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Relationship between Structural and Stress Relaxation in a Block-Copolymer Melt

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The relationship between structural relaxation on molecular length scales and macroscopic stress relaxation was explored in a disordered block-copolymer melt. Experiments show that the structural relaxation time, measured by x-ray photon correlation spectroscopy is larger than the terminal stress relaxation time, measured by rheology, by factors as large as 100. We demonstrate that the structural relaxation data are dominated by the diffusion of intact micelles while the stress relaxation data are dominated by contributions due to disordered concentration fluctuations.

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Polymer materials offer unique insight into the molecular underpinnings of macroscopic mechanical properties because the consequences of molecular motion, which are generally difficult to measure directly, can be readily observed in relatively simple stress relaxation experiments [1]. A quantity of central importance is the so-called longest relaxation time, which characterizes the terminus of the stress relaxation function. In simple systems such as linear homopolymer melts, this relaxation time reflects the time scale for the diffusion of entire polymer chains across length scales comparable to molecular dimensions. In the case of heterogeneous single-phase systems such as disordered block-copolymer melts, the relationship between molecular motion and stress relaxation is complicated due to the spontaneous formation and disappearance of transient structures such as concentration fluctuations, micelles, and concomitant interfaces of varying widths [2]. Stress relaxation in such systems is coupled to both molecular motion and the relaxation of these transient structures. An interesting consequence of this coupling is that structural relaxation can, in principle, be much slower than the terminal stress relaxation. In this Letter we present the first quantitative measurements of both stress and structural relaxation in a block-copolymer melt. The experimentally determined characteristic times for structural relaxation are 1–2 orders of magnitude larger than those for stress relaxation. Thus, the use of the term, ‘‘longest relaxation time’’, that is often used to describe terminal relaxation in disordered block copolymers [3,4] is, perhaps, not appropriate.

Relaxation processes are quantified by the wave-vector (q) dependent dynamic structure factor, $S(q, t)$. $S(q, t)$ is the spatial Fourier transform of the density-density autocorrelation function $\langle \rho_A(\boldsymbol{r}', t)\rho_A(\boldsymbol{r}, 0)\rangle$, where $\rho_A(\boldsymbol{r}, t)$ is the concentration of chain segments of type A at position $\boldsymbol{r}$ and time t. While techniques such as dielectric relaxation [5,6] give insight into relaxation processes, $S(q, t)$ can be measured directly by techniques such as light or x-ray photon correlation spectroscopy (LPCS or XPCS) [7–9], or quasielastic neutron scattering [10]. A large majority of measurements of $S(q, t)$ have been made using LPCS wherein the length scales ($2\pi/q$) that are accessed are in the range of 500 nm [11]. On this length scale, structural relaxation is almost always dominated by diffusion. In contrast, our measurements using XPCS enable the quantification of structural relaxation on molecular length scales (~20 nm). The goal of this Letter is to identify the structural relaxation process that dominates the XPCS signal from our diblock-copolymer melt, and to explore the relationship between structural and stress relaxation.

A polystyrene-*block*-polyisoprene copolymer, SI(7–27), was synthesized and characterized by methods described in Ref. [12]. The weight-averaged molecular weights of the polystyrene and polyisoprene blocks were 6.7 kg/mol and 26.5 kg/mol, respectively. The copolymer melt exhibits an order-disorder transition from hexagonally packed cylinders to disordered micelles at $T_{\mathrm{ODT}} = 70 \pm 2\,^\circ\mathrm{C}$ [13]. The static and dynamic structure factors were measured by small-angle x-ray scattering (SAXS) and XPCS on the 8-ID-I beam line at the Advanced Photon Source (APS), Argonne National Laboratory.

Figure 1 shows the static SAXS intensity profiles, $I(q)$, [where $q = (4\pi/\lambda)\sin(\theta/2)$, $\lambda = 1.65$ Å is the wavelength of the x rays and θ is the scattering angle] obtained at temperatures between 70 °C and 90 °C. In Ref. [13], we presented a thorough analysis of this data set, proving the presence of disordered micelles in this temperature range. Recent theoretical computations by Wang *et al.* [14] enable estimation of the volume fraction of micelles in these systems. Using self-consistent field theory to compute the structure factor of block-copolymer melts with disordered

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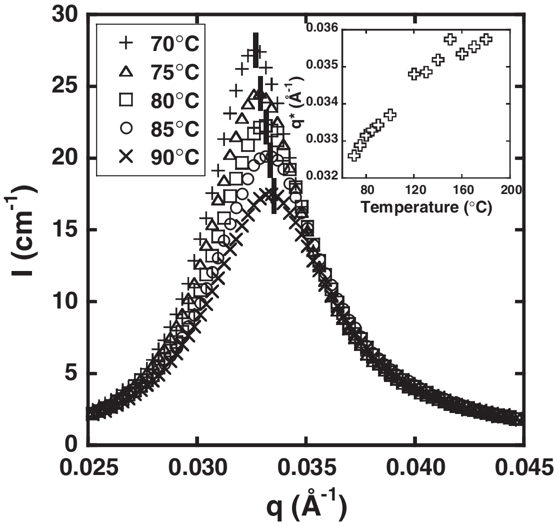

FIG. 1. SAXS intensity, $I(q)$. The peak in the SAXS intensity (q^*), indicated by the vertical bars, shifts to lower q values as micelle volume fraction increases. The inset shows q^* as a function of temperature.

micelles, they showed that the peak in the structure factor, q^*, moves to lower q values as the micelle volume fraction increases. If we assume that our melt has no micelles at 180 °C (the upper limit of our temperature window where we do not observe any signature of micelles) and attribute all of the changes in q^* with decreasing temperature (inset of Fig. 1) to the presence of micelles, we conclude that the upper bound for the micelle volume fraction ϕ_m is 0.07 [15]. Even though the micelle concentration is small, the SAXS signal at q^* is strongly affected by the presence of micelles due to their large scattering power [14].

XPCS was used to measure $S(q, t)$ in the vicinity of q^*. If a single process dominates the relaxation of concentration fluctuations, i.e. $S(q, t) \sim \exp(-t/\tau_{\mathrm{struc}})$, the x-ray scattering intensity time correlation function, $g_2(q, t)$, is given by

$$g_2(q, t) \equiv \frac{\langle I(q, 0)I(q, t)\rangle}{\langle I(q, t)\rangle^2} = 1 + ke^{-2t/\tau_{\mathrm{struc}}(q)}, \qquad (1)$$

where $\tau_{\mathrm{struc}}(q)$ is the characteristic time for structural relaxation. In this Letter, we focus on $\tau_{\mathrm{struc}}(q = q^*)$ (changes in τ_{struc} with q were within experimental error in the narrow range of q values where the XPCS signal could be measured) which we shall refer to as τ_{struc} from now on. Typical measurements of $g_2(q^*, t)$ for SI(7–27), shown in Fig. 2, are in agreement with Eq. (1). The curves in Fig. 2 are least squares fits of Eq. (1) from which we estimate τ_{struc}. Our measurements do not rule out the presence of faster relaxation processes that are below the lower limit of our time window.

Rheological measurements on SI(7–27) were conducted using an ARES Rheometer (Rheometrics Inc.). Our measurements covered the frequency (ω) range from 0.1 to 100 rad s^{-1}. Figure 3 shows the results of the frequency (ω) dependence of the storage and loss shear moduli (G' and G'') of our sample at selected temperatures after time-temperature-superposition (tT) [1,2] of the high-ω data. The high-ω moduli reflect single chain dynamics (as inferred from similarity with homopolymer data [16]). The low-ω moduli are similar to those for the relaxation of concentration fluctuations giving branched master curves of G' and G'' after the tT superposition [2]. The rheological terminal relaxation time $\tau_{\mathrm{tr}} = [G'/\omega G'']_{\omega\to 0}$ is attributed to this relaxation process.

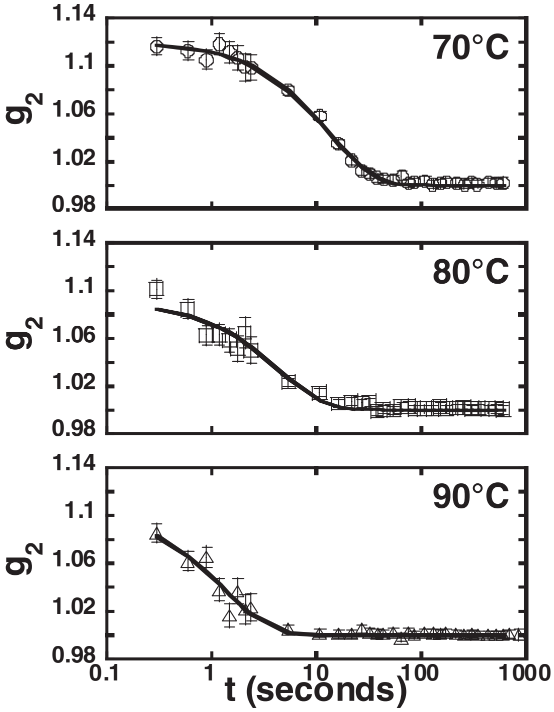

FIG. 2. Typical intensity-intensity time autocorrelation functions, $g_2(q^*, t)$ at 70 °C, 80 °C, and 90 °C.

In Fig. 4, the values of τ_{tr} obtained by rheology are compared to τ_{struc}. It is evident that τ_{struc} is 1–2 orders of magnitude larger than τ_{tr}. The temperature dependences of τ_{struc} and τ_{tr} are similar but not identical. The decrease in τ_{struc} with temperature is less pronounced than that of τ_{tr}.

Stress relaxation in polymers is due to a multitude of relaxation processes, occurring at various time and length scales. XPCS measurements provide a direct measure of the time scale for one of these processes. It has been argued that for systems with peaks in $S(q)$, relaxation times near the critical point would be longest at $q = q^*$ [17]. Pioneering experiments by Anastasiadis and co-workers have shown that this is true for disordered diblock copolymers [7,18]. This provides the qualitative reason for our observation regarding the relative magnitudes of τ_{tr} and τ_{struc}. Quantitative relationships between τ_{tr} and τ_{struc} are contained in the theoretical work of Fredrickson and Larson [19]. In this theory, a Fokker-Planck equation is used to describe the response of a system to simple shear flow, within a Gaussian Hamiltonian approximation. The complex modulus $G^* = G' + iG''$ ($i = \sqrt{-1}$) is given by

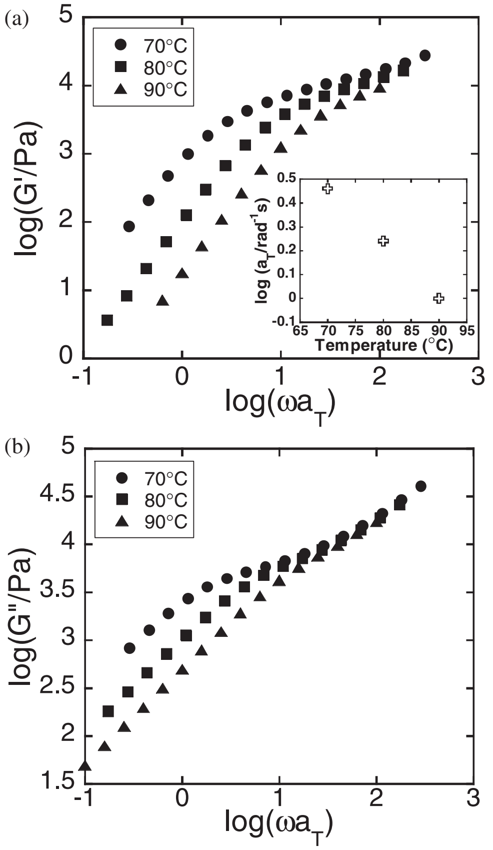

FIG. 3. Time-temperature superposed rheological data on SI(7–27) from 70 °C to 90 °C. (a) Storage modulus $G'(\omega)$. (b) Loss modulus $G''(\omega)$. The inset in (a) shows the shift factor, $\boldsymbol{a}_T$ as a function of temperature.

$$G^*(\omega) = \frac{k_B T \omega}{30\pi^2 R_g^3} \int_0^{x_c} \frac{x^{5/2} S^2(x)}{\omega - 2i\bar{\omega}(x)} \left[\frac{\partial S^{-1}(x)}{\partial x}\right]^2 dx, \quad (2)$$

where R_g is the chain radius of gyration, $x \equiv (qR_g)^2$, $x_c \equiv (q_c R_g)^2$, $q_c \equiv 2\pi/l$, l is the statistical segment length, $S(x)$ is the static structure factor, and $\bar{\omega}(x)$, the rate at which order parameter fluctuations of wave vector q relax at thermal equilibrium, is given by $\bar{\omega}(x) = xg(x)NS^{-1}(x)/2\tau$, where τ is the molecular relaxation time, N is the number of monomers per chain, and $g(x)$ is the Debye function: $g(x) \equiv \frac{2}{x^2}[x + e^{-x} - 1]$. The connection between XPCS and rheological measurements is provided by the fact that if fluctuations dominated the XPCS relaxation $\tau_{\rm struc} = 1/2\bar{\omega}(x)$. We use the term $\tau_{\rm FL}$ to refer to the structural relaxation time based on the Fredrickson-Larson theory, which is given by

$$\tau_{\rm FL} = \frac{\tau_{\rm tr}}{x^* g(x^*) N S^{-1}(x^*)} \left(\frac{\int_0^{x_c} \frac{x^{3/2} N S^{-1}(x)}{g(x)} \left[\frac{\partial S(x)}{\partial x}\right]^2 dx}{\int_0^{x_c} \frac{x^{1/2}}{g^2(x)} \left[\frac{\partial S(x)}{\partial x}\right]^2 dx} \right). \quad (3)$$

The application of Eq. (3) to the disordered micelle phase of block copolymers is not possible because the Hamiltonian and the structure factor for this system [14] are much more complicated than those used in Ref. [19]. However, the effect of simple (nonmicellar) concentration fluctuations on $\tau_{\rm FL}$ can readily be computed using well-established expressions for $S(q)$ [20], and the measured value of $\tau_{\rm tr}$. We take the measured ODT temperature of our system as the spinodal temperature and compute $S(q)$ using the Leibler theory [20,21]. This enables determination of all of the parameters on the right hand side of Eq. (3). The temperature dependence of $\tau_{\rm FL}$ is shown by the dashed curve in Fig. 4. The temperature dependencies of $\tau_{\rm FL}$ and $\tau_{\rm struc}$ are similar and $\tau_{\rm FL}$ is greater than $\tau_{\rm tr}$ at all temperatures. The Fredrickson-Larson theory thus provides a qualitative explanation of our observation that $\tau_{\rm struc}$ is greater than $\tau_{\rm tr}$. The magnitude $\tau_{\rm struc}$ at a given temperature is, however, a factor of 10 larger than that of $\tau_{\rm FL}$. This indicates the need for further analysis.

Our analysis of the XPCS data thus far ignores the presence of micelles. The decay of $g_2(q^*, t)$ of a micellar phase can, in principle, reflect either the dissolution of micelles or the diffusion of intact micelles. The time scale $\tau_{\rm SE}$ for the diffusion of an intact micelle over a distance equal to its radius R_H ($\approx 2\pi/q^*$) can be readily calculated on the basis of the Stokes-Einstein relationship,

$$\tau_{\rm SE} = \frac{\pi R_H^3 \eta_{\rm eff}(T)}{k_B T}, \quad (4)$$

where $\eta_{\rm eff}$ is the effective viscosity of the medium, k_B is the Boltzmann constant, and T is the temperature [23]. In general, $\eta_{\rm eff}$ differs from the rheologically measured terminal viscosity, η_0, because the micelle diffusion itself contributes to η_0. However, since our micelles are dilute ($\phi_m < 0.07$), we may safely assume that $\eta_{\rm eff} \approx \eta_0$ in the evaluation of $\tau_{\rm SE}$ using Eq. (4). In Fig. 5, we compare the $\tau_{\rm SE}$ thus calculated with the experimentally determined $\tau_{\rm struc}$. The agreement between $\tau_{\rm struc}$ and $\tau_{\rm SE}$ at all temperatures is remarkable, considering the uncertainty in R_H and

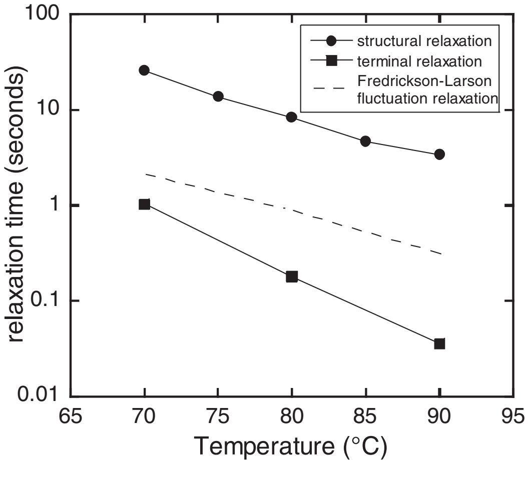

FIG. 4. Comparing the structural relaxation time, $\tau_{\rm struc}$ with the rheological terminal relaxation time, $\tau_{\rm tr}$. Note that $\tau_{\rm struc}$ is 1 to 2 orders of magnitude larger than $\tau_{\rm tr}$. The dashed curve is the structural relaxation time as predicted by the Fredrickson-Larson theory, $\tau_{\rm FL}$.

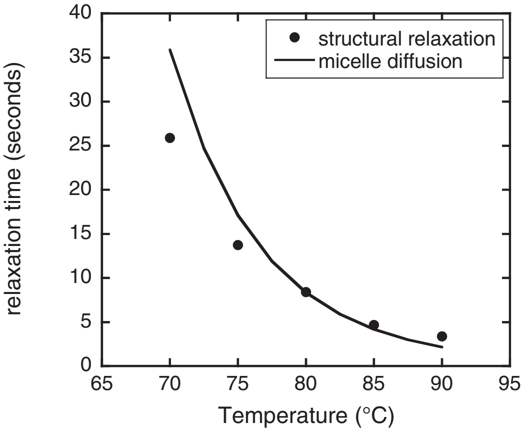

FIG. 5. Comparing τ_{struc} to the Stokes-Einstein diffusion relaxation time, τ_{SE}.

the fact that the Stokes-Einstein relationship applies to rigid spheres diffusing in a homogeneous continuum. We can thus assert that the decay of $g_2(q^*, t)$ is dominated by micelle diffusion, and that the micelle lifetime in our temperature window must be greater than the τ_{struc} values given in Fig. 4. The frequency at which we expect to observe the rheological consequences of micelle diffusion, $\omega = 2\pi/\tau_{\mathrm{struc}}$, was within our experimental frequency window at all temperatures. However, the micelles are dilute ($\phi_m < 0.07$) and thus their diffusion does not contribute significantly to the measured relaxation.

Understanding equilibrium dynamics on molecular length scales affects our understanding of many other phenomena in block copolymers. An example of such a phenomenon is the kinetics of the disorder-to-order transition. In some cases [3,24], large discrepancies have been reported between measured and estimated grain growth rates, if the rheological relaxation times are used in the estimation. Our results indicate that local dynamics on molecular length scales can be significantly slower than those estimated from rheological measurements.

In conclusion, we have used XPCS and rheology to find the relationship between structural and stress relaxation in a block-copolymer melt that contains disordered micelles. We have found that the structural relaxation time can be larger than the longest stress relaxation time by factors as large as 100. A comparison of the Stokes-Einstein micelle diffusion time with τ_{struc} reveals that the structural relaxation mode is dominated by the diffusion of intact micelles.

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