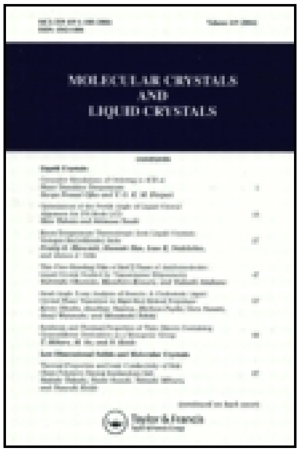

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Rheo-Optical Properties of a Thermotropic Liquid Crystalline Polymer

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RHEO-OPTICAL PROPERTIES OF A THERMOTROPIC LIQUID CRYSTALLINE POLYMER

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ABSTRACT Rheo-optical studies on aligned and unaligned melts of a main chain thermotropic polyester with flexible spacers are discussed in terms of the predictions of the Ericksen-Leslie equations. Experiments show that the material exhibits two different shear-flow regimes depending on the temperature at which the experiments are performed. It is shown, using conoscopy, that the director is flow-aligning at temperatures close to T_{NI} and nonflow-aligning close to a smectic to nematic (T_{SN}) phase transition. The implications of these results are discussed in terms of the change in sign of one of the Leslie viscosity coefficients and interpreted in the framework of the Ericksen-Leslie Theory.

INTRODUCTION

Liquid crystals have long been known to exhibit rather unusual flow behavior[1]. They, for instance exhibit negative first normal stress difference in shear flow, increase in viscosity with decreasing shear rate at low rates of shear, large recoverable strains[2-5]. Polymer nematics, like their low molecular weight counterparts, exhibit a wide range of fascinating macroscopic phenomena. Field-induced instabilities and structural changes are especially interesting. This has led to a flurry of recent efforts aimed at the understanding of these phenomena at a fundamental level[6-8].

In order to understand the complex rheological behavior, rheo-optical properties have been studied to complement the rheology[3,9,10]. Flow birefringence and small angle light scattering have been used, in conjunction with polarized light microscopy[11]. It should be emphasized that all the above experiments were performed on completely unaligned samples,.supporting a large number of defects (which are non-equilibrium structures). This makes the analysis of these experiments non-trivial, if not impossible, and the molecular origin of these unusual phenomena remains unknown.

In contrast, the flow properties of small molecule liquid crystals (SMLC) are well understood. The Ericksen-Leslie theory accounts quite well for the dynamical properties of the nematics[12]. The stress tensor describing the response of a nematic to an imposed flow field is determined completely by six viscosity coefficient (α_1 through α_6), five of which remain independent due to Parodi's relation[13]. In the case of a shear flow, the response of a nematic is primarily dependent on two of the viscosity coefficients, α_2 and α_3. When the product $\alpha_2 \alpha_3 > 0$, the director takes on a stable, steady alignment to the flow direction. The director assumes the familiar Leslie angle θ_0 with the flow direction but remains in the plane containing the velocity gradient (X-Y plane). The angle θ_0 is attained such that at steady state there is no hydrodynamic torque on the director and is given by[12]

$$\tan^2 \theta_0 = \alpha_3/\alpha_2 \qquad (1)$$

However, when the product $\alpha_3\alpha_2 < 0$, there always exist hydrodynamic torques which cause the director to rotate in the shear plane. In this case, the director is predicted to precess indefinitely, while being confined in the shear plane[6,7,8,14,15]. This continuous precession of the director, however, is very unlikely to occur due to the fact that the material has to pay a high price, energetically. In order to minimize the energy the director will go out of the shear plane since the twist elastic constant is small compared to bend or splay. It has been proposed that the director will escape the shear plane before occurance of the so-called 1st tumbling instability[14]. In fact, in experiments with SMLC's and lyotropic LCP, out-of-plane instabilities have been observed and understood in the framework of Ericksen-Leslie theory[16-19].

In the recent past, there have been several attempts to explain the unusual transient rheological properties in terms of "tumbling" behavior. Marrucci and Maffettone[20], using the Doi model, have explained the negative first normal stress as being a consequence of non-linear polymer viscoelasticity. It should be remarked that the Doi-Kuzzu model predicts that polymer nematics will not be flow-aligning. Larson[7], while confirming Marrucci's two-dimensional model, extended it to three-dimensions and demonstrated the transition from director tumbling in the linear limit to steady flow with negative first normal stress difference (N_1) in shear flow, at higher shear rates. Burghardt and Fuller[6] repeated the calculations of Carlsson[14] and extended it to transient experiments which one encounters in the rheological characterization of LCP's. One of their conclusions was that a number of transient data could be explained if one assumes that LCPs do not flow-align in shear flow, i.e. $\alpha_2 \alpha_3 < 0$.

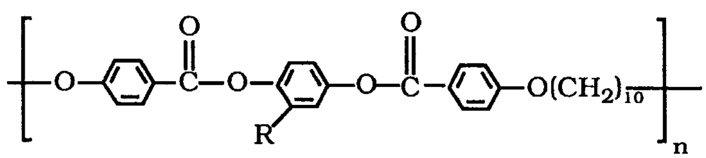
Due to the fact that monodomains are uncommon in LCPs, direct experimental evidence for the sign of α_3 has been lacking for some time. With the availability of single crystals of polybenzobisthiazole[4,19] (PBT) and polybenzylglutamate (PBG), which are lyotropic, there is evidence[6,19] that these materials do go toward the non-flow aligning limit. In the case of PBT[19] several instabilities have been observed, qualitatively similar to the observations of Pieranski & Guyon[18] for a SMLC. In this case it was observed that a spatially periodic structure (phase-grating) was formed (due to secondary flow) for flow normal to the director. Such a periodic structure could also be accessed for flow parallel to the director, provided the velocity (hence the rate of shear) of the plate motion was high[19]. To our knowledge such experiments are still waiting to be done on thermotropic LCPs in an effort to answer questions of flow stability and rheological transients in shear flow.

In this paper the flow properties of a thermotropic polyester, with a stable nematic phase, are studied using unaligned and aligned (monodomain) samples. We demonstrate that the material studied exhibits two shear-flow regimes, tending towards the flow-aligning limit at temperatures close to the isotropic transition temperature (T_{NI}) and tending towards the nonflow-aligning limit at temperatures close to the smectic to nematic temperature (T_{SN}). This kind of flow behavior has also been observed for SMLCs[15,17]. The primary technique is optical microscopy coupled with conoscopy. Conoscopy (or optical crystallography) was used to follow the director motion in response to an applied shear flow.

EXPERIMENTAL

Material

Experimental studies with thermotropic liquid crystalline polymers are plagued with several generic problems which include: (i) insufficient stability of the materials at high temperatures (> 250°C) (ii) high temperatures needed to reach the nematic range; and (iii) lack of transparency of the materials in the nematic range. The material of this study is nematic around 150°C (still high enough to be a nuisance), stable in air for at least a day, and it is also quite transparent. A semiflexible thermotropic liquid crystalline polymer composed of mesogenic groups connected by flexible decamethylene spacer was used, having the repeat unit structure as shown:



Substituents are placed on the mesogenic unit which decrease the transition temperatures, for various transitions. The polymer shows a melting transition at 110°C, a smectic to nematic transition (T_{SN}) at 138°C and a nematic to isotropic transition (T_{NI}) at 158°C[21]. The glass transition temperature could not be determined.

Sample Preparation

Monodomains were prepared between two glass plates coated with SiO_2 at an oblique angle of 75°, forming a grooved surface. The glass plates were repeatedly rinsed with distilled water and dried. On sandwiching the material between two such plates (1" x 5mm x 1mm), the whole assembly was placed in a glass tube inside an oven. Two microscope cover slips served as spacers in defining the sample thickness. This assembly was then placed in a magnetic field at 145° - 150°C for 4 to 5 hours at a field strength of 13.5T at the Francis Bitter National Magnet Lab (Cambridge, Mass), with the magnetic field in the plane of the glass plates. After sufficient time (~ 4 hours), the oven was cooled with the sample at a rate of 25 - 30 K/min to room temperature. The quality of the monodomain was checked by optical microscopy and conoscopy.

Conoscopy

Conoscopy is used to observe the director tilt or twist during flow. For this purpose, a nematic single crystal sample is illuminated with highly convergent laser light (λ=632.8nm) between crossed polars, with the polars at 45 degrees to the optic axis (which is taken to be collinear with the director. The highly convergent beam of light is focused within the sample plane. This enables one to probe the optical properties of the nematic single crystal (uniaxial symmetry) at a wide range of propagation angles simultaneously. For a material with positive birefringence, the path difference δ, is a function of the angle made by the light beam in the cone of light. For a single crystal nematic (with uniaxial symmetry) the conoscopic interference figures take the form of hyperbola-like principal isochromates (curves of zero intensity) placed along the optic axis of the material, and on an axis orthogonal to that axis, see Fig 1. For planar alignment of the director,

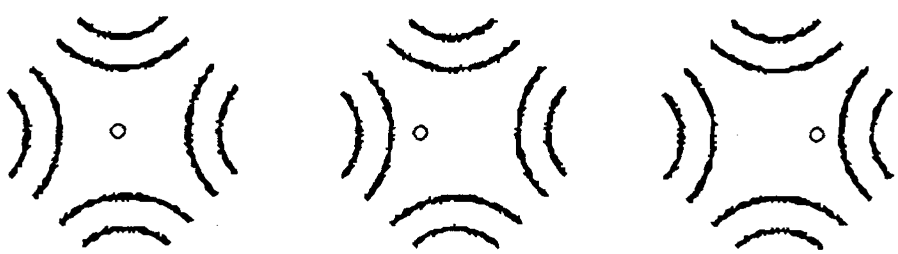


FIGURE 1 Schematic diagram of the interference figures. The circle represents the optic axis of the microscope. From left to right are the figures for a planar alignment, for a flow-aligning nematic and a nonflow-aligning nematic, respectively.

the center of symmetry of the interference figure is collinear with the optic axis of the microscope. Small distortions of the director are revealed by the interference figures, by a shift in the center of symmetry if the distortion is a tilt out of the sample plane, and by a rotation of the interference figures if the distortion is a twist in the sample plane[19]. In the case of a tilt the center of symmetry shifts in a direction normal to the tilt.

A flow cell was constructed to house the sandwich sample described above: The sandwich cell containing the monodomain was placed in an aluminum holder within an aluminum heating block. The the heating block was heated by pencil heaters connected to a temperature controller. The upper plate was translated parallel to the lower plate, providing simple shear flow. A lens (5mm diam, 4.6mm f.l.) was placed below the lower plate to provide the convergent light beam needed for the conoscopic observations. The flow cell was mounted on a polarizing light microscope fitted for conoscopic observation using a 50X objective with a 0.60 numerical aperture (NA)

RESULTS

We report here on the experimental observations on unaligned and well aligned ("monodomain") sample. The sample exhibits the characteristic Schlieren texture observed for nematic phases. On aging (~ 30 min) at that temperature, the texture coarsens, and on further aging (~ 1 hr) parts of the sample go to a homeotropic alignment (director normal to the plates). Quite often most of the sample will go to homeotropic alignment. This process is accelerated if the glass plates had been treated with chromic acid solution and rinsed. As described in the previous section, monodomains with planar alignment were also prepared. Figure 1 shows schematically the interference figure obtained from a monodomain with planar alignment. From the interference figures, it is possible to calculate n_e and n_o separately, but this was not done here. For more details the readers are referred to a paper .by Mattoussi[22].

Flow on Unaligned Material

Shear flow was initiated on unaligned, textured samples between two glass plates. The separation between the plates was about 20 μm. In many experiments (done on a microscope stage) the total displacement of the plate was about 3-4 mm which corresponds to a total shear strain of about 200. It was observed that the density of defects decreased with increasing strain, eventually transforming to a uniformly birefringent fluid under crossed polars (with the polars at 45° to the flow direction). The transformation occured after around 20 - 30 units of strain. Upon cessation of flow large areas (~ 300-500 μm) of the sample remain uniformly birefringent. Regions of varying director profiles are usually separated by line defects. In the regions free of defects having a uniform birefringence one is able to obtain an interference figure indicating that the bulk is free of defects. Quantitative measurements of Δn during flow are in progress. It is also observed that a certain retardation color is transmitted during flow at a constant rate of shear, i.e. Δn is saturated at that rate of shear. The implications of this will be discussed in the following section.

Flow on Aligned Material

Monodomains prepared by aligning in a magnetic field were used in these experiments. On imposing a shear flow (top plate in motion with respect to the bottom plate) on monodomains with planar alignment, the interference figure reveals that the director tilts in the shear plane. For the plate motion going from right to left, the center of symmetry of the interference figures were observed to shift left to right at temperatures 152°C<T<158°C, and from right to left at temperatures 142°C<T<150°C. In general, if the distortion is in the plane of shear the center of symmetry of the interference figures will shift along an axis, normal to the director tilt, but will be contained in the shear plane as is schematically illustrated in Figure 1.

DISCUSSION

The aligned samples obtained as described above have been used to study the response of these materials subjected to shear flow. Two regimes of shear flow have been observed, as indicated by the motion of the center of symmetry of the conoscopic figures during flow. In discussing the observed flow behavior it would prove to be useful to start with the predictions of Ericksen-Leslie theory for nematics subjected to shear flow. We will just cite the salient results that is deemed essential for the discussion.

We consider a flow with the flow direction collinear with the director of a uniformly aligned planar monodomain and is along the x-axis. A velocity gradient, $\kappa = dv_x/dy$ exerts a hydrodynamic torque on the director, which per unit volume is given by[23]

$$T_y^{shear} = (\alpha_3 \cos^2\theta - \alpha_2 \sin^2\theta)\kappa \qquad (2)$$

where θ is the angle between **n** and the velocity **v** in the X-Y plane. This torque is the linearized form of the general equation. For an infinitely thick sample, any velocity parallel to **n** will drive the director to the Leslie angle θ_0 (see eqn1) in the shear plane (X-Y plane) provided the product of $\alpha_2\,\alpha_3 > 0$. With a finite sample thickness, for small velocities, the hydrodynamic torque can be balanced by the elastic torques. Hence at finite velocities the director initially aligned along the X-aixs, aligns within the bulk, in the X-Y plane at an angle such that the hydrodynamic torque on the director vanishes, leading to the Leslie angle as given by equation1. If on the other hand, the product $\alpha_2\,\alpha_3 < 0$, then there exists no angle at which the hydrodynamic torque reduces to zero (as can be seen from equation2) and the material does not exhibit flow alignment, but instead goes towards the nonflow-aligning limit. The transition from the "tumbling limit" to turbulence has been studied in detail by Manneville[14]. Before the first tumbling instability (where the director makes a discontinuous jump in the shear plane) an out-of-plane instability is expected to occur due to the influence of the elastic stress.

In our experiments the sign of α_3 is determined at once by applying a shear flow on the monodomain samples. The center of symmetry of the conoscopic figures is initially displaced along the direction of v for temperatures $142^oC<T<150^oC$ and in the opposite direction for temperatures $152^oC<T<158^oC$. This indicates that in the transient flow conditions reported here, the material exhibits tendency to flow-align in the temperature range $152^oC<T<158^oC$ and crossing over to the nonflow-aligning limit in the temperature range $142^oC<T<150^oC$. Although we do not know the sign of α_2, it has always been found to be negative and greater in magnitude than α_3[12]. Hence two different hydrodynamic problems exist depending on the sign of α_3. The possibility of a sign change has been predicted next to a second-order phase transition from a nematic to a smectic phase, where α_3 is expected to show a positive divergence[24]

The thermotropic polyester used in experiments here, is reported to have a smectic to a nematic phase transition around 138 C[21] [Bhowmik, 1991]. Hence, it is conceivable that the sign of α_3 could go through a change from being negative at temperatures close to T_{NI} and crossing over to being positive close to the smectic to nematic phase transition. The experimental observations are consistent with such a sign change. A related observation not discussed in this paper, but will be published elsewhere[25] is that on imposing an oscillatory shear on a textured sample at about 151°C (±1C), the sample eliminates all the defects and is a defect free sample over large areas (hundreds of microns), with the director taking small excursions along the flow direction. Such behavior is not observed at temperatures close to the smectic phase transition. This again is indicative of the fact that the Leslie coefficient α_3, goes through a sign change.

In fact the Ericksen-Leslie theory is not limited to monodomains. If one has a flow-aligning nematic ($\alpha_2 \alpha_3 > 0$) then the prediction of the Ericksen-Leslie theory for shear flow on a textured sample is identical to that discussed above. This is consistent with the observations reported in the previous section. On shearing a textured sample filled with defects it was observed that the material goes to a defect free sample, uniformly birefringent state at strains >40. Such behavior has been observed in the past on other thermotropic polyesters[26]. It is our contention that the material in those experiments and in our experiments has attained the Leslie angle θ_0, at "steady-state", although the angle was not measured. Such measurements are in progress and will be reported elsewhere. Detailed experiments to study the effects of variation of strain rate, molecular weight and temperature are in progress. The parameters of interest are the twist viscosity, the birefringence and the tilt angle of the director subjected to various shear flows. The temperature dependence of these parameters is of utmost importance to our understanding of the flow properties of these materials.

CONCLUSION

A strong magnetic field was used to achieve the desired (planar) alignment required to study the rheo-optical properties of the liquid crystalline polymer. Using conoscopy we are able to unequivocally answer the question of stability of flow. The polymer used shows flow aligning behavior close to T_{NI} and nonflow-aligning behavior close to T_{SN} in response to transient shear flow between two parallel plates. The behavior is interpreted in terms of the changing sign of one of the Leslie viscosity coefficients, α_3, as a function of temperature. It is shown that the Ericksen-Leslie equations adequately describe the observed results. Systematic experiments are underway to evaluate the effect of various imposed velocities as a function of temperature.

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