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Pattern and Segment Relaxation in a Block Copolymer Melt following Step Shear Flow

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ABSTRACT: The relaxation dynamics of a homogeneous poly(styrene)-poly(butadiene) star diblock copolymer melt following step shear flow is studied as its temperature is lowered through the microphase separation temperature (MST). Transient Raman scattering, birefringence, and mechanical rheometry measurements are used to investigate segment and composition pattern relaxation dynamics. The birefringence was determined to be primarily form birefringence, and its relaxation rate was found to decrease dramatically in the vicinity of the MST. At temperatures close to the MST, the shear stress, first normal stress difference, and segment orientation anisotropy (from Raman scattering measurements) relaxation rates also decreased. Slowing down of the first normal stress difference and segment orientation anisotropy relaxations was found to be less dramatic than that of the birefringence relaxation but more pronounced than that of the shear stress relaxation. A decrease in the relaxation rate of segment orientation anisotropy close to the MST is proposed to result from the coupling of segmental and composition pattern relaxations due to tethering of chain segments to the domain interface.

1. Introduction

When heterogeneous materials such as block copolymers are subjected to flow, the rheological functions display strong temperature-dependent responses that are invariably complex. This complexity is known to result from the participation of structural features on a variety of length scales in the overall rheology. This situation is perhaps best demonstrated in the relaxation of block copolymer melts following step shear flow. In a step shear relaxation experiment, a polymer specimen is subjected to an instantaneous strain and its time-dependent rheological response monitored. This is usually done by measuring stress, birefringence, or some other time-dependent indicator of the configuration distribution of structural units. Steps deformations are unique rheological experiments because the time scale of flow is sufficiently small that structural features on all length scales are perturbed simultaneously.[1,2] The ensuing relaxation therefore reflects the collection of time scales present in the fluid and is usually complex.[3,4]

Spectroscopic rheometric techniques that are capable of isolating the dynamics of selected components in such systems allow for the unraveling of rheological complexity. In this paper, we use Raman scattering spectroscopy to uncouple segmental dynamics from the overall flow response of a poly(styrene)-poly(butadiene) (PS-PBD) block copolymer melt. In addition, simultaneous birefringence measurements are used to investigate the relaxation dynamics of composition fluctuations, and shear and normal stress measurements are used to study bulk rheology. In this study we specifically seek to investigate the effect of the appearance of microphase structure on material properties as the sample temperature is lowered through its microphase separation temperature T_{MST}.

Sources of form and intrinsic birefringence in quiescent block copolymer melts below the MST have been considered previously.[5] At temperatures above the MST, these sources of optical anisotropy are anticipated to either vanish or at most be of negligible magnitude and are replaced by flow-induced anisotropies: intrinsic birefringence resulting from flow-induced orientation of molecular segments and form birefringence from similar orientation of composition fluctuations. In block copolymer melts, such fluctuations (excursions of the local concentration of species from their average values) are expected to become pronounced as the MST is approached. Studies of low molecular weight fluids and binary homopolymer mixtures reveal that as the quiescent cloud-point temperature is approached composition fluctuations made anisotropic by flow regain their equilibrium, random configurations after progressively longer periods of time due to critical slowing down.[6-8] Evidence for similar slowing down also exists in block copolymer dynamics;[8,9] little is known, however, about how proximity to the MST affects block copolymer dynamics following step shear flow.

In the following sections, we study the relaxation dynamics of a PS-PBD block copolymer melt following a single 16% step shear strain. The relaxation of this material is monitored using birefringence. Raman scattering, shear stress, and normal stress difference measurements. As the MST is approached, all of these measurements are expected to be sensitive to the orientation/relaxation of polymer strands and the relaxation of the underlying composition pattern. Form birefringence relaxation, however, results directly from pattern relaxation, and it is therefore anticipated to be most affected by the flow dynamics of composition fluctuations. Moreover, tethering of block copolymer segments to the interface separating domains is anticipated to cause segment relaxation following cessation of flow to be frustrated by slower composition pattern relaxation. Therefore, Raman scattering measurements though only directly sensitive to the orientation/relaxation of polymer chain segments can be affected by pattern relaxation.

2. Experiment

2.1. Sample. The material used in this study was a PS-PBD six-arm star diblock copolymer melt. This copolymer is a research-grade material provided by the Shell Development Co. and has a molecular weight of 27 800 (GPC) per arm, a polydispersity index $(\bar{M}_w/\bar{M}_n)|_{\mathrm{arm}}$ of 1.3, and a styrene content of 30 wt %. The PBD units comprised the inner region of each arm. Static birefringence[5] and low-frequency oscillatory shear measurements[10] revealed that this material disorders at a temperature between 145 and 149 °C, and the mean-field estimate

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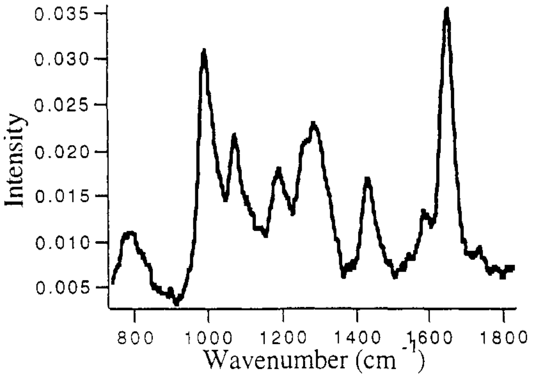

Figure 1. Raman spectrum of a PS–PBD star diblock copolymer melt.

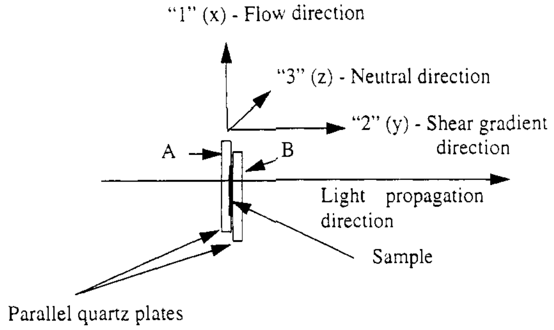

Figure 2. Schematic of shear cell highlighting experimental geometry for optical measurements probing segmental orientation in the 1–3 plane.

of its spinodal temperature is around 135 °C, only some 10–20 °C from the MST.[10,11] Both the MST and mean-field estimate of the spinodal temperature are therefore located well above the glass transition temperature (95 °C) of the material. Electron micrographs obtained from oriented PS–PBD monodomains indicated that the domain structure in the ordered phase consists of PS cylinders in a PBD matrix.[11]

Film specimens approximately 2 mm thick were used for the Raman scattering and birefringence measurements, while specimens 1.2 mm thick were used for the mechanical rheometry experiments. All samples were prepared by solvent casting from a 10 wt % toluene solution containing about 1% Irganox 1010 antioxidant (Ciba Geigy Corp.). Solvent casting was performed at 50 °C using a slow-evaporation technique.

A Raman spectrum of our PS–PBD star diblock copolymer is presented in Figure 1. A number of relatively intense Raman peaks are readily apparent. The Raman peak at 1029 cm^{-1} is characteristic of the C–C aromatic–aliphatic stretching vibration which is unique to the PS block in the present PS–PBD block copolymer. On the other hand, the relatively isolated Raman peak at 1620 cm^{-1} is assigned to the C=C symmetric stretching vibration[12,13] and is characteristic of the PBD block. In ref 5 it was shown that below the MST both Raman peaks could be used to determine static orientation of chain segments in the respective blocks. In the present study, however, only the Raman scattered radiation resulting from the symmetric stretch of carbon–carbon double bonds was found to be appropriate for monitoring transient relaxation of copolymer chain segments following step shear flow. Thus, it was only possible to recover transient segmental orientation information about PBD units. The better quality of the Raman scattered radiation obtained from the C=C stretch presumably results from the slower relaxation of PBD units, compared to the relaxation of the PS segments. Since PBD units comprise the core of the present star block copolymer in the microphase-separated state, PBD units are tethered at both ends and are therefore expected to be most frustrated by the appearance of the microphase pattern, as temperature is lowered through the MST.

2.2. Method. Experimental temperatures were selected to cover a 50 °C range that bracketed the MST. To minimize mechanical history effects, experiments at each temperature were preceded by a quench from the homogeneous phase (30 °C above the apparent MST). The quenched material was allowed to equilibrate before measurements were performed. Equilibration times ranged from 30 min to 2 h and were determined by observing the time required by the birefringence of the quenched material to stabilize.

A plane–Couette flow device was used to generate shear flow in the birefringence and Raman scattering experiments. This device is depicted in Figure 2 and consisted of two quartz plates, between which the sample was sandwiched. These plates were glued to aluminum blocks which were attached to the opposing platforms of a simple translation stage. Step shear was generated by rapidly moving the upper platform "A" relative to the lower one "B" using a computer-controlled stepper motor. A constant strain amplitude of 16% strain was used in all experiments. This arrangement permitted birefringence measurements in the so-called 1–3 plane (Figure 2) and forward Raman scattering measurements to be made simultaneously. Experiments were conducted under a blanket of nitrogen to avoid oxidative degradation of the C=C units in the PBD block.

2.2.1. Stress Measurements. The first normal stress difference and shear stress were measured using a Rheometrics RDA (II) dynamic analyzer. All experiments were performed using 25-mm-diameter parallel disk fixtures. In these experiments, samples were subjected to step strains of 16% and the shear stress and normal stress difference relaxations were monitored as functions of time. As in the birefringence experiments, each measurement was preceded by a quench from the disordered phase.

2.2.2. Raman Scattering and Birefringence Measurements. An experimental arrangement for investigating transient segment orientation in polymeric materials using simultaneous Raman scattering and birefringence measurements has been presented elsewhere.[14] Briefly, this technique involves transient measurement of the Raman scattered polarizations that result from the interaction between polarization-modulated laser light and normal molecular vibration modes present in materials subjected to flow. It can be shown that the Fourier components of the modulation present in the Raman scattered intensity from a given vibration mode are related to the second and fourth moment of the orientation distribution of chain segment vectors and to the birefringence of the material. As pointed out in ref 14, one Fourier component, namely, $I_{2\omega}$, is proportional to a linear combination of the second and fourth moment orientation anisotropies,

$$I_{2\omega} = \frac{1}{2}\langle {\alpha_{xx}}^2 - {\alpha_{zz}}^2 \rangle = \eta^2 I_0 \hat{\epsilon}\left(\langle {u_x}^2 - {u_z}^2 \rangle + \frac{\hat{\epsilon}}{2}\langle {u_x}^4 - {u_z}^4 \rangle \right) \quad (1)$$

Here ω is the polarization-modulation frequency; I_0 is the incident laser intensity multiplied by an instrumental factor; η and $\hat{\epsilon}$ are spectroscopic parameters, which, for a particular vibration mode, depend on the principal values of the Raman tensor and the orientation of the vibration mode with respect to the long segment axis. It can be shown that $I_{2\omega}$ is a monotonic function of segmental orientation, which assumes limiting values of zero for a random distribution of segment vectors and $\eta^2 I_0 \hat{\epsilon}(1 + \hat{\epsilon}/2)$ in the fully aligned state.[11] The $I_{2\omega}$ Fourier component may therefore be used to monitor transient orientation/relaxation of polymer chain segments following small-amplitude step shear flow.

Raman scattering offers another advantage for studying PS–PBD block copolymer melts. This concerns the degradation of the C=C groups at elevated temperatures in the presence of oxygen. The mechanism by which such degradation occurs is well understood and involves the oxidation of carbon–carbon double bonds.[25] By monitoring the intensity of the Raman scattered radiation resulting from the ν_s vibration of these bonds, it was possible to design the sample environment to virtually eliminate degradation during our experiments.

As pointed out earlier, the Raman scattering experimental arrangement also allows for the simultaneous measurement of birefringence. Birefringence relaxation and segmental relaxation can, therefore, be investigated simultaneously, which is useful in the present study because as the MST is approached the birefringence is anticipated to contain both intrinsic and form

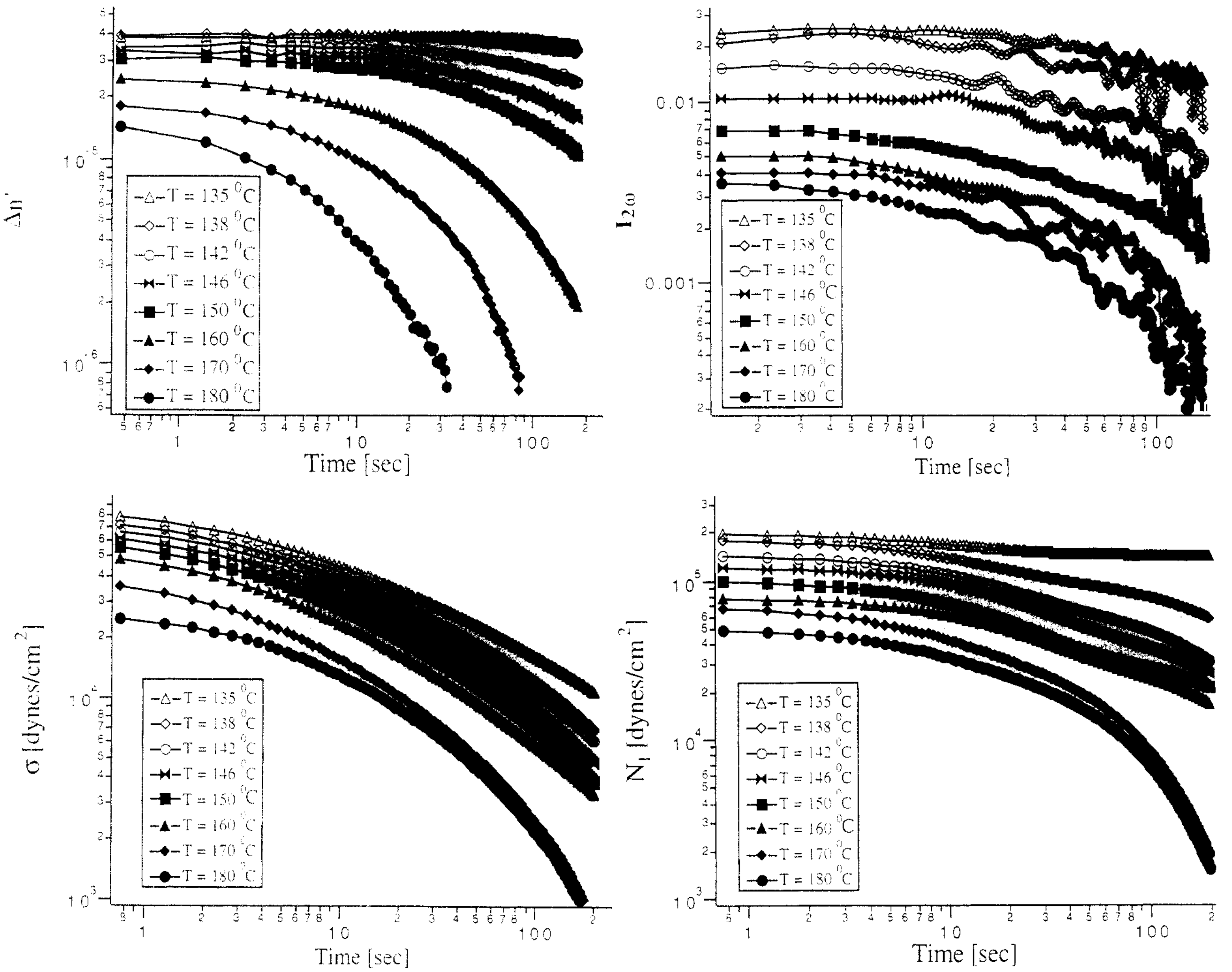

Figure 3. (a) Birefringence relaxation following step shear of PS–PBD at temperatures ranging from 135 to 180 °C. (b) Relaxation of poly(butadiene) segments in PS–PBD following step shear at temperatures ranging from 135 to 180 °C. (c) Shear stress relaxation following step shear of PS–PBD at temperatures ranging from 135 to 180 °C. (d) Relaxation of first normal stress difference following step shear of PS–PBD at temperatures ranging from 135 to 180 °C.

contributions. The intrinsic contribution results from time-dependent changes in the orientation of polymer chain segments and the form contribution from similar changes in the composition pattern.

At temperatures above the glass transition temperature of poly(styrene), the intrinsic segment polarizability anisotropy of PS units is negative[15] and that of PBD units is small and positive.[24] The net effect, assuming additivity of segment polarizabilities,[16,17] is that the overall segment polarizability anisotropy for the copolymer composition used in this study is weakly negative. The intrinsic birefringence of our PS–PBD block copolymer is therefore anticipated to be negative. On the other hand, form birefringence is by definition positive.[18] As a result, depending on the relative magnitudes of the intrinsic and form contributions, the overall birefringence may be either negative or positive. At temperatures well above the MST, chain segments of opposite types mix intimately and one would therefore expect the form contribution to be vanishingly small. The net birefringence resulting from a step strain should therefore be negative. However, as the MST is approached the form contribution is expected to increase. If this increase is sufficiently large, the overall birefringence may be observed to change sign.

In the Results and Discussion section it will be shown that our birefringence measurements following step shear flow yield large positive values for the birefringence retardation at all temperatures considered in this study. This contradicts the expections presented above and appears to imply that significant flow-induced form birefringence is present even at temperatures well into the so-called disordered phase. Since form birefringence in block copolymer systems results from local composition fluctuations made anisotropic by flow, its presence at temperatures above the MST implies that composition fluctuations are present even in the so-called homogeneous phase of the present block copolymer melt.

3. Results and Discussion

For the experimental arrangement used in this work, the birefringence ratio R_{birf} is related to the birefringence retardation, $\delta' = 2\pi d(\Delta n'/\lambda_0)$, by $R_{\mathrm{birf}} = \sin(\delta')$. Here, d is the optical path length; $\Delta n' = n_{xx} - n_{zz}$ is the birefringence; and λ_0 is the wavelength of the incident laser light. Transient values of the birefringence, the Raman $I_{2\omega}$ Fourier component, the shear stress σ, and the first normal stress difference N_1 are presented in Figure 3a–d. Plots are presented for several experimental temperatures and on log–log scales for clarity. For brevity in the following discussion, $I_{2\omega}$, $\Delta n'$, N_1, and σ are collectively termed relaxation functions.

3.1. Birefringence Relaxation. Figure 3a shows that the birefringence is positive at all temperatures. At temperatures well above the MST the shape of the birefringence relaxation function is observed to be only weakly dependent on temperature. At temperatures in excess of 160 °C, the birefringence relaxation is observed to be a strongly decreasing function of time, and plots obtained at different temperatures can be superimposed by horizontal shifting. As the temperature is lowered further, the birefringence changes shape rather dramatically, and at the lowest temperature studied becomes

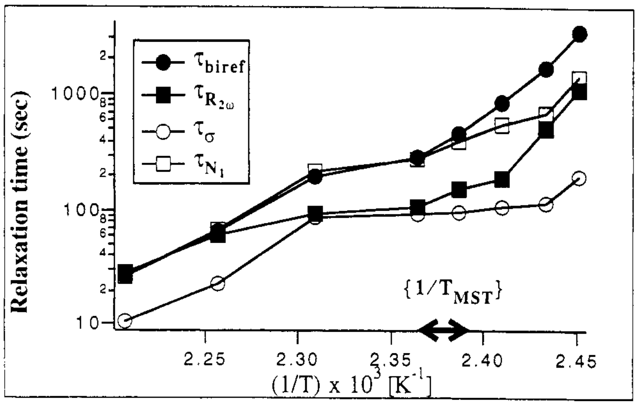

Figure 4. Semilog plot of relaxation time versus inverse temperature. τ_{biref}: birefringence relaxation time. $\tau_{R_{2\omega}}$: relaxation time of chain segment orientation anisotropy obtained from Raman scattering measurements. τ_σ: shear stress relaxation time. τ_{N_1}: first normal stress difference relaxation time.

virtually independent of time. Specifically, as the MST and, perhaps more importantly, mean-field estimate of the spinodal temperature $T_{S,MF}$[10] are approached, the long-time decay time extracted from an exponential fit to the long-time birefringence relaxation is observed to increase dramatically (Figure 4). This increase is paralleled by similar, although not as pronounced, increases in the long-time relaxation times of segment orientation anisotropy, $I_{2\omega}$, and the first normal stress difference. The shear stress relaxation, although sensitive to these transitions, displays a somewhat weaker temperature dependence than the other relaxation functions.

The strong temperature dependence of the birefringence relaxation, as well as its sign, supports the conclusion that the measured birefringence is predominantly form birefringence. As stated earlier, this implies that composition fluctuations are present even well into the so-called homogeneous state.[9] As the mean-field spinodal temperature is approached, the relaxation times of critical fluctuations are expected to increase significantly as a result of critical slowing down. Since the mean-field estimate of the spinodal temperature of the material used in this study is only some 10–19 °C below its apparent MST, such slowing down could explain the increases observed in the form birefringence relaxation time. In fact in an earlier paper, it was contended that critical slowing down may also be responsible for anomalous low-frequency rheological and optical properties of block copolymer melts at temperatures close to the MST. However, current thinking in block copolymer physics, at least for symmetric diblock copolymers, is that fluctuation corrections to the mean-field Hamiltonian cause the spinodal temperature to be pushed toward the absolute zero of temperature.[20] An alternative explanation of anomalous form birefringence relaxation in block copolymer melts close to the MST is lacking.

3.2. Relaxation of Segmental Orientation. Raman scattering measurements are not directly sensitive to the orientation/relaxation of the composition pattern; slowing down of the pattern relaxation therefore cannot entirely explain the unusual decrease in the relaxation rate of $I_{2\omega}$ seen at temperatures close to the MST (Figures 3b and 4). Evidently segmental relaxation and pattern relaxation are coupled. In the present copolymer, such coupling is believed to result from tethering of polymer chains to the interface separating domains.

A mechanism has been recently presented by Witten et al. to explain segmental relaxation in well-entangled, microphase-separated block copolymer melts.[21] These authors proposed that in the microphase-separated state translational diffusion of chain segments is suppressed by tethering and segment relaxation proceeds by a mechanism similar to that observed in highly branched, entangled polymers. If this is correct, the relaxation process should be observed to change from reptational diffusion in the homogeneous phase to a homopolymer starlike relaxation mechanism in the microphase-separated melt. In this latter form of relaxation chain segments lose their orientation by slowly retracting out of oriented confining tubes imposed by neighboring chains.

The presence of a relaxation mechanism similar to that observed in homopolymer stars could explain the unusual increase in the segment relaxation time observed from the Raman scattering measurements. Such a mechanism however requires that chain segments be well entangled and also predicts a nonexponential segmental relaxation function.[22] This latter result is not supported by our experiments, and the block copolymer sample used in this study possesses less than an average of 4 entanglements per chain, which is not usually considered sufficient to characterize the material as being well-entangled.[23] Nevertheless, regardless of the relaxation mechanism pursued by copolymer chains, slowing down of the relaxation of the composition pattern may be envisaged to couple with the relaxation of chain segments through tethering, to yield segmental orientation relaxation times that are larger than otherwise expected. Such coupling is expected to have particularly severe consequences on the relaxation dynamics of microphase-separated star block copolymers because in these materials polymer chains comprising the inner block are tethered both at the central junction point of the star and at the domain interface.

3.3. Stress Relaxation. An additional feature of the theory of Witten et al. is its prediction that the relaxation of chain segments in microphase-separated block copolymer melts should be significantly slower after compression than after pure shear flow.[21] The authors arrived at this result by considering relative differences in interdomain contact of chain segments produced by shear flow and by compression. Shear flow was argued to cause chain segments to orient primarily within their respective domains, and compression, to cause segments to penetrate into domains consisting of the opposite species. Thus, while relaxation of chain segments following step shear requires only local escape from entanglements, relaxation following compression requires diffusion over much larger distances. The relaxation rate of star polymers is known to increase exponentially with increasing molecular weight[21,22] the longer distances copolymer strands are required to diffuse to relieve stress following step compression will therefore result in substantially longer segmental relaxation times.

It is apparent from Figures 3c, 3d, and 4 that the relaxation of the shear stress and first normal stress difference, although similar at temperatures well above the MST, are markedly different at temperatures close to the MST. Specifically, the sensitivity of the relaxation of the first normal stress difference to the MST is clearly greater than that of the shear stress relaxation. Although the actual reason for this difference may well lie in fundamental differences in the sensitivity of these two relaxation functions to critical slowing down,[10] a simple, plausible explanation of this difference can be found in a variant of the argument presented in ref 21 to explain differences in relaxation rates following compression and pure shear flow. N_1 may be more sensitive to the MST because the distances over which chain segments are required to diffuse to relieve normal stresses built up during flow are large enough to cause the restrictions imposed by the tethering of chain ends to be felt by the relaxing copolymer chain. The relaxation of the shear stresses, on the other hand, may require only local diffusion of chain segments and should, therefore, not be as severely affected by tethering. The mechanism by which block copolymer chains relax in the homogeneous phase therefore determines the consequence of the tethering of chain ends on segmental relaxation in the microphase-separated state. If segmental relaxation proceeds by Rouse-like librations in the homogeneous phase, the consequence of tethering on the relaxation of chain segments in the microphase-separated state is not likely to be as severe as if reptational diffusion is the primary mode of relaxation in the homogeneous phase. Low molecular weight linear copolymers are thus not expected to be as good candidates as highly entangled linear block copolymers for exploring further the phenomena presented in this short study.

4. Conclusions

In this paper birefringence, Raman scattering, shear stress, and normal stress relaxation measurements were used to study the influence of the MST on the dynamics of a block copolymer melt subjected to step shear flow. A dramatic increase in the relaxation time of the birefringence was observed in the vicinity of the MST. In addition, form birefringence was observed at temperatures well above the MST, which appear to show that composition fluctuations are present well into the homogeneous phase of our copolymer melt. As the MST is approached, the normal stress relaxation and the chain segment anisotropy, measured using Raman scattering, were found to display similar, though not as dramatic as the form birefringence relaxation, evidence of slowing down. Increases in the relaxation times of these relaxation functions were proposed to result from coupling between composition pattern relaxation and chain segment relaxation. Specifically, we argue that tethering of chain segments at the domain interface frustrates *local* relaxation by reptational diffusion and results in longer relaxation times. Similar ideas were proposed to account for differences in the sensitivities of the step shear stress relaxation and the step-shear first normal stress difference relaxation to the MST.

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