

# Molecular correlations in sheared thermotropic copolyesters showing banded textures

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Banded textures produced in a thermotropic liquid crystal polymer by shearing between glass slides are examined by using both transmission electron and polarized light microscopy. The periodic variation in director orientation about the shear axis, as measured by light microscopy, is shown to be distinctly different from that indicated by electron diffraction. Measurements of birefringence and observation of Zernicke phase contrast indicate periodic variations in optical properties of the polymer, in step with the bands. Such effects are accounted for in terms of a synchronous rotation of the planar aromatic groups about the molecular chain axes. Evidence for an out-of-plane component of molecular orientation is also presented.

(Keywords: liquid crystal polymer; banded texture; synchronous rotation; crossed polars; molecular trajectory)

## INTRODUCTION

Both lyotropic and thermotropic polymers have been shown to exhibit banded textures when subjected to shear or elongational flow<sup>1-4</sup>. The bands, which are readily apparent in the polarizing microscope, lie normal to the shear axis,  $X$ , and are evenly spaced (typically a few  $\mu\text{m}$  apart) when the specimen is oriented with the polarizer or alternatively the crossed analyser parallel to this axis. As the crossed polars are rotated, successive pairs of bands move together, merge and disappear. A detailed analysis of the position of the bands, as a function of polar orientation, indicated a near-sinusoidal form for the divergence angle  $\omega$  (defined as the local angle subtended by the extinction direction to the shear direction)<sup>4</sup>.

For small molecule liquid crystals, the identity of the molecular long axis with the extinction direction is usually assumed; the term 'director' is used synonymously in both cases, although caution in the use of this identity has been advised by Frank<sup>5</sup>. For polymeric liquid crystals, it has recently been shown that the microstructures revealed by optical microscopy of a microtomed section of an extruded pellet are in conflict with X-ray diffraction data, if this identity is assumed: the X-ray diffraction demonstrates that a high degree of orientation along the extrusion direction is present, while optical microscopy shows the extinction direction as wandering randomly throughout the sample<sup>6,7</sup>.

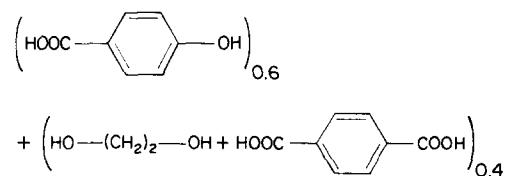
Recognizing this difficulty, a transmission electron microscopy (TEM) study of a thermotropic polymer showing banded textures was undertaken<sup>8</sup>. The presence of bands in dark field images, in which only selected portions of the diffraction pattern contribute to the image, demonstrated that a periodic variation in the local molecular orientation did indeed accompany the si-

nusoidal variation in the local extinction direction. Although at first sight optical microscopy and diffraction data appeared to be compatible in these sheared systems, closer analysis revealed a distinct anomaly<sup>9</sup>. The molecular trajectory indicated by polarized light microscopy was very close to being sinusoidal, whereas electron diffraction measurements suggested a periodic but much more 'flat topped' trajectory.

This paper reports a more detailed examination of this anomaly, with the aim of understanding the molecular microstructure in more detail.

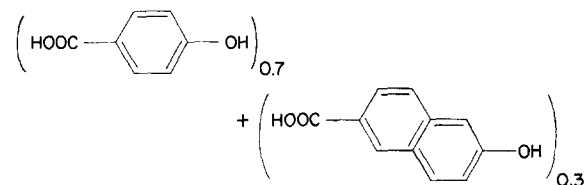
## EXPERIMENTAL

Much of this work focusses on the polymer designated 'B-ET':



[*p*-hydroxybenzoic acid] + [ethylene glycol + terephthalic acid]

It was supplied by Tennessee Eastman Kodak as 'X7G'. Additional investigations in the TEM were carried out on a second polymer, B-N, supplied by ICI:



[*p*-hydroxybenzoic acid] + [hydroxynaphthoic acid]

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Thin films of B-ET for optical microscopy were prepared by shearing the material between glass slides at elevated temperatures, as described in ref. 3. Figure 1 shows the banded texture observed when such a film is viewed between crossed polars with the shear direction  $X$  parallel to the transmission direction of either polar. This specimen orientation will be referred to as the 'orthogonal position'. The position of the dark bands was measured as a function of crossed polar rotation from the orthogonal position. A Berek compensator was used to measure the optical retardation on lines which extinguish when the specimen is in the orthogonal position, and on lines midway in between these. To allow conversion of these data into values of birefringence, the local specimen thickness was estimated by focussing the microscope on the top and bottom surfaces, after appropriate selection of immersion oil and calibration of the focussing knob.

Specimens for TEM were produced by shearing the polymer onto a rocksalt substrate with a glass slide, at a temperature of 300°C. The specimen and slide were quenched to room temperature on a metal block; a carbon coating was evaporated onto the polymer, the rocksalt dissolved, and the film washed in distilled water and picked up on a copper grid. Regions of such specimens thick enough to give contrast in the optical microscope exhibited a banded texture with the same characteristics as that produced in specimens on a glass substrate. Diffraction patterns were produced in a Philips 300 electron microscope operating at 100 kV.

*Development of optical analysis*

If rotation of the crossed polars by an angle  $\omega$  from the orthogonal position produces an intensity minimum at position  $x$  along the shear axis  $X$ , the optical director at  $x$  is inclined at an angle  $\omega$  to the shear direction. The function  $\omega(x)$  is defined as the divergence function. Figure 2 shows two plots of this function, obtained from different parts of a sample of B-ET. For comparison, a sine curve is superimposed on each plot, the amplitude and period



Figure 1 Banded texture in B-ET specimen sheared at 300°C. The specimen is in the orthogonal position between crossed polars, and the bands are normal to the shear direction

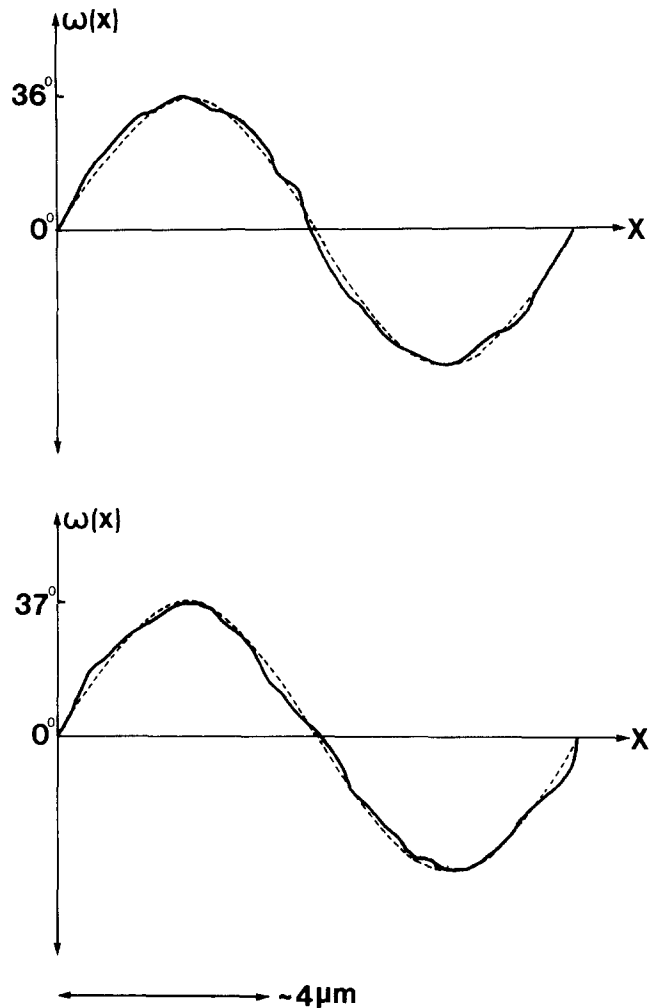


Figure 2 Two plots of the divergence function  $\omega(x)$  prepared from different areas of the sample shown in Figure 1. Experimental readings were taken at 2° intervals of crossed polar rotation. The dashed curves are sinusoidal for reference, having the same amplitude and period as the experimental plots

having been chosen to be equal to that of the experimentally determined function. It can be seen that, to a good approximation for this specimen:

$$\omega(x) = b \sin x$$

with  $b \sim 0.65$

The simplest interpretation is that  $b$  corresponds to the maximum value of  $\omega$ . However, this need not be the case if, through the thickness of the specimen, there is some relative displacement of the microstructure along  $X$ . Consider the following highly simplified model:

Suppose that the specimen consists of two identical layers, in each of which the optical director can be described by a sinusoidal divergence function within the plane of the specimen, but with a relative displacement of the two layers by a distance  $D$  along  $X$ . In this case, the two divergence functions will have the form

$$\omega_1(x') = b' \sin x' \tag{1a}$$

$$\omega_2(x') = b' \sin(x' - D) \tag{1b}$$

Clearly, a realistic description of any through-thickness variations in the structure would need to be continuous,

but the qualitative conclusions drawn from this two-layer model can readily be extended.

To predict the appearance of the superimposed layers in the optical microscope, it is necessary to resolve the incident beam along the vibration directions of the first layer, and to calculate the effect which passing through this layer has on the two rays. The rays are then both resolved along the vibration directions of the second layer, before, finally, the effect of the analyser on the total transmitted intensity can be found<sup>10</sup>. The geometry of the problem is shown in Figure 3 with  $\omega_1$  and  $\omega_2$  defined relative to some arbitrary reference direction. The calculation shows that the total transmitted intensity is a minimum when

$$\omega = \frac{\omega_1 + \omega_2}{2} \quad (2)$$

where  $\omega$  is the angle between the polarizer and the chosen reference direction. Using the explicit forms for  $\omega_1$  and  $\omega_2$  (equations (1a) and (1b)) equation (2) shows that dark bands will occur at positions  $x'$  such that

$$\begin{aligned} \omega(x') &= \frac{b' \sin x' + b' \sin(x' - D)}{2} \\ &= b' \cos \frac{D}{2} \sin \left( x' - \frac{D}{2} \right) \end{aligned} \quad (2a)$$

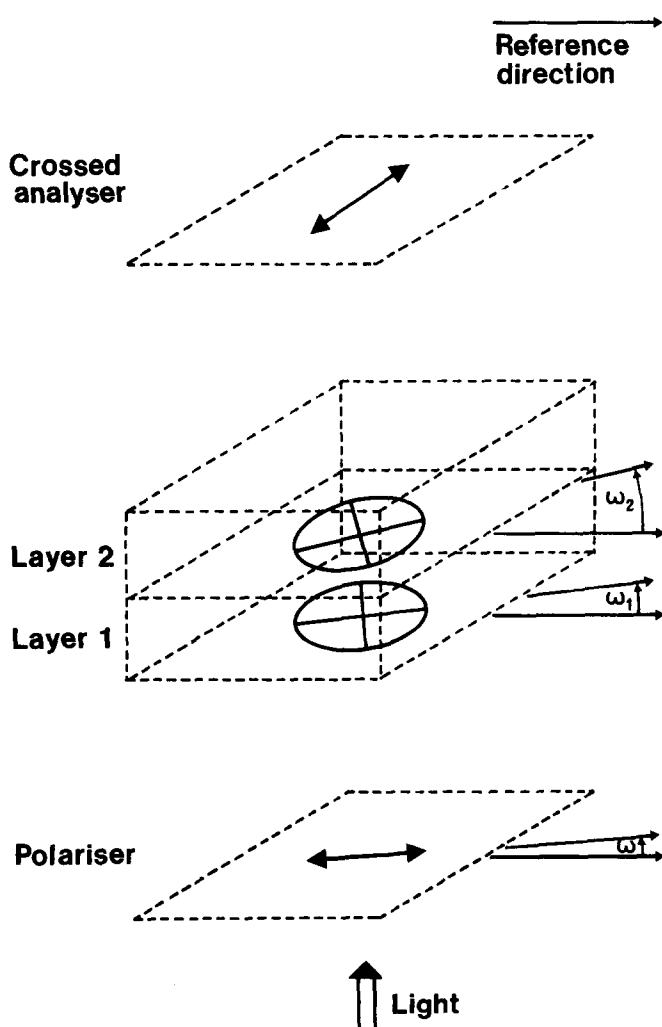


Figure 3 Defining the angles referred to in equation (2)

$$= b'' \sin x''$$

where  $b'' = b' \cos \frac{D}{2}$  and  $x'' = x' - \frac{D}{2}$

Thus a sinusoidal divergence function will still be observed, but with the maximum measured divergence angle,  $b''$ , smaller than the true maximum value  $b'$ . However, the period of the variation remains unchanged. This argument can be extended (see Appendix) to a multilayer structure, i.e. a structure with an essentially continuous displacement function  $D(z)$  through the thickness ( $z$ ) of the specimen, with the same result that any measured maximum value of  $\omega$  must be a lower bound on  $b'$ .

Several pieces of evidence have been assessed in determining whether or not any through-thickness variations are occurring in the specimens of B-ET under discussion. Since the apparent  $b''$  value will decrease as the number of layers increases (equation (A1)), the measured maximum divergence angle should be thickness-dependent (especially in the thinnest regions), if the specimen has this type of structure. There is no evidence for such a dependence from the optical microscopy measurements. Strong support is provided by TEM. Regions suitable for electron diffraction analysis have thicknesses of 1000 Å or less, i.e. the thickness is much less than the period of the banded texture in B-ET (a few  $\mu\text{m}$ ), and hence a superposition of layers is unlikely. Nevertheless, as will be shown by the analysis below (Figure 6d), the spread of in-plane orientations present ( $\pm 35^\circ$ ) agrees closely with the maximum divergence angle measured optically ( $\pm 37^\circ$ ). Again, therefore, there is no evidence to indicate significant through-thickness variations in the structure.

A final demonstration of the absence of layering is afforded by the observation that all areas of the sheared specimens show extinction in white light for some orientation of the crossed polars. Individual layers would be linearly birefringent, having two mutually perpendicular directions along which linearly polarized light can be transmitted without a change in polarization state. The combination of several superimposed linearly birefringent retardation elements of different optical orientations can in general be modelled by superimposing a single linearly birefringent element and a single pure rotator<sup>11,12</sup>. This in turn is equivalent to an elliptically birefringent unit<sup>13</sup>. If linearly polarized light is incident on such a unit, its polarization state will always be altered, whatever the angle between the preferred direction of the polarizer and any reference direction on the birefringent unit<sup>14</sup>, so that extinction is not obtained if the light is subsequently passed through a linear analyser which is crossed relative to the polarizer. In the limiting case of infinitesimally thin layers, with adjacent layers having only a small difference in optical orientation (i.e. the structure is continuously but gradually twisted in any through thickness section), the phenomenon of 'guiding' occurs<sup>15,16</sup>. If linearly polarized light is incident on the bottom surface of such a specimen, the emergent light consists of two linearly polarized components, having the orientations of the local principal vibration directions at the top. Thus the only way that extinction can occur between crossed polars in white light and under conditions of guiding, is for the top surface of the specimen to have an optical orientation differing by an exact multiple of  $\pi$  from that of the bottom layer; given the

method of preparation, there is no reason to suppose that this is the case for the specimens under investigation in this study. The conclusion must therefore be that no significant through-thickness variation of optical orientation occurs in these specimens.

Because of the fine spacing of the bands, it is necessary to consider whether the microscope provides sufficient resolution for a sinusoidal divergence function to be distinguished from one having a different profile. The divergence function plotted in *Figure 2* was obtained from a specimen having a band spacing of  $4\ \mu\text{m}$ . Sheared specimens of B-ET have in fact been produced with band spacings of down to  $0.6\ \mu\text{m}$ , the finer spacings generally being associated with the thinner specimens required for TEM. In all cases, the conoscopic image never showed maxima higher than first order. A non-sinusoidal optical divergence function would necessitate the existence of higher-than-first order components in the Fourier transform (optical diffraction pattern or conoscopic image). In particular, a significant third order should be necessary to produce the 'flat-topped' divergence function required for compatibility with the electron diffraction results to be discussed in the next section. The polarized light microscopy was carried out using an oil immersion lens having a numerical aperture (NA) equal to 1.3, i.e.  $NA = \mu \sin a = 1.3$ , where

$$\begin{aligned} \mu &= \text{refractive index of immersion oil} \sim 1.4 \\ a &= \text{maximum acceptance angle of lens.} \end{aligned}$$

Since the specimen has the geometry of a one dimensional diffraction grating, the equation

$$n\lambda = d \sin \theta$$

applies, where the various terms have their usual meanings in this context.

The highest order which can occur in the conoscopic image corresponds to  $\theta = a$ .

$$\text{i.e. } n\lambda = d \sin a = \frac{1.3d}{\mu}$$

$$\text{or } n = \frac{1.3d}{\mu\lambda} \sim 7 \text{ for } \lambda = 530 \text{ nm (green) and } d = 4\ \mu\text{m}$$

The microscope therefore has sufficient resolving power to detect as high as seventh order maxima in the conoscopic image if the band spacing is  $4\ \mu\text{m}$ . If the band spacing is only  $0.6\ \mu\text{m}$ , only first order maxima are detected. Since we shall be comparing optical results derived from specimens having a  $\sim 4\ \mu\text{m}$  band spacing with TEM results derived from specimens having a  $\sim 1\ \mu\text{m}$  band spacing, we need an independent indication that the molecular orientation is similar in both types of specimen. An X-ray microbeam camera was used to obtain diffraction patterns from both coarsely and finely banded specimens. *Figure 4* shows that there is little difference between the diffraction patterns, and that in each case the main interchain arc peaks strongly on the equator and not on either side of it.

Having established the absence of superposition in the microstructure, and that sufficient optical resolving power is available to reveal higher harmonics of the optical divergence function, it is necessary to consider how this function is related to the molecular trajectory.

Assuming for the present the identity of the optical director with the molecular axis, one can use the measured divergence function to determine the molecular trajectory,  $y(x)$  relative to the shear direction. At each point the relationship is given by

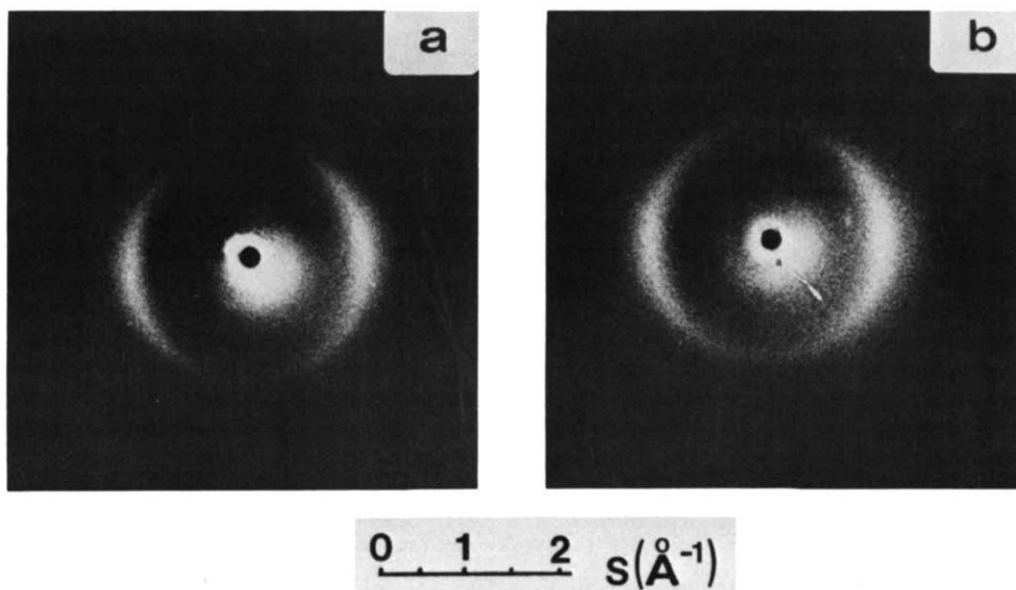
$$\frac{dy}{dx} = \tan \omega \quad (3a)$$

Hence

$$y(x) = \int \tan(b \sin x) dx$$

To simplify the evaluation of this integral, equation (3a) can be rewritten as

$$y(x) = h(x) + C \quad (3b)$$



**Figure 4** X-ray diffraction pattern of sheared B-ET specimens, obtained with a microbeam camera: (a) bands spaced by  $\sim 4\ \mu\text{m}$ ; (b) bands spaced by  $\sim 1\ \mu\text{m}$ . The peaks shown are equatorial; the meridional and other equatorial peaks are very weak in comparison.  $s = 4\pi \sin \theta / \lambda$

where  $C$  is a constant. The form of  $\omega(x)$  suggests that  $y(x)$  is antisymmetric about  $x = \pi/2$ , i.e.  $y(x) = 0$  at  $x = \pi/2$ . This can be achieved if

$$h(x) = \int_0^x \tan(b \sin x) dx \quad (4a)$$

and

$$C = - \int_0^{\pi/2} \tan(b \sin x) dx \quad (4b)$$

This yields

$$y(x) = \int_{\pi/2}^x \tan(b \sin x) dx \quad (5)$$

This integral representation for  $y(x)$  can be evaluated by using the Maclaurin expansion for  $\tan$ , and integrating the resulting series term by term. In carrying out this integration, sufficient terms were taken into account to reduce the error to less than 0.03%. Figure 5 shows the form for  $y(x)$  calculated from equation (5), with  $b = 0.1$  and  $b = 0.65$ . For comparison, cosine curves having the same amplitude and period as these curves are superimposed. From Figure 5 it can be seen that the deviation from a true sinusoidal variation for the molecular trajectory is small for these values of  $b$ . Since  $b \sim 0.65$  for B-ET, it follows that  $y(x)$  will be very close to a sine curve for this polymer.

Comparison with detailed electron diffraction results

If a uniform packing density of molecules in the specimen is assumed, the number of molecules inclined at

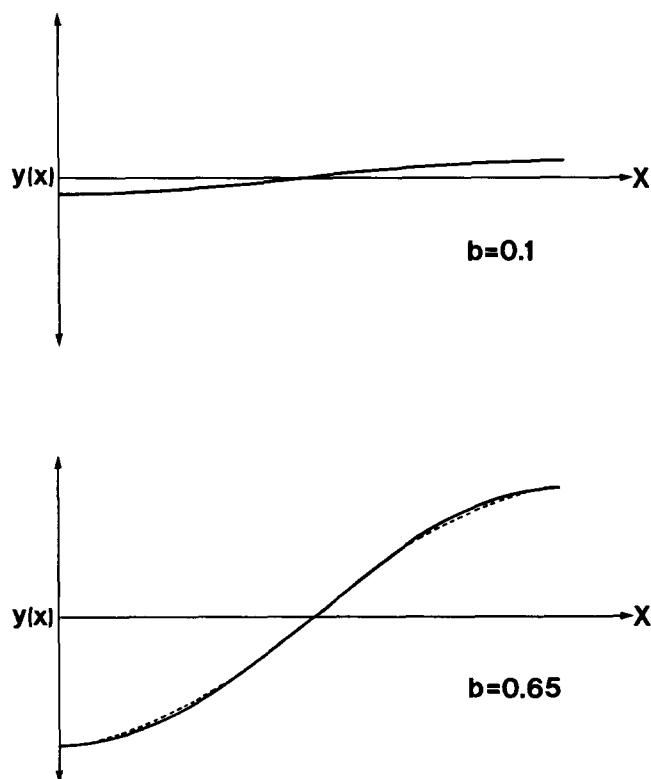


Figure 5 Two plots of  $y(x)$ , as defined by equation (5), versus  $x$ . The broken curves are cosine functions, having the same amplitude and period as the  $y(x)$  vs.  $x$  plots

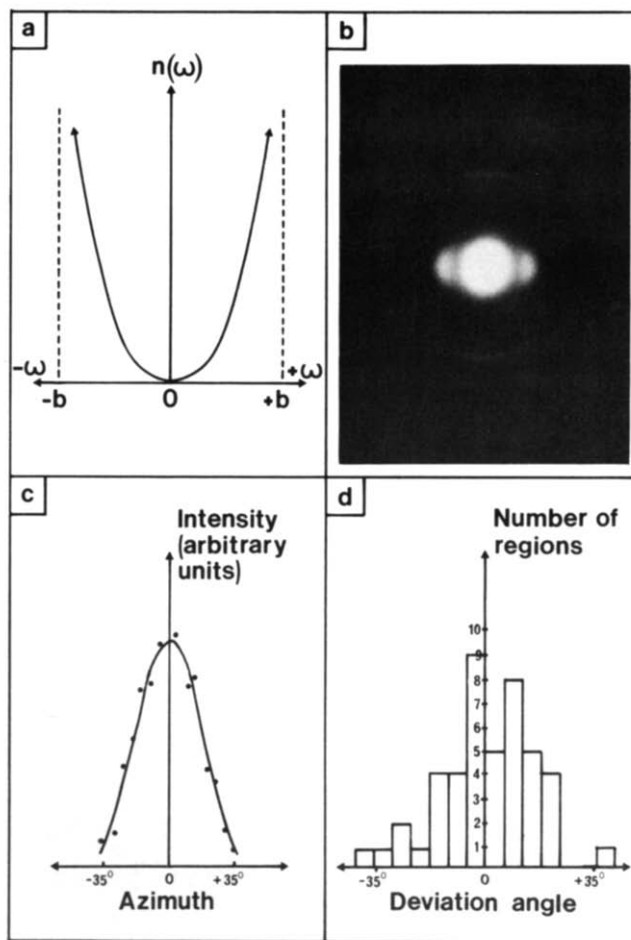


Figure 6 (a) Number density  $n(\omega)$  of molecules as a function of  $\omega$ , for a sinusoidal divergence function. (b) Electron diffraction pattern of B-ET. The shear direction is vertical. (c) Microdensitometry profile of equatorial reflection in electron diffraction pattern of B-ET. (d) Histogram of the number of regions randomly sampled, which possess a deviation angle of  $a$  of the local orientation axis from the overall shear direction, ( $a = 0$ ), obtained from microdiffraction patterns of B-ET

angles between  $\omega$  and  $(\omega + d\omega)$  is proportional to the distance  $dx$  along the shear axis over which this range of angles occurs. This means that for a sinusoidal divergence function the density distribution of molecules as a function of  $\omega$ ,  $n(\omega)$ , can be calculated<sup>9</sup>:

$$n(\omega) \propto \frac{1}{\sqrt{b^2 - \omega^2}} \quad (6)$$

The form of this function is shown in Figure 6a; it has a maxima as  $\omega \rightarrow \pm b$ , and a minimum at  $\omega = 0$ . This implies that there are fewest molecules actually lying along the shear direction  $X$ .

As a consequence of the form of  $n(\omega)$ , it is to be expected that the electron diffraction pattern, which is governed by the orientations present in the sample, will have intensity maxima at the two wings of the equatorial reflection and minimum intensity at the centre. Microdensitometry of the equatorial reflection of B-ET—the electron diffraction pattern is shown in Figure 6b—has been performed to examine the intensity profile; this is shown in Figure 6c. It can be seen that it in no way resembles Figure 6a. On the contrary, it is sharply peaked for orientations corresponding to alignment with the shear direction. The width of the reflection agrees well with the maximum optically-

determined divergence angle of  $37^\circ$ , as discussed above, although the high background intensity in this part of the diffraction pattern makes it impossible to define the width precisely. A similar analysis has previously been performed on a second thermotropic polymer designated B-N (based on hydroxybenzoic and hydroxynaphthoic acid residues) which also shows banded textures<sup>9</sup>, and an intensity profile of similar shape was obtained.

As discussed in ref. 9, several reasons for this discrepancy can be put forward. As was the case for B-N, microdiffraction techniques<sup>9,17</sup> can be used to eliminate the possibility of significant beam damage affecting the polymer during the time required to record the diffraction pattern. Microdiffraction permits random sampling of the local molecular orientation axis (as measured from diffraction patterns obtained from regions  $\sim 150$  nm in diameter) relative to the shear direction  $X$ . A histogram of the number of regions which possess a given misorientation angle can then be plotted, as shown in *Figure 6d*. It is clear that the form of this closely resembles *Figure 6c* but not *Figure 6a*. Beam damage, although possibly affecting the total spread of the equatorial arc in a given microdiffraction pattern, cannot affect the direction of the local orientation axis. Thus the similarity of *Figures 6c* and *6d* confirms that beam damage does not give rise to the discrepancy between the optical microscopy and electron diffraction results.

The electron diffraction data demonstrates that the molecular trajectory must be significantly flatter than a sine curve (i.e. the majority of molecules point along the shear direction), whereas the optical microscopy indicates that the optical director varies sinusoidally. The conclusion that this leads to is that the assumption of an exact equivalence between the optical director and the molecular long axis cannot be correct. It is of course possible that the structure in regions thin enough for electron microscopy ( $< 1000$  Å) may differ from that in regions thick enough to give optical contrast ( $\sim 5$   $\mu$ m). That this is not in fact the case is demonstrated by the X-ray microbeam diffraction patterns shown above in *Figure 4*. Comparison with *Figure 6b* shows the patterns to be essentially similar; the slightly poorer orientation in *Figure 4* is believed to be due to small variations in the local shear direction across the  $75$   $\mu$ m region from which each X-ray diffraction pattern was recorded.

At this stage, therefore, further experiments have to be considered in an effort to resolve the anomaly.

#### *Periodic variations in optical properties*

It is known that the banded texture can be seen, albeit faintly, using Zernike phase contrast<sup>4</sup>. This suggests that the variation in the optical director is not precisely confined to a plane but that it has a through-thickness component which varies with position along the shear direction. One simple model, which would allow for such an out-of-plane component, is to consider the optical director as following a helical rather than a sinusoidal path. Since a helix would project onto the specimen plane as a sine curve, such a model would be consistent with the observed divergence function. However, a helical model would also predict a maximum in  $n(\omega)$  at the two limits of  $\omega$ , and thus cannot resolve the discrepancy.

As mentioned in the Introduction, the incompatibility of optical microscopy with X-ray diffraction data for B-ET has previously been noted<sup>6,7</sup>. The tentative expla-

nation for this effect is that the polymer is not uniaxial. If the optical properties of the material are described by a biaxial indicatrix, then the principal vibration directions at any point may be decoupled from the molecular axis. Biaxiality could arise from rotational correlation of the phenyl rings. That such rotational correlation may occur, has also been suggested by a detailed analysis of X-ray scattering data of B-ET<sup>18</sup>.

If these rotational correlations are present, one possible direct consequence might be some systematic variation in the birefringence of the polymer, in step with the banded texture: the birefringence due to a phenyl ring 'edge on' will be higher than when it is viewed normal to its plane. Measurements of the birefringence were made at positions of a maximum in the divergence function ( $\omega = b$ ), and also where  $\omega = 0$ . It was found that  $\Delta n = 0.036 \pm 0.003$  (10 readings) where  $\omega$  was a maximum, and  $\Delta n = 0.059 \pm 0.004$  where  $\omega = 0$ . The existence of a periodic variation in birefringence along the shear direction can also be demonstrated by setting the microscope up as a 'circular polariscope'<sup>19</sup>: specimens are placed between quarter wave plates having appropriate optical orientations relative to the polarizer and analyser. The periodic variation in birefringence has been thus observed as an equivalent variation in interference colour, with the intensity being independent of the orientation of the specimen relative to the crossed polars.

It is now necessary to consider the structural implications of the 40% variation in birefringence which is periodic with the banded texture.

Firstly, the birefringence changes could represent an out-of-plane component of the divergence function. Returning to the simple helical model, in which the angle subtended to the shear direction is everywhere constant: the in-plane component is minimised where the out-of-plane component will be a maximum, corresponding also to positions where  $\omega = 0$ . This can only lead to a reduction in the birefringence in such regions (assuming optical uniaxiality) and thus cannot explain the observations.

Secondly, it is possible that the periodic birefringence variation is associated with the presence of rotational correlations about the molecular long axes which are synchronous with the changing molecular orientation. If possible out-of-plane effects are excluded for the moment, the data would suggest that the phenyl rings are 'edge on' where  $\omega = 0$ , and flat where  $\omega$  is a maximum. How might such rotational correlation between the phenyl rings affect the electron scattering giving rise to the diffraction patterns? Scattering might be expected to be strongest where phenyl rings are stacked face to face (i.e. the scattering vector is perpendicular to the phenyl ring) and weaker where they are side by side. The effect of this would be to enhance the scattering when the electron beam is parallel to the plane of the phenyl rings relative to positions where it is perpendicular. In turn this implies increased scattering where  $\omega = 0$ , relative to other positions, exactly as is observed in the profile of the main interchain arc.

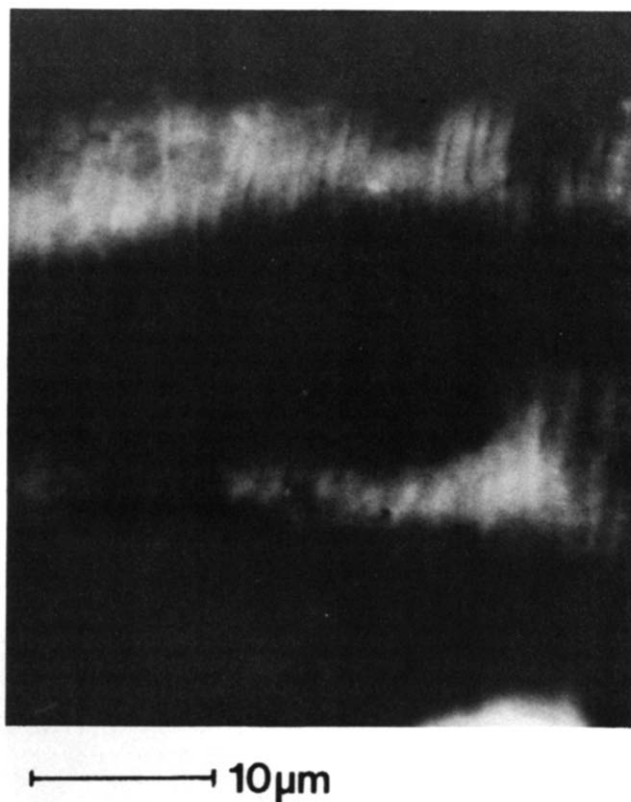
The presence of rotational correlations of the phenyl rings, such that their common plane twists with the molecular backbone, will therefore have two consequences. The molecular director need not be sinusoidally-varying, although the divergence function measured by optical microscopy is, and the intensity at different orientations within the equatorial reflection will

not have an exact correspondence with the number of molecules possessing this orientation (implying a scattering factor varying with orientation). From this it is clear that if such twisting of the plane of the phenyl rings is occurring, neither the optical measurements nor the intensity profile of the diffraction pattern will directly indicate the molecular trajectory; thus their incompatibility is not surprising. It is felt that the flatter-than-sine-curve obtained from the diffraction analysis is a closer representation of the molecular trajectory, because of the similarities in form of *Figure 6c* and *Figure 6d*. Variations in intensity with orientation cannot affect the analysis of *Figure 6d*, thus removing the uncertainty discussed above for the azimuthal profile of the equatorial peak.

Finally, for continuous molecules, a constant flux per unit cross-sectional area implies closer packing where  $\omega$  is a maximum compared with where  $\omega=0$ . The effect is readily illustrated by examining an edge-on view of stacked corrugated roofing sheet, where there will be no contact at the peaks or troughs. Segregation of molecular ends would be able to compensate for the variation in packing density. Furthermore the fact that the birefringence and the intensity of equatorial electron scattering are strongest where  $\omega=0$  would not support a model of a periodic reduction in packing density, even if it were possible in energetic terms.

#### The out-of-plane component

Although it does not explain the sign of the observed periodicity in birefringence when referred to a simple helical model for the molecular trajectory, the possibility of an out-of-plane component for the molecular trajectory remains. It has recently been shown that electron microscopy can be used to examine variations in this out-of-plane component<sup>20,21</sup>. As the molecular orientation deviates from lying within the specimen plane, the scattering cross section for electrons increases, causing increased scattering out of the objective aperture for bright field images. Consequently, regions with a significant out-of-plane component appear darker than neighbouring regions where the molecules lie in the specimen plane. Where only small variations are occurring the contrast can be maximised by tilting the specimen in the microscope about an axis perpendicular to the shear direction. *Figure 7* shows such a tilted bright field image of B-N, where a faint banding is apparent, confirming the existence of an out-of-plane component (contrast due to changes in specimen thickness can be eliminated by viewing at normal incidence<sup>8</sup>). The recording of micrographs such as *Figure 7* is complicated by the occurrence of beam damage, which may itself introduce contrast related to the underlying banded structure. *Figure 8* shows a dark field micrograph (objective aperture placed over one wing of the equatorial arc), and a bright field image of the same area obtained after significant beam damage has occurred. Banding is now clearly apparent in the bright field image, although the period is half that of the original dark field image. Analogous beam damage-induced contrast changes are well known in e.g. polyethylene spherulites<sup>22,23</sup>. The origin of the contrast for irradiated spherulites lies in a systematic variation in the inclination of the *c* axis of the unit cell as the spherulite is traversed, i.e. in a variation in molecular inclination to the specimen plane. Such an explanation for B-N is consistent with a



**Figure 7** Tilted bright field TEM image of B-N obtained by tilting the specimen by 42° about an axis perpendicular to the shear direction

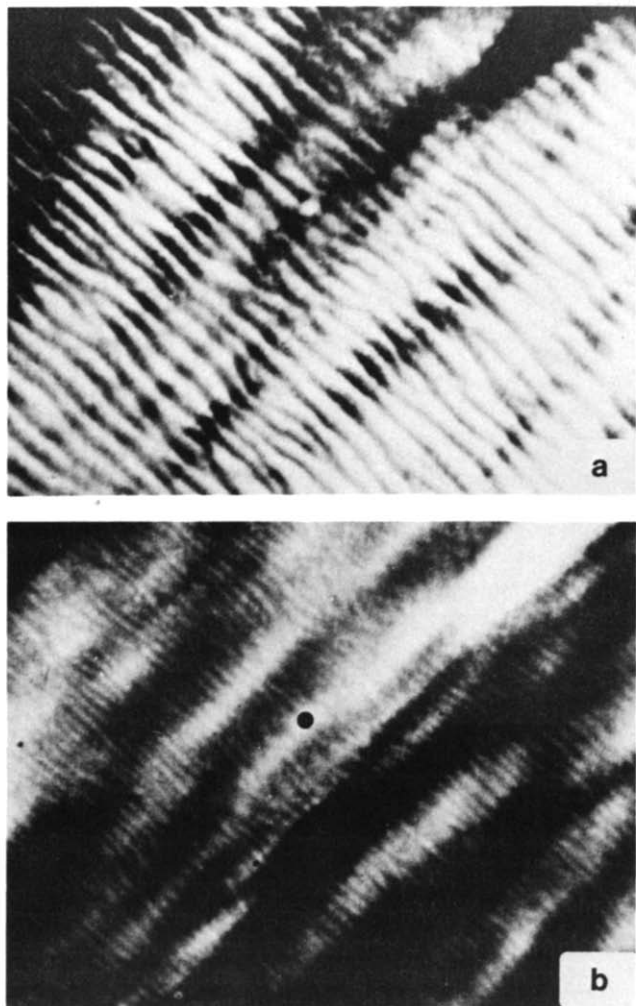
periodic variation in the out-of-plane component of the molecular trajectory accompanying the bands and being enhanced by radiation damage; the halving of the period in *Figure 8b* arises because the bright field image is sensitive only to the absolute magnitude of the out-of-plane component whereas the dark field micrograph distinguishes the sign of the divergence angle from the shear axis. Correlating pairs of micrographs such as *Figures 8a* and *8b* appears to indicate that a maximum out-of-plane component occurs at a minimum in  $\omega$ .

The observation of banding under conditions of Zernicke phase contrast in the optical microscope implies only that refractive index variations are present. These may arise from an out-of-plane component of the optical director, from rotational correlations, or from a combination of these two effects. Invoking the third dimension alone, although consistent with the TEM results, cannot explain the coupling of a maximum in  $\Delta n$  with a minimum in  $\omega$ . Conversely, it seems improbable that rotational correlations alone are responsible for the beam damage-induced contrast seen in the TEM. It therefore seems likely that both effects are present. While a consistent picture, reconciling optical and electron microscopy measurements of the divergence function qualitatively, can be obtained by postulating the existence of rotational correlations, this does not of itself constitute proof of their existence. It nevertheless provides strong additional support for them.

#### CONCLUSIONS

The form of the divergence function in B-ET, deduced from optical microscopy of the shear-induced banded structure, suggests a near-sinusoidal molecular trajectory.





5 μm

**Figure 8** (a) Dark field TEM micrograph (objective aperture positioned over one wing of the equatorial arc) of B-N sheared at 300°C. (b) Bright field image of the same area after the occurrence of substantial beam damage

The orientation of the optical director is approximately constant through the specimen thickness. However, a sinusoidal molecular trajectory is not immediately compatible with selected area electron diffraction results. A tentative explanation is that, for these polymers, lateral rotational correlation of the molecules occurs about their local chain axes and that the correlated molecules twist about the chain axis in step with the period of the banded texture. The study further supports the view that the molecular axis cannot be taken as being synonymous with the local optical director.

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#### APPENDIX

Form of observed divergence function when a sheared specimen consists of a large number of optically identical layers, each being displaced along the shear direction ( $X$ ) by an identical amount relative to the layer below.

Let the specimen consist of  $2^n$  optically identical slices, with the top slice displaced a distance  $D$  along  $X$  relative to the bottom slice.

The relative displacement of adjacent slices is  $\frac{D}{2^n - 1}$ .

There are  $2^{n-1}$  pairs of slices. Consider the pair which have displacements

$$\frac{mD}{2^n - 1} \quad \text{and} \quad \frac{(m+1)D}{2^n - 1}$$

relative to the bottom layer ( $m$  an integer).

The divergence functions for these two layers will have the form:

$$\omega_m(x') = b' \sin \left[ x - \frac{mD}{2^n - 1} \right]$$

and

$$\omega_{m+1}(x') = b' \sin \left[ x - \frac{(m+1)D}{2^n - 1} \right]$$

by analogy with equations (1a) and (1b).

The two layers can be regarded as a single optical unit. Viewed between crossed polars, this will give minimum transmitted intensity when  $\omega$ , the angle between  $X$  and the polarizer, satisfies equation (2).

$$\begin{aligned} \text{i.e. } \omega &= \frac{1}{2} \left\{ b' \sin \left[ x - \frac{mD}{2^n - 1} \right] + b' \sin \left[ x - \frac{(m+1)D}{2^n - 1} \right] \right\} \\ &= \frac{b'}{2} \left\{ 2 \sin \frac{1}{2} \left[ 2x - \frac{(2m+1)D}{2^n - 1} \right] \cos \frac{1}{2} \left[ \frac{D}{2^n - 1} \right] \right\} \end{aligned}$$



$$= b' \left\{ \sin \left[ x - \frac{(2m+1)D}{2^{n+1}-2} \right] \cos \left[ \frac{D}{2^{n+1}-2} \right] \right\}$$

There are  $2^{n-1}$  such units in total. So the original  $2^n$  units can be combined into  $2^{n-1}$  units; the periodicity of the banded structure which would be associated with any of the  $2^{n-1}$  units is the same as that which would be associated with any of the original  $2^n$  units (though the position of the bands relative to an absolute reference point would be different). However, the original maximum divergence angle  $b'$  has now become  $b' \cos \frac{D}{2^{n+1}-2}$ .

The above process of combining layers has to be performed  $n$  times in order to generate a single optical unit which is equivalent to the  $2^n$  original units.

It follows from the case of  $2^n \rightarrow 2^{n-1}$  units that the

spacing of bands will be unchanged by combining layers in this way.

However, the final maximum observed divergence angle will be described by a product of the form

$$b_{\text{observed}} = b' \cos \frac{D}{2^{n+1}-2} \cdot \cos \frac{D}{2^n-2} \cdot \cos \frac{D}{2^{n-1}-2} \cdots \cos \frac{D}{2^2-2} \tag{A1}$$

This result shows that the maximum observed divergence angle will depend on the number of layers being looked at, and that it will decrease as the specimen thickness increases. This will be most noticeable in the thinnest regions of the specimen, since

$$\cos \frac{D}{2^r-2} \rightarrow 1 \quad \text{as} \quad r \rightarrow \infty$$