

Experiment title: Reptation in Polymer Melts Studied by X-ray Intensity Fluctuation Spectroscopy

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Report:

We chose to initiate this program by studying polymer mixtures composed of polystyrene (PS)-polyisoprene (PI) block copolymer and polystyrene homopolymer. The mixtures lie in a micro-phase-separated, micellar region of the phase diagram forming spherical micelles. Here, we report x-ray intensity fluctuation spectroscopy measurements of the equilibrium dynamics of these polymer micelle liquids. The dynamics were investigated for times between one and one thousand seconds, and for wavevectors from 0.003 to 0.015 Å⁻¹, far beyond wavevectors that can be studied with visible light. A wavevector-dependent translational diffusion coefficient was found and analyzed. The results of this experiment convincingly demonstrate the feasibility of carrying out XIFS studies of polymer systems.

Under coherent illumination at ID-10, x-rays scattered from the samples were collected using a CCD array detector. Data were acquired as a series of 1000 one second exposures, separated by 0.24 s for readout and storage. We observe a static speckle pattern at 293 K, corresponding to a frozen arrangement of micelles. By contrast, the graininess characteristic of a speckle pattern is not apparent at 393 K. We may infer that at 393 K the micelles are mobile and that their random thermal motions cause the instantaneous speckle pattern to fluctuate in time, resulting in a smoother intensity variation in a long-time average. Accordingly, to determine the characteristic times of the sample, we computed the normalized intensity autocorrelation function for each CCD pixel as a function of the delay time (t): $g_2(t) = (n+1-t) \sum_{s=t}^n i_s i_{s-t+1} / m_0 m_1$, where n is the number of time steps, i_s is the intensity at time steps, $m_0 = \sum_{s=1}^{n+1-t} i_s$ and $m_1 = \sum_{s=t}^n i_s$. For an isotropic sample, the dynamics depend only on the magnitude of the wavevector (Q). Therefore, to determine the variation versus wavevector, we performed an average overall pixels within successive rings of width $\Delta Q = 0.00032 \text{ \AA}^{-1}$. The resultant, averaged, baseline-subtracted autocorrelation function, obtained at 393 K, for three representative wavevectors is shown versus time in Fig. 1. At each wavevector, the autocorrelation is largest at short times and decays with increasing time. To quantify the behavior, we have fitted each autocorrelation function to a single exponential decay [$g_2(t) = A + B e^{-t/2\tau_Q}$, where τ_Q is the characteristic time at wavevector Q]. The model provides a good description of the data, and we believe that the fitted time constants so-obtained sensibly characterize the decay of intensity autocorrelations.

In Fig. 2(a) are plotted the fitted values of τ_Q versus Q for 393 K and 398 K. The time constants at a given wavevector are different by a factor of roughly 3 at the two different temperatures, consistent with the expected dependence of the matrix viscosity on temperature, but the variation versus wavevector appears similar for both temperatures. The decay times are largest at the smallest wavevectors studied (0.0027 \AA^{-1}), and decrease rapidly for wavevectors increasing to 0.007 \AA^{-1} . Between 0.007 and 0.012 \AA^{-1} , they are approximately constant or increase slightly. Eventually, they decrease again for wavevectors above 0.012 \AA^{-1} .

The observed behavior appears more complicated than for a long-wavelength diffusion process, for which one anticipates $\tau_Q = 1/DQ^2$, where D is a micelle diffusion constant. To make sense of this observation, we note that $1/\tau_Q$ is the width in frequency of the dynamic structure factor $[S(Q, \omega)]$, which exhibits two general properties, pertinent to the discussion: First, the frequency integral of $S(Q, \omega)$ is the static structure factor $S(Q)$. Second, in the classical limit, the second moment of $S(Q, \omega)$ equals $Q^2 k_B T / M$, for all values of Q , as a result of the f -sum rule. In addition, for particles diffusing in a viscous medium, $S(Q, \omega)$ at small wavevectors and frequencies takes the diffusion form

$$S(Q, \omega) \simeq \frac{S(Q)}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}. \quad (1)$$

The frequency integral of Eq. 1 is $S(Q)$. However, Eq. 1 does not obey the f -sum rule. A simple remedy is to suppose that Eq. 1 is valid up to some maximum frequency, Ω , but that $S(Q, \omega) \simeq 0$ for frequencies greater than Ω . With this approximation, the sum rule is satisfied, and, moreover, implies that the diffusion coefficient is wavevector-dependent, so that $\tau_Q \simeq 2M\Omega S(Q) / \pi k_B T Q^2$.

To more thoroughly explore the relationship between $S(Q)$ and τ_Q , we have fitted the scattering cross-section [$d\sigma/d\Omega \sim |F(Q)|^2 S(Q)$, where $F(Q)$ is the form factor of the PI core] versus wavevector, determined from radial averages of the CCD images, to obtain $S(Q)$. The background-subtracted cross-sections at 393 K and 398 K are shown in Fig. 2(b) as open and solid circles, respectively. The solid curve in Fig. 2(b) is the best fit to the data obtained at 398 K. The best-fit parameters so-obtained are: for the core radius, $a = 173 \text{ \AA}$, for the hard-sphere radius, $R = 260 \text{ \AA}$, and for the hard-sphere volume fraction, $\phi = 0.26$. On this basis, we may infer $S(Q)$.

The structure factor inferred from the fit generally mimics the variation of $\tau_Q Q^2$ versus Q (data not shown). Detailed inspection reveals, however, that the peak of $S(Q)$ is more pronounced than that of $\tau_Q Q^2$. Remarkably, similar behavior is found in light scattering studies of dense systems of large colloidal particles, whose interactions approximate those of a hard spheres. In this latter context, the deviation of $\tau_Q Q^2 / S(Q)$ from a constant is ascribed to hydrodynamic interactions between the colloidal particles, mediated by the suspending medium. This suggests the importance of hydrodynamic interactions between micelles in our case, mediated by the flow of the intervening homopolymer matrix.

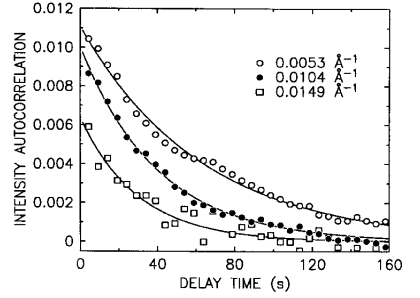


Figure 1: Intensity autocorrelation function vs. time for three wavevectors at 393 K.

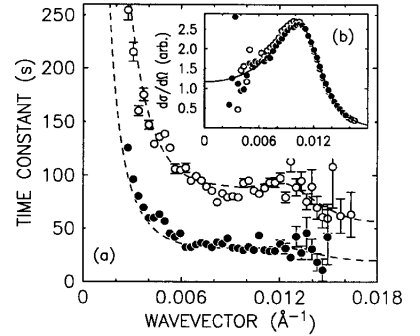


Figure 2: (a) Characteristic time (τ_Q) vs. wavevector (Q) for 17 wt. % PS-PI in 12.7k PS at 393 K (open circles) and 398 K (solid circles). The dashed lines are guides-to-the-eye. (b) Background-subtracted scattering intensity vs. Q . The solid line is the model discussed in the text.