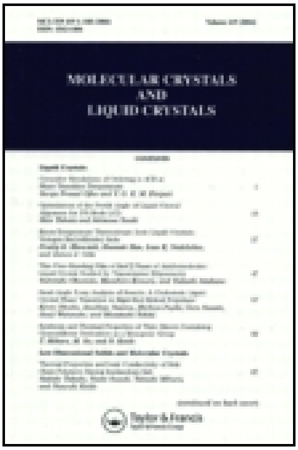

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Light Scattering Properties of Cholesteric Liquid Crystal Films

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Light Scattering Properties of Cholesteric Liquid Crystal Films

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Abstract—It has been observed that cholesteric liquid crystal films exist in two states both of which exhibit characteristic brilliant colors. A transition between the two states can be caused by a variety of disturbances including mechanical perturbation and electrophoretic action.[1] Optical scattering data indicate that the fundamental dispersive cause in both the undisturbed state and the disturbed state is the existence of regions of local order characterized by optically anisotropic layers stacked in a helical fashion. Intensity studies indicate that the angular distribution of helical axes is not isotropic in either state. In the undisturbed state the helical axes lie predominantly in the plane of the surface whereas in the disturbed state the helical axes are predominantly normal to the surface. This is confirmed by microscopic observations which show in the undisturbed state regions (with the dimensions of microns) of large birefringence and no optical activity. The disturbed state exhibits one uniform color between crossed nicols along with dispersive optical activity. Typical materials used were mixtures of cholesteryl nonanoate and cholesteryl chloride. The significance of a reflecting substrate is also treated.

1. Introduction

Certain cholesteric liquid crystal films, when cast from solvent, have a cloudy colorless appearance. Under microscopic study, these films exhibit properties characteristic of the focal conic texture of the cholesteric mesophase. That is, there are regions of local birefringence of the order of a few microns. When these films are disturbed mechanically, the disturbed regions exhibit the characteristic brilliant reflection colors associated with the Grandjean texture of the cholesteric mesophase.[2] If the chemical composition of the mixture is altered, in some cases only slightly, and a reflecting substrate employed, the above sequence is reversed, that is the virgin film is brightly colored (although microscopically it still appears focal conic), and the disturbed film appears colorless.

We have studied these films using optical scattering data, and conclude that the degree of local organization in the disturbed and undisturbed states is the same, and that the effect of disturbance is to reorient the regions of birefringence.

Both disturbed and undisturbed films exhibit color, but whether or not the color is in the visible, depends on chemical composition. The appearance or disappearance of color upon disturbance corresponds to a color shift into or out of the visible as a result of disturbance. A first guess at the mechanism for a discreet color shift would be a change of pitch, p, in the helical scattering structure. We will show that this is not the case, but rather, that a peculiar combination of reorientation plus the effect of a reflective substrate causes the shift.

2. Experimental Procedure

The experimental arrangement is shown in Fig. 1. The sample was mounted vertically on a spectrometer stage. A monochromator was used as a source and a photodiode as a detector. For a given angle of incidence and angle of observation, the wavelength most strongly reflected was recorded. The accuracy was of the order of 100 Å for any given measurement. All data were taken at room temperature in films approximately 5 microns thick. Over 130 measurements were made on each film studied and an attempt was made to study as broad a range of angles and wavelengths as possible. No measurements were made below 4000 Å or above 8000 Å. The system studied consisted of mixtures of cholesteryl nonanoate and cholesteryl chloride and the percent by weight of the cholesteryl chloride will be referred to as α. The disturbed films were studied first. A black plastic substrate was used. The disturbed films reflect

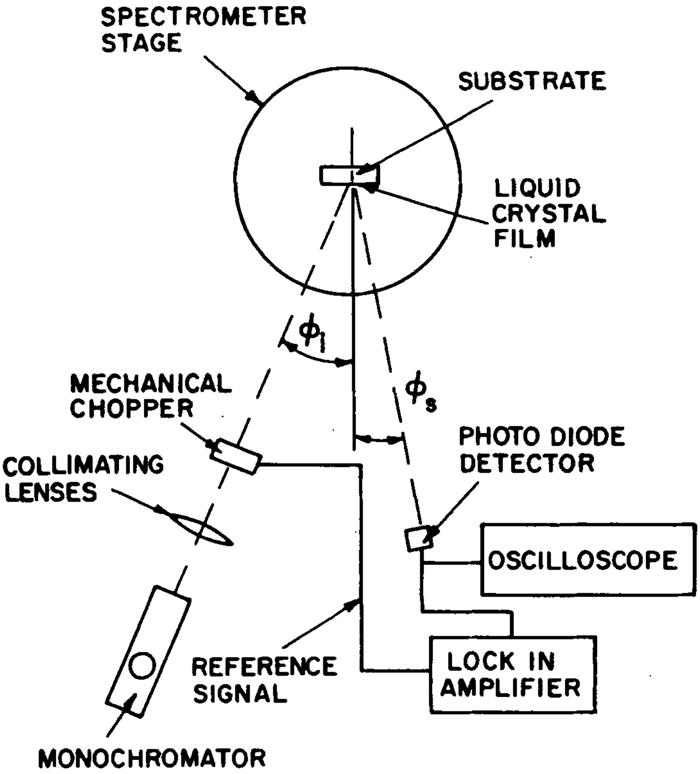

Figure 1. Experimental configuration

colors in the visible over a wide range of angles in the region between 25% cholesteryl chloride and 35% cholesteryl chloride. The data were computer fitted to the formula given by Fergason[3] shown in Eq. (1).

$$\lambda = 2np \cos \tfrac{1}{2}\left\{\sin^{-1}\left(\frac{\sin \phi_i}{n}\right) + \sin^{-1}\left(\frac{\sin \phi_r}{n}\right)\right\} \qquad (1)$$

Here ϕ_i and ϕ_s are the angles of incidence and observation respectively and λ is the observed wavelength. This formula is based on a model of Bragg like scattering regions imbedded in a medium of refractive index n. Each region has an internal helical structure, and the screw axis will be referred to as the normal to the site. The computer gave independent values for pitch and index of refraction. The fit was excellent and confirmed the model. However, this equation tells nothing about the distribution of scattering sites but only relates color to angle of incidence and observation, assuming the presence of scattering sites. We have observed that, although this equation is obeyed for all signals measured, the signal intensity is very strong near specular reflection and very weak away from specular. This implies that most Bragg sites have their normals close to perpendicular to the surface. Of course, there must be some distribution in direction, otherwise the system would act as an interference film and exhibit only specular reflection. However, only a small deviation away from the helical axis being .perpendicular to the surface is required to produce visible reflection at all angles. The refractive fanning effect at the surface enhances this. For these materials the critical angle for total internal reflection is around 40° so a Bragg region tilted only 20° will reflect parallel to the surface. Since we observe a severe decrease in signal intensity a few degrees away from specular, we conclude that the spread in normals is very small. Figure 2 shows the distribution. The microscopic appearance of a disturbed film is consistent with this distribution as will be discussed later.

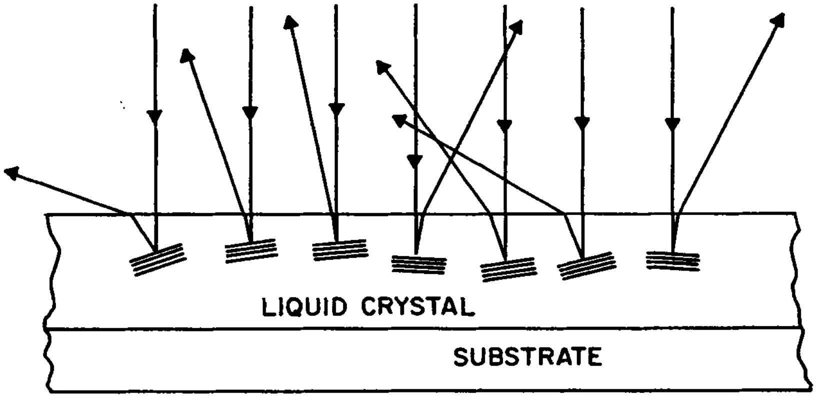

Figure 2. Distribution of scattering sites in a disturbed film

Undisturbed films exhibit visible colors in the range $40 \leqslant \alpha \leqslant 50$ but only when deposited on reflecting substrates. This is not the case in disturbed films, which exhibit colors independent of substrate. The requirement for a reflective substrate implies that either the incident light involved in the Bragg scattering has first been reflected from the substrate, or that after Bragg scattering the observed beam was reflected from the substrate. The geometry for the two cases is equivalent and is shown in Fig. 3.

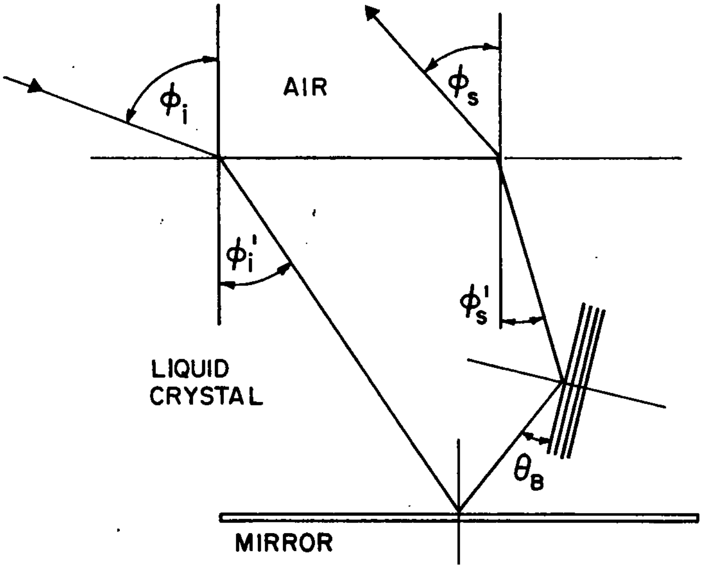

Figure 3. Geometry for scattering from undisturbed films

The data for undisturbed films were taken using an optically flat mirror as a substrate. As a check, the data were fit to the same expression used for disturbed materials. There was no acceptable fit and even the qualitative features of the data were inconsistent with that formula. The expression appropriate to the reflected geometry is given in Eq. (2).

$$\lambda = 2np \sin \tfrac{1}{2}\left\{\sin^{-1}\left(\frac{\sin \phi_i}{n}\right) - \sin^{-1}\left(\frac{\sin \phi_s}{n}\right)\right\} \tag{2}$$

The data taken in undisturbed films fit this expression very well confirming the reflection requirement. Again this formula relates only angles to wavelengths and says nothing about the distribution of scattering centers. In the case of undisturbed films we observed a strong intensity peak in the incident direction. This implies, that the predominant orientation of helical axes is in the plane of the surface. This situation is shown in Fig. 4. Data from these films also give values for pitch. There is a narrow range of chemical composition over which both disturbed and undisturbed films exhibit color in the visible. Measurements in these films indicate that the helical pitch is essentially the same in undisturbed and disturbed films. Furthermore, outside this region the pitch measurements for disturbed films extrapolate into measurements for undisturbed films. These results are shown in Fig. 5. The apparent color shift, attendant with disturbance, then, is caused by a wholesale reorientation of scattering regions such as to Bragg-reflect the light from the substrate into the eyes of the viewer, so, although the pitch of the structure is not changed, the effective angle of incidence is radically changed, and therefore for the same viewing angle, the supported wavelength is greatly changed. Of course, the initial and final colors are independent of film thickness and depend only on chemical composition.

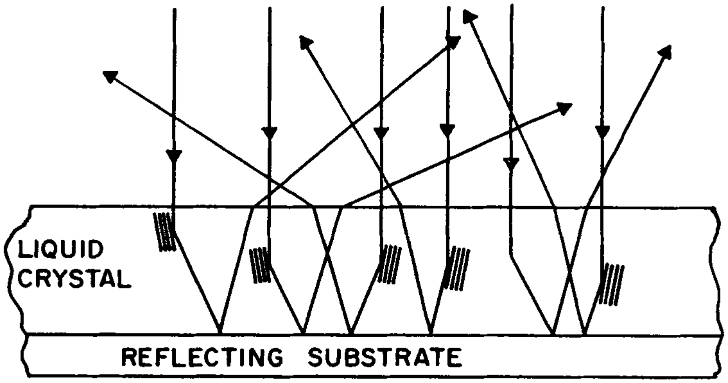

Figure 4. Distribution of scattering sites in an undisturbed film

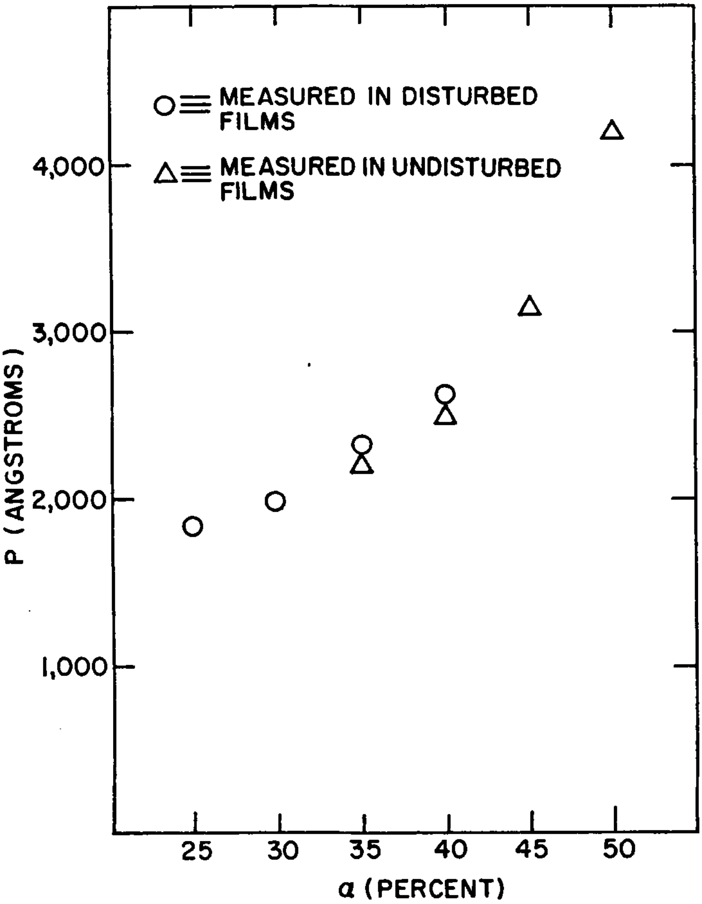

Figure 5. Pitch versus chemical composition

Furthermore, the effect of disturbance causes a large discreet color shift and no intermediate states are stable.

We have studied these films in some detail with the microscope and find an interesting confirmation of the model. This work was done using a Leitz Ortholux polarizing microscope with a 50 × objective and a 25 × eyepiece. This magnification is sufficient to reveal much significant detail in the films. All observed properties of disturbed films are consistent with the optical characteristics associated with the Grandjean plane texture described in the literature.[4] That is, the films exhibit anomalous dispersive optical activity, show a negative uniaxial conoscopic interference figure and even, under high magnification, produce a uniform color between crossed polarizers. If the scattering that produces color, comes from regions of local helical order consisting of stacks of optically anisotropic sheets, then each of these regions is optically equivalent to a birefringent crystallite with the helical axis playing the role of the optic axis. The optical indicatrix, for any one region, is of course an ellipsoid of revolution. One must ask how a large number of these birefringent regions can orient such as to produce the microscopic properties described above. The only orientation distribution of these regions consistent with these observations is that all optic axis are essentially parallel to one another and perpendicular to the film surface. This is precisely the requirement placed on the orientation of these sites from the intensity measurements in reflection data described previously. If, on the other hand, one postulates a random distribution of crystallites, the equivalent microscopic picture would be a potpourri of different color spots each determined by the local orientation. Furthermore, this film could exhibit no macroscopic optical activity, and certainly no conoscopic pattern. We also feel that a parallel or nearly parallel arrangement favors a coalescing of regions into larger units which would produce an even more homogeneous optical appearance. Also, as discussed before, only small deviations from an actual parallel sheet structure are required to produce a reflection signal at other than specular.

Now we turn to the microscopic appearance of an undisturbed film. Here, the optical reflection data required that the optic axis of the scattering centers lie parallel to the plane of the surface. Since these regions are birefringent, between crossed polarizers there should be no extinction unless the optic axis of the region happened to line up with the polarizer or be perpendicular to the polarizer which in general will not be the case.

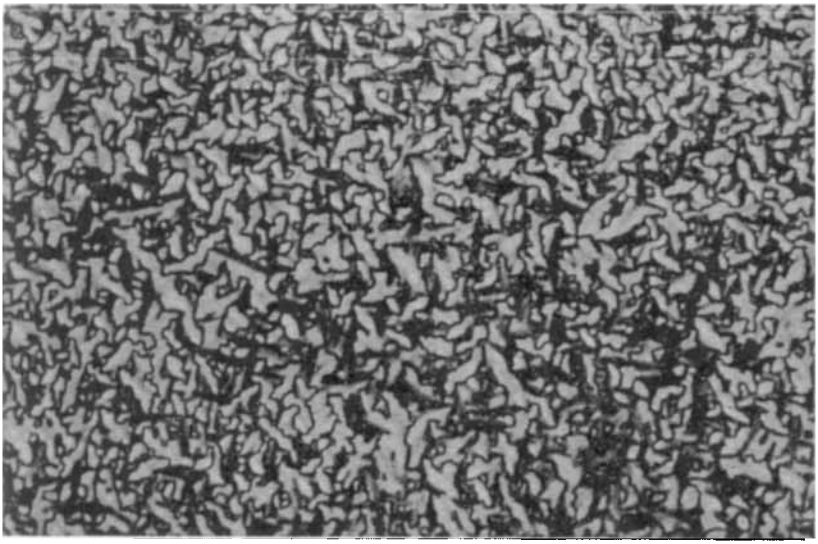

Figure 6. Undisturbed film between crossed polarizers—field of view 50 microns

Figure 6 shows these birefringent regions. Finally, to study the birefringence in more detail a first order red compensator was inserted in the optical path. In this case a birefringent sample either adds to or subtracts from the birefringence of the compensator depending on the relative orientation of fast and slow axes. Here, very distinct regions of local birefringence are observed, the color depending on the orientation of the optic axis relative to the retardation plate. Of course, this structure cannot exhibit optical activity, since the emergent light is not plane polarized but rather in general elliptically polarized and polarized differently in each local region.

Although this microscopic picture corroborates the distribution predicted from optical scattering data, we want to be careful in terms of interpreting the details of these regions. We do not feel that these regions represent separate isolated islands of material like grains of salt but rather that there is continuity between regions and a longer range layer nature to the structure.

Although the distinction between undisturbed and disturbed films in the system studied is clear, in other systems the original film may appear disturbed immediately after solvent evaporation. This is particularly true of films of low viscosity. For example, if significant amounts of oleyl cholesteryl carbonate are mixed into the cholesteryl chloride-cholesteryl nonanoate system the resulting films will be disturbed after evaporation.

In summary, we have shown that certain cholesteric mixtures can exist in two states, both of which exhibit dispersive reflective colors. The transition from one state to the other is accomplished by a mechanical disturbance. The color shift is the result of a major re-orientation of Bragg like scattering regions with no significant change in the helical pitch.

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REFERENCES

1. Haas, W. and Adams, J., *Appl. Optics* 7, 1203 (1968).
2. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals* (Academic Press, Inc., New York, 1962).
3. Fergason, J. L., *Mol. Cryst.* 1, 293 (1966).
4. Friedel, G., *Ann. Phys.* 18, 273 (1922).