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Relationship between Birefringence and the Structure of Ordered Block Copolymer Materials

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Introduction

Recent experiments demonstrate that the order-to-disorder transition (ODT) in block copolymer liquids can be identified by the sharp decrease in the static birefringence of the sample.[1,2] Electron micrographs show that the ordered state that emerges spontaneously when a block copolymer liquid is cooled under quiescent conditions, to temperatures below the order-to-disorder transition temperature (T_{ODT}), is "polycrystalline", consisting of randomly oriented grains:[3] Coherent order is restricted to regions within each grain. While the absence of birefringence in disordered systems is expected owing to the isotropic nature of such materials, the birefringence of polycrystalline ordered materials with no preferential orientation is somewhat unexpected and arises from random changes in the polarization state of the transmitted beam due to the randomly-oriented, optically-anisotropic grains that it encounters.[1,2] Amundson and co-workers[2] used Stokes parameters[4] to explain this effect. Changes in the polarization of the light as it passes through the sample were represented as a "special random walk" on the Poincaré sphere.[4]

The purpose of this paper is to derive an explicit expression for the birefringence of such polycrystalline materials. Jones calculus[4,5] provides a convenient framework for the derivation. We find that, in the limit of weak birefringence, the fraction of the incident light intensity that exits such a sample held between perfectly crossed polarizers is equal to $4\pi^2(\Delta n)^2 L l_{\mathrm{av}}/15\lambda^2$, where Δn is the difference in the refractive indices for light polarized parallel and perpendicular to the optical axis of a single grain, L is the sample thickness (path length of the beam), l_{av} is the characteristic size of the grains, and λ is the wavelength of the light. Birefringence can thus be used to measure average grain sizes in ordered block copolymers provided Δn is known. We also present preliminary experimental evidence that supports the validity of the present analysis.

Analysis

We first examine the optical properties of a single grain. We consider uniaxial grains, and thus our analysis only applies to ordered block copolymer liquids with lamellar and cylindrical microstructures. A unit vector, **n**, that is directed normal to the lamellae (or parallel to the cylinder axes) completely specifies the order in the grains. The optical properties of such grains are well-known.[4,5] Their birefringence can be characterized by the refractive indices for light polarized in directions parallel and perpendicular to **n**, n_{e} and n_{o}, referred to as the extraordinary and ordinary refractive indices, respectively. Form birefringence contributions to n_{e} and n_{o}, in terms of the refractive indices of the microphases, are well-known.[3] Additional contributions due to chain stretching have recently been evaluated.[6]

In the framework of Jones calculus, the polarization of a monochromatic, polarized beam of light propagating in the z-direction is characterized by a two-component column vector **V**.[5] We use the polar and azimuthal angles θ and ψ to describe the orientation of **n** relative to a Cartesian coordinate system (see Figure 1). The effective optic axis is the projection of **n** onto the xy-plane and makes an angle ψ with the x-axis. The change in polarization of a beam after propagating through this birefringent grain can be calculated by operating on **V** with a 2 × 2 matrix $\mathbf{M}(\theta,\psi,l)$.[5]

$$\mathbf{M}(\theta,\psi,l) = \begin{pmatrix} \cos\frac{\Gamma}{2} - i\cos 2\psi \sin\frac{\Gamma}{2} & -i \sin 2\psi \sin\frac{\Gamma}{2} \\ -i\sin 2\psi \sin\frac{\Gamma}{2} & \cos\frac{\Gamma}{2} + i\cos 2\psi\sin\frac{\Gamma}{2} \end{pmatrix} \tag{1}$$

where Γ is the phase shift due to a single grain

$$\Gamma(\theta,l) = 2\pi l(n_{\mathrm{e}}(\theta) - n_{\mathrm{o}})/\lambda \tag{2}$$

l is the length of the grain in the z-direction (see Figure 1), and[5]

$$\frac{1}{n_{\mathrm{e}}^{2}(\theta)} = \frac{\cos^2\theta}{n_{\mathrm{o}}^{2}} + \frac{\sin^2\theta}{n_{\mathrm{e}}^{2}} \tag{3}$$

The polarization $\mathbf{V}'$ resulting from an x-polarized beam propagating through N grains, to first order in Γ, is given by

$$\begin{pmatrix} V'_x \\ V'_y \end{pmatrix} = \prod_{j=1}^{N} \mathbf{M}(\theta_j,\psi_j,l_j)\begin{pmatrix} 1 \\ 0 \end{pmatrix} \approx \begin{pmatrix} 1 - \sum_{j=1}^{N} \frac{i\Gamma(\theta_j,l_j)}{2}\cos 2\psi_j \\ -\sum_{j=1}^{N}\frac{i\Gamma(\theta_j,l_j)}{2}\sin 2\psi_j \end{pmatrix} \tag{4}$$

where the subscript j indicates the properties in the jth grain; the grains are numbered in order of encounter. If we define $\Delta n = (n_{\mathrm{e}} - n_{\mathrm{o}})$ and if $|\Delta n|/n_{\mathrm{o}} \ll 1$, then

$$\Gamma(\theta_j,l_j) \approx \frac{2\pi l_j}{\lambda}\Delta n \sin^2\theta_j \tag{5}$$

When the collection of N grains described by eq 4 and 5 is held between perfectly crossed polarizers, the ratio of the intensity of the exiting beam, I, to that of the beam incident on the sample, I_0, is given by

$$\frac{I}{I_0} \approx |V'_y|^2 = \left(\frac{\pi\Delta n}{\lambda}\right)^2 \Big[\sum_{j=1}^{N} l_j^2 \sin^4\theta_j \sin^2 2\psi_j + \sum_{j=1}^{N}\sum_{\substack{k=1 \\ (j\neq k)}}^{N} l_j l_k \sin^2\theta_j \sin^2\theta_k \sin 2\psi_j \sin 2\psi_k\Big] \tag{6}$$

If there is no correlation between the orientations of

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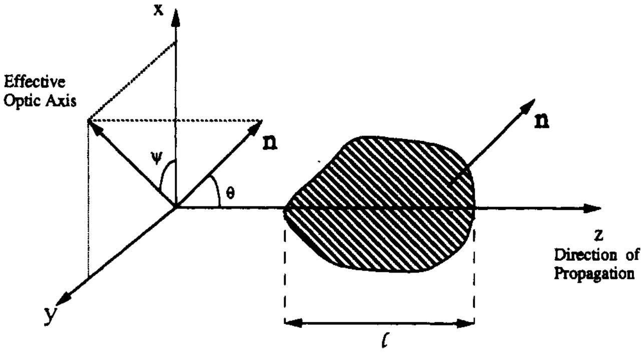

Figure 1. Representation of a grain with orientation **n**, relative to a laboratory Cartesian coordinate frame. The orientation of **n** with respect to the laboratory reference frame is described by polar and azimuthal angles θ and ψ, respectively. The z-axis represents the direction of propagation, the effective optic axis is obtained by projecting **n** onto the xy-plane, and l is the length of the grain in the z-direction.

different grains, the second term vanishes, yielding an expression for I/I_0.

$$\frac{I}{I_0} = \left(\frac{\pi\Delta n}{\lambda}\right)^2 N\langle l^2\rangle\langle\sin^4\theta\rangle\langle\sin^2 2\psi\rangle = \frac{4\pi^2}{15}(\Delta n)^2 N\frac{\langle l^2\rangle}{\lambda^2} \qquad (7)$$

where $\langle\ \rangle$ refers to average values. Equation 7 represents a first-order estimate for I/I_0 and is valid for small $N\langle\Gamma^2\rangle$. Note that only in the limit of weak birefringence do the polarization changes reduce to a random walk.

If L is the path length, then $L = N\langle l\rangle$, and

$$\frac{I}{I_0} = \frac{4\pi^2}{15}(\Delta n)^2\frac{Ll_{\mathrm{av}}}{\lambda^2} \qquad (8)$$

where $l_{\mathrm{av}} \equiv \langle l^2\rangle/\langle l\rangle$.

Equation 8 is the main result of this work. It provides a quantitative explanation for the experimental observations reported in ref 1; i.e., the order-to-disorder transition in block copolymer liquids is accompanied by a sharp decrease in the birefringence of the sample. It also suggests that average grain sizes in ordered systems may be estimated from birefringence measurements.

For typical laser beams, with diameters much larger than the grain size, rays of light emerging from different parts of the sample will have different polarizations because they have encountered a different set of grains.[1,2] Consequently the signal reaching the detector will be averaged over the transverse extent of the beam.

Beam spreading due to diffraction may be significant, but as long as the total power exiting the sample is measured, the analysis presented is correct to first order in Δn.[7]

Experimental Results

In this section we present results of a limited test of the analysis, applying eq 8 to birefringence data obtained from a 52.5 wt % solution of a polystyrene–polyisoprene block copolymer in toluene. The same block copolymer was used in the experiments reported in ref 1. Small-angle X-ray scattering (SAXS) from ordered toluene solutions of the block copolymer is consistent with a lamellar microstructure.[8] The order-to-disorder transition temperature of this solution was obtained by methods outlined in ref 1 and was found to be 64 ± 2 °C.

Figure 2 shows a schematic of the apparatus. The sample was contained in a sealed test tube with a path length of 0.74 cm, which was immersed in a thermostated, index matching fluid. The sample, initially at 70 °C (disordered), was first quenched to an intermediate temperature, T_{in}, for 1 h and then quenched to 39 °C. The quenches were accomplished by switching between two circulating baths set at predetermined temperatures. Thus lower values of T_{in} represent more rapid quenches.

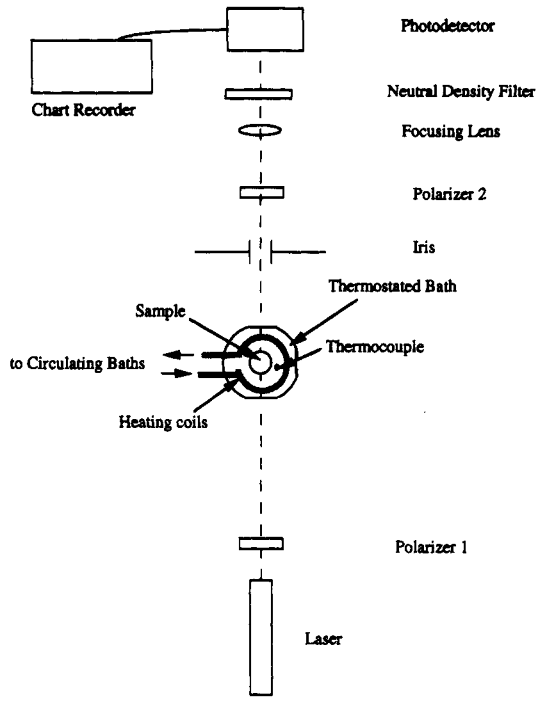

Figure 2. Schematic of the experimental setup (top view).

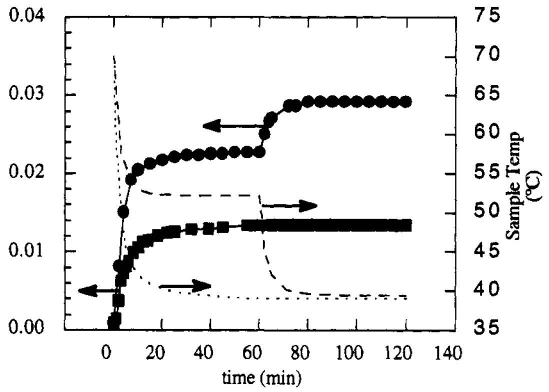

Figure 3. Typical time dependence of birefringence and sample temperature after quenching. (a) Slow quench (T_{in} = 52 °C): big dashes, sample temperature; circles, I/I_0. (b) Rapid quench (T_{in} = 39 °C): small dashes, sample temperature; squares, I/I_0.

Typical birefringence signals and corresponding thermal histories of the sample for the fastest (T_{in} = 39 °C) and slowest (T_{in} = 52 °C) quench are shown in Figure 3. It is expected that faster quenches will yield smaller grains. Our data are consistent with this expectation. The birefringence data and corresponding estimates of grain sizes (l_{av} was calculated using eq 8, with an estimated[9] Δn = 2.4 × 10^{-4}) obtained from different quenches are summarized in Figure 4. These data were acquired 2 h after the initial quench. We believe that these data represent the first attempt to quantify the effect of quenching history on grain structure in ordered block copolymer materials formed under quiescent conditions.

In order to test for any preferred orientation of the grains, we inserted a quarter-wave retardation plate as a compensator between the sample and the analyzing polarizer. Any transmitted signal from orientational bias can be nulled by appropriate rotations of the compensator and analyzer.[2,10] At the settings where the transmitted signal was minimized, a reduction in I/I_0 of approximately 10%

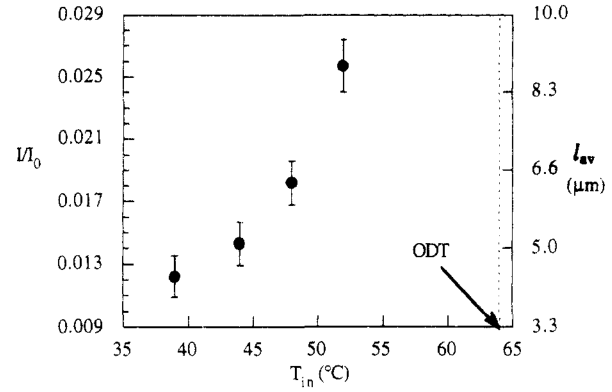

Figure 4. Dependence of birefringence, I/I_0, and estimated grain size, l_{av}, on quenching history.

was typically observed, indicating that about 90% of the observed signal is due to random-walk birefringence and 10% is due to bias in grain orientation. Thus, the average grain sizes displayed in Figure 4 are overestimated by about 10%. The grain sizes obtained by us are consistent with estimates from electron microscopy and SAXS on toluene-cast block copolymer (similar in composition and molecular weight to the one used in this work) films.[11]

Concluding Remarks

An expression relating birefringence and the structure of ordered block copolymer materials formed under quiescent conditions has been derived. The intensity of the light exiting the sample held between perfectly crossed polarizers is found to be directly proportional to the average grain size. The constant of proportionality depends only on material properties that can be obtained independently. Preliminary experiments support the validity of the simplifying assumptions invoked.

Our treatment is not restricted to ordered block copolymers and should be applicable to other materials containing randomly oriented uniaxial grains such as magnetic materials and some liquid crystals and to other forms of electromagnetic radiation.

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References and Notes

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(7) While diffraction effects at grain boundaries are small when Δn is small, they can still contribute to a transverse mixing of orthogonally polarized contributions. The orthogonally polarized electric field at a given point on the detector will be the sum of contributions from all illuminated grains in the sample, although different grains will be weighted differently, depending on location. These contributions can interfere, giving rise to transverse intensity fluctuations. However, as long as all of the diffracted light reaches the detector, the total power collected will be the incoherent sum of the contributions from each illuminated grain. Thus, even when diffraction is included, the integrated signal is, to first order, still a random average over all grains in the sample, and eq 8 is still valid. This statement can be justified by a Born approximation analysis. For systems where Δn is larger, such as liquid crystals, multiple scattering effects become extremely important and cannot be ignored.
(8) Balsara, N. P.; Stepanek, P.; Lodge, T. P.; Tirrell, M. *Macromolecules* **1991**, *24*, 6227.
(9) The thicknesses of polystyrene- and polyisoprene-rich lamellae were estimated to be 125 and 245 Å, respectively, based on SAXS data (ref 8) and block copolymer composition. The refractive indices of the lamellae were estimated in the strong segregation limit (ref 4) and assuming the refractive index of the mixture is given by a volume fraction weighted mean of pure components. Contributions to Δn due to the nonrandomness of the polystyrene and polyisoprene segments have not been included.
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