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Birefringence Detection of the Order-to-Disorder Transition in Block Copolymer Liquids

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ABSTRACT: The order-to-disorder transition (ODT) in a concentrated solution of a polystyrene–polyisoprene diblock copolymer (molecular weights of the polystyrene and polyisoprene blocks are 1.2×10^4 and 1.9×10^4, respectively) in bis(2-ethylhexyl) phthalate is identified by a discontinuous decrease in the static birefringence of the sample upon heating. The location of the ODT is confirmed by rheological measurements; both the storage and loss moduli of the solution show a sharp decrease at the same temperature. Solutions with concentrations ranging from 48 to 61 wt % polymer were examined with the birefringence technique. The measured ODT temperatures for these solutions range from 27 to 178 °C. Small-angle X-ray scattering measurements at temperatures well below the ODT indicate that the ordered solutions have a lamellar microstructure.

Introduction

The spontaneous assembly of block copolymer molecules into periodic structures with long-range order is a subject of continuing interest.[1] While the characteristics of the ordered structures have been analyzed in considerable detail since the 1960s,[2] there are relatively few data on the transition from the disordered to the ordered state. In a pioneering paper in 1981, Leibler predicted that the order-to-disorder transition (ODT) in diblock copolymer melts would be weakly first order with the exception of symmetric diblocks, i.e., diblocks with equal block lengths.[3] Fredrickson and Helfand showed in a subsequent paper[4] that the ODT for perfectly symmetric diblocks was also weakly first order, due to large-amplitude concentration fluctuations, which were not included in Leibler's treatment.

The first experiments indicating that the ODT might be first order were due to Chung and Gale in 1976.[5] They reported discontinuous changes in the temperature dependence of the rheological properties of a poly(styrene–butadiene–styrene) block copolymer. However, there was no direct evidence that the discontinuity was due to the ODT. Most attempts to identify the transition have been based on conventional probes of structure such as small-angle X-ray scattering (SAXS) and small-angle neutron scattering (SANS), where the formation of periodic structures is inferred from peaks in the scattering profiles.[6] Difficulty in locating the ODT with these methods arises because the disordered state is characterized by concentration fluctuations with roughly the same length scale as the periodic concentration profiles found in the ordered state. Furthermore, the ordered materials are typically "polycrystalline", consisting of randomly-oriented grains; coherent order is restricted to regions within each grain. In the vicinity of the ODT, the experimentally-measured powder-averaged scattering profiles obtained from the polycrystalline samples are similar to those obtained in the disordered state.[6,7] In particular, there is no discontinuity in either $I(q_m)$, the intensity at the peak in the scattering profile, or q_m, the scattering vector at the peak, at the ODT. Early estimates of the location of the transition were based on SAXS measurements, in which the ODT was inferred from changes in the slope of the measured dependence of q_m and $I(q_m)$ on temperature.[6,7]

Experiments proving that the ODT was first order were due to Bates and co-workers and came as late as 1990.[8] "Single crystals" of ordered poly(ethylenepropylene)–poly(ethylethylene) diblocks with a lamellar morphology were prepared by shear orientation. SANS from these samples showed that the azimuthally-asymmetric scattering pattern, characteristic of lamellar single crystals, disappeared abruptly at a certain temperature, giving way to an azimuthally-symmetric peak, characteristic of fluctuations in the disordered state. They also found that the low-frequency storage modulus, G', showed a sharp, discontinuous decrease at the same critical temperature, indicating that the ODT could also be identified by rheological measurements.[9]

Although SANS and rheology have been extremely useful in their ability to determine the ODT unambiguously, there are limitations to the types of samples that can be examined by these techniques. To obtain discontinuous changes in the scattering profiles at the ODT, single-crystal samples are required. Rheological determination of the ODT requires shearing the sample at shear levels dictated by the moduli of the sample and instrumental resolution. The shearing process can disrupt the structure being studied. Furthermore, the discontinuous drop in G' is only evident in a certain frequency window, which is system-dependent.[9] The material chosen for investigation must be such that this window falls within the experimentally accessible frequency range. Since the rheology of ordered block copolymer systems is not yet well understood, it may be difficult to predict where this window might lie. Consequently, there appear to be systems in which the measured rheological response does not change discontinuously at the ODT.[10] In such cases, different interpretations of the rheological data in terms of the ODT are possible.[8,10] Additional methods for locating the ODT could be very useful at this juncture.

In this paper, we present evidence that the ODT is accompanied by a discontinuous decrease in the static birefringence. Birefringence in the ordered state pre-

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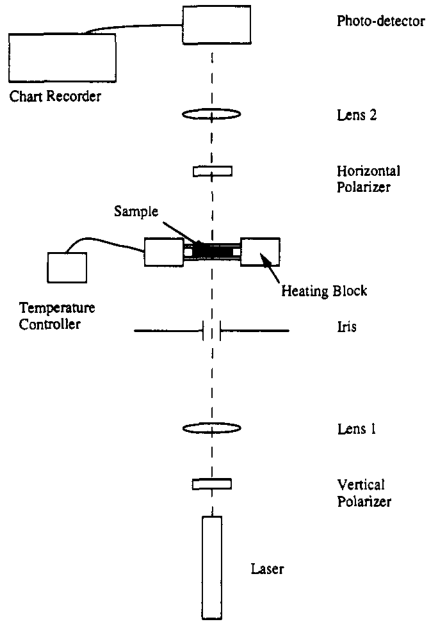

Figure 1. Schematic of the birefringence apparatus used to determine the ODT of the block copolymer solutions.

sumably arises from optical anisotropy within the coherently ordered grains.[11,12] On the other hand, concentration fluctuations in the disordered state are isotropic, and, hence, disordered materials should not be birefringent. Our measurements show that the birefringence of concentrated polystyrene–polyisoprene diblock copolymer solutions decreases discontinuously upon heating beyond a certain temperature, which we identify as the transition temperature from order to disorder. Rheological measurements corroborate this assignment. Both the storage and loss moduli show a discontinuous decrease at the same temperature. SAXS measurements at temperatures well below the ODT indicate that the solutions have a lamellar microstructure. However, the SAXS structure factors of these solutions show no evidence of a first-order transition in the vicinity of the ODT.

Experimental Section

Materials and Sample Preparation. The polystyrene–polyisoprene diblock copolymer used in this study was synthesized by high-vacuum anionic polymerization. Details concerning the synthesis and characterization of this polymer have been reported earlier.[13] The molecular weights of the polystyrene and the high *cis*-1,4-polyisoprene blocks were determined to be 1.2×10^4 and 1.9×10^4, respectively, with polydispersities <1.05, using size exclusion chromatography. The sample is thus designated SI-(12-19). A small amount (<0.5%) of 2,6-di-*tert*-butyl-4-methylphenol was added to prevent degradation of the polyisoprene block. Bis(2-ethylhexyl) phthalate (dioctyl phthalate or DOP) (Aldrich) was washed with aqueous Na_2CO_3 to remove trace acids and vacuum-distilled over $CaCl_2$ at 3 Torr and 200 °C. Solutions of the block copolymer and DOP were prepared using benzene as a cosolvent. After homogenization, the benzene was stripped off in an evacuated desiccator at room temperature. The stripping was stopped when the weight of the remaining solution was slightly less than the sum of the weights of polymer and DOP initially charged (by up to 5%, due to some evaporation of the DOP). This ensures that the remaining solution is essentially benzene-free. (The vapor pressures of benzene and DOP at room temperature differ by 6 orders of magnitude.) Solutions with block copolymer weight fraction, w, ranging from 0.441 to 0.611 were examined. Size exclusion chromatograms of the polymer before and after the experiments showed no evidence of polymer degradation.

Birefringence, Rheology, and SAXS Measurements. A schematic of the apparatus used in the birefringence measurements is shown in Figure 1. The block copolymer solutions were placed between two quartz windows separated by a 1-mm-thick aluminum spacer. A vertically-polarized beam of light from a 15-mW He–Ne laser is directed through the sample, which was housed in an electrically-heated aluminum block. A CN 4700 Omega temperature controller was used to control the sample temperature. Lens 1 was used to diffuse the light beam. Spot sizes at the sample ranging from 2 to 6 mm in diameter were obtained with the help of the iris. The light exiting the sample passes through a horizontal polarizer and is focused onto a photodetector using lens 2. The output of the detector is fed to a chart recorder. The experiment consists of increasing the sample temperature in a stepwise fashion and recording the photodetector output.

The rheological measurements were performed on a Rheometrics RMS 800 instrument, using 50-mm-diameter parallel plates and a fluids transducer, which can resolve torques ranging from 0.1 to 100 gm-cm. Strains of 1% were applied in all the measurements. In some cases, a 2% strain was applied to check for linearity of the viscoelastic response. In all cases, G' and G'' obtained from the two strain levels agreed to within 10%.

The small-angle X-ray scattering experiments were carried out at the Exxon Corporate Research Laboratory using an 18-kW rotating-anode X-ray generator (Rigaku RU300). The monochromator consisted of a vertically-bent pyrolitic graphite (002) crystal which focused the Cu K_α line on the sample. A combination of horizontal and vertical slits was used to define the resolution of the spectrometer and to cut down on tail-scattering of the direct beam. The angular width of the direct beam was $\Delta(2q) = 0.1°$ fwhm (full width at half-maximum), which at small angles corresponds to a width in reciprocal space of $\Delta q \approx (2\pi/\lambda)\Delta(\theta) = 0.00716$ Å^{-1}, where θ is the scattering angle and λ is the wavelength of the X-rays. The in-plane longitudinal and transverse resolutions are given by $\Delta q_h = \Delta q \cos(\theta/2)$ and $\Delta q_k = \Delta q \sin(\theta/2)$. The out-of-plane transverse resolution was set by slits to be $\Delta q_l = 0.13$ Å^{-1}. This configuration allowed us to probe reciprocal space with wave vectors $q = 4\pi/\lambda \sin(\theta/2)$ as small as 0.01 Å^{-1}. The details of the spectrometer and the oven used in the experiments are published elsewhere.[14] The polymer solutions were contained in 10-mm-diameter cylindrical cells with Kapton windows.[15] Sample thickness ranged from 0.8 to 1.5 mm, corresponding approximately to the $1/e$ absorption length for the 8-keV photons.

Results and Discussion

1. Small-Angle X-ray Scattering. Longitudinal SAXS scans through the sample with $w = 0.611$ are shown in Figure 2 as a function of temperature, where intensity is plotted versus q. Figure 2a (top) shows the raw data together with the background, while the background-subtracted data are given in Figure 2b (bottom). The increase in the background at low q is due to the proximity of the detector to the main beam and small-angle scattering from the cell windows. However, the scattered intensity from the samples is typically 5 times larger than the background. Errors due to counting statistics are <1% in the low-q region and smaller than the size of the data points. The two peaks in the scattering curves at 30 and 64 °C are consistent with the first two harmonics of the structure factor of a lamellar phase. The intensity of the second harmonic weakens with increasing temperature and becomes vanishingly small at 111 °C. Figure 3 shows similar plots for the sample with $w = 0.508$. The higher harmonics expected from a lamellar microstructure are not observed in this case at temperatures ranging from 55 to 99 °C.

On the basis of the SAXS data we conclude that ordered solutions have a lamellar microstructure with a spatial period, $d = 2\pi/q_m \approx 370$ Å. (Note that q_m is weakly dependent on concentration and temperature.) We have strong evidence that the solution with $w = 0.611$ is ordered at temperatures below 64 °C. However, it is not clear if the peak in the structure factor observed at 110 °C ($w =$

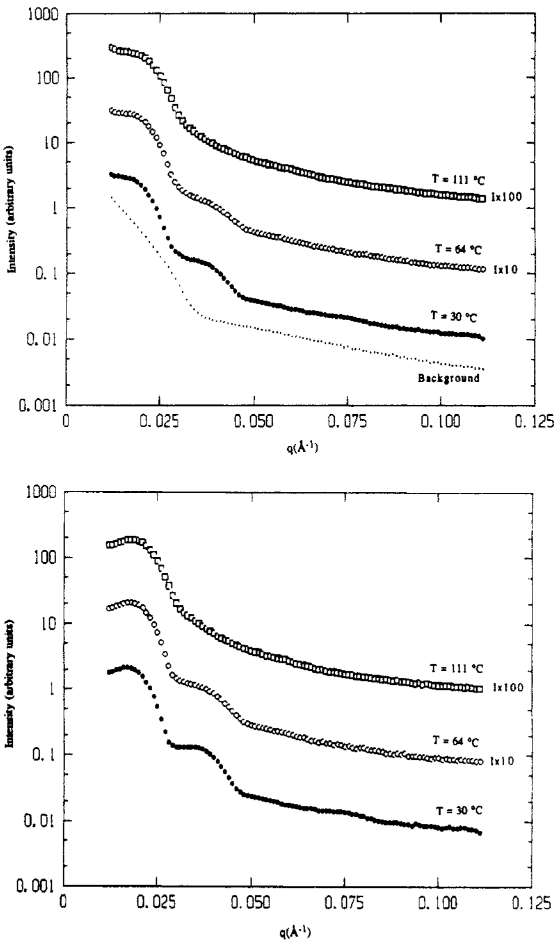

Figure 2. SAXS data from solutions with $w = 0.611$: (a, top) raw scattering data and background scattering; (b, bottom) scattering data corrected for background scattering. The temperatures corresponding to each data set are shown in the figure. The scattering data obtained at different temperatures are shifted vertically for clarity.

0.611) arises from long-range order with the second harmonic disappearing as expected in systems with weakly first-order melting transitions[16] or is due to disordered concentration fluctuations. Similarly, it is not clear whether the solution with $w = 0.508$ is ordered at temperatures between 55 and 99 °C. The experiments described below are aimed at resolving this issue.

The SAXS profiles presented in this section are similar to those obtained from toluene solutions of SI(12-19), which have been reported in previous publications.[13,17]

2. Birefringence. We define a time-dependent birefringence signal, $B(t)$, as

$$B(t) = \frac{V_{\text{sample}}(t) - V_{\text{empty}}}{V_{\text{empty}}} \qquad (1)$$

V_{sample} and V_{empty} are the photodetector outputs with and without the sample. $B(t)$ data obtained from the $w = 0.508$ solution, following a series of temperature jumps, are plotted in Figure 4. The initial and final temperatures for each data set are indicated in the figure. Time zero is defined as the time at which the set point on the temperature controller was changed. It took approximately 3 min for the sample to equilibrate after a 10 °C change in the set point. The sample was allowed to equilibrate at each temperature for at least 15 min.

Raising the sample temperature from 30 to 40 °C results in a decrease in the birefringence, which we attribute to a reorganization of the microstructure in the illuminated part of the sample. For this particular quench, $B(t)$

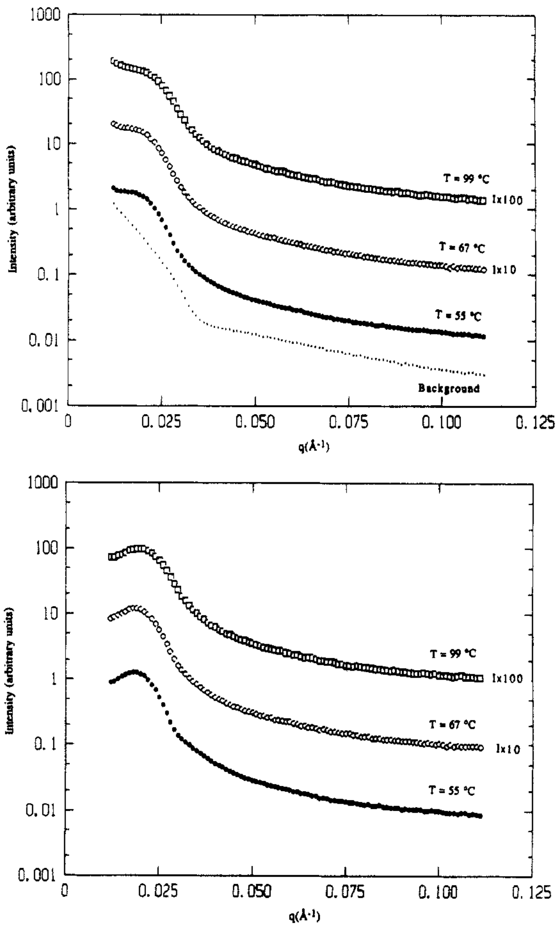

Figure 3. SAXS data from solutions with $w = 0.508$: (a, top) raw scattering data and background scattering; (b, bottom) scattering data corrected for background scattering. The temperatures corresponding to each data set are shown in the figure. The scattering data obtained at different temperatures are shifted vertically for clarity.

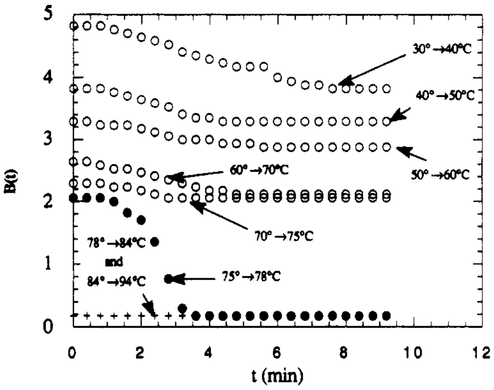

Figure 4. $B(t)$ versus t obtained from solution with $w = 0.508$ immediately after increasing the sample temperature. The initial and final temperatures °C, corresponding to each data set, are indicated in the figure. Open circles represent data obtained from ordered systems. Filled circles represent data obtained from the sample near the ODT. Pluses represent data from disordered systems.

appears to reach an asymptotic value, B_∞, in about 7 min. Subsequent changes in temperature from 40 to 50 °C, 50 to 60 °C, 60 to 70 °C, and 70 to 75 °C resulted in qualitatively similar responses, i.e., $B(t)$ decreasing initially, eventually reaching a finite, asymptotic value. The feature that distinguishes the 75 to 78 °C quench from the above-mentioned quenches is that B_∞ is an order of magnitude lower than that obtained from the solutions below 75 °C. Furthermore, $B(t)$ is not affected by subsequent increases in sample temperature from 78 to

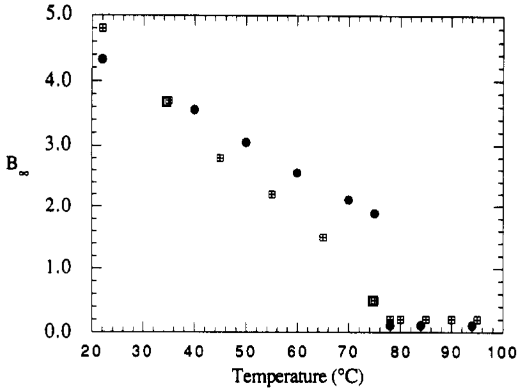

Figure 5. Dependence of B_∞ on temperature from two runs on the solution with $w = 0.508$: filled circles, run 1; hatched squares, run 2.

84 °C and 84 to 94 °C. On the basis of these observations, we conclude that the coherently-ordered grains, responsible for the measured birefringence, disappear between 75 and 78 °C. The ODT for this sample thus occurs at 77 ± 2 °C. The fact that B_∞ is not identically zero in the disordered state could be due to optical imperfections in the sample and optical elements or some residual birefringence that might persist in the disordered state. We define B_0 to be the birefringence of the sample at temperatures above the ODT.

The signal reaching the detector is a measure of the net retardation of the light due to all coherently-ordered grains in the illuminated part of the sample. The summation of the retardations from multiple grains is nontrivial because the principal optical axes of the different grains are not aligned. Thus, light passing through different regions of the sample will be retarded to different extents, depending on the particular properties of the grains that are encountered. There are two possible contributions to the static birefringence of each grain: form birefringence, due to the alternating polystyrene- and polyisoprene-rich domains, and intrinsic birefringence, due to both orientation of the block end-to-end vectors and stretching of the polymer chains in the direction perpendicular to the lamellae. Both contributions should diminish when the material becomes disordered. Folkes and Keller measured the static birefringence of "single crystals" of ordered poly(styrene–butadiene–styrene) block copolymers. In the case of a cylindrical microstructure, the observed signal was in reasonable agreement with theoretical estimates based on form birefringence alone.[11] However, for a lamellar microstructure, roughly comparable contributions from form and intrinsic birefringence were inferred.[18] Recently, Lodge and Fredrickson derived expressions for the intrinsic birefringence of block copolymer microstructures.[19] For the sample examined here, they conclude that the form birefringence should be larger than the intrinsic birefringence by a factor of approximately 3.

The effective retardation due to each grain depends on the orientation of the lamellae relative to the polarization of the incident beam, and therefore it is not surprising that the magnitude of B varies from place to place in a polycrystalline sample. Furthermore, as the waist of the transmitted beam exceeds the typical grain dimension, portions of the beam will experience a different net change in polarization, and the transmitted beam will reflect a mixed polarization state. Hence it is important that the illuminated part of the sample remain constant during each experiment. The temperature dependence of B_∞ obtained from two different experiments on the $w = 0.508$ solution is shown in Figure 5. After the sample was heated to 94 °C in run 1, it was cooled to room temperature and a different spot was examined 2 weeks later. The discontinuity in the birefringence is more clearly evident in run 1 than in run 2. Since $B(t)$ depends on the relative orientation between the lamellae and the plane of polarization, it is possible to "freeze-in" ordered states with relatively low birefringence, as was the case in run 2 at 75 °C. It is difficult to predict the exact temperature dependence of the birefringence because it depends on the response of the lamellae to temperature jumps. The problem is complicated because the chemical composition of the lamellae as well as their orientation could change as a result of the step change in temperature. It is thus best to repeat the measurements until an unambiguous discontinuity is observed. The sample with $w = 0.508$ was run five times. The data obtained in run 2 represents the smallest drop in B_∞ at the ODT. Note, however, that the temperature jump which results in $B_\infty = B_0$ is the same in both experiments. The ODT temperature, T_{ODT}, reported in this study is defined as the midpoint of the temperature jump which results in $B_\infty = B_0 \approx 0$.

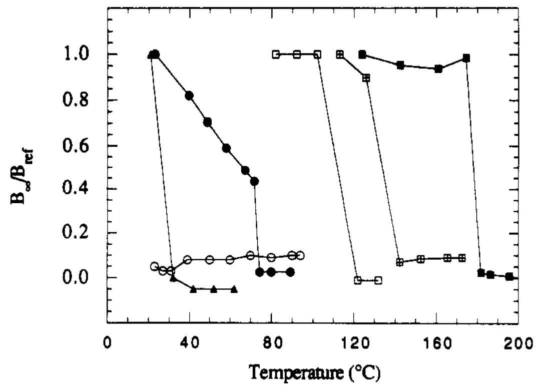

Figure 6. Normalized B_∞ versus temperature for the block copolymer solutions. The B_∞ data obtained from each solution are normalized by a constant B_{ref}, so that all the data could be presented on one plot. Open circles, $w = 0.441$, $B_{ref} = 1.0$; filled triangles, $w = 0.477$, $B_{ref} = 0.8$; filled circles, $w = 0.508$, $B_{ref} = 4.3$, open squares, $w = 0.559$, $B_{ref} = 8.7$; hatched squares, $w = 0.557$, $B_{ref} = 20.0$; filled squares, $w = 0.661$, $B_{ref} = 6.5$. The lines through each data set are meant to serve as a visual guide.

T_{ODT} values of solutions with $w = 0.441$, 0.477, 0.557, 0.559, and 0.611 were inferred from experiments similar to those described above. Each sample was run at least 2 times. In each case the inferred ODTs from both runs were within experimental uncertainty, which is assumed to be the width of the temperature jump resulting in $B_\infty = B_0$. Typical birefringence data obtained from the six solutions are shown in Figure 6. The lack of an appreciable signal from the $w = 0.441$ solution at temperatures ranging from 23 to 94 °C leads to the conclusion that this material is disordered throughout the observed temperature range. All other solutions show a discontinuous decrease in the birefringence at temperatures above room temperature. As might be expected, the time required for the birefringence to reach a stable value (B_∞) after a temperature jump increased with increasing polymer concentration. For the sample with $w = 0.611$, for example, the disappearance of the birefringence took 90 min when it was heated from 174 to 182 °C. The results of the birefringence experiments are summarized in Table I. where T_{ODT} is given as a function of w.

3. Rheology. The rheological properties of the solution with $w = 0.508$ are shown in Figure 7, where G' and G'' are plotted as functions of frequency, ω, for different temperatures. No horizontal or vertical shifts have been applied to the data. At temperatures below 73 °C, the solution exhibits complex rheological behavior, typical of

Table I
ODT Temperatures Determined by Birefringence Measurements

wt fraction of polymer	T_{ODT} (°C)	wt fraction of polymer	T_{ODT} (°C)
0.441	≤23	0.557	134 ± 8
0.477	27 ± 5	0.559	117 ± 4
0.508	77 ± 2	0.611	178 ± 4

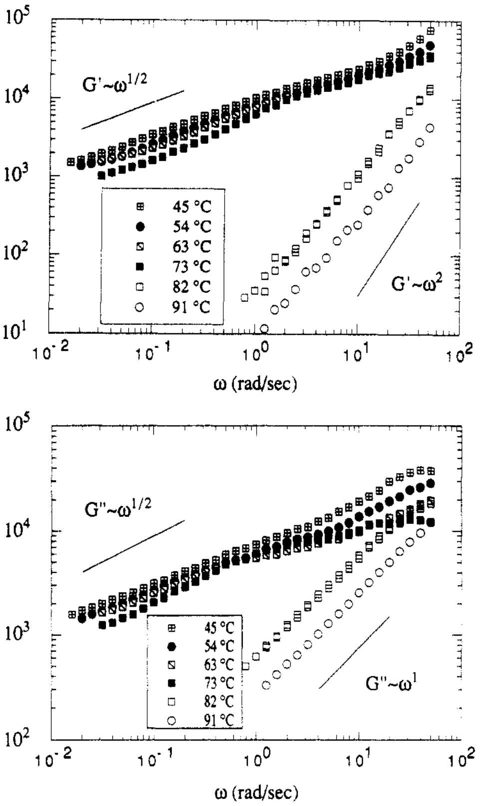

Figure 7. Rheological properties as a function of frequency, ω, for a solution with $w = 0.508$ at different temperatures: (a, top) storage modulus, G'; (b, bottom) loss modulus, G''. The solid lines represent the typical scaling behavior of the moduli at low frequencies in ordered and disordered systems.

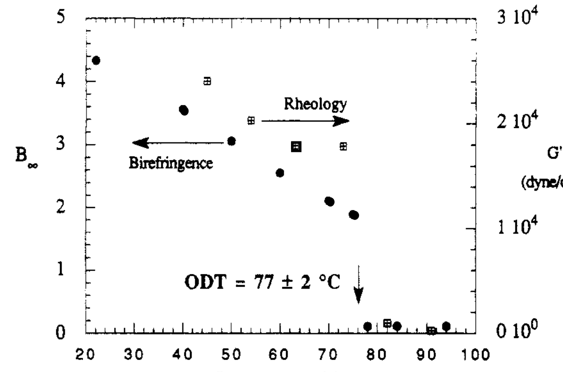

Figure 8. Comparison between birefringence and rheological data (G' at $\omega = 10$ rad/s) obtained from the solution with $w = 0.508$.

ordered block copolymer liquids;[9] G' and G'' scale approximately with $\omega^{1/2}$ at low frequencies. There is a dramatic change in G' and G'' when the sample temperature is changed from 73 to 82 °C, which we attribute to the ODT. The rheological response of the solution above the ODT is similar to that of a "simple" viscoelastic liquid, with $G'' \sim \omega^1$ at low frequencies. Slight deviations from the expected $G' \sim \omega^2$ scaling in Figure 7 (top) are probably due to instrumental limitations in resolving the elastic and viscous responses of a liquid with $G'' \gg G'$. In Figure 8, we compare the temperature dependence of G' at $\omega = 10$ rad/s with one of the B_∞ versus T trajectories obtained from the same sample. It is evident that the two sets of data are consistent with the assignment of 77 ± 2 °C as the ODT temperature for the sample.

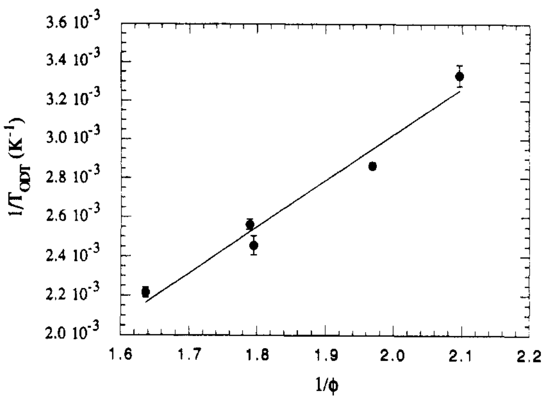

Figure 9. $1/T_{ODT}$ versus $1/\phi$ for the block copolymer solutions.

4. Comparison with Theory. Direct extension of Leibler's theory[3] to concentrated solutions of AB diblock copolymers in a neutral solvent suggests that the ODT occurs when the product $\chi(N_A + N_B)\phi$ reaches a critical value, c, which depends on the composition of the block copolymer,[20] χ is the Flory–Huggins interaction parameter between A and B monomers, N_A and N_B are the number of A and B monomers in a chain, and ϕ is the polymer volume fraction. For the present system, $N_A = 114$, $N_B = 279$, and $c = 15$.[3,21] If we make the usual assumption that $\chi = \alpha/T + \beta$, where α and β are system-dependent constants, then $1/T_{ODT}$ should scale linearly with $1/\phi$.

$$\frac{1}{T_{ODT}} = \frac{c}{\alpha(N_A + N_B)}\left(\frac{1}{\phi}\right) - \frac{\beta}{\alpha} \tag{2}$$

The ODT data obtained from the block copolymer solutions are consistent with eq 2, as demonstrated in Figure 9, where $1/T_{ODT}$ is plotted as a function of $1/\phi$. The solid line represents the best linear fit through the data from which we estimate $\alpha = 16$ K and $\beta = 0.03$. Hashimoto and co-workers have estimated χ between polystyrene and high *cis*-1,4-polyisoprene by fitting the measured SAXS profiles from disordered SI/DOP solutions and bulk SI polymers to Leibler's prediction for the scattering function.[22,23] They obtained α and β values ranging from 13 to 39 K and from −0.040 to +0.002, respectively.

Concluding Remarks

We have demonstrated a new and simple way to identify the order-to-disorder transition in block copolymer liquids. Our experiments show that the static birefringence of lamellar solutions of a polystyrene–polyisoprene diblock copolymer in DOP decreases abruptly upon heating beyond a certain critical temperature. We attribute this disappearance to the order-to-disorder transition. The transition temperatures of solutions with w ranging from 0.477 to 0.611 were estimated from birefringence measurements and were found to be in agreement with theoretical expectations. The transition temperature for the $w = 0.508$ solution was confirmed by rheological measurements. The storage and loss moduli of the solution showed a discontinuous decrease when the temperature was changed from 73 to 82 °C. Birefringence measurements on the same solution gave $T_{ODT} = 77 \pm 2$ °C. On the other hand, the SAXS data from this solution below and above the ODT showed no evidence of a first-order transition.

In principle, the retardation measured in the optical experiments could be caused by phenomena other than linear birefringence, such as dichroism, multiple scattering, or optical activity. However, on the basis of our knowledge of the microstructure of the samples and their chemical composition and the wavelength of the incident light, birefringence is the most likely explanation for the measured signal. It is difficult to envision a mechanism by which the dichroism, the scattered light, or the optical activity in our samples would show a dramatic decrease at the same temperature at which a sharp change in the rheological properties is detected. Furthermore, calculations indicate that both the form[18] and intrinsic[19] birefringence of a poly(styrene–isoprene) lamellar grain are substantial (of the order of 10^{-3}). Also, birefringence has been used to probe order-to-disorder transitions in other self-assembling systems such as liquid crystals and surfactant solutions.[24]

To our knowledge, birefringence is the only probe that registers a discontinuous change in the signal at the order-to-disorder transition in quiescent block copolymer liquids. The experimental setup is simple and inexpensive when compared to SAXS, SANS, or rheology. The simplicity of birefringence measurements was recognized earlier by Pakula et al. in their study of shear-oriented block copolymers.[25] This technique has the potential of being applied to any microstructured block copolymer; even samples that exhibit little or no form birefringence should have a measureable intrinsic birefringence.[19]

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