

**SHEAR-INDUCED ORDERING IN A HOMOPOLYMER BLEND WITH
BLOCK-COPOLYMER SURFACTANT**

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Shear-Induced Order in a Homopolymer Blend with Block Copolymer Surfactant

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Small-angle neutron scattering has been used to investigate the shear response of a low molecular weight A/B homopolymer blend with $A-B$ diblock-copolymer surfactant. In the pure homopolymer limit, long-wavelength critical fluctuations are sheared apart and the flow stabilizes the disordered phase. Above a threshold block-copolymer composition, however, these fluctuations become enhanced by the shear, implying that the flow has a destabilizing effect on the disordered phase. [S0031-9007(97)04737-6]

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In addition to providing practical insight into enhanced polymer miscibility, ternary homopolymer/copolymer mixtures offer a unique opportunity to study phase transitions and ordering in soft materials under shear. This is particularly true of low molecular weight systems that exhibit strong critical fluctuations but still have relaxation rates slow enough to respond to moderate flows. In pure homopolymer blends, it is well established that long-wavelength critical fluctuations are sheared apart in a manner that stabilizes the miscible or disordered phase [1,2]. Fluctuations in disordered diblock-copolymer melts [3], however, are sheared apart in a way that induces ordering [4–7]. Between these two extremes, the behavior is potentially quite rich and complex [8–12]. Here, we use small-angle neutron scattering (SANS) to study the shear response of low-molecular-weight A/B homopolymer blends with $A-B$ diblock-copolymer surfactant. Above a threshold copolymer concentration, the data show an *enhancement* of composition fluctuations under shear, which is attributed to a shear-induced increase in the ordering temperature.

The materials are monodisperse blends of deuterated polystyrene (dPS) and polybutadiene (PB) with degrees of polymerization $N_{\text{dPS}} \approx 9$ and $N_{\text{PB}} \approx 92$. The dPS-PB diblock copolymer is also low-molecular weight, with $N_{\text{dPS-PB}} \approx 45 + 92 = 137$. All three components are unentangled. As determined by transmission electron microscopy (TEM), the melt copolymer is disordered at room temperature (25 °C). Between 0% and 8.6% copolymer by mass, the spinodal temperature as a function of homopolymer content was measured with temperature-jump light scattering, from which we obtain the critical homopolymer composition and critical temperature as a function of copolymer composition [13]. The mixtures used for SANS contained 0% [$\phi_{\text{dPS}} = 0.70$ and $\phi_{\text{PB}} = 0.29$, with $T_{C_a} = (51 \pm 0.5)^\circ\text{C}$], 3% [$\phi_{\text{dPS}} = 0.68$, $\phi_{\text{PB}} = 0.28$, and $\phi_{\text{dPS-PB}} = 0.03$, with $T_{C_b} = (47 \pm 0.5)^\circ\text{C}$], and 8.6% [$\phi_{\text{dPS}} = 0.66$, $\phi_{\text{PB}} = 0.24$, and $\phi_{\text{dPS-PB}} = 0.09$, with $T_{C_c} = (35 \pm 0.5)^\circ\text{C}$] copolymer at critical homopolymer compositions, where ϕ is the volume fraction. We also studied an analogous set of mixtures in which only the diblock was deuterium

labeled [14]. Small amounts ($\phi_{\text{AO}} = 0.01$) of antioxidant were added to all of the samples.

Quasistatic light scattering was also used to measure the time evolution of the spinodal instability in the vicinity of the quiescent critical point [13]. From this, we obtain the spinodal-peak position q_m and intensity $I(q_m)$ as a function of time after shallow quenches just inside the unstable region. At fixed $T_{C_i} - T$, we observe the late time power laws $q_m(t) \sim t^{-\alpha}$ and $I(q_m) \sim q_m^{-d} \sim t^{3\alpha}$ with α ranging from 1 in the pure blend to $\frac{1}{2}$ in the 8.6% copolymer sample, implying that the diblock significantly inhibits the onset of a hydrodynamic growth regime. The suppression of hydrodynamic effects with increasing copolymer content suggests that the coupling between composition and velocity fields decreases in strength with increasing copolymer composition, which should strongly influence the shear response of the mixture.

The SANS measurements were performed at the National Institute of Standards and Technology using a Couette shear cell that is described elsewhere [15]. The temperature was controlled to ± 0.2 K and measurements were taken in the miscible (disordered) phase near the equilibrium stability limit $T_c(0)$. The geometry of shearing is in the x - y plane with the flow in the x direction and the velocity gradient in the y direction. Neutrons incident along the y axis were scattered by the sample and a two-dimensional detector measured the scattering intensity in the x - z plane. The data were first averaged over angular sectors parallel and perpendicular to the flow to detect anisotropy. In all cases, the response was isotropic and the data were azimuthally averaged. Multiple scattering is negligible and the background-corrected intensity is proportional to the structure factor $S(\mathbf{q}, \dot{\gamma}) = \langle \psi_q \psi_{-q} \rangle$, where $\psi(\mathbf{r}) = \phi(\mathbf{r}) - \phi_c$ is the order parameter and $\dot{\gamma} = \partial v_x / \partial y$ is the shear rate.

The random-phase-approximation (RPA) theory of ternary homopolymer/copolymer mixtures is mean field and, thus, inadequate for low-molecular-weight systems [16,17]. An isotropic response in $S(\mathbf{q}, \dot{\gamma})$ over the q range probed by SANS is typically associated with a shift in the stability limit [1]. For the all-PS-labeled mixtures, the low- q miscible-phase scattering intensity was fit to

the Ornstein-Zernike expression

$$S(q) = \frac{S(0)}{1 + \xi^2 q^2} \quad (1)$$

to obtain $\dot{\gamma}$ dependent susceptibilities $S(0)$ and correlation lengths ξ as a function of temperature. In the vicinity of $T_c(0)$, the shear suppressed the low- q scattering in the 0% and 3% copolymer samples. Such behavior is consistent with shear stabilization of thermal fluctuations as previously documented in homopolymer blends [1,15]. In contrast, the shear enhanced the low- q scattering close to $T_c(0)$ in the 8.6% copolymer sample, as shown in Fig. 1.

The shear-induced structure is evident in $S(0)$ and ξ , which decrease with $\dot{\gamma}$ close to $T_c(0)$ in the 0% and 3% samples, but increases with $\dot{\gamma}$ close to $T_c(0)$ in the 8.6% sample, as shown in Fig. 2. Curvature in the inverse susceptibility as a function of $1/T$ indicates a breakdown of mean-field theory [3,18]. In the 8.6% copolymer sample, this curvature decreases as the critical temperature is increased by the flow. At temperatures well above $T_c(0)$, the data from the 8.6% sample suggest shear stabilization, as $1/S(0)$ shows a slight shear-induced increase [Fig. 2(b)]. Close to $T_c(0)$, however, the destabilizing effect of the shear is quite dramatic, suggesting that the reduction of composition fluctuations by the flow drives the system from Ising to mean-field behavior. The interfacial contribution to the Ginzburg-Landau free energy is

$$F_I = \frac{1}{2} \kappa \int |\nabla \psi|^2 dV. \quad (2)$$

As shown in the inset of Fig. 1, the interfacial coefficient $\kappa = \xi^2/S(0)$ exhibits a 20% decrease between 3% and 8.6% copolymer [19]. The T dependence is nonsingular and κ is insensitive to shear. Equation (2) models the leading-order term in the free energy due to gradients in ψ . The decrease in κ with increasing copolymer content

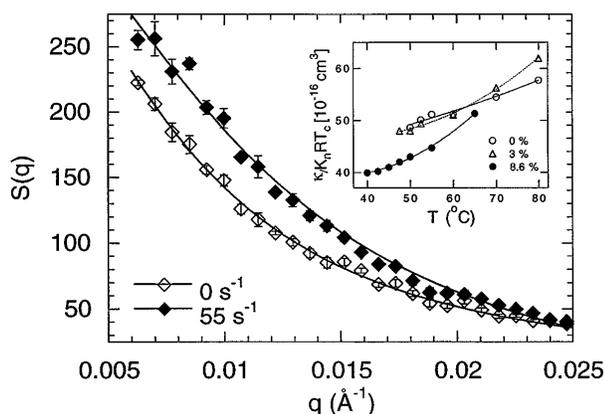


FIG. 1. Shear-induced increase in the low- q scattering intensity in the 8.6% copolymer all-PS-labeled sample. The temperature (40 °C) is 5 K above $T_c(0)$. The lines are fits to Eq. (1). The inset shows the interfacial coefficient κ as a function of temperature and copolymer composition. The units are expressed in terms of $K_n RT_c(0)$, where K_n is the SANS contrast factor between dPS and PB and R is the molar gas constant.

implies that the free-energy cost of an order-parameter gradient is reduced by the diblock.

Figure 3(a) shows the T dependence of the scattering intensity in the equilibrium miscible phase of the 8.6% copolymer block-only-labeled mixture. There was no detectable structure in the 3% block-only-labeled sample. The peak intensity and $2\pi/q_{\max}$ both increase as $T \rightarrow T_c(0)$. In contrast, the same copolymer concentration in a neutral solvent of dioctyl phthalate (DOP) is independent of T [Fig. 3(b)], implying that fluctuations in copolymer composition are coupled to long-wavelength fluctuations in homopolymer composition. In the absence of this coupling, the scattering intensity approximates the form factor of the partially labeled chains, and we model the data in the Fig. 3(a) with

$$I(q) = P(q) \frac{S'(0)}{1 + (\xi' q)^2}, \quad (3)$$

where $P(q)$ is the average of the data in Fig. 3(b). The structure factor $S'(q) = I(q)/P(q)$ is then fit to a Lorentzian to get $S'(0)$ and ξ' , and typical Zimm plots in the vicinity of $T_c(0)$ are shown in the inset of Fig. 3(b).

In this interpretation, the peak in Fig. 3 is due to the correlation-hole effect arising from the partial deuterium labeling of the diblocks [20]. Dividing out the form factor via Eq. (3) significantly reduces the curvature in Zimm plots of inverse intensity vs q^2 and gives a leading-order description in terms of a Lorentzian structure factor $S'(q)$ that contains all of the temperature dependence. This

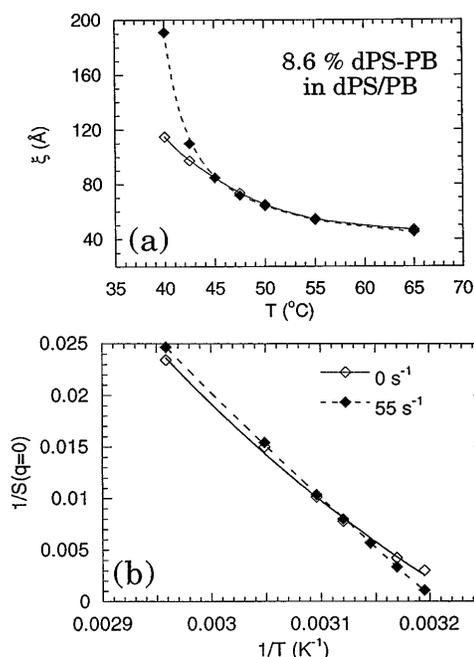


FIG. 2. Shear response of (a) ξ vs T and (b) $1/S(0)$ vs $1/T$ for the 8.6% all-PS-labeled sample, where the error bars are the size of the data markers. The temperature where $1/S(0)$ extrapolates to zero gives the stability limit, and the shear-induced increase in $S(0)$ implies a shear-induced increase in the critical temperature.

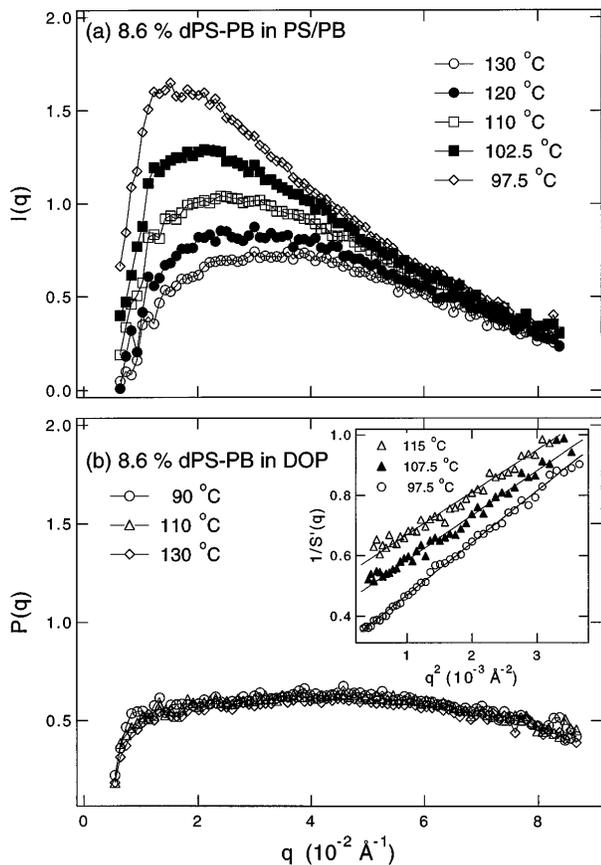


FIG. 3. (a) Temperature dependence of the equilibrium scattering intensity in the 8.6% copolymer block-only-labeled sample. (b) These fluctuations are absent in a neutral solvent of DOP, which gives the partially-labeled-copolymer form factor $P(q)$. The structure factor $S'(q) = I(q)/P(q)$ is fit to a Lorentzian (inset).

treatment is self-consistent, as the q range used in the fitting is much less than $2\pi/\xi'$.

The quantity ξ' measures the spatial coherence of copolymer composition fluctuations induced by critical fluctuations in homopolymer concentration. It is roughly a factor of 5 smaller than ξ and characterizes structural correlations on the size of individual diblocks, as represented schematically in Fig. 4. A comparison of ξ' and

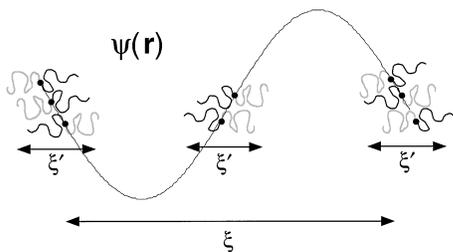


FIG. 4. Schematic representation of block copolymer residing preferentially at the diffuse interface of a homopolymer composition fluctuation that elucidates the difference between the two correlation lengths ξ (all-PS-labeled) and ξ' (block-only-labeled).

ξ as a function of $T - T_c(0)$ is shown in Fig. 5(a), where ξ' has been scaled by a factor of 3. The increase in ξ' as $T \rightarrow T_c(0)$ implies enhanced correlation, and is consistent with a physical picture in which the diblock resides preferentially in regions where $|\nabla\psi|$ exhibits a maximum. The saturation of ξ' in the vicinity of $T_c(0)$ suggests that the extent of these fluctuations is limited, which is consistent with the physical picture depicted in Fig. 4.

As shown in Fig. 5(b), the scattering intensity of the 8.6% block-only-labeled sample is insensitive to shear. The inset shows the shear response of ξ and ξ' in the vicinity of $T_c(0)$, where these two quantities have been reduced by their $\dot{\gamma} = 0$ values. The temperatures are 5 and 1 K away from $T_c(0)$ in the all-PS-labeled and block-only-labeled samples, respectively [14]. The bulk correlation length ξ has been fit to

$$\frac{\xi(\dot{\gamma})}{\xi(\dot{\gamma} = 0)} = \left[1 - a \frac{(\tau\dot{\gamma})}{1 + (\tau\dot{\gamma})} \right]^{-\nu}, \quad (4)$$

with fitting parameters $a = 0.6$, $\tau = 0.7$ s, and $\nu = 0.6$. Equation (4) is derived from an expression for the shear-

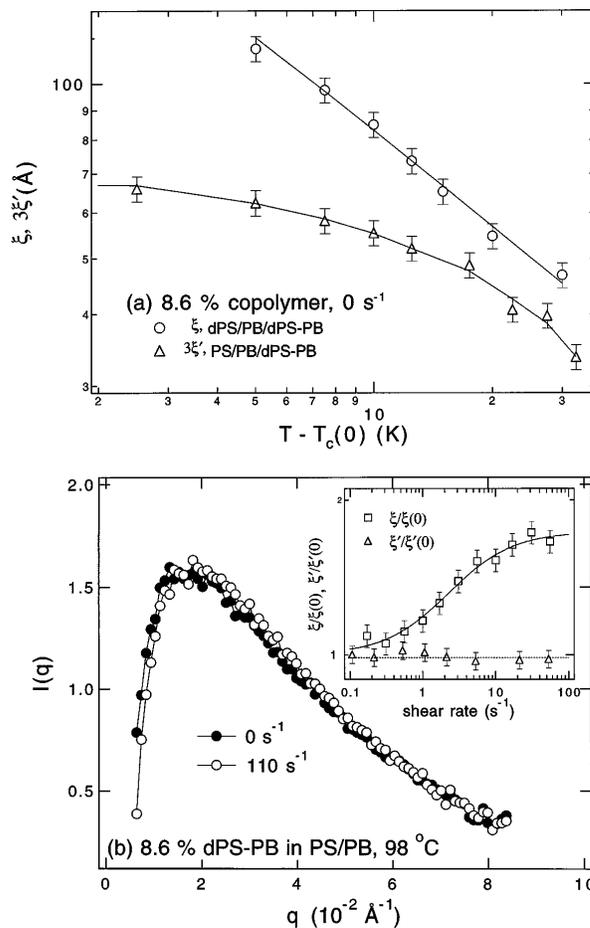


FIG. 5. (a) Log-log plot of ξ' and ξ vs $T - T_c(0)$. (b) The scattering intensity of the 8.6% copolymer block-only-labeled sample is insensitive to shear, and the inset shows the shear response of ξ and ξ' in the vicinity of $T_c(0)$, where the solid line is a fit to Eq. (4).

induced shift in the ordering temperature of copolymer melts [6]. That ξ' is insensitive to shear implies that structural correlations in copolymer composition are stable against the flow. The shear-induced increase in ξ implies that these transient, "micellelike" structures nucleate homopolymer in the presence of the flow field. Below a threshold copolymer concentration, these structures lack interfacial integrity and are sheared apart.

In conclusion, we offer evidence for shear-enhanced composition fluctuations in a low-molecular-weight homopolymer blend with diblock-copolymer surfactant. The tendency for the block to enhance the stability of an interface under flow is reminiscent of shear-induced ordering in pure diblock-copolymer melts. In a qualitative sense, one might envision an equilibrium line of critical points as a function of copolymer content. It is well known that shear moves this line up in the pure-copolymer limit and down in the pure-blend limit, and the results presented here suggested that the former effect emerges at a modest copolymer composition of around 9%. The shear-induced increase in ξ saturates in the strong-shear limit in a manner that is consistent with a high- $\dot{\gamma}$ plateau in the ordering temperature, as predicted in the pure-copolymer limit by Cates and Milner [4]. In contrast to the original mode-coupling scheme of Onuki [21], the Cates-Milner theory does not incorporate hydrodynamics, suggesting that subtle changes in the nature of the coupling between ψ and the velocity field induced by the diblock might lie at the foundation of this effect.

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