Thermotropic polyesters: orientation of poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) fibres

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Orientation of poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate) (50/50 and 67/33) fibres spun from the nematic mesophase is investigated by wide-angle X-ray scattering. Computer-generated sets of model chains and their two-dimensional Fourier transforms are used to interpret the experimental results. It is found that the orientation parameters evaluated from the azimuthal spread of the diffuse equatorial scatter, assigned to the paracrystalline structure in the 'as-made' and heat-treated fibres, underestimate significantly the alignment of chains along the fibre axis.

(Keywords: aromatic polyesters; thermotropic; liquid-crystalline; X-ray diffraction; orientation; chain modelling)

INTRODUCTION

Poly(*p*-oxybenzoate-*co*-*p*-phenylene isophthalate)s (POPI) consist of rod-like *p*-oxybenzoyl (OPCO) and *p*-phenylenedioxy (OPO) units, and of angular isophthaloyl (COMCO) units. Compositions between 50/50 (i.e. [OPCO] = [OPO] = [COMCO] = 0.333) and 67/33 (i.e. [OPCO] = 0.50 and [OPO] = [COMCO] = 0.25) are thermotropic nematogenic materials with a sufficient nematic temperature interval for melt processing[1].

Melt-spun fibres produced from these copolymers lack three-dimensional crystalline order[2]. Features of the equatorial wide-angle X-ray diffraction scattering (WAXS) suggest that the 'as-made' fibres consist of a paracrystalline array of chain molecules aligned along the fibre axis[2]. This was confirmed by analysis of meridional WAXS of these fibres; the observed diffraction traces were in good agreement with one-dimensional Fourier transforms generated from atomic models of extended chains containing *trans* conformations of OPO and OPCO units[3].

Heat treatment of the 'as-made' fibres results in crystallization[2]. The crystalline regions consist of *p*-phenylene isophthalate sequences; they contain about 200 laterally packed chains[2], but their mean apparent thickness is only about 4 nm in the 50/50 fibres and about 2 nm in the 67/33 fibres[3]. Crystallization does not affect significantly the WAXS features assigned to the paracrystalline structure present in the 'as-made' fibres. The structure of heat-treated fibres is therefore regarded as a mosaic of thin crystallites in a paracrystalline matrix[2,3].

The distribution of chain orientation is an extremely important feature of fibres and other shaped articles produced from thermotropic polymers. In the absence of chain folding, it determines, together with chain stiffness and intermolecular shear modulus, the mechanical properties of the shaped articles[4,5]. As shown by Mitchell and Windle[6], quantitative evaluation of orientation parameters for these materials is not a simple task. In particular, these authors pointed out the difficulties in relating the orientation parameters obtained from the azimuthal distribution of the equatorial WAXS to the chain orientation.

This paper is concerned with chain orientation in POPI fibres. Atomic chain models[3] are used for the interpretation of the observed WAXS features.

EXPERIMENTAL

The 'as-made' and heat-treated (30 min at 280°C) fibres prepared from 50/50 and 67/33 copolymers were the same as those used previously[2,3].

Wide-angle X-ray diffraction patterns of fibres were taken with a flat-plate camera.

The optical density of the X-ray diffraction patterns was recorded by means of an image analysis system comprising a video camera (Cohu), interfaced with a personal computer (PC) and a framestore together with software (Semper). The data are stored as an array with typical dimensions for an entire pattern being 512 × 512 pixels, with a grey-level intensity range of 0–255 units. The intensity data are normally converted to an integer format in the form of blocks of data before transfer to the University of Leeds Amdahl mainframe computer. Once the data are transferred, the blocks of data are converted to an array within a program called Raster. The output options for this program were described previously[3]. Data obtained in this way were used for the evaluation of the azimuthal spread of meridional reflections of fibres tilted by 20° from the position perpendicular to the X-ray beam and for the evaluation of the effect of the 2θ position on the azimuthal spread of the equatorial scatter.

The azimuthal intensity profiles $I(\alpha)$ of the equatorial scatter were obtained using a modified Hilger and Watts Y115 diffractometer mounted on a Hiltonbrook DG2

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constant-output generator utilizing Cu K_α radiation. Note that an azimuthal angle of $\alpha = 90°$ corresponds to the equator[6]. For the diffractometer scan, the counter arm was set at a 2θ position corresponding to the maximum of the equatorial scatter (around 20°). The azimuthal intensity $I(\alpha)$ was recorded at 0.2° intervals while the sample was rotated in a vertical plane. Data were corrected for the azimuthal broadening according to Ruland's method[7], using the width of the meridional reflection with a d-spacing of 0.3 nm as a circular broadening function parameter. Using the fibre axis as the reference direction, the orientation parameters $\langle P_2 \rangle$ (i.e. Hermans orientation function, which, in liquid-crystal characterization, is commonly referred to as the order parameter) and $\langle P_4 \rangle$ were evaluated from corrected $I(\alpha)$ data following the procedure described by Mitchell and Windle[6].

The optical birefringence of 50/50 fibres was measured by Erdemir[8] using a Pluta polarizing interference microscope with a Wollaston compensator[9].

CHAIN MODELLING

The procedure for generating atomic models of POPI copolymer chains was described previously[3]. Owing to the complications arising from the presence of angular COMCO units, the modelling has been limited to planar models constructed from *trans* and *cis* conformations of OPCO and OPO units together with the conformation of COMCO units that maximizes the chain extension (see figure 1 in ref. 3). While fully *trans* conformation copolymer chains were feasible, fully *cis* chains were highly non-linear and had to be 'straightened' with *trans* units adjacent to COMCO units; the resulting models were termed '*cis*-based'. From considerations of interactions between the carbonyl oxygen atoms of ester groups and hydrogen atoms of aromatic rings, it follows that such entirely planar conformations are unrealistic[10–13]. In the case of POPI chains it is possible to remove this difficulty by out-of-plane rotation of p-phenylene groups. The required torsion angle is approximately 55°. In the resulting 'quasiplanar' conformations, the m-phenylene groups, ester groups and the virtual bonds representing the p-phenylene groups remain confined to a plane[13]. The chain contours are therefore not affected by the change from a planar to the corresponding 'quasiplanar' conformation. Similarly, this change does not affect the one-dimensional Fourier transforms.

Although one-dimensional Fourier transforms have been computed using the atomic coordinates of model chains[3], the two-dimensional Fourier transforms were obtained more easily from images of sets of chains using the appropriate Semper software.

RESULTS AND DISCUSSION

The observed[2,3] WAXS features assigned to the paracrystalline structure of the 'as-made' fibres and the heat-treated fibres are summarized in *Table 1*. The d-spacings of equatorial peaks PA1 and PA2, associated with intermolecular correlations[6], were obtained by resolution of the equatorial diffractometer traces[2].

The meridional reflections PM1, PM2 and PM3 (which is asymmetrical, and is therefore resolved into two peaks) are related to intramolecular correlations[6]. These reflections are therefore, in principle, most suitable for a quantitative determination of the chain orientation. Unfortunately, the reflection PM1 observed with fibres perpendicular to the X-ray beam is too weak for a reliable measurement of $I(\alpha)$. Reflections PM2 and PM3 do not intercept the sphere of reflections when the fibres are untilted; this itself indicates a high degree of chain orientation. Even with fibres tilted by 20° from the direction perpendicular to the X-ray beam, the azimuthal widths at half-height (w_a) obtained from these reflections do not exceed 8°. Bearing in mind the azimuthal broadening due to the tilt, this means that the chain alignment along the fibre axis must be almost perfect. This conclusion is in agreement with the chain modelling results[3], which showed that the d-spacings of meridional reflections obtained from one-dimensional Fourier transforms of extended-chain models containing *trans* conformations of OPCO and OPO units were in good agreement with the observed d-spacings (*Table 1*). It should be noted that the model chains were repositioned in such a way that the first and last skeletal oxygen atoms were located on the axes used for the Fourier transform, i.e. the model chains were, by definition, perfectly aligned (*Figure 1*).

Evaluation of the azimuthal spread of the equatorial scatter from WAXS patterns showed that within the 2θ range between 19 and 25° (corresponding to d-spacings between 0.46 and 0.36 nm) the w_a values obtained for the 'as-made' fibres remained constant. However, they were considerably larger than expected from the results obtained with the meridional reflections. The $I(\alpha)$ profiles were obtained with the diffractometer at 2θ positions corresponding to the maxima of the equatorial scatter. Their resolution[14] showed that they can be represented by a combination of Gaussian function G_t and Cauchy function C_t, namely $f_t G_t + (1 - f_t) C_t$; the profile function parameters f_t are given in *Table 2*.

Values of the orientation parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ obtained from these $I(\alpha)$ profiles are also listed in *Table 2*. For the 'as-made' fibres a decrease in concentration of the angular disruptor units from [COMCO] = 0.33 in 50/50 composition to 0.25 in 67/33 composition results in a small but probably significant increase of orientation parameters.

Heat treatment causes crystallization (crystallinity of about 17% in 50/50 fibres and 11% in 67/33 fibres[2]). Reflections assigned to the crystalline structure are short vertical streaks rather than arcs[2]; this vertical broadening is due to the small dimensions of the crystallites in the

Table 1 WAXS features assigned to paracrystalline structure in 'as-made' (AM) and heat-treated (HT) fibres: d-spacings (nm); calculated values for meridional reflections were obtained with extended *trans* models[3]

	50/50			67/33		
Feature	AM	HT	Calc.	AM	HT	Calc.
Equatorial						
PA1	0.458	0.448	–	0.444	0.445	–
PA2	0.364	0.355	–	0.371	0.356	–
Meridional						
PM1	0.608	0.609	0.613	0.611	0.612	0.614
PM2	0.301	0.302	0.307	0.307	0.305	0.309
PM3	0.207 0.201	0.209 0.202	0.218 0.205	0.205 0.204	0.205 0.204	0.216 0.206

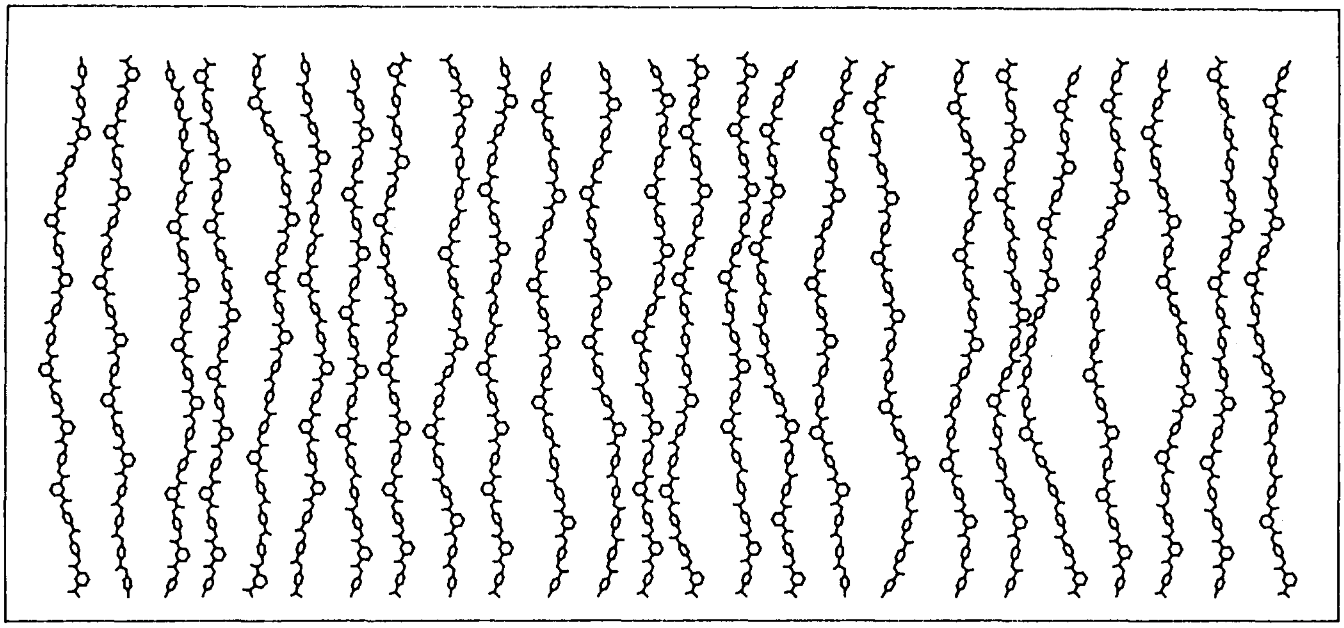

Figure 1 Set of aligned computer-generated chains (50/50 composition, $n=18$, *trans* quasiplanar conformation)

Table 2 Orientation parameters of 'as-made' (AM) and heat-treated (HT) fibres obtained from equatorial scatter at $2\theta \simeq 20°$; f_t is the azimuthal profile function parameter, w_a is the corrected azimuthal width at half-height

	50/50		67/33	
	AM	HT	AM	HT
f_t	0.65	0.67	0.62	0.60
w_a (deg)	23.00	22.40	18.70	18.20
$\langle P_2 \rangle$	0.84	0.85	0.87	0.87
$\langle P_4 \rangle$	0.64	0.66	0.71	0.71

chain direction. Although this precluded a quantitative evaluation of the orientation parameters, it is clear that in both heat-treated fibres the crystallites are highly aligned along the fibre axes. Erdemir[8] found that the optical birefringence of the 50/50 fibres (0.336 ± 0.006) is not affected by the heat treatment. The orientation parameters found for the paracrystalline matrix of the heat-treated fibres do not differ significantly from those obtained for the corresponding 'as-made' fibres (*Table 2*).

The analysis of WAXS showed that the orientation parameters evaluated from the equatorial scatter assigned to the paracrystalline structure underestimate substantially the chain orientation. For a fibre consisting of long, entirely rigid rod-like molecules aligned along the fibre axis, the results obtained from meridional and equatorial WAXS should be in agreement. The chain modelling[3] of POPI copolymers clearly showed that the presence of COMCO angular disruptor units results in a considerable departure from the rod-like character of the molecules. Even if the chain axes are perfectly aligned, the constituent rod-like segments of unequal lengths, joined by the angular units, deviate noticeably from the chain direction. This is illustrated in *Figure 1*, which shows a planar projection of a set of aligned extended 'quasiplanar' chains (*trans* conformation) representing the 50/50 copolymer. Note that the separation of chains has been increased to 1 nm to avoid chain overlap. The two-dimensional Fourier transform of a corresponding larger set of chains shows a sharp meridional reflection due to intrachain correlation. In contrast, the equatorial scatter, arising mainly from the intermolecular correlations between the constituent rod-like segments, is diffuse and shows a considerable azimuthal spread (*Figure 2*). Although the use of a two-dimensional Fourier transform of 'quasiplanar' chains is inevitably an oversimplification, it is clear that it yields features that are qualitatively in accordance with the observed WAXS patterns of POPI fibres (*Figure 2*). This simple approach thus corroborates the conclusion that the orientation parameters evaluated from equatorial WAXS of copolymers containing angular disruptor units do not measure the axial alignment of the chains.

The deviations of copolymer chains from a rigid-rod-like character undoubtedly contribute to the discrepancy between the chain orientation and orientation parameters evaluated from the equatorial scatter. In an attempt to quantify this feature of copolymer chains we used the simple 'quasiplanar' models. Each model chain, consisting of n units, is viewed as a set of m rod-like segments joined together at each end by the m-phenylene group of a COMCO unit (*Figure 3*). Its deviation from rod-like character is then expressed in terms of orientation parameters $\langle P_2 \rangle_c$ and $\langle P_4 \rangle_c$ of the constituent segments with respect to the chain axis (straight line joining the first and last skeletal oxygen atoms). For the evaluation of these parameters, each segment is represented by a vector connecting the centres of the consecutive m-phenylene groups. The angle ϕ_i between each vector and the chain axis is evaluated from atomic coordinates. In the calculation of the mean values of $\langle \cos^2 \phi \rangle_c$ and $\langle \cos^4 \phi \rangle_c$, these vectors are given weightings k_i according to the number of aromatic rings in the corresponding segments. Thus:

$$k_i = n_p + 1$$

where n_p is the total number of rod-like units (OPO and OPCO) in the segment, which also contains half of an

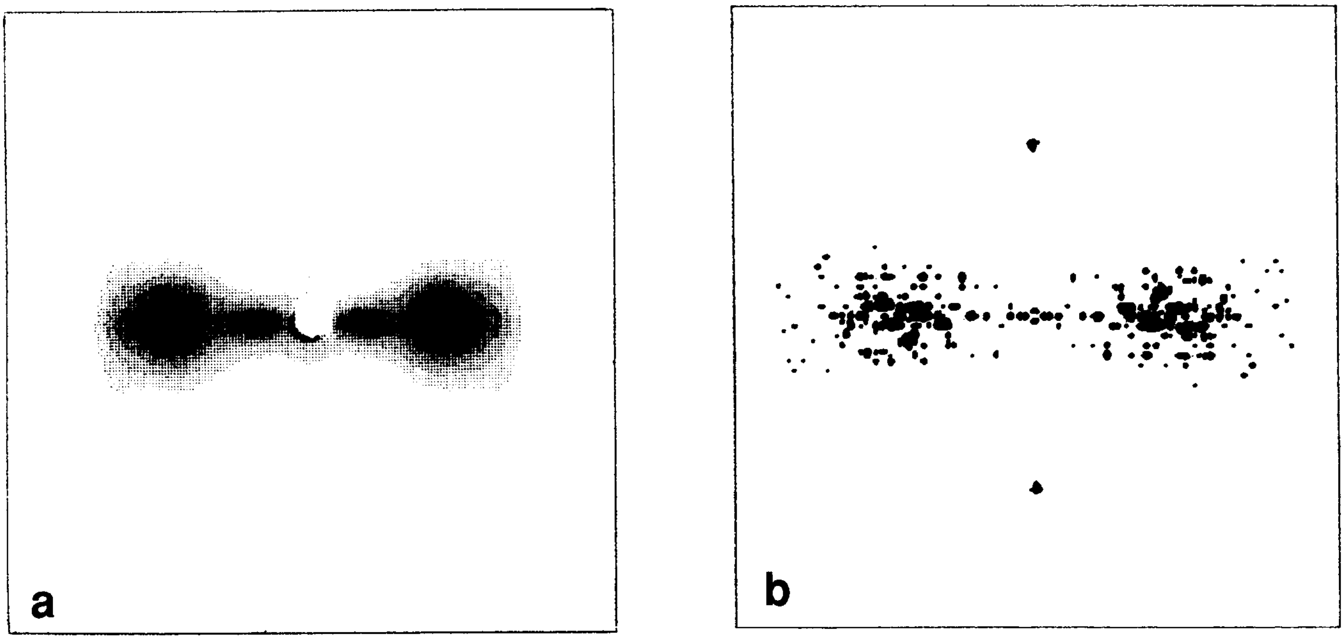

Figure 2 Grey-level representation of WAXS of a 50/50 'as-made' fibre (a) in comparison with a two-dimensional Fourier transform (b) of a corresponding set of aligned model chains; part of this set is shown in *Figure 1*. Fibre axis/chain axes are vertical

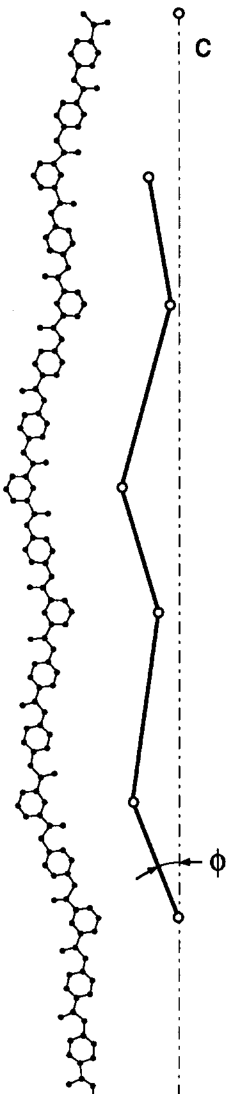

Figure 3 Representation of a model chain (50/50) composition, $n = 18$, *trans* planar conformation) by means of rod-like segments: ϕ is the angle between a segment and the chain axis c

Table 3 Deviations from rod-like character for 50/50 copolymer model chains expressed in terms of orientation parameters $\langle P_2 \rangle_s$ and $\langle P_4 \rangle_s$: mean values and standard deviations for sets of 50 chains; n is the number of constituent units per chain

	trans		*cis*-based	
n	$\langle P_2 \rangle_s$	$\langle P_4 \rangle_s$	$\langle P_2 \rangle_s$	$\langle P_4 \rangle_s$
12	0.910±0.027	0.724±0.078	0.842±0.069	0.540±0.170
14	0.904±0.024	0.709±0.066	0.834±0.042	0.519±0.104
16	0.909±0.024	0.727±0.068	0.840±0.040	0.538±0.095
18	0.900±0.020	0.702±0.047	0.836±0.033	0.523±0.080

angular COMCO unit at each end. Consequently:

$$\langle \cos^q \phi \rangle = \sum_{i=1}^{m} k_i \cos^q \phi_i \Big/ \sum_{i=1}^{m} k_i$$

where $q = 2$ or 4 and $\sum k_i$ is the total number of units between the first and the last *m*-phenylene groups of the chain. By definition:

$$\langle P_2 \rangle_c = (3\langle \cos^2 \phi \rangle_c - 1)/2$$

$$\langle P_4 \rangle_c = (35\langle \cos^4 \phi \rangle_c - 30\langle \mathrm{cs}^2 \phi \rangle_c + 3)/8$$

Finally, the $\langle P_2 \rangle_c$ and $\langle P_4 \rangle_c$ values are averaged for 50 chains to obtain $\langle P_2 \rangle_s$ and $\langle P_4 \rangle_s$.

Note that the mean number of aromatic rings per segment, $\bar{k}$, is equal to the reciprocal value of the concentration of angular units, [COMCO]. Thus, for 50/50 copolymer $\bar{k} = 3$, increasing to $\bar{k} = 4$ for 67/33 copolymer.

Although the investigation of the meridional WAXS showed that extended *trans* conformations are preferred[3], the orientation parameters were also evaluated for the less extended '*cis*-based' models. In this way we obtain the upper and lower limits of deviations from rod-like character for possible non-planar models.

Results obtained for sets of chains representing the 50/50 copolymer are given in *Table 3*. An increase in total number of units per chain from $n = 12$ to $n = 18$ does not affect significantly the $\langle P_2 \rangle_s$ and $\langle P_4 \rangle_s$ values but reduces the variability within each set. The cumulative frequency curves for orientation parameters of *trans* models containing 16 units (i.e. the number corresponding to the correlation length estimated from the radial broadening of meridional WAXS reflections[3]) are shown in *Figure 4*. As expected, the '*cis*-based' models give lower $\langle P_2\rangle_s$ and $\langle P_4\rangle_s$ values compared with the *trans* models. The differences arising from the choice of conformation are highly significant.

Results for 67/33 copolymer chains ($n=16$, 20, 24), shown in *Table 4*, are similar. Note that in this case the correlation length estimated from meridional WAXS corresponds to $n=19$ (see ref. 3). Comparison of the results for the two copolymers shows that a decrease of concentration of angular COMCO units from 0.333 (50/50) to 0.25 (67/33) results actually in decreases in the orientation parameters calculated for the '*cis*-based' models; the differences for $n=16$ are highly significant (0.1% level). For the *trans* models the orientation parameters increased slightly with decreasing concentration of angular units but the differences for $n=16$ are not significant. However, by increasing the number of chains by pooling the data obtained for different chain lengths (using the appropriate weighting), it is found that the differences (*Table 5*) become significant (2% level). *Table 5* also includes data for regular alternating copolymer containing *trans* conformations, for which the differences due to the concentration of angular units are increased. *Figure 5* shows that for regular alternating copolymers (–COMCO–(OPCO)$_z$–OPO–(COPO)$_z$–), where $z=(k-2)/2$, the parameters $\langle P_2\rangle_s$ and $\langle P_4\rangle_s$ increase with increasing length of rod-like segment (i.e. with decreasing concentration of angular units). They approach unity at $k=8$, which corresponds to $[\text{COMCO}]=[\text{OPO}]=1/k=0.125$.

Comparison of orientation parameters evaluated from the equatorial scatter of fibres (*Table 2*) with those expressing the deviations of model chains from the rod-like character (*Table 5*) shows that the '*cis*-based' models underestimate the achieved level of orientation; this is particularly noticeable in the case of $\langle P_4\rangle$ values. Thus, in accordance with the previous results[3], '*cis*-based' models can be ruled out as unrealistic. In contrast, the *trans* models yield $\langle P_2\rangle_s$ and $\langle P_4\rangle_s$ values that exceed those obtained for fibres. While the introduction of non-planar chain conformations would result in lower

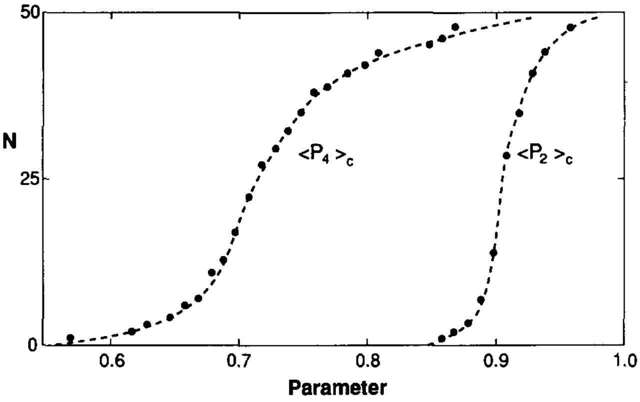

Figure 4 Cumulative frequency curves of $\langle P_2\rangle_c$ and $\langle P_4\rangle_c$ parameters for 50/50 copolymer, *trans* conformation model chains ($N=50$) with $n=16$ units per chain

Table 4 Deviations from rod-like character for 67/33 copolymer model chains expressed in terms of orientation parameters $\langle P_2\rangle_s$ and $\langle P_4\rangle_s$: mean values and standard deviations for sets of 50 chains; n is the number of constituent units per chain

	trans		*cis*-based	
n	$\langle P_2\rangle_s$	$\langle P_4\rangle_s$	$\langle P_2\rangle_s$	$\langle P_4\rangle_s$
16	0.915±0.026	0.743±0.074	0.801±0.042	0.439±0.170
20	0.912±0.026	0.739±0.069	0.798±0.049	0.433±0.117
24	0.913±0.028	0.742±0.078	0.796±0.052	0.439±0.114

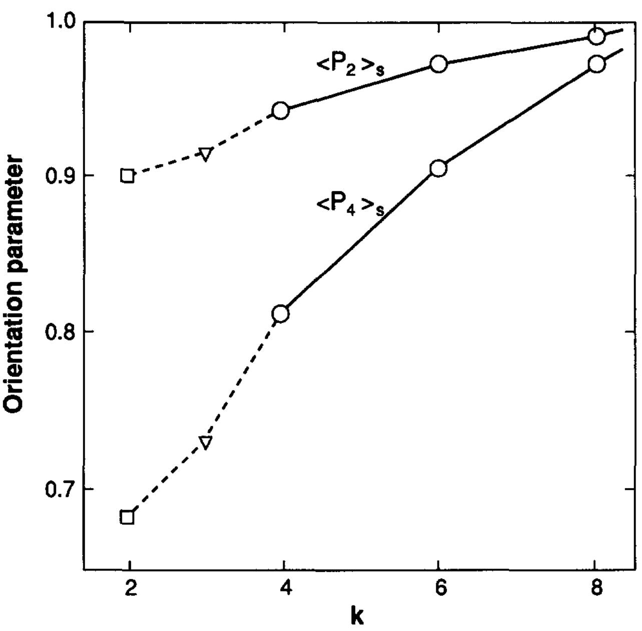

Figure 5 Effect of the number of units in the rod-like segment (k) on the deviation from the rod-like character of *trans* models, expressed in terms of orientation parameters $\langle P_2\rangle_s$ and $\langle P_4\rangle_s$: (□) poly(p-phenylene isophthalate), i.e. (–COMCO–OPO–); (▽) regular alternating copolymer (–COMCO–OPCO–OPO–); (○) regular alternating copolymers (–COMCO–(OPCO)$_z$–OPO–(COPO)$_z$–), where $z=(k-2)/2$

Table 5 Deviations from rod-like character for the specified models and compositions expressed in terms of orientation parameters $\langle P_2\rangle_s$ and $\langle P_4\rangle_s$: mean values and standard deviations for pooled data

	50/50		67/33	
Model	$\langle P_2\rangle_s$	$\langle P_4\rangle_s$	$\langle P_2\rangle_s$	$\langle P_4\rangle_s$
Random, *cis*-based	0.838±0.048	0.530±0.116	0.798±0.050	0.437±0.114
Random, *trans*	0.906±0.024	0.716±0.067	0.913±0.028	0.741±0.076
Regular[a], *trans*	0.914	0.729	0.942	0.813

[a] Unit sequence: (–COMCO–OPCO–OPO–) for 50/50 copolymer and (–COMCO–OPCO–OPO–COPO–) for 67/33 copolymer

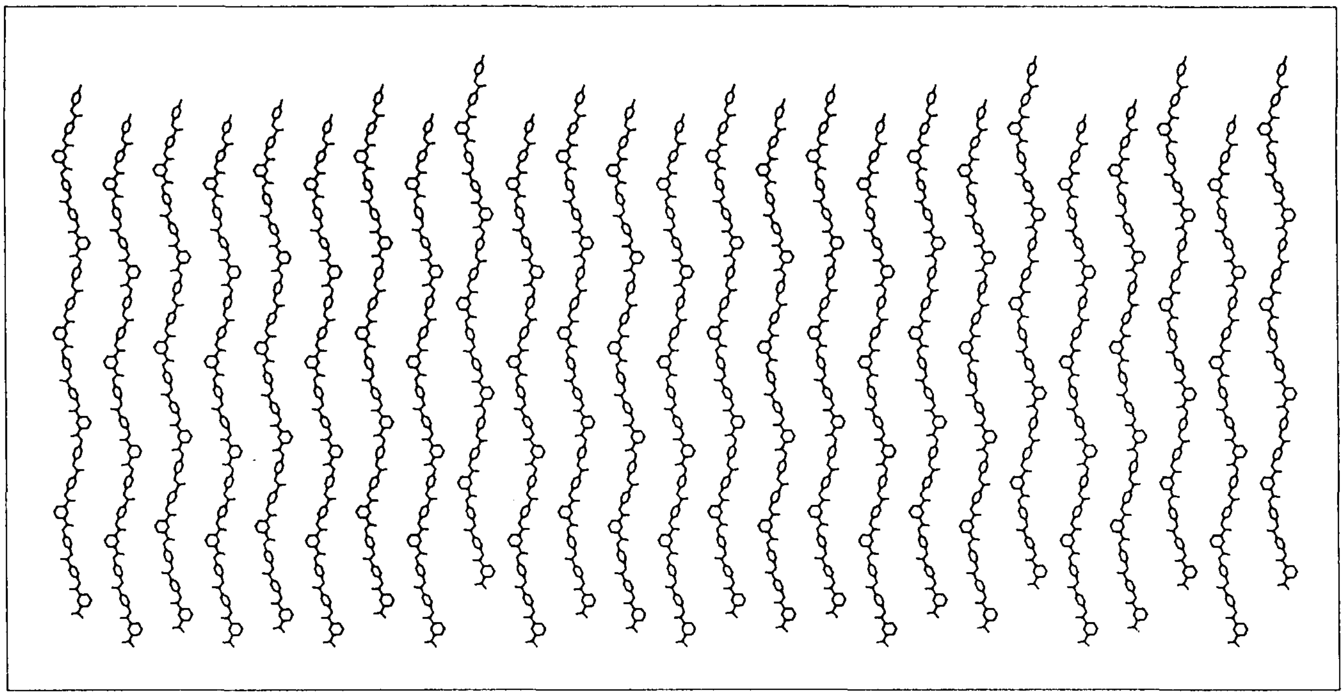

Figure 6 Set of aligned chains (50/50 regular copolymer (–COMCO–OPCO–OPO–), $n=18$, *trans* quasiplanar conformation); random axial displacement of +0.6, +0.3, 0, −0.3 and −0.6 nm relative to the first chain

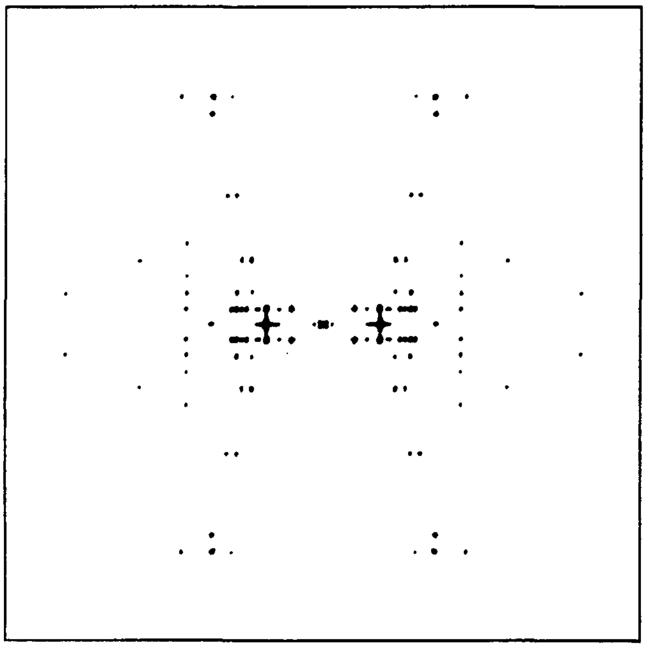

Figure 7 Two-dimensional Fourier transform of a set of chains shown in *Figure 6*

calculated values of $\langle P_2 \rangle_s$ and $\langle P_4 \rangle_s$, we suggest that a more likely explanation is based on the effect of distribution of the length of segments in random copolymers.

Consider a regular 50/50 copolymer with the following sequence of the constituent units: (–COMCO–OPCO–OPO–). In this case, all the segments are of the same length (i.e. $k_i = \bar{k} = 3$). Although the calculated $\langle P_2 \rangle_s$ and $\langle P_4 \rangle_s$ values for the *trans* conformation of the chain are only slightly higher than for random *trans* chains (*Table 5*), a set of such identical regular parallel chains placed in register yields a two-dimensional Fourier transform consisting of sharp reflections. The same applies to other regular copolymers containing angular units and to poly(*p*-phenylene isophthalate) homopolymer, which deviates from rod-like character more than any of the copolymers (*Figure 5*). When random axial displacements of +0.6, +0.3, 0, −0.3 and −0.6 nm (equal probabilities) relative to the first chain are introduced into such a set of regular chains (*Figure 6*), the reflections close to the centre of the two-dimensional Fourier transform (*Figure 7*) become smeared. In a set of extended aligned chains of segments of unequal lengths, the chains cannot be in register (*Figure 1*). Thus, it is suggested that the azimuthal spread of the equatorial scatter observed for fibres produced from random copolymers containing angular disruptor units arises from the combination of both effects, i.e. deviations from rod-like character as well as irregularity of packing due to the distribution of the lengths of segments.

In order to use the modelling approach for a quantitative interpretation of the observing WAXS features, it would be necessary to generate realistic non-planar model chains and then evaluate three-dimensional Fourier transforms for a sufficiently large set of such chains. For copolymers containing angular disruptor units this leads to considerable computational difficulties.

CONCLUSIONS

Comparison of meridional and equatorial WAXS features shows that the orientation parameters evaluated from the azimuthal spread of the equatorial scatter, assigned to the paracrystalline structure in the 'as-made' and heat-treated fibres, underestimates the alignment of chains along the fibre axis.

Models of the copolymer chains deviate considerably from a rod-like character. The constituent chains can be viewed as a sequence of rod-like segments of unequal lengths, joined together by angular units. The alignment of these segments along the fibre axis is poorer than that of the chains. The equatorial WAXS is due to interactions between these segments, and its azimuthal spread cannot be related directly to the chain orientation that is required for interpretation of mechanical properties.

This conclusion is not limited to the copolymers investigated. It also applies to other thermotropic copolymers that contain angular disruptor units or deviate from rod-like character for other reasons.

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