Optical effects and molecular ordering in the ringed spherulites of mixtures of cholesterol and nematic *p*-anisaldazine

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Abstract : In this paper we discuss the results of our investigations with ringed spherulites formed in the solid phase of pure cholesterol and also in the mixture of cholesterol and nematic p-anisaldazine. The observed ringed spherulite textures are found to exhibit upto four orders of optical diffraction. Using polarizing microscope, the ring spacing d of the ringed spherulites were measured as a function of concentration of p-anisaldazine in the total weight of the mixture. The nature of the molecular order in the ringed spherulites has also been explained using two sensitive optical interference techniques. The optical birefringence measured for pure cholesterol in the solid phase varies from 0.0134 to 0.0163 as the wavelength is changed from 553 nm to 440 nm.

Keywords : Spherulites, birefringence, molecular ordering, liquid crystals, phase grating.

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1. Introduction

It has been known for a long time that many cholesteric compounds and their mixtures and also some polymer samples exhibit spherulite textures with ring structure [1-8]. Gaubert (1931) had first observed the ringed spherulites in the case of pure cholesterol sample, by rapid solidification of the molten sample. However, the formations of the ring structures in this pure sample were not regular and uniform and consisted of numerous wrinkles. Gaubert [9] had suggested that the spherulites with regular ring structures having a suitable helical pitch could be obtained by the addition of some amount of impurities (for example, p-anisaldazine, Alantolactone, etc). He had also observed optical diffraction in the above cases but he had not reproduced any diffraction photograph or micro photograph. In this paper we report some of the observed optical effects and also the composition dependence of the helical pitch in the system containing cholesterol and a nematic p-anisaldazine. The helicoidal nature of the molecular structure in these systems is also confirmed by using the same interference techniques described by us earlier [7].

2. Experimental results and discussion

In our experiment, we have used the commercially available cholesterol sample and p-anisaldazine after purifying them by recrystallization from their solutions in benzene. The

specimens were prepared by having the samples between the slide and cover glass and the molten samples were allowed to cool at room temperature of approximately 28°C. The optical observations were made using the polarizing microscope. The sample of pure cholesterol when cooled from its isotropic melt, exhibits ringed spherulites of very large ring spacing ($d \simeq 230$ μm) (see Figure 1.) The ring-structures of these spherulites are not
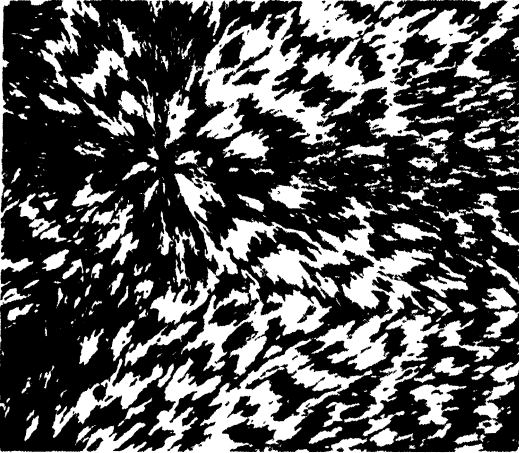

Figure 1. Microphotograph of ringed spherulites of pure cholesterol. Crossed polars (ring spacing $d \simeq 230$ μm).

regular and uniform. As suggested by Gaubert [9], therefore, the samples of various concentrations of cholesterol and p-anisaldazine were prepared. The mixtures of the above two compounds give rise to spherulite textures with reasonably uniform ring structures (see Figure 2). The ring structures also exhibit polarisation effect with regard to their visibility.
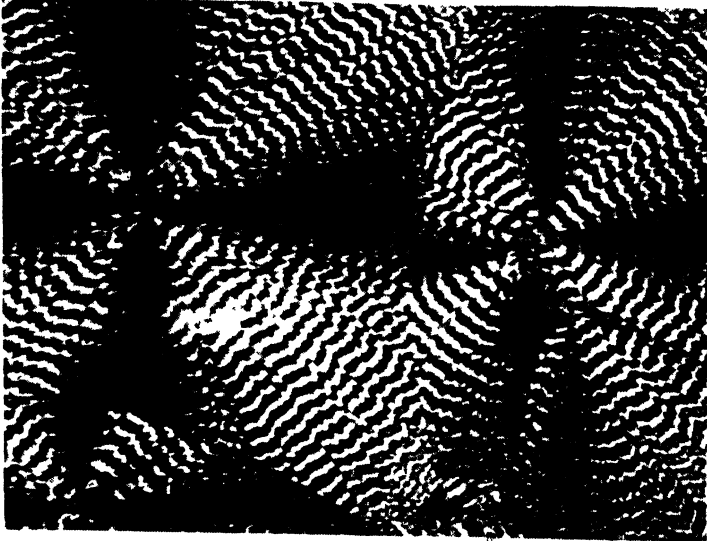

Figure 2. Microphotograph of ringed spherulites of a mixture of cholesterol and p-anisaldazine (15%). Crossed polars (ring spacing = 17 μm).

The ring spacings for samples of various concentrations were measured directly using the polarizing microscope. The observed ring spacing d or the pitch of the helix p (= $2d$) was found to decrease with the increase of the concentration of p-anisaldazine, in the total weight of the mixtures (see Figure 3).
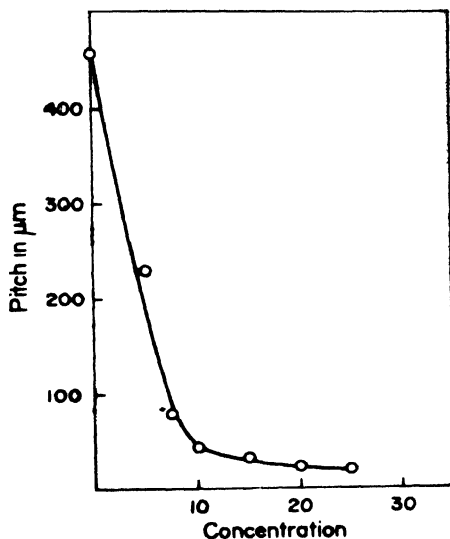

Figure 3. Variation of helical pitch with the concentration of p-anisaldazine.

Further, the ringed spherulites behave as phase gratings and give rise to optical diffraction as a consequence of the periodic variation of the refractive index, for light polarized transverse to the radial direction. Figure 4 exhibits the different orders of the
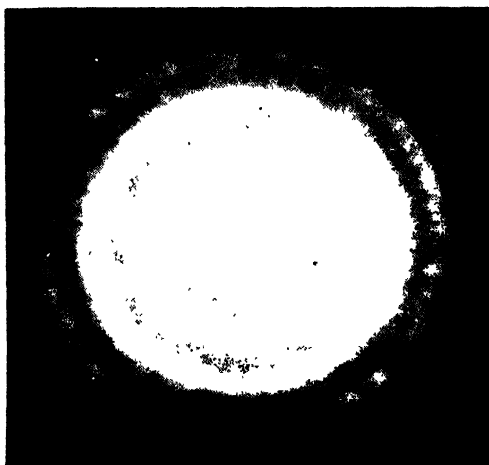

Figure 4. Diffraction pattern obtained with a spherulite texture shown in Figure 2 and using incident light of λ = 5461 Å.

6A (5)

diffraction spectra recorded using the unpolarized 5461Å radiations of the mercury arc. The polarization of the diffraction rings along the radial direction is also observed by interposing a polarizer with its vibration direction along the horizontal, in the path of the light incident on the specimen. In the following are presented results to show that the refractive index is indeed variable continuously and in a periodic fashion.

In the case of cholesteric compounds and their mixtures, the periodic variation of the refractive index was confirmed unambiguously by us with the aid of an elegant interference experiment, the complete details of which are given in an earlier paper [7]. Therefore, only a brief outline of the principle of the experiment is given here. It is well-known that when a birefringent crystal (with its principal directions horizontal and vertical) is kept between crossed polars at 45° to the vertical, the spectrum of white light transmitted through the combination exhibits a series of extinctions (Figure 5a) which satisfy the equation [10],

Figure 5(a).   Banded spectrum obtained with a crystal of $BaSO_4$ ($t = 0.16$ cm) kept between crossed polars. The left end corresponds to the red region of the spectrum.

Figure 5(b).   Banded spectrum showing the periodic shift of the extinctions observed with a ringed spherulite of a sample containing 5% p-anisaldazine.

$$m \lambda_o = t\Delta n_o .$$ (1)

Here, t and Δn_o denote respectively the thickness and the birefringence of the crystal (Barite $BaSO_4$). λ_o is the wavelength at which extinction occurs and m is an integer. If a spherulite is interposed in juxtaposition with the birefringent crystal in the above combination, additional path difference arises and the wavelengths of the extinctions shift their positions periodically. Figure 5(b) exhibits the periodic shift of the extinction towards the red. For each sinusoidal band in Figure 5(b), the wavelength difference $(\lambda_1-\lambda_o)$ between the points of extreme excursion satisfies the relation [7],

$$m (\lambda_1 - \lambda_o) = t_1 \Delta n_1 .$$ (2)

Here, Δn_1 is the birefringence associated with the spherulite of thickness t_1. The value of $(\lambda_1 - \lambda_o)$ in the above equation for any sinusoidal band can be easily determined from the measured values of wavelengths corresponding to the two extreme excursions. Using eq. (2) and employing the same procedure discussed earlier [7], it was possible to determine the values of Δn_1 of the ringed spherulites of pure and doped samples which are graphically

represented in Figure 6. As may be seen from this figure the birefringence associated with the spherulites of pure and doped samples vary differently. This can be generally expected for the fact that the pure sample exhibits spherulites of non-uniform ring structure. Further in the case of doped sample the molecule of p-anisaldazine endow the ring structure with uniform pitch for the helicoidal arrangement about each radial direction. As a result the oscillatory strength, which determines the dispersion of birefringence, is small in the spherulites of pure sample when compared to the doped sample.
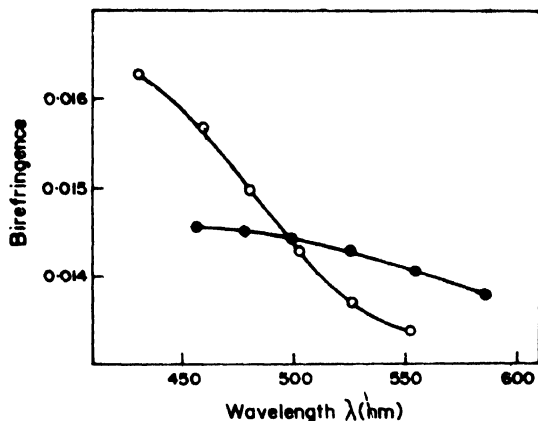

Figure 6. Variation of the birefringence Δn_1 with wavelength (i) pure cholesterol —o—, (ii) with 5% p-anisaldazine —•—

Using the Babinet compensator it is also observed that the spherulites of pure cholesterol and its mixture with p-anisaldazine give rise to interference fringes [7] which exhibit the periodic shift. From the measurement of extinctions, the birefringence and the phase shift associated with the spherulite of sample containing 5% p-anisaldazine were found to be respectively 0.0138, and 3.74 radians, for $\lambda = 589$ nm. These values are in good agreement with those determined using the banded spectrum method.

Acknowledgment

References

[1]   A Keller 1955 *J. Polymer Sci.* 17 291; 17 351

[2]   H D Keith and F J Padden 1958 *J. Polymer Sci.* 31 415

[3]   R S Stein and M B Rhodes 1960 *J. Appl Phys.* 31 1873

[4]   R S Stein and A Plaza 1960 *J. Polymer Sci.* 45 519

[5]   R S Stein, M B Rhodes and R S Porter 1968 *J.Colloid Interface Sci* 27 336

[6]   D Revannasiddaiah, M S Madhava and D Krishnamurti 1977 *Mol. Cryst. Liq. Cryst.* 39 87

[7]   D Krishnamurti, M S Madhava and D Revannasiddaiah 1978 *Mol Cryst Liq Cryst* 47 155

[8]   G Chiu, R G Alamo and L Mandelkern 1990 *J. Polymer Sci.* 28 1207

[9]   M P Gaubert 1931 *Compt. Rend.* 192 1576

[10]   M A Wooster and /. Breton 1970 *Experimental Crystal Physics* (Oxford : Clarendon press) p 13