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Dynamic Light Scattering from Ternary Polymer Blends: Critical Behavior and Bicontinuous Microemulsions

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SUMMARY: We have used dynamic light scattering to study the dynamics of ternary polymer blends consisting of poly(dimethylsiloxane) (PDMS) and poly(ethylethylene) (PEE) homopolymers and a PDMS-PEE diblock copolymer nearly symmetric in composition. The intensity autocorrelation functions for the binary blend are single-exponential, and the associated correlation length ξ scales with reduced temperature ε in accordance with the Ising universality class (i.e., $\xi \sim \varepsilon^{-\nu}$, with $\nu = 0.63$). An addition of copolymer depresses the critical temperature, but also increases the magnitude of ν. For compositions within the microemulsion channel, ξ exhibits a distinct maximum with decreasing temperature, near the Lifshitz line obtained from the static structure factor. For a particular composition, there is a "re-entrant" microemulsion, as the system passes into and then out of the phase-separated region upon cooling.

Introduction

Multicomponent polymer blends are technologically very important, as they offer relatively direct routes to tailoring physical properties. Due to the low combinatorial entropy of mixing associated with long chain molecules, most polymer pairs are not miscible. Consequently, it is often advantageous to stabilize a dispersion of one component in another by using a macromolecular surfactant, such as a block copolymer. Furthermore, as has recently become apparent, it is possible to utilize copolymers to direct the system to adopt more controlled and varied morphologies[1], such as bicontinuous microemulsions[2]. The microemulsion phase appears as a narrow channel in a phase diagram as a function of copolymer concentration, intermediate between a swollen lamellar phase on the copolymer-rich side and a phase-separated mixture on the other. Furthermore, this composition range coincides with the regime where the mean-field theory anticipates an isotropic Lifshitz point[3,4], i.e., a point where disordered, uniformly ordered, and periodically ordered phases meet[5]. Indeed, in one system a

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Lifshitz-like behavior was found in a region within one degree of the expected Lifshitz point[6], even though fluctuations are expected to destroy the Lifshitz point in favor of phases such as the bicontinuous microemulsion.

Experimental

The polymer samples were prepared by living anionic polymerization following standard procedures, as described elsewhere[7]. The number-average molecular weights determined by NMR were 2 130 for poly(dimethylsiloxane) (PDMS), 1 710 for poly(ethylethylene) (PEE), and 10 400 for the PDMS-PEE diblock (52% PDMS by volume). Mixtures of equal volumes of PDMS and PEE were prepared with the following volume fraction of copolymer: 0, 0.042, 0.071, 0.092, and 0.10. The mixtures were dissolved in pentane and filtered through 0.45 micron filters into duste-free light scattering cells. The cells were sealed after extraction of pentane in vacuum.

The viscosity of the sample with copolymer volume fraction 0.10 was measured on a Rheometric Scientific DSR from 25 to 150 °C using parallel plates with diameter 25 mm. Viscosities for the other compositions were estimated assuming the same T dependence, and scaling to the appropriate sample weight average molecular weight assuming Rouse dynamics (i.e., $\eta \sim M$).

The dynamic light scattering (DLS) instrument used was described elsewhere[8,9]. The autocorrelation functions of the scattered light intensity, $g^{(2)}(q,t)$ were analyzed either by fitting to a single exponential decay, or by the regularized nonlinear inverse Laplace transformation program REPES[10], which is similar to the routine CONTIN[11], except that it fits the intensity correlation function $g^{(2)}(t)$ directly (instead of taking the square root of $g^{(2)}$ to generate $g^{(1)}$).

Theory

For symmetric systems considered in this study ($N_A = N_B = N$, $\phi_A = \phi_B$, and $f_A = 1/2$), the phase diagram can be displayed[4,12] as a plot of T vs. ϕ_H and is schematically presented in Figure 1. Here, N_i and ϕ_i are the degrees of polymerization and volume fractions of component i, f_A is the fraction of polymer A in the copolymer, and $\phi_H = \phi_A + \phi_B$ is the total volume fraction of homopolymer. For $\alpha = N/N_{AB} < 1$, the (longer) copolymer is effective in compatibilizing the homopolymer blend, and is also capable of forming mesophases[4].

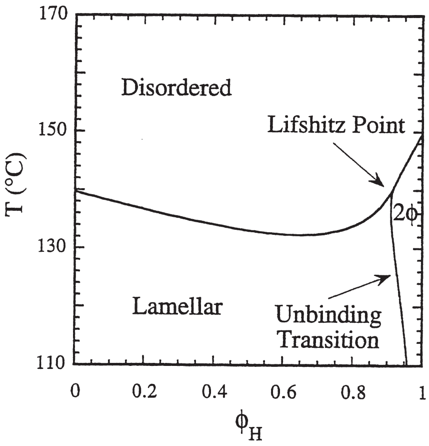

Fig. 1: Theoretical mean-field phase diagram for a symmetric homopolymer/ homopolymer/ block copolymer blend with equal volume fractions of each homopolymer, with $\alpha = 0.2$. The unbinding transition separates the lamellar and two-phase (2ϕ) regions and meets the order-disorder transition and stability lines at an isotropic Lifshitz point.

Figure 1 represents a mean-field description of the symmetric ternary mixture. Experimentally, fluctuations destroy the lamellar structure in the vicinity of the unbinding transition, leading to the appearance of a bicontinuous microemulsion in a channel, which is approximately vertical and with a narrow width of a few percent around the unbinding transition. Also, both 2 and 3-phase windows appear in the phase-separated regime.

In the dynamic light scattering experiments, the range of accessible wavevectors corresponds to lengthscales considerably larger than the constituent molecules, and one probes the rise and decay of spontaneous collective concentration fluctuations of PEE and PDMS segments. In the case that the dynamic structure factor S(q,t) is described by a single exponential, the decay rate Γ may be written generically as

$$\Gamma = q^2 (\Lambda/S(q)) \tag{1}$$

where Λ is an Onsager coefficient (that may depend on q) and S(q) is the static structure factor. For binary polymer blends at the critical composition, the results follow Eq. 1 as has been shown for several systems[9,13]. Furthermore, the resulting diffusivity, $D = \Lambda/S$, follows the Kawasaki-Stokes-Einstein form[9]

$$D = kT/(6\pi\eta\xi) \tag{2}$$

which defines a dynamic correlation length, ξ. This correlation length exhibits a broad crossover from mean-field ($\xi \sim \varepsilon^{-1/2}$) to Ising scaling ($\xi \sim \varepsilon^{-0.63}$) around a Ginzburg temperature a few degrees above T_c, just as the static correlation length determined from S(q) does. Here, ε is the reduced temperature, $\varepsilon = (T-T_c)/T$.

Results

The DLS correlation functions were all well described by single exponential decays, and the decay rate Γ was proportional to q^2 with zero intercept. This validates the use of Eq. (2) to extract the correlation length, using the measured viscosity as a function of T. The resulting values of ξ are compared as a function of temperature in Fig. 2.

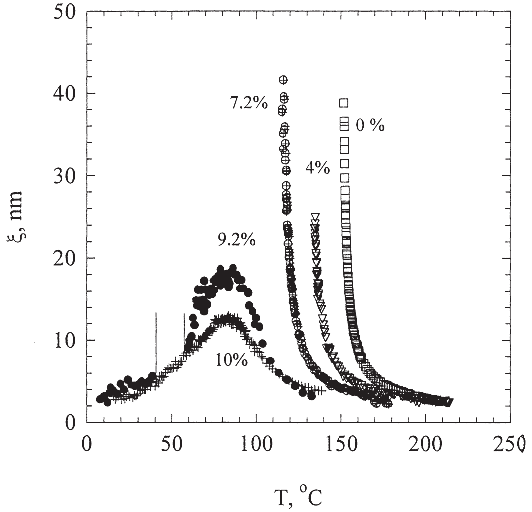

Fig. 2: Dynamic correlation length ξ as a function of temperature for five symmetric blends with the volume fraction of copolymer indicated. The vertical lines indicate the phase-separated gap for the mixture with 9.2 % of the copolymer.

For the blends with 0, 4 and 7.2 % of the copolymer added, the functional form of $\xi(T)$ is similar, but the magnitudes of ξ significantly decrease with increasing copolymer concentration at fixed T. This is directly attributable to the reduction in T_c, observable in Fig. 2, upon the addition of copolymer. However, it turns out that the functional form of $\xi(T)$ is not independent of copolymer concentration. Distinct deviations from the Ising-like behavior are apparent as T_c is approached; an example is shown in Fig. 3 for the blend containing 7.2 % of the copolymer. Interestingly, the magnitude of the apparent exponent ν is becoming larger than 0.63, hence the deviation is not a trend toward the mean-field "Lifshitz-like" behavior[6] ($\nu = 0.25$). Recently, a similar deviation of the critical exponents in static scattering on the same system was reported[14]. Physically, one can view this as the presence of copolymer opposing the growth of fluctuations, due to the compression of copolymers at the interface as the amount of interface decreases.

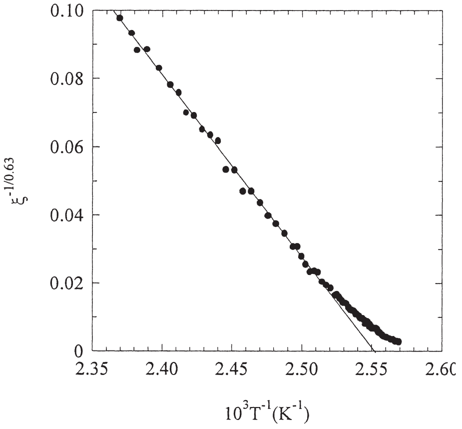

Fig. 3: Dynamic correlation length ξ (in nm) raised to the power -1/0.63 as a function of inverse temperature for the symmetric blend with 7.2 % of the copolymer. As the phase boundary is approached there are clear deviations from the Ising behavior (the straight line fit).

The situation is different for the mixture containing 9.2 % and 10 % of the copolymer, see Fig. 2. The increase in ξ as T_c is approached is arrested at a temperature near 90 °C and ξ decreases on further cooling. The resulting maximum of ξ near 83 °C is clearly associated with the transition into the microemulsion phase. This conclusion is supported by the appearance[15] of a peak in the static structure factor S(q) from SANS for this sample below 80 °C which is characteristic of microemulsion phases[16] and is reminiscent of the transition from $q^* = 0$ to $q^* > 0$ at the LP anticipated by mean-field theory[3]. The mixture with 9.2 % of the copolymer exhibits an additional feature: there is a gap on the corresponding curve in Fig. 2 between about 35 and 65 °C over which interval the sample passes into the two-phase regime (see Fig. 1). Below 35 °C, the mixture is again in the microemulsion phase which is, therefore, "re-entrant". Such behavior was not found for the other samples. The boundary between the phase-separated region and the microemulsion phase in a phase diagram is thus not a vertical line. The two transitions between the microemulsion region and phase separated region are first order, thus no divergence of the correlation length is observed in their vicinity.

Conclusion

We have shown that the main effects on the dynamics of adding copolymer to a binary blend are: (i) suppressing the stability limit and, therefore, the critical slowing down at a given temperature, (ii) changing the apparent values of the critical exponents, and (iii) stopping the divergence of the dynamic correlation length for a composition corresponding to the microemulsion channel. For a narrow range of copolymer compositions, near where the mean-field theory anticipates an isotropic Lifshitz point, ξ exhibits a distinct maximum with decreasing temperature.

Acknowledgments

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