Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: Donald B. Dupré & James R. Hammersmith (1974): Optical properties of the Magnetotropic Nematic Phase of Poly-γ-Benzyl-ζ-Glutamate, Molecular Crystals and Liquid Crystals, 28:3-4, 365-382

To link to this article: http://dx.doi.org/10.1080/15421407408082832

Mol. Cryst. Liq. Cryst., Vol. 28, pp. 365-382
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Printed in Dordrecht, Holland

Optical properties of the Magnetotropic Nematic Phase of Poly-γ-Benzyl-L-Glutamate

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(*Received January 21, 1974*)

Above a critical concentration in certain solvents poly-γ-benzyl-L-glutamate (PBLG) forms a lyotropic liquid crystal of the cholesteric structure. In the presence of sufficiently strong electric or magnetic fields this liquid crystal undergoes a mesomorphic phase transition to nematic order. Reported are the results of our long term observations of bulk samples of liquid crystalline PBLG subjected to strong magnetic fields. We have observed visually magnetohydrodynamic processes that occur on several very different time scales: (a) the slow cholesteric-nematic phase transition, (b) a more rapid reorientation in the acquired nematic condition, and (c) a critical orientation of nematic PBLG with unusual anisotropic optical effects and high, but directional, thermal sensitivity. The phenomena are accounted for in terms of molecular order and dynamics of the associated polypeptide helices.

Due to its ready availability and good solubility characteristics poly-γ-benzyl-L-glutamate (PBLG) has undoubtably been the most extensively studied synthetic polypeptide. The macromolecule is known to adopt an α-helical configuration in a number of solvents of low enough dielectric constant so as not to interfere with the primary organization of the sterically favorable rod-shaped polymeric backbone and the delicate secondary structure of pendent side chains. As a result of this unique geometry, PBLG in helogenic solvents is characterized by an anisotropic refractive index and dielectric and diamagnetic susceptibility.

At sufficiently high concentrations of polymer, PBLG forms lyotropic liquid crystals exhibiting, in appropriate solvents or solvent mixtures, properties similar to all three major liquid crystal classes: i.e. the nematic, smectic, and cholesteric mesophases (Table 1). It is curious that a mesophase develops even in some solvents (e.g. dichloroacetic acid) that do not, in more dilute solution, support the necessary helical configuration of the macromolecule.

TABLE I

Lyotropic liquid crystal solutions of poly-γ-benzyl-L-glutamate

Structure	*Solvent*
Cholesteric	$CHCl_3$, CH_2Cl_2, dioxane, m-cresol, DCA, DMF
Nematic	CH_2Cl_2 : dioxane (1 : 4 vol.)[a]
Smectic	C_6H_6

[a] Racemic mixture of D and L isomers also forms nematic

Many of the liquid crystalline properties of this polypeptide can be understood on the basis of the nature of constituent macromolecules and solvent interactions; others require the invocation of illusive surface effects that are presently inadequately characterized or appreciated.

Reported here are the results of our long term observations of bulk samples of liquid crystalline PBLG subjected to strong magnetic fields. We have observed visually several magnetohydrodynamic processes that occur on very different time scales: (a) the slow cholesteric-nematic phase transition, (b) a more rapid reorientation in the acquired nematic condition, and (c) a critical orientation state of nematic PBLG with unusual anisotropic optical effects and high, but directional, thermal sensitivity. The phenomena are accounted for in terms of molecular order and dynamics of the associated polypeptide helices.

OPTICAL PROPERTIES OF CHOLESTERIC PBLG SOLUTIONS

The optical properties of undisturbed cholesteric PBLG solutions have been well studied. Robinson[1-4] found that sufficiently concentrated solutions of the polypeptide in appropriate solvents behave *in some aspects* as cholesteric liquid crystals. They display, for example, high optical rotatory powers (as high as 10^4 °/mm) not accountable for on the basis of the properties of individual PBLG molecules. This suggests a form optical rotation of a twisted macromolecular superstructure within the medium. When viewed in the polarization microscope the cholesteric phase is characterized by regions of regular striations arranged in a swirl-like, or fingerprint pattern. The optical retardation has been shown to vary in a regular manner between equidistant lines of extinction. The observations are consistent with a regular variation of refractive index along the axis of a helicoidal molecular superstructure that meanders throughout the medium. The distance between the striations, S, which is one half the pitch of the structure is of the order of $3-100\ \mu$ for PBLG and depends on concentration in an inverse manner ($S \sim 1/C^2$).

Liquid crystal PBLG solutions however do not exhibit dramatic iridescent color when viewed in reflected white light (Bragg reflection from internal molecular planes) or selective scattering and transmission of circularly polarized light: properties distinctive of many other thermotropic cholesterics. Their absence is due to the fact that S is well beyond the wavelength of light even for concentrated solutions of the polymer. Attempts to get S in the optical region by concentrating the polymer result in opaque gels. These latter typically cholesteric properties are however seen in solutions of the ethyl isomer of polyglutamic acid.[4]

FIELD INDUCED CHOLESTERIC TO NEMATIC PHASE TRANSITION OF PBLG

As indicated above individual PBLG macromolecules in the helical conformation have anisotropic dielectric[5] and diamagnetic[6, 7] susceptibilities, which are in both cases positive. As a result they will tend to align themselves in an applied electric or magnetic field such that their long axes are parallel to the field direction. Liquid crystalline solutions subjected to sufficiently high fields may therefore be made to transform to nematic order with the director of the molecular aggregates more or less parallel to the field axis. The phenomenon is presumably a result of the dilation of the helical pitch of the cholesteric superstructure with increasing field strength. At some critical field strength the mesophase would be expected to loose the high optical rotatory power and diffraction properties associated with the cholesteric phase. The phenomenon of field induced phase transition may be termed electro- or magnetotropism, in analogy to the more usual lyotropic or thermotropic mesomorphic transitions which occur with changes in solvent concentration or temperature. The critical magnetic field strength (H_c) for this event has been theoretically shown by deGennes[6] to be inversely proportional to the pitch of the undisturbed cholesteric structure. For most cholesterics of moderate periodicity the critical field can be as high as 100 kG and the effect is not observable. In PBLG solutions, however, the pitch (or S) is already beyond the wave length of light, considerably reducing the field requirements for the transition. The field induced cholesteric to nematic transition of this lyotropic liquid crystal has in course been followed by NMR,[7-10] IR dichroism,[11, 12] optical methods,[13] and most recently by the techniques of laser light beating spectroscopy.[14] The critical magnetic field for liquid crystal PBLG has been recently determined by Duke and DuPré[15] and Guha-Sridhar, Hines, and Samulski.[16] The precise value of H_c was found to be dependent on temperature, concentration of polymer, and molecular weight. For the solutions

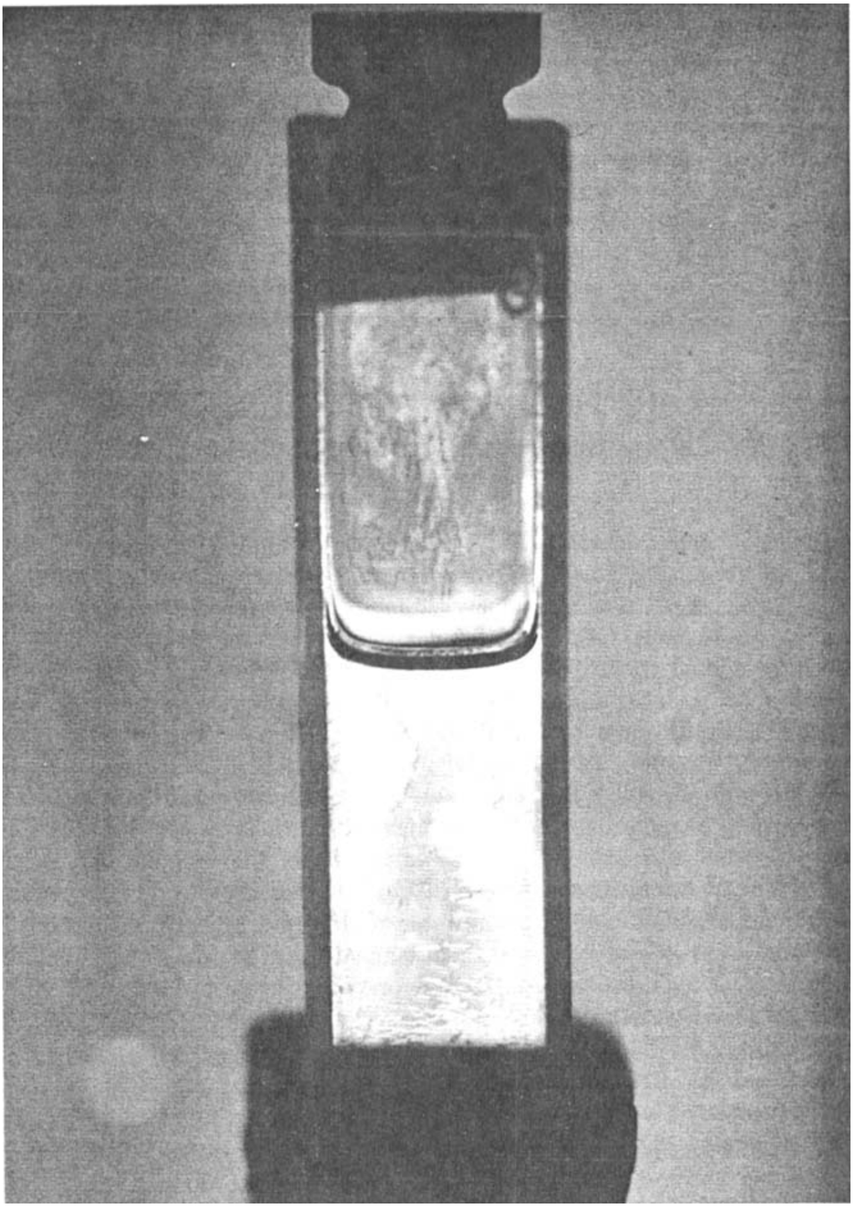
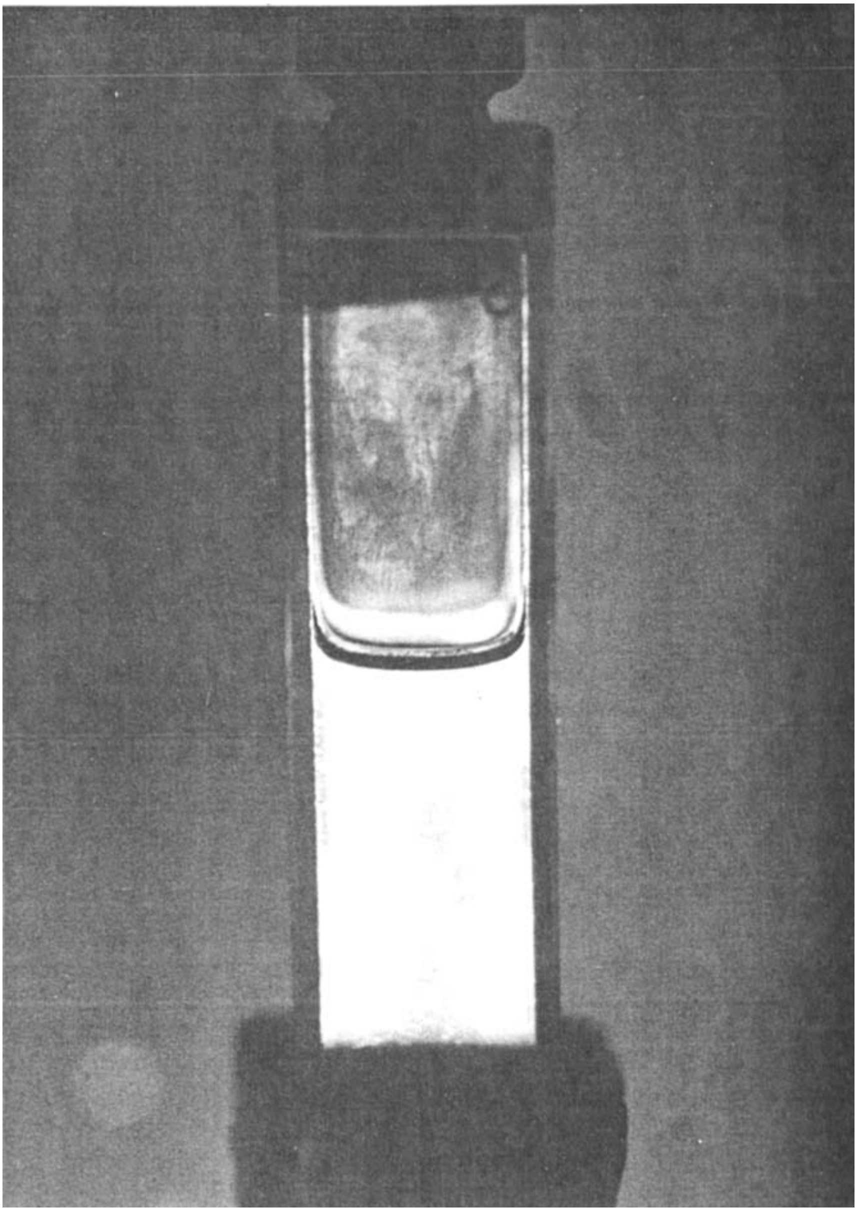


FIGURE 1 Optically active wall blotches in nematic PBLG. View is between crossed polars, perpendicular to an applied magnetic field of 12 kG. In photograph on the left one polar has been rotated 10° to the left. The photograph on the right corresponds to a 10° rotation to the right of the same polar. Note retention of the pattern with a reversal of light an dark regions. The sample is contained in a standard 1 cm pathlength spectrophotometric cell.



of this study, H_c is less than 5 kG. The critical electric field for the transition occurs around 350 V/cm.[13, 14] It should be noted that even in strong fields the transition to nematic order is slow, taking as long as 100 hours before equilibrium is attained. Addition of trace amounts of trifluoroacetic acid markedly reduces the equilibration time.[16, 17]

VISUAL OBSERVATIONS

PBLG of molecular weight 310,000 was obtained from Pilot Chemicals, Inc. and used without further purification. Liquid crystal solutions of 13.7% (w/v) in millipore filtered chloroform were prepared in 1 cm x 1 cm x 3 cm spectrophometric cells which were ultrasonically cleaned after a chromic acid rinse in acetic acid and high purity deionized water. It should be noted that PBLG samples in most of the studies cited above were of small volume, held in containers with large surface to sample contact. In an effort to reduce the influence of boundaries and surfaces, our samples were prepared in bulk.

Upon preparation PBLG solutions are non-uniform and striated. After several weeks of maturation, samples become uniformly bright but colorless when viewed between crossed polars. This is characteristic of the high optical rotatory power of lyotropic liquid crystals in the cholesteric state. The absence of brilliant iridescent color sometimes seen in light reflected from cholesteric solutions of some esters of polyglutamic acid is an indication that the helical pitch of the superstructure in our undisturbed samples is indeed beyond the wavelength of light.

After maturation samples were subjected for an extended period of time to a strong magnetic field (12 kG), well above H_c, applied perpendicular to two of the cell wall faces. Visual observations were made with the sample placed between crossed polars, parallel and perpendicular to the field axis, in transmitted white light. When it was necessary to remove the cell from the magnet for field parallel observation, the sample was quickly returned to the same position between the poles.

The magnetotropic cholesteric-nematic phase transition was visually evident in textural changes in the solution. Samples became clearer and more uniform as the directors of the molecular aggregates themselves became more uniformly disposed, reducing fluctuations in the spatial components of the refractive index that normally lead to strong light scattering in this and other liquid crystals.

After several weeks residence time in the field observations were again made in transmitted white light with the sample placed between mutually perpendicular polars. Curious optical effects appeared which were dramatically different parallel and perpendicular to the field axis.

The view perpendicular to the field was one of regions of light and dark polygonal areas extending the height of the sample in a stable pattern (Figure 1).

These blotches were of macroscopic dimensions covering areas as large as 0.5 cm^2. Some had a slight green or pink coloration. There was no evidence of blotch boundaries when the sample was viewed in unpolarized light. When the polarizers were tilted slightly (± 10°) to the left and the right of the extinction position, a reversal of the light and dark regions occurred with the zone boundaries maintained. Careful observation revealed that the blotches were optically active wall domains of equal but opposite optical rotatory power that could be transformed from light to dark by equal clockwise or counterclockwise rotation of the polars from orthogonality. We found this effect curious in that at this field strength PBLG has been clearly shown to a nematic liquid crystal which should not exhibit optical activity on such a scale. A review of the literature uncovered a report of a similar observation on large droplets of a thermotropic nematic liquid crystal, p-azoxyanisole (PAA), when viewed in polarized light under the influence of a horizontal magnetic field.[18] The appearance of field generated optically active nematic domains is identical to that of Figure 1. Subsequent theoretical explanation of the phenomenon by the workers[18, 19] referenced was one of polar ordering of the asymmetric molecules preferentially parallel and anti-parallel to the magnetic field in D and L regions. The origin of the optical activity of the p-azoxyanisole molecule itself was attributed to its approximate C_s symmetry (the molecule contains an approximate reflection plane[20]).

Our observations on lyotropic PBLG, however, indicate the phenomenon is purely a surface effect. It is evident that in these large cells one is looking through an arrangement of optically active blotched regions on the front surface of the cell towards others of similar appearance on the rear. The parallax effect at these dimensions is clear. Latter and very recent observations by the same group on another thermotropic nematic, 4′-methoxybenzylidene-4-butylaniline (MBBA), confirm the aspect of our study.[21] The authors did find however that the optical rotatory power of PAA was dependent on the sample thickness, suggesting in this case a bulk effect. A model was put forth for the room temperature nematic (MBBA) in which the optical activity was accounted for in terms of a gradual twist of the nematic director from surface alignment near normal to the boundary to one in the interior that is in parallelism with the applied magnetic field. The twist occurs in two senses as a result of the influence of two types of surface domains. This model for MBBA is reenforced by a recent paper of Bouchiat and Langevin-Cruchan[22] who demonstrated that there are two preferential directions of surface alignment of MBBA, symmetric with respect to the normal and tilted at an angle of approximately 75° from the surface. The model however does not account for the authors observations on PAA where the molecules are known to lie parallel to supporting surfaces. Likewise the model is inconsistent with liquid crystal PBLG where the macromolecules also naturally rest with their long axes in a plane parallel to surfaces.[8, 23]

The physical basis for only two preferential surface-sense orientations of the liquid crystal remains unclear. We are reminded here of the remark in the recent review of liquid crystal properties by Brown[24] *et al* that 'boundary conditions are so important that we can say that the thermodynamic state of the liquid crystal is not defined unless the boundary conditions are specified.' Such a specification will be complicated enough, the difficulty of the solution of the resultant boundary valve problem notwithstanding. Note should be taken of some experimental work that has been done with liquid crystals[25] on prepared or 'well-conditioned' supporting surfaces.

One might argue that the residual optical activity observed in a naturally cholesteric liquid crystal such as lyotropic PBLG is due to insufficient alignment of the bulk of the sample by the magnetic field (12 kG in this case). Other spectroscopic investigations of magnetic ordering in PBLG solutions speak to the contrary however.

NMR analysis[10] of the degree of order of liquid crystal PBLG solutions subjected to the magnetic field of the spectrometer put some 90% of the PBLG macromolecules with their long axes within ± 20% of the magnetic axis. X-ray data[12] on films cast from liquid crystal solutions in applied magnetic fields of 7 and 10 kG also indicate almost complete alignment (80–85%) of the macromolecules.

More striking was the view between crossed polars parallel to the field axis. Almost complete extinction was observed when the sample was viewed directly along the axis of the applied magnetic field. This was a further confirmation that the sample was in substantial nematic order. As the components of the refractive index perpendicular to the macromolecular helical axis are equal, optical extinction should result as in the case of a uniaxial single crystal when viewed along its *c*-axis. Color however was seen when the sample was viewed slightly off axis indicating a recovery of components of the refractive index not perpendicular to the rod axis. If the sample was thermally insulated between the pole faces the colors appeared uniform over the width and height of the cell except at the meniscus boundary where irregular and complicated surface conditions result in a small swirl contortion of multi-color. The precise color seen is a very sensitive function of the angle of observation. Note should be made that these are retardation colors, not due to diffraction effects as in the cholesteric phase of some solutions of polypeptides homologous to PBLG.

Macromolecular alignment and the resultant retardation color in polarized light was noted to be very sensitive to thermal disturbances. In our setup the PBLG samples were maintained in the magnet slightly below room temperature. If observations were made outside the magnet for more than a few seconds color uniformity was lost with evident pattern alterations proceeding inward from the warming cell surfaces (Figure 2). Deliberate thermal perturbation of a cell wall results in rapid color response (Figure 3). Even thermal gradients set up by air

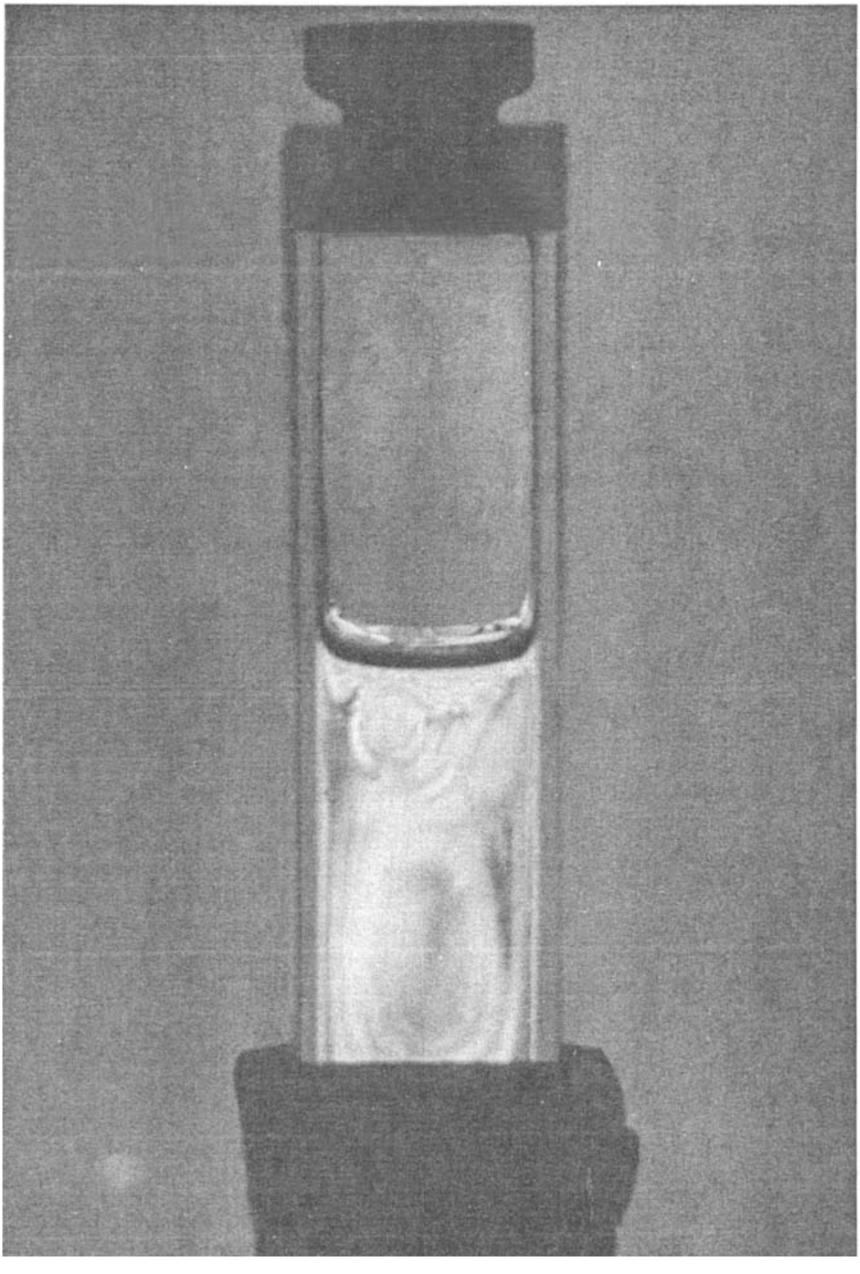


FIGURE 2 Birefringent pattern seen parallel to the axis of applied magnetic field.

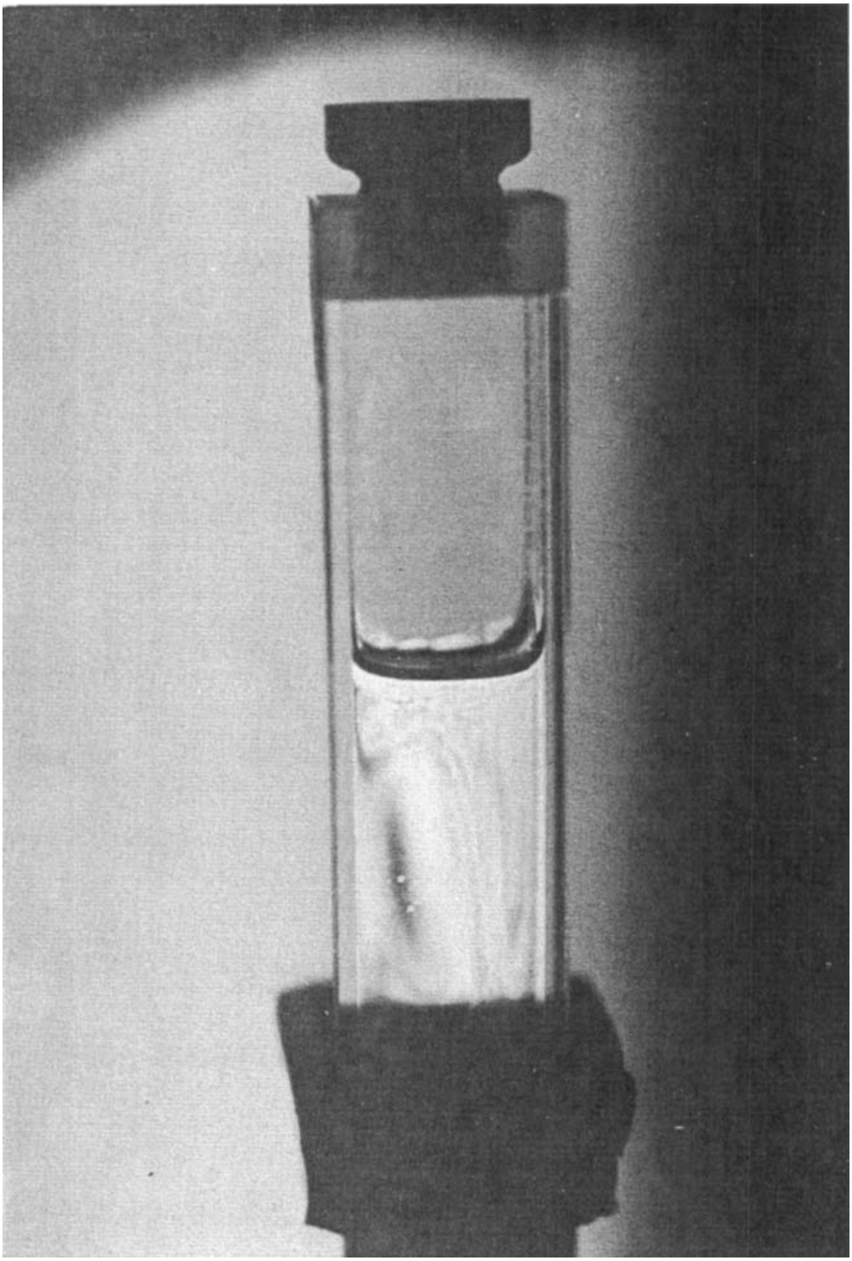
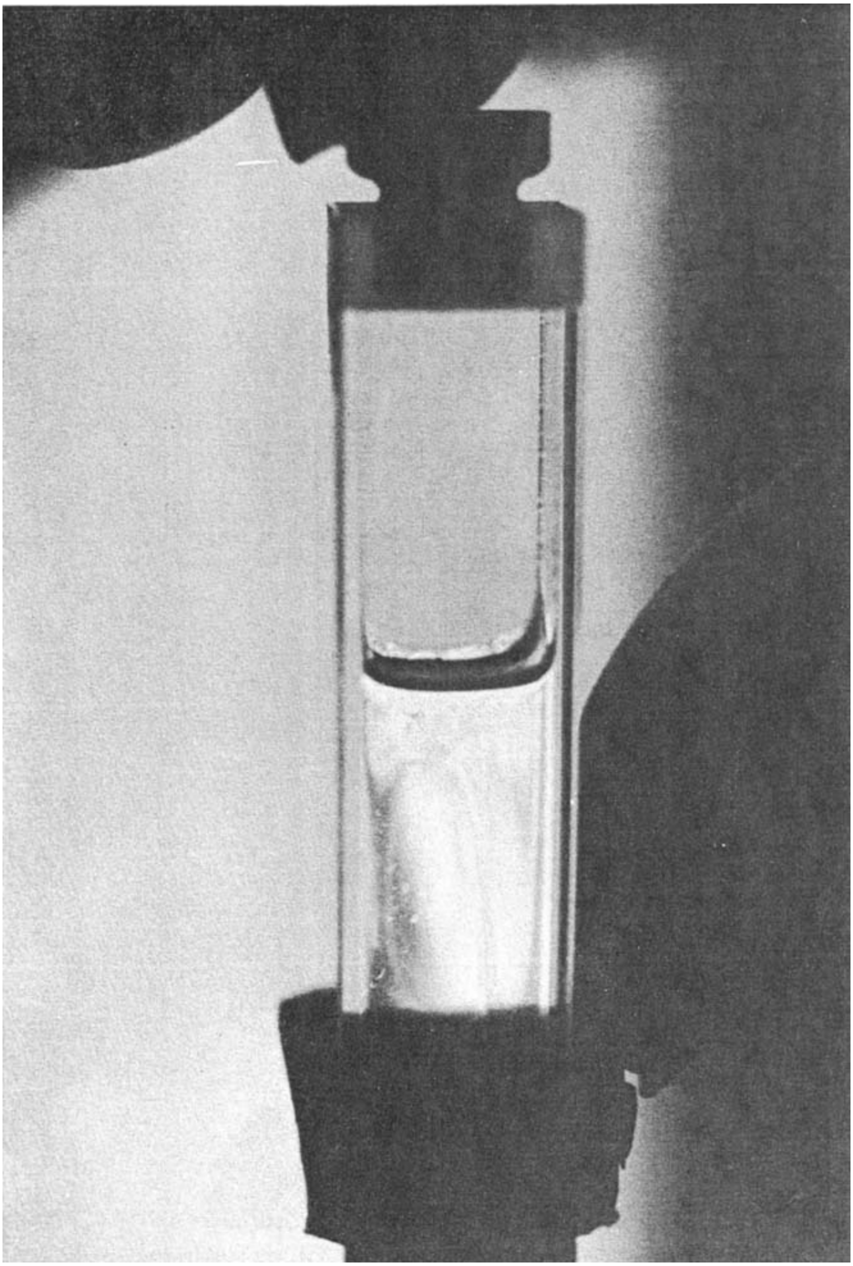


FIGURE 3 Effect of deliberate thermal perturbation on the birefringent pattern.



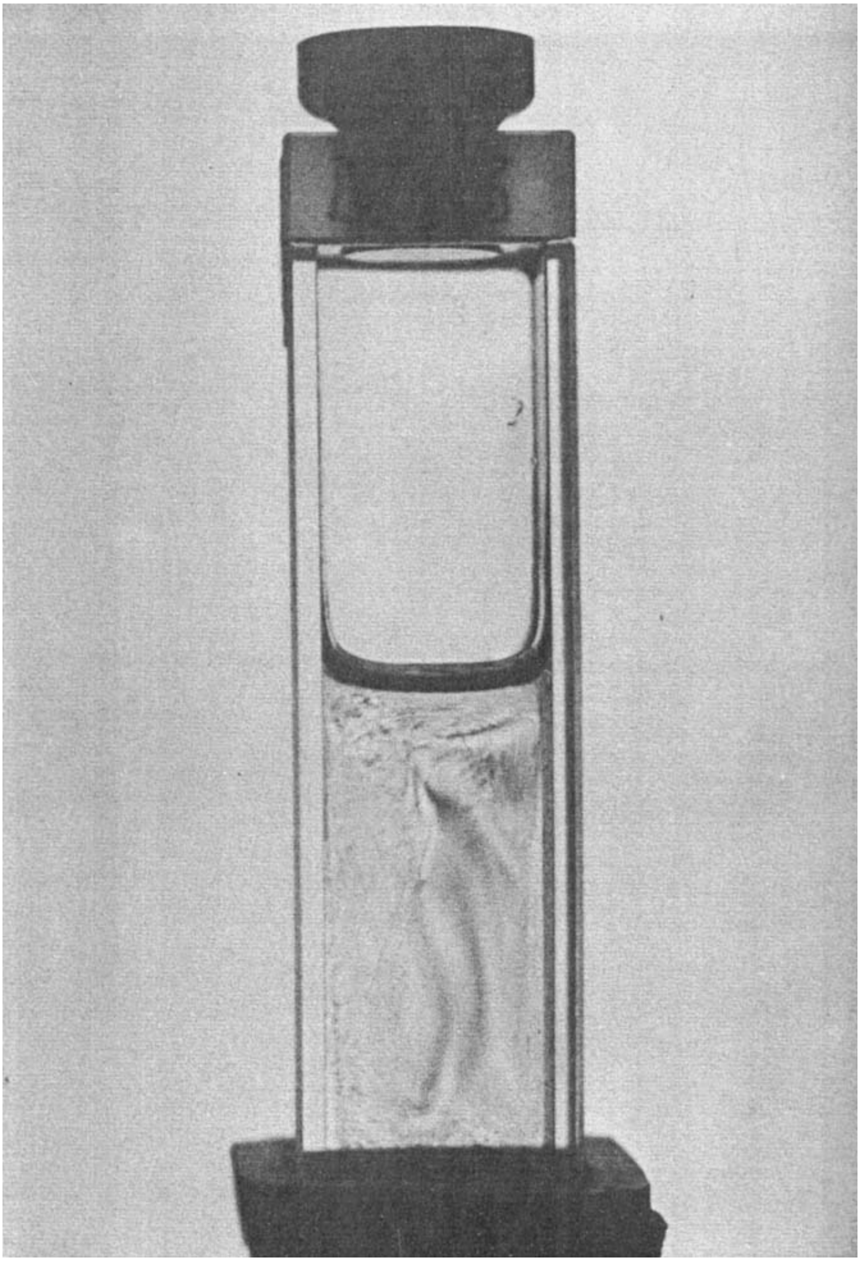
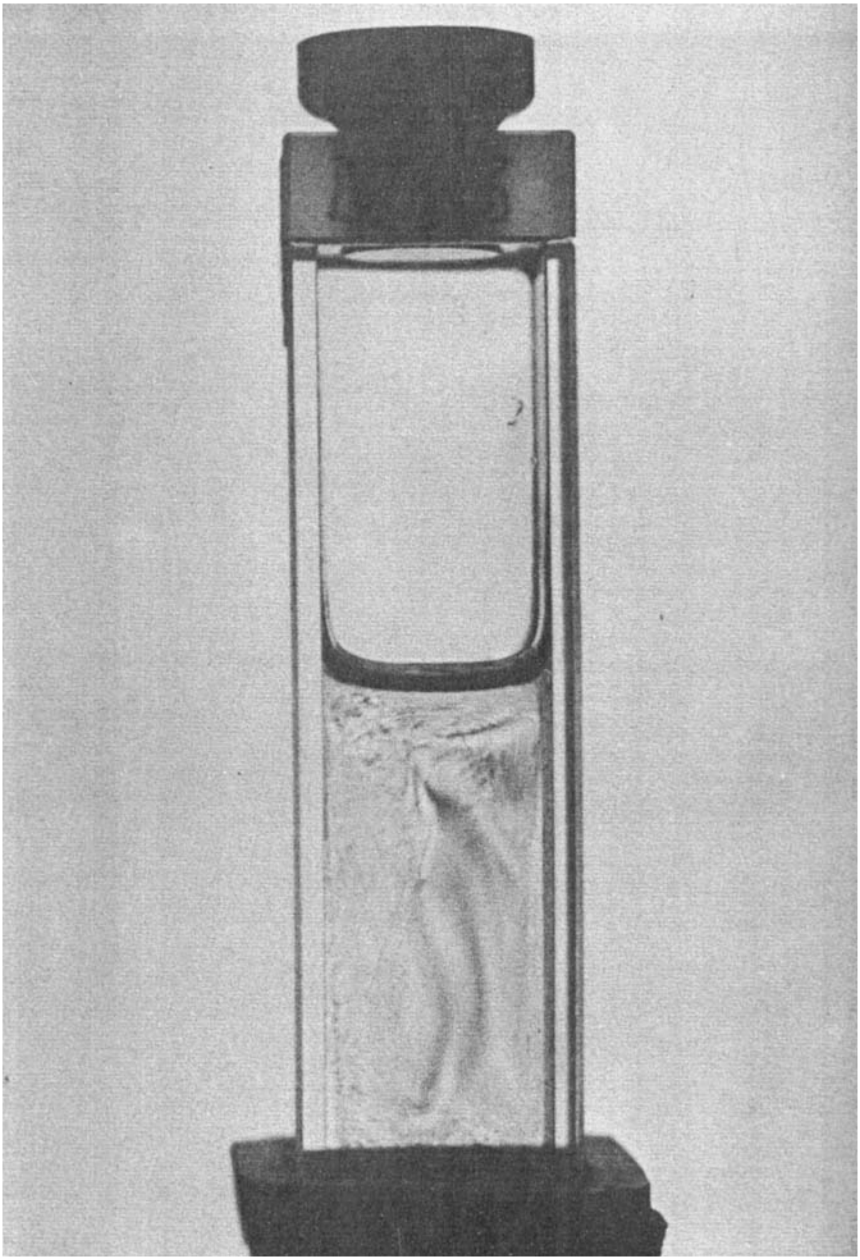


FIGURE 4 Front and rear views of a typical field-parallel birefringent pattern illustrates that the effect is not a result of cell boundaries as in the field-perpendicular case. The disturbance is carried all the way through the 1 cm cell.



currents registered in a color response. As our magnet is water cooled, a sample left exposed between the pole faces in the colder months was subject to a downwards air flow which cooled the cell walls relative to the cell center. The resultant convection currents set up in the liquid crystal a regular, birefringent swirl pattern parallel to the magnetic field (Figure 2). No such effect was evident perpendicular to the field axis. The birefringent pattern extends outwards from a central oval which itself may be extinguished between the polars. Smaller partially colored contortions were also frequently observed. The pattern along the field direction extended throughout the volume of the cell and was clearly more than just a surface boundary effect (Figure 4). When the polars were rotated the colors went over into one another continuously. This swirl or elliptical vortex pattern was also seen in natural light but the sample was otherwise colorless. In this critically aligned condition nematic PBLG when viewed parallel or near parallel to the major director is a very sensitive optical register to thermal fluctuations.

The presence of birefringent color in this bulk sample when the view is slightly off axis represents a recovery of the longitudinal component of the refractive index tensor of the macromolecule ($n_{\parallel} > n_{\perp}$) and a fortunate phasal difference between the ordinary and extraordinary components of white light as they make their way through the 1 cm pathlength cell. It seems unusual however to observe such retardation color in a sample of this thickness ($\sim$ 1 cm). This is an indication that the component of $\Delta n = n_{\parallel} - n_{\perp}$ recovered is quite small. The precise retardation color seen in a birefrigent specimen is proportional to the birefrigence (Δn) and thickness. As the thickness of the sample increases interference colors go through a series of orders of vivid color (Newton's colors) that gradually pass into pastel and eventually white. For quartz where Δn is only 0.009, color separation is lost in samples thicker that about 1 mm. The precise component of Δn that one sees is dependent upon the orientation of the PBLG axes with respect to the viewer. These orientations in the critically aligned condition are apparently quite sensitive to disturbances such as thermal gradients. In observing the sample along and at slight angle to the field direction one goes from a condition of extinction of polarized light when the view is parallel to the nematic director to one in which an off-axis component of Δn and therefore color is seen. A slight change in this component (resulting from a change in viewing angle or thermal perturbation) is manifested by rapid change in color. Note should be made that if the macromolecular aggregates are not set up in proper orientation with the field (as in the case of insufficiently matured samples) such differences in overall refractivity of the sample would not be so extreme, and the resultant optical effects less vivid.

The observations suggest that the molecular arrangement of the polypeptide helices in the liquid crystal imposes considerable constraints on macromolecular rotational motion. X-ray studies[2] on the liquid crystal phase of this polypeptide

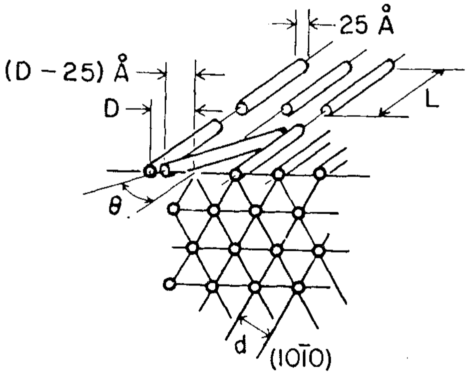


FIGURE 5 Schematic representation of rodlike polypeptide molecules packed on a hexagonal net where L = the length of a rod, rod diameter = 25 Å, d = spacing between (10$\bar{1}$0) planes, $D = 3d/\sqrt{3}$, and $\theta = \sin^{-1}[(D-25)/(L/2)]$.

have shown that the rodlike molecules pack in something near an hexagonal arrangement as schematically illustrated in Figure 5. The cholesteric twist is superimposed upon these more local structures which are nevertheless of sufficiently large and ordered to give sharp X-ray reflections. The distance, d, between the (10$\bar{1}$0) planes of the hexagonal net was found to be dependent on concentration in the manner:[2]

$$d^2 = \frac{W\sqrt{3} \times 10^{24}}{2N_0 q} \cdot \frac{1}{C} \qquad (1)$$

where d is in Å; $W = 219$, the residue weight; N_0 = Avogadro's number; $q = 1.5$ Å, the length of the projection per residue along the axis of the α-helix; and C is the concentration of polymer in g/100 ml. Assuming that an applied magnetic field acts only on the torsion of the cholesteric superstructure and does not affect macromolecular packing, one may calculate the degree of mobility available to an individual PBLG rod in our aligned samples. The distance, $D = 2d/\sqrt{3}$, between the centers of nearest neighbor rods may be determined for a given polypeptide at a given concentration from Eq. (1). On the hexagonal net the long rodlike molecule is allowed to execute only a very small rotation, θ (defined in Figure 5), about an axis through its center before coming into contact with its nearest neighbor. For our solutions θ turns out to be only 1.08°. This low degree of freedom of movement allows us to understand the difficulty in obtaining uniform liquid crystal solutions and the slowness of ordering in applied fields. A large number of highly anisotropic molecules must be made to accommodate one another in a regular geometric structure with little individual rotational mobility. In the presence of an applied field large clusters of slowly moving macromolecules are induced to reorient to attain uniformity with the field axis.

Birefringent color change in the ordered sample is the result of the influence of temperature upon the mean square angular displacement of the rods, $\overline{\theta^2}$. Following a calculation similar to that of Hines and Samulski,[26] for a given time interval t, $\overline{\theta^2} = 4\,D_r t$, in a random walk formulation where D_r is the rotational diffusion constant of the macromolecule. D_r of a rodlike particle in a medium of viscosity η has been determined by a modification of the Stokes–Einstein relation:[27]

$$D_r = \frac{k_B\,T\,[\ell n\,(2p) - \lambda]}{4\pi\eta(L/2)^2}\ \text{in sec}^{-1}$$

where L is the length of the rod, p is the axial ratio and λ a constant of the order of unity. For our solutions, $\overline{\theta^2} = 3.77$.

A macromolecular reorientation process on a much shorter time scale was also followed visually when the sample was rotated in the magnet while in the nematic phase. When the liquid crystal was turned 90° in the field a rapid and continuous destruction of the pattern described above was seen to begin after 1–2 minutes. Birefringent regions become confused and diffuse with colors in the central region of the vortex persisting longer than those on the outer borders. The surface blotches then parallel to the new field axis disappeared. The field was dark although not perfectly extinct with a salt and pepper appearance (Figure 6). Curious parallel striations were seen to run up and down the length of the cell. These striations were probably a result of cell surface preparation but may reflect a more fundamental property of the liquid crystal. They could result, for example, from lines of 'disinclination' or optical discontinuity separating molecular aggregates that rotate to the left from those that rotate to the right in the re-establishment of alignment with the new field axis. As the PBLG molecule has no diamagnetic polarity it does not matter in which way it turns to restore registration with the field. Repeated 90° rotations in the field produced identical molecular reorientations which were essentially complete in 10–12 minutes. A reorientation process in PBLG on such a time scale has been followed by other workers in the NMR study cited above.[10] We suspect that we have followed the same macromolecular reorientation process visually. If samples were allowed to remain in any one of these new orientations for another 3–4 days the field perpendicular blotches and field parallel birefringent vortices returned. The general characteristics outlined above were always recovered.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund administered by the American Chemical Society, and to Research Corporation for support of this research.

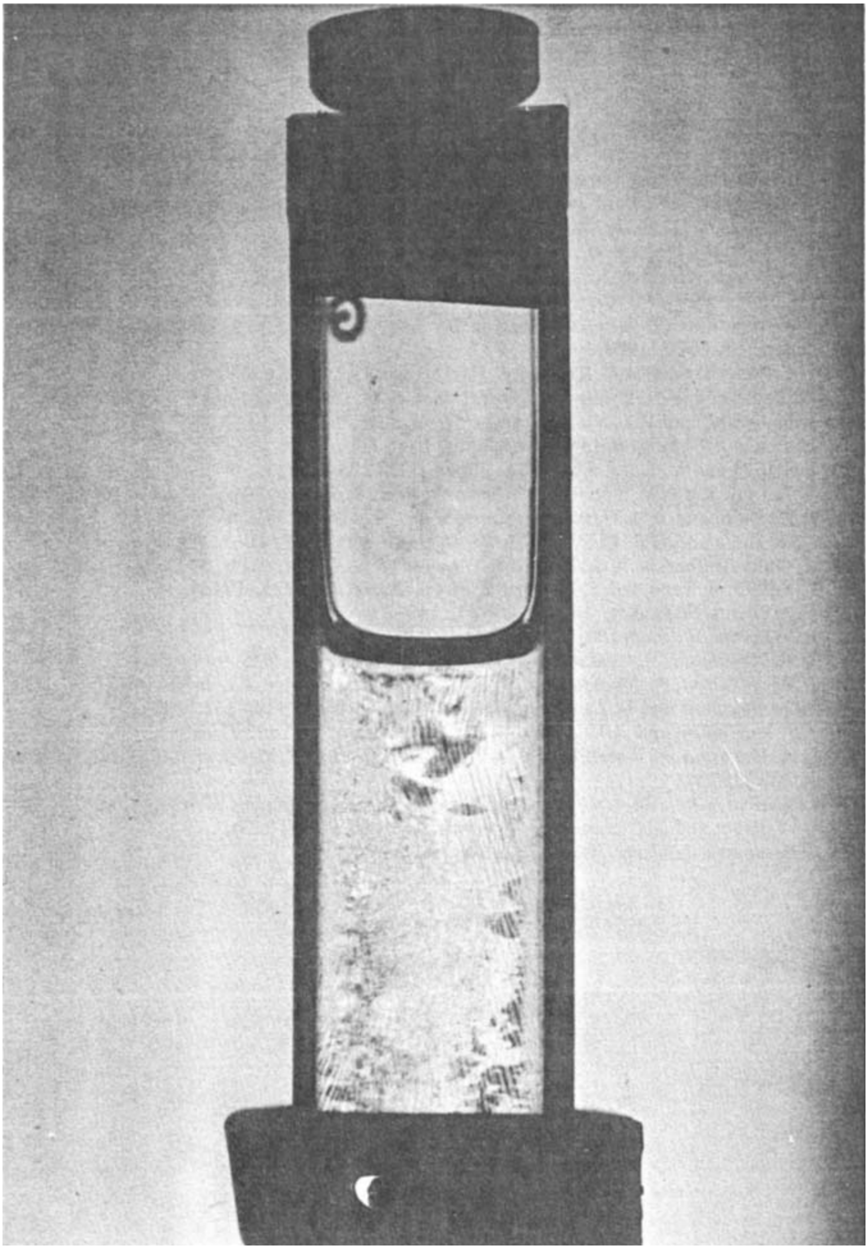


FIGURE 6 View between crossed polars 1–2 minutes after the cell is rotated 90° in the field. Parallel striations running up and down the length of the cell may be lines of discinclination separating molecular aggregates that rotate to the left from those that rotate to the right to restore registration with the field.

The authors are also indebted to Professor E. T. Samulski of the University of Connecticut for many helpful discussions on the nature of this unusual liquid crystal system.

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