Mechanical and Optical Rheometry of Polymer Liquid-Crystal Domain Structure

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ABSTRACT: Complementary mechanical and optical rheometric techniques are used to examine the domain structure of two lyotropic polymer liquid-crystalline samples. The mechanical methods involved both shear and first normal stress measurements, and the optical experiments employed conservative linear dichroism. The experimental protocol used transient simple shear flows where the shear rate was either suddenly reversed in sign or stepped up to a higher value. In either case, pronounced oscillations of the same period were observed in both the mechanical and optical measurements. The periods, if measured in strain units, were observed to be independent of *strain rate* and suggested a suspension-like behavior. Since the conservative linear dichroism can be identified with the polarization-dependent scattering of light by the defect structure in the samples, these results offer strong evidence that this structure dominates the rheological response.

Introduction

The rheology of polymer liquid crystals (PLCs) is characterized by many qualitative differences compared with isotropic polymeric liquids. Among these rheological properties are apparent yield stresses,[1,2] negative first normal stress differences,[3-6] and pronounced oscillations in stress following the inception and stepwise change of simple shear flow.[7-9] Understanding the physical processes responsible for this behavior is complicated due to the variety of phases and structural entities which liquid crystals can manifest and the difficulty in reproducing many of the observed phenomena. Furthermore, it has proven difficult to identify which rheological responses appear to be general in nature and not specific to particular systems.

In this respect, the polydomain structure of PLCs has long been argued to be responsible for their unique rheology. Although the precise origin of domains in PLCs is the subject of current investigation, the concept of arrays of disclinations has gained some degree of acceptance in recent years. Here one refers to the presence of defects in the form of line disclinations where the director $\mathbf{n}(\mathbf{x})$ specifying local ordering of polymer chains is discontinuous over a small region in space. Recent transmission electron microscopy techniques have been able to visualize these disclinations.[10] Following Marrucci,[11] one can define an effective domain as an average volume element containing the minimum number of disclinations, which produces a zero net orientation in the director. A common picture of a domain consists of two pairs of line defects of equal and opposite strength, $S = \pm^1/_2$. The strength S is the multiple of 2π through which the director will rotate upon intercepting a disclination in the plane normal to the line defect.[12] A quiescent fluid consisting of an assembly of such domains will be macroscopically isotropic in the director field even though, on the scale of a single disclination, the fluid is highly ordered.

Initial interpretations of yield stress phenomena and oscillatory stresses following flow start up have attributed this behavior to a suspension-like character associated with the flow response to domains. Such explanations are appealing and have lead to the construction of simple domain-based constitutive models,[11,13] which can predict some of the qualitative aspects of experimental observations. However, the use of mechanical measurements alone to elucidate the role of domain structure in the rheology has the disadvantage of not being able to unambiguously separate out the contributions of the polydomain structure and the individual macromolecules constituting the domains. In this paper, conservative linear dichroism is explored as a complementary measurement capable of responding to the domain structure alone.

Dichroism refers to polarization-dependent attenuation of light and is linked to the imaginary part $\mathbf{n}''$ of the refractive index ensor $\mathbf{n} = \mathbf{n}' - i\mathbf{n}''$. Light can be attenuated by either scattering or absorption, and both mechanisms lead to dichroism in anisotropic materials. Dichroism arising from polarization-dependent scattering is termed conservative whereas polarization-dependent absorption is referred to as intrinsic or consumptive dichroism. In either case, dichroism is strongly wavelength dependent. This is unlike birefringence, the optical anisotropy associated with the real part, $\mathbf{n}'$ of the refractive index tensor $\mathbf{n}$, which is only weakly dependent on wavelength. It is often possible to locate a range of wavelengths where form contributions to the dichroism by scattering dominate over the intrinsic effects due to absorption. This is in contrast to birefringence, where it is generally not possible to separate intrinsic contributions from form effects.

Polymer liquid crystals normally exhibit substantial scattering due to the presence of defects. Flow-induced anisotropy of disclinations will cause the scattering to be polarization dependent and should result in both conservative dichroism and a form contribution to the birefringence. Intrinsic dichroism, on the other hand, can be negligible since many PLCs do not absorb significantly in the visible wavelengths. Both intrinsic and scattering effects will contribute to the birefringence, and for that reason this optical anisotropy is not particularly useful for considering the dynamics of domain structure. Nevertheless it has been used rather extensively for that purpose.[2]

In the following sections, measurements of conservative linear dichroism are presented on two lyoptropic PLCs subjected to transient simple shear flow. These measurements are complemented by mechanical measurements of stress in order to identify the contributions of polydomain structure to the rheology of these materials.

Experimental Section

Materials. Two lyotropic PLC samples were studied. The first sample (sample A) consisted of a 12% solution by weight

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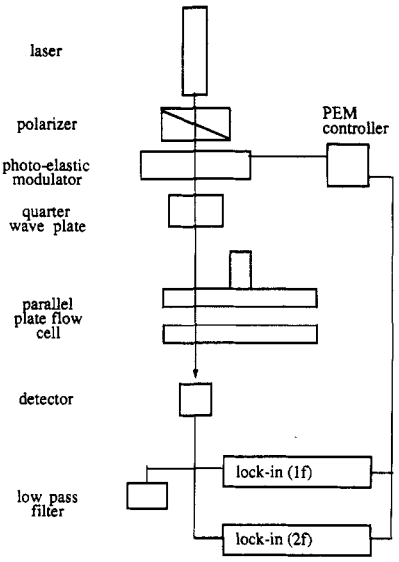

Figure 1. Optical apparatus for the measurement of flow-induced dichroism.

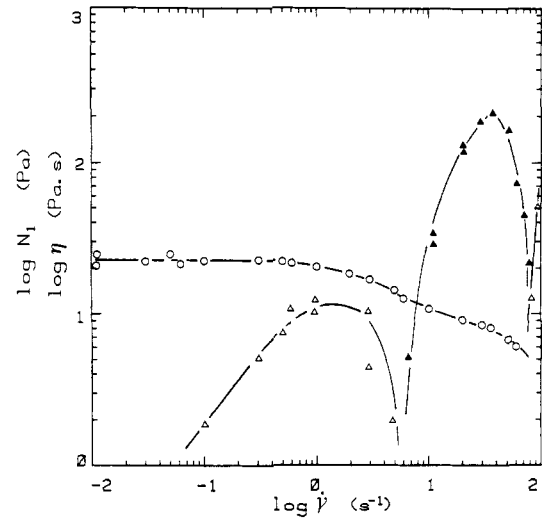

Figure 2. Steady-state shear viscosity, η (circles), and first normal stress difference, N_1 (triangles), as a function of shear rate, $\dot{\gamma}$. The open triangles are positive values, and the solid triangles are negative values.

of poly(γ-benzyl L-glutamate) (PBLG) in *m*-cresol. This polymer had a molecular weight of 250 000 and a critical concentration for an isotropic to nematic phase transition of 8%. The same sample has been the object of extensive rheological studies.[5,7,8,14] The second solution (sample B) was a racemic mixture of PBLG and PBDG in *m*-cresol at a concentration of 20% by weight. The molecular weight of the PBLG was 345 000 and of the PBDG was 310 000. When a single enantiomer is dissolved in *m*-cresol a cholesteric structure develops. This structure transforms into a nematic during shear.[3] A racemic mixture of L- and D-glutamate forms a nematic structure even at rest.

Optical Rheometer. The optical measurements were carried out at Stanford University. The instrument used to make measurements of conservative linear dichroism has been described in ref 15 and is shown in Figure 1. The instrument operates by modulating the polarization of the light with a photoelastic modulator (PEM). The combination of a polarizer, PEM, and quarter-wave plate oriented as described in Figure 1 produces linearly polarized light which rotates rapidly at a frequency of 50 kHz. Following the sample, the light is sent to a detector. The intensity has the following form

$$I = I_{dc} + I_{\omega} \sin \omega t + I_{2\omega} \cos 2\omega t + \cdots \quad (1)$$

The amplitudes

$$I_{\omega} = 2J_1 I_{dc} \tanh \delta'' \sin 2\theta \quad (2a)$$

$$I_{2\omega} = 2J_2 I_{dc} \tanh \delta'' \cos 2\theta \quad (2b)$$

are functions of the sample extinction $\delta'' = 2\pi\Delta n'' d/\lambda$, and the sample orientation θ is relative to the flow direction. This angle is measured in the plane of the electric vector, normal to the direction of light propagation. $\Delta n''$ is the dichroism, d is the sample thickness, and λ is the wavelength of the light (0.632 nm). The amplitudes I_{ω} and $I_{2\omega}$ are measured by using phase-sensitive detectors, and J_1 and J_2 are calibration constants. The signal I_{dc} is the mean transmitted light intensity through the sample and is measured with a low-pass filter.

The flow cell consisted of two 1-in. disks of the fused quartz spaced 2 mm apart. The flow was generated by rotating the lower disk. The light was sent parallel to the axis of rotation and at a radial distance of 1 cm from the center of the disks. Due to symmetry considerations, the angle θ was always observed to be zero, and only the measurement of $I_{2\omega}$ was required. Knowledge of the shear rate required determination of both the gap separation and the radial position of the light beam. Uncertainty in these two values led to an error in the shear rates of ±10%.

It should be noted that the use of the parallel disk flow geometry meant that the electric vector in the optical measurements was in the (1,3) plane, that is, the plane containing the flow and neutral directions. It would be valuable to conduct similar measurements using a Couette cell with light propagating along the vorticity axis in order to determine the state of structure in the (1,2) plane. The necessary flow cell to conduct such measurements is currently under construction.

Mechanical Rheometer. The rheological experiments were performed at the University of Leuven on a Rheometrics mechanical spectrometer 705 F. A cone and plate geometry (angles of 0.02 and 0.04 rad) was used to ensure a constant shear history throughout the sample. This is a prerequisite for transient rheological experiments. The temperature was kept constant at 293.0 K.

Experimental Protocol. Studies of the evolution of structure in transient flow conditions normally provide important information which is not available from steady flow measurements. In order to properly carry out transient flow measurements on PLCs it has proven to be difficult to obtain reproducible initial conditions. This was demonstrated in ref 7 and 8, where the start-up from rest of the 12% PBLG solution showed pronounced, damped oscillations prior to the steady state; these oscillations were, however, not reproducible from run to run. For that reason a presheared initial condition was used with the sample being sheared at a lower shear rate before a step change to a higher shear rate. With this protocol, reproducible results could be obtained if the preshear condition was established over sufficiently large total strains (typically over 100 strain units). A second transient flow procedure which can produce reproducible results is a flow reversal where the sample is first sheared for a large total strain (again over 100 strain units) at which point the shear rate is suddenly reversed in sign and continued for the same total strain in the opposite direction. Both types of transient flows were used in this study for the mechanical and optical measurements.

Results

Mechanical Measurements on Sample A. Sample A has been studied extensively under steady-state conditions as well as in transient flow experiments.[5,7,8,14] Only those results which are relevant for comparison with the optical data will be presented here. It has been verified that all the measured values are bulk properties of the material under consideration and that boundary effects were not important.

Figure 2 shows equilibrium values for the viscosity and the first normal stress difference (N_1). The most prominent feature is the occurrence of a negative normal stress in the intermediate shear rate region. Negative normal stresses are now well documented for various polymeric liquid crystals.[3,6]

Two types of transient experiments are important for the subsequent discussion: flow reversal and stepwise

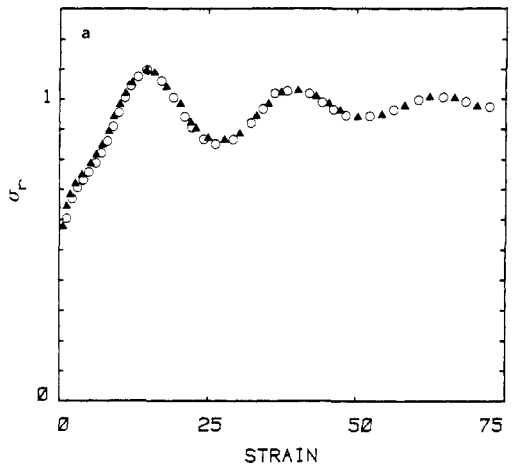

Figure 3. Normalized shear stress versus strain immediately following the sudden reversal of simple shear flow. The shear rates used were 1.0 (circles) and 0.5 s^{-1} (triangles).

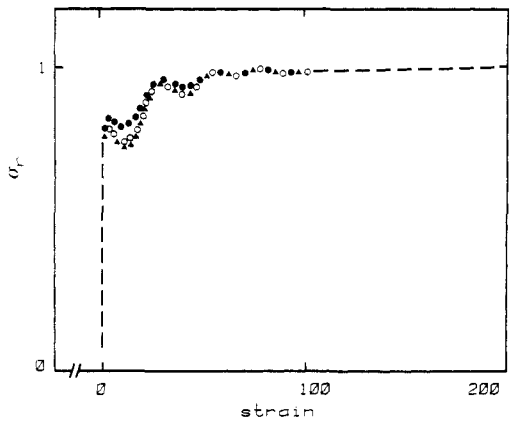

Figure 4. Normalized shear stress versus strain following a step-up in shear rate from 0.05 to 0.2 (solid circles), 0.5 (open circles), and 1.0 s^{-1} (triangles).

increase in shear rate. In both types of experiments the initial conditions of the material are well defined by the previous shearing. The reduced shear stresses upon reversal of the flow direction are displayed in Figure 3. The applied shear rates in the Newtonian region, and the response is plotted versus strain. A complex transient pattern with multiple overshoots is observed. The curves can be scaled approximately with strain. The period of the oscillatory pattern amounts to 25 strain units.

Stepwise increases in shear rate can also shed some light on the complex transient behavior of this class of materials. The results for transient shear stresses upon increasing the shear rate, with the initial as well as the final shear rate in the Newtonian region, are represented in Figure 4. As in the flow reversal experiments, the curves have a compex damped oscillatory pattern which can be scaled with strain at the final shear rate. It has been established that when the final shear rate is outside the Newtonian region the period of the oscillation tends to shift to smaller values.[16]

Optical Measurements on Sample A. The turbidity of sample A, as indicated by measurements of I_{dc}, was found to be constant during the flow experiments. Figure 5 shows the dichroism measured during flow reversal experiments for shear rates of 0.375 and 75 s^{-1}. The dichroism is plotted against total strain, and the arrows in the figure indicate the points where the flows in each experiment were reversed. At sufficiently low shear rates, the dichroism is observed to respond in a manner similar to the result shown for $\gamma = 0.375$ s^{-1}. Each experiment was started from rest, and the dichroism was initially zero.

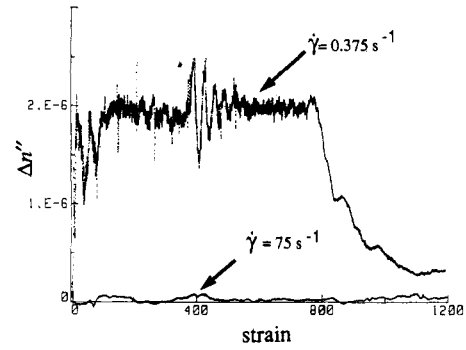

Figure 5. Dichroism versus strain during flow reversal experiments for two shear rates. The pronounced oscillations occurring at approximately 400 strain units indicate the position of the flow reversal.

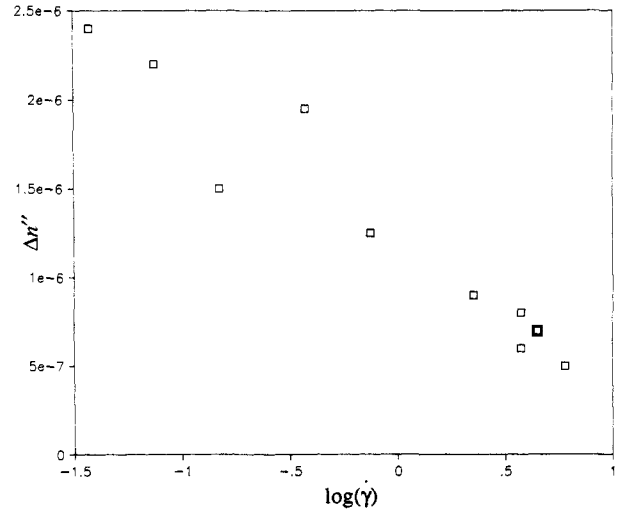

Figure 6. Steady-state dichroism versus the shear rate.

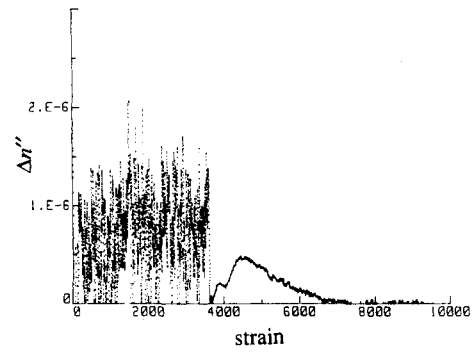

Figure 7. Dichroism versus strain during a flow reversal experiment at a shear rate of $\dot{\gamma} = 6$ s^{-1}. These data indicate a chaotic, time-dependent behavior until the flow was stopped at 3800 strain units.

Following a period of damped oscillations, the dichroism reached a steady value and underwent pronounced, damped oscillations upon the reversal of flow. In the reverse direction the dichroism again evolved to its former steady-state value. After the flow was arrested, the dichroism relaxed to zero.

The steady values of the dichroism are plotted against shear rate in Figure 6. The dichroism was observed to decrease with shear rate until a shear rate of 6 s^{-1}, where the dichroism was found to be highly fluctuating and did not achieve a steady value. The flow reversal experiment at this shear rate is reproduced in Figure 7. It is important to note that a shear rate of 6 s^{-1} was the point at which the first normal stress difference became negative, as indicated in Figure 2. At higher shear rates the dichroism

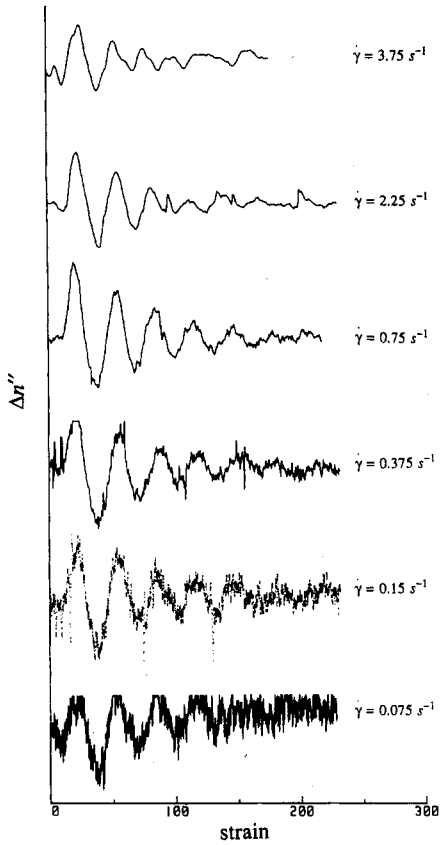

Figure 8. Dichroism versus strain immediately following the reversal of simple shear flow.

continued to be fluctuating but also declined in magnitude. The region of highly fluctuating dichroism coincides with the region of negative normal forces (Figure 2). At even higher shear rates ($\geq$75 s^{-1}) the dichroism becomes very small, but the signal is stable once more. Here as well, there is a correspondence with the normal force data, as N_1 again becomes positive in this shear rate region. The data indicate the dichroism is a decreasing function of the shear rate over the entire range studied, although scatter in this measurement prevents a firm conclusion on this point. The shear viscosity, on the other hand, is shear rate independent in this range and becomes shear thinning above a shear rate of 1 s^{-1}.

The damped oscillations following a flow reversal are plotted against strain in Figure 8 for shear rates ranging from 0.075 to 4.5 s^{-1}. The oscillation can be superimposed almost perfectly up to a shear rate of 2.25 s^{-1} after which the period decreases slightly with shear rate before becoming erratic at γ = 4.5 s^{-1}. Below 2.25 s^{-1} the period is 30 strain units, which is close to the period of 25 strain units found in the shear stress measurements (Figure 3). Given the uncertainty in the shear rates in the optical experiments, this differnce is within experimental error. Comparing the oscillations in Figures 3 and 8, the dichroism and shear stress oscillations are in phase with their maxima and minima occurring at the same strains. The mechanical and optical data also show approximately four to five oscillations before damping to steady values. The damping is also largely shear rate independent.

Each flow reversal experiment included a start up from rest and cessation of flow. The transient response following the start-up also showed an oscillatory response with periods of oscillation of the same magnitude as occurring following flow reversal (see Figure 5). The details of the transient response, however, were not reproducible from run to run due to the difficulty of ensuring identical initial

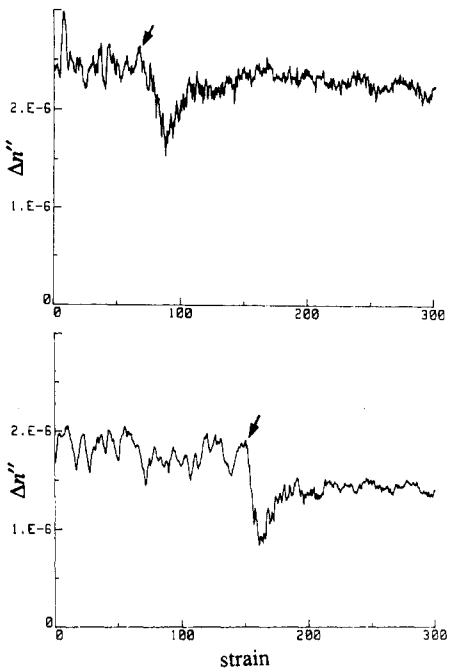

Figure 9. Dichroism versus strain following a step-up in shear rate from $\dot{\gamma}$ = 0.0375 to (a, top) $\dot{\gamma}$ = 0.375 and (b, bottom) $\dot{\gamma}$ = 0.75 s^{-1}. In each the strain has been calculated by using the final shear rate. The arrows indicate the strain at which the flow rate was stepped up.

conditions in the rest states. Long time effects also hampered the generation of reproducible transients in the mechanical measurements.[7,8]

Upon cessation of flow the dichroism was found to relax to zero over a time scale much larger than the period of oscillation. This indicates that the rest state is characterized by a director field which is macroscopically isotropic. This is in contrast to birefringence, which relaxes to a finite rest state value reflecting local ordering of the polymer chains on the length scale of disclinations.[2] The overall dichroism relaxation curves, however, were not reproducible from run to run although the initial time scale for relaxation varied inversely with the previous applied shear rate. A similar relation was also observed for the slow part of the stress relaxation.[8] On the other hand, the shear stress relaxation was reproducible from run to run. This difference is likely due to the fact that the dichroism is measured over a small region in space defined by the light beam diameter (0.8 mm) whereas the stress measurement is an average over the entire surface of the plate in the cone and plate viscometer.

Two sets of step-up experiments were performed. In each case the sample was presheared at $\dot{\gamma}$ = 0.0375 s^{-1} for a total of 10^4 s. At this time the shear rate was stepped up to 0.375 and 0.75 s^{-1}, respectively. The responses in the transition region are shown in Figure 9, where the dichroism is plotted against strain calculated by using the final shear rates. These transients are also seen to scale with strain with an observed minimum occurring in at strain of 13–15 strain units following the step-up. An oscillatory response, as seen in the shear stress measurements (Figure 4), did not occur in the dichroism. The two types of measurements produced results in the step-up experiments which were out of phase with the response obtained following flow reversal. That is, they first produced an undershoot following a step-up in shear whereas following flow reversal a maximum was first observed.

Optical and Mechanical Measurements on Sample B. Flow reversal experiments were also performed on the racemic mixture. The response of this sample was found

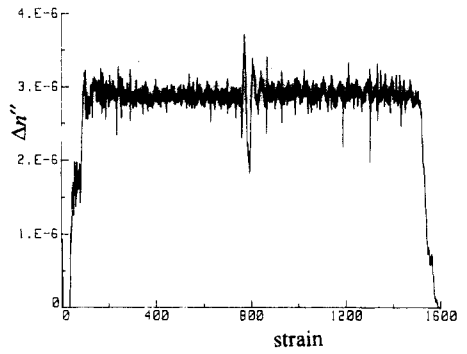

Figure 10. Dichroism versus strain for a flow reversal experiment on the racemic sample B. The shear rate was $\dot{\gamma} = 3.75\ s^{-1}$ and was reversed at approximately 800 strain units.

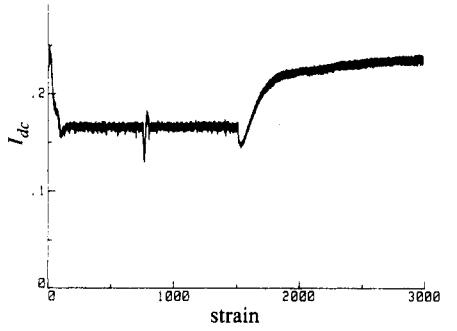

Figure 11. Mean transmitted intensity, I_{dc}, in arbitrary units for the same conditions described in the caption for Figure 10.

to be qualitatively similar to the cholesteric solution with the exception that the mean transmitted light intensity, I_{dc}, defined in eq 1 was a strong function of shear rate and time. Figures 10 and 11 show the dichroism and I_{dc} as functions of time for a flow reversal experiment at $\gamma = 3.75$ s^{-1}. The general features of these data were also observed in experiments with shear rates from 0.075 to 3.75 s^{-1}. Both the dichroism and transmitted intensity underwent damped oscillations which scaled with strain as demonstrated in Figure 12. The period of the oscillations was 34 strain units.

No extensive rheological data are available on sample B. However, a similar racemic mixture has been studied by Kiss and Porter.[2] They measured the steady flow value for η and N_1 and obtained the same general characteristics as we observed for sample A. The critical shear rate for the sign change in N_1 is 10–20 s^{-1}. Limited experiments performed in Leuven confirm their results. Flow reversal also resulted in a damped oscillatory pattern which scaled with strain but with a slightly larger period (28 strain units for sample B versus 25 strain units for sample A).

Discussion

The oscillatory behavior reported here and its scaling with strain is reminiscent of the dynamics of suspensions of nonBrownian, rigid, particles. For these systems, the period of oscillations can be directly interpreted in terms of particle geometry, which controls the angular velocities of the particles. Furthermore, the damping of the oscillations is a direct indication of dispersion in particle geometries, nonnegligible Brownian motion, or particle–particle interactions.[15] Although such a simple interpretation cannot be directly carried over in the present problem, the period of the oscillations, when measured in strain, is clearly a material property of the polymer liquid crystals. Very recently Marrucci[17] has examined the Leslie–Ericksen model of liquid crystals.[18] That model describes an anisotropic fluid through the director field

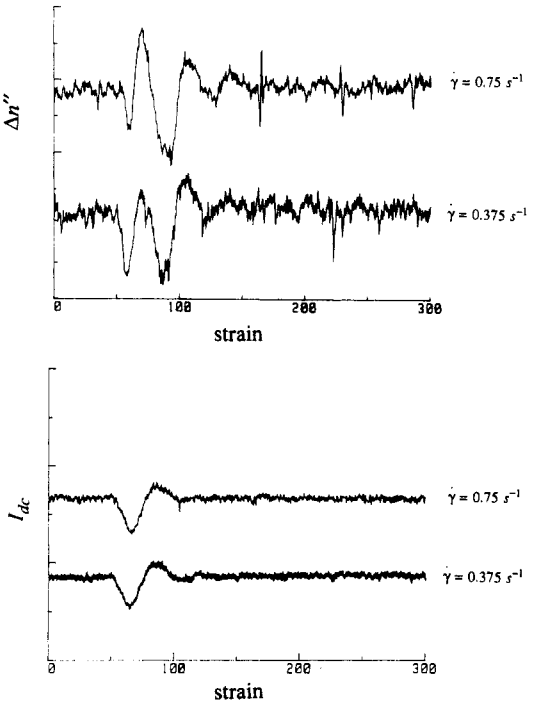

Figure 12. (a, Top) Dichroism versus strain in the vicinity of the flow reversal for two shear rates for the racemic mixture. (b, Bottom) Mean transmitted intensity, I_{dc}, in the vicinity of the flow reversal for two shear rates for the racemic mixture.

which is made to satisfy a simple torque balance involving hydrodynamic and elastic forces. Neglecting the Frank elasticity term, Marrucci has demonstrated that this model is capable of predicting oscillatory responses so long as certain criteria on the coefficients appearing in the model are met. In particular, the period of oscillations is predicted to be a material property which depends on the ratio of two of the Leslie–Ericksen coefficients (specially, α_2/α_3). Precisely the connection to the material properties, however, is not clear. The interpretation in terms of aspect ratio, as in the case of rigid particles, would not appear to apply, for example, since one would not expect anisotropic domain structures to naturally form.

The Marrucci version of the Leslie–Ericksen model predicts undamped oscillations, whereas the oscillations were observed to eventually dampen. This would be expected if the properties of the domains (size, shape) are polydisperse, causing phase mixing of individual contributions. Interactions between neighboring domains could also cause phase mixing. If the density of defects is higher in the more concentrated racemic mixture, this latter mechanism would also explain why that sample is damped more quickly than sample A.

The correspondence of the oscillatory behavior of both the shear stress and dichroism gives strong evidence that the domain structure of polymer liquid crystals contributes significantly to the rheology of the materials. The fact that the dichroism and shear oscillate in phase suggests that maxima and minima in the shear are associated with maxima and minima in the degree of domain orientation. An indication of the relative contributions of domain structure and individual molecules may be inferred by the relaxation behavior of both characteristic properties. The shear stress relaxed in two stages: a fast, initial process which was shear rate independent in the Newtonian region, followed by a slower process with a relaxation time inversely proportioned to the shear rate.[8,14] The dichroism only showed the slower process, suggesting that the faster relaxation in the shear stress may represent the contri-

bution of improved alignment of individual molecules. The inverse dependence of the slower relaxation time scale on the shear rate suggests that the domains are being reduced in size by hydrodynamic forces.

Unfortunately, dichroism measurements made at a single wavelength cannot distinguish between changes in domain anisotropy and changes in their density. Domain multiplication and reduction have both been observed to occur as a result of flow,[19] and any coupling of these two possibilities cannot be unambiguously interpreted with this measurement. Since conservative dichroism can be expected to be a strong function of the ratio of the size of the scattering structures to the wavelength, scanning wavelength would offer the possibility of directly determining the population densities of domains according to their size. Such an experiment would be valuable in understanding the reasons why the transmitted light intensity decreased with flow rate of the more highly concentrated, racemic mixture.

Although many features of the dichroism and shear stress measurements were similar, a few noticeable differences were observed. In particular, reproducible results could often be obtained in the mechanical measurements during conditions where the measurement of dichroism resulted in irreproducible and often chaotic signals. This occurred during relaxation following flow cessation and during flow as the shear rates approached values where the first normal shear difference crossed from positive to negative values. The most probable explanation for these differences is that the stress measurements are averages over the entire surfaces of a force transducer whereas the dichroism measurement is made over a localized volume element. This would cause possible spatial variations to be averaged in the mechanical measurements, which would minimize or eliminate the temporal variations which might result.

An additional point of difference between the optical and mechanical measurements was that, whereas flow reversal and step changes in shear rate produced similar mechanical effects, the same was not true for the optical measurements. This is related to the fact that the dichroism is a rather weak, decreasing function of shear rate while the shear stress is a strong, increasing function of this parameter. For that reason, a step change in shear rate would not be expected to result in a large transient. A flow reversal, on the other hand, produces a dramatic restructuring of the fluid and leads to large effects in both the mechanical and optical measurements.

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Registry No. PBLG (homopolymer), 25014-27-1; PBLG (SRU), 25038-53-3; PBDG (homopolymer), 30869-19-3; PBDG (SRU), 31724-32-0.

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Self-Consistent Field Theory of Surfaces with Terminally Attached Chains

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ABSTRACT: Considering a planar surface with many terminally attached polymer chains at a distance d to another planar surface, we have solved numerically the differential equation for the probability distribution function of an effective chain within the self-consistent field approximation. We have calculated (a) segmental density profiles of the chains and (b) free energy of interaction vs d profiles for both repulsive and attractive two-body excluded volume interaction and for both adsorbing and nonadsorbing surfaces. The contributions from the osmotic and bridging effects to the free energy–d profiles are systematically calculated, and the results are compared with experiments on forces between surfaces bearing polystyrene in near-Θ solutions and with block copolymers.

1. Introduction

The configurations of terminally attached polymer chains at an interface have attracted considerable interest[1] both experimentally and theoretically in view of their role in colloidal stability, copolymer morphology, adhesives, etc. The chain configurations in the proximity of surfaces are

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