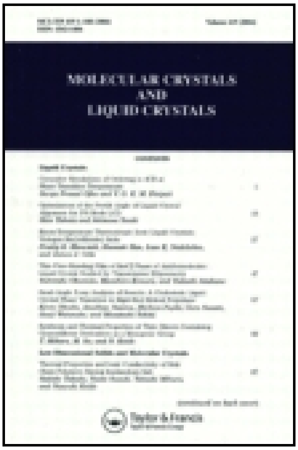

# Molecular Crystals and Liquid Crystals

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# Some Optical Properties of Dispersed Cholesteric Liquid Crystals

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High iridescence has been achieved by the dispersion of cholesteric liquid crystals in polyurethane elastomers. A model based on Frank's disclination theory is proposed whereby the aggregate size and pitch determine a textural change from a spherulitic texture to an "aligned" plane texture as the size of the dispersed aggregate decreases. This is accomplished by the different free energy relationships of radial and surface defects in the dispersed state. Discussion of the model and experimental observations center on the morphological, chemical and physical parameters which determine high iridescence of dispersed cholesteric liquid crystals and hence the effect of these parameters on the topological role of defects in attaining high iridescence.

## INTRODUCTION

Cholesteric liquid crystals in the plane texture display the interesting and useful property of selectively scattering white light into brilliant iridescent colors. This property finds utility in thermal mapping, bio-medical and non-destructive testing, and other applications. In order to protect the liquid crystals from contamination by dust and other foreign elements, it is desirable to disperse the cholesteric liquid crystal within a transparent polymer matrix which can be formed into re-usable thin films.

There are numerous polymers in which one can successfully disperse cholesteric liquid crystals[1] and subsequently form thin films. The problem, however, is that once dispersed the liquid crystals, even when present in high concentrations, generally exhibit a lower intensity and iridescence than "naked" cholesteric liquid crystals in the plane texture. However, it has been shown that polyurethane formulations having uniformly dispersed cholesteric liquid crystal aggregates smaller than 2–3 $\mu$ in diameter provide highly iridescent reflections similar to those of "naked" liquid crystals. We have also observed that this iridescence in polyurethanes is often time-dependent, increasing with time.[2] These observations have led to the question the relationship between iridescence and structure in cholesteric dispersions within polyurethanes.

Cholesteric liquid crystals are known to form several different textural arrangements when spread on a free surface or placed between glass plates.[3] The cholesteric plane texture is composed of twisted two-dimensional nematic layers where the optic axis is everywhere perpendicular to the glass plates. When the pitch of the helix in the plane texture is of the proper dimension for Bragg scattering of visible light, the structure reflects highly iridescent colors. With the cholesteric focal conic texture (also called the "undisturbed" texture), however, the optic axis is parallel to the glass plates,[4] and the texture does not reflect iridescent colors and has a milky appearance since the repetitive pitch planes are not at the correct angle for Bragg scattering.

When cholesteric liquid crystals are dispersed in a polymer or liquid matrix, however, the liquid crystal tends to form into spherical drops. The boundary conditions of this spherical geometry create different textural structures. Robinson[5] has shown that cholesteric phases of poly-benzyl-L-glutamate solutions tend to form what he calls "spherulitic" textural droplets. Bouligand[6] has shown other textural arrangements in dispersed droplets of cholesteric liquid crystal.

The spherulitic texture may be considered to be an intermediary molecular structural distribution between the Grandjean planar texture and the focal conic or "undisturbed" state.

## EXPERIMENTAL

Experiments have been carried out by dispersing cholesteric liquid crystals within urethane monomers, with subsequent polymerization into polyurethane elastomeric liquid crystalline dispersions, (PUELCD). Typical PUELCD formulations have been reported elsewhere.[2,7]

Liquid crystals used were cholesteryl linoleate and a mixture of cholesteryl linoleate and cholesteryl chloride, dispersed 30% by weight in polyurethane elastomers formed from toluene diisocyanate monomer and polyol having molecular wieghts of 3000, and a functionality of 3. The procedure was to dilute the polyurethane-liquid crystal solids content to 50% in toluene. Once homogeneity of the solution was reached, it was cast onto a substrate, a glass microscope slide in the case of microscopic observations. Films were cast, either as uniformly thick films (0–200 $\mu$) or in a gradient. Solvent evaporation and polymerization took place at room temperature with a varying humidity.

Macroscopic observation was carried out with subjective visual observation, aided by the rotation of a $\frac{1}{4}\lambda$ plate in front of a polarizing filter. The degree of extinction represents the degree of order achieved from the Bragg scattering of the sample from various angles. This was supplemented by continued heating and cooling cycles of the samples on a bipolar temperature-controlled stage (Cambion). Microscope observations were carried out at room temperature ($\simeq$24°C) by polarization photomicroscopy (Nikon PoH).

It is worth noting, and relevant to discussions presented in this paper, that thousands of experiments have been performed on PUELCD systems over the past 5 years in these laboratories. Many observations, particularly on the time-dependence of iridescence have been carried out on diverse systems, employing many varieties of liquid crystal in many different types of polyurethane matrices.

## OBSERVATIONS

We have concluded from our observations that under suitable conditions in polyurethane there is a critical size range (2–3 $\mu$ in diameter) for dispersed aggregates of cholesteric liquid crystal reflecting visible light. Above this critical size range aggregates display a spherulitic structure which creates a low iridescence color reflection. Below this critical size range aggregates display what we call an "aligned" texture which reflects highly iridescent colors in contradistinction to the spherulitic texture.

Plate 1 shows a spherulitic texture between crossed polarizers in polyurethane. This texture has been described in detail by Robinson.[8] The spherulitic texture is made possible by a high energy radial disclination as first described by Frank[9] as a $n = 4$ disclination. The optic axis in the spherulitic texture runs radially out from the center of the droplet such that it is everywhere normal to the interfacial surface. The long axis of the interfacial molecules are everywhere tangent to the spherical aggregate surface.

Plate 2 is a photomicrograph between crossed polarizers showing dispersed cholesteric liquid crystal aggregates smaller than 2–3 $\mu$ in diameter in polyurethane. Here we have a return to a structure similar to naked liquid crystals where the optic axis inside an individual aggregate runs in only one direction, which we call the "aligned" texture. For optimal iridescence in the aligned texture it is desirable to have the optic axis in as many aggregates as possible perpendicular to the film surface.

In most polyurethanes, 2–3 $\mu$ seems to be the critical size diameter for textural change. However, deviations from this behavior do occur. While we believe this scale factor is of major importance, the formation of textures

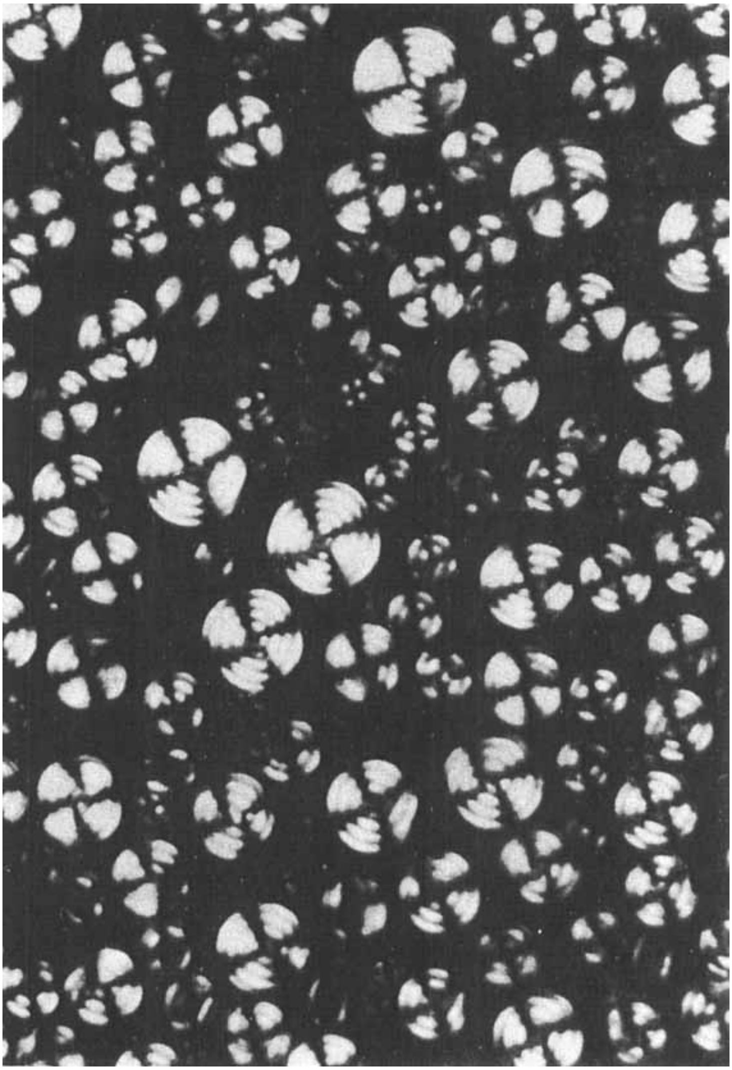

PLATE 1 30% Cholesteryl linoleate/cholesteryl chloride mixture dispersed in polyurethane elastomer. × Nicols. mag. × 200

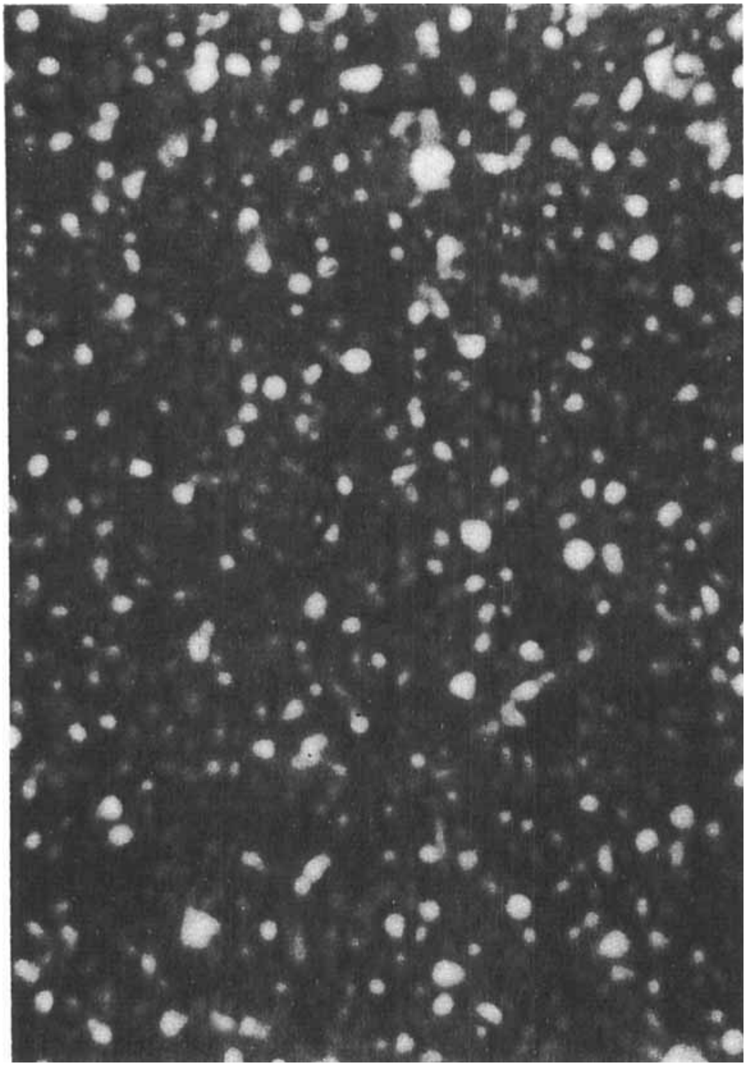

PLATE 2 30% Cholesteryl linoleate dispersed in polyurethane elastomer. × Nicols. mag. × 315 within dispersions is undoubtably effected by other parameters such as surface tension, polymer structure, aggregate shape, and interfacial conditions between the liquid crystal and polymer.

Another interesting observation concerning the iridescence of cholesteric dispersions is the effects of time. Often the iridescence of dispersions within polyurethanes have been observed to gradually but continually increase over weeks and months.[2] This is not a transitory but permanent increase and is stable upon repetitive heating and cooling cycles. Some samples are in excellent condition after five years.

## A MODEL SYSTEM

In order to explain the textural changes observed in polyurethane as aggregates fall below $\simeq 3\ \mu$ in diameter, a model system, based on disclination theory, predicts a textural change as aggregate size changes. In the construction of this model the following has been assumed: that the liquid crystal molecules are rod-like and, as in the spherulitic texture, that the polymer interface imposes a major orientation on the interfacial layer of liquid crystal molecules such that the long axis of the rod-like interfacial molecules are always tangent to the spherical aggregate interface. One possible arrangement of molecules in the aligned texture which meets these assumptions is made possible by a continuous $n = +1$ disclination running in a helical sense up the side of the aggregate (see Figure 1).

The free energy of this proposed "aligned" texture and the spherulitic texture can be modelled by assuming that the primary difference in free energy between the two lies in the disclination formations. The relative energy values for the disclinations may be calculated from Frank's[9] observation that the energy of a disclination is proportional to the value of $|n|^2$. Thus if we compare a $n = +4$ with a $n = +1$ disclination, a unit length

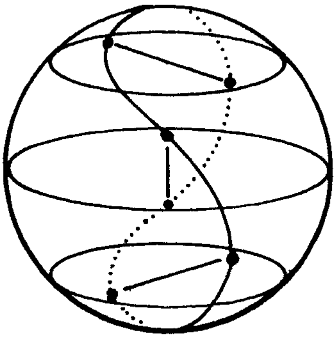

FIGURE 1 $n = +1$ disclination of model "aligned" texture.

of a $n = +4$ will have 16 times the energy of a unit length of a $n = +1$ disclination. The length of the spherulitic $n = +4$ disclination is equal to the radius of the dispersed aggregate. The length of the $n = +1$ disclination in the proposed "aligned" texture is a function of both aggregate size and pitch as is given below.

$$L_{n=+1} = 2r\int_0^{\pi} \sqrt{\rho^2 \sin^4 \phi + 1}\, \mathrm{d}\phi \qquad \text{where} \quad \rho = \frac{2\pi r}{p}.$$

This equation expresses the length ($L$) of the disclination (as in Figure 1) for a condition of spherical co-ordinates where a cholesteric liquid crystal of pitch ($p$) is aligned in an aggregate of radius ($r$), where $\Theta$ defines the helical displacement from layer to layer and $\varnothing$ defines an angle with its stationary axis normal to $\Theta$.

Figure 2 shows the energy of the disclinations or the free energy of the textures as a function of aggregate size. For cholesterics having specific

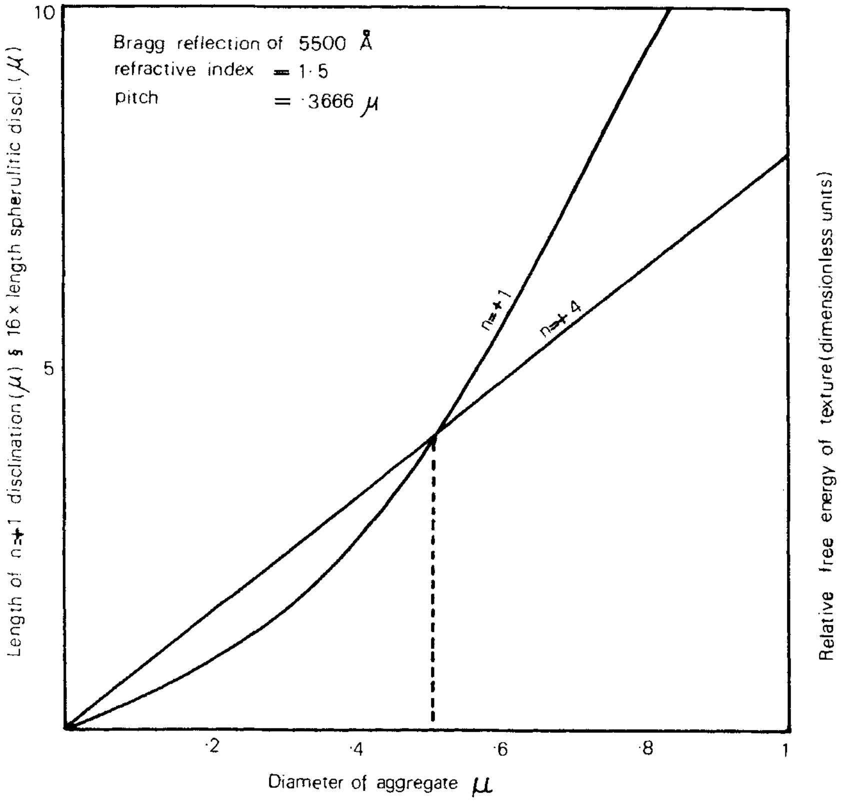

FIGURE 2 Dependence of texture formation on aggregate size.

pitch values there is a critical aggregate size above which the spherulitic texture is stable and below which the aligned texture is stable. If the values for visible light of 5500 Å are plotted, the theoretical critical aggregate size is 0.509 $\mu$ in diameter, which is somewhat smaller than the 2–3 $\mu$ which we observe in polyurethanes.

## DISCUSSION

A model system is proposed that demonstrates a textural change with changes in scale or pitch, although predicted values fall somewhat below observed values. Other model systems are possible assuming other types of disclinations, such as $n = +2$, or for different boundary conditions such as interfacial molecules lying perpendicular as opposed to tangent with the interfacial surface, or for variable boundary conditions that may be created by a "soft" interface.

The physico-chemical basis for time-dependent ordering of the PUELCD systems is not fully understood. However, observations indicate that there may be morphological changes produced by the second order bonding mechanism of the elastomer,[10] causing a compressive distortion to the aggregate which may serve as a means of anchoring or "pinning" of surface disclinations to the aggregate wall. Dion[11] has recently shown that the compression effect on the cholesteric helix is 0.5 nm/atm in the region from 0–1 atmosphere. This is concurrent with observations of PUELCD systems where an upward shift of the cholesteric mesophase has been reported.[2,7] One might postulate a distortion of an aggregate from a spherical towards an oblate or prolate form, and this obviously complicates the idealized spherical model proposed.

On the other hand an argument can be made for chemical interactions underlying the upward shift of the cholesteric mesophase. For example on the initial mixing of a temperature-insensitive mixture of cholesteryl esters a shift to shorter wavelengths is usually observed, and this shift is retained on polymerization of the elastomer. A time-dependent increase in iridescence is also observed. Sarada's[12] work describes effects of polymer additives upon the scattering intensity of cholesteric structures including some additives displaying time-dependent effects upon reflected intensities.

A further time-dependent parameter could be caused by effects between the polymer chains and liquid crystal molecules. Blokland[13] has shown that polyurethane elastomers exhibit some degree of molecular order, which could have an effect upon liquid crystal structure. The molecular interactions of the macromolecular chains and liquid crystal molecules might also depend on the hydrophilicity and lipophilicity of the two components, the resultant parameter (as yet unmeasured) being the interfacial tension between the elastomer and liquid crystal.

## CONCLUSIONS

High iridescence in PUELCD systems has been correlated with aggregate scale and time. Morphological, chemical and physical effects have been postulated as possible relevant parameters towards an understanding of the role of topological defects in the ordering of cholesteric dispersed aggregates. The conclusions to this report are exemplified in the facile observation in white light of 3rd and 5th order Bragg reflections in PUELCD systems[14] illustrating the high degree of order achievable.

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