On predicting the optical diffraction pattern from thermotropic specimens having a banded texture

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Specimens of a sheared and annealed thermotropic copolyester were examined in the polarizing microscope. The optical diffraction pattern associated with the periodic microstructure (banded texture) was observed in the objective back focal plane. The significant features of the diffraction pattern can be predicted analytically in terms of the in-plane periodic variation of optical orientation in the specimen. We explain how the relative intensities of the different diffracted orders depend on the orientation of the crossed polars relative to the specimen shear direction. For specimens in which the optical orientation varies sinusoidally with position along the unique axis, we derive the diffraction pattern exactly, and we explain why second and higher orders are not normally observed.

(Keywords: banded texture; optical diffraction pattern; Fourier transform; crossed polars; liquid crystalline polymers)

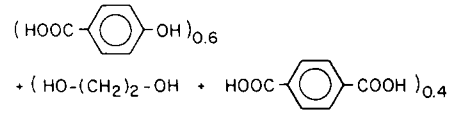
INTRODUCTION

It is a widely documented fact that both lyotropic and thermotropic liquid crystalline polymers can show a microscopic banded texture after shearing, especially if viewed between crossed polars[1–8]. Progress has been made in relating the observed microstructure to the appearance of the optical diffraction pattern as seen in the objective back focal plane when using a Bertrand lens[2,4]. In particular, explanations have been sought to account for the absence of a zero order in the diffraction pattern when the shear axis is parallel to the transmission direction of either polar. These analyses have however been almost entirely qualitative, and they have not addressed the possibility of second or higher orders. Indeed, these have not been observed, either because the microstructure is so fine that orders higher than first cannot be accommodated by the objective aperture (e.g. in the case of 'Kevlar' [Du Pont trademark]), or because the particular form of the one-dimensional periodicity of intensity in the microstructure is such that higher orders are too weak (e.g. in the case of many as-sheared thermotropic copolyesters).

In the present study, we identify banded textures which give second and third orders (as well as zero and first) in the optical diffraction pattern. A generalised method is developed to predict the intensities of all the diffracted orders, as a function of crossed polar rotation, for a specimen having one-dimensional periodicity in its optical texture.

EXPERIMENTAL

Specimens were prepared from the following random copolyester:



Material was sheared at 250°C, between glass microscope slides. It was held at this temperature for 5 h before being quenched to room temperature on a copper block. The specimens were examined and photographed (*Figure 1*) between crossed polars in a Carl Zeiss (Jena) microscope. The corresponding optical diffraction patterns (*Figure 2*) were imaged in the same instrument with the help of a Bertrand lens. All observations were made in *white* light, and the specimens were thin enough that all contrast was between black and low-order whites.

The optical diffraction patterns show four clear orders (0 to 3), though not all are visible at all rotations of the crossed polars (*Figure 2*). When the transmission direction of either polar is parallel to the shear direction, only the first and third orders are visible. Their intensity decreases, and that of the zero and second increases, as the crossed polars are rotated away from this orientation. When the specimen is in the 45° orientation between the crossed polars, only the latter two orders can be seen.

This behaviour of the bands as the crossed polars are rotated is similar to that documented[4,7] for specimens of the same polymer quenched directly after shear; this indicates that the orientation of the in-plane components of the principal axes of the optical indicatrix changes periodically as a function of position measured along the shear direction. However, whereas this variation was near-sinusoidal in the sheared and quenched specimens, *Figure 1* is more suggestive of a symmetrical sawtooth function for the sheared, annealed and quenched material.

ANALYSIS AND DISCUSSION

Consider a region of specimen in which the optical director is at an angle ϕ relative to the polarizer transmission direction. Let the specimen be observed between crossed polars. The locally transmitted amplitude is described by the following standard

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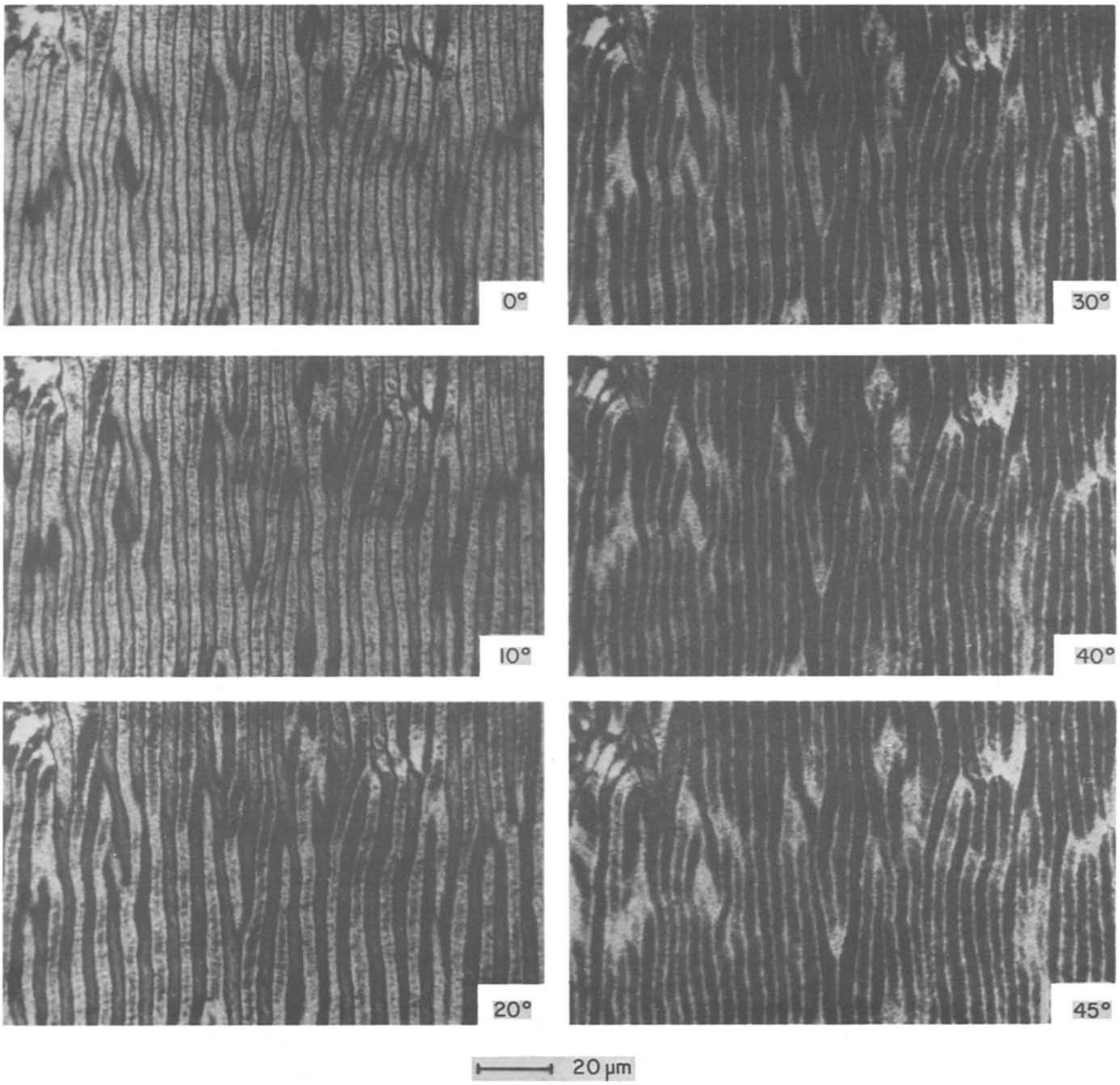

Figure 1 Specimen of sheared and annealed thermotropic copolyester, photographed at room temperature between crossed polars. The six micrographs show the same field of view. Initially, the transmission direction of the polarizer was parallel to the specimen shear direction (left to right); the angle through which the crossed polars were rotated (anticlockwise) from this orientation is marked on each frame

equation[4,9]:

$$A=\left[\frac{A_0}{2}\sin 2\phi\right][\exp i\omega t-\exp i(\omega t-\delta)]$$

where A_0 = incident amplitude and δ = phase lag which the specimen introduces between the components of light travelling along the two vibration directions.

Let the specimen have a variation in optical orientation relative to a reference axis X (the shear direction), and let this variation be periodic with position measured along X. The specimen is defined as being in the 'orthogonal position' when X is parallel to the transmission direction of the polarizer. A 'divergence function' $f(x)$ then describes how ϕ varies with position x measured along X; it need not necessarily have the sinusoidal form deduced for sheared thermotropic liquid crystal polymer specimens in previous studies[4,7].

The transmitted amplitude, as a function of x when the specimen is viewed in the orthogonal position between crossed polars, is now:

$$A(x)=\frac{A_0}{2}\{\sin 2f(x)\}\{\exp i\omega t-\exp i[\omega t-\delta(x)]\}$$

In writing δ as a function of x, we recognize that the birefringence of the sample may also vary periodically with x (ref. 7), and that there may be variations in thickness too.

If the crossed polars are rotated by θ relative to the orthogonal position, then $\phi=f(x)+\theta$, where f and θ are measured in the same sense relative to X. The transmitted amplitude, in the most general case, is then:

$$A(x)=\frac{A_0}{2}\{\sin 2[f(x)+\theta]\}\{\exp i\omega t-\exp i[\omega t-\delta(x)]\} \quad (1)$$

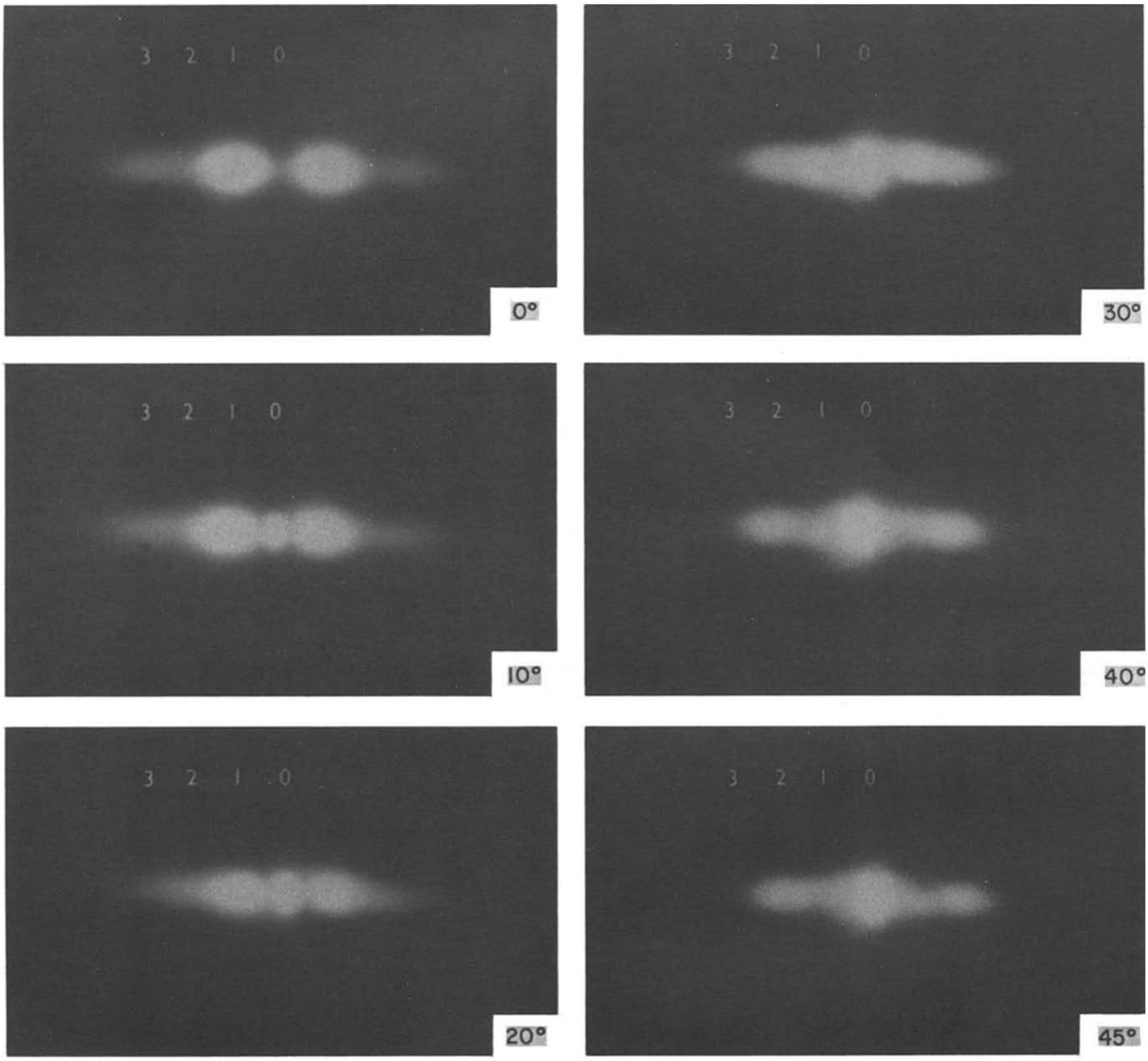

Figure 2 Optical diffraction patterns corresponding to the six micrographs in *Figure 1*. They were imaged by using a Bertrand lens to access the back focal plane of the microscope objective. White numerals are used to indicate the orders to which particular diffraction maxima belong

The amplitude distribution in the back focal plane of the objective (for an infinite object) is now found by calculating the Fourier transform of equation (1):

$$A(k)=\int_{-\infty}^{\infty}\frac{A_0}{2}\{\sin 2[f(x)+\theta]\}\times\{\exp i\omega t-\exp i[\omega t-\delta(x)]\}\{\exp ikx\}\mathrm{d}x \tag{2}$$

where k is a measure of position in the back focal plane of the objective, measured along a direction K in reciprocal space. K is parallel to X. If $A'(k)$ denotes the complex conjugate of $A(k)$, the quantity $A(k).A'(k)$ gives the corresponding intensity variation as a function of position in the back focal plane—in other words, it describes the optical diffraction pattern of the specimen. (It has become practice to refer to this synonymously as the 'conoscopic image', though the latter term should strictly be reserved for the case where the optical diffraction pattern of a (single crystal) specimen is being viewed in *convergent* light). The optical diffraction pattern of the specimen, as recorded on photographic film or the retina of the eye, contains no information about the relative phases of the constituent orders. If one were to Fourier transform this recorded pattern, one would consequently obtain the autoconvolution of the original object function. The Fourier transform of the recorded diffraction pattern would therefore necessarily always be centrosymmetric, regardless of whether or not there is a centre of symmetry in the object.

In equation (2), the quantity $\delta(x)$ can be written as:

$$\delta(x)=\frac{2\pi d(x)}{\lambda}[\mu_{\max}(x)-\mu_{\min}(x)]$$

where $d(x)$ = specimen thickness at position x; μ = refractive index, measured along a vibration direction at position x; λ = wavelength of light incident on specimen.

It therefore follows that the amplitude (and intensity) distribution *in the objective back focal plane* may not simply depend on the in-plane component of the divergence function. It may also be affected by any out-of-plane component, by any spatial variation in the local molecular correlations, and by any variation in thickness. For the purpose of this initial analysis, equation (2) can be simplified by *ignoring* any point-to-point changes in relative phase which the specimen may introduce into the light that it transmits. In practice, this requires a specimen of constant thickness, sufficiently thin to exhibit only low-order interference colours. Provided that any birefringence variations have the same spatial periodicity as the divergence function, their effect would be to modify the relative *intensities* of the diffracted orders, rather than their positions in the objective back focal plane; this is a result fundamental to the operation of blazed optical diffraction gratings[10].

Hence, treating the specimen as an amplitude object only, we can write equation (2) in the following simplified form:

$$A(k)=C\int_{-\infty}^{\infty}\{\sin 2[f(x)+\theta]\}\{\exp ikx\}\mathrm{d}x$$

where C is a constant

$$=C\cos 2\theta\int_{-\infty}^{\infty}[\sin 2f(x)][\exp ikx]\mathrm{d}x$$

$$+C\sin 2\theta\int_{-\infty}^{\infty}[\cos 2f(x)][\exp ikx]\mathrm{d}x \qquad (4)$$

Both the integrals in equation (4) are the Fourier transforms of periodic functions. Furthermore, the divergence function $f(x)$ is itself periodic. For the sake of mathematical convenience, we choose x to be scaled so that the period of $f(x)$ is 2π.

Now $f(x)$ is antisymmetric about $x=0$ and symmetric about $x=\pi/2$. So $2f(x)$ and also $\sin 2f(x)$ are antisymmetric about $x=0$ and symmetric about $x=\pi/2$, and have a period of 2π.

In general, for any infinite periodic function $g(x)$,

$$\mathscr{F}[g(x)]=\mathscr{F}[g(x)+T],$$

where T is the period of $g(x)$. So

$$\int_{-\infty}^{\infty}[\sin 2f(x)][\exp ikx]\mathrm{d}x=\int_{-\infty}^{\infty}[\sin 2f(x+2\pi)][\exp ikx]\mathrm{d}x$$

Substituting $x+2\pi=z$ (i.e. $x=z-2\pi$ and $\mathrm{d}x=\mathrm{d}z$) gives:

$$\int_{-\infty}^{\infty}[\sin 2f(x)][\exp ikx]\mathrm{d}x$$

$$\equiv\int_{-\infty}^{\infty}[\sin 2f(z)][\exp ik(z-2\pi)]\mathrm{d}z$$

$$=[\exp(-2\pi ik)]\int_{-\infty}^{\infty}[\sin 2f(z)][\exp ikz]\mathrm{d}z$$

$$\equiv[\exp(-2\pi ik)]\int_{-\infty}^{\infty}[\sin 2f(x)][\exp ikx]\mathrm{d}x \qquad (5)$$

(Since we are dealing with a definite integral, the value does not depend on the variable used.)

Equation (5) can only be true if:

$$\int_{-\infty}^{\infty}[\sin 2f(x)][\exp ikx]\mathrm{d}x$$

is zero (or, in other words, if the Fourier transform of $\sin 2f(x)$ is zero), or if:

$$\exp(-2\pi ik)=1$$

(in which case the Fourier transform of $\sin 2f(x)$ can be non-zero).

It follows that non-zero solutions require:

$$-2\pi ik=2\pi im$$

where m is an integer. So

$$k=m \qquad (6)$$

We also know that $\sin 2f(x)$ is antisymmetric about $x=0$ and that it is symmetric about $x=\pi/2=T/4$. So all cosine components and all even sine components of its Fourier transform are zero[11]. Only odd orders will therefore be present in its Fourier transform, and equation (6) is reduced further to:

$$k=m,\ \text{where } m \text{ is an odd integer.} \qquad (7)$$

The values of k for which the second term of equation (4) is non-zero can now be found, by a similar argument to that used above for the first term. We have seen that $2f(x)$ is antisymmetric about $x=0$ and symmetric about $x=\pi/2$, with a period of 2π. Therefore, $\cos 2f(x)$ is symmetric about $x=0$. It has a period of π [rather than 2π as was the case for $\sin 2f(x)$], and it is neither symmetric nor antisymmetric about $x=\pi/4=T/4$.

By analogy with the derivation of equation (6), non-zero solutions require:

$$-\pi ik=2\pi im$$

where m is an integer. So

$$k=2m \qquad (8)$$

Since $\cos 2f(x)$ is symmetric about $x=0$, all sine components of its Fourier transform are zero[11]. However, it is neither symmetric nor antisymmetric about $x=\pi/4=T/4$, so that there are no further restrictions on equation (8).

The first term of equation (4) is non-zero if equation (7) is satisfied:

i.e. $k=\ldots, -5, -3, -1, +1, +3, +5, \ldots$

These solutions represent the odd-order maxima in the optical diffraction pattern. The second term of equation (4) is non-zero if equation (8) is satisfied:

i.e. $k=\ldots, -6, -4, -2, 0, +2, +4, +6, \ldots$

These solutions represent the even-order maxima in the optical diffraction pattern.

The $[\cos 2\theta]$ factor in the first term of equation (4) shows how the intensity of the odd orders depends on the orientation of the crossed polars relative to the orthogonal position. The intensity of these orders (proportional to $\cos^2 2\theta$) must be a maximum when $\theta=\pm n\pi/2$, and zero when $\theta=\pi/4\pm n\pi/2$ (where n is an integer). Similarly, the $[\sin 2\theta]$ factor in the second term of equation (4) explains the behaviour of the even orders: their intensity (proportional to $\sin^2 2\theta$) is zero when $\theta=\pm n\pi/2$, and it is a maximum when $\theta=\pi/4\pm n\pi/2$.

The intensities of the odd and even diffracted orders visible in *Figure 2* can be seen to follow this predicted behaviour qualitatively as the crossed polars are rotated. It is however not possible to *quantify* the absolute magnitudes of the intensities easily, since there is some overlap of intensity from the different orders. (The maxima are broadened because the object is of finite extent and not perfectly periodic.) Also, there is an indeterminate level of background scattering.

THE SPECIAL CASE OF A SINUSOIDAL DIVERGENCE FUNCTION

We turn now to the well-documented sinusoidal divergence function deduced for sheared thermotropic liquid crystal polymer specimens in previous studies[4,7]. The optical diffraction pattern of such specimens only ever showed detectable zero and first order maxima. In this case the divergence function can be written in the form: $f(x)\approx b\sin x$, where b is a constant.

The maximum possible amplitudes of the odd diffracted orders (i.e. their amplitudes when $\theta=n\pi/2$) are given by the Fourier coefficients of $[\sin 2f(x)]$, as implied by the first term of equation (4) and the results deduced in the previous section. To obtain the Fourier coefficients, we write:

$$\sin 2f(x)=\sum_{r=-\infty}^{\infty} C_r \exp(2\pi i r x/T)$$

where T is the period of $[\sin 2f(x)]$. The Fourier coefficients C_r are given by:

$$C_r=\frac{1}{T}\int_{-T/2}^{T/2}[\sin 2f(x)][\exp(-2\pi i r x/T)]\mathrm{d}x$$

From the derivation of equation (5), T is known to be equal to 2π. The maximum possible amplitude of each diffracted order is therefore given by:

$$C_r=\frac{1}{2\pi}\int_{-\pi}^{\pi}[\sin(2b\sin x)][\exp - irx]\mathrm{d}x$$

$$=\frac{1}{2\pi}\int_{-\pi}^{\pi}[\sin(2b\sin x)][\cos(rx)-i\sin(rx)]\mathrm{d}x$$

$$=\frac{1}{2\pi}\int_{-\pi}^{\pi}[\sin(2b\sin x)][\cos(rx)]\mathrm{d}x$$

$$-\frac{i}{2\pi}\int_{-\pi}^{\pi}[\sin(2b\sin x)][\sin(rx)]\mathrm{d}x \qquad (9)$$

The first term of equation (9) contains the integral of an antisymmetric function (the product of a symmetric function and an antisymmetric function), evaluated in an interval having zero as its midpoint. It is therefore equal to 0. The second term of equation (9) contains the integral of a symmetric function, also evaluated in an interval having zero as its midpoint. One may therefore write:

$$C_r=\frac{-i}{2\pi}\int_{-\pi}^{\pi}[\sin(2b\sin x)][\sin(rx)]\mathrm{d}x$$

$$=-\frac{i}{\pi}\int_{0}^{\pi}[\sin(2b\sin x)][\sin(rx)]\mathrm{d}x$$

$$=-\frac{i}{\pi}[1-(-1)^r]\frac{\pi}{2}[J_r(2b)] \qquad (10)$$

(from Tables in ref. 12; J_r is a Bessel function of order r).

$$=-iJ_r(2b)$$

where r is an odd integer.

C_r is seen to be zero for n even, consistent with the fact that we are dealing with the odd diffracted orders. Similarly, the maximum possible amplitudes of the even diffracted orders (i.e. their amplitudes when $\theta=\pi/4\pm n\pi/2$) are given by the Fourier coefficients of $[\cos 2f(x)]$. We therefore write:

$$\cos 2f(x)=\sum_{s=-\infty}^{\infty} C_s \exp(2\pi i s x/T)$$

The Fourier coefficients C_s are given by:

$$C_s=\frac{1}{T}\int_{-T/2}^{T/2}[\cos 2f(x)][\exp(-2\pi i s x/T)]\mathrm{d}x$$

From the derivation of equation (8), T is known to be equal to π. Hence:

$$C_{2s}=\frac{1}{\pi}\int_{-\pi/2}^{\pi/2}[\cos(2b\sin x)][\exp(-2isx)]\mathrm{d}x$$

$$=\frac{1}{\pi}\int_{-\pi/2}^{\pi/2}[\cos(2b\sin x)][\cos(2sx)-i\sin(2sx)]\mathrm{d}x$$

$$=\frac{1}{\pi}\int_{-\pi/2}^{\pi/2}[\cos(2b\sin x)][\cos(2sx)]\mathrm{d}x$$

$$-\frac{i}{\pi}\int_{-\pi/2}^{\pi/2}[\cos(2b\sin x)][\sin(2sx)]\mathrm{d}x \qquad (11)$$

The second term of equation (11) is zero. This leaves:

$$C_{2s}=\frac{1}{\pi}\int_{-\pi/2}^{\pi/2}[\cos(2b\sin x)][\cos(2sx)]\mathrm{d}x$$

$$=\frac{2}{\pi}\int_{0}^{\pi/2}[\cos(2b\sin x)][\cos(2sx)]\mathrm{d}x$$

$$=\frac{2}{\pi}\frac{\pi}{2}[J_{2s}(2b)] \qquad \text{(from Tables).}$$

We can therefore write:

$$C_r=J_r(2b) \qquad (12)$$

where r is an even integer. This result is consistent with the fact that we have been considering the even diffracted orders.

Equations (10) and (12) show that the amplitudes of the different diffracted orders depend on b, the maximum value of the divergence function. *Figure 3a* shows values of $|C_r|^2$ (maximum intensity) plotted as a function of $2b$ ($0\lesssim 2b\lesssim\pi$), corresponding to maximum divergence angles in the range $0\lesssim b\lesssim\pi/2$). Measurement[4] of b generally yields values in the range $0.35\lesssim b\lesssim 0.65$, so that the area between the vertical broken lines in *Figure 3a* is of particular interest. *Figure 3b* shows the expected intensities when $\theta=0$ (i.e. when the specimen is in the orthogonal position and the even orders are therefore absent). *Figure 3c* shows the situation for $\theta=\pi/4$.

The intensity curves show clearly that one can expect to observe zero and first order optical diffraction maxima from these specimens, and that higher orders, though present, may be too weak. However, were the maximum divergence angle to be as large as 1 radian, one would find that the first and second orders are strongest, with the zero order now being too weak to observe. On the other hand, for a maximum divergence angle as low as 0.1 radian, it is doubtful whether anything other than the zero order would be seen.

The observation of only zero and first orders in the optical diffraction patterns of these specimens is therefore not just a simple consequence of taking the Fourier transform of a sine function—such an explanation[4] can

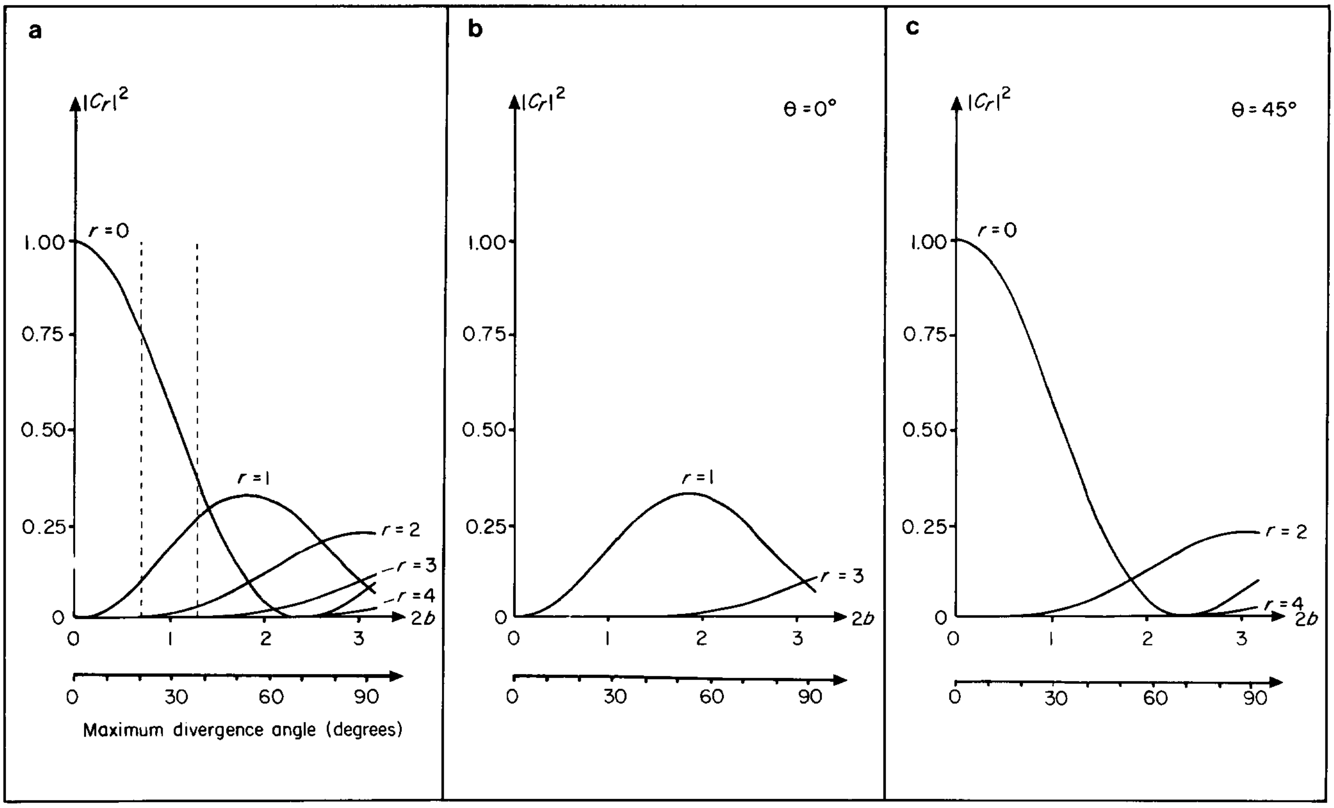

Figure 3 (a) Values of $|C_r|^2$ (maximum intensity of diffracted order r) plotted as a function of $2b$ (and the related maximum divergence angle). Curves were plotted according to equations (10) and (12), using published tables, ref. 13. The values lying between the vertical broken lines relate to typical observed specimens. (b) Curves from (a) which are relevant to specimens viewed in the orthogonal position between crossed polars. (c) Curves from (a) which are relevant to specimens rotated through 45° from the orthogonal position

only be approximate. The intensity distribution in the objective back focal plane also depends on the transmission characteristics introduced by the presence of the crossed polars, so that one in fact has to consider the Fourier transform of a 'sine of sine' function.

COMPARISON WITH SPECIMENS HAVING A NON-SINUSOIDAL DIVERGENCE FUNCTION

Figures 1 and *2* were obtained from a specimen with a symmetrical sawtooth-like divergence function; the contrast changes as a function of crossed polar rotation suggest an alternating divergence angle of approximately $+40^\circ$ and -40° relative to the shear direction.

Were the divergence function sinusoidal, with a maximum divergence angle of $\pm 40^\circ$, *Figure 3* suggests that the intensity of the zero order at $\theta = \pi/4$ would be similar to that of the first order at $\theta = 0$. The maximum intensity of the second order should be a factor of six or so lower, and the third order should be almost imperceptible.

Figure 4 consists of contour plots prepared from the optical diffraction patterns in *Figure 2*. The plots were drawn with the help of an image processing system[14] which reads in data directly from photographic negatives via a microdensitometer. The contour levels were chosen (after appropriate calibration of the film sensitivity) so that the interval between any adjacent pair corresponds to a twofold increase in intensity. Overlap of intensity from the different orders makes it impracticable to calculate an integrated intensity for each of the orders, but some estimated comparison on the basis of their relative peak intensities is possible. It is apparent that the maximum intensities of the zero and first orders are indeed similar, and that the maximum intensity of the second order is perhaps an order of magnitude lower. However, the third order is almost as evident as the second.

The observed optical diffraction pattern appears to be a sensitive guide to the profile of the divergence function, and can be used to complement results deduced from observation of the banded texture between crossed polars.

CONCLUSIONS

(1) The optical diffraction pattern of sheared specimens having a one-dimensional divergence function consists of discrete maxima when the specimens are viewed between crossed polars.

(2) The odd order maxima are most intense when the polarizer (or crossed analyser) transmission direction is parallel to the shear direction. The even orders are brightest when the crossed polars are rotated by $\pi/4$ from this orientation.

(3) In the special case of specimens having a sinusoidal divergence function, the maximum intensities $I_{r,\max}$ of the various diffracted orders can be calculated exactly, subject to reasonable assumptions being made. For the r^{th} order maximum, $I_{r,\max}$ is proportional to $[J_r(2b)]^2$, where b is the maximum value of the divergence function.

(4) The observation that specimens with a sinusoidal divergence function show only zero and first order diffracted maxima is a consequence of their particular values of b.

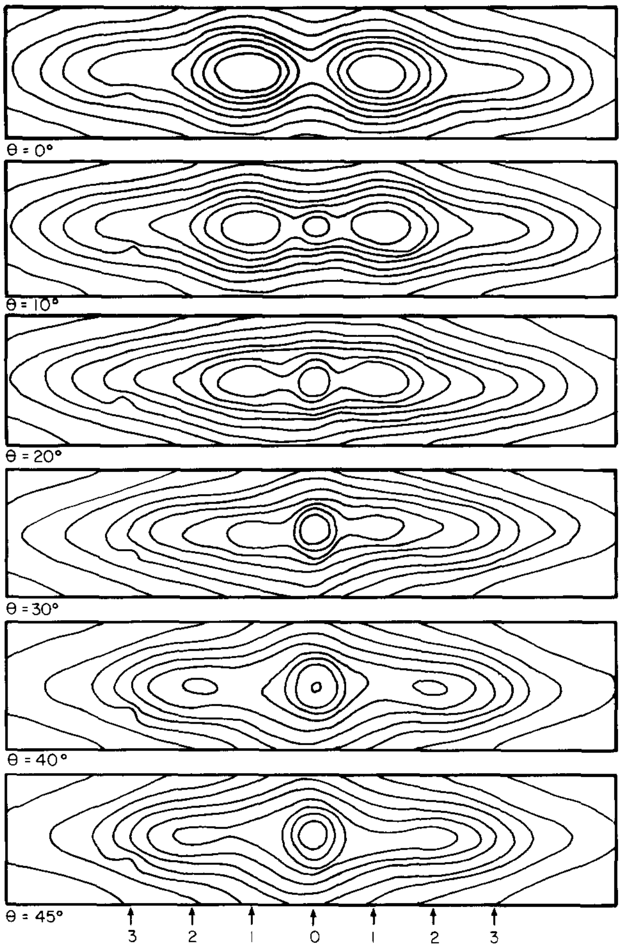

Figure 4 Intensity contour plots prepared from the six optical diffraction patterns shown in *Figure 2*. The interval between successive contours corresponds to a twofold increase in intensity

(5) The relative intensities of maxima in the observed optical diffraction pattern are sensitive to the profile of the divergence function.

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REFERENCES

1 Kiss, G. and Porter, R. S. *Mol. Cryst. Liq. Cryst.* 1980, **60**, 267
2 Simmens, S. C. and Hearle, J. W. S. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 871
3 Donald, A. M., Viney, C. and Windle, A. H. *Polymer* 1983, **24**, 155
4 Viney, C., Donald, A. M. and Windle, A. H. *J. Mater. Sci.* 1983, **18**, 1136
5 Shimamura, K. *Makromol. Chem. Rap. Commun.* 1983, **4**, 107
6 Graziano, D. G. and Mackley, M. R. *Mol. Cryst. Liq. Cryst.* 1984, **106**, 73
7 Viney, C., Donald, A. M. and Windle, A. H. *Polymer* 1985, **26**, 870
8 Horio, M., Ishikawa, S. and Oda, K. *J. Appl. Polym. Sci.* (*Symp.*) 1985, **41**, 269
9 McKie, D. and McKie, C. H. 'Crystalline Solids', Nelson, London, 1974, Ch. 12
10 Hutley, M. C. 'Diffraction Gratings', Academic Press, London, 1982, Ch. 2
11 Riley, K. F. 'Mathematical Methods for the Physical Sciences', Cambridge University Press, Cambridge, 1974, Ch. 8
12 Gradshteyn, I. S. and Ryzhik, I. M. 'Table of Integrals, Series, and Products', Academic Press, New York, 1980
13 Abramowitz, M. and Stegun, I. A. 'Handbook of Mathematical Functions', Dover, New York, 1965
14 Saxton, W. O. and Koch, T. L. *J. Microsc.* 1982, **127**, 69