Role of Director Tumbling in the Rheology of Polymer Liquid Crystal Solutions

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ABSTRACT: The role of director tumbling in the dynamic response of polymer liquid crystals is investigated. A flow experiment on an oriented monodomain confirms director tumbling in liquid crystalline poly(benzyl glutamate) solutions. Mechanical and optical rheometric techniques are used to investigate the behavior of textured liquid crystal solutions in slow shear flows. Director tumbling in this system is shown to play a major role in determining the rheological behavior, particularly in that it results in large distortions in the director profile, leading to significant distortional elastic effects. The rheological data are interpreted in terms of general scaling arguments based on the assumption that the director field responds over a length scale associated with the texture rather than the macroscopic flow dimension. Comparison of our results with model calculations using the Leslie–Ericksen continuum model further suggests that the texture length scale is refined in response to increased shear rates, as a mechanism for limiting distortional free energy in the shear flow; rheooptical evidence for this texture refinement is described. A broad range of experimental data may be explained by these arguments, including a widely observed relaxation scaling law.

1. Introduction

A clear understanding of the rheological behavior of liquid crystalline solutions of rodlike polymers has proven to be a challenging and, as yet, unrealized goal of much research during the past 15 years. Unusual experimental observations in polymer liquid crystal (PLC) solutions include pronounced oscillatory responses in stress and structure in transient flows, studied extensively by Moldenaers and co-workers for both poly(benzyl glutamate) (PBG) and (hydroxypropyl)cellulose (HPC) liquid crystal solutions,[1-4] and negative values of the first normal stress difference (N_1) in steady shear flow at high shear rates, first seen in PBG solutions by Kiss and Porter[5,6] and also found more recently in HPC solutions as well.[7] The hypothesis that oscillatory responses in these systems are related to tumbling of the liquid crystal director[1] has been considerably reinforced by the recent analyses by Marrucci and Maffettone[8] and Larson[9] that indicate that the observation of negative N_1 is also related to director tumbling. Thus, director tumbling likely plays a central role in the rheology of liquid crystal polymer solutions.

Director tumbling arises naturally out of the linear continuum theory of Leslie and Ericksen[10,11] when the Leslie coefficient α_3 takes on positive values. In this case, the hydrodynanic limit of the director evolution equation takes the same form as the equation governing the orientation of an axisymmetric particle in creeping flow, leading to the well-known Jeffery orbits in shear flows.[12] Thus, in the presence only of hydrodynamic torques, the director would rotate in a closed trajectory, resulting in an indefinite oscillatory response in the macroscopically observed material functions. The occurrence of negative values of N_1 in PLC solutions has been recently shown by Marrucci and Maffettone[8] to be predicted by the well-known Doi molecular model for nematic solutions of rodlike polymers.[13] In order for the Doi model to make this prediction, the usual decoupling approximation for the fourth-moment tensor of the orientation distribution function must be avoided. Marrucci and Maffettone avoided the need for this approximation by reducing the problem to two dimensions and solving directly for the orientation distribution function of the rods, while Larson has extended this work to the full three-dimensional problem by expanding the orientation distribution function in spherical harmonics and solving numerically for the expansion coefficients.[9] Both analyses yield a region of negative N_1 at intermediate shear rates in the nonlinear regime, in good agreement with experiment. The linear predictions of the Doi model are critically dependent on whether the decoupling approximation is adopted. When it is used, the Doi model predicts flow alignment of the director in shear flow, with negative α_3,[13,14] while when it is avoided, director tumbling is predicted.[15] Indeed, the calculations of Larson show a transition from director tumbling at low shear rates to steady shear flow with negative N_1 at higher shear rates.[9]

Despite the strong evidence for director tumbling in PLC solutions, direct confirmation of tumbling has been difficult, due to the high defect density generally exhibited by these materials. Dynamic light scattering studies on uniformly oriented monodomains have provided more detailed information on the Leslie coefficients of polymeric nematics,[16-19] but these studies are unable to determine whether the PLC exhibits tumbling.[20] Flow experiments on initially uniform monodomains have shown much promise for the elucidation of the shear flow properties of PLC solutions.[21,22] In the first part of this paper, we describe a simple flow experiment on a PBG nematic monodomain that confirms director tumbling for this system. We then turn to rheological experiments on textured PBG solutions.

Despite the fundamental importance of studies on oriented monodomains, their direct utility toward the interpretation and prediction of the flow behavior of PLC's is limited, since rheological characterization and practical utilization of these materials generally involve samples exhibiting a textured structure due to a high density of defects in the director field. Our goal in this paper is to formulate some general hypotheses about the dynamic response of textured PLC's in shear flows, relying heavily on the knowledge that PBG solutions exhibit director tumbling. It has been shown that while the rigorous Doi molecular model predicts tumbling at low shear rates, it is expected that flow alignment is recovered due to nonlinear viscoelastic effects at high shear rates.[9] In this high shear rate regime, molecular viscoelastic models appear to capture the major features of the response. Hence we focus here on unusual observations in textured PBG

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solutions that may be seen at *low* shear rates and consequently look to the linear continuum theory of Leslie and Ericksen for insight into the underlying physical phenomena.

Director tumbling is expected to have a profound effect on the flow barrier of PLC's at low shear rates. In the converse case of a flow-aligning nematic, hydrodynamic torques in the shear flow promote a uniform orientation of the nematic at the flow alignment angle.[23] It would be expected that prolonged exposure to shear flow would tend to anneal away defects in a textured nematic. For a tumbling nematic, no such unifying tendency exists; instead, hydrodynamic torques always act to rotate the director in the shear field. Rather than promoting uniform alignment, shear flow is expected to have a destructive effect on the macroscopic alignment of the liquid crystal. The role of elasticity associated with distortions in the director field is dramatically different for tumbling and flow-aligning systems. In flow-aligning nematics at large Ericksen number (ratio of hydrodynamic to elastic torques on the director), the director field is determined predominantly by the hydrodynamic torques, with the effects of distortional elasticity confined to small orientational boundary layers.[24] Indeed, the expectation that polymer liquid crystals would almost invariably be governed by high Ericksen numbers due to their high viscosity has been cited as a reason for neglecting distortional elastic effects in polymeric systems.[25] However, the role of distortional elasticity is much more profound in tumbling nematics. In the absence of elastic torques on the director, a tumbling nematic would exhibit no steady state in shear flow but rather a periodic response associated with the tumbling of the director. Introduction of constraints on the director field due to, for instance, boundary effects on the director orientation prevent the director from rotating indefinitely due to the distortions introduced in the director profile and the corresponding elastic torques.[26] Whereas elastic effects are confined to small boundary layers in flow-aligning nematics, they influence the entire director profile in tumbling systems. Thus, a direct consequence of tumbling at low shear rates in polymer liquid crystals is that we expect distortional elasticity to be a large factor in determining the rheological behavior.

We have recently performed model calculations of transient shear flows for tumbling nematic liquid crystals in order to develop qualitative information about the balance between hydrodynamic and elastic torques and the effects of distortional elasticity on the rheological response.[27] The Ericksen number, defined qualitatively by $Er = \alpha\dot{\gamma}d^2/K$, is the critical parameter for determining the key features of the transient response. Here, α is a characteristic viscosity, $\dot{\gamma}$ is the shear rate, K is a characteristic elastic constant, and d is the length scale over which the director field may respond to the hydrodynamic torques exerted by the shear flow. At moderately large Er, hydrodynamic torques are sufficiently strong to rotate the director through several multiples of π before elastic torques reach sufficient magnitude to balance them. The transient response exhibits oscillations, reflecting variation in the viscous properties of the nematic as the director rotates toward its steady state. When the hydrodynamic torques are removed, the director profile relaxes toward its initial condition under the influence of elastic torques. This rotation of the director during relaxation is coupled to the viscous response and consequently leads to macroscopic relaxation phenomena such as stress relaxation and constrained recoil through which the stored distortional elastic energy is dissipated. These processes occur on the characteristic time scale for relaxation of the director profile, approximately equal to $\alpha d^2/K$. In textured PLC's, the director field is disrupted over a length scale associated with the defect density, typically on the order of a micron, and consequently much smaller than the macroscopic sample size. We have proposed that it is this texture length scale that is relevant in determining the local response of the director field to shear flow and that the dynamic behavior should be interpreted by using Ericksen numbers and relaxation time scales based on this local length scale. A qualitative model for the rheological behavior of textured PLC's in slow flows has been developed based on this central hypothesis,[27] and we will summarize its key elements in the discussion of the present experimental observations.

Our experimental studies of textured PBG solutions combine both mechanical and rheooptical characterization techniques. The optical technique used is flow dichroism, anisotropy in the attenuation of light associated with light scattering from scattering centers oriented or stretched in the flow direction. Moldenaers and co-workers have demonstrated that this technique is useful for monitoring the structural response of PBG solutions,[1] and we use it here as a probe for the dynamic behavior of the PLC in transient flows. Here we extend this technique by allowing for the wavelength of light to be varied. This innovation allows us to investigate how the length scale of the texture responds to shear flow, a key element in the model described above.[27] Our mechanical experiments focus on constrained recoil. Larson and Mead have argued that the large strain recovery observed in PLC solutions at low shear rates reflects distortional elasticity,[28] and our model calculations have identified a mechanism by which this elastic energy may be transferred into strain recovery through the relaxation of the director profile.[27] Here we seek to clearly establish the link between director field relaxation and constrained recoil and use these relaxation processes as probes of the structural response of the PLC in shear flows.

2. Experimental Section

2.1. Samples. Two liquid crystalline solutions of PBG in *m*-cresol have been studied. The first is a 20 wt % racemic PBG solution, with a polymer consisting of equal weights of 248 000 molecular weight PBLG and 200 000 molecular weight PBDG. The use of a racemic mixture in this solution avoids formation of a cholesteric phase due to the optical activity of the polymer and allows the resulting nematic PLC to form an oriented monodomain. The second solution is a 12 wt % PBLG solution, using the 248 000 molecular weight PBLG, and is very similar to that studied extensively by Moldenaers and co-workers.[1-4] Since it contains only the L optical isomer, this solution is cholesteric at rest. It has been reported that cholesteric PBG solutions are transformed into nematics under shear flow;[6] the similarity in behavior between the nematic and cholesteric solutions studies here suggests that the rheological behavior of this 12 wt % solution is insensitive to its cholesteric structure at rest. All chemicals were obtained from Sigma Chemical Co. The 12 wt % solution is just above the transition to an anisotropic phase, while the 20 wt % solution is well within the nematic phase.

2.2. Monodomain Formation. Monodomains of the 20 wt % nematic PBG solution were prepared by a procedure similar to that outlined by Taratuta et al.[29] A small amount of the solution was placed between two coated glass substrates, separated with a Teflon spacer of the desired thickness, and the sample was held together in an aluminum cell. The sample was then placed in a high-field NMR magnet for at least 8 h. Field strengths of either 47 or 55 kG were used. Two types of substrates were used. One type was prepared according to the method of Taratuta et al.,[29] consisting of a glass slide coated first with a layer of SiO vacuum evaporated at a glazing angle of incidence. On top of the SiO layer, a polymer layer was plasma deposited from C_2H_4 gas. These substrates were kindly supplied by Professor R. B. Meyer. Monodomains were also prepared by using

substrates consisting of a glass slide upon which a polymer layer was deposited from a CHF_3 plasma.

It is believed that the hydrophobic polymer coating on the glass slides eliminates specific interactions between the PBG molecules and the polar glass surface that result in perpendicular alignment in the absence of this surface treatment, and thus allows a parallel boundary condition to be established. Annealing in a strong magnetic field promotes uniform alignment of the liquid crystal and a uniform texture with no defects. The SiO precoating helps enhance the orientation of the sample, but this layer is not necessary for the formation of uniformly oriented samples.[29] The monodomains prepared by the above procedure exhibited a uniform appearance and extinction as the samples were rotated between crossed polarizers in a polarizing microscope. Section 3.1 describes the flow experiment performed on these monodomains that demonstrates director tumbling in this solution. All optical and mechanical rheological experiments discussed in subsequent sections were carried out with textured PBG solutions.

2.3. Basis for Scanning-Wavelength Linear Dichroism. The optical polarimetry techniques most often applied to problems in rheology have been flow birefringence and dichroism, referring to flow-induced anisotropy in the real and imaginary parts of the refractive index tensor associated with retardation and attenuation of light, respectively.[30] Although it has been used rather extensively for this purpose, flow birefringence is ill-suited for studying textured polymer liquid crystals. Most importantly, the strong optical anisotropy of these materials at rest makes it virtually impossible to isolate flow-induced changes in the degree of alignment. In a highly textured PLC, the light beam will pass through many "domains" with possibly varying optical orientation, thus giving the sample complicated optical properties that would be strongly sensitive to small changes in the polydomain texture. Finally, defects in PLC's scatter light strongly, leading to a substantial conservative dichroism when the domains are oriented by flow.[1] This anisotropic light scattering will also cause birefringence associated with the texture, so that flow birefringence in a textured PLC will be sensitive to multiple levels of structure. Flow dichroism on the other hand will only arise from anisotropic light scattering provided wavelengths that are absorbed are avoided.

It is well-known that the defects and disclinations in textured PLC solutions scatter light strongly. Alignment or stretching of these scattering centers in the flow direction will introduce anisotropy in the attenuation caused by this scattering that we quantitatively measure as a dichroism. However, scattering off of orientational fluctuations in nematics is also polarization dependent, leading to an anisotropic turbidity even in the absence of texture. Measurement of principal turbidities in nematics has been used to determine elastic constants for a variety of systems.[31-33] To characterize this effect in our solution, defect-free monodomains of thickness 1 mm have been prepared from the nematic 20 wt % PBG solution according to the method described in section 2.2. Anisotropy in the attenuation was measured both by direct turbidity experiments with a He–Ne laser as a light source and by measuring the dichroism with a commercial polarimeter, described below. The dichroism exhibited by the native nematic in the absence of defects was found to be approximately 4×10^{-7}.[20] As will be subsequently seen, this is much smaller than the dichroism observed under flow of the 20 wt % PBG solution in the presence of texture, particularly in that it represents a maximum observable value for a uniformly aligned sample. Thus, the flow dichroism measured in these experiments may be associated with anisotropy in the polydomain texture.

Advantage may be made of the fact that the light scattering that gives rise to dichroism is wavelength dependent. For instance, in dichroism measurements on concentrated suspensions of spherical particles oriented by an external field, varying the wavelength probes different length scales of the anisotropic part of the pair distribution function.[34] Similarly, Meeten has shown that dichroism caused by light scattering from an anisotropic body is a strong function of the relative magnitude of the particle size and wavelength of light. Calculations in the Rayleigh–Debye approximation indicate that the dichroism associated with scattering from oriented spheroids shows a maximum when the wavelength and particle size are of the same order of magnitude.[35]

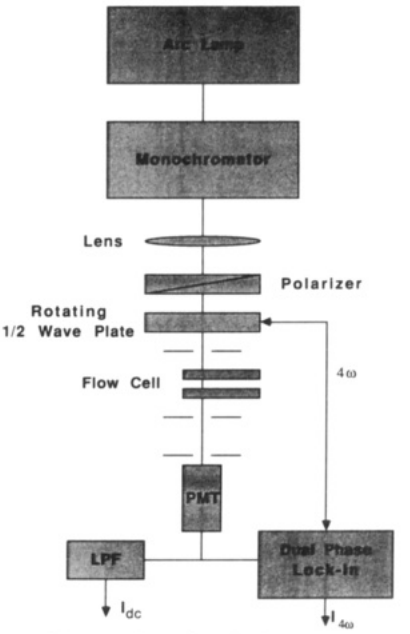

Figure 1. Variable-wavelength polarimetry apparatus for the measurement of linear dichroism under shear flow.

Different length scales in a complicated system may thus be selectively probed by varying the wavelength used. The structure of a textured PLC under flow is certainly too complicated to make direct use of these limiting-case theories, but varying the wavelength used in observing flow dichroism in textured PLC's under flow should allow different length scales in the polydomain texture to be investigated and, in particular, determination of how the dominant length scale responds to varying shear rate.

2.4. Optical Experiments. Figure 1 shows the optical apparatus built to perform dichroism measurements as a function of wavelength. Light in the visible spectrum is supplied by a xenon arc lamp, and the desired wavelength is selected by a grating monochromator. Light exiting the monochromator is focused by a lens and passes through incident polarization optics consisting of a linear polarizer oriented at 90° with respect to the flow direction and a half-wave plate rotating with angular velocity ω in a high-speed air turbine. This half-wave plate is fabricated to be approximately achromatic in the visible spectrum by laminating three normal half-wave plates together following the strategy discussed by Title.[46] The PLC solution is sheared in a rotating parallel-disk flow cell, with a gap of 1 mm. Apertures before and following the flow cell define the light beam in the experiment. After passing through the flow cell, the intensity of the light is measured by a photomultiplier tube with a high-speed amplifier.

The use of high-speed rotary polarization modulation has been thoroughly discussed by Fuller and Mikkelson.[36] Light leaving the rotating half-wave plate is linear polarized, with a polarization vector that rotates at angular velocity 2ω. The sheared PLC exhibits dichroism with principal axes parallel and perpendicular to the flow direction; as the polarization vector rotates, the intensity of the transmitted light fluctuates due to the polarization dependence of the attenuation. Assuming that the principal axes of the birefringence and dichroism are coaxial, analysis of the optical system leads to the following expression for the light intensity measured by the photomultiplier:

$$I = I_{dc}[1 + R_1 \cos(4\omega t) + R_2 \sin(4\omega t)] \quad (1)$$

where the two factors R_1 and R_2 depend on the optical properties of the sample:

$$R_1 = \cos(2\chi) \tanh(\delta'') \quad (2)$$

$$R_2 = \sin(2\chi) \tanh(\delta'') \quad (3)$$

Here, χ is the angle made by the principal axis of the imaginary refractive index tensor and the flow direction, and δ'' is known

as the *extinction*, related to the dichroism, $\Delta n''$, through

$$\delta'' = \frac{2\pi\Delta n'' d}{\lambda} \quad (4)$$

During flow, the symmetry of the shearing geometry dictates that $\chi = 0$, so that the information about the structural anisotropy will be carried in the factor R_1.

Experimentally, the intensity signal is split to a low-pass filter that measures the mean transmitted intensity and a dual-phase lock-in amplifier that measures the in-phase and out-of-phase components of the oscillating portion of the intensity signal. A phase reference is generated by an optical sensor that measures the rotation rate of the rotating half-wave plate and electronics that generate a square wave signal at 4 times this frequency. The outputs from the lock-in amplifier and low-pass filter are read into a microcomputer through an A/D converter and stored for subsequent analysis. R_1 and R_2 are determined by normalizing the lock-in outputs by the mean transmitted intensity, allowing straightforward calculation of the dichroism. Both the monochromator and the flow cell are driven by computer-controlled stepping motors.

Some optical experiments were performed on a commercial polarimeter, the Rheometrics optical analyzer. This instrument uses a He–Ne laser for a light source and hence requires no lens or apertures to define a light path. The intensity is measured by a high-speed photodiode. In other respects, the instrument is similar in design to the variable-wavelength instrument in Figure 1.

2.5. Mechanical Experiments. Constrained recoil and steady-state viscosity experiments were carried out on a Rheometrics stress rheometer (RSR). This is a controlled-stress rotational viscometer, particularly suited for the measurement of elastic recoil. The test fixture was a 40-mm-diameter cone and plate with a cone angle of 0.04 rad. Mewis and Moldenaers have demonstrated the necessity of shearing PLC solutions through large strains to obtain reproducible results.[2] Thus, in recoil experiments, a constant stress was applied for sufficient time to allow 150 strain units of flow before removal of the stress and measurement of the strain recovery. The effects of instrument inertia in constant-stress rheometers have been analyzed recently.[28,37] Larson and Mead describe conditions under which inertial effects may be ignored;[28] due to the large diameter and small cone angle of the fixture used here, the effects of instrument inertia should be negligible for the recovery data presented in this work. A small number of steady viscosity and flow reversal experiments were carried out on a Rheometrics mechanical spectrometer (RMS). The test fixture for these experiments was a 50-mm-diameter cone and plate with a cone angle of 0.097 rad.

3. Results

3.1. Demonstration of Director Tumbling. The flow experiment to determine tumbling is motivated by considering the hydrodynamic torque exerted by a shear flow on the director of a nematic oriented in the flow direction. As discussed by Skarp and co-workers,[38,39] this torque is proportional to the Leslie coefficient α_3. Tumbling occurs when $\alpha_3 > 0$, and the hydrodynamic torque acts to rotate the director through the flow-vorticity plane, while for $\alpha_3 < 0$, the torque acts in the opposite sense, rotating the director toward the flow alignment angle. If a small shear displacement is applied to a nematic initially oriented in the flow direction, the optical axis of a tumbling nematic will rotate in the same sense as the shear flow vorticity, while a flow-aligning nematic will rotate in the opposite direction.

The sense of the rotation of the director field may be determined by observing the displacement of the hyperbolic interference fringe pattern produced by passing convergent polarized light through the sample and then through an analyzer (a conoscopic optical arrangement). This approach was used by Skarp and co-workers to see the transition between tumbling and flow alignment as a function of temperature in the low molecular weight liquid crystal 8CB[38] and by Berry and Srinivasarao in flow studies

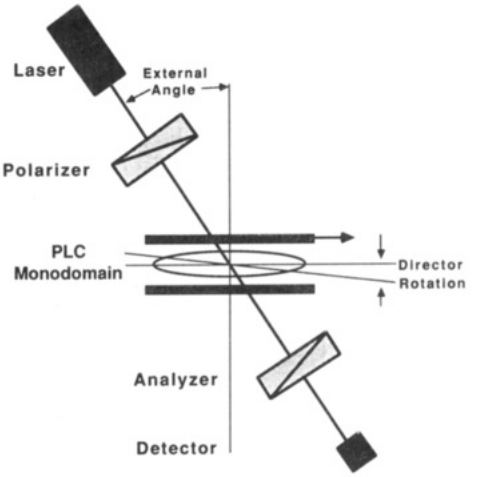

Figure 2. Optical arrangement used to detect direction of director rotation upon application of a small shear displacement.

on PBT monodomains.[22] For weakly birefringent materials, the conoscopic patterns may be visualized through interference colors under white light illumination.[40] For strongly birefringent materials these colors are washed out and monochromatic illumination such as an expanded laser beam is used to generate a series of fringes associated with the phase retardation passing through multiple orders of π as a function of the angle of incidence of the illumination. Our PBG solution is moderately birefringent. While we were unable to visualize the conoscopic patterns in a polarizing microscope under white illumination, there was insufficient optical anisotropy to generate multiple interference fringes in an expanded laser beam configuration similar to that used by Skarp and co-workers. For this reason, we have developed a simple modification of the conoscopic optics technique that does allow us to determine the sense of director rotation and that offers very high sensitivity to small director rotations.

Figure 2 schematically illustrates the principle of the technique. The oriented liquid crystal is represented by its uniaxial refractive index ellipsoid. When viewed from above, the sample exhibits an optical anisotropy given by the birefringence of the nematic. If the optical path is rotated in the shear plane away from normal incidence by some external angle as indicated in Figure 2, the apparent optical anisotropy will decrease. In this case, rotation of the director in a clockwise sense (tumbling) will *decrease* the optical anisotropy further, while rotation in a counterclockwise sense (flow alignment) will *increase* the optical anisotropy. Using this oblique light path, it is therefore possible to distinguish between tumbling and flow alignment. The optical anisotropy is monitored by using a simple crossed polarizer photometric arrangement, consisting of a laser, two crystal prism polarizers oriented at +45° and −45° with respect to the shear plane, and a photodiode detector. Calculations using the optical properties of our PBG monodomains (exhibiting a birefringence of approximately 0.01) indicate that significant changes in the light intensity are expected for director rotations as small as $^1/_2$°, so that this optical arrangement is particularly well-suited for detecting tumbling.[20]

This experiment has been performed on oriented monodomains of the 20 wt % PBG solution of thickness 250 μm. The monodomains were subjected to shear displacements in this optical apparatus by slowly driving the top plate by hand with a micrometer. Shear rates were kept low to avoid nonlinear effects, but even at these low deformation rates, the influence of the parallel boundary condition should be confined to small boundary layers near the slides, due to the extremely slow relaxation times

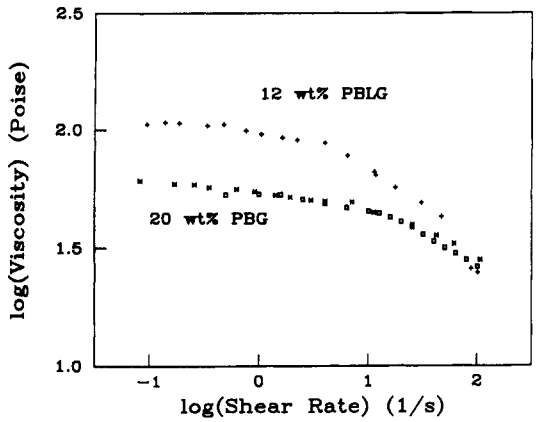

Figure 3. Steady-shear viscosity vs shear rate for poly(benzyl glutamate) solutions: (+) RSR, 12 wt %; (*) RSR, 20 wt %; (□) RMS, 20 wt %.

expected for the director profile under the influence of distortional elasticity. We observed that (i) intensity changes were easily detectable for small shear strains less than $^1/_2$ strain unit, (ii) the sense of the intensity changes was always consistent with tumbling, and (iii) intensity changes were approximately reversible with small reversed strain displacements. On this basis, we conclude that the 20 wt % PBG solution under consideration does exhibit director tumbling.

Similar experiments have been performed by Berry and Srinivasarao on a liquid crystalline PBT solution, using standard conoscopic observation.[22] Under some circumstances, they have observed that initially the director rotates in a sense consistent with flow alignment but that after a small amount of strain the director rotates in the opposite sense. More extensive experiments on this system under a wide range of conditions suggest that the PBT solution also shows director tumbling.[41] In our experiments, there was no indication of any strain-dependent changes in the response such as those reported by Berry and Srinivasarao.

Confirmation of director tumbling in PLC solutions is of both theoretical and practical importance. It provides a direct test of the abilityof molecular models to describe the dynamic behavior of these systems and, along with the analyses of Marrucci and Maffettone[8] and Larson,[9] illustrates the shortcomings of the decoupling approximation as applied to the Doi model. From a more practical standpoint, the tendency toward tumbling will have a profound impact on the rheological behavior of textured PLC solutions. Due to their structural complexity, detailed understanding of the dynamic response of textured PLC's remains far out of reach. However, knowledge that hydrodynamic torques always act to rotate the director can make an important contribution in interpreting experimental observations in textured systems; such interpretation is the subject of the remaining sections of this paper.

3.2. Steady-Flow Behavior. Figure 3 shows the steady-shear viscosity as a function of shear rate for the two PBG solutions, incorporating data from both the stress rheometer and mechanical spectrometer. Both solutions exhibit a Newtonian plateau at low shear rate, followed by a region of shear thinning at higher shear rate. The onset of shear thinning indicates the beginning of the nonlinear regime in which the finite molecular relaxation time plays a large role in determining the rheological behavior. As has also been observed by Moldenaers and Mewis,[42] there is no sign of so-called region I shear thinning at low shear rates. Finally, we see that the viscosity of the 12 wt % solution is *higher* than the 20 wt % solution, reflecting

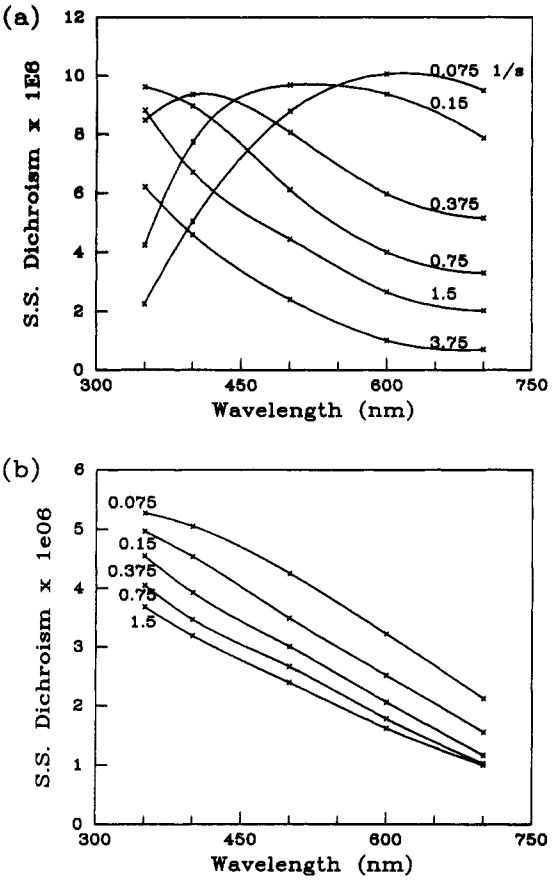

Figure 4. Steady-state dichroism vs wavelength at indicated shear rates: (a) 20 wt % PBG; (b) 12 wt % PBLG.

both its higher average molecular weight and the fact that the viscosity of PLC solutions decreases with increasing concentration above the isotropic to liquid crystal transition.

Figure 4 shows the steady-state dichroism as a function of wavelength for a variety of shear rates. The data of Figure 4a for the 20 wt % PBG solution clearly show a maximum in dichroism as a function of wavelength at low shear rates. As the shear rate is increased, the maximum is shifted to lower wavelengths, until it passes beyond the range accessible to the instrument. Such data strongly suggest that the length scale of the texture giving rise to the scattering is refined in response to increased shear rate. Data for the 12 wt % solution in Figure 4b show similar qualitative features, with curves shifted to shorter wavelengths with increased shear rate, although no maxima as a function of wavelength is observed with this solution. The refinement of texture length scale in response to increased shear rates has been well documented in thermotropic PLC's by Alderman and Mackley,[43] and similar observations have been reported by Larson and Mead from direct microscopic visualization of shear flow in textured PBG solutions.[28] This texture refinement figures significantly in the scaling arguments developed to interpret the transient data discussed in the remainder of this paper.

3.3. Transient Response; Flow Reversals. Transient flow experiments on textured polymer liquid crystals are difficult due to the lack of a well-defined initial condition in the liquid crystal structure. Moldenaers and co-workers have demonstrated the utility of sudden changes in shear rate to study the transient response in PBG solutions, since preshearing the sample results in an initial condition that is very reproducible.[1-4] In this work, we choose a flow reversal experiment as the basic tool to study the transient response of our PBG solutions. The shear stress observed upon reversal of shear flow of our 20 wt % ra-

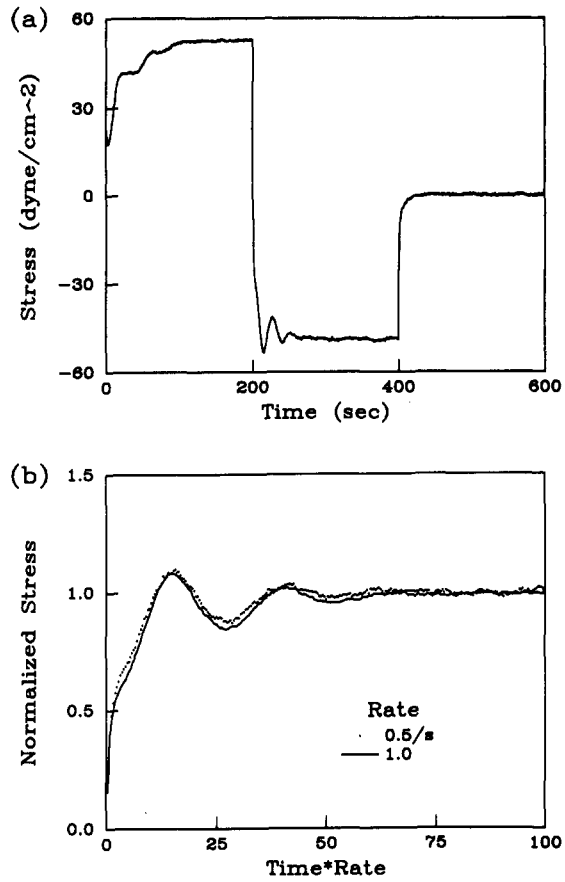

Figure 5. Shear stress response in a flow reversal experiment on 20 wt % PBG solution in the mechanical spectrometer: (a) full experiment showing flow inception, reversal and relaxation, shear rate = 1 s^{-1}; (b) normalized stress following reversal vs shear strain for two different shear rates. Note shear strain scaling of oscillations.

cemic solution is shown in Figure 5. In Figure 5a, the entire flow reversal experiment is given. Upon flow inception at time zero, an oscillatory response is observed; this initial transient is not reproducible due to its dependence on the structure of the PLC at rest. Upon flow reversal at a time of 200 s, a pronounced damped oscillatory response is observed during the approach to the corresponding steady-shear stress of opposite sign. Finally, at 400 s, flow is stopped, and a fairly nondescript stress relaxation phenomena is observed. Moldenaers and Mewis have recently examined stress relaxation in PBG solutions in more detail and find in general that it may be divided into fast and slow contributions;[44] we will discuss their findings in section 4, following the presentation of our relaxation studies in section 3.4.

The oscillatory response may be investigated in greater detail by plotting the normalized stress following the reversal for two separate shear rates as a function of the shear *strain* elapsed following the reversal, as shown in Figure 5b. As can be seen, the oscillatory response scales with the elapsed shear strain. This is in line with the many observations of Moldenaers and Mewis of oscillatory responses in transient flows that scale with strain.[1-4] We also note that the oscillatory response for the two shear rates is nearly identical, despite the two fold change in shear rate.

Flow reversal experiments have also been carried out in the optical apparatus. An example of a typical experiment is presented in Figure 6 for the 20 wt % solution, exhibiting several features that merit discussion. First we note that after the flow is turned on, up to dimensionless time of 400, R_2 is equal to zero, as expected due to the symmetry

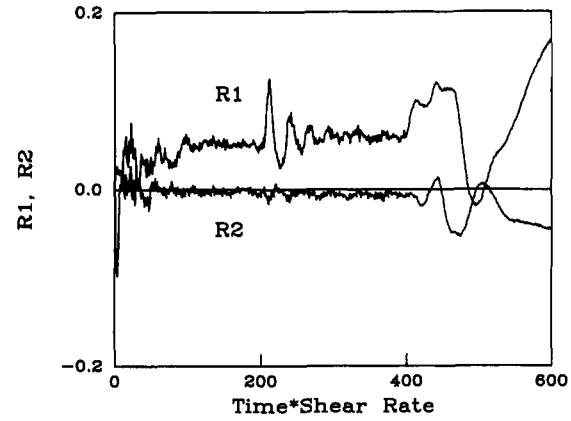

Figure 6. Experimental data in optical flow reversal experiment. R_1 and R_2 as defined in eqs 2 and 3. Flow is reversed at dimensionless time = 200 and stopped at time = 400. Shear rate = 1.5 s^{-1}, wavelength = 500 nm.

imposed by the flow. Thus, information about the optical anisotropy is carried in R_1. Next, we see that upon reversal of the flow direction at a dimensionless time of 200, a strong oscillatory response is observed, similar in nature to that observed in the mechanical experiments. A poorly defined set of oscillations is observed upon flow inception; as is the case mechanically, this transient is irreproducible, while the oscillatory response observed upon flow reversal after extensive shearing is very reproducible. Finally, we note the complicated behavior observed upon cessation of flow at dimensionless time 400. The most striking feature is that R_2 becomes substantially nonzero, indicating that the principal optical axis moves away from the flow direction. Once this occurs, the assumptions inherent in the optical analysis of the polarimetry experiment are violated, and the functions R_1 and R_2 may also be influenced by the large birefringence in the sample, making any further analysis of these data impossible. In any event, it is clear that the structural relaxation of the PLC is a good deal more complicated than suggested by the stress relaxation observed in Figure 5a.

The oscillatory responses following flow reversal may again be examined by plotting the response for various shear rates against the shear strain elapsed following the reversal. In Figure 7, we see that for both the 20 and 12 wt % solutions there is excellent scaling of the oscillations with strain over a very wide range of shear rates. We also note that the oscillatory response persists well into the linear region noted by the Newtonian plateau in steady-shear viscosity in Figure 3. Finally, we see that as was the case with the stress oscillations, the number of the oscillations is seen to be very nearly independent of the shear rate. On the basis of this similarity between the optical and mechanical response, it is clear that the oscillatory behavior in the shear stress reflects rather fundamental structural oscillations in the PLC.

We have seen in Figure 4 that varying the wavelength allows different length scales in the texture to be probed. In Figure 8, we present the oscillatory response observed at various wavelengths for both the 20 and 12 wt % solutions. It is seen that the oscillation frequency is independent of the wavelength of the observation; thus all length scales within the polydomain texture exhibit oscillations with the same period. From Figures 5 and 8a, the tumbling period for the 20 wt % PBG solution is approximately 27 strain units, while Figure 8b indicates a shorter period of 23 strain units for the 12 wt % PBLG solution.

3.4. Relaxation Phenomena and Scalings. In this section, we turn our attention to relaxation phenomena in

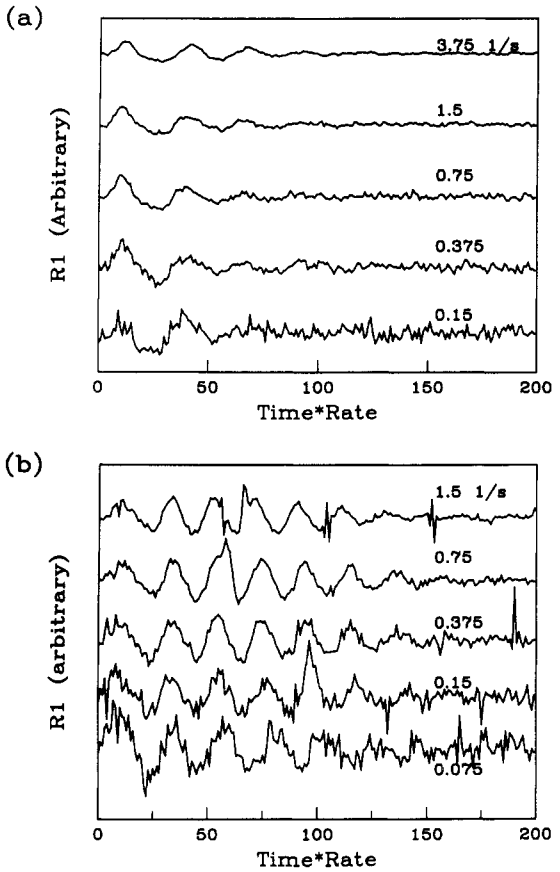

Figure 7. Oscillations in optical response vs shear strain following flow reversal at indicated shear rate: (a) 20 wt % PBG solution; (b) 12 wt % PBLG solution. Wavelength = 600 nm.

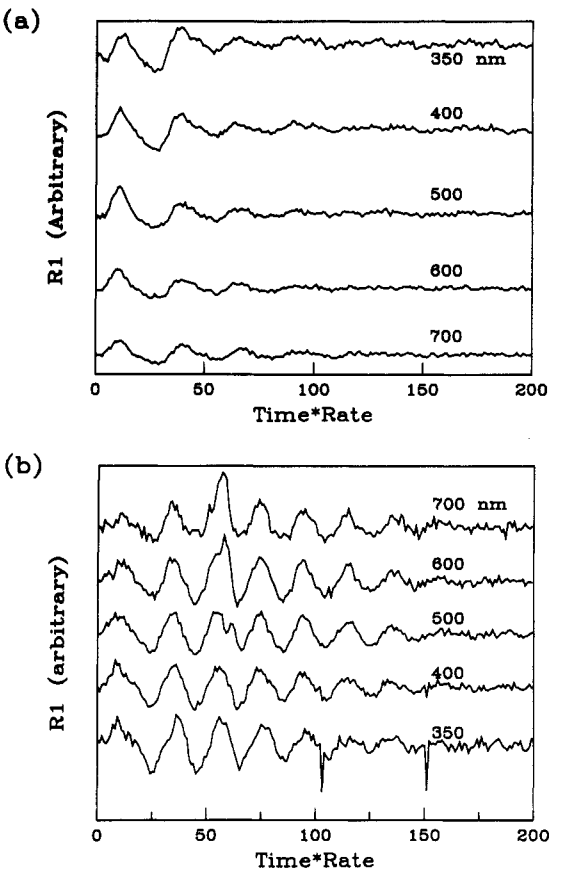

Figure 8. Oscillations in optical response vs shear strain following flow reversal at indicated wavelength: (a) 20 wt % PBG solution, shear rate = 1.5 s^{-1}; (b) 12 wt % PBLG solution, shear rate = 0.75 s^{-1}.

PBG solutions. Constrained recoil data for the 20 wt % PBG solution taken with the stress rheometer are shown in Figure 9. As the previously applied shear stress and hence shear rate decreases, any elastic recovery associated with molecular viscoelasticity should become negligible, so that the elastic recoil seen in Figure 9 predominantly reflects distortional elasticity. Similar to data published recently by Larson and Mead,[28] these data are unusual in three respects. First, the magnitude of the strain recovery is quite large, indicating a significant storage of elastic energy at these low shear rates. Second, the magnitude of the strain recovery is independent of shear rate. Finally, the data obey a relaxation scaling law, such that the various curves collapse when time is scaled by the previously applied shear rate, as shown in Figure 9b. The 12 wt % PBLG solution exhibits a similar behavior pattern, except that the magnitude of the strain recovery is somewhat lower.[20] All of these observations will be explained in a self-consistent picture in section 4.

The characteristics of the oscillatory response may be probed through interrupted shear flow experiments, carried out in the dichroism apparatus. A sample is sheared until steady state is reached, whereupon flow is interrupted for a predetermined amount of time. Upon flow resumption, an oscillatory response is observed, the strength of which depends on the delay time. Figure 10 shows the optical response observed upon flow resumption following a series of delays with the 12 wt % PBLG solution. For a very short interruption in flow, the system merely resumes the prior steady-state dichroism, with no sign of oscillations. As longer delays are allowed, oscillations appear upon flow resumption, increasing in strength as the delays are lengthened. These experiments thus probe the relaxation of the structural entity responsible for the oscillatory response.

Similar experiments conducted at different shear rates may be compared by quantifying the strength of the oscillatory response. The amplitude of the observed oscillations upon flow resumption is normalized by that seen for delays long enough that the amplitude does not grow significantly further. The fractional recovery of the oscillation amplitude may then be associated with the degree of relaxation of those structural features responsible for the oscillatory response. Such data are plotted in Figure 11 for both the 20 and 12 wt % solutions. As can be seen, the recovery of oscillations upon flow resumption follows a similar scaling law as the constrained recoil data, in that curves for various shear rates superimpose when time is scaled by the shear rate. Furthermore, when normalized strain recovery data for these two solutions are plotted on the same figures (the solid curves in Figure 11), we note that the time scales for strain recovery and the recovery of oscillations in the interrupted flow experiment are essentially identical, suggesting that these two very different phenomena have a common origin. We will return to this point in the following section.

4. Discussion

The experiment in section 3.1 conclusively shows that the director of our PBG nematic solution is subject to tumbling in a shear flow field. In this section, we develop qualitative arguments regarding how this tendency toward director tumbling may manifest itself in highly textured nematics. Despite the complicated nature of the director profile in a textured PLC, hydrodynamic torques will still promote rotation of the director in the shear flow field. The presence of defects and disclinations would, however, limit the degree to which the director field is able to respond to the hydrodynamic torques by rotating. For instance,

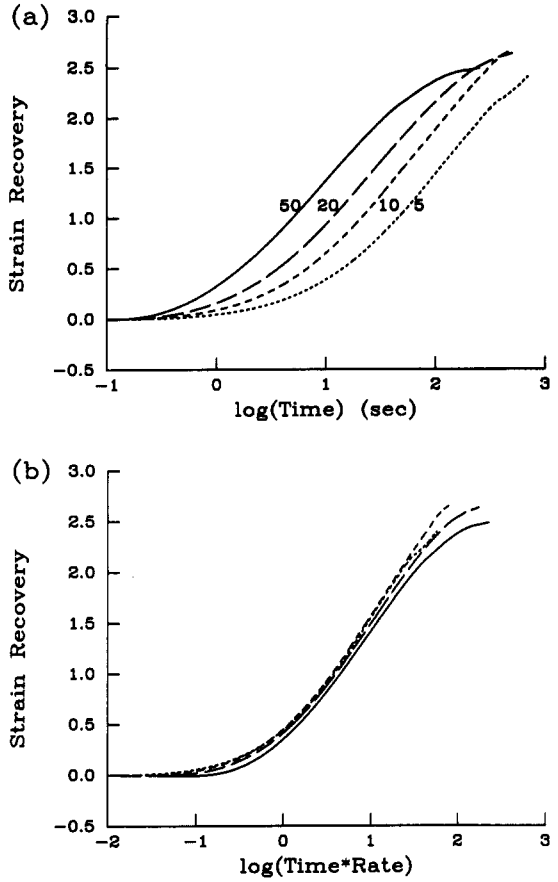

Figure 9. Strain recovery upon removal of indicated shear stress for 20 wt % PBG solution: (a) recovery vs time; (b) recovery vs time scaled by the previously applied shear rate.

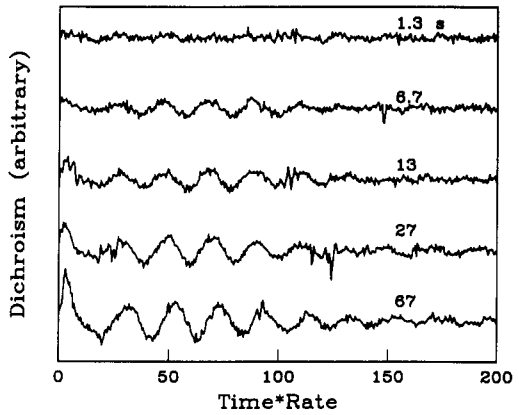

Figure 10. Optical response in interrupted shear flow experiments on 12 wt % PBLG solution. Dichroism vs shear strain following flow resumption after interruption of indicated delay time. Shear rate = 0.75 s^{-1}, wavelength = 500 nm.

in the immediate vicinity of a disclination line, the local topology imposed by the disclination would be incompatible with continuing rotation of the director. Farther away from defects, the director field is less constrained and may respond to the hydrodynamic torques to some degree by rotating in the shear flow. We have hypothesized that the constraining effects of defects on the director field would be similar to those imposed by boundary-induced orientations on the director field in monodomain flows of tumbling nematics.[27] Under this assumption, the balance between hydrodynamic torques that promote tumbling and distortional elastic torques arising due to the nonhomogeneous response of the director field is determined by a length scale associated with the texture rather than the macroscopic flow dimension. Our interpretation of experimental results on textured PLC's

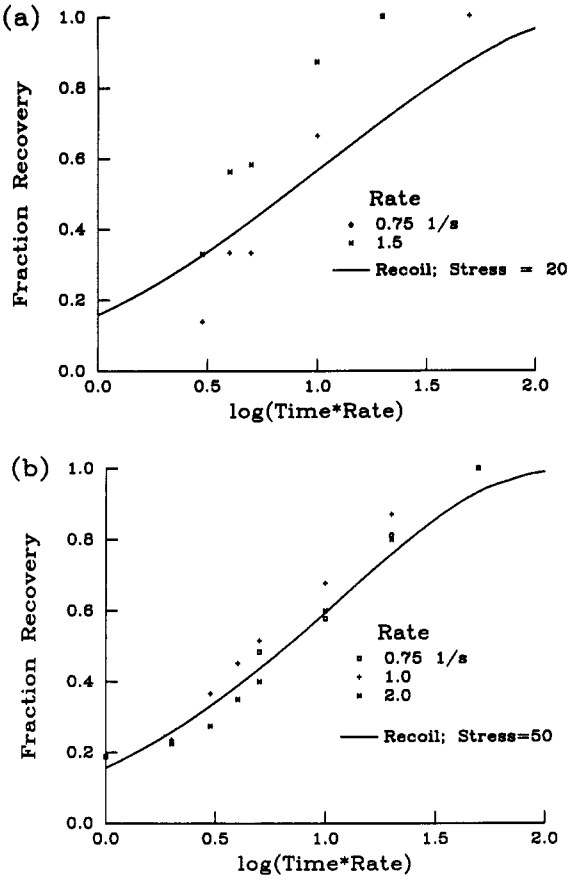

Figure 11. Fractional recovery of oscillatory response in interrupted flow experiments plotted against delay time scaled by shear rate: (a) 20 wt % PBG solution; (b) 12 wt % PBLG solution. Solid curves are normalized strain recovery data.

therefore rests on the assumption that the dynamic response of the director field is governed by a *local* Ericksen number, based on a length scale determined by the defect density. This assumption seems reasonable in that it merely reflects the absence of long-range correlations in orientation in a textured sample and hence the expectation that the response of the director field should be determined only by its local environment.

Director tumbling provides an immediate and straightforward explanation for the oscillatory responses seen in section 3.3 as well as in numerous previous studies of PBG solutions.[1-4] The oscillatory response associated with director tumbling at low shear rates is expected to scale with shear strain, as has been seen in experiments. The tumbling frequency at low shear rates should be a material parameter, determined by the linear Leslie coefficients.[9,15] Thus, the oscillation period should be independent of the length scale over which the observation is made. The independence of the oscillation period on wavelength in the dichroism data of Figure 8 suggests that, indeed, all length scales within the textured PLC are tumbling at the same frequency. Furthermore, the linearized Doi model predicts that the tumbling period should increase with increased concentration (and hence molecular alignment). The fact that our data do indicate an increase in oscillation period with concentration is consistent with the predictions of the Doi model as well as the hypothesis that these macroscopically observed oscillations in the transient response are manifestations of local tumbling in the director field. Of course, the microscopic details of how the director field and texture respond to the competing effects of hydrodynamic and distortional elastic torques would be extremely complicated. The cholesteric nature of the 12 wt % PBLG solution precludes a monodomain

flow experiment of the sort described in section 3.1; however, the strong oscillatory response that has been well documented in this type of solutions and observed here is compelling evidence that the tendency for tumbling in PBG solutions is not restricted to nematic solutions of racemic polymer samples but may be taken as a general phenomenon in this model system.

Our model calculations have indicated that the degree of director rotation and hence the number of oscillations should be proportional to the Ericksen number, reflecting the balance of hydrodynamic to elastic torques.[27] On the basis of the zero-shear viscosities seen in Figure 3, typical elastic constants on the order of 10^{-6} dyn, and a macroscopic flow dimension of 1 mm, an Ericksen number of around 10^5 is obtained for a shear rate of 0.1 s^{-1}. Thus, if the macroscopic length scale were relevant, the director would rotate to an extraordinary degree, and the oscillatory response would persist far longer than is observed. Instead, we advocate the use of a local Ericksen number based on the texture length scale and that would have a much more reasonable order of magnitude. The fact that the number of oscillations is seen to be independent of shear rate in Figures 5b and 7 suggests that the local Ericksen number governing the response is independent of shear rate. For this to be the case, the texture length scale d would have to decrease as $\dot{\gamma}^{-1/2}$. In Figure 4 we have presented evidence that the length scale of the texture does in fact decrease with increased shear rate, consistent with the hypothesis that Er based on the texture length scale is constant. The relaxation data provide additional evidence supporting the existence of a saturation Ericksen number. The data in Figures 7 and 8 show that the 12 wt % solution exhibits a larger number of oscillations than the 20 wt % PBG solution. This would imply that hydrodynamic torques are relatively stronger than elastic torques in this system. This is not unreasonable in light of the larger viscosity shown by the 12 wt % solution, as well the likelihood that this less concentrated solution may exhibit smaller elastic constants.[18]

We turn now to the discussion of the strain recovery data of Figure 9. We first note that the large magnitude of the constrained recoil may be attributed to director tumbling. Our model calculations for tumbling nematics show that large amounts of strain recovery are expected even at modest Ericksen number, since a significant amount of elastic distortional energy is introduced into the director field by the hydrodynamic torques that always act to rotate the director.[27] These calculations indicate that the amount of strain recovery for a tumbling nematic is roughly proportional to the Ericksen number. This is reasonable in that the recoil is driven by the elastic free energy stored in the shear flow at steady state, associated with distortions in the director profile that increase with Er. Adopting our model assumptions that (i) the director response is governed by an Ericksen number based on a local length scale associated with texture and (ii) this local Ericksen number saturates, we would expect that the amount of strain recovery would be independent of shear rate. As seen in Figure 9, this is precisely what is observed experimentally in PBG solutions, as was first noted by Larson and Mead.[28]

The origin of the constrained recoil suggested by comparison with our model calculations is that strain recovery is driven by a coupling of the viscous response of the liquid crystal with the relaxation of the distorted director profile under the influence of elastic torques upon removal of the applied hydrodynamic field.[27] In order to check this hypothesis, it would be useful to have an independent measure of the relaxation of the director profile. The interrupted shear flow experiments in section 3.4 serve such a purpose. The reappearance of oscillations reflects the partial relaxation of the director profile under the influence of distortional elasticity. The extent to which the oscillations appear upon flow resumption may be taken as a measure of the extent to which the director profile has relaxed. Model calculations of interrupted flow in fact show similar partial recovery of the oscillatory response, reflecting the partial relaxation of the director profile.[27] The fact that constrained recoil occurs on exactly the same time scale as the director field relaxation is compelling evidence that the relaxation of the director field in fact drives the strain recovery.

The most important consequence of the assumption of a saturated local Ericksen number relates to the time scale of relaxation processes associated with director field relaxation. Our model calculations indicate that the director field relaxes on a time scale on the order of $\alpha d^2/K$. We have proposed that the relevant length scale determining the transient response of the director field is that associated with the texture, while adopting a saturation Ericksen number implies that this texture length scale decreases with increasing shear rates. Combining these assumptions leads to the prediction that the characteristic time for director field relaxation should be inversely proportional to the previously applied shear rate, or equivalently, that relaxation phenomena observed at various shear rates should have a common time dependence when time is scaled by the previously applied shear rate. This is precisely what was observed in both types of relaxation experiments, as may be seen in Figures 9 and 11. Such relaxation scaling laws have been widely discussed,[28,42,44] but no explanation for their origin has been put forward. The fact that this prediction follows directly from our general scaling arguments about the local Ericksen number with no additional assumptions is strong evidence for the self-consistency of this approach toward interpreting data.

Moldenaers and Mewis have recently investigated stress relaxation phenomena in a PBLG solution.[44] They conclude that stress relaxation occurs with two distinct time scales, where the slower portion of the relaxation exhibits the sort of scaling with shear rate described above. This suggests that this slower relaxation component is associated with relaxation of the director profile. Our model calculations indicate that director relaxation induces a macroscopic stress relaxation upon flow cessation. In these calculations, the stress initially drops to approximately 20% of its steady value, followed by a smooth decrease.[27] This is in good agreement with the observation of Moldenaers and Mewis that the slowly relaxing component constitutes a relatively small fraction of the steady value of the stress (see also Figure 5a). While our calculations indicate a discontinuous initial drop of the stress, Moldenaers and Mewis see a rapid but finite initial relaxation. We suggest that this initial relaxation is associated with molecular viscoelasticity, whereas the slower component reflects the relaxation of the director profile. Finally, we note that PLC's generally show evidence of extremely long time relaxation processes, particularly in structural measurements.[3,42,45] An example is the optical data presented in Figure 6. While the director field relaxation in this system occurs relatively quickly, the structure is seen to evolve over much longer periods of time. We suggest that the initial stages of relaxation reflect first molecular and next director field relaxations, subject to the texture length scale determined by the previously applied flow. Once the flow-induced rotation of the director field has relaxed, one expects that the high flow-induced defect density will begin to anneal away under the influence of the elasticity associated with the quiescent

texture. This provides a possible explanation for why gradual structural changes reflected in the evolution of the dynamic moduli following shear flow occur on a much longer time scale than stress relaxation or strain recovery.[28,42]

We would finally like to propose a possible explanation for the existence of a saturation Ericksen number. The extent to which hydrodynamic torques rotate the director is proportional to the Ericksen number; thus, a saturation Ericksen number essentially means that there is a limit to the extent to which distortion may be introduced into the director profile. Our inference and evidence of texture refinement suggest that any attempt to increase the local Ericksen number further through increasing the shear rate is balanced by the sample adopting a higher defect density, thus reducing the length scale governing the response of the director profile. The introduction of a new defect in a quiescent textured polymer liquid crystal would increase the elastic energy of the system and hence require energy to be expected. We propose that, under flow, new defects are generated when the elastic energy generated by the flow-induced distortions in the director field exceeds that required to nucleate a new defect in the texture. Steady flow at the saturation Ericksen number thus occurs when the defect density is sufficiently high that hydrodynamic torques are unable to generate enough additional elastic energy by rotating the director to introduce new defects into the texture.

5. Conclusions

A simple flow experiment on a PBG liquid crystal solution monodomain confirms director tumbling in this system. Tumbling is shown to strongly influence the rheological response of textured PBG solutions at low shear rates. The pronounced oscillatory response observed in transient flows of these materials is a direct manifestation of tumbling of the liquid crystal director within the textured structure. Since large amounts of distortion of the director field are introduced by hydrodynamic torques that always promote director rotation, distortional elastic effects play a significant role in the rheological response of these materials, most notably in relaxation phenomena. Comparison of the time scales for director field relaxation as probed in interrupted flow experiments and constrained recoil indicates that strain recovery is driven by the relaxation of the distorted director field. Our results have been discussed in terms of a qualitative scaling model that assumes (i) the texture length scale controls the dynamic response of the director field and (ii) the texture length scale is refined with increasing shear rate as a result of an increased defect density nucleated by energy associated with flow-induced distortion in the director profile. Independent evidence of texture refinement is seen in the wavelength and shear rate dependence of the steady-state dichroism. These assumptions allow a self-consistent interpretation of the experimental observations discussed here, and, in particular, they yield a prediction of relaxation scaling laws that have been widely observed in PLC solutions.

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