Texture Refinement in a Sheared Liquid-Crystalline Polymer

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Introduction

There has been much recent interest in the optical properties of textured anisotropic materials. Birefringence has been used to study the order–disorder transition in block copolymers, where despite the macroscopically random orientation in unaligned samples, light is transmitted between crossed polarizers.[1,2] This has been explained in terms of random polarization changes associated with the textured character of the sample.[2-4] Indeed, Balsara and co-workers have shown that this experiment provides a means of estimating grain sizes in randomly oriented textured materials.[3]

In a rather different context, flow birefringence studies of molecular orientation in textured polymer liquid crystals (PLCs) are also characterized by a failure of extinction conditions,[5] presumably again due to a heterogeneous optical texture.[6] In this case, however, flow introduces a strong bias in orientation, so that the average orientation state is highly anisotropic, with a large total retardation.[5] Our motivation here is to examine whether failure of extinction conditions might also be used as a probe of texture length scale in this situation, where analyses for macroscopically random orientation[3,4] do not apply. Similar issues are also expected if flow birefringence is to be used to study macroscopic orientation in block polymers during flow alignment.

While the analysis of Balsara and co-workers[3] may be slightly modified for the case of high domain orientation, their analysis is formulated in such a way that a restriction is placed on the total retardance of the sample. Since this condition is clearly not satisfied in sheared PLC solutions,[5] we present a derivation based on a slightly different set of assumptions that leads to the same result, but with the capability to describe systems of large total retardation *provided the degree of domain misalignment is sufficiently small.* Experiments are reported on a sheared textured PLC solution to test the scalings of this relationship and to study texture refinement under flow.

Analysis

We adopt the problem description and notation of Balsara et al.[7] A composite sample consists of N optically uniaxial grains, each oriented at polar and azimuthal angles θ_j and ψ_j with respect to a Cartesian coordinate system where light propagates along the z axis. Here we treat the case where grains are only slightly misaligned away from the x axis, so that ψ_j is small, and $\theta_j = \pi/2 + \varphi_j$, where φ_j is small. Keeping only terms $O(\psi_j^2)$, the change in polarization induced by a single grain is characterized by its 2×2 Jones matrix:[8]

$$\mathbf{M}_j = \begin{pmatrix} \exp\{-i\Gamma_j/2\} + i2\psi_j^2 \sin \Gamma_j/2 & 2i\psi_j \sin \Gamma_j/2 \\ 2i\psi_j \sin \Gamma_j/2 & \exp\{i\Gamma_j/2\} - i2\psi_j^2 \sin \Gamma_j/2 \end{pmatrix} \tag{1}$$

For small birefringence $|\Delta n| = |n_e - n_o| \ll n_o$,[3] the single-grain retardance is given to $O(\varphi_j^2)$ by

$$\Gamma_j = \frac{2\pi l_j}{\lambda} \Delta n (1 - \varphi_j^2) \tag{2}$$

where l_j is the optical thickness of grain j, and λ is the wavelength.

The Jones matrix for the composite sample is

$$\mathbf{M} = \prod_{j=1}^{N} \mathbf{M}_j = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} \tag{3}$$

where the four components are given by

$$\underset{(M_{11})}{M_{22}} = \exp\left\{ \underset{(-)}{+} \frac{i}{2} \sum_{j=1}^{N} \Gamma_j \right\} \underset{(-)}{+} \sum_{j=1}^{N} 2i\psi_j^2 \sin \frac{\Gamma_j}{2} \times \exp\left\{ \underset{(-)}{+} \frac{i}{2} \sum_{k \neq j} \Gamma_k \right\} - \sum_{j=1}^{N-1} \sum_{k>j} 4\psi_j \psi_k \sin \frac{\Gamma_j}{2} \sin \frac{\Gamma_k}{2} \times \exp\left\{ \underset{(-)}{+} \frac{i}{2} \left[\sum_{m<j;\, m>k} \Gamma_m - \sum_{j<n<k} \Gamma_n \right] \right\} \tag{4a}$$

$$\underset{(M_{12})}{M_{21}} = \sum_{j=1}^{N} 2i\psi_j \sin \frac{\Gamma_j}{2} \exp\left\{ \underset{(-)}{+} \frac{i}{2} \left[\sum_{k>j} \Gamma_k - \sum_{m<j} \Gamma_m \right] \right\} \tag{4b}$$

While the random orientation case has been described as a random walk[2] of the polarization state or formalized as a diffusive process[4] on the surface of the Poincaré sphere, the highly oriented case has some important qualitative differences. In particular, the behavior depends critically on the initial polarization state. To illustrate, if we evaluate $\mathbf{M}$ in the limit where there is no misalignment of grains, we recover

$$\mathbf{M} = \begin{pmatrix} \exp\{-(i/2) \sum_{j=1}^{N} \Gamma_j\} & 0 \\ 0 & \exp\{+(i/2) \sum_{j=1}^{N} \Gamma_j\} \end{pmatrix} \tag{5}$$

which is just the Jones matrix for a retarder with total retardance Γ equal to the sum of the individual grains, oriented along the x axis. If light polarized at 45° with respect to the x axis enters the sample, a phase shift is introduced, such that if an analyzer oriented at −45° is placed following the sample, the transmitted light intensity is

$$I^{\perp}(45°,-45°)/I_0 = \sin^2(\Gamma/2) \tag{6}$$

When Γ is sufficiently large, the polarization state passes through multiple orders, which correspond to multiple circuits around the surface of the Poincaré sphere, as illustrated by path A in Figure 1. Note that since the leading terms in eq 4 retain the complex exponential

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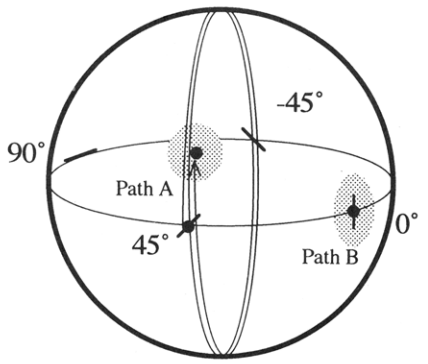

Figure 1. Schematic illustration of influence of highly oriented textured sample on light polarization, represented on the surface of the Poincaré sphere. Path A shows the case in which the incident linear polarized light is oriented at 45° with respect to the sample orientation direction, while path B shows the case where the incident light is linearly polarized along the sample direction. Note that birefringence experiments in ref 5 are described by path A, while the present experiments are represented by path B.

dependence on the total retardation, this expression for **M** can properly account for multiple orders in retardation. A small misalignment of domains ($\psi_j \neq 0$) introduces small perturbations to the polarization as it circuits the sphere, leading to a gradual spreading of polarization states; the situation is analogous to a convection/diffusion process at high Peclét number.

The qualitative behavior is very different when the incident light is polarized along the x axis (path B in Figure 1). If there is no misalignment, there will be no perturbation in the polarization state at all, and light will be completely extinguished when it passes through a crossed analyzer at 90°:

$$I^{\perp}(0°,90°)/I_0 = M_{21}M^*_{21} \tag{7}$$

where the asterisk denotes the complex conjugate. Small misalignment of domains causes a small spreading of polarization states in the neighborhood of the original point on the Poincaré sphere, without any complications associated with the large average orientation. Equation 4b for this case then gives

$$I^{\perp}(0°,90°)/I_0 = 4\sum_{j=1}^{N}\psi_j^2 \sin^2\frac{\Gamma_j}{2} + 8\sum_{j=1}^{N}\sum_{k>j}\psi_j\psi_k \sin\frac{\Gamma_j}{2}\sin\frac{\Gamma_k}{2}\cos\left(\sum_{m=j}^{k-1}\frac{\Gamma_m + \Gamma_{m+1}}{2}\right) \tag{8}$$

Provided there are no correlations in the misalignment of domains about the x axis, ψ_j is equally likely to be positive or negative, and the second term vanishes.

We now make an additional assumption that the retardance of each individual grain $\Gamma_j < 1$ (note that it is still possible for the *total* retardance, $N\Gamma_j$, to be large). Combining with eq 2 and keeping only the leading order term, we find

$$I^{\perp}(0°,90°)/I_0 = 4\pi^2(\Delta n)^2\frac{Ll_{av}}{\lambda^2}\langle\psi^2\rangle \tag{9}$$

where $L = N\langle l\rangle$ is the total optical path of the textured sample, $l_{av} \equiv \langle l^2\rangle/\langle l\rangle$ is the average texture length scale,[3] and $\langle\psi^2\rangle$ is the mean-square misalignment in the x–y plane (slight misalignment *out* of the x–y plane does affect this result to leading order). The complementary experiment

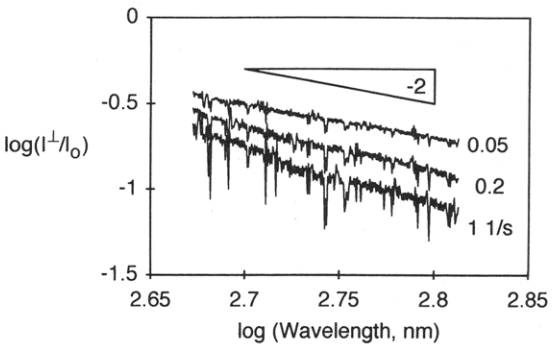

Figure 2. Wavelength dependence of light intensity transmitted between crossed polarizers (0°,90°) at indicated shear rates. Reference curve shows λ^{-2} dependence. Sample thickness = 0.94 mm.

of light intensity transmitted between parallel polarizers oriented along the x direction may be analyzed to give

$$I^{\parallel}(0°,0°)/I_0 = M_{11}M^*_{11} = 1 - I^{\perp}(0°,90°)/I_0 \tag{10}$$

Equation 9 is virtually identical to the result obtained by Balsara et al.,[3] with differences only in geometric factors. Indeed, their penultimate result will yield eq 9 directly for the case of high average orientation. The present analysis, however, shows that this result is not necessarily dependent on the assumption that the total retardance of the sample be small. Instead, this result is expected to hold for $N\langle\Gamma_j^2\rangle\langle\psi^2\rangle \ll 1$, which may be satisfied via *either* conditions of small retardance or small misalignment.

Experimental Section

In the case of random domain orientations, there is effectively only one unknown, the average texture length l_{av}.[3] In the present case, eq 9 shows that the transmitted light intensity depends on both the texture length scale and the degree of misalignment of domains ($\langle\psi^2\rangle$). Thus, investigations of how l_{av} scales with shear rate are possible only if (i) an independent measure of the shear rate dependence of $\langle\psi^2\rangle$ is available or (ii) $\langle\psi^2\rangle$ is independent of shear rate. In our previous studies of molecular orientation in PLC solutions under shear, we observed a regime at low rates where birefringence is constant, suggesting that the distribution of domains is independent of shear rate;[5] the experiments conducted here are restricted to this regime. It must be noted that the macroscopic birefringence in this regime suggests a greater degree of misalignment than rigorously admitted by the above analysis.[5] Milner's comprehensive approach could treat this situation;[4] however, it would be necessary to assume a particular form for the grain distribution function, and numerical integrations would be required, at the expense of much generality. We proceed therefore in the hope that the scalings embodied in eq 9 are sufficiently robust that they are not significantly altered by a somewhat greater degree of grain misalignment.

The sample used is a 13.5 wt % solution of poly(γ-benzyl-D-glutamate) [PBDG, Sigma lot 110H5531, M = 298 000] dissolved in m-cresol. The sample is sheared in a rotating parallel disk flow cell constructed from optical windows; strains of at least 200 units are applied prior to measurements.[5] Light intensity transmitted between crossed or parallel polarizers is measured as a function of wavelength using a white light source and photodiode array.[5] Experiments are also reported using a HeNe laser, where a lens is used to focus all transmitted light onto a photodiode detector. Both crossed (0°,90°) and parallel (0°,0°) polarizers are employed, and eqs 9 and 10 are used to normalize the data.

Figure 2 shows the wavelength dependence of the transmitted light intensity at three shear rates. Also shown is a curve with a λ^{-2} dependence. The data satisfy the inverse square dependence quite well, although there are deviations at shorter wavelengths. This probably results from the need to correct for baseline offset in the diode array, combined with a weak source intensity at

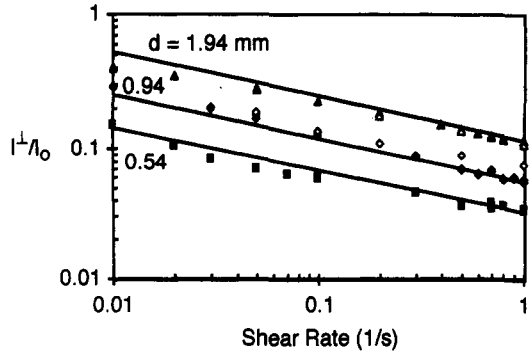

Figure 3. Light intensity transmitted between crossed polarizers (0°,90°) as a function of shear rate, for sample thicknesses 1.94 (▲), 0.94 (♦), and 0.54 (■) mm. Wavelength = 633 nm. Lines are drawn using the formula $C\gamma^{-0.33}$, with values of C in proportion 1.94:0.94:0.54. Open symbols are data from spectrographic optical train; filled symbols use HeNe laser illumination.

short wavelengths.[5] It should be noted that because of the somewhat poorly defined character of the white-light beam, there is no good way to collect all diffracted light in the detector, which is necessary if the above analysis is expected to apply.[7] In Figure 3, the spectrographic results at 633 nm are compared with the HeNe laser experiments, where great care is taken to collect all diffracted light. We find good agreement between the two optical trains.

Provided that $\langle\psi^2\rangle$ is independent of shear rate, variations in transmitted light intensity with shear rate may be directly attributed to changes in l_{av} according to eq 9. Figure 3 shows intensity as a function of shear rate, for several different sample thicknesses. Note that for the thickest sample, a significant fraction of the incident light intensity passes through crossed polarizers, violating the conditions placed on the analysis. For the thinner samples, a linear dependence is seen on the double log plot, suggesting texture refinement according to the scaling law $l_{av} \sim \gamma^{-0.33}$. Our data are also in good agreement with the prediction that the transmitted light intensity should be proportional to the sample thickness, as seen by the solid lines, drawn using a linear dependence on L.

Discussion

It is important to reiterate that the assumptions upon which the analysis are based are not fully satisfied in the experiments. Independent measurements of macroscopic birefringence indicate that $\langle\psi^2\rangle$ is not rigorously small, and for thicker samples in particular, too large a fraction of light passes through the sample. Despite these limitations, the predicted dependences of transmitted light intensity on sample thickness and wavelength are quite well satisfied by the data, indicating that application of the analysis to these data may have some justification. Subject to these provisos, this technique provides a rare opportunity to directly quantify how length scale varies with shear rate. The exponent −0.33 is rather different from the value −0.5 suggested by the scaling of relaxation processes in textured PLCs.[9] At this point it is impossible to conclude whether this discrepancy is real, or a consequence of the limitations in the present analysis.

More generally, we recall an important characteristic of this analysis. Light intensity transmitted between crossed polarizers depends on *two* quantities, the texture length scale and the degree of domain misalignment. In the present case, independent measurements indicate that $\langle\psi^2\rangle$ is constant, allowing in principle the shear rate dependence of l_{av} to be determined. It is noteworthy that if $\langle\psi^2\rangle$ were indeed rigorously small, the macroscopic birefringence would saturate, becoming insensitive to the degree of misalignment. There would then be no way to isolate changes in l_{av} and $\langle\psi^2\rangle$. Thus, while the conditions of the experiments described here are not ideal, they may be as close to an optimum compromise as is possible in this system. Recent work has shown that reasonable self-consistency is achieved between estimates of block copolymer grain sizes obtained from birefringence and the angular dependence of diffracted light;[10] this suggests diffraction as a complementary technique to study texture refinement in sheared PLCs.

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