Molecular Alignment of Polymer Liquid Crystals in Shear Flows. 2. Transient Flow Behavior in Poly(benzyl glutamate) Solutions

K. Hongladarom and W. R. Burghardt*

Department of Chemical Engineering, Northwestern University, Evanston, Illinois 60208

Received August 3, 1992; Revised Manuscript Received October 27, 1992

ABSTRACT: Flow birefringence is used to study the degree of molecular orientation in transient shear flows of liquid crystalline solutions of poly(benzyl glutamate) (PBG). Experiments are confined to the low shear rate regime in which it is known that such solutions exhibit director tumbling. Our optical results exhibit characteristics common to PBG solutions, including oscillatory responses that scale with shear strain and relaxation processes that scale inversely with the previously applied shear rate. The measured degree of orientation is compared with the transient predictions of the linear Larson and Doi tumbling polydomain model [Larson, R. G.; Doi, M. *J. Rheol.* 1991, *35*, 539], which is known to qualitatively reproduce transient stress behavior well. Our results reveal some shortcomings of the model regarding its predictions of molecular orientation. Our most startling observation is a significant *increase* in molecular orientation upon cessation of shear flow. This increase in orientation provides a straightforward explanation for the gradual decrease in dynamic moduli that is observed following cessation of shear flow. This result is in direct contradiction with conclusions drawn by Asada and co-workers on similar PBG solutions [Asada, T.; Onagi, S.; Yanase, H. *Polym. Eng. Sci.* 1984, *24*, 355]. We attribute this discrepancy to ambiguity in birefringence measurements resulting from multiple retardation orders; we have employed a spectrographic birefringence technique that eliminates this source of uncertainty. This work is an extension of an accompanying paper on steady-state flow behavior.

1. Introduction

Polymer liquid crystal (PLC) solutions of rodlike polymers exhibit a wide range of unusual rheological behavior. In steady shear flows at high deformation rates, nonlinear viscoelastic interactions between shear flow and the molecular orientation probability distribution function give rise to complex normal stress behavior, most notably regimes in which the first normal stress difference is negative[1–8] and the second normal stress difference is positive.[3,8] In addition to these remarkable nonlinear effects, PLC solutions also exhibit peculiar rheological behavior in the linear, low shear rate regime. Among the unusual observations are damped oscillatory responses in stress and structure that scale with shear strain in transient flows,[7,9–12] large shear strain recoveries with magnitudes that are independent of the previously applied shear rate,[12,13] stress relaxation that persists much longer than the molecular relaxation time,[14] and gradual evolution of dynamic moduli following cessation of shear flow.[5,7,11,13,14] The relaxation processes are noteworthy in that they can occur over time scales as long as hours and that these long time scale relaxation phenomena follow a scaling law in which the characteristic relaxation time is inversely proportional to the previously applied shear rate.[13]

Much of the unusual rheological behavior seen in PLC solutions at low shear rates has been attributed, at least to some extent, to the phenomenon of director tumbling. In tumbling nematics, there is no preferred molecular orientation induced by a shear flow field, but rather hydrodynamic torques act to rotate the director (a unit vector, $\mathbf{n}$, denoting the average molecular orientation direction). In the absence of other torques, such as those associated with applied fields or spatial variations in the director field $\mathbf{n}(\mathbf{r})$, the tumbling motion of the director is equivalent to the well-known Jeffery orbits of suspension mechanics that describe the rotation of ellipsoidal particles in shear flow. Under these conditions, the director would rotate indefinitely, accompanied by oscillations in the mechanical stresses. To date, director tumbling has been confirmed experimentally in two systems, by following the initial rotation of the director upon application of slow shear flow to initially homogeneous monodomains (defect-free samples).[12,15] Tumbling provides an immediate explanation for the observed stress oscillations in transient flows. Moreover, the scaling of these oscillations with shear strain is a direct consequence of the linearity of the viscous response of nematics at low shear rates.

Unlike flow experiments on monodomains that have been used to confirm director tumbling, rheological studies invariably employ samples that are initially *textured*, with a high defect density that disrupts the orientation of the polymer liquid crystal over length scales on the order of 1–10 μm (such a structure is often referred to as a *polydomain*). The presence of texture introduces two significant complications in the low shear rate behavior of PLC's. First, the director field suffers considerable spatial distortions simply owing to the presence of the defects, even in the absence of flow. Elastic effects associated with director field distortion (Frank elasticity[16]) will therefore necessarily play a role in the dynamic behavior of textured PLC's. In shear flow of textured nematics, the director field is unable to respond to hydrodynamic torques by indefinite rotation in a tumbling orbit due to the additional constraints placed on the director field by the presence of defects and/or boundary-imposed orientations. In such a situation, as the director locally rotates in response to hydrodynamic torques, distortions in the director field would be introduced, generating elastic torques that eventually balance hydrodynamic torques and lead to a steady state.[17] Burghardt and Fuller have performed calculations using the linear Leslie–Ericksen model in a highly idealized geometry to study the characteristic features of this torque balance and the associated transient rheological behavior.[18] These calculations show qualitative agreement with many of the experimental observations discussed above. In particular, the mechanisms of dissipating stored distortional elasticity through relaxation phenomena are revealed through these model calculations.

---

* Author to whom correspondence should be addressed.

0024-9297/93/2226-0785$04.00/0

The second complication associated with the presence of texture in PLC solutions used for rheological studies is that the measured mechanical response includes contributions from a distribution of domain orientations. Since the Leslie–Ericksen calculations of Burghardt and Fuller were based on an idealized monodomain geometry, the detailed results of their calculations bear little resemblance to typical experimental observations on textured PLC solutions.[18] Larson and Doi recently developed a model that addresses this issue by formally averaging the linear Leslie–Ericksen continuum theory over a domain orientational probability distribution function.[19] This approach rests on a hypothesis that the characteristic length scales associated with the macroscopic flow fields and the texture are sufficiently separated that this averaging process may be carried out at a "mesoscopic" length scale: large enough to include a large number of "domains", yet small compared to the macroscopic flow dimensions. While this model incorporates the essential physics of PLC rheology at low shear rates (director tumbling and distortional elasticity), the averaging process necessitates the introduction of phenomenological forms for terms involving distortional elasticity. Even using the simplest possible choices for these terms, however, the model makes predictions of damped stress oscillations in transient flows and constrained recoil that are in excellent agreement with experiment.[19] The Larson and Doi model also explicitly incorporates *texture refinement*, the hypothesis that the length scale associated with the texture decreases (or equivalently, the defect density increases) as the shear rate increases within the linear regime.

It should be noted that some of the characteristic features of PLC rheology that have been described thus far are not always observed. While solutions of poly(benzyl glutamate) (PBG) and (hydroxypropyl)cellulose (HPC) have been shown to be quite similar to one another in their rheological behavior (see references cited above), much of this behavior is not observed in solutions of poly(phenylenebenzobisthiazole)(PBT) that have been extensively studied by Berry and co-workers.[20] This is of particular interest in that tumbling at low shear rates has been confirmed in PBG and PBT solutions,[12,15] and one would expect therefore that they would exhibit greater similarities in bulk rheological behavior. Oscillatory transients and large strain recovery have been observed in polyaramid solutions by Picken; however, the detailed behavior is quite different from PBG solutions.[29] Here we focus on PBG solutions, where the rheological behavior appears to be well described by available models.

In this paper we describe measurements of molecular orientation in transient flows of liquid crystalline poly(benzyl glutamate) solutions, using the technique of flow birefringence. The preceding paper introduced a spectrographic birefringence technique particularly well suited for studying materials with high optical anisotropy and described measurements of molecular alignment in steady shear flow.[21] The nonlinear regime was extensively studied to elucidate the connections between molecular orientation and unusual normal stress phenomena at high shear rates. Here we focus on transient flow phenomena in the linear regime. The Larson and Doi tumbling polydomain model has proven to be effective at describing bulk rheology at low shear rates. At the same time, it makes specific *predictions* about the transient changes in molecular alignment that accompany the mechanical response. Our birefringence measurements provide a direct test of these predictions. We are also interested in relating mechanical rheological observations to changes in the microscopic structure in a more general sense. For instance, measurements of changes in molecular orientation following shear flow cessation provide insights into the origin of the observed evolution of dynamic moduli following shear flow.

2. Transient Predictions of Orientation

In this section we provide examples of calculations of stress and molecular orientation using the Larson and Doi polydomain model.[19] The primary structural variable in this model is the mesoscopic order parameter tensor, $\bar{\mathbf{S}}$, defined as

$$\bar{\mathbf{S}} \equiv \langle \mathbf{nn} \rangle - {}^{1}/_{3}\boldsymbol{\delta} \tag{1}$$

where $\langle ... \rangle$ represents an average over a domain orientation probability function $\bar{\psi}(\mathbf{n})$, and $\boldsymbol{\delta}$ is the unit tensor. $\bar{\mathbf{S}}$ thus provides a measure of anisotropy in the domain orientation distribution function. In our experiments, we interrogate shear flow with a polarized light beam that propagates along the shear gradient direction. Assigning coordinates as flow direction (1), gradient direction (2), and vorticity direction (3), our measured birefringence then reflects structural anisotropy in the 1–3 plane. If all domains were oriented along the flow direction, eq 1 would predict anisotropy in the mesoscopic order parameter tensor $\bar{S}_{11} - \bar{S}_{33} = 1$, corresponding to perfect alignment. Experimentally, this situation would correspond to a uniformly oriented monodomain, with the maximum possible birefringence obtainable in an unperturbed quiescent sample. In a textured sample under flow, $\bar{S}_{11} - \bar{S}_{33}$ will be less than 1, reflecting the disruption in orientation associated with a distribution of domain orientations. Assuming that the *microscopic* degree of orientation, characterized by a molecular order parameter, S, is unperturbed by the flow (that is, that the Weissenberg number is small), the birefringence measured in textured PLC solutions under flow should be directly proportional to $\bar{S}_{11} - \bar{S}_{33}$. See the preceding paper for a more extensive discussion of the relationship between birefringence and the molecular orientation state in textured PLC's.[21]

The principal components of the Leslie–Ericksen model are a torque balance that determines the director field and a constitutive relationship between the applied deformation, the director field, and the resulting mechanical stresses (this relationship is linear in velocity gradient).[16] Larson and Doi derived an evolution equation for the mesoscopic order parameter by multiplying the torque balance by $\mathbf{n}$ and averaging over $\bar{\psi}(\mathbf{n})$. The resulting equation involves the mesoscopic averages $\langle \mathbf{nh} \rangle$ and $\langle \mathbf{hn} \rangle$, where $\mathbf{h}$ is the "molecular field" that arises due to inhomogeneity in $\mathbf{n}(\mathbf{r})$.[16] These terms consequently represent, in an average sense, the effects of distortional elasticity. Larson and Doi introduced phenomenological forms for these terms, leading to the result

$$\frac{\mathrm{d}}{\mathrm{d}t}\bar{\mathbf{S}} = \boldsymbol{\omega}^{\mathrm{T}}\cdot\bar{\mathbf{S}} + \bar{\mathbf{S}}\cdot\boldsymbol{\omega} + \lambda[{}^{2}/_{3}\mathbf{D} + \mathbf{D}\cdot\bar{\mathbf{S}} + \bar{\mathbf{S}}\cdot\mathbf{D} - 2\bar{\mathbf{S}}:\mathbf{D}(\bar{\mathbf{S}} + {}^{1}/_{3}\boldsymbol{\delta})] - \epsilon l\bar{\mathbf{S}} \tag{2}$$

All but the last term on the right-hand side of eq 2 represent the hydrodynamic torques, averaged over the domain distribution function. The *tumbling parameter*, $\lambda \equiv (\alpha_5 - \alpha_6)/(\alpha_3 - \alpha_2)$ distinguishes tumbling ($\lambda > 1$) from flow aligning ($\lambda < 1$) behavior and is expressed in terms of the linear Leslie coefficients, α_i. $\mathbf{D}$ is the rate of deformation tensor, while $\boldsymbol{\omega}$ is the vorticity tensor. The final term in eq 2 represents the averaged effects of distortional elasticity and is taken to be proportional to the defect density $l \sim 1/a^2$, where a is the characteristic texture length scale. The defect density is hypothesized to follow its own evolution equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}l = II_{\mathrm{D}}l - l^2 \qquad (3)$$

where II_{D} is the second invariant of the rate of deformation tensor. This equation has the properties that (i) it predicts texture refinement at steady state, such that a varies as $\dot{\gamma}^{-1/2}$, where $\dot{\gamma}$ is the shear rate, and (ii) it predicts that defects anneal away in the absence of flow (l decreases monotonically when $II_{\mathrm{D}} = 0$).

Dimensional analysis of the Leslie–Ericksen model reveals that the relevant dimensionless group governing the response of the director is the Ericksen number, $Er = \alpha\dot{\gamma}a^2/K$, representing the ratio of hydrodynamic to elastic torques (K is a characteristic elastic constant). This Ericksen number is written using the texture size as the length scale appropriate to a discussion of textured PLC's in relatively large gaps. Dimensional considerations also reveal that the only characteristic time that can be formed from the material properties in the linear limit (where molecular relaxation times are no longer relevant) is $t_c = \alpha a^2/K$. The texture refinement scaling $a \sim \dot{\gamma}^{-1/2}$ consequently ensures that the widely observed relaxation scaling law $t_c \sim \dot{\gamma}^{-1}$ is obeyed.[13] Texture refinement furthermore suggests that the local Ericksen number is independent of shear rate. Comparisons of experimental data with model calculations support this outlook, in that it correctly suggests that the magnitude of strain recovery and the number of oscillations in transient flows should be independent of shear rate.[12] In the context of eq 2, the parameter ϵ determines the balance between elastic and hydrodynamic effects and is consequently analogous to the inverse of this hypothesized saturation Ericksen number.[18]

The final equation of the Larson and Doi model is a constitutive equation for the domain-averaged stress tensor:[19]

$$\bar{\tau} = 2\mu\mathbf{D} + 2\mu_1\mathbf{D}:\bar{\mathbf{S}}(\bar{\mathbf{S}} + {}^1/_3\delta) + {}^2/_3\mu_2\mathbf{D} + \mu_2(\bar{\mathbf{S}}\cdot\mathbf{D} + \mathbf{D}\cdot\bar{\mathbf{S}}) - {}^1/_2(\alpha_2 + \alpha_3)\epsilon l\bar{\mathbf{S}} \qquad (4)$$

In this expression, μ_i are combinations of the Leslie viscosities α_i with dimensions of viscosity. We have eliminated a term that represents a direct contribution from distortional elastic stresses, $\bar{\tau}^d$, from the expression given by Larson and Doi.[19] This term has no major influence on the shear stress behavior of the model; in fact, in the idealized shear flow geometry used by Burghardt and Fuller, the shear component of the distortional stresses was identically zero.[18] However, elastic-driven relaxation of the director profile is coupled with the viscous response of the nematic. Mechanical manifestations of distortional elasticity such as recoil and stress relaxation are thus predicted even in the absence of a direct contribution of Frank stresses.[18] The final term of eq 4 incorporates these effects phenomenologically.

In the preceding paper, we have evaluated the steady-state predictions of the Larson and Doi model for molecular orientation in shear flow.[21] At steady state, the scaling properties of eqs 2 and 3 dictate that the mesoscopic order parameter tensor is constant and that only the texture length scale depends on shear rate. These predictions appear to be in excellent agreement with experimental results, although the degree of molecular alignment predicted by the model is somewhat larger than that observed experimentally.[21] In transient flows in which the shear rate is changed, the predicted transient response involves a redistribution of domains, in conjunction with possible changes in texture length scale. However, the components of the order parameter always return to the same steady-state value, unless shear flow is ceased. We illustrate several features of the model's behavior through a series of calculations of a variety of transient flows. For the sake of completeness, we include stress calculations using eq 4; however, it is not necessary to calculate stresses to solve for the orientation state, and we will be primarily interested in predictions of the quantity $\bar{S}_{11} - \bar{S}_{33}$, which may be compared directly with our experimental results. Equations 2 and 3 are solved by Runge–Kutta integration; at each time step, the stress tensor may be calculated from eq 4. The Leslie coefficients, α_i, are evaluated by the linearized Doi model analysis of Kuzuu and Doi as a function of dimensionless concentration, c/c^*.[22] For these calculations we use parameters $\epsilon = 0.03$ and $c/c^* = 1.122$, which have been shown to provide reasonable predictions of oscillatory stresses and strain recovery.[19]

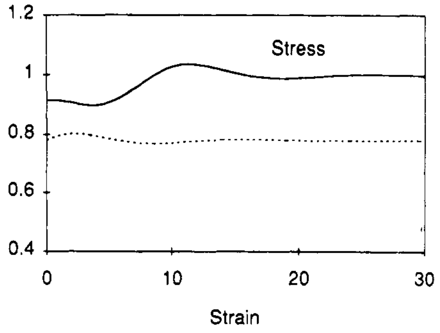

Figure 1. Larson and Doi model predictions of normalized shear stress and $\bar{S}_{11} - \bar{S}_{33}$ plotted vs shear strain following a 5-fold step increase in shear rate.

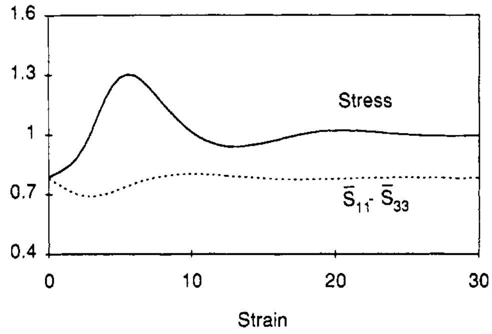

Figure 2. Larson and Doi model predictions of normalized shear stress and $\bar{S}_{11} - \bar{S}_{33}$ plotted vs shear strain following reversal in shear flow direction.

Figure 1 shows the calculated response that accompanies a 5-fold step increase in shear rate. Normalized shear stress and anisotropy in the mesoscopic order parameter tensor are both seen to exhibit damped oscillations as they approach their steady-state values. This type of behavior has been extensively studied by Moldenaers and Mewis in transient flows.[9] The agreement between the Larson and Doi model and experiment is excellent, except for the strain period of the oscillations.[19]

Figure 2 shows the calculated response upon reversal of the direction of shear flow. The predicted stress behavior is again in excellent qualitative agreement with experimental observations.[10,11] Accompanying the damped oscillations in stress are similar oscillations in the quantity $\bar{S}_{11} - \bar{S}_{33}$, reflecting the transient redistribution of domains toward a new steady state. Upon application of the reversal, the average molecular orientation in the flow direction is predicted to initially decrease. This may be easily interpreted in terms of the steady-state predictions of the model. As shown in the preceding paper, at steady

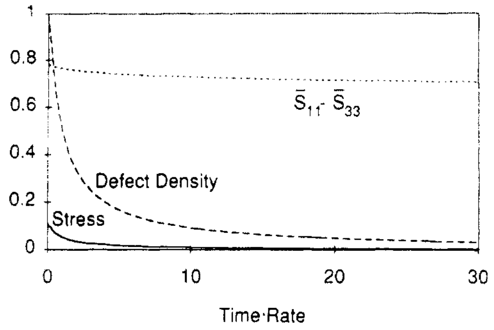

Figure 3. Larson and Doi model predictions of normalized shear stress, $\bar{S}_{11} - \bar{S}_{33}$, and defect density plotted vs scaled time following cessation of shear flow.

state the domains are predominantly oriented close to flow direction (see Figure 2 of ref 21). Upon reversal of the shear flow direction, the domains will rotate in concert under the influence of tumbling toward their new steady-state orientation. When viewed from "above" (i.e., along the gradient direction), this will result in a temporary decrease in orientation projected onto the 1–3 plane.

Comparing Figures 1 and 2, the damped oscillations in $\bar{S}_{11} - \bar{S}_{33}$ are much stronger for the flow reversal than for the step change in shear rate. This is reasonable, since a reversal involves a more severe perturbation to the orientation state; the domains must flip from one orientation to another. For the step change, the mesoscopic order parameter tensor upon resumption of steady state is exactly the same as that before the step change. Moldenaers and co-workers in fact have observed that structural oscillations are much more pronounced for reversals than for step changes.[10]

Figure 3 shows the calculated response following cessation of shear flow. While Larson and Doi calculated recoil phenomena following removal of an applied shear stress,[19] they did not perform relaxation calculations of the type shown here. These calculations reveal a finite stress relaxation phenomenon driven by distortional elasticity. This prediction is in qualitative agreement with the detailed Leslie–Ericksen model calculations by Burghardt and Fuller[18] and with the observation of a slowly relaxing component of shear stress in PBG solutions by Moldenaers and Mewis.[14] In polymeric systems, it is expected that the predicted instantaneous drop from the steady-state shear stress to roughly 10% of this value would be modulated to some extent by molecular viscoelasticity; the observations of Moldenaers and Mewis bear this out.[14] In addition, due to the relaxation scaling implicit in the Larson and Doi model, this slowly relaxing component of the shear stress should follow the inverse shear rate scaling law; again, this expectation is borne out by experiment.[14] Figure 3 also shows the relaxation of the defect density, l. In the absence of flow, eq 3 provides that l will monotonically decrease. According to eq 4, the relaxation of shear stress observed in Figure 3 is predominantly driven by the decreasing defect density. This is somewhat different from the interpretation of stress relaxation suggested by the Leslie–Ericksen calculations of Burghardt and Fuller, where relaxation of director profile distortions at a constant texture length scale is responsible for stress relaxation.[18]

The structure of eq 2, and in particular the final term reflecting distortional elastic effects, is such that the mesoscopic order parameter tensor tends to become isotropic in the absence of flow. This prediction reflects a widely held expectation that any flow-induced bias in domain orientation would tend to decay once the flow is removed, under the influence of the high innate defect density. There have been numerous experimental reports that flow-induced orientation is ultimately lost upon cessation of shear flow,[23-26] but to the best of our knowledge only three cases where this process has been quantified in PLC solutions. Flow birefringence measurements of decaying orientation are reported for solutions of poly(benzyl glutamate)[27] and (hydroxypropyl)cellulose,[28] while, more recently, X-ray scattering has been used to study decaying orientation following shear flow of polyaramid solutions.[29] In addition, Viola and Baird used X-ray scattering in thermotropic PLC's to demonstrate a rapid decay of molecular orientation following cessation of extensional flow.[30] In the Larson and Doi model, the randomizing process is driven by distortional elasticity and consequently proportional to the defect density, which is seen to decrease rapidly in Figure 3. As a result, $\bar{S}_{11} - \bar{S}_{33}$ is calculated to decay at increasingly slow rates, until it becomes essentially constant. The Larson and Doi model has no structure capable of describing the widely studied phenomena of band formation following shear flow.[6,31-33]

3. Experimental Section

3.1. Materials. We have studied transient behavior in four solutions of poly(benzyl glutamate). Two solutions use a racemic mixture of PBDG and PBLG, with viscosity-average molecular weight 301 000 (denoted PBG(301k)), while two solutions use a sample of the single optical isomer PBLG, with viscosity-average molecular weight 236 000 (denoted PBLG(236k)). Solution concentrations of 13.5 and 20% by weight were used. These solutions are the same for which steady-state birefringence and mechanical rheological properties were measured in the preceding paper.[21] To summarize briefly, the birefringence in all solutions was roughly constant in the low shear rate, tumbling regime and showed a transition to a higher average orientation state as the shear rate increased. This transition was closely correlated with transitions in the normal stress behavior and was thus identified as a manifestation of the transition from tumbling behavior at low shear rates to flow alignment at high shear rates.[21] In the present work, measurements are confined to the low shear rate plateau region for all solutions, where it is expected that the dynamic behavior is dominated by director tumbling.

3.2. Optical Experiments. We have devised a modification of the crossed and parallel polarizer optical arrangement used by Asada and co-workers[27,34] to measure flow birefringence in sheared PLC solutions; the reader is referred to the previous paper for a full discussion of the technique.[21] To summarize briefly, the light intensity transmitted between either crossed (⊥) or parallel (‖) polarizers (oriented with optic axes at 45° with respect to the flow direction) is measured as a function of wavelength using a diode array spectrograph. Collection of both crossed and parallel spectra allows normalization of the data to remove any dependence on the intensity spectrum of the incident light, the transmission spectra of the optical elements, the attenuation of light by the sample, and the spectral response of the diode array detector. For a sample with birefringence Δn and thickness d oriented along the flow direction, the normalized spectra take the following form:

$$N^{\perp} = \frac{I^{\perp}}{I^{\perp} + I^{\parallel}} = \sin^2(\pi \Delta n d/\lambda) \tag{5}$$

$$N^{\parallel} = \frac{I^{\parallel}}{I^{\perp} + I^{\parallel}} = \cos^2(\pi \Delta n d/\lambda) \tag{6}$$

where $I^{\perp}$ and $I^{\parallel}$ are the raw measured transmitted intensity spectra. For an ideal birefringent sample, the normalized spectra oscillate out of phase between extremes of 0 and 1 as a function of wavelength. By fitting the wavelength dependence of these oscillations, the birefringence may be extracted. To obtain acceptable fits of data using these equations, the additional wavelength dependence associated with the dispersion in birefringence $\Delta n(\lambda)$ must be included; in this work we use the dispersion relationship determined in the preceding paper for

PBG solutions.[21] This allows for an excellent fit of the wavelength dependence of the normalized spectra for all solutions studied. Reported values of birefringence are for a wavelength of 633 nm.

In textured PLC solutions under shear, variability in optical properties from one light path to another within the beam causes polarization mixing that reduces the amplitude of the oscillations in normalized spectra.[21] We quantify these effects using a peak-to-peak amplitude A that ranges from 0 for the case where no distinction is observed between the spectra $I^{\perp}$ and $I^{\parallel}$ to 1 for the case where the sample behaves according to eqs 5 and 6 as an ideal birefringent element. In reality, a small amount of baseline offset in the diode array signal prevents the condition $A = 1$ from occurring, even when an ideal retarder is used (see Figure 4 of ref 21).

The sample is sheared in a rotating parallel-plate flow cell consisting of two optical windows separated by a gap of approximately 1 mm. The light beam is displaced away from the axis of rotation and consequently interrogates a shear flow that is locally homogeneous, while the polarization vector is sensitive to optical anisotropy in the flow–vorticity plane. The lower plate is rotated by a computerized microstepping motor of high precision and reproducibility. Transient experiments are conducted twice in order to obtain spectra for both parallel and crossed polarizers. The experimental protocols are such that the flow cell always completes an integral number of revolutions in any given flow period; thus, corresponding crossed and parallel spectra are collected at exactly the same flow cell position. This is necessary due to a slight (≈5%) variation in sample thickness as a function of flow cell rotation due to imperfect cementing of the windows (see Figure 4). In a typical experiment, the sample is presheared for over 200 strain units and then subjected to some transient change (step up in shear rate, flow reversal, or flow cessation). This change is coordinated with the initiation of computerized data acquisition to collect spectra during the transient response. The entire experiment is then repeated to obtain the complementary spectra. For long time scale relaxation measurements, it becomes possible to manually collect both crossed and parallel spectra fast enough to resolve gradual changes in birefringence without repeating the whole experiment. For shorter time scale relaxation experiments, the automated data acquisition procedure described above is employed. All spectra are stored into computer memory in real time and subsequently written to disk files. These files may be accessed later for analysis to determine how the birefringence changes with time during the transient experiments. Recording a single spectrum by the diode array requires around 20 ms; this provides more than adequate temporal resolution for the work presented here. We note in addition that this approach allows measurements of transient orientation changes much more quickly than the manual compensation technique used by Onogi and co-workers[28] and the X-ray scattering measurements of Picken and co-workers.[29]

3.3. Mechanical Experiments. Extensive steady-state rheological measurements on these solutions are presented in a preceding paper.[21] In this work, we have carried out a limited number of shear stress and dynamic modulus measurements in transient shear flows in order to make comparisons between the transient structural and mechanical responses of the PLC solutions. We have followed well-established protocols introduced by Moldenaers and Mewis,[5,9] and our results are entirely consistent with previous mechanical observations on liquid crystalline poly(benzyl glutamate) solutions. These experiments were performed using a Bohlin VOR rheometer using a torsion bar transducer designed for low-torque, fluids applications. The experiments were carried out using a cone and plate fixture with 30-mm diameter and 2.5° cone angle.

4. Results and Discussion

4.1. Flow Reversals. Figure 4a shows the birefringence as a function of shear strain following a reversal in flow direction for the 20% PBG(301k) solution at a shear rate of 1 s^{-1}. Strong damped oscillations are observed initially with a period of roughly 26 strain units, which is in the range that has been associated with director tumbling.[12] These give way to a periodically oscillating birefringence with a period of around 75 strain units. This latter period corresponds exactly to one rotation of the flow cell; these persistent oscillations are thus identified with a slight variation in sample thickness as a function of the rotation of the flow cell. The amplitude of the oscillations would correspond to a 5% variation in sample thickness. Naturally, this also corresponds to a periodic variation in shear rate of 5% as well; however, these data are taken in a regime in which the steady-state birefringence is essentially independent of shear rate,[21] so that this should not affect our results. To make sure the initial transient damped oscillations are not unduly influenced by this superimposed

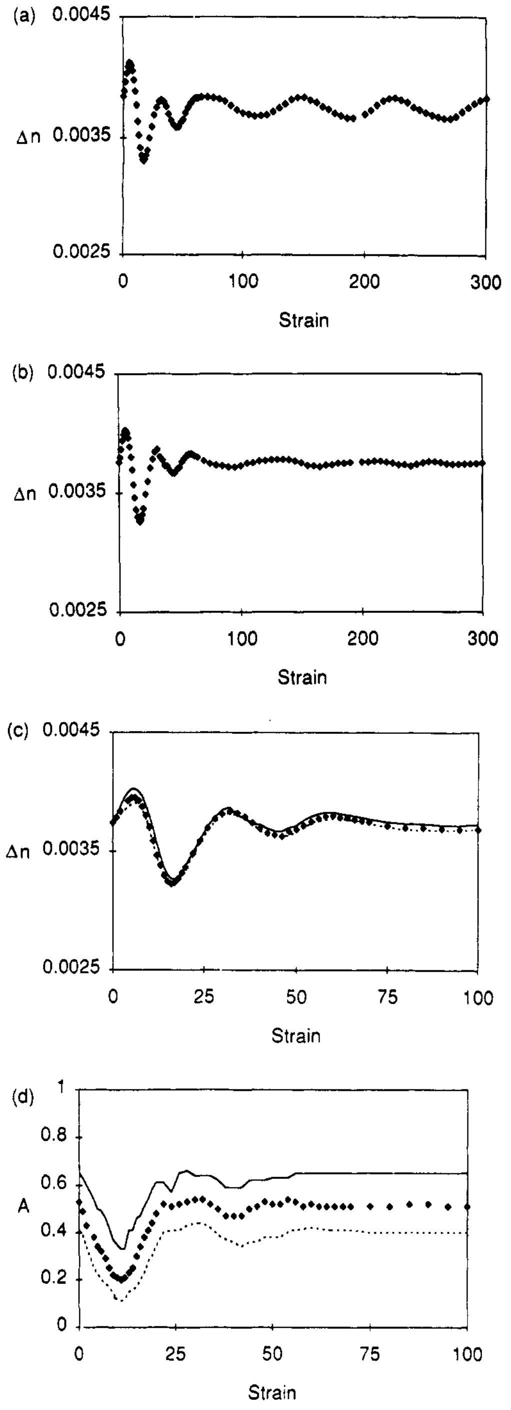

Figure 4. Response of 20% PBG(301k) solution to flow reversal. (a) Birefringence vs shear strain following reversal at a shear rate of 1 s^{-1}. (b) Same data corrected for variation in sample thickness. (c) Corrected birefringence vs shear strain following reversals at 0.2 (- - -), 0.4 (◆), and 1 s^{-1} (—). (d) Amplitude of oscillations in normalized spectra vs shear strain; same symbols as in (c).

variation in sample thickness, the long-term data may be used to generate a periodic correction factor to the sample thickness used to extract the birefringence, which is then applied to the entire range of the data. The results of this correction process are shown in Figure 4b. This procedure suppresses the long-time oscillations associated with the thickness variation; the basic features of the initial damped oscillations are unaffected.

Figure 4c shows the results of similar experiments conducted at several shear rates, drawn so as to make the initial transient more clear. Not surprisingly, the oscillatory response scales with shear strain, and the number of oscillations is independent of the previously applied shear rate; both of these observations are in line with previous observation of oscillatory behavior in both stress and structure in PBG solutions.[9-12] The presence of oscillations is a natural consequence of director tumbling, while the dampening of the oscillations is most likely associated with distortional elastic effects, as described by the Larson and Doi model, for instance.[19] However, while the general behavior is in agreement with the expectations of this model, we observe that the degree of orientation initially *increases* upon reversal of the flow direction, while the Larson and Doi model predicts a *decrease* in orientation (see Figure 2). As discussed in section 2, this prediction of the Larson and Doi model is closely linked to its steady-state prediction of a distribution of domain orientations accumulated close to the flow direction. In the preceding paper, it was shown that this picture overpredicts the steady-state degree of anisotropy. Recent microscopic visualization of texture in sheared PBG solutions by Larson and Mead suggests a more structured domain orientation distribution function, with domains predominantly *misaligned* with the flow direction.[35] It is likely that the discrepancy between Figures 2 and 4 is simply another indication that additional structure needs to be built into the Larson and Doi model in order for it to provide a more accurate representation of the orientation state in textured PLC's under shear. The fact that the mechanical behavior calculated in Figure 2 agrees with experiment suggests that stress predictions do not provide the most rigorous test of the model.

Figure 4d shows the behavior of the amplitude of the oscillations in the normalized spectra associated with the birefringence data in Figure 4c. The variation in the average degree of polarization mixing with shear rate is in line with the steady-state data presented in the preceding paper.[21] The redistribution of the degree of orientation that follows the flow reversal is associated with a temporary increase in the degree of polarization mixing (i.e., a decrease in A). As the texture adapts to the new flow direction, its detailed structure changes in such a way so as to reduce A; however, it is difficult to make a hypothesis as to what sort of structural rearrangements might yield this result. The polarization mixing observed during relaxation is even more severe (section 4.3).

We close this section by showing birefringence data for the 13.5% PBG(301k) solution following flow reversal in Figure 5. In all respects, the behavior is similar to that seen in Figure 4c. In particular, we observe that in this solution as well there is a clear *increase* in orientation immediately following the reversal. Qualitatively similar behavior is also seen in the 13.5% and 20% PBLG(236k) solutions, which is to be expected in light of the previously observed similarity between samples made of single isomers and racemic mixtures.[12]

4.2. Step Changes. Figure 6 shows birefringence as a function of shear strain following step increases in shear rate. Again, a damped oscillatory pattern which scales with shear strain is observed. The results here are more consistent with the predictions of the Larson and Doi model (as shown in Figure 1) than the reversal experiments. In particular, the birefringence exhibits an initial increase following the step change, in agreement with the model predictions. Detailed comparison between Figures 1 and 6 reveals subtle differences in that the first maximum in birefringence appears to occur somewhat later in the experiment than would be anticipated from the model calculations. Comparison of Figures 5 and 6 indicates that oscillations in birefringence following reversals are much larger than those observed following step changes in unidirectional shear rate. This observation is consistent with the Larson and Doi predictions of Figures 1 and 2 and is expected, since a flow reversal imposes a need for more substantial structural rearrangements of the domain orientation distribution function. Furthermore, the appearance of stronger oscillations for reversals is consistent with the previous experimental work of Moldenaers and co-workers, who studied transient changes in texture by conservative linear dichroism.[10]

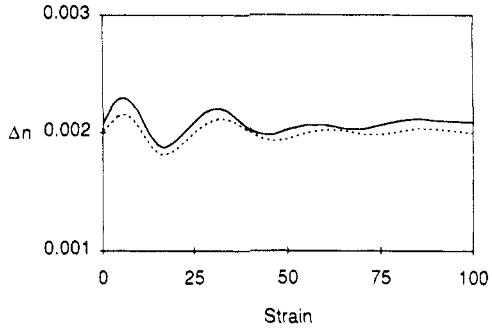

Figure 5. Birefringence vs shear strain following flow reversals at 0.2 (- - -) and 1 s^{-1} (—) for 13.5% PBG(301k) solution.

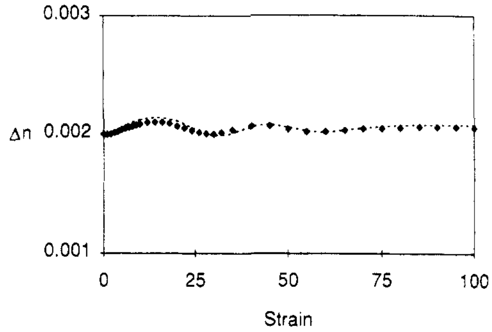

Figure 6. Birefringence vs shear strain following step up in shear rate from 0.2 to 1 s^{-1} (- - -) and from 0.4 to 1 s^{-1} (◆) for 13.5% PBG(301k) solution.

4.3. Relaxation Behavior. Figure 7 presents "raw" transmitted intensity spectra (although in normalized form) observed at intervals following cessation of shear flow for three of the solutions we have studied. In all cases, the previously applied shear rate was in the range of the low shear rate plateau in steady-state birefringence discussed in the preceding paper. In anticipation of the widely observed inverse shear rate relaxation scaling law that accompanied relaxation processes in PBG solutions,[13] we consistently report time following flow cessation in dimensionless form, $\dot{\gamma}t$, where time has been scaled by the previously applied shear rate $\dot{\gamma}$.

In each case, the initial behavior upon flow cessation is similar. An increasing number of oscillations observed in the normalized spectra is invariably seen. According to eqs 5 and 6, this must be associated with an increase in

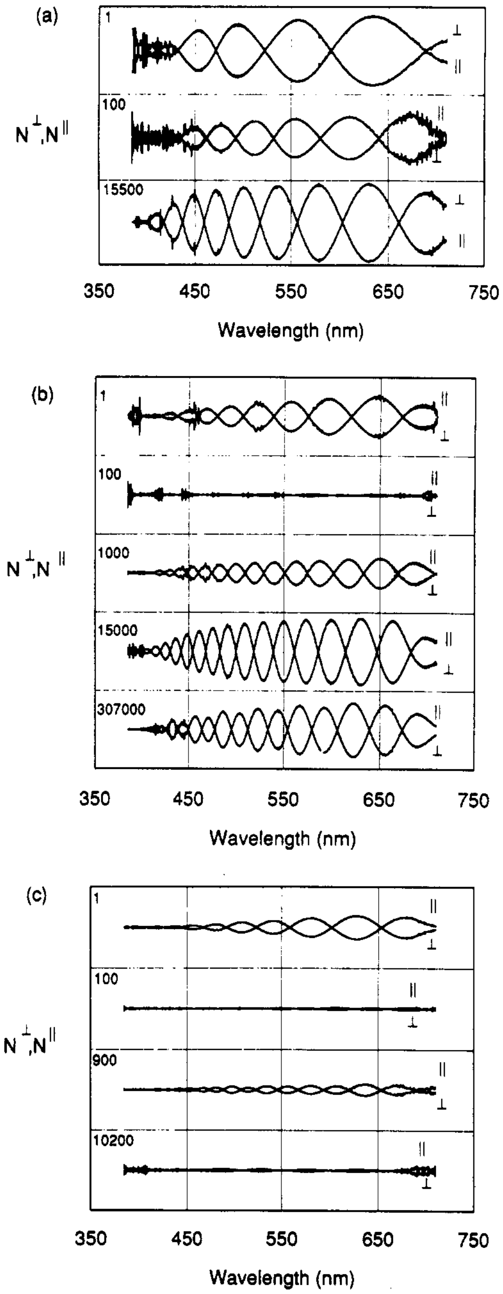

Figure 7. Normalized transmitted intensity spectra taken at indicated scaled time following cessation of shear flow: (a) 13.5% PBG(301k) solution, $\dot{\gamma}$ = 0.2 s^{-1}; (b) 20% PBG(301k) solution, $\dot{\gamma}$ = 0.4 s^{-1}, (c) 20% PBLG(236k) solution, $\dot{\gamma}$ = 0.4 s^{-1}. For each pair of spectra, ordinate varies from 0 to 1 between gridlines.

birefringence, and consequently an increase in the degree of molecular orientation in the flow direction. During the initial stages of the relaxation process, the amplitude of the oscillations decreases and reaches a minimum at dimensionless times near 100. After this, the amplitude increases, indicating that the optical properties of the textured PLC more closely approximate those of an ideal retarder. In the case of the racemic PBG solutions, the optical properties become very nearly ideal and stay that way for quite an extended period of time. Eventually, however, we again observe increased polarization mixing. In Figure 7b, the final spectra (dimensionless time = 307 000) exhibit a slight decrease in the amplitude of the oscillations, but also a small displacement of the curves relative to one another. As shown in the preceding paper, this corresponds to a slight rotation of the optical axis away from the flow direction.[21] It is not surprising that after this extended length of time following flow cessation (roughly 3.5 days in this case) the original orientation direction induced by flow has been "forgotten". The PBLG solutions tend to show a return of polarization mixing sooner than the racemic PBG samples. In particular, Figure 7c shows that polarization mixing almost completely degrades the spectra at a dimensionless time as "short" as 10 200.

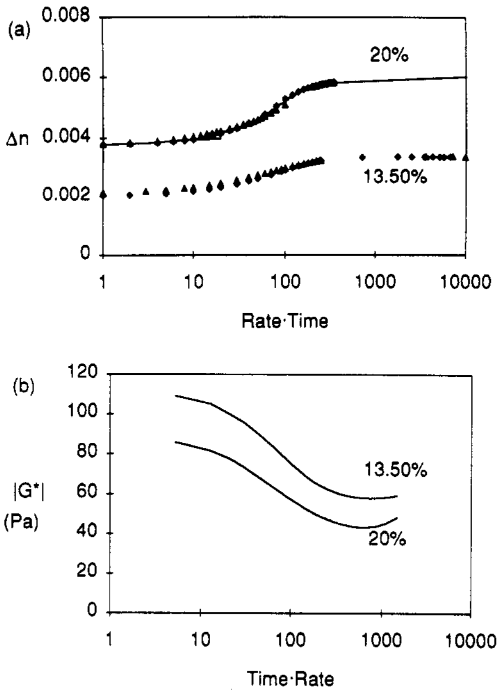

Figure 8. Relaxation following cessation of shear flow of PBG(301k) solutions. (a) Birefringence vs scaled time (symbols refer to previous shear rate: 0.2 (◆), 0.4 (—), and 1 s^{-1} (▲)). (b) Magnitude of complex modulus, $|G^*|$ vs scaled time (2 Hz).

The birefringence exhibited by the solutions may be obtained by fitting normalized spectra such as those in Figure 7 to eqs 5 and 6. Even when the amplitude has been substantially reduced by polarization mixing, it is possible to expand the scale of the spectra and obtain excellent fits to the wavelength dependence of the observed oscillations. Results of such analyses for relaxation following shear flow at a variety of shear rates in the linear regime are presented in Figure 8a for the racemic PBG solutions (birefringence data for the PBLG solutions are nearly identical). As qualitatively suggested by the spectra in Figure 7, the birefringence is seen to increase substantially from its prior steady state to a much higher value. In all cases, the characteristic time scale for this increase is around 100 dimensionless units. Given the extensive reports of relaxation time scaling in PBG solutions, it is not surprising to observe that results for experiments at different shear rates essentially superimpose when plotted vs scaled time.

In light of previous reports of *decreasing* orientation following cessation of shear flow, these results are somewhat surprising.[27-30] Even more remarkable is the degree of orientation observed. In the preceding paper, the birefringences of uniformly oriented, defect-free monodomains of the two racemic PBG solutions were measured to be 0.0035 ± 0.0002 and 0.0059 ± 0.0003 for the 13.5% and 20% solutions, respectively.[21] Comparison with Figure 8a indicates that the birefringence ultimately achieved during flow relaxation in these solutions is equivalent to that seen in a monodomain, within experimental error.

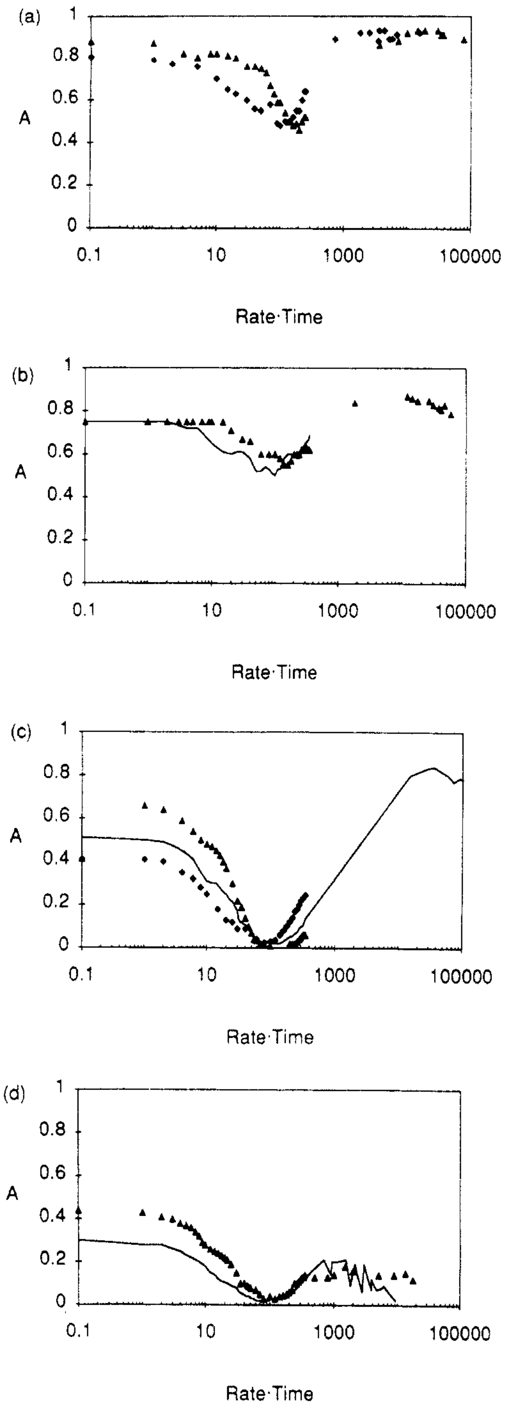

Figure 9. Amplitude of oscillations in normalized spectra vs scaled time following cessation of shear flow. Symbols the same as in Figure 8. *A* is evaluated from data in the spectral range 600–650 nm.

The polarization mixing apparent in Figure 7 is quantified by the amplitude *A* of the oscillations observed in the normalized spectra. This quantity is plotted vs scaled time in Figure 9 for all four solutions studied. These graphs reveal a characteristic dip in amplitude that occurs in the dimensionless time range of 60–200. The initial value of *A* reflects the degree of polarization mixing observed at steady state.[21] Again, the qualitative features of these data show the relaxation time scaling characteristic of PBG solutions. As noted above, the PBLG solutions show a final reemergence of polarization mixing earlier than the PBG solutions of corresponding concentration. This is particularly evident in the 20% PBLG solution, where unlike the other solutions, a large recovery in *A* following the initial drop is not seen. It is known that PBLG solutions exhibit a cholesteric mesophase at rest that is easily transformed into a nematic under flow. The more rapid reemergence of significant polarization mixing during the relaxation of these solutions may result from a transition back into a cholesteric phase. The high degree of orientation revealed by the birefringence in Figure 8a is of course inconsistent with a fully cholesteric structure. However, once *A* becomes sufficiently small, it is no longer possible to extract any measure of birefringence, so that determination of possible subsequent reductions in degree of orientation becomes impossible.

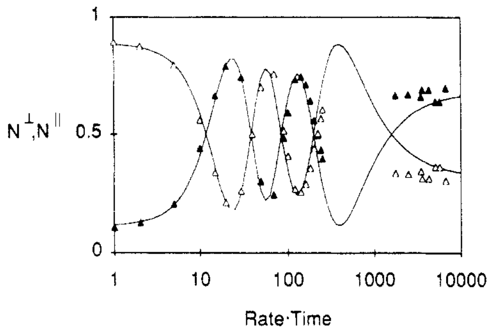

Figure 10. Intensity transmitted at $\lambda = 633$ nm between crossed (▲) and parallel (△) polarizers vs scaled time following cessation of shear flow of 13.5% PBG(301k) solution at 0.2 s^{-1}.

The simultaneous monotonic increase in birefringence and more complex behavior pattern in *A* suggests that to a significant degree the two variables reflect different structural features. It is clear that the birefringence reflects the average degree of molecular orientation, but the origin of behavior in Figure 9 is less clear. The formation of a larger scale, banded texture[31–33] is consistent with our observations, since this would result in substantial heterogeneity from one light path to another and a large amount of polarization mixing. The time scale over which the dip in *A* occurs is in line with published kinetics of band formation.[33] To our knowledge, an increase in average molecular orientation accompanying band formation has not been reported. In addition, the large recovery of *A* in most cases (Figure 9) indicates that any banded texture that may be formed eventually gives way to a strongly homogeneous structure with high orientation. It is possible that direct microscopic visualization experiments on thicker samples may provide greater insights into the nature of these textural rearrangements.[33,35]

We have noted that Asada and co-workers had previously concluded that birefringence decreases in PBG solutions following cessation of shear flow.[27] We believe that their conclusion was arrived at erroneously, due to ambiguities associated with multiple retardation orders in birefringence measurements at a single wavelength. In Figure 10, we have recast data from one or our relaxation experiments into the form that would have been measured by Asada and co-workers using the same crossed and parallel polarizers technique, but using only a single wavelength of 633 nm (Figure 10 should be compared with Figure 3 from ref 27). During relaxation, the intensity transmitted between crossed or parallel polarizers exhibits oscillations as the sample retardation changes. Asada and co-workers associated these oscillations with a *decrease* in retardation, and subsequent figures in their paper show many examples of calculations based on this assumption.[27] It is clear from eqs 5 and 6, however, that a similar pattern would be observed for an increase in retardation, and in fact the full spectra in figure 7 unambiguously demonstrate the birefringence does in fact *increase* during relaxation, as quantified in Figure 8. We feel that this clearly demonstrates the advantages of the spectrographic technique we have employed to the study of liquid crystalline polymers, where orientational changes associated with applied flow may not be as straightforward as those in isoptropic polymeric systems.

Our observation of an increasing degree of molecular orientation along the flow direction during shear flow relaxation provides a direct explanation for the origin of the long time scale reduction in dynamic moduli reported in poly(benzyl glutamate) solutions by Moldenaers and Mewis[5] and more recently by Larson and Mead.[13] One normally would expect that preshearing would break down structure in complex materials and consequently that dynamic moduli would increase following flow cessation as structure is re-formed. In addition, a structural interpretation of these results is complicated by the fact that opposite behavior is observed in HPC solutions; moduli are observed to increase following cessation of flow.[7,11] Figure 8 shows both optical and mechanical rheometric data on relaxation following shear flow of our 13.5% PBG(301k) solutions. The behavior pattern in the evolution of the amplitude of the complex modulus is in close accord with the prior studies mentioned above. Comparison of the time scales of the increase in orientation and the decrease in moduli indicates that this behavior is closely correlated. Larson and Mead have calculated the linear viscoelastic predictions of the Doi molecular model and demonstrated that the dynamic moduli are extremely sensitive to the molecular orientation direction.[36] This is expected, as the orientational dependence of viscosity in liquid crystals is one of their most characteristic properties.[16] A large drop in bulk dynamic moduli would be expected to accompany a significant increase in the degree of molecular orientation along the flow direction, since the viscosity of liquid crystals is lowest in this configuration.

Our measurements have been confined to the linear low shear rate regime. The evolution of dynamic moduli has also been studied for higher previous shear rates than we have employed. It is seen that at low shear rates, the initial values of the moduli are roughly insensitive to the previous shear rate, but as the nonlinear regime is entered, the initial moduli that are observed upon flow cessation are somewhat lower.[5,13] In the preceding paper, we have shown that in the nonlinear regime, the sheared PBG solutions undergo a transition to a higher orientation state.[21] It would consequently be expected that upon flow cessation, initial moduli would be lower due to the increased initial orientation, in agreement with the reported observations. These results suggest that the dynamic moduli in textured PBG solutions are predominantly determined by the average degree of orientation along the flow direction. Moldenaers has recently reported studies of oscillation superimposed on steady shear flow that, in conjunction with the steady flow orientation behavior reported in the preceding paper, generally support this conclusion.[37]

Moldenaers and Mewis[11] and Grizzutti and co-workers[7] have observed increasing dynamic moduli following flow cessation in HPC solutions. Based on the above arguments, it is tempting to suggest that this may reflect a decrease in molecular orientation along the flow direction during relaxation in this system. Indeed, Onogi and co-workers report flow birefringence measurements showing a decrease in orientation following shear flow in HPC solutions (it is unlikely that the compensation technique utilized in their work would lead to ambiguity in differentiating between an increase or decrease in flow alignment.[28] HPC has a much stronger tendency to form a cholesteric phase in the absence of shear flow than PBLG; optical experiments indicate the reformation of the cholesteric texture in HPC solutions occurs relatively quickly.[38] Significant differences in relaxation behavior between cholesteric HPC and nematic PBG are thus not necessarily surprising. On the other hand, Picken and co-workers have also quantified a decreasing degree of molecular orientation along the flow direction following flow cessation in *nematic* polyaramid solutions using X-ray scattering.[29]

To our knowledge, this is the first report of such substantial increases in orientation during relaxation of a sheared, textured PLC solution. In many ways, this result is quite appealing. The lowest free energy state of nematic liquid crystals is in a uniformly oriented condition; textured samples with large spatial distortions in the director field are energetically unfavorable. In the preceding paper we have shown that tumbling at low shear rates reduces the degree of orientation; why then should the liquid crystal *not* return to a more highly oriented condition when the flow is removed? Assuming orientational defects (possibly in the form of line disclinations) are not removed by flow, which seems reasonable at least in the low shear rate tumbling regime, one would expect that they would assert themselves upon flow cessation by promoting an orientationally heterogeneous structure, such as is typically observed in micrographs of quiescent PLC's. Similarly, a uniformly oriented structure should in principle only result if care is taken to establish uniformly oriented boundary conditions. Having made no attempts to do so in the present situation, it is to be expected that the boundaries would also act to promote a heterogeneous structure. These arguments for and against formation of a highly oriented structure following shear flow should in principle be applicable to any textured solution of a nematic PLC. That our observations in PBG solutions are exactly opposite the behavior seen in polyaramid solutions by Picken and co-workers[29] is apparently yet another indication of the limits of our understanding of these rheologically complex materials.

5. Conclusions

We have studied the degree of molecular orientation in transient flows of liquid crystalline poly(benzyl glutamate) solutions at low shear rates, using the technique of flow birefringence. Damped oscillations which scale with strain are observed in birefringence following step changes in the shear rate and reversal of the shear flow direction, as predicted by the Larson and Doi tumbling polydomain model.[19] Stronger oscillations are observed in reversals than in step changes, in agreement with the model. However, we observe an initial increase in orientation along the flow direction following flow reversal, in contrast to the Larson and Doi model prediction of a decrease. We believe that this discrepancy is an indication that the steady-state domain orientation distribution predicted by the model does not capture the detailed structure of PBG solutions sheared at low shear rates.[35]

We have quantitatively measured a pronounced increase in molecular orientation along the flow direction upon cessation of shear flow in all solutions studied. This increase in orientation follows a well-established relaxation scaling law typical of PBG solutions.[13] The spectrographic birefringence technique that was employed eliminates ambiguities associated with multiple retardation orders which we believe had previously led to the wrong conclusion in a similar previous study.[27] The birefringence ultimately approaches that observed in uniformly oriented monodomains, within experimental error. This increase in orientation along the flow direction provides a direct explanation for previous observations of gradual reductions in dynamic moduli following cessation of shear flow in similar systems. The increase in birefringence is accompanied by a substantial but temporary increase in the degree of polarization mixing, likely associated with the transient formation of banded textures.

Acknowledgment. We acknowledge the contributions made to this work by helpful discussions with Dr. Ronald Larson, Dr. Paula Moldenaers, and Professor Jan Mewis. The low molecular weight PBLG sample was provided by Dr. R. G. Larson and Prof. J. J. Magda. We thank Dr. C. Herb for access to the Bohlin rheometer. Financial support was provided in part by the National Science Foundation (Grant CTS-9109898) and by the June and Donald Brewer Junior Professorship.

References and Notes

(1) Marrucci, G.; Maffettone, P. L. *Macromolecules* **1989**, *22*, 4076.
(2) Marrucci, G.; Maffettone, P. L. *J. Rheol.* **1990**, *34*, 1217.
(3) Larson, R. G. *Macromolecules* **1990**, *23*, 3983.
(4) Kiss, G.; Porter, R. S. *J. Polym. Sci., Polym. Phys. Ed.* 1978, *65*, 193.
(5) Moldenaers, P.; Mewis, J. *J. Rheol.* **1986**, *30*, 567.
(6) Navard, P. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 435.
(7) Grizzuti, N.; Cavella, S.; Cicarelli, P. *J. Rheol.* **1990**, *34*, 1293.
(8) Magda, J. J.; Baek, S.-G.; De Vries, K. L.; Larson, R. G. *Macromolecules* **1991**, *24*, 4460.
(9) Mewis, J.; Moldenaers, P. *Mol. Cryst. Liq. Cryst.* 1987, *153*, 291.
(10) Moldenaers, P.; Fuller, G. G.; Mewis, J. *Macromolecules* **1989**, *22*, 960.
(11) Moldenaers, P.; Mewis, J. *Proc. Xth Int. Cong. Rheol.* **1988**, *2*, 134.
(12) Burghardt, W. R.; Fuller, G. G. *Macromolecules* **1991**, *24*, 2546.
(13) Larson, R. G.; Mead, D. W. *J. Rheol.* **1989**, *33*, 1251.
(14) Moldenaers, P.; Mewis, J. *J. Non-Newtonian Fluid Mech.* **1990**, *34*, 359.
(15) Srinivasarao, M.; Berry, G. C. *J. Rheol.* **1991**, *35*, 379.
(16) De Gennes, P.-G. *The Physics of Liquid Crystals*; Clarendon: Oxford, 1974.
(17) Carlsson, T. *Mol. Cryst. Liq. Cryst.* **1984**, *104*, 307.
(18) Burghardt, W. R.; Fuller, G. G. *J. Rheol.* **1990**, *34*, 959.
(19) Larson, R. G.; Doi, M. *J. Rheol.* **1991**, *35*, 539.
(20) Berry, G. C. *Mol. Cryst. Liq. Cryst.* **1988**, *165*, 333.
(21) Hongladarom, K.; Burghardt, W. R.; Baek, S. G.; Cementwala, S.; Magda, J. J. *Macromolecules*, previous paper in this issue.
(22) Kuzuu, N.; Doi, M. *J. Phys. Soc. Jpn.* **1984**, *53*, 1031.
(23) Kiss, G.; Porter, R. S. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 267.
(24) Graziano, D. J.; Mackley, M. R. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 73.
(25) Alderman, N. J.; Mackley, M. R. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 1.
(26) Takebe, T.; Hashimoto, T.; Ernst, B.; Navard, P.; Stein, R. S. *J. Chem. Phys.* **1990**, *92*, 1386.
(27) Asada, T.; Onogi, S.; Yanase, H. *Polym. Eng. Sci.* **1984**, *24*, 355.
(28) Onogi, S.; White, J. L.; Fellers, J. F. *J. Non-Newtonian Fluid Mech.* **1980**, *7*, 121.
(29) Picken, S. J.; Aerts, J.; Doppert, H. L.; Reuvers, A. J.; Northolt, M. G. *Macromolecules* **1991**, *24*, 1366.
(30) Viola, G. G.; Baird, D. B. *J. Rheol.* **1986**, *30*, 601.
(31) Marrucci, G.; Grizzuti, N.; Buonaurio, A. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 263.
(32) Ernst, B.; Navard, P. *Macromolecules* **1989**, *22*, 1419.
(33) Gleeson, J. T.; Larson, R. G.; Mead, D. W.; Kiss, G.; Cladis, P. E. *Liq. Cryst.* **1992**, *11*, 341.
(34) Asada, T.; Muramatsu, H.; Watanabe, R.; Onogi, S. *Macromolecules* **1980**, *13*, 867.
(35) Larson, R. G.; Mead, D. W. *Liq. Cryst.*, in press.
(36) Larson, R. G.; Mead, D. W. *J. Rheol.* **1989**, *33*, 185.
(37) Moldenaers, P.; Mewis, J. *J. Rheol.*, to appear.
(38) Asada, T.; Toda, K.; Onogi, S. *Mol. Cryst. Liq. Cryst.* **1981**, *68*, 231.