polymer papers

# Measurement of molecular orientation in thermotropic liquid crystalline polymers

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Procedures for obtaining molecular orientational parameters from wide angle X-ray scattering patterns of samples of thermotropic liquid crystalline polymers are presented. The methods described are applied to an extrusion-aligned sample of a random copolyester of poly(ethylene terephthalate) (PET) and *p*-acetoxybenzoic acid. Values of the orientational parameters are obtained from both the interchain and intrachain maxima in the scattering pattern. The differences in the values so derived suggest some level of local rotational correlation.

**Keywords** Liquid crystalline polymer; orientation measurement; X-ray scattering; thermotropic copolyester; random copolymer; molecular orientation

## INTRODUCTION

The ease of development of high molecular alignment is a characteristic of the liquid crystalline state. For polymeric liquid crystalline systems this property may be exploited for the development of high modulus materials[1,2], the levels of modulus and strength achieved depending largely upon the degree of molecular alignment[3]. To characterize these materials it is necessary to have simple and direct procedures for the evaluation of molecular orientation. We differentiate here between the chain orientation averaged over the sample volume and defined with respect to an external coordinate system such as the extrusion or extension axis, and the chain orientation in the region of and defined with respect to each chain segment. The former will be termed global the latter local. Whilst the degree of local correlation is of undoubted importance for full structural characterization, it is the global orientation which controls the anisotropy of bulk properties.

For samples subjected to uniaxial orientation, whether by extrusion or tension, it is sufficient to define the distribution of chain segment axes about the deformation axis. It is usual and most convenient to describe the distribution of these directors in space by exploiting the properties of a series of orthogonal harmonic functions, $P_{2n}\langle\cos\alpha\rangle$, where $\alpha$ is the angle between the director of the orienting unit and the unique axis of the specimen, and $P_{2n}$ a Legendre polynomial. Only even harmonics are required for a distribution function with uniaxial and inversion symmetry. The full orientation distribution $D(\alpha)$ may be reconstructed by a weighted summation:

$$D(\alpha)=\sum_{n=0}^{\infty}(4n+1)\langle P_{2n}(\cos\alpha)\rangle P_{2n}(\cos\alpha) \qquad (1)$$

Although many techniques have been developed to determine chain orientation in polymeric systems, only those using wide-angle X-ray scattering (WAXS) have the ability to give the complete orientation distribution function through its harmonic components. It has been the practice to utilise the arcing of the equatorial peak in the WAXS pattern which arises from *interchain* interferences. However such an analysis requires a *local* uniaxial symmetry about each chain segment and a knowledge of the local packing. In this paper we show that precise orientational and other structural information may also be derived from the meridional peaks in the WAXS pattern which arise from interferences within chains and that only *global* uniaxial symmetry need be assumed. Measures of orientation from meridional and equatorial peaks in the WAXS of an extruded pellet of a random copolyester of poly(ethylene terepthalate) and *p*-acetoxy benzoic acid are presented and compared.

## EXPERIMENTAL

The liquid crystalline polymer used in this study was a random copolyester of 40 mol% poly(ethylene terepthalate) (PET) and 60 mol% *p*-acetoxy benzoic acid (PABA), prepared by Eastman Kodak Company[4]. The X-ray measurements have been made at room temperature using melt extruded pellets of the copolyester, which exhibited a marked degree of axial alignment.

The X-ray scattering intensity data were obtained using a symmetrical transmission diffractometer, and then smoothed, corrected and normalised using the procedures described previously[5]. The data in the form of an $s$-weighted reduced intensity function $si(s,\alpha)$ are shown in *Figure 1*. There are two very prominent features in this pattern, namely the peak intensifying onn the equator at $s=1.4$ Å$^{-1}$ corresponding to *interchain* correlations[6], and the peak on the meridian at $s=30$ Å$^{-1}$ arising from *intrachain* interferences. The absence of significant lateral sampling of the meridional peaks, indicates molecules which are preferentially aligned but not longitudinally correlated. The uniaxial symmetry of the pellet about the extrusion axis is shown in the X-ray transmission pattern

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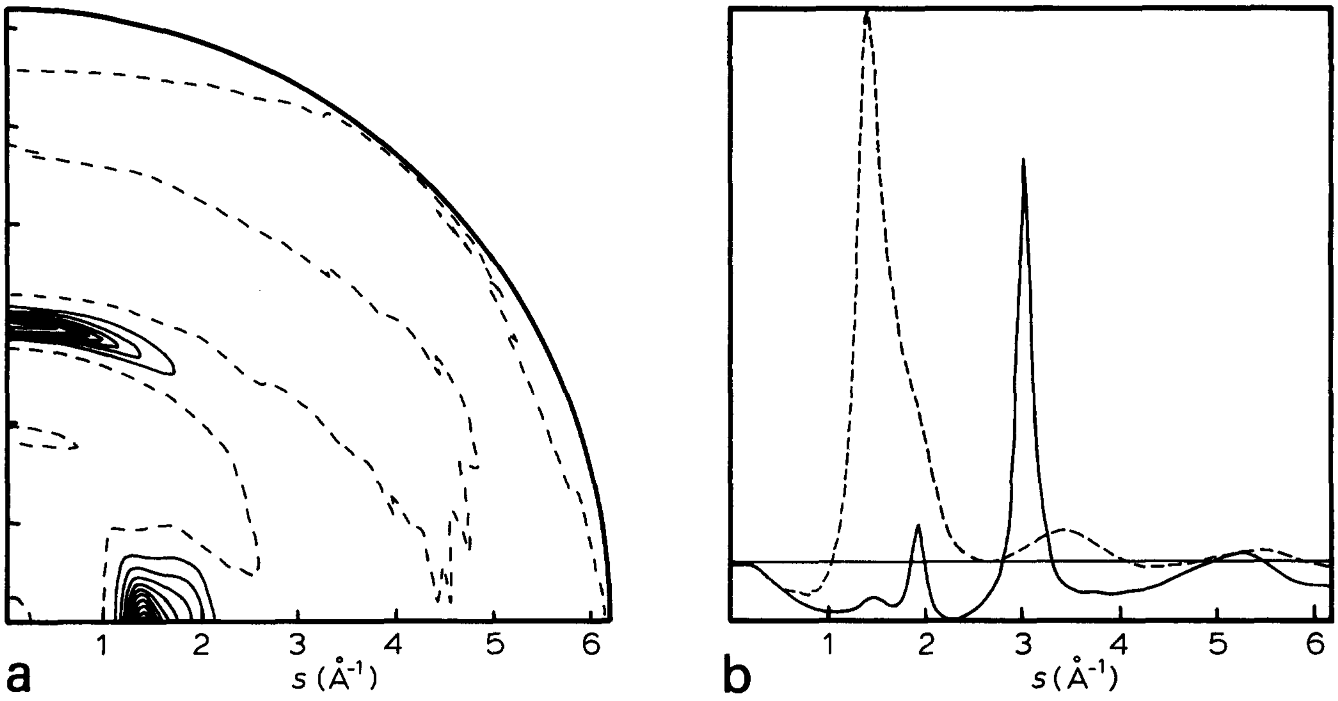


*Figure 1* (a) *s* weighted reduced intensity function $si(s,\alpha)$ for melt extruded pellet of 60 mol% PABA and 40 mol% PET. (b) The meridional (–) and equatorial (---) sections of the scattering (a)

shown in *Figure 2*, which was taken with the X-ray beam parallel to the extrusion axis. There is an even distribution of intensity about the ring which corresponds to the interchain peak at $s=1.4$ Å$^{-1}$. The level of homogeneity of orientation within the sample is shown by the two patterns of *Figure 3*, which compare the surface layers of the cylindrical pellet with material from near to the central axis. It should be pointed out however that although these particular samples showed uniformity of orientation, extruded themotropic polymers frequently show a skin-core texture in which the surface layers are highly oriented while the central core is nearly isotropic[7]. It follows that where skin-core textures are present, a single global measure of orientation may be misleading.

## BASIC THEORY

The scattering pattern $I(s,\alpha)$ may be considered as the scattering from a perfectly aligned sample of the structure, $I^m(s,\alpha)$, smeared or convoluted with the orientation function, $D(\alpha)$:

$$I(s,\alpha)=I(s,\alpha)=I^m(s,\alpha) \tag{2}$$

The scattering function $I(s,\alpha)$ has cylindrical and inversion symmetry and may be expressed as a series of even order Legendre polynomials:

$$I(s,\alpha)=\sum_{n=0}^{\infty} I_{2n}(s)P_{2n}(\cos\alpha) \tag{3}$$

where

$$I_{2n}(s)=(4n+1)\int_0^{\pi/2} I(s,\alpha)P_{2n}(\cos\alpha)\sin\alpha\,\mathrm{d}\alpha \tag{4}$$

Similar components $I^m_{2n}(s)$ for the structural unit may also be evaluated. It has been shown[8-10] that if $I(s,\alpha)$, $I^m(s,\alpha)$ and $D(\alpha)$ are expressed in this way then the convolution (2) may be written:

$$I_{2n}(s)=\frac{2\pi}{4n+1}I^m_{2n}(s).D_{2n} \tag{5}$$

where $D_{2n}$ can be obtained in an analogous manner to

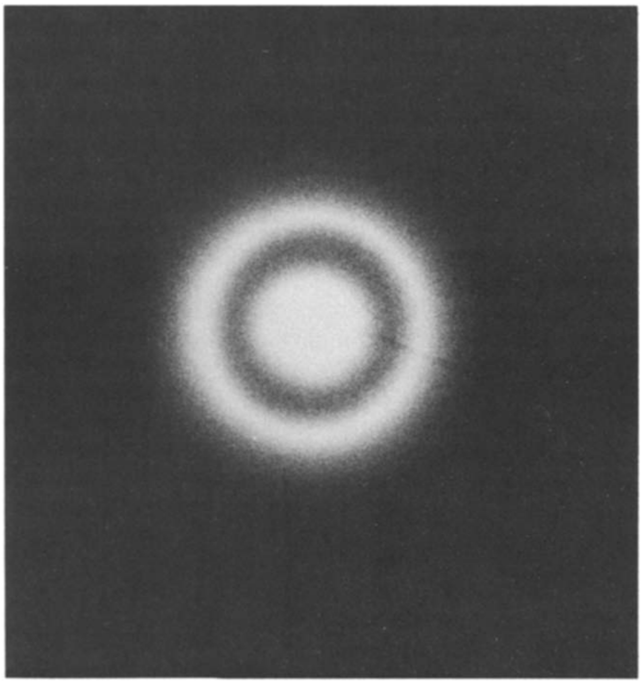


*Figure 2* Transmission X-ray diffraction pattern of an extruded pellet with the incident beam parallel to the extrusion direction

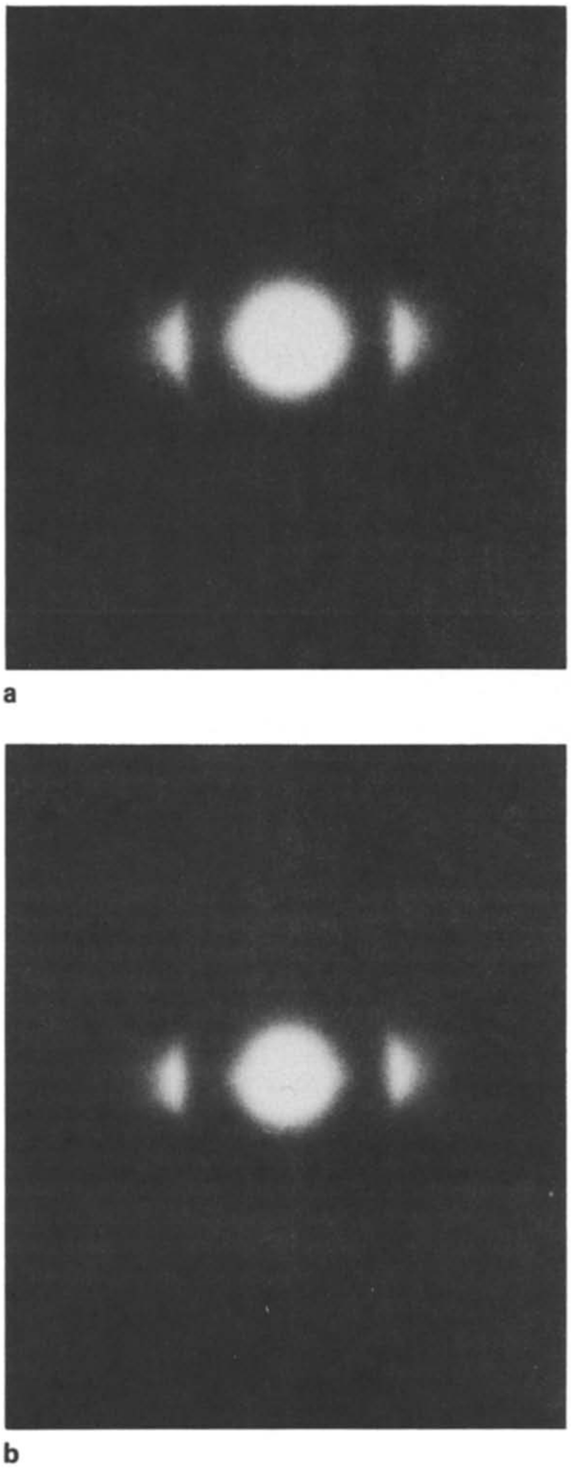


***Figure 3*** Transmission X-ray diffraction patterns of sections of an extruded pellet with the incident beam normal to the extrusion direction, (a) near skin and (b) near centre

$I_{2n}(s)$ with $D(\alpha)$ being normalized such that

$$\frac{1}{2\pi} = \int_0^{\pi/2} D(\alpha)\sin\alpha\,\mathrm{d}\alpha \qquad (6)$$

The simple relationship shown in equation (5) is *only* valid over an $s$ range in which the scattering arises solely from a single structural unit for which $I^m(s,\alpha)$ is the scattering and is not complicated by interunit correlation. However, with this restriction the orientation parameters $D_{2n}$ may be obtained at any $s$ value as a series of quotients. Since $I_{2n}(s)$ may be derived from the experimental scattering pattern the problem of measuring the orientation reduces to the calculation of coefficients $I^m_{2n}(s)$. It may be more convenient in some cases to rewrite equation (5) in terms of the amplitudes $\langle P_{2n}(\cos\alpha)\rangle$ of the spherical harmonics, thus:

$$\langle P_{2n}(\cos\alpha)\rangle_D = \langle P_{2n}(\cos\alpha)\rangle / \langle P_{2n}(\cos\alpha)\rangle_m \qquad (7)$$

The application of this procedure to oriented thermoplastics has already been described in detail[11-13].

## EVALUATION OF $I^m(s,\alpha)$ OR $\langle P_{2n}(\cos\alpha)\rangle_m$

It is evident that in order to evaluate $I^m_{2n}(s)$ it is necessary to assume a structural model. This necessity is common to all methods of measuring orientation, for not only is it useful to know what structural unit the orientation function relates to, but it is also required for normalizing the experimental observations, for example the use of the intrinsic birefringence in optical methods.

The scattering pattern (*Figure 1*) shows two principal features, the equatorial peak of interchain chain origin at $s \sim 1.4$ Å$^{-1}$ and the meridional peak at $s \sim 3.1$ Å$^{-1}$. For a structure of spatially uncorrelated relatively rigid molecules, the information required for a structural model of *intra*chain effects is considerably less than that required for an interchain model. Nevertheless it is the latter, through the use of the azimuthal variation of the equatorial interchain intensity as a measure of chain orientation, which has received most attention in the literature[14-16]. The procedures for analysing the interchain and intrachain scattering will be considered in turn.

### *Interchain scattering*

The equatorial peaks represent spatial correlations between chains. The arcing of the diffuse maxima is thus related to the orientation distribution of these spatial correlations rather than that of the chains themselves. The extent of spatial correlations, as determined from the width of the interchain peak ($s \approx 0.5$ Å$^{-1}$), is of the order of two or three chain diameters: a correlation volume of 10–20 molecules. If we make the assumption that there is no rotational correlation between adjacent molecules we can assign $\langle P_{2n}\rangle'$ to describe the molecular orientation within this correlation volume, and $\langle P_{2n}\rangle''$ as the measure of the orientation distribution of correlated volumes. The true molecular orientation is then given by:

$$\langle P_{2n}\rangle = \langle P_{2n}\rangle' \langle P_{2n}\rangle'' \qquad (8)$$

Thus unless the level of local molecular orientation within the scattering unit is known it is not possible to obtain the global molecular orientation parameters.

However if we assume the molecules to be aligned perfectly on a local scale, the scattering $I^m(s,\alpha)$ (for infinitely long molecules) will be completely confined to the equatorial plane, and thus[10]

$$\langle P_{2n}\rangle^m = \frac{(2n!)}{(-1)^n 2^{2n}(n!)^2} \qquad (9)$$

The values for the first 4 terms are listed in *Table 1*. The use of these 'correction factors' requires a local orientation which is perfect. If it is not, the experimentally determined orientation distribution will be sharper than the true molecular distribution function.

For finite length molecules or long chains which are not straight there will be a smearing of the interchain peak out of the equatorial plane along the direction of the meridional axis, the extent of the smearing being inversely proportional to the correlation length. Leadbetter and Norris[16], and De Vries[17], in a study of small molecule liquid crystals (where the correlation length $\sim 20$ Å) concluded that, for all but the most highly 'ordered' systems that is ($\langle P_2 \rangle > 0.8$), the smearing will be negligible. However to calculate the precise corrections for polymeric systems requires a knowledge of the intrachain correlation function, and how the smearing from such a function interacts with the relatively broad (within the equatorial plane) interchain peak.

The scattering intensity measured at $s \sim 1.5$ Å$^{-1}$ will contain both structural contributions and incoherent scattering and it is common practice to use the intensity level for $\alpha = 0°$ as the 'background level'. This may be reasonable for medium to high levels of orientation, for which the azimuthal variation of intensity has reached an asymptotic value, but for lower levels of orientation in particular such practice may result in too sharp a distribution, while neglecting the background would obviously result in too broad a distribution. An alternative approach may be to correct the intensities for geometric effects (polarization, absorption, multiple scattering) and then to normalize the intensities to electron units[5]. The calculated incoherent contribution can then be subtracted from the normalised curve. Alternatively the intensity of the incident X-ray beam could be calculated in electron units[18] thus removing the necessity of recording the complete scattering pattern.

In summary, if one is prepared to make a number of reasonable assumptions the molecular orientation parameters may be obtained from the azimuthal variation in intensity of the equatorial maxima by the use of simple correction factors (*Table 1*). However the limitations of using the equatorial information need to be carefully considered in the light of all available structural information.

*Table 1* Correction factors $\langle P_{2n} \rangle^m$ for an interchain peak assuming perfect local orientational order

| $n$ | $\langle P_{2n} \rangle^m$ |
|---|---|
| 1 | −1/2 |
| 2 | 3/8 |
| 3 | −5/16 |
| 4 | 35/128 |

### *Intrachain scattering*

For a model for the intrachain scattering it is only necessary to know the structural information relevant to an isolated molecule. For the relatively rigid molecules which form liquid crystalline polymers the number of conformational parameters is limited. This is particularly true for scattering centred on the meridian; since this scattering represents a projection onto the unique axis of the molecular structure, and hence depends only upon conformational parameters which affect the positional coordinates along the molecular axis. However the scattering components $I^m_{2n}(s)$ must represent an 'average' molecule, taking into account any variation in chemical sequences and conformational parameters.

The molecular segments of the PABA/PET copolymer are shown in *Table 2*. Bond angles and bond lengths may be obtained from structural studies on similar compounds[19–21]. The main conformational parameters which are not clearly defined, namely the rotations of the phenyl groups[22] will not greatly affect the meridional scattering. The scattering components $I^m_{2n}(s)$ may be obtained for $N$ atoms[24,25]:

$$NI^m_{2n}(s) = (-1)^n(4n+1)\sum_j^N\sum_k^N f_i(s)f_k(s)j_{2n}(r_{jk}s)P_{2n}\cos(\alpha_{jk}) \tag{10}$$

using the procedures described elsewhere[5]. For the calculated scattering we shall use the reduced intensity function $si(s,\alpha)$ and its harmonics $si_{2n}(s)$. These functions weight more evenly the features of the scattering patterns.

The distribution of molecular segments along the chains is taken as random[4,23], with the level of intrachain spatial correlation at 40–50 Å[6]. To account for the irregular positioning of the sequences of the random copolymer, chains comprising 150 segments or 3000 atoms were used, although only distances between atoms separated by less than $m$ atoms were incorporated in the calculation. This restriction is justified by the limited intrachain spatial correlation as defined by the breadth of the meridional peaks. *Figure 4* shows the first four components calculated, using equation (10), for a chain with $m \approx 50$. The positions of the peaks in these curves match the intrachain features of the experimental $si_{2n}(s)$ shown in *Figure 5*. The scattering pattern $si(s,\alpha)$ obtained by summing the calculated component of *Figure 4* using equation (3) is shown in *Figure 6*: the meridional features are in good agreement with the experimental intensity plot of *Figure 1*.

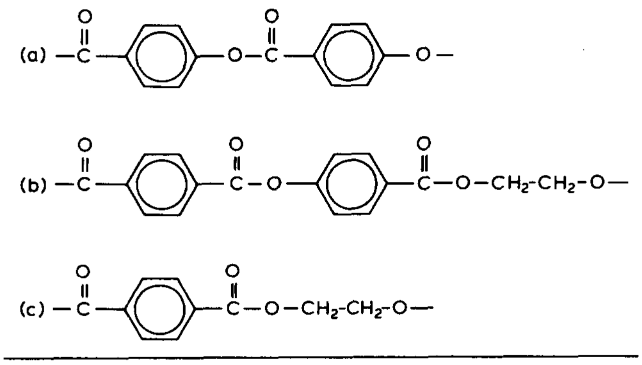
In order to obtain the 'correction factors' $\langle P_{2n} \rangle^m$ for use with the experimental factors $\langle P_{2n} \rangle$, allowances must be made for the independent scattering both coherent and incoherent, thus

$$\langle P_{2n} \rangle^m = I_{2n}(s)/\{I_0(s) + \sum_i f_i^2(s) + I_{\text{comp}}(s)\} \tag{11}$$

where $\sum_i f_i^2(s)$ is the independent scattering for a 'repeat unit' and $I_{\text{comp}}$ is the Compton scattering.

Although from equation (5) it is possible to obtain the orientational parameter from the ratios of $\langle P_{2n} \rangle / \langle P_{2n} \rangle^m$

*Table 2* Molecular segments on the random copolyester 60 mol% PABA, 40 mol% PET



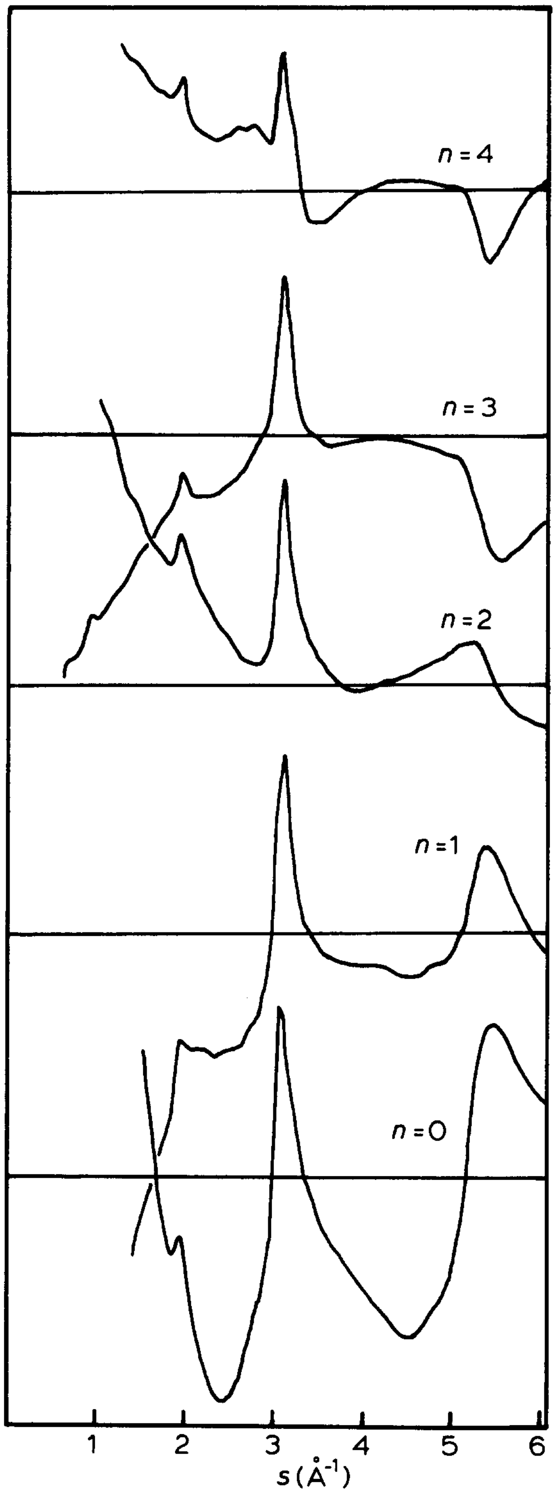


*Figure 4* $si_{2n}^{m}(s)$ curves with $n=0, 1, 2, 3, 4$, calculated for a random chain copolyester model with the segment shown in *Table 2*, using the procedures described in the text

over a range of $s$, it is more convenient to restrict the calculation of the ratios to the $s$ values corresponding to maxima in the scattering pattern.

The breadth (in terms of $\Delta s$) of the meridional peaks may vary with the level of the molecular alignment, as an off-meridional component of a layer line may contribute to the intensity in the meridian as a result of misorientation. Consequently it is important to match the breadths of the peaks in the calculated function to the experimental version through the use of the harmonic components $i_{2n}(s)$.

*Figure 7* shows the variation in the half height full width of the peak at $s \approx 3.1$ Å$^{-1}$ in the calculated function $i_2(s)$ for a range of spatial correlations 25–60 Å. *Figure 8* shows the corresponding variations in the correction factors' $\langle P_{2n} \rangle^m$ calculated using equations (10) and (11) for the same range of spatial correlations ($n = 1,2,3$).

Although these factors are for the PABA/PET copo-

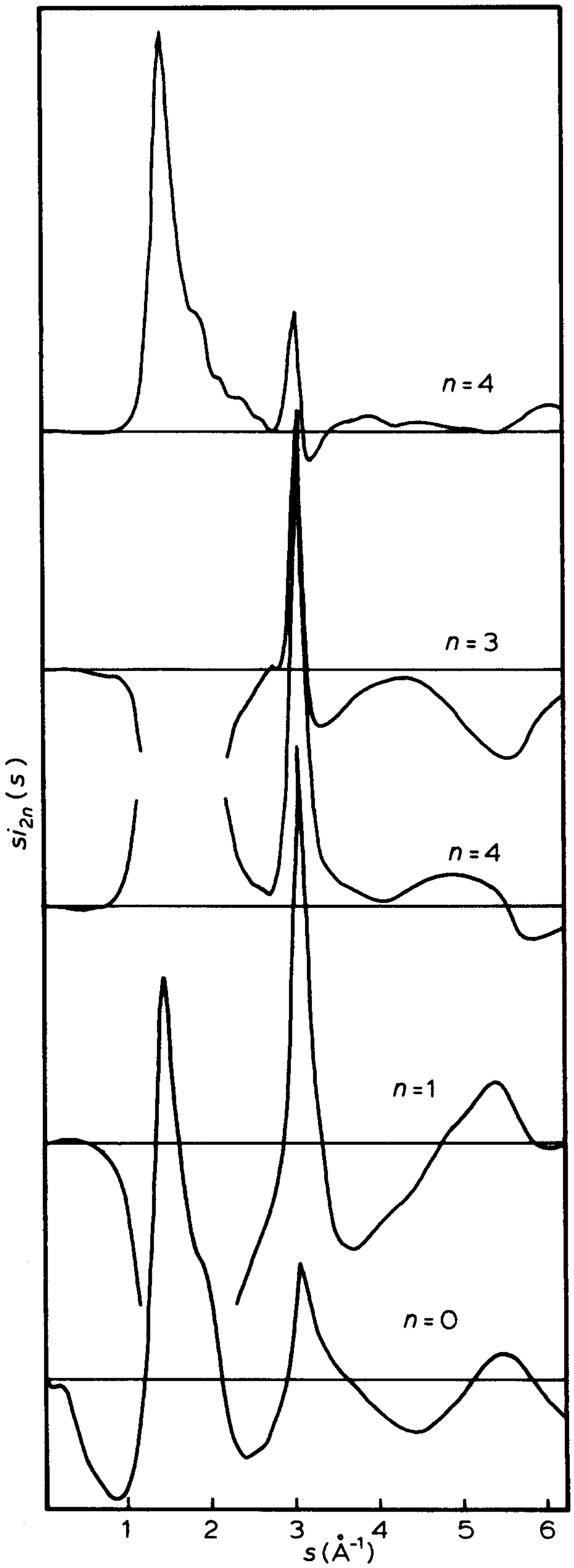


*Figure 5* Experimental $si_{2n}(s)$ curves derived from the data shown in *Figure 1a*

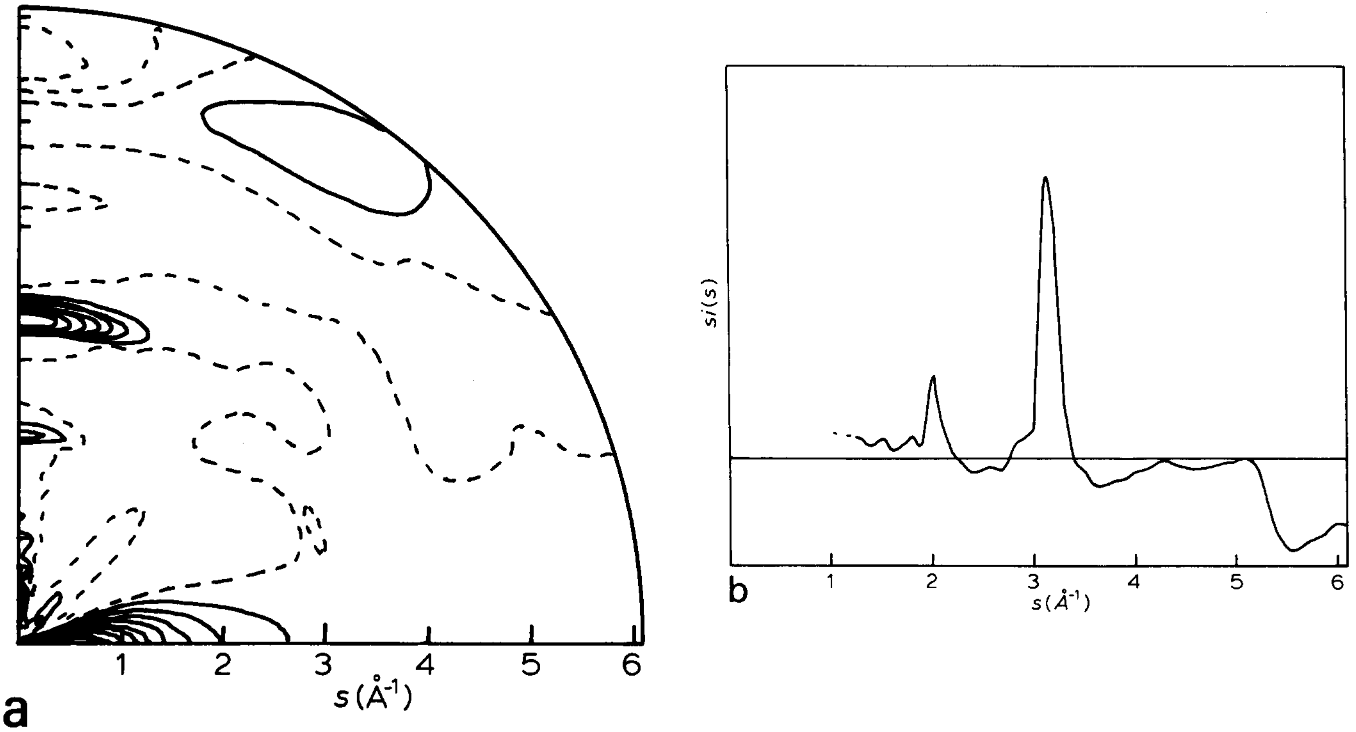


*Figure 6* (a) The calculated s-weighted reduced intensity function $si^m(s,\alpha)$ reconstructed from the harmonics component of *Figure 4* using equation (3). (b) Meridional section of the scattering (a)

lymer, it is expected that broadly similar values would be obtained for other phenylene based LCPs. The observed half width in the experimental patterns can thus be used to refine the values of the 'correction factors' $\langle P_{2n} \rangle^m$.

## RESULTS

### *Interchain scattering*

The azimuthal distribution of the scattered intensity of the equatorial maxima at $s = 1.4$ Å$^{-1}$ is shown in *Figure 9*. Adopting the level of intensity for $\alpha = 0°$ as the background level, the first three $\langle P_{2n} \rangle$ components derived from this profile are shown in *Table 3*, together with the correction factors used (equation (11)) and hence the true orientation parameters. Using the technique more terms could be evaluated and the distribution function calculated. The numerical reliability of these results is high, as the measurements are taken for the most intense part of the pattern, and at a relatively low scattering vector where the level of the Compton scattering is not high.

### *Intrachain scattering*

Using the data displayed in *Figures 7* and *8* with a half height breadth of the experimental function $i_2(s)$ at $s = 3.1$ Å$^{-1}$ of 0.196 Å$^{-1}$ gives the correction factors shown in *Table 4*. The molecular orientation $P_2$ of 0.64 is significantly lower than that measured from the interchain peak. Although these data are for a higher scattering vector, the peak intensity is the substantial and accordingly the numerical reliability is good. The intrachain peak at $s = 2.0$ Å$^{-1}$ was not used, as it is not clearly separated from the interchain peak, although in terms of position and relative intensity it was matched well by the calculated functions.

## DISCUSSION

It is clear that the level of molecular orientation in the PABA/PET pellet is substantial although this orientation is not apparent when the microstructure of microtomed slices is viewed between crossed polars[26]. However, the detailed analysis, while showing the relative ease with which orientational parameters may be obtained from the azimuthal variation in the interchain peak, does indicate a discrepancy with the parameters obtained by a more thorough analysis of the meridional maxima. Small variations might be expected through slight inadequacies

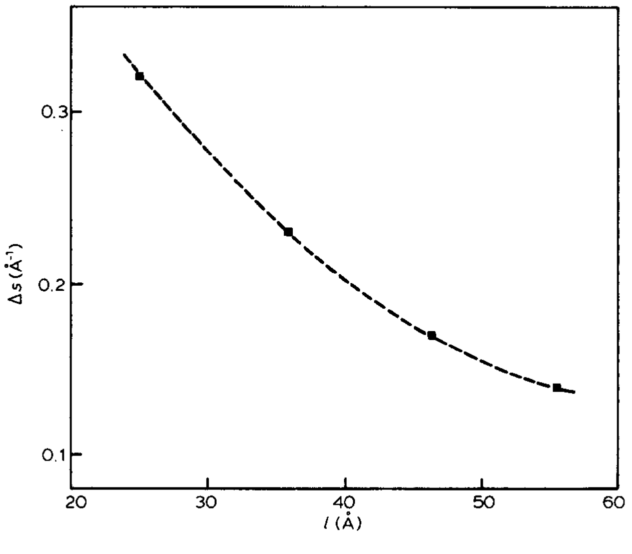


*Figure 7* Plot of the half height breadth of the peak at $s = 3.0$ Å$^{-1}$ in the calculated $si_2(s)$ curve against the correlation length of the model

of the intrachain scattering model used. However a difference amounting to >20% clearly indicates a more fundamental cause. Indeed, even cursory inspection of flat plate diffraction photographs of this type of thermotropic copolyester reveals that the meridional maxima are less well oriented than the equatorial.

The route to the orientational parameter *via* the intrachain scattering is sound if lengthy, whereas the basis for obtaining values for the same parameters using the interchain peak involves a number of assumptions and the first step in understanding the discrepancy is to question these.

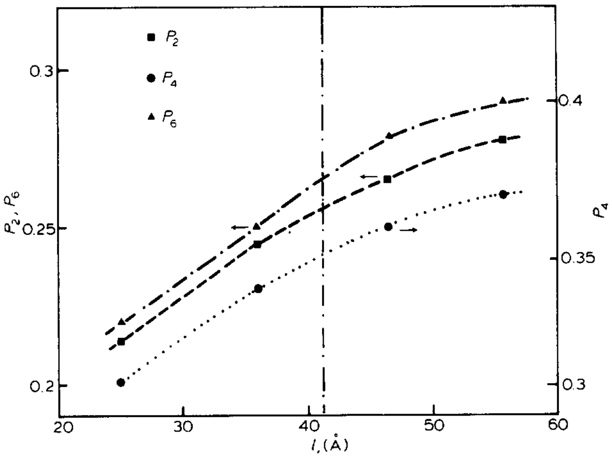


*Figure 8* $\langle P_{2n}\rangle^m$ term derived from model calculation for varying correlation lengths. The vertical broken line represents the correlation length determined from the experimental scattering

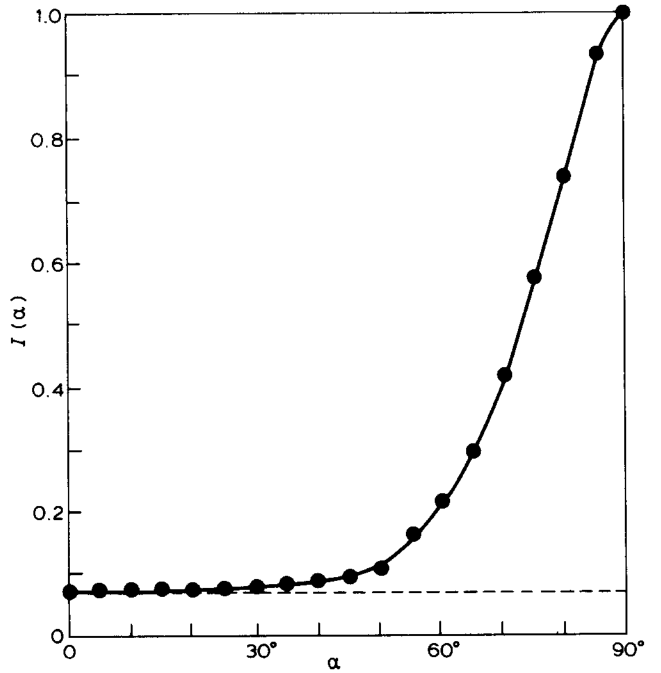


*Figure 9* Azimuthal distribution of intensity measured for a pellet with $s = 1.4$ Å$^{-1}$. The broken line represents the 'background' level assumed in the analysis

*Table 3* Values used to determine the orientation parameters from the interchain peak at $s = 1.4$ Å$^{-1}$

| $n$ | $\langle P_{2n}\rangle$measured | $\langle P_{2n}\rangle^m$ | $\langle P_{2n}\rangle^{\text{equat}}$ |
|---|---|---|---|
| 1 | –0.390 | –0.5 | 0.78 |
| 2 | –0.180 | –3/8 | 0.48 |
| 3 | –0.080 | –5/16 | 0.27 |

In determining the orientation from the azimuthal profiles of the equatorial peaks the assumption is made that the molecules within the correlation volume for the peaks (a few chains) show perfect local orientational order. A lack of perfection in local orientation, while contributing to the arcing of meridionals, would not of itself smear the equatorials. It should also be remembered that although some theories of nematic ordering envisage a relatively high level of local orientation[27], this is not always the case as for example in the mean field approach of Maier–Saupe[28]. If the discrepancy between the orientation shown by meridional and equatorial peaks is to be accounted for in terms of a lack of perfect local orientational order, then the parameters describing the local orientation will be given by:

$$\langle P_{2n}\rangle_{\text{local}} = \langle P_{2n}\rangle_{\text{merid}}/\langle P_{2n}\rangle_{\text{equat.}} \qquad (12)$$

For the sample examined in this work, the values of $\langle P_{2n}\rangle_{\text{local}}$ consistent with this explanation are listed in *Table 5*.

Another assumption implicit in the use of equatorial maxima to give molecular orientation is that the molecules have local axial symmetry. This is in addition to the necessity for global uniaxiality if the analysis is to be performed in terms of even order spherical harmonics. The effect of absence of local axiality on the azimuthal profiles of equatorial maxima can be seen by considering an extreme example. If one assumes a sheet structure, in which the sheets all lie parallel to the unique specimen axis and interference between the sheets accounts for the equatorial peak, then there will be no azimuthal smearing of the equatorials which will of course indicate perfect alignment. At the same time the molecular axes need not be well aligned about the specimen axis within each sheet, in which case they will be represented by substantial arcing of the meridional peak. In a more realistic model the sheet orientation would perhaps not be perfect, but the essential point is that any coupling between non-axial local structure (and thus non-axially symmetric diffraction) and the perfection of molecular orientation will mean different degrees of azimuthal smearing of the equatorial and meridional diffraction maxima.

A model based on non-uniaxiality of the local structure as a consequence of rotational correlation between neigh-

*Table 4* Values used in determining the molecular orientation from the intrachain peak at $s = 3.1$ Å$^{-1}$

| $n$ | $\langle P_{2n}\rangle$measured | $\langle P_{2n}\rangle^m$ | $\langle P_{2n}\rangle^{\text{merid}}$ |
|---|---|---|---|
| 1 | 0.165 | 0.256 | 0.644 |
| 2 | 0.115 | 0.35 | 0.329 |
| 3 | 0.050 | 0.266 | 0.188 |

*Table 5* Values of parameters describing local orientation

| $n$ | $\langle P_{2n}\rangle^{\text{merid}}$ | $\langle P_{2n}\rangle^{\text{equat.}}$ | Level of molecular orientation in equatorial correlation volume |
|---|---|---|---|
| 1 | 0.644 | 0.78 | 0.83 |
| 2 | 0.329 | 0.48 | 0.69 |
| 3 | 0.188 | 0.27 | 0.69 |

bouring molecules has recently been suggested to account for the absence of a direct link between overall molecular orientation and the birefringence observed in a thin slice parallel to the axis of the same type of oriented specimen as used in this study[25]. For these reasons this second explanation of the meridional/equatorial discrepancy is favoured.

## SUMMARY

A method has been developed which enables chain orientation to be measured from the aximuthal arcing of the X-ray scattering peaks associated either with correlations within a single chain, or the spatial correlation between chains. The intrachain or meridional X-ray scattering provides a convenient and accurate method of assessing the molecular orientation of liquid crystalline polymers. For the PABA/PET pellet examined, the $P_2$ orientation parameter was 0.64. However this was considerably lower than the value of 0.8 obtained by the more usual method of utilising the equatorial interchain peak at $s = 1.4\ \text{Å}^{-1}$. It is likely that the discrepancy is the result of non-uniaxial local symmetry about each chain segment, which leads to an exaggerated value for the orientation parameter when derived from the interchain peak.

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## REFERENCES

1 Acierno, D., La Mantia, F. P., Polizzotti, G., Ciferri, A. and Valenti, B. *Macromolecules* 1982, **15**, 1455

2 Shaefgen, J. R., Bair, T. I., Ballou, J. W., Kowlek, S. L., Morgan, P. W., Panar, M. and Zimmerman, Z. 'Ultrahigh Modulus Polymers', Eds. A. Ciferri, I. M. Ward, Applied Science, London, 1979, p. 173

3 Ward, I. M. *Proc. Phys. Soc.* 1962, **80**, 1176

4 Jackson, W. J. and Kuhfuss, H. F. *J. Polym. Sci. Polym. Chem. Edn.* 1976, **14**, 2043

5 Mitchell, G. R. and Windle, A. H. *Colloid Polym. Sci.* 1982, **260**, 754

6 Mitchell, G. R. and Windle, A. H. *Polymer* 1982, **23**, 1269

7 Mitchell, G. R. and Mackley, M. R. unpublished work

8 Deas, H. D. *Acta Cryst.* 1952, **5**, 54

9 Ruland, W. *Colloid Polym. Sci.* 1977, **255**, 833

10 Lovell, R. and Mitchell, G. R. *Acta Cryst.* 1981, **A37**, 135

11 Mitchell, G. R. and Windle, A. H. *Polymer* 1983, **24**, 285

12 Brown, D. J. and Mitchell, G. R. *J. Polym. Sci. Polym. Lett. Edn.*, 1983, **21**, 341

13 Windle, A. H. 'Developments in Oriented Polymers—1' Ed. I. M. Ward, Applied Science, London, 1982

14 De Lord, P. and Falgueirettles, J. *C. R. Habd. Sean. Acad. Sci.* 1965, **260**, 2468

15 Leadbetter, A. J. and Wrighton, P. G. *J. de Physique* 1979, **40**, C3-234

16 Leadbetter, A. J. and Norris, E. K. *Molecular Physics* 1979, **38**, 669

17 De Vries, A. *J. Chem. Phys.* 1972, **56**, 4489

18 Warren, B. E. 'X-ray Diffraction', Addison Wesley, 1965, p. 172

19 Daubeny, R. P., Bunn, C. W. and Brown, C. J. *Proc. Roy. Soc.* 1954, **226**, 531

20 Adams, J. M. and Morsi, S. E. *Acta Cryst.* 1976, **32B**, 1345, 1976

21 Kaiser, J., Richter, R., Lemke, G. and Golic, L. *Acta Cryst* 1980, **36B**, 193

22 Hummel, J. P. and Flory, P. J. *Macromolecules* 1980, **13**, 479

23 McFarlane, F. E., Nicely, V. A. and Davies, T. G. 'Contemporary Topics in Polymer Science', Eds. E. M. Pearce and J. R. Schaefgen, Plenum, New York, p. 109

24 de Gennes, P. G. *C. R. Acad. Sci.* (*Paris*) 1972, **274**, 142

25 Pynn, R. *J. Phys. Chem. Solids* 1973, **34**, 735

26 Viney, C., Mitchell, G. R. and Windle, A. H. *Polymer* 1983, **24** (*Commun*), 145

27 Faber, T. E. *Proc. R. Soc. London* 1981, **A375**, 579

28 Chandrasekhar, S. 'Liquid Crystals', Cambridge University Press, London, 1977, p 44