Structural analysis of an oriented liquid crystalline copolyester

Geoffrey R. Mitchell and Alan H. Windle
Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge CB2 2QZ, UK

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Wide angle X-ray scattering from an aligned sample of a random copolyester is presented, together with an analysis of the derived cylindrical distribution function. High local orientational correlation of chains is observed, although the global orientation is less marked. There is some evidence of lateral biaxiality, which is compared with that predicted for theoretical studies of liquid crystalline structures.

Keywords Liquid crystalline polymers; X-ray scattering; biaxial nematic; PET–PABA copolyester; cylindrical distribution function; oriented mesophase

INTRODUCTION

Random copolymers are currently being developed which exhibit microstructures similar to those seen in conventional low molecular weight liquid crystalline materials. Although such copolymers have been broadly characterized in terms of their optical and thermal properties[1–4], comparatively little work has hitherto been directed at an understanding of the local molecular organization. This paper reports initial results of structural investigations on one of these polymers: a 40/60 polyethylene terephthalate (PET) and *p*-acetoxybenzoic acid (PABA) copolymer[5].

Careful analysis of wide angle X-ray scattering (WAXS) can provide a detailed description of the local structure in polymeric systems, particularly over the range 1–50 Å. The analysis is facilitated if the sample is oriented, for the scattering can then be resolved into those features which intensify along the draw direction, (on the meridian), and hence arise from correlations within chains, and those which intensify normal to the draw direction (on the equator) which are a consequence of chain packing. This partitioning is the cornerstone of the X-ray analysis of crystalline fibres and it has also been exploited for non-crystalline polymers[6]. High degrees of preferred molecular orientation can be readily produced in the material under investigation which is thus particularly suitable for WAXS analysis.

SAMPLE

The material used in this study was prepared by Eastman Kodak Company[5] from 40 mol % PET and 60 mol % PABA, which produced a copolymer consisting of the segments shown in *Scheme 1*. Jackson and Kuhfuss[5] indicate on the basis of n.m.r. investigations, that these segments are arranged randomly along the chain. They classified the material as liquid crystalline on the basis of (a) lack of sharp WAXS peaks, (b) no melting endotherm, (c) the turbid nature of the 'melt' above 275°C coupled with a low viscosity in this temperature range.

The stereochemical geometry of the ester linkages ensures that any bond rotation while perhaps rendering the phenyl groups non coplanar will not affect the trajectory of the molecule. This particular copolyester contains CH_2 linkages which could be considered 'flexible links'. However a consideration of the conformations sterically viable, indicate that although the $-O-CH_2-CH_2-O-$ sequence is very flexible its restricted length means that it permits the chain to do no more than hinge every 20–30 Å. Furthermore it is unlikely that these flexible segments occurring randomly within the chain are sufficiently long to provoke segregation of the aromatic and aliphatic segments, a feature common in many low molecular weight liquid crystalline compounds.

The material does not crystallize on cooling, and optical textures observed at room temperature on quenching are characteristic of those seen at room temperature by hot stage microscopy[4,7]. All X-ray measurements have been made at room temperature using melt extruded pellets of the copolyester which exhibit a marked degree of axial alignment.

X-RAY ANALYSIS

Quantitative X-ray intensity measurements on liquid crystalline polymers are few[8]. Wang and Yeh[9] have calculated a radial distribution function from X-ray scattering data for a nominally isotropic sample of the same copolyester as used in this investigation. They concluded that the material shows lateral order of up to 60 Å.

Good intensity data are a prerequisite to any study which involves structural analysis. For this investigation we utilised a similar experimental and data reduction procedure to that recently developed for aligned non-crystalline polymers[10,11]. The WAXS was measured using a symmetrical transmission diffractometer equipped with an incident beam graphite monochromator, pinhole collimation, stepscan facilities and an Eulerian cradle which enabled the sample to be rotated in a plane normal to the plane containing both

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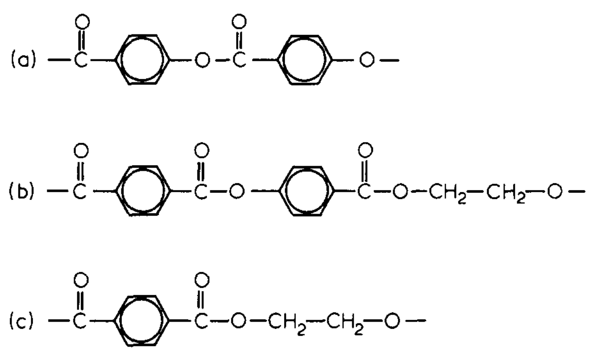

Scheme 1 Molecular segments of the random copolyester 60 mol % PABA 40 mol % PET[5]

incident and scattered beams. Using CuKα radiation, the intensity was measured as a function of both 2θ and α, where α is the angle measured away from the normal to the plane containing the incident and scattered beams (i.e. $\alpha=0$ meridian, $\alpha=\pi/2$ equator). The data were collected at intervals of 1° in 2θ corresponding to a range of s of 0.2–6.2 Å^{-1} ($s=4\pi\sin\theta/\lambda$) and 9° in α. (To provide a check on peak positions and width scans were made for $\alpha=0$, and $\pi/2$ at intervals of 0.2° 2θ.) The data were smoothed and interpolated onto an equal interval grid with $s=0.05$ Å^{-1} and $\alpha=\pi/80$ radians, and were corrected for absorption[12], polarization[13] and multiple scattering[14]. The corrected data were then normalized to electron units using a modified form of the Krogh Moe method[11,15].

The data in the form of an s-weighted reduced intensity function $si(s,\alpha)$ is shown in *Figure 1a*. There are two main features: a peak on the equator at $s=1.4$ Å^{-1} which extends almost parallel to the meridian, and a peak on the meridian at $s=3.0$ Å^{-1} which is slightly arced. In *Figure 1b* meridional and equatorial sections are shown through the intensity surface of *Figure 1a*. The meridional section shows clearly another peak at $s=2.0$ Å^{-1}, while the equatorial section indicates that the main peak at $s=1.4$ Å^{-1} consists of 2 components. There is apparently a sharper component at $s=1.4$ Å^{-1} and a broader component at the higher scattering vector of $s=1.7$ Å^{-1}. There is also a somewhat weaker equatorial peak at $s=3.7$ Å^{-1}.

The immediate conclusion which may be drawn from this pattern is that the material is well oriented, while the lack of lateral sampling of the meridional peak suggests that there is no longitudinal (as opposed to orientational) correlation of adjacent chains.

The width at half height (Δs) of the meridional reflections can, by using the expression $l=2\pi/\Delta s$[16] give an indication of the lower limit to the length (l) of coherent periodicity in the extension direction. This length is of the order 40–50 Å. However, the breadth of the equatorial is comparable, for example, with that of the interchain peak in the scattering from an isotropic melt of polyethylene[17].

A cylindrical distribution function (*CDF*) is the real space distribution of the self convolution of the variation of the electron density from its mean value. It is expressed in terms of cylindrical coordinates (in this case spherical-polar) and is generated by transformation of the intensity function $si(s,\alpha)$. A *CDF* calculated from the intensity data of *Figure 1a* and using the procedure described elsewhere[10] is shown in *Figure 2a*. The general appearance of the *CDF* is similar to that expected for the packing of rods. It is evident that the correlation along a given chain is greater than that between adjacent chains. There are inter-chain peaks on the equator at 4.5, 9.5, 14, 18 ... Å. They are elongated by about ±8 Å in the meridional direction which together with the extent of the lateral order indicates a high degree of *local* chain alignment. The regularity along the meridional axis is clearly shown. The arcing of the meridional peaks is mainly due to the range of chain orientations present in the specimen as a whole. The fact that it is more pronounced than the arcing of the equatorial maxima is significant. It suggests that there are regions of the specimen which are better ordered laterally and are responsible for the persistent equatorial correlation extending beyond 20 Å and that in these regions the chains are rather better aligned with the extrusion axis than in the specimen as a whole.

It is general practice to utilize the azimuthal distribution of the intensity of the equatorial peak in order to obtain a measure of the orientation distribution function[18,19]. A uniaxial distribution function can be conveniently expressed as a series of Legendre polynomials P_{2n} ($\langle\cos\alpha\rangle$). It is possible to obtain values for all components in the series using the method recently described[18]. The more significant terms are given in *Table 1*. The function, $D(\alpha)$, calculated using a series of 14 terms is shown in *Figure 3*. It is a density function which takes account of the lower probability, even in an isotropic sample, of orientations close to $\alpha=0$ compared to those

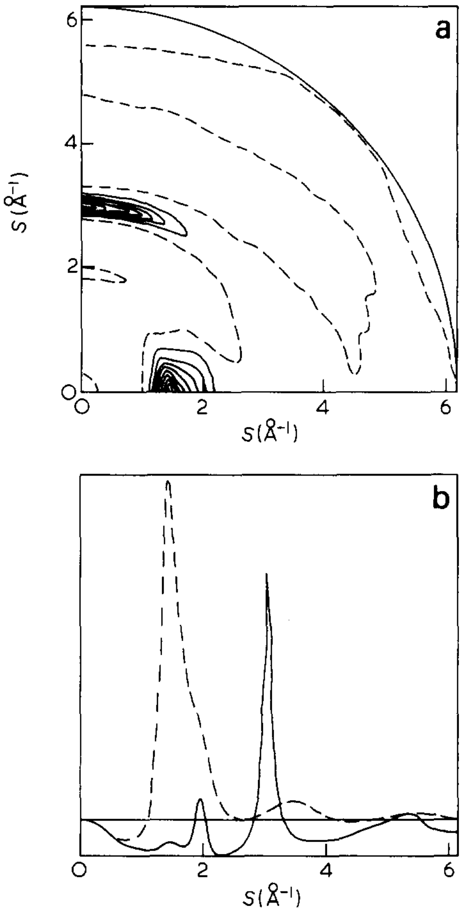

Figure 1 (a) Experimental s weighted reduced intensity function $si(s,\alpha)$ for a melt extruded pellet of random copolyester (40 mol % PET 60 mol % PABA) measured at room temperature. Broken contours are negative. (b) Meridional (——) and equatorial (– – –) sections of the intensity function $si(s,\alpha)$ shown in *Figure 1a*

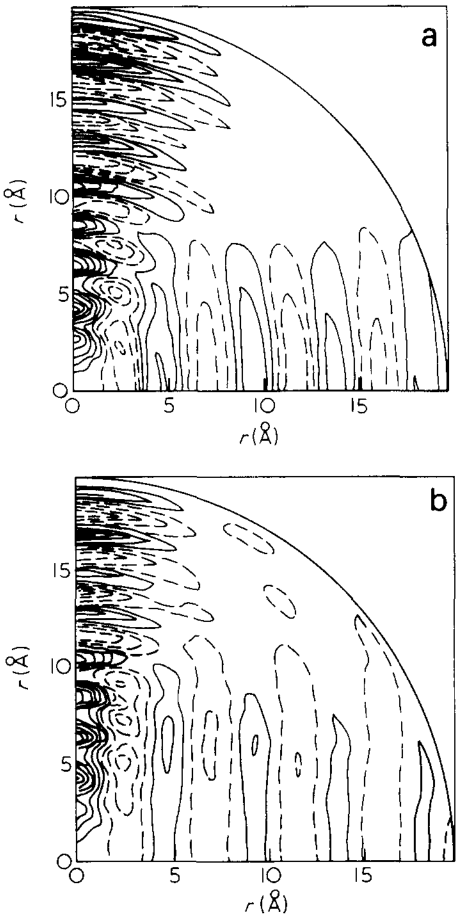

Figure 2 (a) Cylindrical distribution function derived from the experimental intensity function $si(s,\alpha)$ shown in *Figure 1a*.
(b) The cylindrical distribution function resulting from the numerical deconvolution of *Figure 2a* to remove the effect of global molecular misalignment

approaching $\alpha = \pi/2$. By weighting $D(\alpha)$ with $\sin\alpha$ the number distribution function, $N(\alpha)$, is obtained, and this is also shown in *Figure 3*. It is clear that despite the degree of chain orientational correlation apparent in the *CDF*, the overall orientation is far from perfect.

It has been shown[10,20,21] that if the *CDF* is expressed in spherical polar coordinates, the apparent alignment in the *CDF* may be improved by deconvoluting the *CDF* with the effective orientation distribution function. The results of this technique are shown in *Figure 2b*. It is readily apparent that the arcing of the meridional peaks is considerably reduced but not eliminated. The interchain peaks are elongated in the meridian direction extending to ±10 Å, and all vestiges of arcing have been removed.

Comparison of the meridional spacings in the *CDF* with those of model chains, together with a consideration of the scattered intensity distribution along the meridian suggests that the distribution of the chemical components of the copolymer is random. There is no indication of substantial segregation of the chain segments.

FURTHER DISCUSSION

The wide angle X-ray scattering and the resulting *CDF*'s show that the molecules of the copolymer pellet are aligned towards the extrusion axis. There are significant levels of lateral and interchain order. In general the level of order is similar to that seen in small molecule nematic structures[22]. However, a closer study of these data leads to additional qualifications. As discussed above, the *CDF* reveals the high level of local orientational correlation which is present, at least in some regions of the specimen, despite a lower level of orientation in the pellet as a whole. Furthermore there is evidence of some degree of longitudinal correlation (register) between neighbouring molecules, for example the vertically elongated equatorial peaks show maxima at a meridional displacement of about ±6 Å in the numerically deconvoluted presentation (*Figure 2b*).

In the scattering pattern (*Figure 1a*), the equatorial peak appears to have two components: a sharp one at $s = 1.4$ Å^{-1} and a broader one at $s = 1.7$ Å^{-1} with evidence of a corresponding second order maximum at $s = 3.4$ Å^{-1}. It is possible that the duplex nature of the main equatorial peak indicates some measure of biaxial packing which involves rotational correlation between adjacent chains. If such correlation is pronounced and extensive, then it may be realistic to think of the structure as stacked sheets, each made up of aligned oriented molecules, which are able to slip over each other during deformation or elevated temperature flow. In a first attempt to test this possibility, an aligned pellet was extensively compressed ($\lambda = 4$) normal to the prevailing molecular axis. X-ray diffraction of the deformed pellet with the beam parallel to the original molecular axis showed only very limited orientation. It was manifest as a slight ovality of the equatorial ring, perhaps sufficient to support the view that the two components of the peak arise from the disparate axes of the molecular cross section but not sufficient to suggest the presence of long range rotational correlation

Table 1 Values for the principal coefficients of the series of Legendre polynomials representing the orientation distribution function derived from the equatorial peak in the WAXS for the copolyester segment

n	$\langle P_{2n}(\cos\alpha)\rangle$
1	0.58
2	0.37
3	0.22

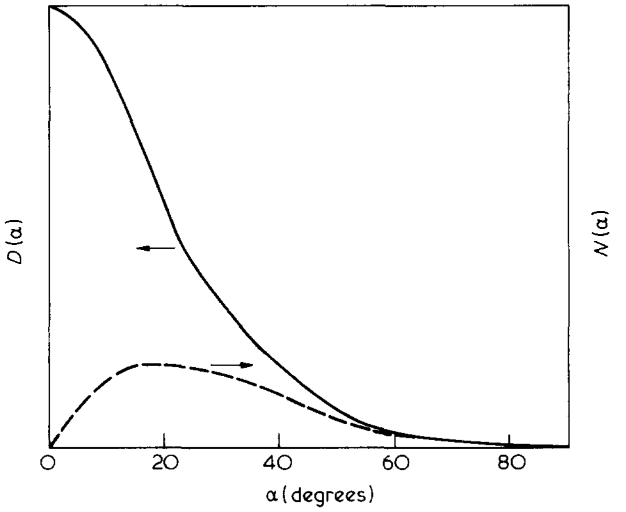

Figure 3 Experimentally derived molecular orientation distribution function $D(\alpha)$ (——) and $N(\alpha)$ (– – –) where $N(\alpha)\sin\alpha$, for the melt extruded copolyester pellet

which is preserved during deformation. Furthermore, the implication of such rotation correlation that all the backbone phenyl groups are planar, is incompatible with the sterically viable chain conformations in the 60/40 copolyester examined. Phenyl groups which are linked by an ester group are sterically prevented from coplanar orientation. The potential lath-like nature of the molecule will therefore be opposed at ester linkages, and either the perfection or the range (or both) of any biaxial rotational correlations will be correspondingly limited.

If a level of biaxial order does exist in this liquid crystal polymer, then the question of classification arises. It is well established [for example see refs 23, 24] that highly anisotropic molecules (generally length/breadth >6) will at critical temperatures or concentration levels form nematic type structures. At lower temperatures other mesomorphic structures, for example, smectic A and C, have been observed for low molecular weight liquid crystalline material. In general nematogens are composed of aromatic groups (which are definitely not cylindrical), and it has been proposed[25] and evaluated theoretically that an additional biaxial nematic phase should be seen[25–30]. For small molecule materials, any biaxial packing will almost certainly be accompanied by longitudinal correlation, and thence crystallization. Random copolymerization discourages longitudinal register and thus makes it more likely that a non-crystalline biaxial nematic phase can occur.

The implications within the context of aligned liquid crystalline polymers of a nematic phase with some level of biaxiality have still to be worked out, and it is not yet clear what detailed relationship such a structure would have to the observed optical textures. However it is probable that rotational correlation would only persist in a limited temperature range, above which the structure reverts to nematic.

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