Shear-Induced "Homogenization" of a Diluted Polymer Blend

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The miscibility of a diluted polymer blend under steady shear has been investigated in the two-phase region using fluorescence and phase-contrast microscopy. Critical exponents describing the shape of the coexistence curve and the shift of the critical temperature $\Delta T_c(\dot{\gamma})$ were compatible with expectations based on renormalization group and mode-coupling theories, but the introduction of a reduced variable description of ΔT_c suggested a tendency for T_c to saturate at high shear rates. [S0031-9007(97)02774-9]

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The effects of shear on the critical temperature T_c has been studied in small molecule binary mixtures as well as polymeric blends [1–4]. Because of the relatively large influence of shear and the slow dynamics of polymeric systems, it has been possible to perform more comprehensive measurements on bulk [3] and diluted [4] polymer blends using a combination of small angle neutron scattering and dynamic light scattering techniques. A comparison [5] of experimental results obtained in the one phase region with the theory of Onuki and Kawasaki [6] indicates a remarkable consistency. However, many questions remain about the influence of shear on the phase stability of mixtures. For example, the *combined* influence of additives (e.g., solvent for the blend) and shear on the phase stability of mixtures and the nature of mode-coupling effects in the unstable regime have received limited attention. The present paper considers these problems based on the existing Onuki-Kawasaki framework.

Previous measurements [2] on diluted polymer blends in the unstable regime under conditions of steady shear showed a marked decrease of scattering intensity at high rates of shear. This shear-induced "homogenization" effect was interpreted in terms of a shift of the phase boundary with shear, as in earlier shear-scattering measurements on small molecule mixtures in the one-phase region [1]. The effect of droplet distortion on the shear-scattering measurements was minimized by considering the projection of the scattering data along the vorticity direction. Estimates of the integrated intensity along this direction from shear light scattering measurements showed a tendency to strongly decrease and then to saturate at high shear rates. The characteristic shear rate $\dot{\gamma}_c$, corresponding to this saturation point, was then employed along with theoretical arguments to estimate the shift of the phase boundary with shear. While this procedure led to estimates of the critical temperature shifts with shear that were apparently consistent with the Onuki-Kawasaki (OK) theory [6], it seems unclear to us whether the diminished scattering intensity ("homogenization") reflected a true shift of the phase boundary or merely the breakup of droplets under shear to a scale undetectable by light scattering measurements. Since this kind of scattering intensity measurement depends on the history of the shearing measurement, the procedure of extrapolation, and the sensitivity of the detection system, it seems necessary to seek other measurement techniques which more directly reflect the location of the phase boundary to determine the true meaning of shear-induced "homogenization." More basically, we have the question of whether the coexistence curve actually shifts with $\dot{\gamma}$.

In this paper we investigate the miscibility of a blend in the two-phase regime. Fluorescence and phase-contrast microscopy provide real-space images of the two-phase morphology under shear. Information about the local polymer composition is determined from the fluorescence intensity, and observation of droplet deformation under shear with phase-contrast microscopy allowed us to determine a shear stress relaxation time.

Polystyrene (PS) was purchased from Varian [7] with molecular weight $M_W = 96\,000$ [8] and polydispersity $M_W/M_n = 1.02$. We labeled the PS with the fluorescent dye, 4-chloro-7-nitrobenzofurazan (NBD chloride) following the method described in Ref. [9]. The aminomethylated polystyrene intermediate was reacted with NBD chloride and purified via a precipitation method. The monomer ratio of PS to NBD was calculated to be 300 to 1. Gel permeation chromatography (GPC) revealed that the labeling process leads to a slight change in the molecular weight and polydispersity, such that $M_W = 110\,000$ and $M_W/M_n = 1.08$. The polybutadiene (PB) had a molecular weight $M_W = 22\,000$ and a comparable polydispersity. The fluorescence microscope utilized a bandpass excitation filter (480 ± 20 nm), a dichroic mirror (reflects light 480 ± 20 nm), a long-pass emission filter (cutoff wavelength 510 nm), and a 300 watt xenon (ORL illuminator 6000) excitation light source. Phase-contrast and fluorescence microscopy data were collected using techniques described elsewhere [10]. Images were recorded onto videotape (super VHS) and then digitized using a frame grabber.

The coexistence curve for the quiescent NBD-PS/PB/DOP mixture (8% total polymer in solution by mass)

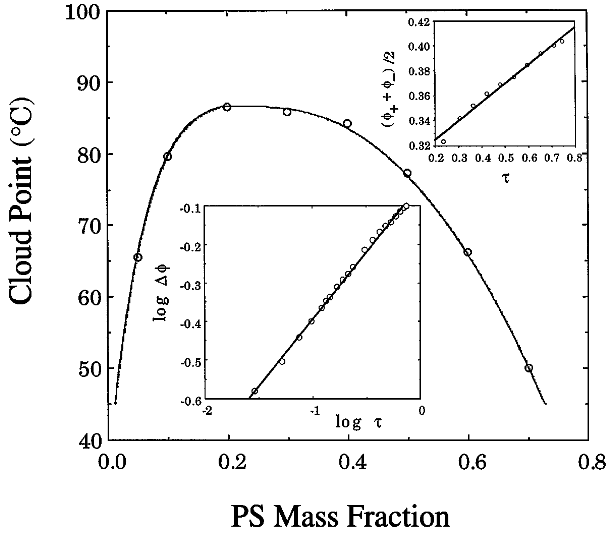


FIG. 1. Phase diagram of NBD-PS/PB (1:1 mass ratio) in DOP. The main figure shows the coexistence curve (determined by optical turbidity measurements) where the blend is treated as a pseudobinary system. The total polymer concentration is 8% by mass. The insets show the composition difference $\Delta\phi$ between the coexisting phases and their average $\overline{\phi}$ versus reduced temperature, $\tau = |T - T_c|/T_c$.

was measured with optical microscopy, and is shown in Fig. 1. The critical composition corresponds to roughly 30/70 PS/PB by weight, and the critical temperature was found to equal 86.5 °C. The order parameter exponent β (inset Fig. 1) was determined from a power-law fit of the composition difference $\Delta\phi$ as a function of reduced temperature, $\tau = |T - T_c|/T_c$, leading to the relation,

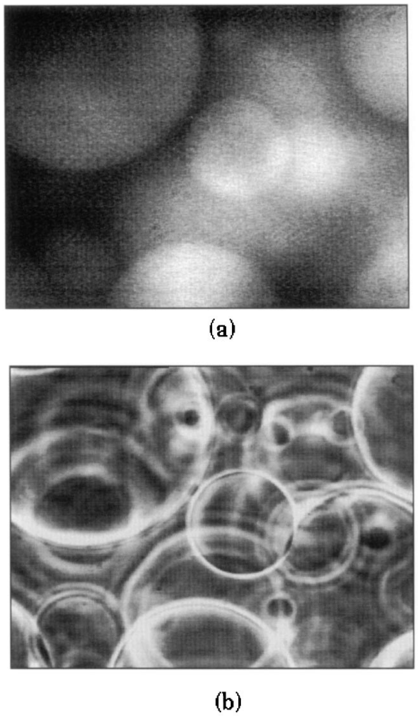
$$\Delta\phi(\dot{\gamma} = 0, T) = 0.90\tau^{\beta}, \qquad \beta = 0.35 \pm 0.01\,, \quad (1)$$

where the stated confidence interval [11] corresponds to 2 standard deviations in the fitting procedure. The value of β determined is intermediate between the Ising value [12] $\beta \approx 0.326 \pm 0.002$ and the fully Fisher-renormalized value [13] $\beta_F \approx 0.366$ expected for a highly diluted binary-fluid mixture. A previous measurement of the correlation length exponent ν by dynamic light scattering [14] for a comparable PS/PB/DOP diluted blend (without dye labeling) gave $\nu \approx 0.68$, which is likewise intermediate between the Ising ($\nu \approx 0.63$) and fully Fisher-renormalized value ($\nu_F \approx 0.71$) [13,15]. Similar β values have been determined for diluted small molecule mixtures [16].

The asymmetry of the coexistence curve was characterized by the average of the coexisting compositions, $\overline{\phi} \equiv (\phi_+ + \phi_-)/2$, which has a linear ("rectilinear diameter" [17]) dependence on τ,

$$\overline{\phi} = \phi_c + 0.15\tau, \qquad \phi_c = 0.295\,. \quad (2)$$

This serves as a useful method of locating the critical composition and is important in the development below. Figure 2 shows fluorescence and phase-contrast micrographs of phase-separated droplets. The bright domains (a) are the PS-rich phase. By monitoring the fluorescence intensity differences it is possible to deduce the composition differences between the phases under steady shear. The droplets become increasingly distorted with shear, and this effect becomes more pronounced near the critical point where the interfacial tension is small. For the modestly large quenches used here (≥30 °C below the phase boundary) the distortion is small enough that the fluorescence intensity difference between droplet and matrix can be accurately measured. The fluorescence intensity ratio is very sensitive to small composition changes undetectable with ordinary light scattering.


(a)

(b)

FIG. 2. Fluorescence and phase contrast micrographs of PS enriched droplets in the unstable regime for a mass fraction of 8% NBD-PS/PB in DOP at 22 °C. The bright regions in the fluorescence microscope image (a) show the NBD-PS rich droplets, while the dark continuous phase corresponds to the PB rich phase. The droplet morphology is clearer in the phase contrast image (b).

The relative-polymer-composition ratio R between the PS-rich domains and the PB-rich continuous phase is obtained from the fluorescence-emission intensities I_f of the PS enriched and PS depleted phases,

$$R \equiv \phi_+/\phi_- = \exp\{\alpha[I_f(\text{PS-rich}) - I_f(\text{PS-poor})]\}\,, \quad (3)$$

where α is a calibration constant. The composition difference $\Delta\phi(\dot{\gamma}, T)$ under steady shear is readily determined to equal

$$\Delta\phi(\dot{\gamma}, T) = 2[(R - 1)/(R + 1)]\overline{\phi}\,. \quad (4)$$

Figure 3(a) shows $\Delta\phi$ versus τ determined from fluorescence-emission-intensity measurements based on

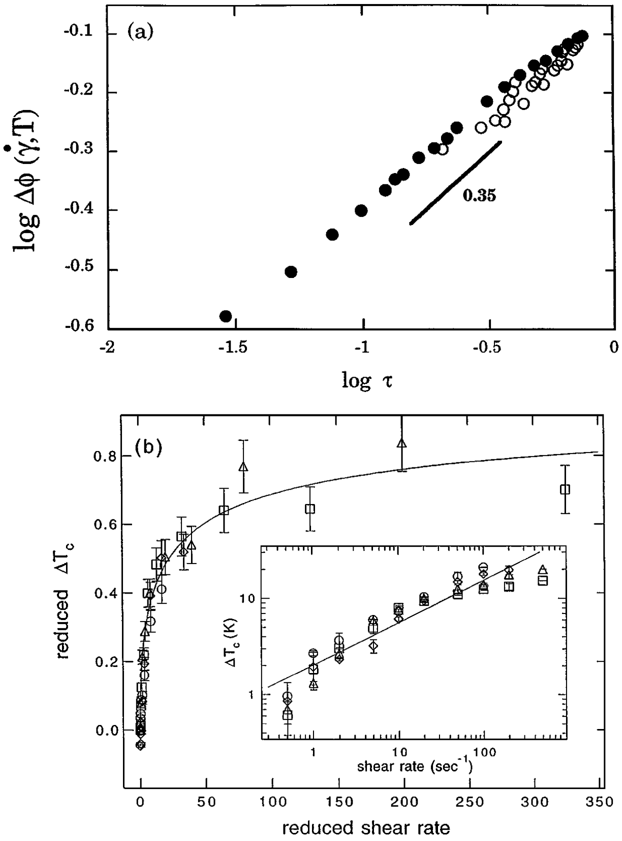


FIG. 3. Influence of shear on composition $\Delta\phi$ and the critical temperature shift ΔT_c. (a) The change of the droplet composition with shear $\Delta\phi(\dot\gamma, T)$ obtained from Eq. (4) is shown versus the reduced temperature $\tau = |T - T_c(\dot\gamma)|/T_c(\dot\gamma)$. Filled circles show quiescent data while open circles show shear data for several temperatures in the two-phase regime (22, 30, 40, and 50 °C). (b),(inset) Power-law fit of $\Delta T_c(\dot\gamma)$ versus $\dot\gamma$ based on expectations from mode-coupling theory and the reduced ΔT_c plot corresponds to Eq. (7). The symbols discriminate data for different temperatures: (○, 22 °C; ◇, 30 °C; △, 40 °C; □, 50 °C).

Eq. (3). $\Delta\phi(\dot\gamma, T)$ and $\Delta T_c(\dot\gamma)$ can be obtained by placing an estimated value of $\overline{\phi}$ into Eqs. (4) and (2), then iterating this procedure until the change of these values is small enough to be neglected. The value of $\overline{\phi}$ from Eq. (2) was used as the initial value in this recursion. This procedure gave a relation similar to the quiescent case,

$$\Delta\phi(\dot\gamma, T) = 0.85\tau^{\beta'}, \qquad \beta' = 0.35 \pm 0.05. \qquad (5)$$

The statistically determined error is optimistic, and we believe the total error could be as large as 0.07 due to systematic errors. The shift of the critical temperature from its quiescent value $T_c(\dot\gamma = 0)$ obtained by this procedure leads an apparent power law shown in Fig. 3(b),

$$\Delta T_c \equiv T_c(\dot\gamma = 0) - T_c(\dot\gamma) \approx (1.52 \pm 0.36)\dot\gamma^{0.44\pm0.05}, \qquad (6)$$

where the prefactor has an order of magnitude similar to the value reported by Takebe *et al.* [2] for PS/PB/DOP. The critical temperature shift exponent is notably smaller than the mode-coupling value for undiluted mixtures [1,5]. However, Fisher renormalization should increase ν, as mentioned above, leading to a smaller shear exponent, $1/3\nu = 0.47$, consistent with Eq. (6).

Although the power law Eq. (6) provides a rough description of $\Delta T_c(\dot\gamma)$ over intermediate shear rates, the scatter is rather large and the data suggest a tendency for ΔT_c to saturate for large $\dot\gamma$. Experimental errors become appreciable at high shear rates ($\dot\gamma \geq 500\ \mathrm{s}^{-1}$) where the droplets become small and the fluorescence intensity changes become difficult to measure, but the tendency for ΔT_c to saturate seems to occur at lower shear rates where we are confident in our measurements. We then examined the saturation effect more closely by introducing a reduced shear variable $\overline{\gamma} = \dot\gamma\tau_c$ where the stress relaxation time τ_c was determined from direct observation of droplet deformation under shear, as described in a previous paper [18]. The scatter in ΔT_c becomes substantially reduced with the introduction of $\overline{\gamma}$, and the tendency for ΔT_c to saturate at high shear rate becomes more apparent. The reduced $\Delta T_c(\dot\gamma)$ shift is well described by the approximant,

$$\Delta T_c(\overline{\gamma})/\Delta T_c(\overline{\gamma} \to \infty) = (\overline{\gamma}^{0.44}/5)/[1 + (\overline{\gamma}^{0.44}/5)], \qquad (7)$$

which is similar to an expression introduced previously to describe the shift of the order-disorder transition in block copolymers under steady shear [19]. Equation (7) is consistent with the expected scaling of mode-coupling theory at low shear rates [see Eq. (6) and Ref. [4]], but leads to a saturation of T_c at high shear rates, $\Delta T_c(\dot\gamma \to \infty) \approx 25$ °C. It is clear that the shift of T_c predicted by mode-coupling theory cannot hold indefinitely since the critical temperature must be positive, and a tendency for ΔT_c to saturate is reasonable. This observation invites further theoretical and experimental work on the high shear rate regime to understand and further verify this "saturation effect."

The present measurements were restricted to relatively deep quenches because of the tendency for the fluorescence of the NBD probe to be quenched at high temperatures ($T \geq 50$ °C). This restriction could be overcome by higher solvent dilution or by adjusting the polymer molecular weights, and further studies along this line are planned. Despite these limitations, it is clear that fluorescence microscopy can detect composition changes even at low rates of shear where these changes are small, and that the method provides a powerful and conceptually well-defined method for probing the phase coexistence of fluids under shear.

It should be appreciated that the present measurements do not conform to the narrow conditions required by the OK theory. This theory was developed for the one-phase region "near" the critical point where the shear rates are assumed to be sufficiently low that the steady state is "near" the quiescent equilibrium state. These assumptions allow the use of the ϕ^4 field theory as an appropriate model of the long wavelength composition fluctuations in the vicinity of the critical point, and this shear range restriction allows the neglect of inertial effects and other mode-coupling effects which can be expected at high shear rates where the fluid becomes strongly driven. The OK theory also does not treat diluted mixtures where the conventional Ising-type critical behavior can become strongly modified, leading naturally to questions of how the composition-velocity field mode couplings become modified in such systems.

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