Optical Effects and Molecular Ordering in Spherulites

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Optical Effects and Molecular Ordering in Spherulites

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The optical behaviour of spherulite textures exhibited by mixtures of cholesteryl acetate and cholesteryl ethyl carbonate is investigated. The observed optical effects arise due to a helicoidal arrangement of the molecules along the radial directions of the spherulites, the long axes of the molecules being oriented transverse to the radial directions. The helicoidal nature of the structure is strikingly demonstrated by two sensitive interference experiments wherein sinusoidal interference fringes are observed. The observed results are in agreement with the theory developed for the interference effects.

1 INTRODUCTION

In a recent paper[1] we had reported the circular diffraction of light, its polarization and other optical effects exhibited by spherulites formed in the case of mixtures of cholesteryl acetate and cetyl alcohol in the solid phase. The observed optical effects were interpreted as a consequence of the molecules being arranged in a helicoidal structure along the radial directions of the spherulite, the long axes of the molecules being transverse to the radial directions. The helicoidal nature of the structure was inferred from the facts that the diffracted light as well as the ring structures observed with the spherulites were extinguished along the radial directions corresponding to the vibration direction of the incident light, when plane polarized light was incident on the spherulite.

This paper reports the results of our more extensive investigations with spherulites formed in the solid phase by mixtures of cholesteryl acetate and cholesteryl ethyl carbonate (CEC), exhibiting up to six orders of diffraction, whereas only one order of diffraction was reported by us earlier, owing to the periodicity of the helicoidal arrangement there being only about 10^4 Å. Herein is presented strikingly direct evidence with regard to the helicoidal

nature of the molecular arrangement, with the aid of two optical interference methods.

2   RING STRUCTURE AND OPTICAL DIFFRACTION

In our experiments, we have used the commercially available cholesteryl acetate and CEC, after purifying them by crystallization from benzene solutions. The clearing points of cholesteryl acetate and CEC are 117 and 103°C respectively. In the course of our preliminary studies, it was noticed that the mixtures of the above two compounds, gave rise to spherulite textures with large spacings of the ring structures and that the ring-spacing varied with the ratio of the components of the mixture. Therefore, mixtures with different compositions were prepared and their clearing points and ring-spacings (equal to one half of the pitch of the helicoidal structure) were determined. The ring-spacings could be measured either directly or determined from the angle of diffraction of monochromatic light by the spherulite. The values of the pitch calculated from the angle of diffraction are consistent with the measured values of the ring-spacings ($P/2$). Figure 1 exhibits the variation of the clearing points and the pitch as a function of the weight-percentage of CEC (in the total weight of the mixture). The clearing points and the pitch are reckoned to be accurate to within ± 0.5°C and $\pm 0.2\mu$. Over a narrow range of temperatures it was possible to observe the planar texture also after heating the spherulite, and it was confirmed that the phase transitions from solid to cholesteric and then to isotropic phases were reversible. It is observed that the pitch increases sharply in the region of concentrations between 40 and 50%. With higher concentrations, the spherulite textures become highly imperfect and we have not investigated these cases. It is well-known that the pitch of the helical structure in the cholesteric mesophase is temperature dependent. But, here the pitch of the helicoidal structure of the spherulites is essentially temperature independent.

For observation of the spherulites in the solid phase under the polarizing microscope, the specimens were prepared between microscope slide and cover glass without any spacer, the thickness of the sample being about 25μ. The techniques adopted for the preparation of the specimens and recording the optical effects were identical to those described in our previous paper. Unlike the case of the mixtures of cholesteryl acetate and cetyl alcohol, the growth of the spherulites from the planar texture, especially, at the higher concentrations, was rather slow (taking up to one hour). Further, the spherulite textures reported here are stable, whereas in the case of mixtures of cholesteryl acetate and cetyl alcohol, they are metastable. Figures 2(a) and 2(b) are typical of the more spectacular ring structures with large spacings
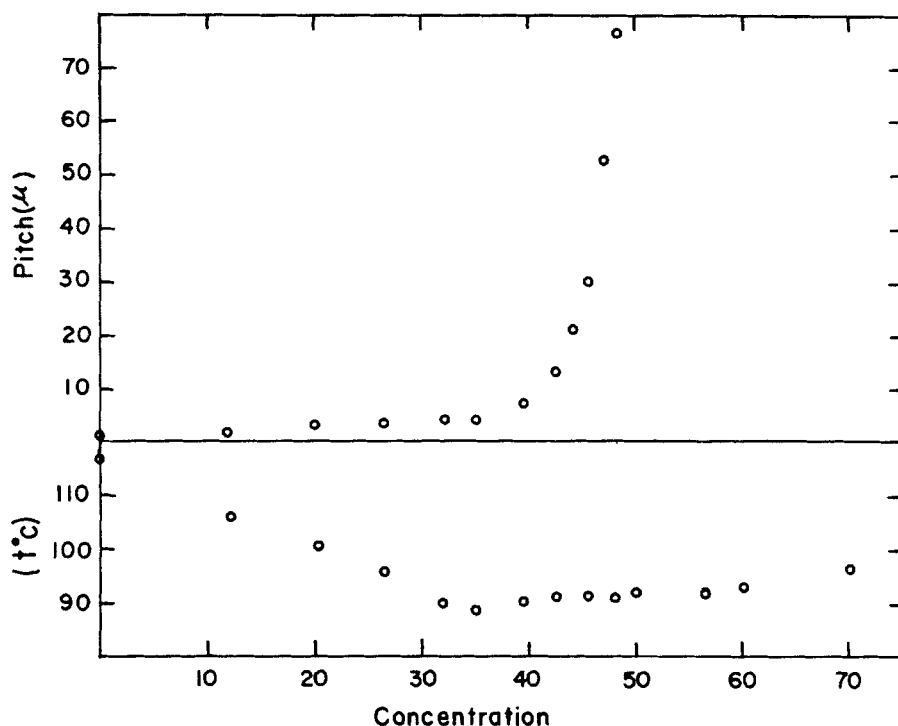
FIGURE 1 Variation of the clearing points and the pitch with concentration.

exhibited by spherulites of mixtures having a concentration in the region of 35 to 50%. The photographs were obtained respectively

1) with unpolarized white light incident on the specimen and

2) with the specimen between crossed polars, using a polarizing microscope.

Thick specimens gave rise to less regular patterns owing to overlap of growth in different layers. The ring structures exhibit polarization effects with regard to their visibility. Figure 2(c) showing this effect was obtained using plane polarized incident light, the vibration direction being horizontal. No analyzer was used. The ring structure is visible only along directions which are away from the horizontal direction, i.e., the vibration direction of the polarizer.

Figure 3(a) exhibits the different orders of diffracted light obtained with spherulites of the mixture, using unpolarized 5461 Å as the incident light. Figure 3(b) was obtained by interposing a polarizer with its vibration direction along the horizontal, in the path of the light incident on the
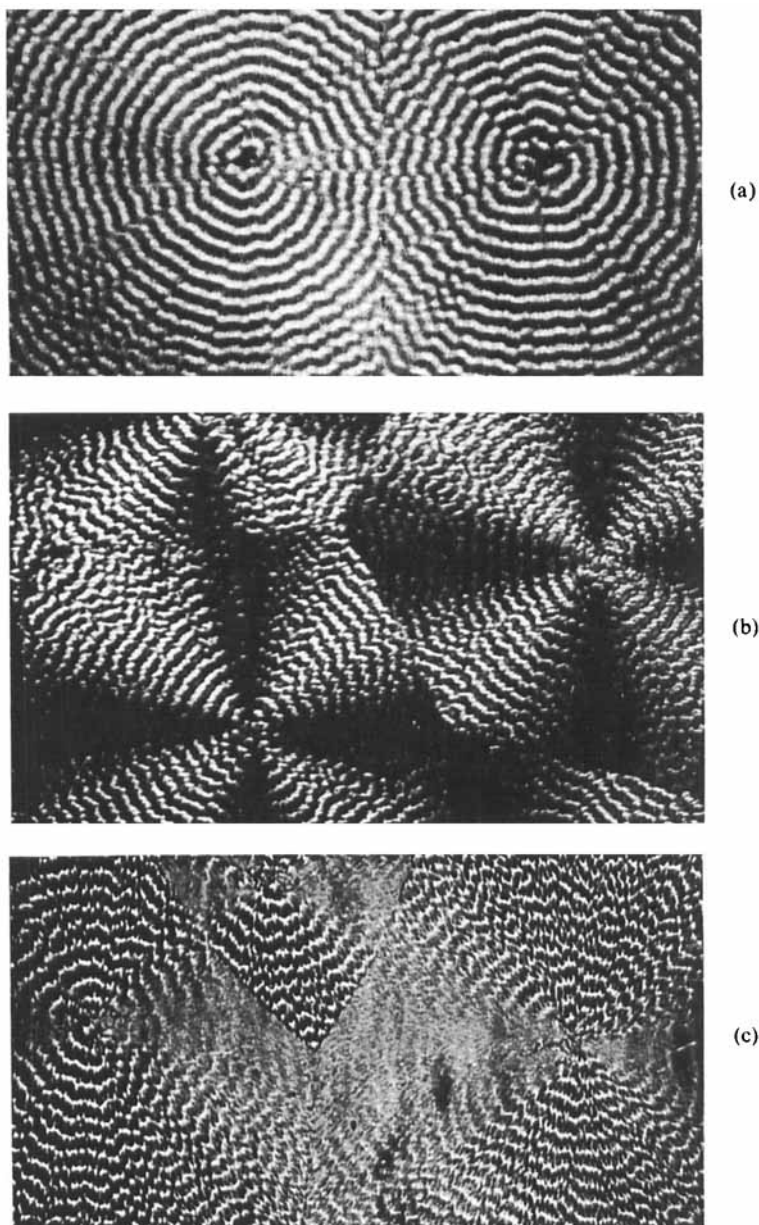
FIGURE 2   Microphotographs of the spherulite texture of a specimen (with 48.3 % of CEC). The value of the pitch $P = 76.6 \mu$. (a) Using unpolarized white light. 61x. (b) Specimen between crossed polars. 53x. (c) Using plane polarized incident light, the vibration direction being horizontal. 59x.
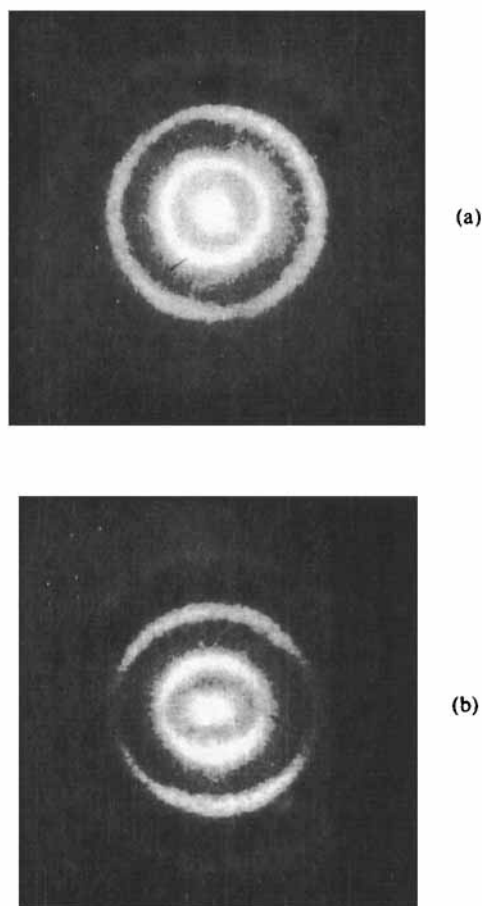
FIGURE 3 Diffraction pattern of a spherulite specimen (with 39.5 % of CEC), using light of wavelength 5461 Å; here, $P = 7.4 \mu$. (a) With unpolarized light. (b) With plane polarized light, the vibration direction being horizontal.

specimen. The extinction of the diffraction rings along the radial directions close to the vibration direction of the polarizer may be noticed. Unlike the case of the mixtures of cholesteryl acetate and cetyl alcohol, the diffraction rings here are not sharp, due to the facts that

1) the pitch of the helicoidal structure is not perfectly uniform and

2) the ring structures have radial defects and are not perfectly circularly symmetric, and consist of sectors with the rings having numerous wrinkles.

Further, the rather uneven extinctions in the dark cross as observed between crossed polars, indicate that the orientations of the long axes of the molecules in several regions are not exactly transverse to the radial directions. The optical effects exhibited by mixtures of lower concentration with smaller ring-spacings are less spectacular, but similar to the effects reported here.

We have already described in our previous paper the features observed with pure cholesteryl acetate. With pure CEC, the planar texture, on cooling to the solid phase, is transformed into an imperfect zig-zag ring structure as shown in Figure 4(a). However, this ring structure is metastable and in the course of an hour is transformed into a different texture (probably crystalline), shown in Figure 4(b).
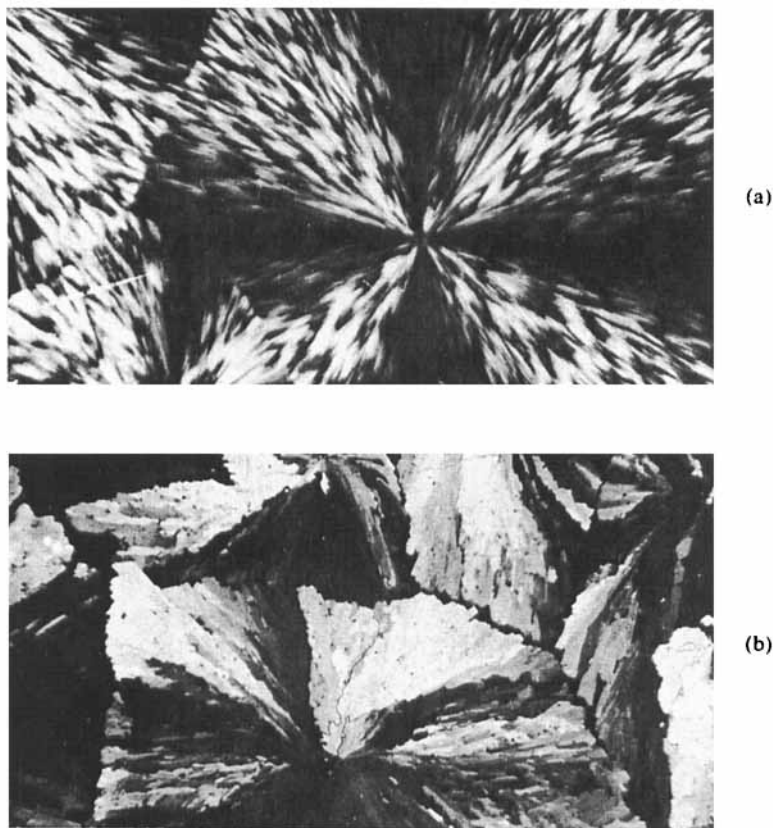

(a)

(b)

FIGURE 4 (a) Microphotograph of the spherulite texture exhibited by pure CEC, with the specimen between crossed polars. 45x. (b) Microphotograph of the texture obtained after transformation of the metastable texture in 4(a). The specimen was between crossed polars. 45x.

3 LOW ANGLE OPTICAL SCATTERING

The low angle optical scattering by spherulites of cholesteryl acetate was studied by Rhodes et al.[2] and scattering patterns were reported by them corresponding to (i) the polarizer and analyzer being vertical (V_v) and (ii) the polarizer being vertical and the analyzer being horizontal (H_v). The typical cross and four-leaf clover patterns respectively obtained in the above two cases have been interpreted as consistent with a structure having different radial and tangential refractive indices.[3] With a similar experimental arrangement as used by them, similar patterns have been obtained by us also. Figures 5(a) and 5(b) reproduce respectively the patterns recorded by us in the two cases V_v and H_v, using 6328 Å radiations of a He—Ne laser. The patterns extend here over an angular diameter of about 4°. Although the scattering patterns and the other optical effects described above indirectly confirm the helicoidal nature of the molecular orientation, it was felt by us that especially in the case of spherulites with large spacings, the molecular orientation could be more directly ascertained by sensitive interference methods and in the following sections are discussed our experimental results in this regard.

(a)   (b)
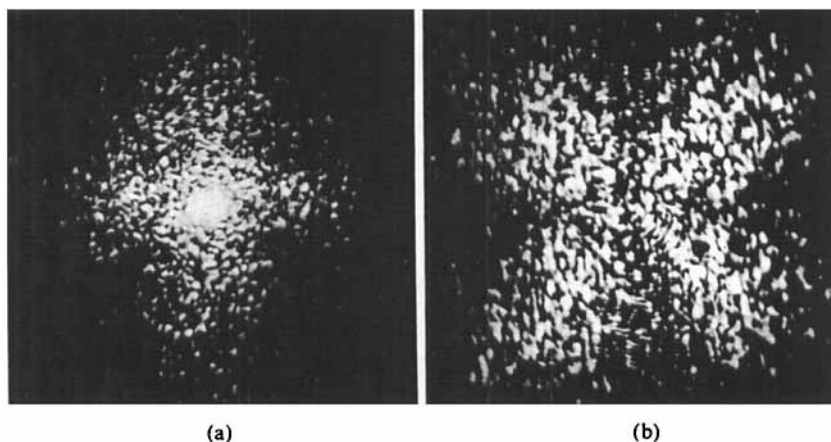
FIGURE 5   Low angle scattering by a spherulite sample (with 12.2% of CEC). (a) V_v and (b) H_v.

4 MOLECULAR ORIENTATION—USING THE BABINET COMPENSATOR

We shall consider here an ideal two-dimensional spherulite with circular symmetry and uniformity of ring spacing. Let the long axis of a molecule at a distance **r** from the centre of the spherulite make an angle $\phi(r)$ with the

normal to the plane of the spherulite. If the radial helicoidal structure has a smooth variation of ϕ along the radius, it may be assumed that

$$\phi(r) = \frac{2\pi r}{P}, \tag{1}$$

where P is the pitch of the helicoidal structure. For light incident normally on the spherulite at any point $\mathbf{r}$, the two principal vibration directions are respectively along the radius and transverse to it. These two vibrations shall be referred to as the radial and transverse components hereafter. The refractive index for the radial component is denoted by $n_\perp$, since the long axis is always oriented transverse to the radial direction. The constancy of the refractive index for the radial component is the reason for the absence of the ring structure along radial directions corresponding to the vibration direction of the incident light, when plane polarized light is incident normally on the specimen, [vide, Figure 2(c)]. The refractive index n for the transverse component is easily shown to be given by

$$n^2 = n_\parallel^2 n_\perp^2 [n_\parallel^2 \cos^2 \phi(r) + n_\perp^2 \sin^2 \phi(r)]^{-1}, \tag{2}$$

where $n_\parallel$ and $n_\perp$ respectively correspond to the refractive indices for vibrations parallel to the long axes and for vibrations transverse to the long axes of the molecules. From Eq. (2) it is seen that the refractive index n alternates between $n_\perp$ and $n_\parallel$ with a period equal to the ring-spacing i.e., one half of the pitch of the helicoidal structure. It is this alternation of n along the radial direction, which is responsible for a cylindrical lens-like focusing effect, giving rise to the ring structures. Using Eqs. (1) and (2) it may be shown that the birefringence $(n - n_\perp)$ at any point along the radial direction is representable (to a good approximation) by the equation,

$$\Delta n = \Delta n_0 \sin^2\left(\frac{2\pi r}{P}\right), \tag{3}$$

where $\Delta n = (n - n_\perp)$ and $\Delta n_0 = (n_\parallel - n_\perp)$. For a thickness t_1 of the specimen the phase difference between the transverse and radial components is given by

$$\delta_1 = \frac{2\pi t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi r}{P}\right), \tag{4}$$

where, $\delta_1 \geq 0$.

It is well-known[4] that when a Babinet compensator is oriented so that the motion of the wedge is along the horizontal direction and when crossed polarizers are introduced on either side of the compensator with their vibration directions at 45° to the principal vibration directions of the compensator, equally spaced vertical interference fringes are observed with

monochromatic light. The intensity of light transmitted by the Babinet compensator under the conditions described above is given by,

$$I = A^2 \sin^2\left(\frac{\delta_2}{2}\right) \tag{5}$$

A^2 being a constant of proportionality. δ_2 is the phase difference introduced by the compensator between the horizontal and the vertical components of vibration. The dark bands of the interference pattern satisfy the condition that $\delta_2 = 2m\pi$, where m is an integer. δ_2 can be positive or negative and it is a linear function of the horizontal distance x from the band corresponding to $\delta_2 = 0$, (i.e., the achromatic dark band observed with white light). δ_2 is equal to $2\pi x/x_0$, where x_0 is the uniform band spacing, (0.104 cm).

In the present case, owing to the thickness of the specimens as well as the ring-spacing being small, we had to adopt special methods to establish and determine the small alternating phase difference between the transverse and radial components. Let us consider the effects which arise in the case of an experimental arrangement, wherein we have a monochromatic source followed sequentially by a polarizer, a spherulite specimen, a microscope which focuses the enlarged image of the spherulite (magnified about 50 times) on the wedge of the Babinet compensator, the Babinet compensator and an analyzer. The polarizer and analyzer are crossed, their vibration directions being at $45°$ to the horizontal and vertical. In the above, the Babinet compensator is oriented so that the motion of the wedge is along the horizontal direction. Suitable apertures are introduced in the path of the beam in order to secure the depth of focus of the enlarged image formed on the wedge of the Babinet compensator. Because the magnified image of the spherulite is focused on the compensator, every point at a particular distance $\mathbf{r}$ from the centre of the spherulite is associated with a corresponding point $\mathbf{r}'$ in the image plane, $\mathbf{r}'$ being measured from the corresponding point of the centre of the image of the spherulite. If $P/2$ is the ring-spacing of the spherulite and $P'/2$ is the ring-spacing of the enlarged image, $r/P = r'/P'$, since r and P are magnified to the same extent. The transverse and radial components of vibration passing through the spherulite at a point $\mathbf{r}$ suffer a phase difference δ_1 and the same relative phase difference will be preserved between the two components as they arrive at the point $\mathbf{r}'$ on the image plane. When these two components enter the Babinet compensator, each one of them splits into the horizontal and vertical components and pass along the direction normal to the compensator. A phase difference δ_2 is now introduced between the horizontal and vertical components due to the passage of the components through the Babinet compensator. The value of δ_2 will be determined by the horizontal distance x of the point $\mathbf{r}'$ (in the image plane) as measured from the original position occupied by the dark band ($\delta_2 = 0$), before the

introduction of the spherulite specimen, [vide Figure 6(a)]. The expression for the transmitted intensity can easily be derived, by resolving the incident light along the principal directions and by including the proper phase factor (at each stage) corresponding to the passage of the beam through the spherulite and the Babinet compensator. The transmitted intensity is given by,

$$I = \frac{A^2}{2} [1 - \sin^2 2\alpha \cos \delta_2 - \cos 2\alpha \sin \delta_1 \sin \delta_2$$

$$- \cos^2 2\alpha \cos \delta_1 \cos \delta_2], \tag{6}$$

where α is the angle made by $\mathbf{r}$ (or $\mathbf{r}'$) with the horizontal direction.

In the absence of the spherulite, i.e., $\delta_1 = 0$, Eq. (6) reduces to Eq. (5) as is to be expected. In the absence of the Babinet compensator, i.e., $\delta_2 = 0$, Eq. (6) reduces to the well-known equation,[5]

$$I = A^2 \cos^2 2\alpha \sin^2\left(\frac{\delta_1}{2}\right) = A^2 \sin^2 2\beta \sin^2\left(\frac{\delta_1}{2}\right), \tag{7}$$
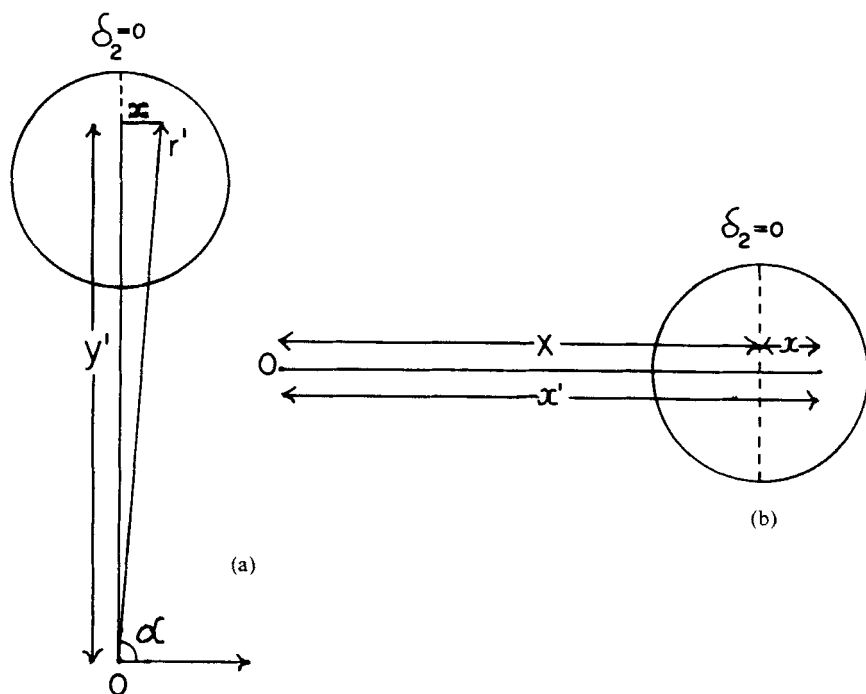

FIGURE 6   A diagrammatic representation of the two cases corresponding to (a) $\alpha \simeq \pi/2$ and (b) $\alpha = 0$. The circle represents the aperture of the Babinet compensator. O is the centre of the magnified image of the spherulite formed on the wedge of the Babinet compensator.

where β is the angle made by $\mathbf{r}$ with the vibration direction of the polarizer, i.e., $\beta = \pm(\pi/4 - \alpha)$, since the polarizer is at an angle $45°$ to the horizontal. Equation (6) gives rise to three cases of special interest which we shall discuss here.

Case (i): When $\alpha = \pi/4$, Eq. (6) reduces to Eq. (5), so that we should observe the vertical bands characteristic of the Babinet compensator. When the portion of the enlarged image of the spherulite, corresponding to the region at $45°$ to the horizontal was brought to focus on the wedge of the Babinet compensator, the characteristic vertical bands were observed.

Case (ii): When $\alpha = \pm(\pi/2)$, the intensity expression reduces to

$$I = A^2 \sin^2\left(\frac{\delta_1 + \delta_2}{2}\right). \qquad (8)$$

Here,

$$\delta_1 = \frac{2\pi t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi r'}{P'}\right)$$
$$= \frac{2\pi t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi y'}{P'}\right), \qquad (9)$$

since $r' \simeq y'$ in the region of $\alpha = \pm \pi/2$. Further, $\delta_2 = 2\pi x/x_0$. A diagrammatic representation of this case is shown in Figure 6(a). The intensity is equal to zero at all points for which $\delta_1 + \delta_2 = 2m\pi$, where m is an integer. This condition gives,

$$\frac{2\pi t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi y'}{P'}\right) + \frac{2\pi x}{x_0} = 2m\pi, \qquad (10)$$

i.e.,

$$x = mx_0 - \frac{x_0 t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi y'}{P'}\right). \qquad (11)$$

For $m = 0$, it may be seen that the contour of the dark band is a sinusoidal curve being shifted to one side of the original vertical band at $m = 0$. The bands corresponding to $m = \pm 1$ will also be shifted in a similar fashion. This is indeed what is observed, when the portion of the image corresponding to the region $\alpha = \pi/2$ and sufficiently far away from the centre of the spherulite is brought into focus on the wedge of the Babinet compensator. Figure 7(a) exhibits the vertical sinusoidal dark bands in the centre of the field of view. The bands get distorted as one moves away from the centre because α is no longer equal to $\pi/2$, and the approximation $r' = y'$ does not hold good any longer.
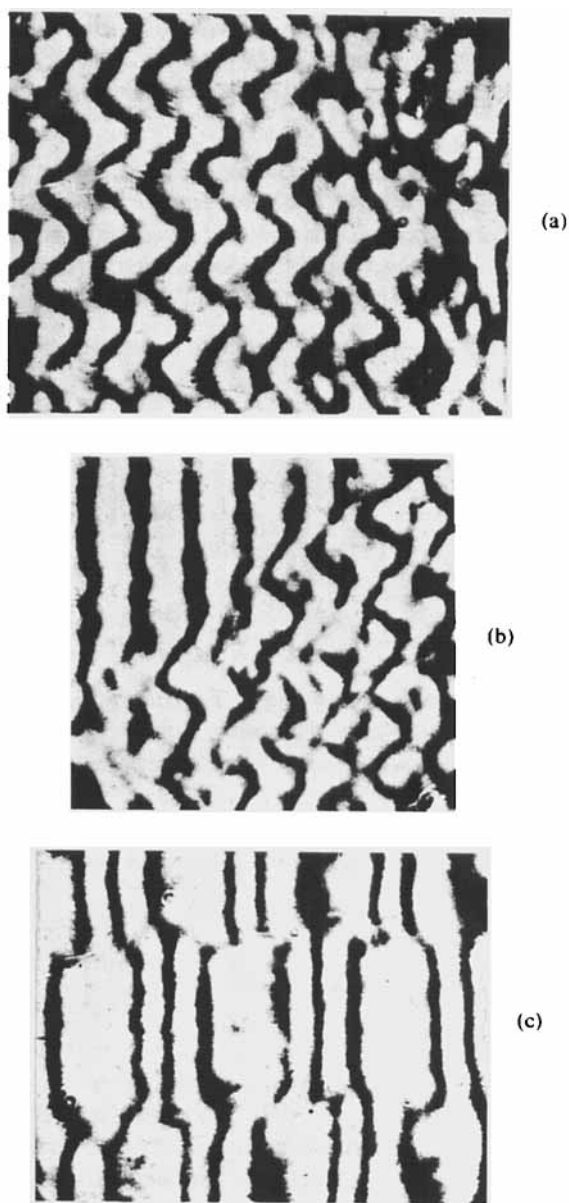
FIGURE 7   Interference patterns obtained with a spherulite specimen (with 48.3 % of CEC), using the Babinet compensator and with radiations of 5893 Å. (a) The sinusoidal dark bands, (b) The sinusoidal dark bands of one spherulite is contiguous with the straight bands of another spherulite, (c) Bunching of the bands observed in the case when $\alpha = 0$.

The sinusoidal nature of the curve in Figure 7(a) is clear evidence of the sinusoidal change of the phase difference δ_1 along the radial direction, y'. Physically the origin of the sinusoidal curve may be explained as arising from the superposition of the two phase differences δ_1 and δ_2, the former varying sinusoidally along the vertical direction and the latter linearly along the horizontal direction, so that the shift of any fringe in the central region of the Babinet compensator varies sinusoidally as one passes along the vertical direction. In Figure 7(a) the peak to peak vertical distance (for the sinusoidal curve at the centre) corresponds to one half of the magnified pitch of the spherulite. Figure 7(b) also shows a region where the vertical bands (belonging to another spherulite, and with $\alpha = \pi/4$ for that region) are present. It may be seen that the vertical bands are almost tangential to the sinusoidal bands. The latter are shifted with respect to the vertical bands to one side only as predicted by Eq. (11), the shift being equal to zero when $\Delta n = 0$. In fact, when any thin specimen with positive birefringence, with the higher index direction along the horizontal, is introduced in front of the Babinet compensator the achromatic dark band ($\delta_2 = 0$) is found to shift to the left. The presence of sinusoidal bands on the left of the vertical bands seen in Figure 7(b), confirms the fact that the transverse component with its vibration direction along the horizontal is the one for which the refractive index is higher. Therefore, the long axis should be transverse to the radial direction. The points on the sinusoidal curve which are along the same line as the vertical bands, correspond to points at which the orientations of the long axes of the molecules are normal to the plane of the spherulite, so that here $\Delta n = 0$. On the other hand, the maxima shifted to the left of the corresponding straight vertical bands in Figure 7(b) represent points where the orientation of the long axis is in the plane of the spherulite, so that here $\Delta n = \Delta n_0$.

The horizontal distance between the maxima and the minima (extremes of excursion) of the sinusoidal curve at the centre of Figure 7(a) corresponds to $t_1 \Delta n_0 x_0/\lambda$, as may be seen from Eq. (11). From measurements of x_0 and the above horizontal distance, the maximum value of the phase difference between the transverse and radial components, i.e., $2\pi t_1 \Delta n_0/\lambda$, was calculated to be on an average equal to 4.26 radians for 5893 Å. The value of $2\pi t_1 \Delta n_0/\lambda$ as calculated from a different experimental method discussed in the next section, turns out to be 4.24 radians for the same specimen, being in agreement with the former value.

We have reproduced here only some of the best photographs illustrative of the presence of ideally regular helicoidal structure over a few ring-spacings. It is not uncommon to find spherulites with radial defects and with wrinkled ring structures which are sometimes discontinuous and staggered with respect to one another in adjacent sectors. In such cases the sinusoidal curves

are regular and continuous only over a few ring-spacings. Distortions or discontinuous changes in the sinusoidal curve are observed at points where sector boundaries or defects are present.

Case (iii): When $\alpha = 0$, Eq. (6) reduces to

$$I = A^2 \sin^2\left(\frac{\delta_2 - \delta_1}{2}\right), \qquad (12)$$

where

$$\delta_1 = \frac{2\pi t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi r'}{P'}\right)$$

$$= \frac{2\pi t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi x'}{P'}\right),$$

and

$$\delta_2 = \frac{2\pi x}{x_0}.$$

Figure 6(b) is a diagrammatic representation of this case. The intensity is zero when $\delta_2 - \delta_1 = 2m\pi$, where m is an integer. The above condition leads to the relation,

$$\frac{x}{x_0} - \frac{t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi x'}{P'}\right) = m. \qquad (13)$$

Since $x' = x + X$ as shown in Figure 6(b), it may easily be seen that,

$$x' = mx_0 + X + \frac{x_0 t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi x'}{P'}\right). \qquad (14)$$

This is a nonlinear equation involving the superposition of a linear term with a sinusoidally varying term and it is evident that under such circumstances, the values of x' which will satisfy the above equation for $m = 0$, $+1$, $+2$ etc., need not in general be evenly spaced. Figure 7(c) shows such a case where groups of three bands occur closer and farther apart along the horizontal direction. The middle portion of Figure 7(c) corresponds to $\alpha = 0$. A similar effect is also observed in the same figure in the region of α slightly greater or less than zero. The origin of this latter feature is not quite clear. It is possible that the regions above and below $\alpha = 0$, may belong to a different sector of the spherulite with the ring-spacing being out of step with the middle region as is observed sometimes.

5 MOLECULAR ORIENTATION—USING BANDED SPECTRUM

It is well-known[6] that when a birefringent material is kept between crossed polarizers with their vibration directions at 45° to the vertical and horizontal and when the principal vibration directions of the birefringent medium coincide with the vertical and horizontal directions respectively, the spectrum of the white light transmitted by the system exhibits characteristic vertical dark bands at different wavelengths. In fact, such a phenomenon cannot be observed here with the spherulite specimens alone, because the specimens are too thin to give significantly large phase differences. Therefore, a modified experimental arrangement was used. The experimental set-up essentially consisted of a tungsten filament lamp, followed sequentially by a polarizer, a cleavage plate of a crystal of barium sulphate (1.6 mm thick), the spherulite specimen, a microscope which focuses the enlarged image of the spherulite (magnified about 50 times) on the slit of the spectrograph, an analyzer and a spectrograph. The polarizer and analyzer are crossed with their vibration directions being at 45° to the horizontal and vertical. The cleavage plate of the birefringent crystal of barium sulphate was oriented normal to the beam with the principal vibration directions along the vertical and horizontal, the refractive index corresponding to the horizontal direction being greater than the index corresponding to the vertical direction.

Let δ_2 be the phase difference introduced between the horizontally and vertically polarized components passing normally through the crystal of barium sulphate. When the region of the spherulite corresponding to $\alpha = \pm \pi/2$ is focused on the slit of the spectrograph (i.e., $r' = y'$) the phase difference δ_1 between the transverse and radial components passing through the spherulite is given by Eq. (9), i.e.,

$$\delta_1 = \frac{2\pi t_1 \Delta n_0}{\lambda} \sin^2\left(\frac{2\pi y'}{P'}\right). \tag{15}$$

Here, y' is parallel to the length of the slit. Δn_0 is, in general, a function of λ. Under these circumstances, it is easy to derive an expression for the transmitted intensity. The intensity is given by,

$$I = A^2 \sin^2\left(\frac{\delta_1 + \delta_2}{2}\right). \tag{16}$$

The intensity is equal to zero when $\delta_1 + \delta_2 = 2m\pi$.

In the absence of the spherulite, the intensity is constant along the y' direction for a given wavelength and is given by,

$$I = A^2 \sin^2\left(\frac{\delta_2}{2}\right). \tag{17}$$

Vertical dark bands are observed in the spectrum at wavelengths which satisfy the equation,

$$t_2 \Delta n_2(\lambda) = m\lambda, \tag{18}$$

where m is an integer and t_2 and $\Delta n_2(\lambda)$ correspond to the thickness of the cleavage plate and the difference between the refractive indices for the horizontally and vertically polarized components passing through it.

In the absence of the spherulite, let us consider a particular dark band of given m at $\lambda = \lambda_0$ so that,

$$t_2 \Delta n_2(\lambda_0) = m\lambda_0. \tag{19}$$

In the presence of the spherulite the condition for the intensity to be equal to zero, is givn by $\delta_1 + \delta_2 = 2m\pi$. Hence, we get.

$$t_2 \Delta n_2(\lambda) + t_1 \Delta n_0(\lambda) \sin^2\left(\frac{2\pi y'}{P'}\right) = m\lambda. \tag{20}$$

Since the phase difference introduced by the specimen of the spherulite is usually less than 2π, the same value of m will be involved in Eqs. (19) and (20) and $(\lambda - \lambda_0)$ is small. From Eq. (20) it is evident that when y'/P' takes half integral or integral values, $\lambda = \lambda_0$. Therefore, we have,

$$m\lambda_0 + (t_1 \Delta n_0) \sin^2\left(\frac{2\pi y'}{P'}\right) = m\lambda. \tag{21}$$

In the above, we have not explicitly considered the dispersion of birefringence in the region $(\lambda - \lambda_0)$ but have assumed that $t_2 \Delta n_2(\lambda) = m\lambda_0$ and $t_1 \Delta n_0(\lambda) = t_1 \Delta n_0(\lambda_0)$. Hence, for a given m,

$$m(\lambda - \lambda_0) = t_1 \Delta n_0 \sin^2\left(\frac{2\pi y'}{P'}\right). \tag{22}$$

From Eq. (22) it is evident that in the field of view of the spectrograph one should observe dark bands with the wavelengths of extinction in each one of them varying sinusoidally along the vertical direction, i.e., parallel to the slit of the spectrograph. Again, it may be noticed from Eq. (22) that in the case of each band, the oscillatory shift is towards the red region with respect to the original position of the vertical band observed in the absence of the spherulite. These features are illustrated in Figure 8 which also shows for comparison the banded spectrum observed with the crystal of $BaSO_4$ only. The shift towards the red is clear for the first three bands in the red and yellow regions. Beyond these regions, the shift with respect to the straight bands is not quite unidirectional. This indicates that the long axes may not be exactly transverse to the radial direction. The greater dispersion in the region of short
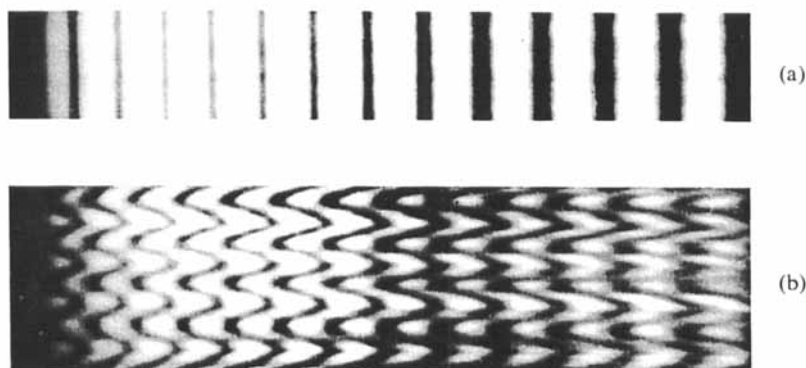
FIGURE 8   (a) Banded spectrum of white light obtained with a crystal of $BaSO_4$ between crossed polars. The first dark band in the red region (the left side) corresponds to $m = 29$ with $\lambda = 6210$ Å. (b) Banded spectrum consisting of sinusoidal bands, obtained with a specimen with 48.3% of CEC.

wavelengths is probably the reason for the above anomalous behaviour manifesting itself in the region of shorter wavelengths rather than in the red and yellow regions. With highly enlarged photographs it was possible to confirm by measurements, that the bands in the red region are almost perfectly sinusoidal. The points of extreme excursions of each sinusoidal band towards the short wavelength side, having almost the same wavelength as the vertical band, correspond to those points on the spherulite, where the molecules have their long axes almost normal to the plane of the spherulite. The points of extreme excursions towards the red correspond to those points on the spherulite where the long axes are in the plane of the spherulite. The peak to peak vertical distance corresponds to one half of the magnified pitch.

For each sinusoidal band, the wavelength difference between the points of extreme excursion satisfies the following relation obtainable from Eq. (22).

$$m(\lambda - \lambda_0) = m\Delta\lambda = t_1\Delta n_0. \tag{23}$$

Hence, from $\Delta\lambda$ and m it is possible to calculate the maximum value of the phase difference between the transverse and radial components i.e., $2\pi t_1\Delta n_0/\lambda$. By assuming that $m\lambda = $ constant, and by preparing a chart of $\log \lambda$ with the measured values of λ of the vertical bands, and matching it with another chart of $\log m$ (drawn to the same scale for various integral values of m), it was possible to obtain uniquely perfect coincidences between $\log \lambda$ and $\log m$ for all the bands in the region 4800 to 6200 Å. Hence, the value of m for each band was ascertained unambiguously. The average value of $(2\pi t_1\Delta n_0/\lambda)$ was found to be 4.24 radians, in satisfactory agreement with the value of 4.26 radians mentioned previously. It was not possible to determine t_1

quite accurately. Using an estimated value $t_1 = 15\mu$, Δn_0 was found to be 0.027 for 5893 Å, in the case of a mixture with a concentration of 48.3% of CEC. The magnitude of Δn_0 estimated here is of the same order as of the values reported in the case of cholesteryl compounds.[7]

6   CONCLUDING REMARKS

The observed sinusoidal bands, the nature of their shift with respect to the straight bands, the optical effects observed with polarized light in the case of the ring structures and the optical diffraction establish conclusively the helicoidal nature of the orientation of the long axes of the molecules for the spherulites studied here. Spherulite textures have been observed by us in the case of other compounds and their mixtures in their solid phase. The values of the pitch of the helicoidal orientation of the long axes are found to be different in different cases. For example, in the case of

   1) cholesteryl propionate,

   2) cholesteryl palmitate,

   3) cholesteryl stearate, the values of the pitch are 1.5, 2.2 and 12μ respectively.

It is proposed to investigate these cases and cases of other mixtures in order to obtain information with regard to the typical features exhibited by them.

References

1. D. Revannasiddaiah, M. S. Madhava, and D. Krishnamurti, *Mol. Cryst. Liq. Cryst.*, **39**, 87 (1977).
2. M. B. Rhodes, R. S. Porter, W. Chu, and R. S. Stein, Proceedings of the Second International Liquid Crystal Conference (Gordon and Breach Science Publishers, London, New York, Paris, 1968), Part II, p. 731.
3. R. S. Stein, M. B. Rhodes, and R. S. Porter, *J. Colloid and Interface Science*, **27**, 336 (1968).
4. N. H. Hartshorne, and A. Stuart, *Crystals and the Polarising Microscope* (Edward Arnold Publishers Ltd., London, 1960), p. 295.
5. M. Born and E. Wolf, *Principles of Optics* (Pergamon Press, 1970), IV Edn., p. 696.
6. W. A. Wooster and A. Breton, *Experimental Crystal Physics* (Clarendon Press, Oxford, 1970), p. 13.
7. G. Pelzl and H. Sackmann, *Z. Phys. Chem.* (Leipzig), **254**, 354 (1973).