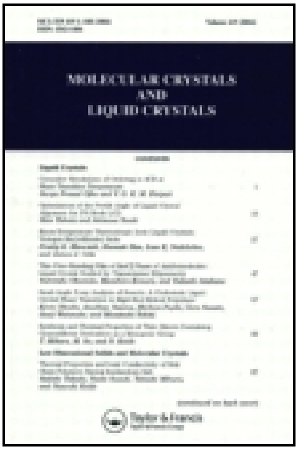

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Optical Behaviour of Spherulite Textures of Cholesteryl Acetate Doped with Cetyl Alcohol

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Optical Behaviour of Spherulite Textures of Cholesteryl Acetate Doped with Cetyl Alcohol

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Optical diffraction rings are observed in the solid phase with spherulite textures of cholesteryl acetate and cholesteryl acetate doped with varying amounts of cetyl alcohol, the rings being intense and sharp in the case of the latter. The diffracted light is polarized with its vibration direction transverse to the radial direction of the spherulite. When observed under the polarizing microscope, the textures exhibit fine circular rings corresponding to the periodic nature of the structure along each radial direction. It emerges from the observed results that in the spherulites, along each radial direction the molecules are arranged in a helicoidal structure. In the case of the doped samples, the cetyl alcohol molecules endow the structure with a more uniform pitch for the helicoidal arrangement about each radial direction. The spherulite textures of doped samples are found to be metastable and they undergo a slow transformation to a fibrillar crystalline texture, the domains of which give rise to diffraction of light at small angles.

1 INTRODUCTION

It is well known that in the cholesteric mesophase the molecules are arranged parallel to one another within planes and that in the successive planes the direction of the orientation of the long axes of the molecules rotates smoothly leading to a helical structure which is responsible for the characteristic optical properties of the cholesteric mesophase. Sackmann *et al.*[1] have confirmed the helicoidal nature of the structure from their studies on the optical diffraction patterns exhibited by magnetically oriented mixtures of cholesteryl chloride and cholesteryl myristate. In their experiments, when light was incident in a direction parallel to the planes of the cholesteric structure and perpendicular to the axis of the helix, optical diffraction patterns were observed by them, the effects being analogous to the diffraction of light by ultrasonic waves as observed by Debye and Sears.[2] Spherulite textures are exhibited by concentrated solutions of poly-γ-benzyl-L-glutamate (PBLG) and characteristic optical diffraction and other effects were observed in this case by Robinson.[3-4] Optical effects by ringed spherulite textures in polymers have been studied by a number of investigators.[5-12] The scattering of light by spherulite type of optical textures exhibited by cholesteryl acetate was investigated by Rhodes *et al.*[13] However, diffraction effects similar to those observed in the case of polyethylene[8] have not been reported by Rhodes *et al.* in their studies with cholesteryl compounds. In the present paper, we discuss our observations on the optical behaviour of pure cholesteryl acetate and cholesteryl acetate doped with cetyl alcohol and the results presented here are very similar to those reported in the case of ringed spherulites of polymers.

2 EXPERIMENTAL

In our experiments we have used commercially available cholesteryl acetate and cetyl alcohol purified by recrystallization, the melting points of the samples being 117° and 50°C respectively. In all the experiments described herein, the specimens were prepared by having the samples between the microscope slide and cover slip and the molten samples were allowed to cool on the stage of the microscope at the room temperature of approximately 28°C. No spacer was used between the slide and the cover slip and the thickness of the specimen was about 50 μ. However, it was confirmed with thick specimens prepared by using spacers of thicknesses up to 150 μ that there were no significant changes in the optical effects described in the following. Figure 1 shows the variation of the clearing points of the monotropic mixture of cholesteryl acetate and cetyl alcohol for different percentages by weight of the cetyl alcohol (in the total weight of the mixture).

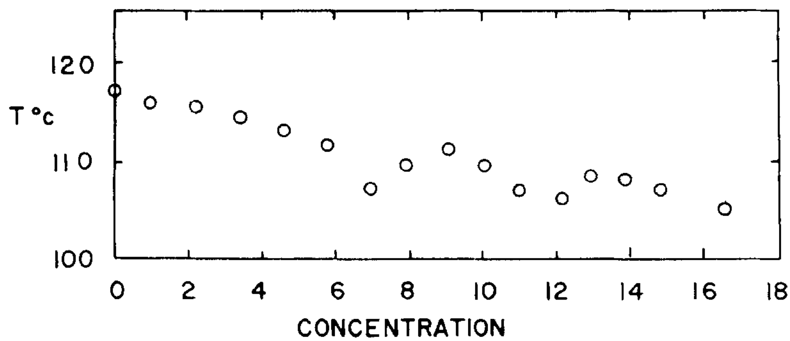


FIGURE 1 Clearing points as a function of the percentage weight of cetyl alcohol in the mixture. Clearing temperatures are accurate to within ±0.5°C.

3 SPHERULITE TEXTURES

Spherulite textures are characterised by a radial growth of the substance about a centre of nucleation with specific orientation of the molecules along each radius. But the higher refractive index can lie along or transverse to the radius, and between crossed polars spherulite textures exhibit a black Maltese cross. In the case of cholesteryl acetate, at the setting point the field of view appears at first as a cloud of greyish colour. Subsequently at different centres of nucleation, growth occurs radially and these spherulites ultimately coalesce to form a network, the individual spherulites being separated by boundaries which are conic sections. It was observed by Rhodes *et al.*[13] that quenching of the specimen (rapid cooling) results in the formation of a large number of small spherulites which are stable even at room temperature. This state is analogous to the "glassy" or quenched state prepared by Sackmann *et al.*[1] by rapid cooling of the mixtures of cholesteryl chloride and cholesteryl myristate, although the specimens prepared by them were magnetically oriented and corresponded approximately to a planar texture. Very slow cooling gives rise to textures which appear somewhat similar to the spherulite texture, but with a difference in that the texture exhibits coarse radial fibrils which appear to be crystalline and these are referred to as fan-shaped fibrillar textures. Using a polarizing microscope with crossed polars, it is observed that the individual fibrils exhibit extinctions parallel and perpendicular to the fibrils. Often the spherulite texture and the fan-shaped fibrillar textures are found to coexist in the case of a sample of pure cholesteryl acetate allowed to cool at room temperature from the molten phase. This is illustrated in Figure 2. In order to investigate the spherulite textures in detail, it occurred to us that doping of the host material with a long chain molecule of approximately the same length as cholesteryl acetate might result in the formation of spherulites without the simultaneous occurrence of the fan-shaped textures. Cetyl alcohol was chosen as the impurity to be added and the above expectation was found to be reasonably justified. Figure 3 exhibits the spherulite textures obtained with a sample containing 2.4% of cetyl alcohol by weight, as observed between crossed polars with a polarizing microscope. The photograph shown in Figure 3 was taken in the solid phase at room temperature after allowing the molten sample to cool on the stage of the microscope at room temperature. The texture may be termed as metastable in that in the course of a few days it is transformed into a fibrillar texture as shown in the photograph in Figure 4a.

Rhodes *et al*[13] report that the direction of the highest refractive index is transverse to the radial directions of the spherulites shown in Figures 2 and 3. They mention also that it was possible in some cases to grow spherulites having a banded structure interpretable in terms of a helicoidal twist about

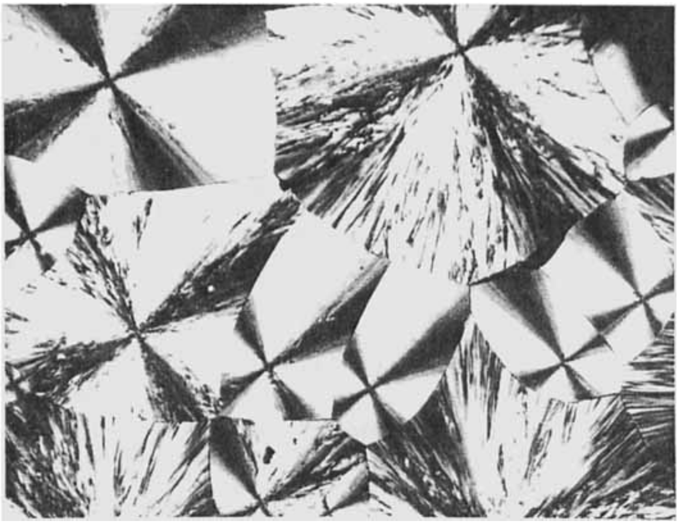


FIGURE 2 Texture of pure cholesteryl acetate between crossed polars. 60 ×.

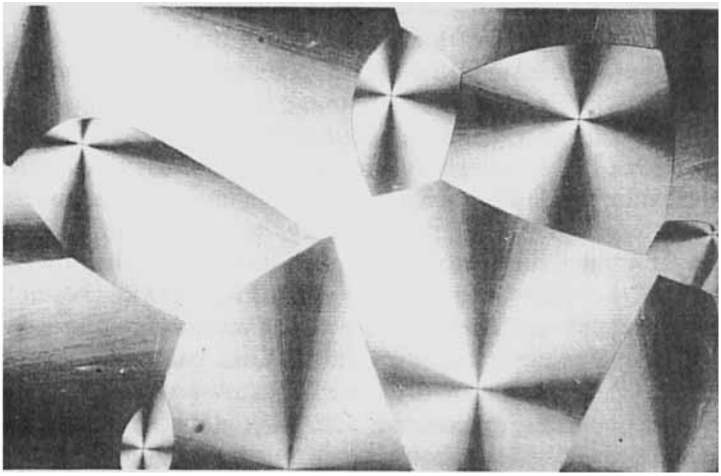


FIGURE 3 Texture of a mixture of pure cholesteryl acetate and cetyl alcohol (2.4 %) between crossed polars. 45 ×.

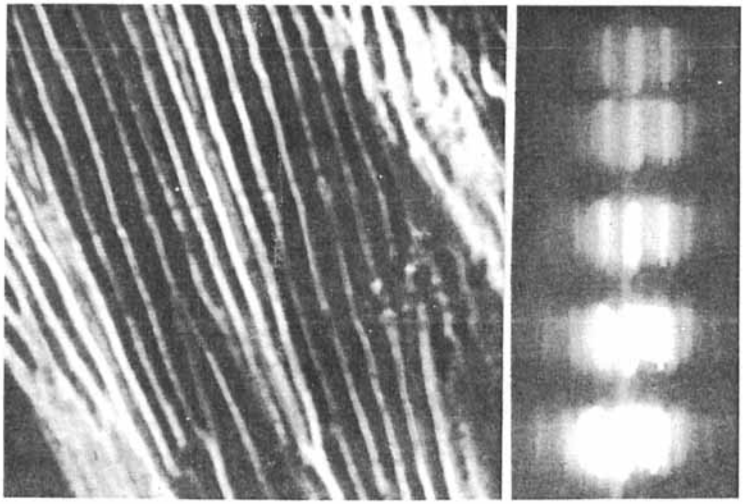


FIGURE 4 (a) Fibrillar texture of a mixture of pure cholesteryl acetate and cetyl alcohol (13%) between crossed polars. 90×. (b) Diffraction pattern given by the texture in (a) photographed with sodium yellow light.

the radial directions of the spherulites. The continuity of these rings throughout the spherulites is interpreted as indicating the continuity of the phase of the twist. However, they have not mentioned about observing any optical diffraction effects, nor have they reproduced any photographs of the banded structures for any of the cholesteryl compounds studied by them.

4 OPTICAL DIFFRACTION BY SPHERULITE TEXTURES

Although the spherulite textures can be examined by observing through the polarizing microscope, a most striking effect is noticeable by just looking at the sample on the stage of the microscope. The doped sample exhibits a spectacular play of colours or iridescence due to the diffraction of the light passing through the sample. With pure cholesteryl acetate this was weakly visible and liable to be missed. If one observes a polychromatic source of light like the mercury arc through a doped sample exhibiting spherulite textures by keeping the slide close to the eye, sharp diffraction rings are seen corresponding to the different wavelengths of the mercury arc. With pure cholesteryl acetate the diffraction rings are wide and weak. The diffraction patterns obtained with pure and doped samples are illustrated in Figures 5 and 6a. The photographs were obtained by using collimated light passing

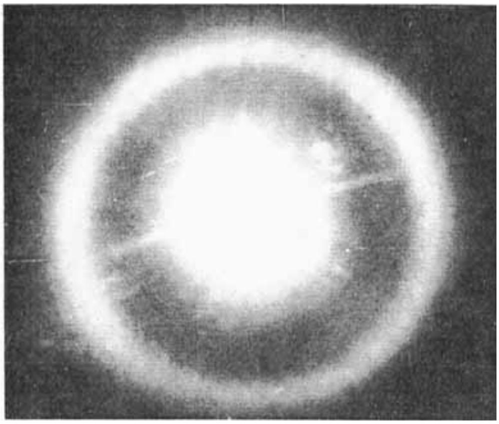


FIGURE 5 Diffraction pattern obtained with spherulite textures of pure cholesteryl acetate using light of wavelength 4358 Å.

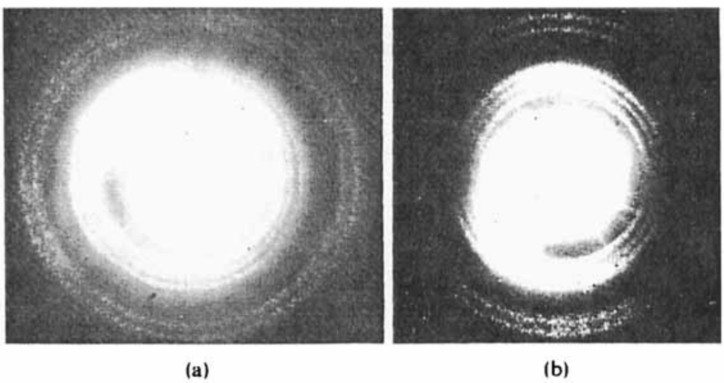


FIGURE 6 (a) Diffraction pattern obtained with a doped sample (with 4.7 % of cetyl alcohol), using unfiltered radiations from a mercury arc. (b) Diffraction pattern obtained with the same sample, but with a polaroid with its vibration direction horizontal interposed in the path of the diffracted light.

through a pinhole kept in front of the specimen. We have observed the diffraction rings in the backward direction also; but we have not obtained any photographs since these are rather weak and the experimental geometry for photographing them is inconvenient. Another interesting feature which can be observed is that the diffracted light along any direction is polarized with its vibration direction transverse to the corresponding radius of the spherulite. Figure 6b exhibits the polarization of the diffraction rings. The photograph was obtained by placing a polaroid in the path of the diffracted light, the vibration direction of the polaroid being horizontal. The optical diffraction patterns described above are exhibited by the doped samples up to a concentration of about 50 % of cetyl alcohol. However, at concentrations above 30 % the diffraction rings become progressively weak and the spherulite textures become somewhat distorted and it appears that there is a tendency for the cetyl alcohol to segregate on solidification of the sample.

Obviously, the diffraction rings have their origin in the spherulite texture which behaves as a circular diffraction grating. The periodic nature of the structure of the spherulites along the radial direction became evident from the circular rings which were observed through the polarizing microscope with a high power objective (60 ×). This feature for the pure and doped samples is shown in Figures 7 and 8 obtained by using crossed polars. The circular rings are observable even with unpolarized white light, although the contrast is poor (see Figure 9). The visibility of the circular rings is not exactly the same over all the regions owing to the existence of radial faults and also due to the fact that all regions are not simultaneously in good focus, when a high power objective is used. Further, usually the spacing of the rings is somewhat larger near the centre of the spherulite but is practically uniform over the entire remaining areas of the spherulite.

It was found that the fan-shaped fibrillar textures of pure cholesteryl acetate do not give rise to diffraction rings and no fine circular rings are observed through the polarizing microscope. However, in the regions where

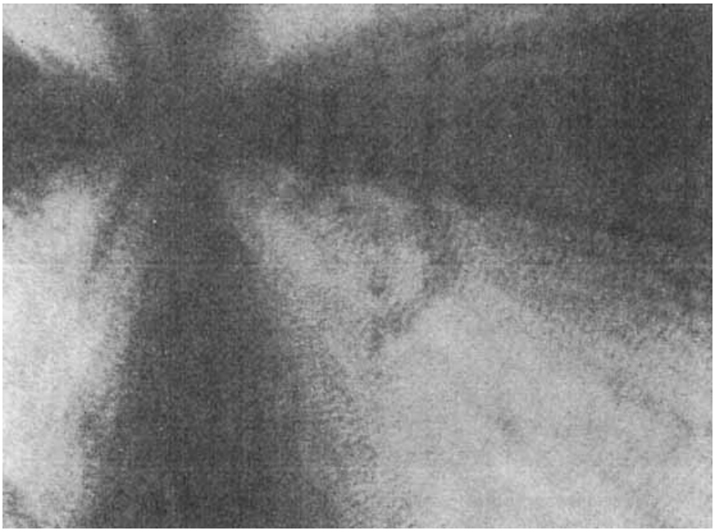


FIGURE 7 Microphotograph of a spherulite of pure cholesteryl acetate between crossed polars. 1520 ×.

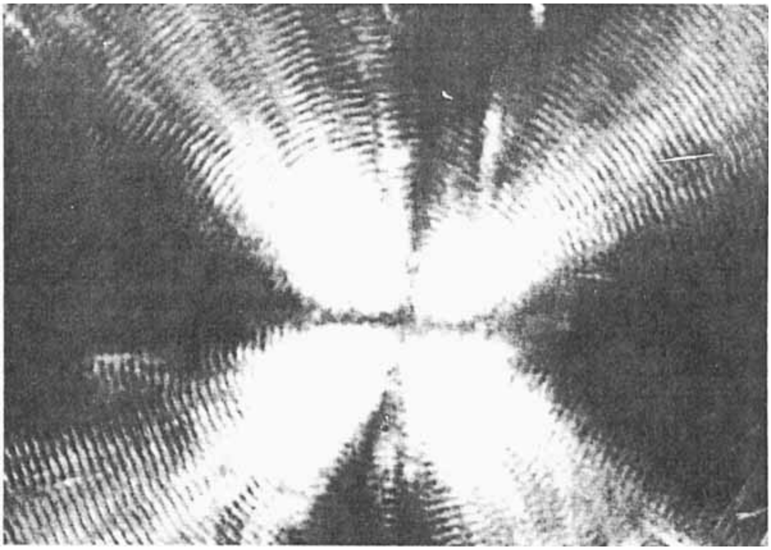


FIGURE 8 Microphotograph of a spherulite of a doped sample (with 2.4% cetyl alcohol) between crossed polars. 1290 ×.

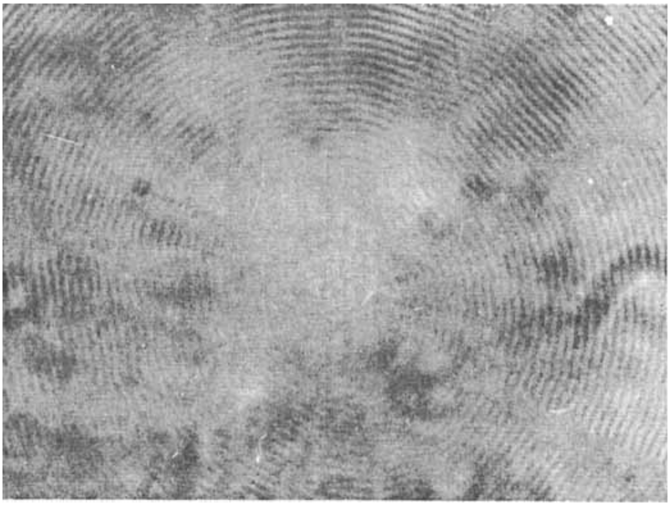


FIGURE 9 Microphotograph of a spherulite of a doped sample (with 2.4% cetyl alcohol) using unpolarized white light. 1290 ×.

the spherulite textures were present, fine circular rings were observed but with poor definition as shown in Figure 7. The fibrillar textures (Figure 4a) obtained by slow transformations of the spherulite texture in the case of doped samples exhibit a diffraction pattern at small angles only. The optical diffraction is due to the fibrillar domains which are about 50 μ in size. Figure 4b shows the diffraction pattern obtained with monochromatic light (5893 Å), the pattern having been photographed for different exposures.

5 DISCUSSION

The foregoing results are explainable as follows. Along each radial direction of the spherulite the molecules are arranged in planes normal to the radial direction with their long axes transverse to the radius and the direction of the long axes of the molecules rotates smoothly in successive planes in passing along each radius. For the focal conic textures of the cholesteric mesophase, Gray[14] has envisaged such a helicoidal structure. The fine circular rings observed under the microscope arise in a fashion analogous to the Becke line effect, owing to the periodic variation of the refractive index along the radial direction, as already explained by Robinson in the case of PBLG solutions. The periodic variation of the refractive index along each radial direction for light polarized with its vibration direction transverse to the radius is responsible for the diffraction of light. With light polarized with its vibration direction along the radius, no diffraction arises at any point along that radius, because the vibration direction is always transverse to the molecular axes for the molecules along that radius and hence no optical heterogeneity is involved. As is to be expected from the above explanation, we find that when only a polarizer or only an analyzer is used, extinction of the diffracted light is obtained only along the direction corresponding to the vibration direction of the polarizer or that of the analyzer. With crossed polarizers the diffraction pattern consists of four arcs at 45° to the polarizer and analyzer axes. A similar result is reported by Moore and Gieniewski[8] in the case of ringed spherulites of unstrained polyethylene.

The molecular arrangement described above is further confirmed by the following interesting features observed by us. When only a polarizer was used, the visibility of the circular rings was found to be better along directions which are more away from the vibration direction of the incident light (best around 90°). In fact, the circular rings are totally absent along the direction parallel to the vibration direction of the polarizer. Figure 10 which was obtained by using only a polarizer along the horizontal direction exhibits these features. These features arise as a consequence of the fact that the

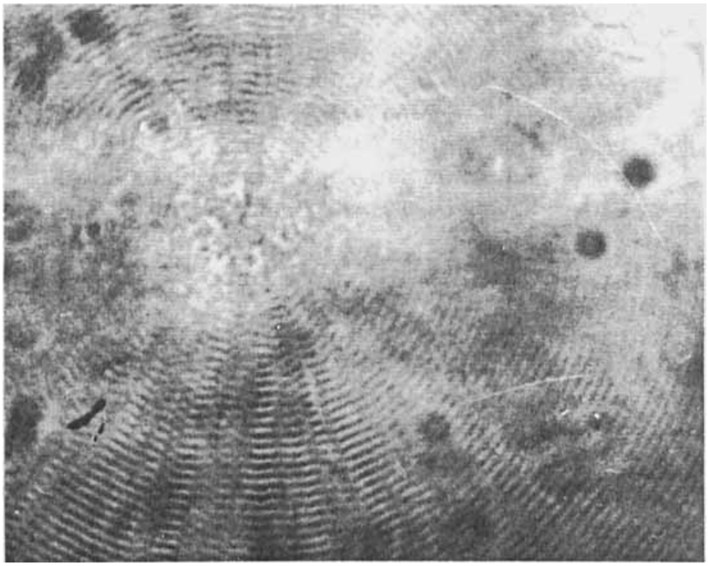
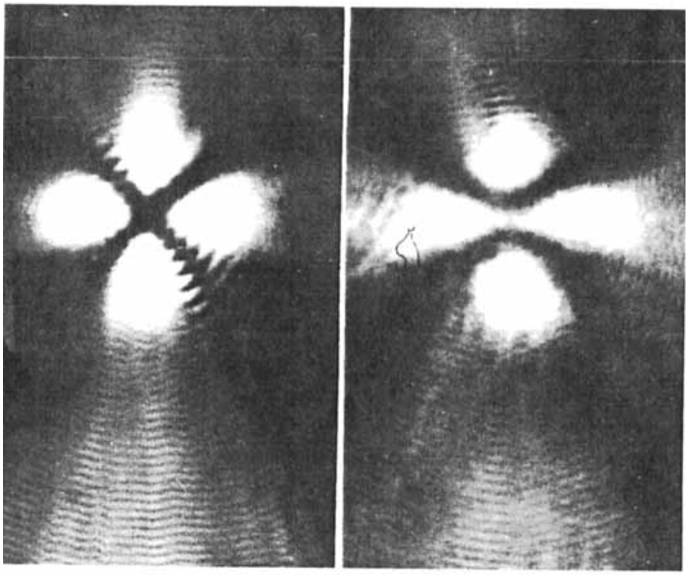


FIGURE 10 Microphotograph of a spherulite of a doped sample (with 2.4% cetyl alcohol) obtained with polarized white light, the direction of vibration of the polarizer being horizontal. 1480 ×

refractive index of the periodic structure alternates more drastically for radial directions away from the vibration direction. For the radial direction parallel to the polarizer, no optical heterogeneity is involved and hence no Becke line effect arises.

It may be remarked here that Clough *et al.*[12] have given a theory of the scattering of light by two dimensional ringed spherulites and good agreement is found between their theory and the experimental results of Moore and Gieniewski.[8] Their theory predicts that the intensity of scattering is a maximum when the condition, $\lambda = d \sin \theta$, is satisfied. Here, λ is the wavelength of light, d is the ring spacing and θ is the angle of diffraction. The ring spacing d corresponds to one half of the pitch of the helicoidal structure around the radial direction. The diffraction and the associated polarization effects observed by us are consistent with the theory of Clough *et al.*[12] corresponding to a helicoidal arrangement of the long axes of the molecules about each radial direction, the long axis being transverse to the radial direction.

Although we have mentioned above that the molecular axes are transverse to the radial direction and lie along the planes normal to it, there are evidences to show that this is not always strictly conformed to. The radial faults and zig-zag cross (shown in Figure 11a) and the isogyres similar to the



(a) (b)

FIGURE 11 Microphotographs of spherulites of a doped sample between crossed polars. (a) Zig-zag nature of the Maltese cross. 1300 ×. (b) Biaxial type of extinction. 1290 ×.

biaxial figure (shown in Figure 11b) indicate that sometimes deviations from the ideal molecular arrangement described above, do occur. This feature is also confirmed by the fact that sometimes the diffracted light is not perfectly polarized with its vibration direction transverse to the radial direction; the diffracted light is composed of also a very weak component with its vibration direction parallel to the radial direction.

The pitch distance of the helicoidal arrangement about the radial directions may be calculated from the equation, $\lambda = (P/2)\sin\theta$, where λ is the wavelength of light, P is the pitch of the helix and θ is the angle of diffraction. The pitch can also be deteremined from the photographs exhibiting the fine circular rings by measuring the spacing between the rings which should correspond to $P/2$. For a specimen doped with 2.4% of cetyl alcohol, the two values of the pitch thus determined are 1.83 μ and 1.84 μ and agree very well. Table I shows the agreement in the values of the pitch calculated from the diffraction rings of different wavelengths obtained with a sample doped with 2.4% of cetyl alcohol. For pure cholesteryl acetate the value of the pitch is about 1.6 μ. In the case of doped samples, the values of the pitch are higher and lie in the region of 1.7 to 1.9 μ. It is found that in the case of doped samples the pitch is practically uniform over the area of each spherulite; however, the pitch varies by about ± 0.05 μ for the different spherulites

TABLE I

Pitch calculated from the angles of diffraction for different wavelengths in the case of a doped sample with 2.4% of cetyl alcohol.

λ in Å	3650	4047	4358	5461	5780
θ	23°28′	26°19′	28°17′	36°25′	39°4′
P in μ	1.83	1.83	1.84	1.84	1.83

in different regions observed with any particular doped sample. Hence, we are not giving any curve representing the variation of the pitch with concentration.

The poor definition of the fine circular rings and the wide and weak optical diffraction rings observed with the spherulites of pure cholesteryl acetate indicate that the pitch of the radial helicoidal arrangement in this case is not very uniform. The fan-shaped fibrillar textures of pure cholesteryl acetate appear to be crystalline as may be inferred from the extinctions observed between crossed polars parallel and perpendicular to the individual fibrils. The absence of both optical diffraction and the ring structures also confirms that the molecular arrangement in the fibrils is different from that in the case of spherulite textures.

Finally, the following remarks may be made. The pitch of the helicoidal structure is considerably smaller in the case of cholesteryl acetate than in the case of PBLG solutions where it is of the order of 10 μ. Higher orders of diffraction are not observed by us owing to the pitch being very small here. We have confirmed that doping of cholesteryl acetate with stearyl alcohol also leads to optical effects which are essentially similar to those described above and investigations with stearyl alcohol as impurity are in progress.

Acknowledgements

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References

1. E. Sackmann, S. Meiboom, L. C. Snyder, A. E. Meixner, and R. E. Dietz, *J. Amer. Chem. Soc.*, **90**, 3567 (1968).
2. P. Debye and F. W. Sears, *Proc. Nat. Acad. Sci. U.S.*, **18**, 409 (1932).
3. C. Robinson, *Trans. Faraday Soc.*, **52**, 571 (1956).
4. C. Robinson, *Proceedings of the First International Conference on Liquid Crystals* (Gordon and Breach Science Publishers, London, New York, Paris, 1965) p. 147.
5. H. D. Keith and F. J. Padden, *J. Polymer Sci.*, **39**, 101 and 103 (1959).
6. A. Keller, *J. Polymer Sci.*, **39**, 151 (1959).
7. F. Price, *J. Polymer Sci.*, **39**, 139 (1959).

8. R. S. Moore and C. Gieniewski, *J. App. Phys.*, **36**, 3022 (1965).
9. R. S. Stein and M. B. Rhodes, *J. App. Phys.*, **31**, 1873 (1960).
10. R. S. Stein and A. Plaza, *J. Polymer Sci.*, **45**, 519 (1960).
11. R. J. Clark, R. L. Miller, R. S. Stein, and P. R. Wilson, *J. Polymer Sci.*, **42**, 275 (1960).
12. S. Clough, J. J. Van Aartsen, and R. S. Stein, *J. App. Phys.*, **36**, 3072 (1965).
13. 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.
14. G. W. Gray, *Molecular Structure and the Properties of Liquid Crystals* (Academic Press, London and New York, 1962), p. 52.