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MAGNETIC FIELD INDUCED INSTABILITY ON AN ALIGNED NEMATIC SOLUTION OF A RODLIKE POLYMER

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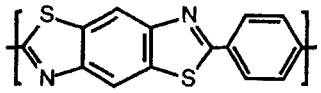
Abstract The reorientation of an initially well aligned nematic rodlike solution of the rodlike poly(1,4-phenylene-2,6-benzobisthiazole), PBT, in an external magnetic field in the sample plane is studied. For angle β between the magnetic field **H** and the initial director **n** less than 45 degrees, the reorientation occurs by a homogeneous twist distortion of the director field, permitting assessment of the Frank elastic constant K_T and the Leslie viscosity η_T. For larger β, the reorientation is nonhomogeneous, with a component of the distortion out of the sample plane, resulting in a phase-grating, made manifest by its focusing effects for transmitted light.

INTRODUCTION

A number of phenomena involving an instability in fluids perturbed by external field result in a dynamic order that emerges when the system is far from equilibrium.[1] An instability resulting from the application of a magnetic field in the twist geometry on a lyotropic nematic liquid crystalline polymer is discussed here. The instability considered has certain similarities to those in similar nematic produced by an electric field[2] or a thermal gradient.[3] In each case, the instability manifests itself as a spatially periodic structure. The nematic studied here is formed by dissolving long, rodlike molecules, poly(1,4-phenylene-2,6-benzobisthiazole), PBT, in a solvent (methane

sulphonic acid, MSA), above a certain critical concentration φ_{NI} (volume fraction) for the formation of nematic phase.[4]



PBT

A nematic liquid crystal exhibits long range orientational order, with no long range positional order. In the solutions of interest here, the rodlike chains are oriented more or less parallel to one another. The average direction of orientation, or the director **n**, can be aligned to form a single-crystal nematic by surface interaction, as well as by an external magnetic field which couples through the anisotropy of the magnetic susceptibility. The field (magnetic or electric) induced reorientation of the director in a thin liquid crystal film, called the Freedericksz transition,[5a] is frequently used to determine the Frank elastic constants, which characterize the curvature elasticity associated with a nematic phase. Application of such a field sets up a competition between the forces resulting from the field and those due to the surface orientation. A distortion is expected if the magnitude of the applied field exceeds a critical value $H_{c,v}$, where

$$H_{c,v} = (\pi/d)(K_v/|\Delta\chi_a|)^{1/2} \qquad (1)$$

with d the separation between the bounding plates, K_T, K_S and K_B the Frank elastic constants for twist, splay or bend distortions, respectively, and $\Delta\chi_a$ the anisotropy in diamagnetic susceptibility per unit volume.[5a] One arrangement used has a magnetic field normal to the director, and in the sample plane, resulting in a twist distortion under ideal circumstances, permitting determination of K_T from the critical field $H_{c,T}$ if $|\Delta\chi_a|$ is known.

When a field with magnitude $H>H_{c,T}$ is applied, any small perturbation in the initially uniform alignment can begin to grow exponentially[5a], with a rate inversely proportional to an effective viscosity for that reorientation process. For a simple twist distortion, uniform rotation of the director does not generate flow, and involves

only the rotational viscosity η_T. In the case of small molecule nematics, the twist viscosity is only sightly larger than the shear viscosity η_{SH}, whereas in the case of polymeric nematics η_T can be much larger than η_{SH}.[6,7] Hence the rate of uniform reorientation can be very much smaller than competing modes of reorientation, giving rise to transient periodic structures. A periodic response can, in fact, occur more rapidly than the uniform reorientation, to a number of factors. Rotation of the director in either direction lowers the free energy due to the imposed magnetic field, but involves the twist viscosity. A nonuniform distortion with a periodic pattern, such as that resulting from counter rotating zones, is produced by fluid flow coupled to molecular reorientation, with the shear viscosity replacing the twist viscosity in the latter. The difference in the viscosities will be large for polymeric systems, and hence periodic responses are ubiquitous.[6] The periodic modes involve additional elastic distortions, absent with a continuous rotation mode of the director. The wavelength will then be determined by a balance of the elastic and viscous torques, with the fastest growing response giving the periodic distortion, analogous to spinodal decomposition, as previously noted.[7] Short wavelengths involve large gradients for the director, and large wavelengths have considerably higher viscosities. The balance of the elastic and viscous torques, will develop an optimum wavelength for the fastest response.[7] In the simpler form of wavelength selection, the system develops shorter wavelengths as the driving field strength increases. This has been observed to be the case for solutions of polybenzylglutamates (PBG) and tobacco mosaic virus (TMV).[7,8]

The instability is more complex with PBT solutions than that observed with PBG or TMV solutions. With PBT, the application of magnetic field in the twist geometry creates a phase-grating in a direction parallel to the applied field. The optical character of this instability is very similar to those of the electrohydrodynamic instability reported for small molecule nematogens,[9] although the structures reported here are transient. To our knowledge, the structures observed for PBT solutions in the twist geometry have not been reported for any other material.

Before discussing the nature of the instability, we consider the response to an applied field at a small angle β (less than 35 degrees) between the applied field **H** and the director **n**. Under such conditions, the distortion may avoid the reorientation coupled flow, producing a continuous twist distortion. Measurements of the growth of the distortion following imposition of the external magnetic field, or relaxation of the distortion on removal of the external field will be discussed, providing estimates of K_T/η_T.

EXPERIMENTAL

Materials. Monodomains, or single-crystal, nematic solutions of PBT in MSA, were prepared by modifying the procedure described elsewhere,[10] see below. Two different molecular weights PBT samples were used in this study: intrinsic viscosities $[\eta]$ of 1800 mL/g and 900 mL/g, weight average molecular weights M_w of 34,500 and 23,000 and weight average contour lengths L_w of 140 nm and 95 nm respectively. The solutions used had weight fractions w of 0.051 for the higher molecular weight, Sample 57, and 0.045 for the lower molecular weight, Sample 43.

Solutions of PBT exposed to moisture deprotonate, resulting in precipitation of the polymer from solution.[11] Hence the solutions had to be kept dry. This was accomplished by construction of a special cell consisting of rectangular glass tubing (Vitro Dynamics, Rockway, NJ) fitted with Leur joints which could be sealed with a ground glass cap. The cap was further sealed with an epoxy resin that cured in a few minutes. This procedure was found to be effective in keeping the contents moisture free over extended periods (e.g., years).

In the preparation of well-aligned solutions of PBT, the nematic solution is slowly extruded into the tubing. The pressure-driven extrusion of the nematic solution creates an extensional flow at the advancing front.[10,12-14] This flow produces an alignment of the nematic fluid near the surfaces as the fluid advances through the rectangular tubing. Fluorescence emission anisotropy was used to probe the effectiveness of the alignment since the fluorescence

emission is polarized principally along the molecular long axis.[15] The fluorescence emission anisotropy is given by the ratio of the fluorescence intensities polarized parallel and normal to the director. Since the incident light intensity used to excite the fluorescence was reduced by absorption by a factor e after penetration by about one wavelength into the sample, the fluorescence emission anisotropy provides a probe of the alignment of molecules near the surface. On cessation of the pressure-driven flow, the fluorescence emission anisotropy of 4 to 6 for surface areas of $\approx$ 8 mm^2 over the entire sample reveals a high degree of uniform alignment near the surfaces. The anisotropy depended on the pressure used in the pressure-driven extrusion flow. Although the surfaces are aligned, the bulk is far from a uniform alignment, exhibiting a fine, grainy texture, and being strongly birefringent and turbid. However, the alignment at the surface was sufficient to produce an aligned monodomain if the sample was allowed to age for a prolonged period of time (20-30 days). The time required for the monodomain can be shortened by subjecting the sample to a strong magnetic field (4.7 or 7 T) on cessation of flow, with the field direction along the flow axis. In this way, the magnetic field reinforces the alignment tendency provided by the surface layers. This procedure resulted in a well-aligned sample after about 8 hrs in a 7T field or 16 hrs in a 4.7T field. The alignment was evaluated by polarized light microscopy using both orthoscopic and conoscopic optics.[16] It was necessary to use a laser source (632.8 nm) in the latter case owing to the large retardation in the samples studied, e.g., $\Delta n = 1.42$ w, for $0.03 < w < 0.06$.[14] Monodomains so obtained are indefinitely stable, and scatter light weakly.[10]

In the preceding, it is important that the sample be placed in the magnetic field soon after the cell is filled. If the sample is allowed to anneal toward the aligned state outside the field, under the influence of the aligned surface layers, and then placed in the magnetic field after a few hours, characteristic structures will remain in the fluid after most of it has been aligned along the magnetic field. As shown in Fig. 1, these have an elliptical form, with relatively sharp vertices along the long axis. They appear to

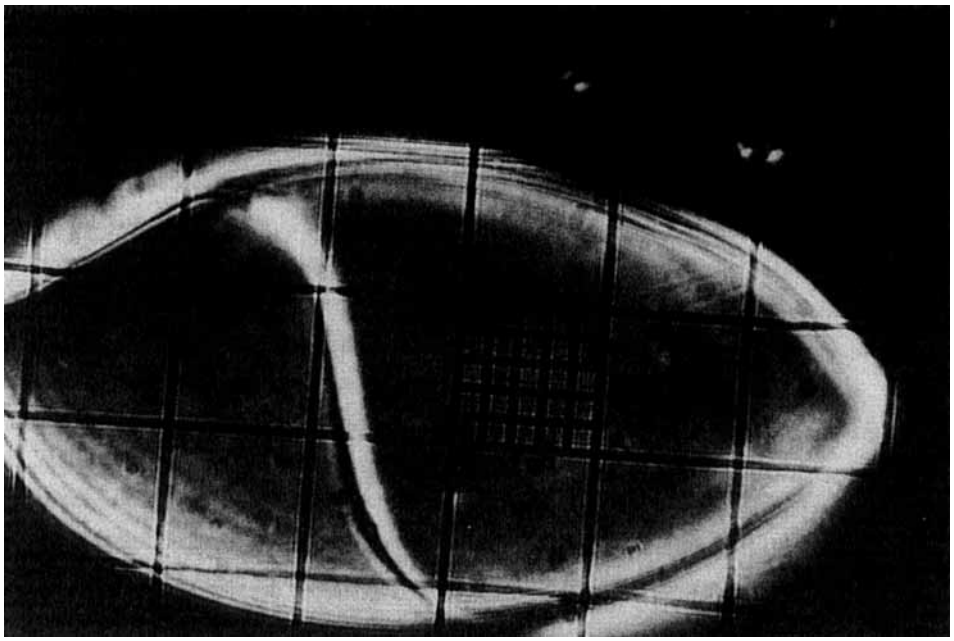


FIGURE 1 Defect structure obtained when a partially aligned sample is placed in a magnetic field. The large grid is 40μm.

be very thin, with dichroism in the plane of the structure at 90 degrees to that of the bulk nematic. Although they may vary in size, the ratio of the major to minor axes appears to be invariant, and equal to 2.3 to 2.4 for the samples studied here, independent of the field strength. The defects tended not to change size with time in the field, but rather all of the imperfections tend to migrate toward one end of the cell, where they disappear. They are probably transported along the direction of least perfect alignment in the cell. Elliptical defects attributed to domain walls have been observed in the splay-geometry,[17] and analyzed for several geometries.[18] For the geometries studied, the ratio of the major to minor axes of the defect is equal to the square root of the two elastic constants involved in the defect structure, and is invariant to the field strength; a similar behavior may explain the result observed here.

Methods: Due to the large birefringence of the samples studied, orthoscopic polarized light microscopy could not be used to follow small twist distortions of the director field.[19] By contrast, small distortions of the director field are revealed by rotation of the conoscopic interference figures about its center of symmetry as the director field is rotated in the sample plane, or by translation of the pattern if the director field tilts out of the sample plane. For uniaxially symmetric materials such as that for the undistorted, planar aligned nematic of interest here, the conoscopic interference figures are hyperbola-like principal isochromates (curves of zero intensity) placed along and orthogonal to the optic axis (or director) of the material. For a material with positive birefringence, and retardation $\delta = 2m\pi + \delta'$ for light propagating normal to the sample plane, m being an integer and $0 < \delta' < 2\pi$, the successive fringes along the optic axis have retardation $2m\pi$, $2(m-1)\pi$, ..., 2π on moving away from the center, and those along the orthogonal axis have retardation $2(m+1)\pi$, $2(m+2)\pi$, ... on moving outward. For the samples studied here, m=20 or more, depending on the solution concentration and the cell thickness.

For a continuous rotation of the director field, the rotation Φ_{ROT} of the interference figures is given by[20]

$$\tan 2\Phi_{ROT} = \langle \sin 2\varphi \rangle / \langle \cos 2\varphi \rangle \qquad (2)$$

where φ is the twist angle, and the angular brackets denote the average of twist $\varphi(z)$ through the sample thickness z ($-d/2 \le z \le d/2$). For a material at equilibrium in a field imposing a continuous twist distortion, with maximum twist $\varphi(0) = \varphi_{max}$ in the midplane of the sample and zero twist $\varphi(d/2) = \varphi(-d/2) = 0$ at the surfaces, Φ_{ROT} may be expressed as[20]

$$\tan 2\Phi_{ROT} = \frac{2\sin(\varphi_{max})}{2E(\pi/2, \sin \varphi_{max}) - F(\pi/2, \sin \varphi_{max})} \qquad (3)$$

where F and E are the complete elliptic integrals of the first and the second kinds, respectively. In this analysis, $\varphi(z)$ is essentially given

by $\varphi_{max}\cos(\pi z/d)$ for small φ_{max}, though the rigorous expression is more complicated.[21] For the range of φ_{max} of interest here, calculations with Eqn (3) show that φ_{max} may be approximated from the measured Φ_{ROT} by the simple expression $\varphi_{max} = 1.57\Phi_{ROT}/(1 + 0.14\Phi_{ROT}^2)$ within 3% error (with Φ_{ROT} in radians). By comparison, a bulk rotation of the director field, such that $\varphi(z) = \varphi_{UNF}$ at all z, gives $\Phi_{ROT} = \phi_{UNF}$ for the range of retardations of interest here. For the sake of completeness, the translation Δ of the center of symmetry of the fringe pattern from the optic axis of the microscope is related to an average of the tilt $\theta(z)$ of the director out of the sample plane. For a uniform tilt ($\theta(z) = \theta_{UNF}$), $\Delta/D\Omega_{NA} = n_I(\sin\theta_{UNF})$, where D is the diameter of the field of view, Ω_{NA} is the numerical aperture of the objective (here 0.60), and n_I is the average refractive index of the sample.[16]

To induce a twist distortion, the samples were placed in a magnetic field (7T) for a short time (5 to 15 minutes). The samples were then removed from the field, and the relaxation of the director to the original alignment was followed using the rotation of the interference figures as a function of time. The image was viewed on a video monitor, and recorded on magnetic tape. The rotation angle was determined to within 0.1 degrees by noting the rotation of the sample required to bring the displayed pattern to a reference orientation. In addition, the image was photographed at intervals, so that the interference figures could be superposed with respect to their overall symmetry to determine the rotation.

In the experiments done to measure the growth of the twist distortion, the samples were subjected to a magnetic field at a fixed angle β, and the rotation of the director monitored conoscopically as a function of time. The samples are taken out of the field periodically for conoscopic measurements. Care was taken to insure that the sample extinguished light (white light) along the unperturbed director in orthoscopic optics (a consequence of the adiabatic limit[19]). The sample was rotated to give extinction under white light and then held in that position as the polarizers and the light source are changed to conoscopic optics to obtain the interference figures from

which the rotation angles were measured. All the measurements were made at room temperature (about 20°C).

RESULTS

Reorientation Without Flow. The consoscopic interference figures remained visible, and underwent a smooth rotation about their center when the samples were placed in a magnetic field (H = 4.7 or 7 T; $H >> H_{c,T}$) in the sample plane, with **H** at small angle β (< 35 degrees) to the director $\mathbf{n}_0$. Growth and relaxation of twist experiments were done for Sample 43, but only the growth of twist was done for Sample 57. On relaxing for a long time (weeks) on

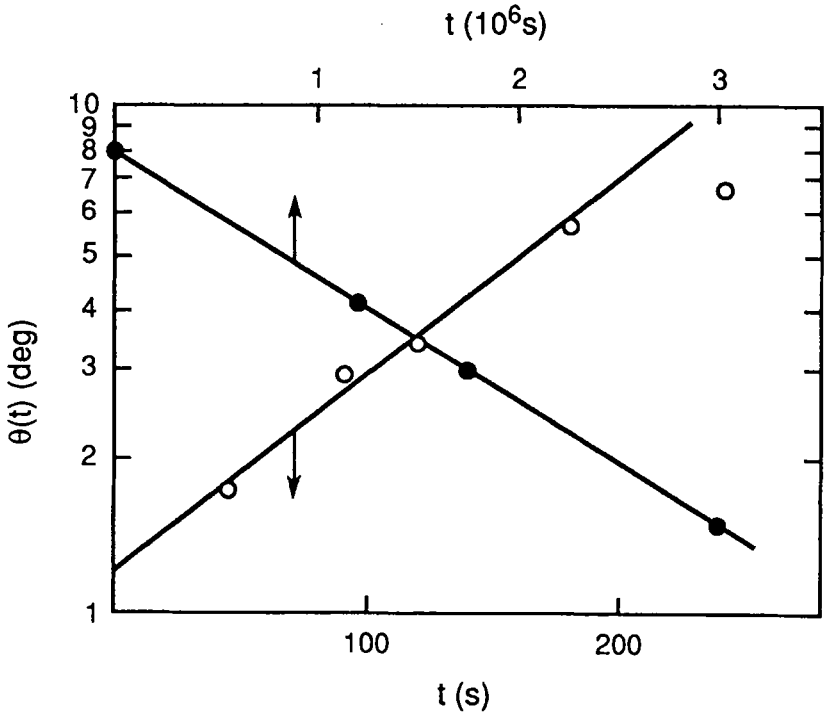


FIGURE 2 The growth (unfilled), with β=36 degrees and H = 4.7 T, and relaxation (filled) of a twist distortion induced in a fully aligned nematic solution of PBT (Sample 43) under the influence of a magnetic field (From Ref. 13)

removal of the external magnetic field, the interference figure relaxed to its unperturbed alignment. Fig. 2 shows the growth and relaxation observed with Sample 43 for a field (4.7 T) applied for a short time (2 to 5 min). For longer application of this field (about 2hrs), the director is essentially aligned uniformly along the field, except at the boundaries, i.e., $\varphi(z) \approx \varphi_{UNF}$ except for z close to d/2 or -d/2. In such a case, the rotation angle of the interference figures is the same as the angle at which the magnetic field was applied, but the fluorescence emission anisotropy remained the same before and after the application of a magnetic field, showing that the surface alignment had not changed.

The twist angle $\varphi(z,t)$ of the director at height z following imposition of an external magnetic field has been analyzed using the Ericksen-Leslie constitutive equation to give:[5b,22]

$$\varphi(z,t) = \varepsilon\varphi_M f(z/d)\ \exp(t/\tau_T')\{1 + u(t)\}^{-1/2} \qquad (4)$$

$$u(t) = \varepsilon^2[\exp(2t/\tau_T') - 1] \qquad (5)$$

where $\tau_T' = \tau_T(h^2 - 1)$, with $\tau_T = \eta_T d^2/\pi^2 K_T$, $h = (H_f/H_{c,T})$, with $H_f = H\sin\beta$, ε is a small number associated with thermal fluctuations of the director, f(z/d) is approximately given by $\cos(\pi z/d)$, and φ_M is equal to $\varphi(0,\infty)$, the maximum value of $\varphi(z,t)$ at the midplane (z = 0) for $t/\tau_T' >> 1$, i.e., $\varphi_M \leq \beta$. For small t/τ_T', $\varphi(z,t) \propto \exp(t/\tau_T')$, permitting evaluation of τ_T'. The twist angle $\varphi(z,t')$ of the director at time t' after removal of the external field can be represented as[5b]

$$\varphi(z,t') = \varphi_M f(z/d)\exp(-t'/\tau_T) \qquad (6)$$

It is evident that evaluation of K_T/η_T requires an estimate for $H_{c,T}$ for the growth of twist distortion, but not for the relaxation. Hence, data on both growth and relaxation permit evaluation of K_T/η_T and $H_{c,T}$, thereby providing values of both K_T and η_T if $\Delta\chi_a$ is known. From the data shown in Fig. 2, the critical field $H_{c,T}$ is calculated to be 0.55kG for Sample 43, which gives the K_T in Table 1 using $|\Delta\chi_a| = 5.0 \times 10^{-7}$

erg/G^2cm^3. The latter, based on preliminary measurements for Sample 43, is comparable to the larger $|\Delta\chi_a|$ reported for aromatic

Table 1 Parameters for the Nematic PBT Solutions[1]

Sample	w	L_w (nm)	d (μm)	$H_{c,T}$ (kG)	K_T (pN)	η_T (kPa.s)
57	0.051	140	300	1.80	1,500	7000.
43	0.045	95	300	0.55	140	27.6

1 Calculated with $|\Delta\chi_a| = 5.0 \times 10^{-7}$ cgs units, see text.

compounds.[26] The same value of $|\Delta\chi_a|$ is used to analyze the data reported in Table 1 for Sample 57 as its concentration is similar.

Reorientation With Flow. Application of a field ($H > H_{c,T}$) in the twist geometry with $\beta > \pi/4$, led to a spatially periodic structure in all cases studied with aligned nematic solutions of PBT. The periodic structure consists of bands orthogonal to the initial director. These bands are visible without the aid of an analyzer, using either naturally polarized incident light, or incident light polarized along the unperturbed director. Inspection of the inhomogeneous distortion using light focused at various planes z in the sample revealed the existence of two planes in which sets of bright lines could be observed, one above the midplane (z=0) of the sample, and one below the midplane, the intensity modulation in these two plane being exactly out of phase. No structure was visible at other heights from the midplane. The stripes were not visible for polarization of the incident light orthogonal to n_o. A micrograph and a schematic diagram of the periodic structure obtained with $\beta = \pi/2$ are given in Figs. 3 and 4, respectively. The stripes are not completely regular, as can be seen by the visible defect (edge dislocation) in Fig. 3, but they do have an approximate periodicity ($\lambda_x/2$) of about 60-70 μm along the unperturbed director (the x axis). The wavelength λ_x of the

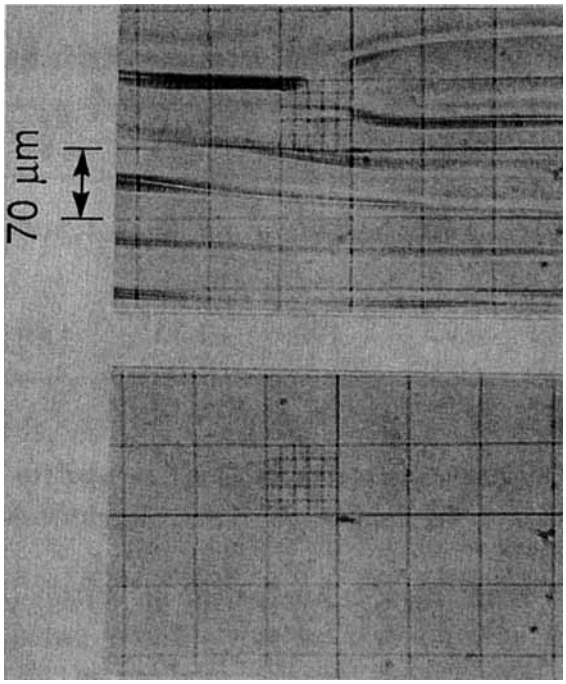


FIGURE 3 Banded pattern produced in the focal plane of a phase-grating created in a nematic solution of PBT in the twist geometry in a magnetic field.

Table 2 Phase-Grating Band Wavelength

Sample	H (kG)	d (µm)	λ_x (µm)	Sample	H (kG)	d (µm)	λ_x (µm)
	17.2	300	120		10.3	300	120
57	17.2	400	120	43	8.7	300	120
	17.2	700	120		7.2	300	120
	10.3	300	120				
	8.7	300	120				
	7.2	300	120				

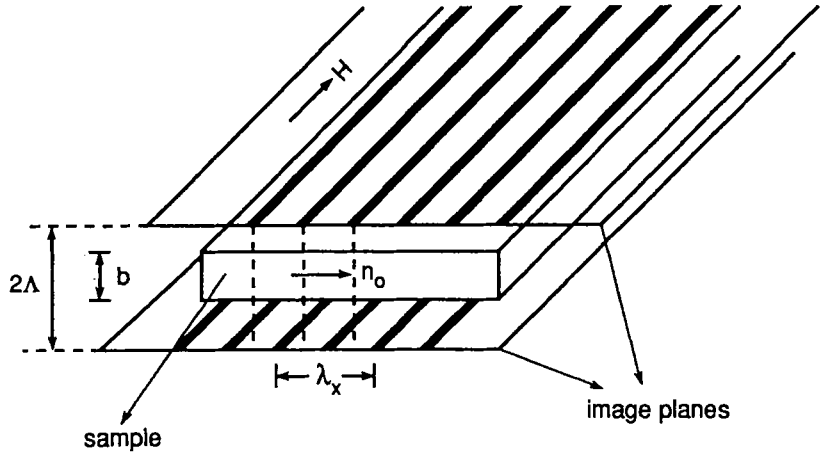


FIGURE 4 Schematic drawing of the focusing produced by a phase-grating. The bright and dark stripes in the image plane represent focused and defocused images (or virtual images) of the light source. From Ref 12.

stripes appeared to be independent of the applied field strength over the range studied (0.7T < H < 2.2T, for Sample 43, and 0.5T < H < 2.2T for Sample 57). For sample thickness d > 200 μm, λ_x is insensitive to the sample thickness, see Table 2.

The preceding observations have certain similarity to behavior observed in several other cases: for an electric field applied normal the sample plane;[9] in certain cases with a temperature gradient between the bounding plates;[24] in oscillatory shear flow;[23] in simple shear with flow normal to the director;[23] and in Kevlar fibers spun from solution.[25] In each case, the liquid crystal acts as a lattice of parallel cylindrical lenses, forming a phase-grating to produce real and virtual images of the light source used to probe the sample.

Fluorescence depolarization measurements were carried out on the distorted samples (Sample 57, with λ_x about 120μm), with 488 nm excitation. Since the 488 nm beam traverses all the way through the sample, the resulting fluorescence provides information on the director in the bulk. Using the microscope in the fluorescence mode

(reflected mode), it was found that the stripes were visible with maximum contrast on rotating the sample by 20 degrees from the easy axis of the analyzer, indicating the presence of an in-plane rotation of the director.

Evidence for an in-plane rotation (twist distortion) also comes from the flow pattern observed during the formation of the phase grating. The flow pattern was observed by visualizing the motion of the dust particles when Sample 43 was exposed to a 0.72T field. It was observed that the flow pattern was quite complex, with motion in all 3-dimensions, with a large component in the field direction. A 3-dimensional flow pattern must certainly give rise to a complicated director pattern, perhaps in all 3-dimensions.

The inhomogeneous distortion did not appear instantaneously on application of the field, but only after a certain time t_D, dependent on the field strength H. For $t < t_D$, the interference fringes did not appear to change, but they progressively disappeared for $t > t_D$. The interference fringes in the quadrant containing the optic axis distorted first. After about 2hrs under a field strength of 0.35T, the interference figures were completely destroyed. Observation of the sample with white light polarized along the unperturbed director, did not reveal the phase grating at that stage, but the grating was well formed after about 4hrs. Extrapolation of H^2 versus $1/t_D$ to zero $1/t_D$ (i.e., an infinite time for the onset of the distortion) gave an intercept H_o^2, with $H_o \approx H_{c,T}$.

The bright lines are found to be in focus with coordinates $[x,z] = [(m \pm 1/4)\lambda_x, \Lambda]$ and $[x,z] = [(m/2)\lambda_x, -\Lambda]$ above and below the midplane, respectively. Here, m is an integer, λ_x is the wavelength of the stripe periodicity, and Λ and $-\Lambda$ are the positions of the focal planes of the bright lines above and below the sample, respectively. The depth Λ of the focal plane of the image depends on both the field strength and the time in the field, and Λ may be smaller or larger than d/2. Fig. 5 shows a plot of twice the focal length plotted against H^2t, where t is the time in the magnetic field H (Sample 57, at 12 and 14.4 kG). As seen in Fig. 5, the wavelength λ_x was decreased abruptly by a factor after a certain time in the field.

Experiments performed using Sample 43 also produced the spatially periodic structures, having identical optical characteristics to those described above. A major difference between the two

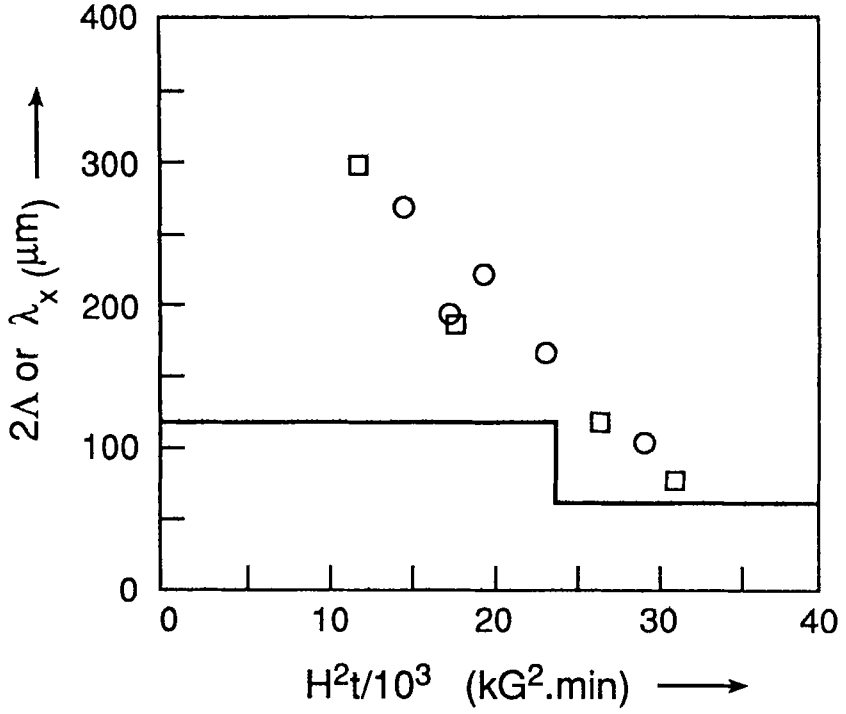


FIGURE 5 The separation 2Λ of the image planes produced by the phase-grating (circles and squares) and the half-period λ_x (solid line) of the bands as a functions of the product H^2t: 12.2 and 14.0 kG for squares and circles, respectively.

samples is in the wavelength observed for the samples. For Sample 43, the wavelength Λ is about 120 μm for fields above 0.5T. The pattern is irregular for fields below 0.5T, with the pattern exhibiting regions with varying wavelengths. It is not known whether Sample 57 would exhibit similar behavior at low fields.

At long times in the field, the periodicity of the stripes is destroyed, and loop disclinations develop, with the planes containing

the loops oriented normal to the original director $\mathbf{n}_0$. At still longer times the loop defect structure is replaced by line defects pinned at the bounding surfaces.

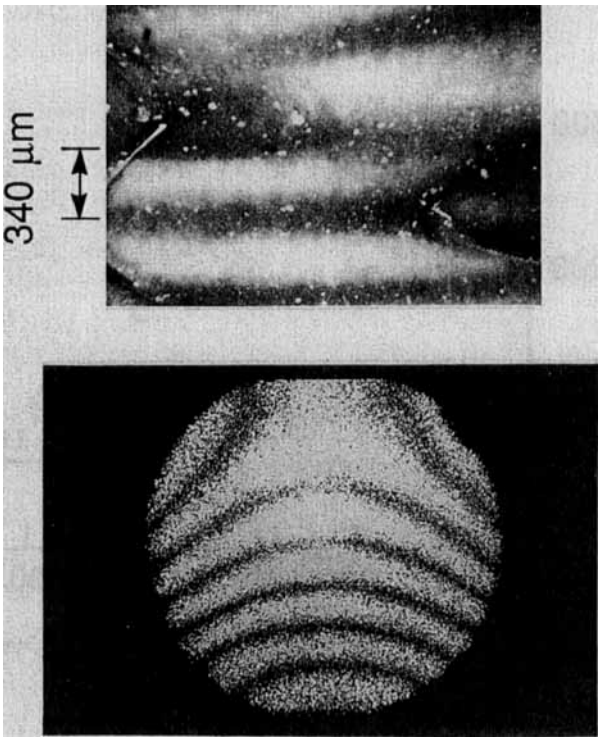


FIGURE 6 The banded interference figures observed after a PBT solution had been annealed for a long time in a magnetic field.

A second type of transient structure was also observed with Sample 43. At very long times (> 4 weeks) the phase grating was eliminated, but regions free of this texture exhibited stripes under crossed polars, reminiscent of observations with PBG solutions.[7] Fig. 6 shows the stripes and the conoscopic figure obtained from such a region.

DISCUSSION

Reorientation without Flow. The results reported above show that the director field in the nematic solution of PBT can be reversibly distorted by an external field, provided that the disturbance is not forced too aggressively. The values of K_T reported in Table 1 are large in comparison with those for small nematogens. This is to be expected, since the elastic constants are expected to scale with $B_2\nu/D \propto cL/D$, where B_2 is the second virial coefficient, ν is the number density of rods in solution, and D is the diameter of the rod:

$$K_\mu = (kT/D)B_2\nu k_\mu(S) \tag{7}$$

where μ = S, T, or B, and k_μ depends on S for rodlike molecules interacting through a hard-core potential: e.g., $k_T \approx 0.031(4S-1)$.[13,27] The ten-fold difference in K_T given in Table 1 is unexpected since $B_2\nu/D \propto cL/D$ is not expected to be very different for the two solutions studied, and birefringence measurements show that S is nearly independent of c for solutions of a given PBT, and close to unity for the range of conditions used here.[13]

For $h \gg 1$, the growth rate of the distortion gives $\tau_T/(h^2 - 1) \approx \eta_T H_f^2|\chi_a|$, permitting comparison of η_T of different samples, with the results given in Table 1. For rodlike molecules interacting through a hard-core potential,

$$\eta_\mu = \eta_{ISO}(1 - S)^2 H_\mu(S) \tag{8}$$

where $H_T = 30S^2/(5S - 2)$ according to one model.[13,28] Here, η_{ISO} is expected to be proportional to $c^3L^{5.8}$ for rodlike chains.[13] Thus, if S is not too different, as anticipated, the ratio of η_T is expected to be about 15 for the two samples studied here, by comparison with the ratio of 250 observed--the large ratio of the K_T values increases the calculated η_T value.

Reorientation With Flow. The imposition of an external magnetic field at angle $\beta > \pi/4$ inevitably led to inhomogeneous distortion of the

director field. Transient structures with inhomogeneous distortion of the director field have been reported for other polymer solutions.[7,29] In an inhomogeneous transient distortion reported for nematic solutions of PBG[7] in the twist geometry ($\beta = \pi/2$), the director remains in the sample plane adopting a distortion such that the distortion angle φ depends both on the height z from the midplane of the sample, and the position x along the axis defined by the unperturbed director--in this distortion, the director does not rotate out of the sample plane. A first-order analysis of this transient structure based on a reorientation driven flow of the nematic fluid led to the result[7,30,31]

$$\varphi(z,x,t) = \varphi_o \exp(t/\tau_x)\cos(\pi z/d)\cos(\pi x/\lambda_x) \qquad (9)$$

for the fastest growing mode at short times. Here, φ_o is some (small) initial amplitude arising from thermal fluctuations, λ_x and τ_x are the characteristic wavelength and time constant, respectively, for the growth of the fastest growing mode. The calculated $\varphi(z,x,t)$ predict the appearance of the periodic distortion observed under crossed polarizers. The linear analysis[7] provides expressions for λ_x/d and τ_x as a functions of $h = H/H_{c,T}$ and certain of the Frank elastic constants and the Leslie viscosities. The linear theory does not adequately represent the observed wavelengths. A nonlinear analysis[30,31] accounts for deviations from the linear theory, with two distinct stages in the evolution of the transient structures. The instability is dominated by the anisotropic viscosities initially, and by the anisotropic elasticities in the later stages

The instability with solutions of PBT is more complicated than the one observed with PBG solutions, involving a distortion in three dimensions, and producing a phase-grating. This distortion involves reorientation coupled with a circulatory flow, with adjacent vortices being antiparallel. A cross-section of the idealized flow pattern (two-dimensional), and the associated equivalent lens for the distortion are shown in Fig. 7. In the case of an electrohydrodynamic instability, the director tilt $\theta(z,x)$ produced by a reorientation induced flow was expressed in the form[32]

$$\theta(z,x) = \theta_0 \cos(\pi x/\lambda_x)\cos(\pi z/d_{eff}) \quad (10)$$

there being no distortion in the y-direction in that case. With this $\theta(z,x)$, the the refractive index $n_e(\theta)$ for light polarized along the x-axis, and propagating along the z-axis, can be written as

$$n_e(\theta) = \left\{\left(\frac{\cos\theta}{n_E}\right)^2 + \left(\frac{\sin\theta}{n_O}\right)^2\right\}^{-1/2} \quad (11)$$

where n_E and n_O are extraordinary and ordinary refractive indices, respectively, θ_0 is the maximum tilt angle of the director out of the sample plane, and d_{eff} is an effective sample thickness. The optical path length was calculated by integration of $n_e(\theta)$ through the sample,[32] producing a diverging lens at $x = 0$ and a converging lens at $x = \pm\lambda_x/4$. The focal length f of the lenses is equal to Λ. The calculated f using the refractive index profile provides a measure of θ_0: $\Lambda^{-1} = f^{-1} = \pi^2\Delta n\theta_0{}^2 d_{eff}/\lambda_x{}^2$, where $d_{eff} = \lambda_x$ if $\lambda_x < d$, or $d_{eff} = d$ otherwise.

The focal length observed for PBT solutions decreased with increasing time in the field, whereas λ_x was invariant until a certain time t_Λ, at which point λ_x suddenly decreased by a factor of two. These observations imply that the tilt angle θ_0, increases as a function of time in the magnetic field for $t < t_\Lambda$. Using the relation given above, the observed Λ correspond to θ_0 in the range 30 to 40 degrees for Sample 57, with θ_0 increasing with the time at 14 kG. A possible explanation for the sudden reduction of λ_x would have the sudden formation of two smaller vortices stacked up on each other to replace a vortex with too large a θ_0. This would result in the wavelength reduction and decrease the tilt angle in each of the smaller vortices, thus relieving the excess splay energy. Such a flow pattern has been suggested in the case of electrohydrodynamic instabilities.[33] Studies of fluorescence emission as a function of the height in the sample using a confocal scanning optical microscope in the fluorescent mode might provide a method to assess the existence of such a structure.

In the early stages of the inhomogeneous distortion under a small external field ($H/H_{c,T} \approx 6$-9) , the fringes along the optic axis were lost first, reminiscent of shear flow normal to the director for PBT solutions.[14,15] This suggests that the fastest growing mode is

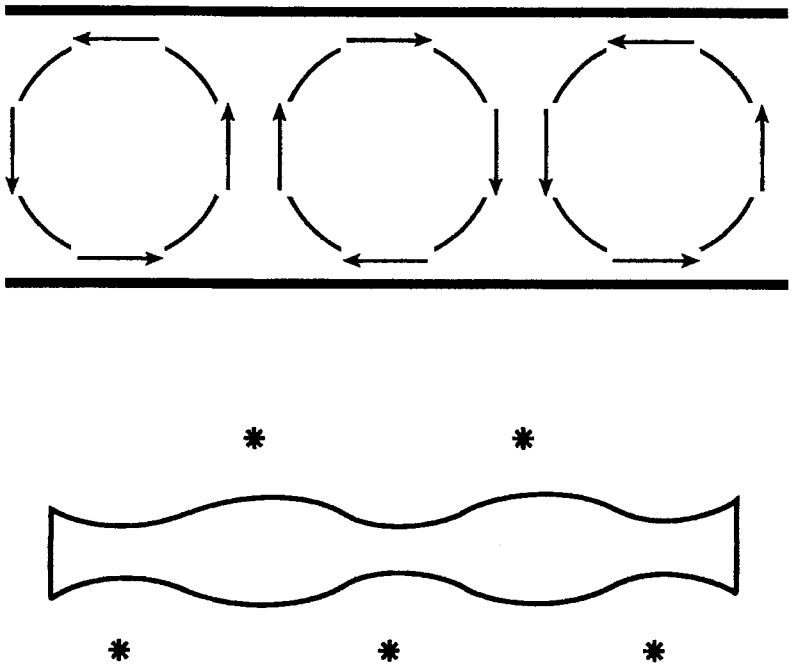


FIGURE 7 Schematic drawings showing the reorientation induced flow vortices (upper) and the corresponding lens structure (lower).

probably the periodic tilt, since the interference figures would have revealed a twist distortion, had there been one. This observation is consistent with a mechanism in which the initial stages are dominated by the occurrence of anisotropic viscosities.[30,34]

After Sample 43 was held under a small external field ($H/H_{c,T} \approx 9$) for four weeks, the phase-grating relaxed away, but alternating bands, perpendicular to the initial director $\mathbf{n}_0$, could be visualized between crossed polars, oriented at $\pi/4$ to $\mathbf{n}_0$, as shown in Fig. 6,

with a wavelength $\lambda_x/d \approx 1$. Moreover, the conoscopic interference figures reformed, revealing a substantial tilt of the director out of the sample plane, in the plane perpendicular to $\mathbf{n}_0$. Since the interference figures were formed with light collected across a diameter of $\approx 3\lambda_x$, any small rotation of the director in opposite directions in areas of bright and dark bands could not be detected; some such feature could, however, explain the presence of the interference bands observed under crossed polars. For example, the interference bands are similar to those observed for PBG solutions[7] and attributed to a twist distortion, with twist angle $\varphi(z,x,t)$ given by Eqn. (7). At still longer times, disclinations appeared at the surfaces of the cell and the periodicity of the bands was destroyed, along with the conoscopic figures. The preceding behavior is not observed under a stronger field ($H/H_{c,T} > 15$) rather, the sample becomes filled with disclinations as the phase-grating is lost.

The disappearance of the phase-grating and the appearance of the reformed conoscopic figures under reorientation with small $H/H_{c,T}$ shows that after standing in the field for an extended period, the periodic tilt out of the sample plane is replaced by a more-or-less uniform tilt. The periodic distortion relaxes in favor of a more uniform one, with the director still tilted out of the sample plane, and rotated with $\varphi \approx \pi/2$, but oscillating periodically along the axis of the unperturbed director to produce the interference bands observed between crossed polars.

CONCLUSIONS

The study reported here shows that application of a magnetic field at $\pi/2$ to the director (twist geometry) results in an instability, creating a phase grating. The reorientation creating the phase-grating is coupled to a complex three-dimensional flow pattern, giving rise to a three-dimensional director pattern. Most of the phenomena are unique to PBT solutions thus far, but may be expected with other similar materials. If the magnetic field is applied at a small angle (< 45°) to the director, reorientation occurs without coupled flow. The

growth and relaxation of twist distortion was used to evaluate K_T/η_T. Both K_T and η_T are considerably larger than the values reported for other polymeric systems. No theoretical treatment is available for these observations.

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