Isotropic Lifshitz Behavior in Block Copolymer-Homopolymer Blends

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(Received 27 September 1995)

A series of mixtures composed of a symmetric A-B diblock copolymer and a symmetric blend of A and B homopolymers was investigated by small-angle neutron scattering. Mean-field theory predicts that a line of lamellar-disorder transitions with wave-vector instability $q^* > 0$ will meet a line of critical points with $q^* = 0$ in the three-component mixture at an isotropic Lifshitz point. Mean-field Lifshitz behavior ($\gamma = 1$ and $\nu = \frac{1}{4}$) was observed in the disordered state at the anticipated composition to within 1 K of the phase transition.

PACS numbers: 61.41.+e, 61.12.Ex, 64.60.Cn, 64.70.Kb

Fundamental to the study of critical transitions, where a system orders as a field (i.e., temperature) is varied, is the categorization of distinct universality classes. Each class possesses a unique set of critical exponents that describes how the various measurable quantities scale as the transition is approached. Two decades ago Hornreich, Luban, and Shtrikman [1] addressed the critical behavior that occurs when a wave-vector instability $\mathbf{q}^*$ in the ordered state evolves continuously from a fixed value $\mathbf{q}_0$, as an appropriate nonordering field is varied. Here, the locus of critical transitions, the λ line, is divided into $\mathbf{q}^* = \mathbf{q}_0$ and $\mathbf{q}^* \neq \mathbf{q}_0$ branches by a special multicritical point denoted as the Lifshitz point (LP) with its own set of characteristic exponents. A general review of Lifshitz phenomena has been presented by Selke [2]. LP behavior has been suggested for a variety of systems including liquid crystals [3,4], ferroelectrics [5], magnets [6], microemulsions [7], polyelectrolytes [8], and block copolymer-homopolymer mixtures [9,10]. To our knowledge an isotropic LP ($m = d$, where m represents the number of dimensions in which the wave-vector instability occurs and d is the space dimension) has never been realized experimentally. In this Letter, we report experiments on symmetric diblock copolymer-homopolymer blends that demonstrate mean-field isotropic Lifshitz behavior.

The Ginzburg-Landau free-energy density for a symmetric isotropic system described by a scalar ($n = 1$) order parameter, $\psi(\mathbf{r})$, can be represented by

$$F(\psi) = a_2\psi^2 + a_4\psi^4 + a_6\psi^6 + \cdots + c_1(\nabla\psi)^2 + c_2(\nabla^2\psi)^2 + \cdots, \qquad (1)$$

where the coefficients, $a_2, a_4, a_6, \ldots, c_1, c_2, \ldots$, are system (and temperature, pressure, etc.) dependent [2]. At an ordinary critical point $a_2 = 0$, with all remaining coefficients positive. Such a critical point separates a disordered state from one that is uniformly ordered with $q^* = 0$. Ferromagnets, binary liquid mixtures, and single-component fluids display ordinary critical points with well-established scaling exponents. At a Lifshitz (critical) point both a_2 and c_1 vanish, signaling the incipient development of a nonuniform ordered state with finite wave vector $q^* > 0$. Thus the LP is a special type of critical point that connects three distinct phases: disordered ($a_2 > 0$), uniformly ordered ($a_2 < 0, c_1 > 0$), and periodically ordered ($a_2 < 0, c_1 < 0$). Actual physical realizations of these states include paramagnetic, ferromagnetic, and helical in certain magnetics ($n \geq m = d - 1$) [2]; nematic, smectic-A, and smectic-C in liquid crystal mixtures ($n = m = 2$, $d = 3$) [3,4]; disordered, two-phase, and lamellar in properly constructed block copolymer-homopolymer mixtures ($n = 1$, $m = d = 3$) [9,10] (see Fig. 1).

Isotropic Lifshitz behavior was first proposed for block copolymer-homopolymer blends by Broseta and Fredrickson [9]. A symmetric A-B diblock copolymer contains $N_{A\text{-}B}$ repeat units evenly divided between chemically distinct A and B blocks. It forms a lamellar phase at low temperatures with periodicity $D = 2\pi/q^*$, and disorders upon heating. Binary mixtures of equal size linear homopolymers ($A + B$, where $N_A = N_B = N$) produce a symmetric phase diagram that contains an ordinary critical point at an A volume fraction $\phi_{A,c} = \frac{1}{2}$. Within mean-field theory, blending the two symmetric systems connects the homopolymer critical point and the block copolymer order-disorder transition (ODT) by a λ line of second-order transitions (see Fig. 2); here, ϕ represents the overall volume fraction of homopolymer. When $\alpha \equiv N/N_{A\text{-}B} < 1$, the $q^* = 0$ and $q^* > 0$ branches of the λ

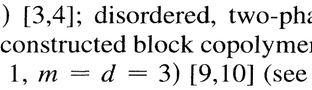

FIG. 1. Ordered state of a block copolymer-homopolymer blend. The lamellar microstructure, $q^* > 0$, reduces to two-phase coexistence in the limit of $q^* = 0$.

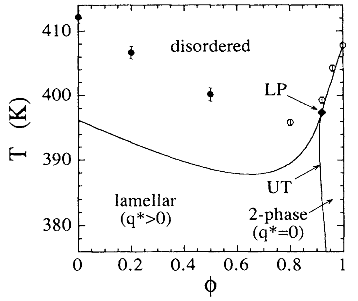

FIG. 2. Phase diagram for the block copolymer-homopolymer blends in terms of temperature and homopolymer volume fraction. Open and filled circles denote experimental phase transitions between ordered and disordered states measured by SANS and rheology, respectively. Theoretical phase boundaries are shown with solid lines. The diamond denotes the Lifshitz point (LP) below which an unbinding transition (UT) separates lamellar and two-phase regions.

line meet at a LP, as illustrated in Fig. 2 for $\alpha = 0.208$. (Theory predicts a tricritical point when $\alpha > 1$ and a Lifshitz tricritical point when $\alpha = 1$ [9,10].) Above the λ line the system is disordered. Adding homopolymer to the lamellar phase continuously increases D (i.e., decreases q^*), up to the unbinding transition (UT) where the system separates into two phases. We have calculated the UT that appears in Fig. 2 using self-consistent mean-field theory [11]. One end of the UT terminates at the LP, and the other intersects a three-phase envelope (well below the low-temperature limit of Fig. 2) where swollen lamellae ($q^* > 0$), A-rich ($q^* = 0$), and B-rich ($q^* = 0$) regions coexist.

This picture ignores the effects of fluctuations that are known to destroy the second-order character of the ODT [12–14]. Moreover, the isotropic LP has an upper critical dimension $d_u = 8$ [1], whereas claims for the lower critical dimension vary: $d_\ell = 1$ [15], $d_\ell \geq 2$ [16], and $d_\ell = 4$ [17]. Nevertheless, fluctuation effects are generally suppressed in polymer melts (the Ginzburg parameter scales as $N^{-1/3}$, N^{-1}, and $N^{-2/5}$ for diblock copolymers, binary homopolymer mixtures, and the associated LP, respectively [10]) making the three-component system illustrated in Fig. 1 an ideal candidate for investigating isotropic Lifshitz behavior.

Nearly monodisperse ($M_w/M_n < 1.05$) polyethylene (PE) and poly(ethylenepropylene) (PEP) homopolymers were synthesized using standard techniques [18], yielding $N_{\text{PE}} = 392$ and $N_{\text{PEP}} = 409$ calculated based on a four-carbon repeat unit, subject to approximately 5% error. Small-angle neutron scattering (SANS) measurements have established a critical temperature of $T_c = 406.9 \pm 0.5$ K and a critical composition of $\phi_{\text{PE},c} = 0.50 \pm 0.03$. The Flory-Huggins segment-segment interaction parameter used in computing the phase diagram shown in Fig. 2, $\chi = 6.82T^{-1} - 0.0118$, was determined from SANS data obtained with a $\phi_{\text{PE}} = 0.50$ mixture above T_c using established procedures [19]. This symmetric blend displayed mean-field behavior to within 1 K of the critical temperature.

The PE-PEP diblock copolymer used in this study has been described in a recent publication [20]. It contains a deuterated PE block with $N_{\text{PE-PEP}} = 1925(\pm 5\%)$, and has an ODT at 412 ± 1 K. The value $\alpha = 0.208$ used in preparing Fig. 2 was obtained from $N = (N_{\text{PE}} N_{\text{PEP}})^{1/2}$ and $N_{\text{PE-PEP}}$. Polymer blends were coprecipitated from a good solvent and dried under vacuum.

The λ line was determined by SANS and rheological measurements, and the results are included in Fig. 2. Disordering of lamellae is accompanied by a significant drop in the dynamic elastic modulus, G', which provides a convenient means of locating the ODT [14,20]. This method was used to identify T_{ODT} for $0 \leq \phi \leq 0.5$. SANS experiments were performed on mixtures with $0.8 \leq \phi \leq 1$ at the Risø National Laboratory (Roskilde, Denmark) using $\lambda = 10.6$ Å wavelength neutrons ($\Delta\lambda/\lambda = 0.09$) and an area detector. Blend specimens were sealed in quartz cells (1 mm path length) and held in a temperature-controlled (±0.5 K) brass oven that contained neutron beam access holes fitted with aluminum foil windows. This oven assembly was calibrated with a thermocouple mounted in a sample cell. SANS data were corrected for transmission, sample thickness, background, and empty cell scattering, were azimuthally averaged, and placed on an absolute intensity scale based on a calibrated secondary standard [19]. These results are presented as a function of the magnitude of the scattering wave vector $|\mathbf{q}| = q = 4\pi\lambda^{-1}\sin(\theta/2)$, where θ is the scattering angle. Here we focus on two of the blends studied.

Figure 3(a) illustrates the scattering intensity, $I(q)$, obtained from the $\phi = 0.80$ blend. At the highest measurement temperature (430.4 K) a broad plateau of intensity is evident in the low-q regime. As the temperature was reduced a peak appeared, at first growing slowly with decreasing temperature, then rapidly, until between 396.7 and 394.8 K when a higher-order reflection developed. By 390.8 K, three orders of reflections were apparent, consistent with a lamellar morphology. These results indicate that $T_{\text{ODT}} = 395.8 \pm 1$ K at $\phi = 0.80$.

The $\phi = 0.916$ mixture did not produce a SANS peak in the q range examined. Instead, the intensity grew most rapidly upon cooling at the lowest values of q, reminiscent of ordinary critical scattering. In general, the structure function $[S(q) \propto I(q)]$ for a critical mixture is given by [7]

$$S^{-1}(q) = 2a_2 + 2c_1 q^2 + 2c_2 q^4 + \cdots, \qquad (2)$$

where a_2, c_1, and c_2 appear in Eq. (1). In the long wavelength and $\phi \longrightarrow 1$ limits, Eq. (2) takes on the familiar Ornstein-Zernike form while at the LP composition, $\phi_{\text{LP}} = (1 + 2\alpha^2)^{-1}$ [9], c_1 vanishes and $S^{-1}(q)$ becomes linear in q^4. Figure 3(b) illustrates the latter behavior for the $\phi = 0.916$ mixture, which lies within

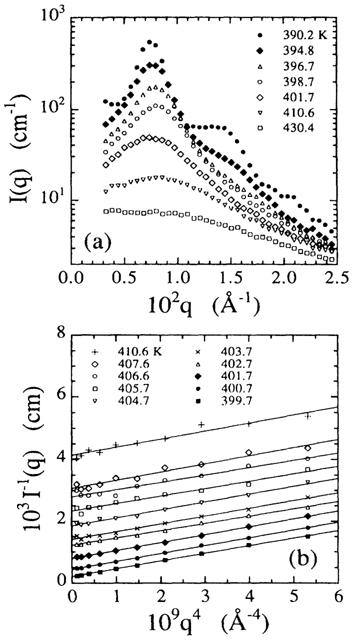

FIG. 3. Selected SANS intensities for temperature sequences at (a) $\phi = 0.800$ and (b) $\phi = 0.916$. The development of a peak at $q^* > 0$ followed by high-order reflections in (a) confirms a disorder-lamellar transition, while the linear dependence on q^4 (solid lines) in (b) indicates $c_1 = 0$ in Eqs. (1) and (2), consistent with Lifshitz behavior.

experimental error of the calculated ϕ_{LP}. We have extracted $S^{-1}(0)$ and the correlation length $\xi = (4c_2/a_2)^{1/4}$ [7] from the intercepts and slopes, respectively, of these linear data. Both q^2 and q^4 terms were necessary to model the $\phi = 0.96$ SANS data while the $\phi = 1$ mixture produced Ornstein-Zernike scattering (not shown). Figure 4 (inset) illustrates that $S^{-1}(0)$ is linear in T^{-1} over the entire experimental range, extrapolating to $T_{\mathrm{LP}} = 399.2$ K. Between 399.7 and 398.7 K the form and temperature dependence of $S^{-1}(q)$ changed significantly, suggesting that the system had crossed the λ line, within 1 K of the mean-field LP. The critical exponents, $\gamma = 1.01 \pm 0.02$ and $\nu = 0.24 \pm 0.01$, were obtained using T_{LP} as shown in Fig. 4. These values are consistent with mean-field isotropic Lifshitz behavior, $\gamma = 1$ and $\nu = \frac{1}{4}$ [1,10].

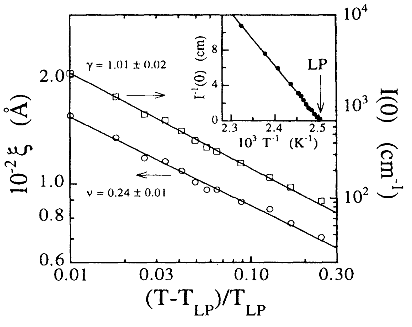

FIG. 4. Logarithmic plots of the correlation length (ξ) and zero-angle scattering intensity [$I(0)$] in terms of reduced temperature for $\phi = 0.916$, yielding the exponents ν and γ, respectively. T_{LP} is obtained from the inset. The mean-field Lifshitz (critical) point exponents are $\gamma = 1$ and $\nu = \frac{1}{4}$.

Both the form of the λ line (i.e., a minimum in T_{ODT} for $0 < \phi < \phi_{\mathrm{LP}}$) and the actual Lifshitz point (LP) composition are anticipated by the mean-field theory of Broseta and Fredrickson [9]. (The absolute deviation in T_{ODT} between theory and experiment may reflect a quantitative failure of the former, although the disparity is barely outside the experimental errors associated with $N_{A\text{-}B}$ and N.) However, we cannot claim that an isotropic Lifshitz point actually exists at the extrapolated mean-field value T_{LP}. The UT that emerges from the LP cannot survive the effects of fluctuations that will be encountered at the λ line. The lamellar phase near the unbinding transition consists of alternating domains rich in homopolymer separated by diblock monolayers. Mean-field theory suggests that the A and B domains swell to macroscopic dimensions as the UT is approached while the thin diblock monolayers remain flat, parallel, and equally spaced. (The UT occurs when the lamellar phase has been reduced to two domains.) This progression cannot continue for domain spacings, D, much larger than the persistence length of the diblock monolayer [21]. Instead, a transition will occur where the monolayers disorder, producing a channel of structured disordered phase (i.e., microemulsion [7]) that covers the UT and the LP. This would preclude a true Lifshitz point and imply that $d_\ell \gtrsim 3$ for this class of mixtures.

This work has demonstrated the utility of block copolymer-homopolymer mixtures in the pursuit of Lifshitz behavior. Our results revealed mean-field behavior remarkably close to an apparent Lifshitz critical point. These findings indicate that considerably smaller molecules should be used if access to fluctuations is desired. This system also provides the unique opportunity to examine a Lifshitz tricritical point [10] at $\alpha = 1$, which is likely to be more stable against fluctuations because a three-phase window replaces the unbinding transition in Fig. 2.

We are grateful to G. H. Fredrickson and M. Schick for useful conversations. This work was supported by the National Science Foundation (NSF/DMR-9405101) and the Center for Interfacial Engineering (CIE), a NSF-sponsored Engineering Research Center at the University of Minnesota. F. S. B. and K. A. also benefited from a NATO travel grant.

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