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Birefringence and Diffraction of Light in Ordered Block Copolymer Materials

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ABSTRACT: The scattering of light from ordered block copolymer materials, consisting of irregularly shaped birefringent grains with randomly oriented optic axes, is analyzed theoretically and experimentally. We show that independent estimates of the characteristic grain sizes can be obtained from the far-field angular spread of the diffracted light and from the total orthogonally polarized scattered power. Experimental measurements on ordered polystyrene–polyisoprene diblock copolymer solutions in toluene support the predictions of the theory. Grain sizes estimated from diffraction and total power measurements are in agreement. Such measurements should aid in the physical characterization of ordered block copolymer materials, as well as other random anisotropic media.

I. Introduction

Block copolymer materials can spontaneously self-organize into ordered, periodic structures.[1] Large "single crystals" of such a material, formed by extrusion, were first observed to be birefringent by Folkes and Keller in 1971.[2] In contrast, recent studies have confirmed the presence of birefringence in macroscopically isotropic ordered block copolymer materials.[3-6] Such materials are formed if the ordering process is conducted in the absence of external fields. Coherent order is restricted to finite regions that are referred to as grains. A light beam propagating through such a sample encounters a large number of randomly oriented, optically anisotropic grains. In an earlier paper,[5] an expression was derived for the birefringence of such samples using the framework of Jones calculus. It was shown that if such samples are illuminated with plane-polarized light, the fraction of the incident power transmitted through a crossed polarizer is proportional to the average size of a grain. Thus, birefringence measurements could be used to estimate grain size if the strength of the optical anisotropy of the grain were known. In that treatment, the diffraction of the light beam as it propagates through the sample was ignored.

The purpose of this publication is to provide a more complete description of the interaction between light and a randomly birefringent medium, specifically including scattering effects. The treatment of light scattering from randomly anisotropic media has been reviewed by Flygare and Gierke[7] and by Nieto-Vesperinas.[8] A rigorous treatment of this phenomenon is contained in the work of Goldstein and Michalik.[9] Our treatment uses this theory as a starting point to obtain a quantitative relationship between the spatial spread of the far-field orthogonally polarized transmitted beam and the characteristic size of the grains in block copolymers. The typical grain sizes we have observed are an order of magnitude larger than the wavelength of the incident light, so that we can restrict our treatment to small scattering angles (paraxial approximation). This approximation and the use of a transverse correlation function simplify the treatment and allow us to present general results for the scattered intensity that are simple in form and can be tested by experiment. We show that the angular spread is inversely proportional to the average grain size and is independent of the strength of the optical anisotropy of the grains. It thus provides a direct measure of grain size. In addition, when the far-field intensity is integrated, we obtain an expression for the total power that is in agreement with the results of our earlier study.[5] Our treatment is an extension of the pioneering work of Stein and co-workers on light scattering from crystalline and other anisotropic polymers,[10-14] including block copolymers.[15]

We present experimental birefringence and diffraction data, obtained from an ordered solution of a polystyrene–polyisoprene block copolymer in toluene. We find that the grain size determined by diffraction is comparable to that determined by birefringence. This agreement lends validity to the concept of a characteristic grain size, even though the actual grain shapes are probably highly irregular and grain boundaries are not always well-defined.

II. Theory

The sample's anisotropic optical characteristics are represented by a random diadic permittivity,

$$\overleftrightarrow{\epsilon}(r) = \bar{\epsilon} + \delta\overleftrightarrow{\epsilon}(\mathbf{r}); \quad \mathbf{r} = [x, y, z] \qquad (1)$$

whose mean value, $\bar{\epsilon}$, is homogeneous and isotropic. The spatially random part, $\delta\overleftrightarrow{\epsilon}$, induces polarization changes and diffraction of an incident monochromatic wave of angular frequency ω. Within the sample, the incident field is polarized in the x direction and propagates in the z direction:

$$\mathbf{E}_{\text{incident}} = \hat{\mathbf{x}}\, U_0(x,y)\, e^{ikz} \qquad (2)$$

The index of refraction, n, and the propagation constant k are

$$n = (\bar{\epsilon}/\epsilon_0)^{1/2}; \quad k = n\omega/c \qquad (3)$$

The incident field amplitude, U_0, typically has a Gaussian distribution in the x–y plane. Under experimental conditions, its width is sufficiently broad that the entire sample is in its near field; thus we may assume negligible diffraction spread of the input Gaussian beam over the entire length of the sample. We define a grain as a contiguous region over which the sample's optical properties—direction of optic axis and refractive index components—are constant. Each realization of the sample has irregular groupings of grains that contribute coherently to the field at the detector, thereby forming a speckled intensity pattern.

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The statistical ensemble expectation value[8] of the intensity, $\langle I\rangle$, at the detector is an average over these patterns. If the anisotropy axes of the grains are random, uniformly distributed in angle and uncorrelated, the scattered intensity per unit solid angle in the direction θ relative to the incident beam is given by[9,10]

$$\frac{d\langle I(\theta)\rangle}{d\Omega} = k^4\langle\Delta^2\rangle P_0 L_s\int_0^\infty r^2\,dr\,C(r)\frac{\sin(Kr)}{Kr} \qquad (4)$$

In this expression, L_s is the sample length, P_0 is the total incident power, and $C(r)$ is the correlation function that characterizes the statistical properties of the grains. This expression, based on the Born approximation, is valid when the length of a typical grain times the difference in the two refractive indices of the anisotropic grain is a small fraction of the wavelength.[8] The grain geometry is described by the *shape factor* $f_i(\mathbf{r})$ defined by

$$f_i(\mathbf{r}) = \begin{cases} 1 & \textit{for } \mathbf{r} \textit{ within ith grain} \\ 0 & \textit{otherwise} \end{cases} \qquad (5)$$

The correlation function is given by

$$C(|\mathbf{r}' - \mathbf{r}''|) = \langle f_i(\mathbf{r}')\, f_i(\mathbf{r}'')\rangle \qquad (6)$$

It depends on the distance $|\mathbf{r}' - \mathbf{r}''|$, having a maximum of unity at $\mathbf{r}' = \mathbf{r}''$ and decreasing to zero as the distance exceeds the characteristic linear dimension of the grains. The parameter K is defined by

$$K = 2k\sin(\theta/2) \qquad (7)$$

The quantity, Δ_i, whose square is averaged in eq 4, is proportional to the component of the polarization induced in the ith grain by the incident field (which is polarized along x) that is perpendicular to the direction of propagation of the scattered ray and is passed by a polarizer in the scattering light path:

$$\Delta_i = \mathbf{a}\cdot(\mathbf{s}\times(\mathbf{s}\times\delta\overset{\leftrightarrow}{\epsilon}(\mathbf{r}_i)\cdot\hat{\mathbf{x}}))/\bar{\epsilon} \qquad (8)$$

where $\mathbf{a}$ is a unit vector along the axis passed by the analyzer, $\mathbf{s}$ is a unit vector in the direction of the scattered light, $\hat{\mathbf{x}}$ is a unit vector in the direction of the incident field polarization, and $\mathbf{r}_i$ is a vector to the interior of the ith grain.

The grain sizes in our sample are large compared to the wavelength, so that the scattered field can be taken as paraxial. Thus, in eq 8, $\mathbf{s}$ can be approximated by a unit vector in the z direction, and we have

$$\langle\Delta^2\rangle = \langle(\delta\epsilon_{y,x})^2\rangle/(\bar{\epsilon})^2 \qquad (9)$$

where y is the analyzer axis.

Since we are dealing with paraxially scattered beams, it is useful to express the scattered intensity in terms of the transverse coordinates, $\rho = [x, y]$, in the detector plane. In the paraxial limit eq 4 can be transformed to

$$\langle I(\rho,L)\rangle = \left(\frac{k^2}{4\pi L}\right)^2\langle\Delta^2\rangle P_0 L_s\int_\infty d\rho'\,C_T(\rho')\,e^{-ik\rho\cdot\rho'/L} \qquad (10)$$

where L is the distance from the sample to the detector plane and the *transverse* correlation function, $C_T(\rho)$, is given by

$$C_T(\rho) = \int_{-\infty}^{\infty} dz\,C(\rho,z) \qquad (11)$$

Integrating the exponential factor in eq 10 over ρ leads to a delta function in ρ' and the total collected power, P, is

$$P = \int_\infty d\rho\,\langle I(\rho,L)\rangle = \frac{k^2}{4}\langle\Delta^2\rangle P_0 L_s C_T(0) \qquad (12)$$

The quantity $C_T(0)$ can be interpreted as a characteristic length of the grains:

$$C_T(0) = 2\int_0^\infty dr\,C(r) \equiv l_{av} \qquad (13)$$

If we substitute eq 13 into eq 12 and use the result[5,7,10]

$$\langle\Delta^2\rangle = \frac{4}{15}\left(\frac{n_e - n_o}{n}\right)^2 \qquad (14)$$

where n_e and n_o are the refractive indices for light polarized parallel and perpendicular to the optic axis of a grain, respectively, we get for the fraction of the incident power transmitted by a crossed polarizer

$$\frac{P}{P_0} = \frac{4\pi^2}{15}(\Delta n)^2\frac{L_s l_{av}}{\lambda_0^2} \qquad (15)$$

where $\Delta n = n_e - n_o$ and λ_0 is the wavelength of the incident light in free space. Equation 15 is the same as the result [eq 8, ref 5] of Balsara et al., which was obtained without accounting for diffraction effects (see Appendix 1).

According to eq 10 the far-field intensity distribution is proportional to the Fourier transform of the transverse correlation function. We can determine the shape of the local transverse correlation function from the inverse transform of the normalized far-field distribution:

$$\frac{C_T(|\rho|)}{C_T(0)} = \frac{\int_\infty d\rho'\,\langle I(\rho',L)\rangle e^{ik\rho\cdot\rho'/L}}{\int_\infty d\rho'\,\langle I(\rho',L)\rangle} \qquad (16)$$

The observed far-field distributions are well approximated by Gaussians. If we assume the form

$$I(\rho,L) = I(0)\,e^{-(1/2)(\rho/w_{\text{far-field}})^2} \qquad (17)$$

the originating correlation function is also a Gaussian given by

$$C(r) = e^{-(1/2)(r/w_{\text{average grain}})^2} \qquad (18)$$

where

$$w_{\text{average grain}} = \frac{\lambda L}{\pi}\frac{1}{w_{\text{far-field}}} \qquad (19)$$

and $\lambda = \lambda_0/n$ is the wavelength of the incident light in the medium. This expression assumes that both source and observation points are in the medium of index n. In practice, the detector is in air, and the sample is immersed in an index-matching fluid that extends beyond the sample to an interface with air. If this interface is in the far field of a typical grain, then the angular spread of the diffracted beam beyond that plane is the same as if a grain of the same size were in air. The effect on eq 19 is to replace λ by λ_0.

The transverse Gaussian correlation function is

$$C_T(\rho) = (2\pi)^{1/2}w_{\text{average grain}}\,e^{-(1/2)(\rho/w_{\text{average grain}})^2} \qquad (20)$$

From eqs 13 and 20, we obtain

$$C_T(0) = (2\pi)^{1/2}w_{\text{average grain}} = l_{av} \qquad (21)$$

Thus we have two independent ways of measuring l_{av}: from the far-field intensity profile using eqs 19 and 21 and from the birefringence measurement using eq 15.

In order to get additional physical insight into the size of the actual grains, we define an equivalent grain shape function, $f_{\text{equiv}}(\mathbf{r})$, as one that leads to the same normalized intensity distribution as the sample grains. The function must satisfy the relation

$$\left[\int d\mathbf{r}'\,f_{\text{equiv}}(\mathbf{r}')\,f_{\text{equiv}}(\mathbf{r}+\mathbf{r}')\right]_{\text{angle average}} = C(r) \qquad (22)$$

The average over angles leads to a transverse correlation

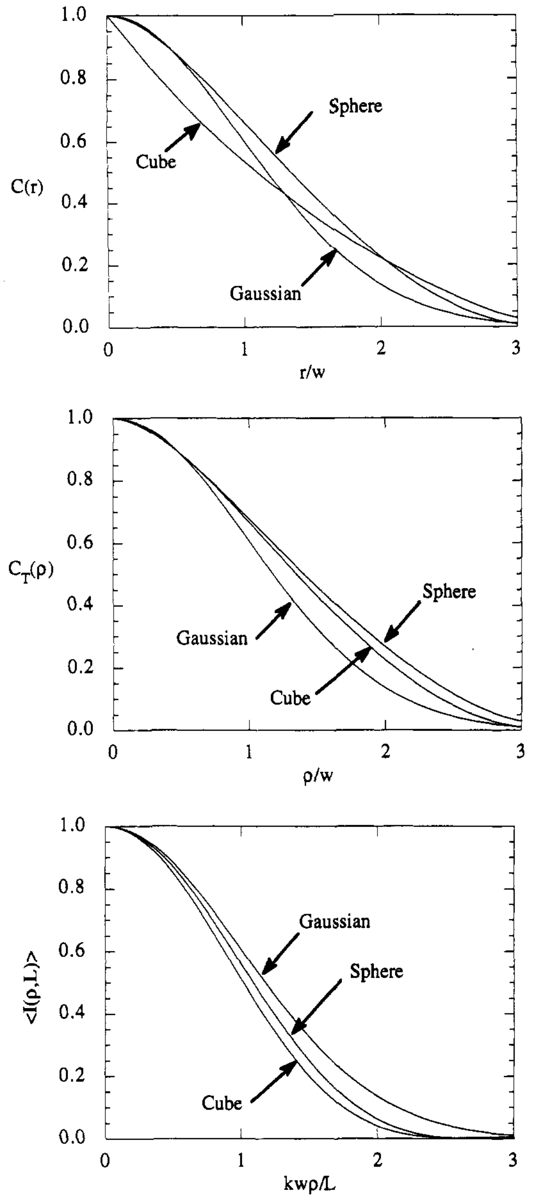

Figure 1. Correlation functions and far-field intensities for Gaussian grains of width w, spherical grains of diameter $3.34w$, and cubic grains of side $2.80w$. (a) Correlation functions. (b) Transverse correlation functions, normalized to unity at $\rho = 0$. (c) Far-field intensities, normalized to unity at $\rho = 0$.

function with azimuthal symmetry. Specific grain dimensions were chosen by requiring that $C_T(0)$, calculated from eq 22, be equal to $C_T(0)$ for a Gaussian of width w. When applied to a sphere of diameter d and a cube of side s, we obtain $d = 1.33l_{av} = 3.34w$ *and* $s = 1.12l_{av} = 2.80w$; $w_{\text{average grain}}$ may be interpreted as roughly one-third the physical dimensions of a grain. In Figure 1a, we plot the correlation functions for the sphere, cube, and Gaussian. In Figure 1b we plot the corresponding transverse correlation functions, and in Figure 1c the corresponding normalized far-field intensity distributions. Although the correlation function for the cube differs in form from that of the sphere and Gaussian, the far-field distributions are all similar in form because the transverse correlation functions are similar. A lack of sensitivity of the far-field intensity distribution to grain shape is evident.

III. Experimental Section

A. Polymer Synthesis. A polystyrene–polyisoprene diblock copolymer was synthesized by anionic polymerization under high vacuum, using *sec*-butyllithium as the initiator and methanol as the terminator. The polystyrene block was synthesized first, followed by the polymerization of the polyisoprene block. An aliquot of the reaction mixture containing poly(styryllithium) precursors of the polystyrene block was isolated and terminated with methanol, before the addition of isoprene. Both reactions were carried out at room temperature, in a 70:30 cyclohexane/benzene mixture. Standard high-vacuum procedures were used to purify the solvents and reagents used in the synthesis.[16] The block copolymer used in this study will be referred to as SI-(7.5–7.5). The numbers in parentheses refer to the molecular weight in thousands of the polystyrene and polyisoprene blocks, respectively.

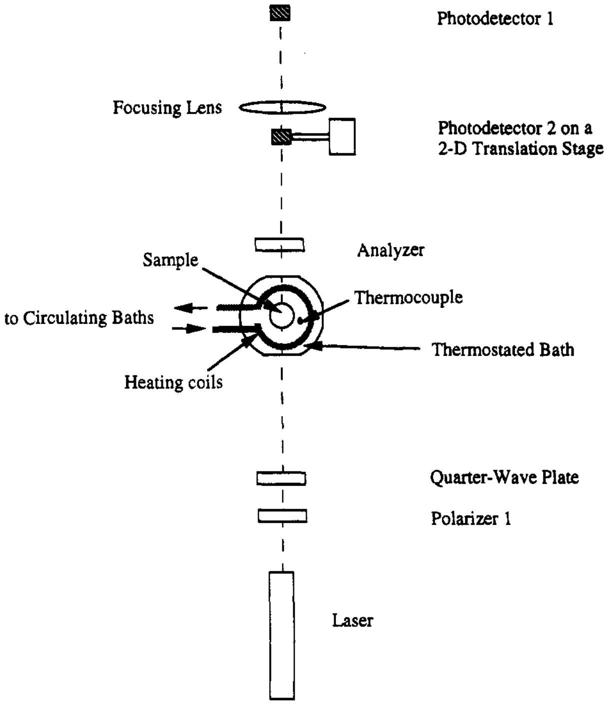

Figure 2. Schematic of experimental setup (top view).

The molecular weight and polydispersity of the polystyrene block were obtained from GPC measurements on the polystyrene precursor. The GPC was calibrated using polystyrene standards. The composition of the block copolymer was obtained by ^{1}H NMR. The polydispersity of the block copolymer was estimated from GPC measurements using the polystyrene calibration curve. The polydispersities of the polystyrene precursors, as well as the block copolymer, were less than 1.06. The reaction conditions used here give a predominantly (93%) 1–4 polyisoprene block.[17] A small amount (<0.5%) of 2,6-di-*tert*-methylphenol was added to the block copolymer to prevent degradation of the polyisoprene block.

B. Optical Measurements. The optical characteristics of an 89.4 wt % solution of SI(7.5–7.5) in toluene were measured to test the theoretical ideas presented in section II. Based on previous experiments on ordered solutions of polystyrene–polyisoprene block copolymers in toluene, we expect the ordered SI(7.5–7.5)/toluene solutions to have a lamellar microstructure.[3,18,19] The order-to-disorder transition temperature, T_{ODT}, of this solution was obtained by methods outlined in ref 3 and was found to be 39.5 ± 0.5 °C.

A schematic of the apparatus used for the optical measurements is shown in Figure 2. A beam of light from a 15-mW HeNe laser ($\lambda_0 = 633$ nm) was directed through a horizontal Glan air-spaced prism polarizer and then through the sample, which was housed in a thermostatted, index-matching fluid bath. A quartz quarter-wave retardation plate (compensator) was placed in the beam path, between the first polarizer and the sample. Initially it was set with its optic axis horizontal, parallel to the incident plane of polarization, and thus it did not alter the polarization of the incident beam. The light exiting the sample passed through a large area, dichroic vertical polarizer (analyzer). The sample was temperature controlled with the help of heating coils connected to circulating fluid baths. The temperature changes were accomplished by switching between two circulating baths set to predetermined temperatures. The polymer solution was contained in a sealed test tube with a path length of 0.74 cm.

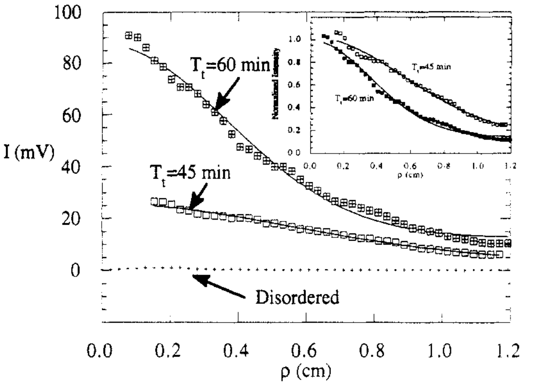

Figure 3. Far-field orthogonally-polarized scattered intensities as a function of the transverse coordinate, ρ. Experimental data, represented by square symbols, are fit to Gaussians (solid lines). Squares represent data for two different tempering times, T_t. The inset shows the same data normalized to unit peak value, making the difference in width more apparent. The plus symbols represent scattering data from a disordered sample.

The experiment consisted of disordering the sample by heating it to 45 °C and then cooling it to 37 °C, which was just below the ODT temperature of the solution. The sample was tempered at 37 °C for a variable length of time and then quenched to 28 °C. The tempering time, T_t, was varied from 30 to 60 min. The birefringence of the sample was monitored throughout the process by collecting the light exiting the analyzer, focusing with a large diameter lens onto a photodiode. The transient signal from photodetector 1 and the sample temperature were fed to a computer (Macintosh II ci) via a LabView data acquisition board.

Cooling the sample to 37 °C caused an increase in the birefringence signal that was qualitatively similar to our earlier measurements.[5] One would expect longer tempering times to lead to larger grains. Our birefringence data are consistent with this expectation. The birefringence signal at 28 °C reached a stable value after about 1 h for all T_t. At that point, the compensator and analyzer were adjusted to minimize the contribution to the transmitted power from bias in grain orientation[4,5] and typically resulted in a 10% decrease in the measured signal. The transverse spatial intensity distribution of the scattered light was obtained by translating photodetector 2 vertically, in steps of 0.25 mm, and recording the output voltage at each location. A 1-mm aperture was attached directly in front of this photodetector. This aperture was large enough to average out the intensity fluctuations due to speckle. The laser beam axis was located by momentarily uncrossing the analyzer and moving the aperture to the point of maximum intensity. The distance from the sample output plane to the detector aperture was 10.5 cm.

IV. Results and Discussion

Typical scattering profiles obtained from the block copolymer solution at 28 °C are shown in Figure 3. The scattered intensity $I(\rho)$ is plotted as a function of ρ, the transverse distance from the beam axis, for T_t = 45 and 60 min. The data obtained from the disordered solution (at 45 °C) are shown for reference. The curves through the data are best fits to a Gaussian profile:

$$I(\rho,L=10.5\text{ cm}) = I_0 e^{-(1/2)(\rho/w_{\text{far-field}})^2} + I_b \qquad (23)$$

I_0, $w_{\text{far-field}}$, and I_b were treated as fitted parameters, and $w_{\text{average grain}}$ was obtained using eq 19.

The scattering profiles obtained from different regions in the sample were nearly identical, with estimates for $w_{\text{far-field}}$ agreeing to within 5%. All scattering profiles appeared to be azimuthally symmetric and consisted of a fine speckle pattern. A small, central bright spot was observed in the scattering pattern from all the ordered solutions; this spot was nearly extinguished after the compensator and the analyzer had been adjusted for minimized transmitted power. That it was not completely extinguished indicates a complexity in the sample that has not been accounted for theoretically. However, the power contained in the minimized central spot was estimated to be less than 1% of the scattered optical power and thus did not introduce significant error in our power measurements. In our fits of the far-field intensity profile, however, we did not include scattering data from the region $0 < \rho < 0.1$ cm.

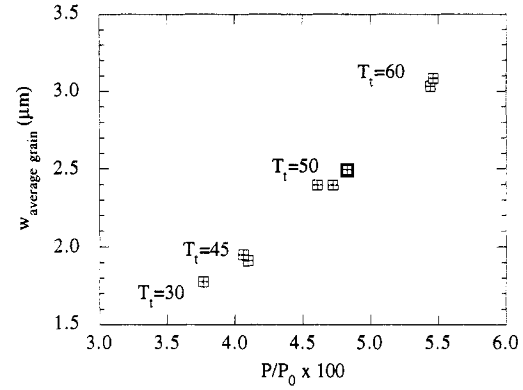

Figure 4. Transverse grain width obtained from diffraction measurement versus fraction of total power transmitted through crossed polarizers. Four groups of points represent different tempering times, T_t. Within each group, a square symbol represents the result of an individual quench, indicating the reproducibility of the measurements.

Table I. Comparison of the Average Grain Sizes Obtained from Birefringence and Diffraction for Different Tempering Times, T_t

	measured grain size (μm)[a]	
T_t (min)	birefringence l_{av}	diffraction $(2\pi)^{1/2} w_{\text{average grain}}$
30	11	8.5
45	12	9.0
50	13	11
60	15	14

[a] The error associated with the measurements is about 5%.

We note that the diffraction measurement provides an estimate of the *transverse* dimensions of a grain, while the birefringence measurement provides an estimate of the *longitudinal* dimensions, although we would expect these two measures to be comparable. The qualitative agreement between the birefringence and the scattering measurements is depicted in Figure 4, where $w_{\text{average grain}}$ is plotted as a function of P/P_0 for all of the quenches. Each data point represents an average of at least two measurements from different regions of the sample. Longer tempering times should lead to larger grains. Both the birefringence and scattering measurements are consistent with this expectation, since l_{av} is proportional to P/P_0. In order to extract a grain size from birefringence measurements, we need an estimate of Δn. In Appendix 2, we estimate it to be 2.7×10^{-4}. To extract a grain size from the diffraction measurements, we use the quantity $(2\pi)^{1/2} w_{\text{average grain}}$ to represent the transverse size of an average grain (see eq 21). In Table I we present both l_{av} and $(2\pi)^{1/2} w_{\text{average grain}}$ as a function of tempering time. Considering the uncertainty in the estimate of Δn and the other approximations involved, the agreement between the two estimates of average grain size is encouraging and suggests the confirmation of the basic features of our model.

V. Concluding Remarks

Expressions relating birefringence and diffraction of light to the structure of ordered block copolymer materials have been derived. The total optical power exiting a sample held between crossed polarizers is shown to be directly proportional to the grain size, while the angular spread of the far-field diffraction pattern is shown to be inversely proportional to the grain size. The former result confirms the conclusion of our earlier study in which diffraction was ignored.[5] Experimental data suggest that these two measures of the grain size are comparable, providing support for the concept of grains in these materials. The diffraction measurement is particularly useful, since it is independent of the strength of the optical anisotropy, Δn. These two measures can together also allow the determination of Δn. (Such a determination is equivalent to the procedure using the Porod invariant described in refs 11 and 20.) If grain sizes are on the order of the wavelength of the light, the scattering is no longer restricted to small angles. In that case, the paraxial approximation is no longer valid. The theory can be easily modified to cover this regime, although the resulting expressions are not as simple. Also, a finite detector aperture would make it experimentally difficult to collect all of the scattered power in a birefringence measurement.

Further information can be extracted from the scattered intensity distributions than we have attempted to demonstrate in this paper. The use of two-dimensional CCD detectors, coupled with two-dimensional Fourier analysis, would allow a more accurate determination of the transverse correlation function. Other polarization components of the scattered field can also be detected and used to probe other phenomena, such as isotropic refractive index fluctuations.[10,11] Such optical measurements may provide new insight into the nature of ordered block copolymer materials, as well as other random anisotropic media. Also, ordered block copolymer systems can provide model materials for testing scattering theories.

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Appendix 1. Relation between $C_T(0)$ and the Average Length of a Grain

To relate the ensemble expectation value, $C_T(0) \equiv l_{av}$, to the corresponding quantity that appears in eq 8 of ref 5, the ensemble average and sum over grains are performed in the reverse order from the calculations which led to eq 4. If we sum over grains before doing the ensemble average and equate the two resultant expressions (which must be equal if the sample is statistically homogeneous and isotropic), we get the relation

$$P_0 L_s l_{av} = \langle \sum_i I_0(\rho_i)\, a_i \overline{l_i^2} \rangle \tag{A1.1}$$

where $I_0(\rho_i)$ is the incident intensity at the location of the ith grain, a_i is the projected area of the ith grain on a plane perpendicular to z, and

$$a_i \overline{l_i^2} = \int \mathrm{d}\rho\, \left(\int \mathrm{d}z\, f_i(\rho,z)\right)^2 \tag{A1.2}$$

The quantity $\overline{l_i^2}$ is the square of the width (along z) across the ith grain averaged over the projected area. If we consider a single column of N grains with equal areas, then we obtain

$$l_{av} = N\langle \overline{l^2} \rangle / L_s \tag{A1.3}$$

which is identical to the expression given in ref 5.

Appendix 2. Estimation of Δn

As has been pointed out in earlier publications,[3-5] Δn has contributions due to intrinsic and form birefringence. Since the ordered solutions were only 11.5 °C below T_{ODT}, we expect form birefringence to dominate. From the work of Amundson et al.[4] and Fredrickson et al.,[21,22] it can be shown that Δn for concentrated block copolymer solutions just below the ODT is given by

$$\Delta n = 0.443\phi^2 (R_g^{\,3} \rho_c)^{-2/3} \Delta n_{ss} \tag{A2.1}$$

where ϕ is the copolymer volume fraction, R_g and ρ_c are the radius of gyration of the copolymer and the number of chains per unit volume, respectively, in the melt, and Δn_{ss} is the form birefringence of a grain in the strong segregation limit. For the system under consideration, we estimate $R_g = 38$ Å, $\rho_c = 3.77 \times 10^{-5}$ chains/Å^3, and $\Delta n_{ss} = 1.25 \times 10^{-3}$. Equation 19 (p 707) of ref 23 for the form birefringence of a lamellar system was used to obtain Δn_{ss}. The refractive indices of the polystyrene-rich and polyisoprene-rich phases were estimated under the assumption that toluene was distributed uniformly in both microphases and that the square of the refractive index of a phase is given by the volume fraction weighted averages of the squares of the refractive indices of the pure compounds. Hence $\Delta n = 2.7 \times 10^{-4}$.

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