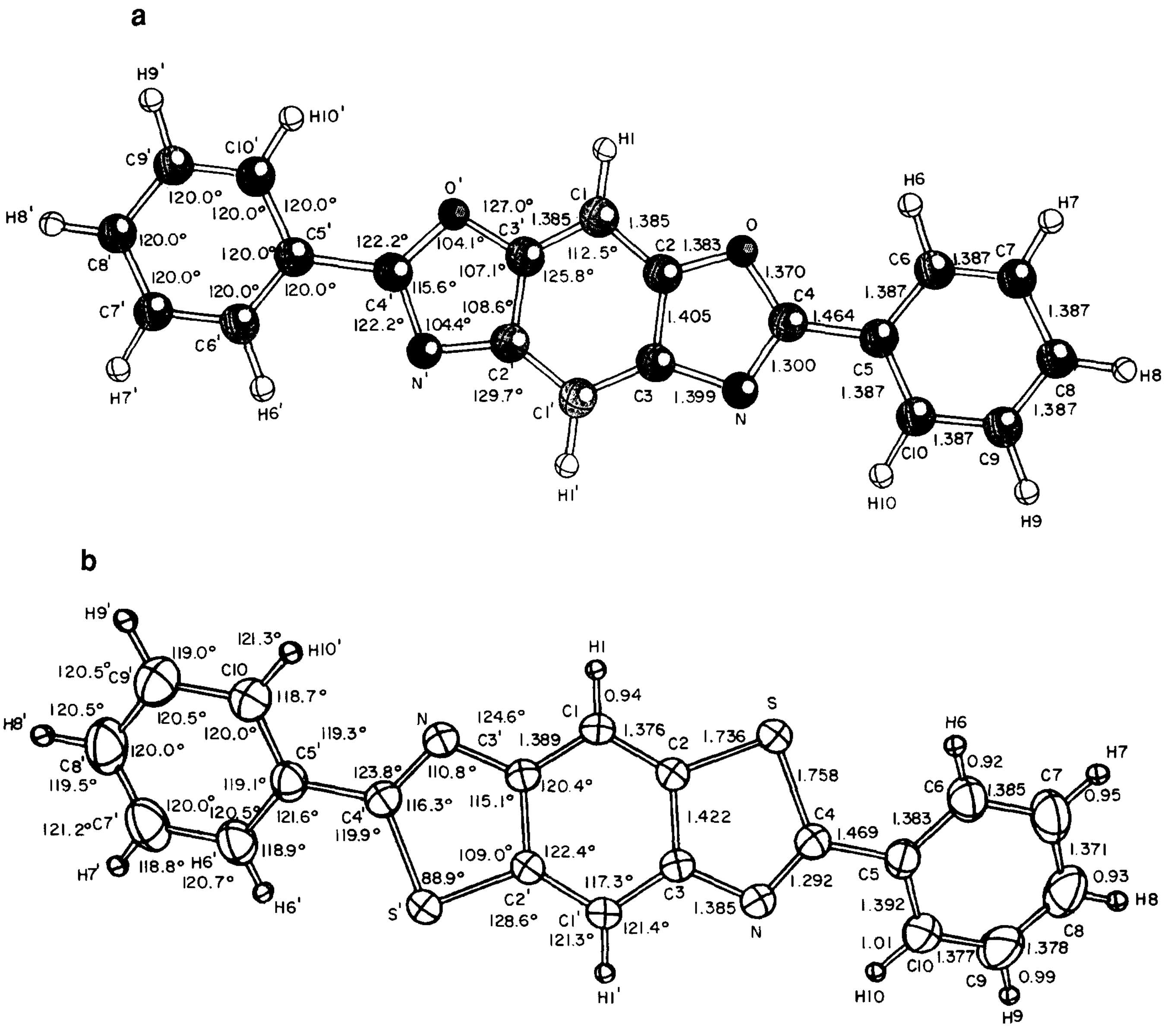

Figure 9 Backbone structures of (a) benzobisoxazole, (b) benzobisthiazole (derived from refs. 21 and 13 respectively)

numerical simulations[16–19] indicating that for a unidirectional polymeric system a plate-like ordered phase would show an off-axis radial four-point SAXS intensity pattern.

The absence of the off-axis radial four-point SAXS pattern for thermally annealed PBT is intriguing. One of the plausible reasons may be the difference in the backbone of PBO and PBT molecules. As illustrated in *Figure 9*, the PBO backbone is known to be colinear, and its heteroaromatic and phenylene moieties are coplanar[21]. However, the PBT backbone is not colinear (the neighbouring repeat unit shifts about 0.06 nm). In addition, there is a 30° torsion-angle offset between its neighbouring heteroaromatic and phenylene moieties[13]. Upon annealing, the colinear and coplanar PBO molecules are expected to have less steric hindrance and be more mobile than the PBT molecules to adjust themselves into a crystalline phase. This could account not only for the absence of the radial four-point SAXS pattern but also for the absence of a three-dimensional crystalline phase in annealed PBT (or ABPBI–PBT–ABPBI) fibres.

Finally, some general observations should be made. The correlation with mechanical properties is less certain, since both PBO and PBT fibres have the same degree of improvement of tensile properties upon annealing, but only annealed PBO fibres have the distinct SAXS pattern. Even though this report only focused on heteroaromatic polymers of coil-like and rod-like molecules, in addition to oriented polyethylene and polyurethane–urea copolymer, we have also seen the radial four-point SAXS pattern for polyester fibres. The convention in attributing forward SAXS intensity to elongated voids in fibres also needs to be examined more closely. Scattering from the fibrillar structure of the fibres is also expected to contribute to the forward SAXS intensity.

CONCLUSIONS

Thermal annealing of fibres of the heteroaromatic oxazole polymers ABPBO and PBO induces a unique off-axis radial four-point SAXS pattern. The off-axis angle is independent of annealing temperature; it is 50° for ABPBO fibres and 63° for PBO fibres. This SAXS pattern is attributed to the formation upon annealing of plate-like crystallites which tilt towards the fibre axis. This agrees with numerical modelling of SAXS intensity for unidirectional semi-crystalline polymeric systems, and with ABPBO and PBO fibre crystallite sizes determined by selected-area electron diffraction. The absence of this distinct SAXS pattern for annealed PBT (or ABPBI–PBT–ABPBI) fibres is believed to be due to the PBT backbone, which is neither colinear nor coplanar, hindering molecular mobility for a crystalline phase upon annealing. A significant improvement in tensile modulus has been consistently realized for annealed heteroaromatic fibres, regardless of the existence of the off-axis radial four-point SAXS pattern.

ACKNOWLEDGEMENTS

The authors express deep appreciation for generous support from the Materials Laboratory, Wright Research and Development Center. The fibre tensile properties were measured by M. E. Hunsaker of the Materials Laboratory, and are adopted from the preceding article co-authored with her. The selected-area electron diffraction was performed by T. Haddock and S. J. Krause, Arizona State University. A. V. Fratini, University of Dayton, is also thanked for useful discussion on conformations of PBO and PBT molecules.

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