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Optical and Mechanical Properties of a Star Diblock Copolymer Melt in Oscillatory Shear Flow

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ABSTRACT: Mechanical rheometry and birefringence measurements are used to study the low-frequency dynamics of a homogeneous, star diblock copolymer melt as it is cooled through its microphase separation temperature (MST). Anomalous low-frequency behavior in both mechanical and optical properties are observed at temperatures close to the MST. We conclude that a general condition must be satisfied before unusual low-frequency behavior is observed, namely that the time scale of flow must be less than the relaxation time of structural features perturbed by flow. Furthermore, because of the similarities between the low-frequency dynamics of the present star diblock copolymer and those of linear diblock and triblock copolymers, we also conclude that block copolymer architecture does not play a critical role in determining the low-frequency behavior of these materials.

1. Introduction

In the vicinity of the microphase separation temperature (MST), homogeneous block copolymer melts exhibit unusual optical and rheological properties. Well-known examples include large changes in optical anisotropy,[5] dramatic increases in loss (G'') and storage (G') moduli,[1–4] and unusual frequency scalings of G'' and G' in the so-called terminal frequency regime[1–5]. Anomalous changes in rheological properties are particularly important because they appear to be universal to all block copolymer morphologies and architectures and have in fact become a standard method for locating the MST.[6] Singular behavior in the viscometric coefficients that occur as the MST is approached is significantly more pronounced for dynamically sheared diblock copolymer melts than for low-molecular weight, critical fluid mixtures and polymer blends.[11–15] It is believed that this difference makes it easier to measure singular changes in rheological properties of block copolymer melts and underscores the fact that block copolymers do not belong to the same universality class as do low-molecular weight fluid mixtures and polymer blends. For example, while the low-frequency dynamic moduli of homopolymer melts typically scale as $G'' \sim \omega$ and $G' \sim \omega^2$, the dynamic moduli of block copolymer melts exhibit frequency scalings that are temperature dependent. At temperatures significantly higher than the MST ($T >$ MST $+30\ °C$), homopolymer-like scalings are preserved, and as the temperature is lowered through the MST, these scalings change dramatically, $G'' \approx G' \sim \omega^{\alpha}$, where the exponent α varies from 0.7 to 0.4 depending on the temperature.

In this study, mechanical rheometry and dynamic birefringence measurements are used to investigate the role played by the MST in determining low-frequency dynamics of a star diblock copolymer melt in shear flow. In so doing, it is shown that anomalous low-frequency behavior previously reported for diblock (1-arm star) and triblock (2-arm star) are readily observed for hetero-arm star diblock copolymers. The remarkable qualitative similarities between these anomalies and those previously reported for diblock and triblock copolymers leads us to conclude that in the vicinity of the MST details of block copolymer architecture are not crucial for understanding their low-frequency dynamics. In this study we, therefore, ignore architectural details and focus instead on understanding the role played by slowly relaxing, structural features in the low-frequency behavior of block copolymer melts. Dynamic birefringence measurements are also shown to provide important information about the low-frequency flow-response of microphase separated block copolymers.

In the following sections, it is proposed that anomalous low-frequency rheological properties of block copolymer melts result from the enhanced contribution of slowly relaxing structural features to the overall dynamics close to the MST. The precise mechanism by which the relaxation of such features is slowed down close to the MST depends on the specific nature of the features in question. For example, if the MST and mean-field spinodal temperatures are close, as they are in symmetric critical diblock copolymers, composition fluctuations become large close to the MST and slowing-down results from a decrease in the quiescent thermal decay rate of composition fluctuations, which is proportional to the inverse of the structure factor; the structure factor diverges, at least in theory, at the mean-field spinodal temperature. On the other hand, slowing down may be caused by large sluggish grains, which result from microphase separation, that relax very slowly, if at all, after being perturbed by flow.

If slowing-down results from an increase in the relaxation time of composition fluctuations, this would obviously imply that anomalies previously associated with an approach to the MST may actually result from proximity to the mean-field spinodal. Indeed the closeness of the mean-field spinodal temperature and MST for symmetric, critical diblocks may explain why these observations have in the past been associated with the MST. On the other hand, slowing-down that results from the appearance of a microphase structure would be most dramatic at the MST, provided that the material is not in a supercooled state during experiments. In either case, the origin of unusual terminal frequency scalings of the loss and storage moduli in block copolymers are believed to be similar to that of the high frequency scalings of these quantities for simple polymer fluids. We conclude that *a universal condition must be satisfied for "anomalous" low-frequency scalings to be observed in block copolymer melts*. Specifically, the *characteristic time scale of flow* ($\dot{\gamma}^{-1}$) *must exceed the longest relaxation time of structural features perturbed by flow.*

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2. Experimental Section

2.1 Sample. The sample used in this study was a polystyrene–polybutadiene six-arm, star diblock copolymer. This polymer is a research grade material provided by the Shell Development Co. and has an arm molecular weight of 27 800 g/mol (GPC), polydispersity index of 1.3, and styrene content of 30 wt %. Film specimens approximately 0.3-mm thick were prepared by solvent casting from a 10 wt % toluene solution that contained 1% Irganox 1010 antioxidant (Ciba Geigy Corp.). Solvent casting was done at 50 °C using a slow evaporation technique that lasted for a period of 2 weeks. Films were further dried under vacuum at a temperature of 90 °C for 48 h and then annealed under a constant load at a temperature of 120 °C for a period of 6 h. These films were found to contain large, uniformly birefringent sections (approximately 5 mm × 25 mm), and electron microscopy indicated that the morphology of this material consists of polystyrene (PS) cylinders in a matrix of polybutadiene (PBD). Static birefringence and dynamic mechanical measurements indicated that this material disorders at a temperature between 145 and 149 °C. The relatively large uncertainty in locating the MST resulted from the fact that changes in the birefringence at the MST were found to be less dramatic[7] than those previously observed for polystyrene–polyisoprene (PS–PI) diblocks.[4] In fact, the largest changes in static birefringence appeared to occur at the glass transition temperature of the PS block; indicating the presence segmental alignment, perhaps resulting from chain stretching, at temperatures below T_g. As a result of the uncertainty in locating the MST, temperatures in the range 145 to 149 °C will be referred to as the apparent MST of this material.

2.2 Birefringence Measurements. The birefringence of compositionally heterogeneous materials, such as block copolymer melts, are of two distinct types, "form" and "intrinsic". Form birefringence results from anisotropy in the spatial correlation of segment density and has the following origin in block copolymer melts. The dielectric constant, ϵ, is related to the density, ρ, through the Clausius–Mossotti relation, $(\epsilon-1)/(\epsilon+2) = A\rho$. Therefore, composition fluctuations present in block copolymer melts result in a spatially varying dielectric tensor. In the absence of an external perturbing field, wave vectors of the associated composition pattern assume all possible orientations, and the dielectric tensor is isotropic. In the presence of shear flow, however, composition fluctuations are rendered anisotropic, yielding an anisotropic dielectric tensor. Anisotropy in the dielectric tensor results in an anisotropic refractive index tensor ($n_{\alpha\mu}n_{\mu\beta} = \epsilon_{\alpha\beta}$) which in turn leads to the observation of form birefringence in the deformed material. At temperatures below the MST, form birefringence results largely from anisotropy in the microphase pattern. Intrinsic birefringence, on the other hand, results from flow-induced anisotropic alignment of molecular segments at all temperatures.

In practice, intrinsic birefringence dominates form birefringence for most systems.[10] However, if the rate of shear, $\dot{\gamma}$, is chosen such that it is less than the inverse of the longest molecular relaxation time ($\dot{\gamma}\tau_r < 1$) the time during which segments remain aligned will be shorter than the time required by the flow field to align them. Thus, the contribution of "intrinsic" birefringence to the overall birefringence is minimized. For the same reason, if the frequency of the strain used in an oscillatory shearing flow is less than the inverse of the longest molecular relaxation time, the measured birefringence will be predominantly "form" birefringence. This permits the study of flow-induced anisotropy in critical fluctuations using birefringence measurements.

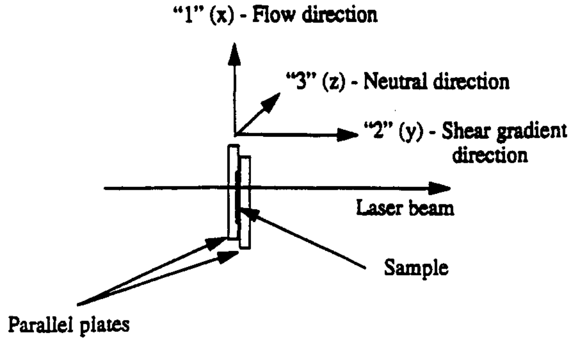

Figure 1. Geometry for 1–3 birefringence measurements; "laser beam" denotes direction along which light propagates.

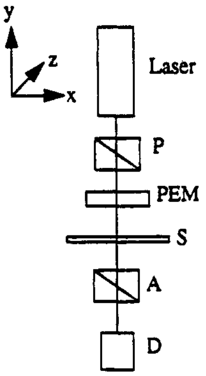

Figure 2. Optical train for measuring birefringence: "laser" HeNe laser; "P", linear polarizer oriented along "x"; "PEM", photoelastic modulator oriented at +45° to "x"; "S", oscillatory shear cell; "A", analyzing polarizer oriented at −45° to "x"; "D", photodiode.

Dynamic birefringence measurements were performed on block copolymer films produced using the method outlined in section 2.1. These measurements were made at temperatures covering a 50 °C range that bracketed the apparent MST. To minimize mechanical history effects, measurements 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. Equilibrium times ranged from 30 min to 2 h and were determined by observing the time it took for the birefringence of the quenched material to stabilize. Birefringence measurements were preformed using the 1–3 geometry (Figure 1). The optical train used in this study has been described elsewhere[12] and is presented in Figure 2. For this arrangement, the time-dependent birefringence response to oscillatory shear flow can be shown to be of the form[11,12]

$$\Delta n'(t) = (\Delta n')^d + (\Delta n')' \cos(2\omega t) + (\Delta n')'' \sin(2\omega t) \quad (1)$$

where ω is the frequency of the applied strain. The quantities $(\Delta n')^d$, $(\Delta n')'$, and $(\Delta n')''$ were obtained by Fourier transforming the measured time-dependent birefringence. In this work, these quantities will occasionally be referred to as the birefringence moduli. For all but the lowest temperature studied, strain amplitudes were adjusted to ensure that strains in the linear viscoelastic regime were used. Strain amplitudes satisfying this condition varied from 42% strain (at high temperatures) to 6% (at the lowest temperature studied). In the low-frequency regime, the lowest strain at which birefringence measurements possessed suitable quality was found to be 8%, which places measurements at the lowest temperature in the weakly nonlinear regime. Linearity was verified by stress–strain measurements.

2.3 Mechanical Measurements. Dynamic mechanical properties of block copolymer films were studied at various temperatures using a Rheometrics RDA II dynamic analyzer. All measurements were performed using a parallel plate geometry. The same procedures used in the birefringence experiments to reduce the influence of mechanical history and to ensure linearity of the strain amplitude were used in the mechanical experiments. In these measurements it was possible to use strains as low as 0.1% and still achieve reasonable signal-to-noise. As a result, measurements at all temperatures fall in the linear regime.

To verify that the PS–PBD samples do not degrade during the course of our experiments, measurements at high temperatures (above 150 °C) were repeated at lower, equivalent, temperatures using concentrated solutions (85%) of PS–PBD in DOP (a good solvent for both blocks).[9] At this concentration, the MST was found to be shifted to 110 °C, thereby permitting disordered phase measurements to be made at more convenient temperatures. The magnitudes and shapes of the dynamic moduli were found to be identical to those obtained for the disordered, undiluted material. This reassures us that no appreciable thermal degradation of the material occurs under the conditions of our experiment.

For materials that obey the stress-optical rule, constitutive equations predict the following relationships between the birefringence moduli and mechanical moduli

$$(\Delta n')^d \propto G' \tag{2}$$

$$(\Delta n')' \propto G'(\omega) - 1/2\, G'(2\omega) \tag{3}$$

$$(\Delta n')'' \propto G''(\omega) - 1/2\, G''(2\omega) \tag{4}$$

Here, ω is the shear frequency. The constant of proportionality in eqs 2–4 is related to the stress-optical coefficient and is the same for all moduli. As a result of these relations, birefringence moduli may be used to determine the storage and loss moduli of materials that satisfy the stress-optical rule.[12] Furthermore, because of the complex dependence of $(\Delta n')'$ and $(\Delta n')''$ on G' and G'', respectively, these moduli display features not present in G' and G''. Only one of these features is of importance to the following discussion; we will elaborate only on it here. The reader is referred to ref 12 for more examples.

For entangled homopolymer melts, and at high frequencies, G' is approximately independent of frequency; $G'(\omega)$ is, therefore, larger than $1/2\ G'(2\omega)$, which results in a positive value for $(\Delta n')'$. In the terminal frequency regime, G''s frequency scaling changes to ω^2. Thus, immediately after the inception of terminal behavior (frequency slightly lower than the inverse of the longest molecular relaxation time), $1/2G'(2\omega)$ becomes larger than $G'(\omega)$, and $(\Delta n')'$ changes sign. In practice, the frequency at which this sign change occurs is found to coincide roughly with the inverse of the longest molecular relaxation time of monodisperse homopolymer melts. Although PS–PBD block copolymer melts are not expected to obey the stress optical rule,[13] in the next section we report sign changes in $(\Delta n')'$ similar to those observed for homopolymer melts. At temperatures exceeding the MST, the frequency at which these sign changes occur roughly coincides with the inverse of the molecular relaxation time extracted from step shear relaxation experiments. As temperature approaches the MST, a second sign change becomes apparent at lower frequency. By analogy to the homopolymer observations, we assign this second sign change to the appearance of a second, slower relaxation process as the MST is approached.

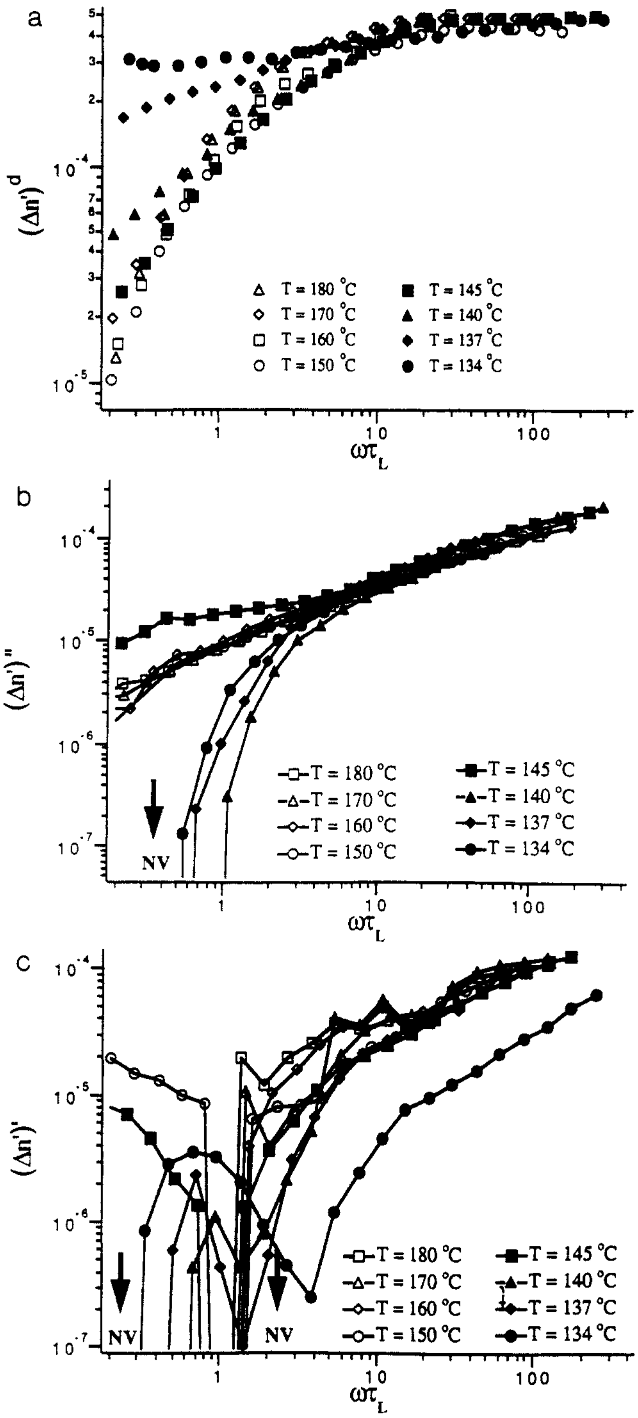

Figure 3. (a) Experimental $(\Delta n')^d$ vs dimensionless frequency for temperaturesmranging from 134 to 180 °C. (b) Experimental $(\Delta n')''$ vs dimensionless frequency for temperatures ranging from 134 to 180 °C. NV indicates that $(\Delta n')''$ changes sign and becomes negative. (c) Experimental $(\Delta n')'$ vs dimensionless frequency for temperatures ranging from 134 to 180 °C. NV indicates that $(\Delta n')'$ changes sign and becomes negative.

3. Results

3.1 Birefringence Measurements. Birefringence moduli obtained using the procedure described in section 2.1 are presented as a function of dimensionless frequency in Figure 3a–c. Frequencies were nondimensionalized using relaxation times, τ_L, determined from low-amplitude step shear/relaxation experiments.[7]

It is apparent from Figure 3a that at temperatures in excess of 150 °C, plots of $(\Delta n')^d$ versus dimensionless frequency roughly superimpose unto a single curve which scales as $(\omega\tau_L)^{1.90\approx 2.0}$ for dimensionless frequencies below a value of about 1. This behavior is in agreement with terminal frequency scalings observed for homopolymer mixtures[12] and is expected for disordered block copolymers. At temperatures below 150 °C, plots of $(\Delta n')^d$ versus dimensionless frequency superimpose onto a single curve only at high frequencies. At low frequencies, the frequency scaling of $(\Delta n')^d$ begins to deviate from the scalings observed at high temperatures. In this region, a "power law" scaling regime ensues where $(\Delta n')^d \sim (\omega\tau_L)^{\alpha}$. The exponent α varies from 0.64 to 0.12 as the temperature is lowered. The magnitude of $(\Delta n')^d$ is also observed to increase dramatically as the temperature is lowered through the apparent MST. These observations, although unusual by homopolymer standards, are expected for block copolymer melts. Indeed, the relationship between $(\Delta n')^d$ and G' presented in section 2.3 for homopolymer melts that obey the stress-optic rule would appear to indicate that these findings are in some sense related to those previously reported for G' for other block copolymer architectures.

At high temperatures ($T \geq 150$ °C) plots of $(\Delta n')''$ versus dimensionless frequency also approximately collapse onto a single curve. In the low-frequency regime this curve scales linearly with dimensionless frequency (Figure 3b). At a temperature of 145 °C, the low-frequency scaling of $(\Delta n')''$ is observed to change dramatically, while at still lower temperatures it abruptly changes sign. The frequency at which the sign change occurs is an increasing function of temperature and is lower than the inverse of the longest relaxation time.

The frequency dependence of $(\Delta n')'$ (Figure 3c) is somewhat more complex than those observed for $(\Delta n')^d$ and $(\Delta n')''$. At high temperatures ($T > 150$ °C) it displays a single sign change that occurs at a dimensionless frequency close to 1.0. At temperatures lower than 160 °C $(\Delta n')'$ is observed to undergo two sign changes: the first sign change occurs at $\omega\tau_L \approx 1.0$ and the second at a lower dimensionless frequency $\hat{\omega}_2$. It is apparent that $\hat{\omega}_2$ is an increasing function of temperature. The first sign change, as well as the value of the dimensionless frequency at which is occurs, can be rationalized in terms of the discussion presented in section 2.3. As pointed out earlier, the value of the frequency at which this sign change occurs roughly coincides with the reciprocal of the longest molecular relaxation time for monodisperse molecular weight distributions. For this reason, the appearance of a second sign change in $(\Delta n')'$ appears to indicate that a second relaxation process, with relaxation time greater than the first, becomes important as the MST is approached. Judging from the temperature at which this process first appears, this relaxation is most likely that of composition patterns made anisotropic by flow. Although similar sign changes observed for $(\Delta n')''$ have no parallels in the study of homopolymer melts, their appearance for a disordered block copolymer melt close to its MST appears to indicate that they are of the same origin as those observed for $(\Delta n')'$.

These observations, including the reduction of $\hat{\omega}_2$ with decreasing temperature, can be predicted, at least qualitatively, by crude fluctuation based dynamical mean-field theories.[15] The presence of an apparent slower relaxation mode in the dynamics of the present block copolymer close to its MST is consistent with results reported earlier from photon correlation spectroscopy measurements on poly(dimethylsiloxane-*b*-methylethylsiloxane) diblock copolymer melts.[14]

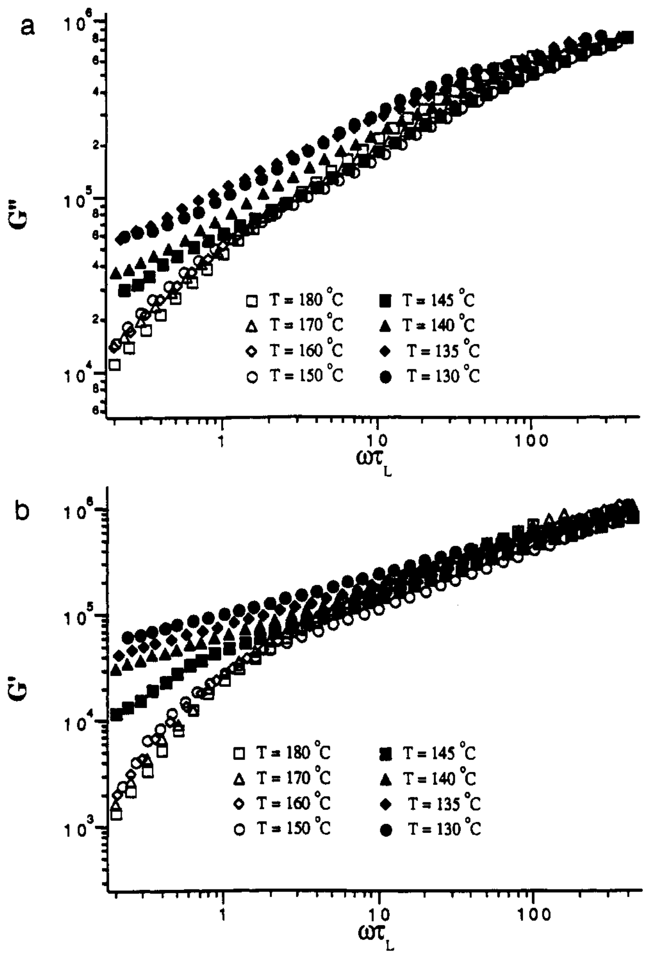

Figure 4. (a) Experimental G'' vs dimensionless frequency for temperatures ranging from 130 to 180 °C. (b) Experimental G' vs dimensionless frequency for temperatures ranging from 130 to 180 °C.

3.2 Mechanical Measurements. Values of the dynamic moduli obtained using the procedures described in section 2.3 are presented as a function of dimensionless frequency in Figure 4a,b. The same procedure used for nondimensionalizing frequency in the birefringence measurements was repeated for these measurements. As observed for the displacement component of the birefringence ($(\Delta n')^d$), plots of G'' and G' versus dimensionless frequency superimpose onto a single curve for temperatures greater than or equal to 150 °C. At these temperatures, the low-frequency scalings are those expected for homopolymer melts. At temperatures less than 150 °C, however, G'' and G' both increase dramatically and display anomalous low-frequency scalings: $G'' \sim \omega^{\alpha}$ and $G' \sim \omega^{\Gamma}$, where α varies from 0.6 to 0.35 and Γ from 0.8 to 0.43. We believe that these unusual low-frequency scalings have the same origin as the anomalous low-frequency behavior of the birefringence moduli, namely the appearance of slowly relaxing structural features at the MST.

It is possible to obtain a rough estimate of the χ parameter for the present PS–PBD six-arm star diblock copolymer from published temperature dependent values of the χ parameter for PS–PBD diblocks, PS–PBD random copolymers, PS/PBD blends, PS–PI diblock copolymers, and PS–PI six-arm star diblock copolymers.[8,9] Results from these studies yield the following expression for χ, $\chi = 0.0181 + 3.540/T$, where T is the absolute temperature. Mean-field theory predicts that the spinodal of a six-arm star diblock copolymer, with the same composition as the

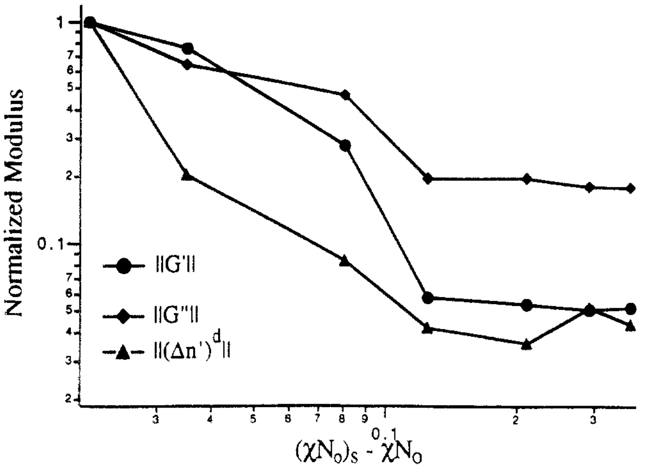

Figure 5. Experimental normalized moduli vs temperature distance from the mean field spinodal temperature.

one used in this study, occurs at $(\chi N_0)_s = 11.78$.[15] N_0 is the total number of monomer units present in each arm of the copolymer and has a value of 440 for the star-diblock used in this study. The mean-field spinodal temperature, T_s, of this material is thus expected to be 135.2 °C; some 10–14 °C lower than its apparent MST. Using small-angle X-ray scattering (SAXS) measurements, Hashimoto and co-workers have observed a separation of 18–20 °C between these temperatures for a PS–PI star diblock copolymer melt of similar composition and comparable molecular weight.[9]

Normalized low-frequency amplitudes of $(\Delta n')^d$, G'', and G' are presented as a function of temperature distance from the mean-field spinodal temperature in Figure 5. All amplitudes are determined at a dimensionless frequency of 0.2. Two distinct regions are observed: at temperatures above 150 °C, these quantities are all independent of temperature, while for temperatures in the range 130–150 °C, they all increase rapidly with decreasing temperature. In the latter interval, the following scalings are observed, $\|(\Delta n')^d\| \sim ((\chi N_0)_s - \chi N_0)^{-1.84}$, $\|G''\| \sim ((\chi N_0)_s - \chi N_0)^{-0.82}$, and $\|G'\| \sim ((\chi N_0)_s - \chi N_0)^{-1.53}$, where $(\chi N_0)_s$ is the value of χN_0 at the spinodal.

4. Discussion

As pointed out earlier, a number of the qualitative observations reported in this paper are consistent with the predictions of simple dynamical mean-field theories.[15] Such theories, however, suffer serious quantitative limitations because noncritical contributions to the birefringence and mechanical moduli are not included and, for nonsymmetric block copolymers, the mean-field spinodal temperature may fall well below the MST making it difficult to neglect the contribution of structures that result from microphase separation. Nevertheless, it is useful to consider the form of the fluctuation contribution to the low-frequency loss and storage moduli predicted by such theories:[15,17] $G'' \sim G_0''(S)\,[(\omega/\bar{\omega})/(\omega^2 + \bar{\omega}^2)]$ and $G' \sim G_0'(S)[\omega^2/(\omega^2 + \bar{\omega}^2)]$. Here $\bar{\omega}$ is the quiescent thermal decay rate of composition fluctuations and G_0' and G_0'' are functions of the structure factor S.

The similarity of these forms to those of the mechanical moduli predicted by the Rouse model for simple polymer fluids is readily apparent;[10,17] $G'' = \sum_i G_i[(\omega/\Gamma_i)/(\omega^2 + \Gamma_i^2)]$ and $G' = \sum_i G_i[\omega^2/(\omega^2 + \tau_i^2)$. Here G_i is the modulus associated with the ith Rouse mode, $\Gamma_i = 1/\lambda_i$, and λ_i is a characteristic molecular relaxation time. For slow modes, corresponding, for example, to the collective motion of all strands constituting a polymer chain, the Rouse model predicts that $\lambda_i \propto i^{-2}$ and that G_i is independent of i and the following frequency scalings are recovered for the dynamic moduli

$$\omega \ll \Gamma, \begin{cases} G' \sim \omega^2 \\ G'' \sim \omega \end{cases} \quad \text{(liquid-like response)}$$

and

$$\omega \gg \Gamma, \begin{cases} G' \sim \omega^0 \\ G'' \sim 0 \end{cases} \quad \text{(solid-like response)}$$

For "intermediate" frequencies, where frequency and relaxation time are of the same order of magnitude, $G'' \sim G' \sim \omega^{1/2}$. In fact, it can be shown that any model that predicts $\lambda_i \propto i^{-\alpha}$ and G_i = constant will yield moduli that scale as $G'' \sim G' \sim \omega^{1/\alpha}$ for "intermediate" frequencies.

It is, therefore, apparent that if the quiescent decay rate of composition fluctuations becomes smaller than experimentally accessible frequencies, as it would close to the mean-field spinodal temperature, the low-frequency scalings of the moduli produced by composition fluctuations become similar to the high-frequency scalings predicted for simple polymer fluids by the Rouse model. Thus, as the spinodal temperature is approached, fluctuations cause the so-called "terminal" frequency regime to be progressively pushed to lower frequencies, which results in the appearance of power-law frequency scalinngs at the lowest experimentally accessible frequencies.

5. Summary

In this work, dynamic birefringence and mechanical measurements are used to study the dynamics of a star diblock copolymer melt subject to oscillatory shear flow. It is shown that anomalous low-frequency scalings of the dynamic mechanical moduli similar to those observed in diblock and triblock copolymer melts are also observed in star diblock copolymers. Anomalous low-frequency dynamics is also observed in the various dynamic birefringence moduli. We use ideas from the Rouse model for simple polymer fluids to argue that such scalings occur whenever the experimental frequencies become comparable to the relaxation rate of structures perturbed by flow. Although we point out that a number of the qualitative features of our experimental observations are consistant with the predictions of dynamical mean-field theories for composition fluctuations, quantitative discrepancies as well as the asymmetry of the present copolymer make it impossible to ascertain the exact cause of these anomalies. Nevertheless, in light of the apparent similarities of the low-frequency dynamics observed for the present star architecture and those observed in linear copolymers, we conclude that architectural details do not play a great role in determining the low-frequency dynamics of these materials.

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