Polymeric Bicontinuous Microemulsions

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High molecular weight block copolymers can be viewed as macromolecular surfactants when blended with thermodynamically incompatible homopolymers. This Letter describes the formation of polymeric bicontinuous microemulsions in mixtures containing a model diblock copolymer and two homopolymers. Although we attribute development of this equilibrium morphology to the effects of fluctuations, mean-field theory provides a quantitative strategy for preparing the bicontinuous state at blend compositions near an isotropic Lifshitz point. [S0031-9007(97)03788-5]

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Subtle variations in the morphology of many soft materials can produce dramatic changes in physical properties and function. Lipid membranes, emulsions, colloidal dispersions, and foams are representative examples [1–3] of such systems, each constructed through a combination of short-range, liquidlike packing and some degree of long-range, solidlike order. This delicate balance is often mediated by amphiphilic molecules that modify specific interfacial characteristics such as curvature and tension [3]. Bicontinuous microemulsions, created by mixing appropriate amounts of oil, water, and a suitable amphiphile, contain a particularly intriguing morphology composed of undulating interfaces with vanishingly small mean curvature [1–4]. Small variations in component concentrations or temperature can destroy this state, and change the flow behavior, ionic conductivity, and other transport properties by many orders of magnitude. Despite more than a decade of research, this complex state of soft matter is not completely understood, particularly regarding the quantitative application of theory to experiment [4].

Conceptually, mixtures of high molecular weight homopolymers and block copolymers are closely related to traditional microemulsions. A-B diblock copolymers (these molecules contain a long sequence of type A monomers followed by one of type B monomers) are known to localize at the interfacial boundary separating discrete phases rich in A and B homopolymers [5]. The associated reduction in interfacial tension, and the imposition of a preferred interfacial curvature, can lead to two-phase morphologies with prescribed sizes and shapes that mimic the behavior of low molecular weight surfactant and soap solutions. However, the strongly overlapping chain conformations of molten polymers favor mean-field theoretical approaches, as illustrated by the remarkably successful treatments of pure block copolymer phase behavior [6]. In a previous Letter [7], we reported on the critical scattering from a symmetric A-$B/A/B$ ternary blend near the anticipated isotropic Lifshitz conditions. Surprisingly, this mixture exhibited mean-field behavior to within experimental resolution. Here we describe a more comprehensive investigation of this system near the predicted Lifshitz point, and show a catastrophic failure of mean-field theory, coincident with the fluctuation-induced formation of a bicontinuous microemulsion. We are not aware of prior experimental evidence of this morphology in bulk three-component polymeric systems under equilibrium conditions [8]. Previous studies that report cocontinuous phase morphologies have relied on kinetically restricted processing strategies [8], such as interfacial growth, high-shear mixing, and solvent casting, which can obscure the underlying equilibrium thermodynamic state.

Polymer blend phase behavior is influenced by a daunting array of experimental variables that includes component molecular weight and concentrations, block copolymer symmetry, temperature, and pressure. Here we focus on mixtures containing nearly equal size poly(ethylene) (PE) and poly(ethylenepropylene) (PEP) homopolymers ($N_{\mathrm{PE}} = 392$ and $N_{\mathrm{PEP}} = 409$ are the number-averaged degrees of polymerization) and a symmetric (i.e., $50/50$) PE-PEP diblock copolymer ($N_{\text{PE-PEP}} = 1925$); these N values are based on a four-carbon repeat unit and subject to about 5% error. Each compound is characterized by a polydispersity index of less than 1.1. We refer to a single mean homopolymer value $N_{\mathrm{H}} = (N_{\mathrm{PE}} N_{\mathrm{PEP}})^{1/2}$ throughout this Letter. Deuterium labeling of PE, and the PE block of PE-PEP, provided neutron scattering contrast. Synthesis and characterization of such saturated hydrocarbon compounds is described elsewhere [9].

Four parameters control the phase behavior of this system at constant pressure: the concentration of each component and the temperature. These are typically displayed in a "phase prism" [4], with the concentrations forming a triangular base and temperature the vertical axis. We have restricted our attention to a two-dimensional isopleth that slices symmetrically through this prism at a fixed ratio $\phi_{\mathrm{PE}}/\phi_{\mathrm{PEP}} = 1$, where ϕ_{PE} is the volume fraction of the PE homopolymer. This condition, along with the volumetric constraint $\phi_{\mathrm{PE}} + \phi_{\mathrm{PEP}} + \phi_{\mathrm{PE\text{-}PEP}} = 1$, reduces the number of thermodynamic variables to temperature and the total homopolymer volume fraction $\phi_{\mathrm{H}} = \phi_{\mathrm{PE}} + \phi_{\mathrm{PEP}} = 1 - \phi_{\mathrm{PE\text{-}PEP}}$, and these parameters define the two-dimensional phase diagrams shown in Fig. 1. The solid curves in the inset of this illustration were calculated using self-consistent mean-field theory [10,11], as reported previously [7].

Within the temperature range covered by our experiments, mean-field theory anticipates three thermodynamic regions: a single disordered phase at high temperatures, two disordered liquid phases rich in PE and PEP at high ϕ_{H} and low temperatures, and a single ordered lamellar phase at low ϕ_{H} and low temperatures. Adding homopolymer swells the flat lamellae thereby increasing the layer spacing, which within the mean-field theory diverges at the unbinding transition (UT). (In certain situations, such as at low temperatures or when $N_{\mathrm{H}} \geq N_{A\text{-}B}$ near the disordered state, separation into two or three phases may preempt unbinding [12].) Two lines of second-order phase transitions separate the high and low temperature portions of the theoretical phase diagram, intersecting the UT at an isotropic Lifshitz multicritical point (LP) [13]. In the present case, the mean-field theory [11] yields $\phi_{\mathrm{H,LP}} = 0.92$.

We have used small-angle neutron scattering (SANS) to characterize the phase behavior of the symmetric PE-PEP/PE/PEP ternary mixtures around the LP composition. These experiments were conducted at the Risø National Laboratory (Roskilde, Denmark) using established procedures [9]. Representative SANS data acquired from $\phi_{\mathrm{H}} \leq 0.91$ mixtures at 120 °C are presented in Fig. 2. This illustration also shows how the characteristic spacing $d = 2\pi/q^*$ varies with ϕ_{H}, where q^* is the scattering wave vector at the peak intensity. For $\phi_{\mathrm{H}} \leq 0.89$ these scattering patterns contain at least one higher-order reflection, at $2q^*$, consistent with a lamellar morphology. Lamellar-to-disorder transition temperatures were associated with the loss of higher-order diffraction, along with distinct changes in rheological properties [9]. In theory [14] and practice [9,15] fluctuation effects destroy the second-order character of this order-disorder transition, which must also create a two-phase region when $\phi_{\mathrm{H}} > 0$. However, our experiments indicate that this two-phase window spans less than 1 °C since coexisting lamellar and disordered phases were not observed. Accordingly, a narrow channel has been used to identify this phase boundary in Fig. 1.

At ϕ_{H} of 0.90 and 0.91, the SANS patterns contain just one peak over the entire span of temperatures probed ($118 \leq T \leq 160$ °C), indicative of a disordered phase as identified in Fig. 1.

Qualitatively different SANS patterns were recorded for $0.916 \leq \phi_{\mathrm{H}} \leq 1$. In the one-phase regime these mixtures produced structure factors that varied smoothly from an Ornstein-Zernike ($\phi_{\mathrm{H}} = 1$) to a Lifshitz

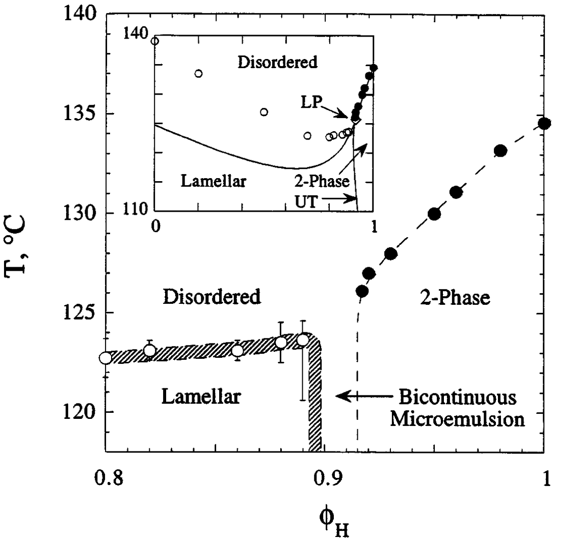

FIG. 1. Phase behavior of symmetric PE-PEP/PE/PEP mixtures where ϕ_{H} denotes the volume fraction of homopolymer. Symbols (○) and (●) identify first- and second-order transitions, respectively, and the dashed curves delineate the associated phase boundaries. The shaded portion indicates a two-phase region. A mean-field theoretical calculation, represented by the solid curves in the inset, locates the unbinding transition, and two lines of critical points that converge at an isotropic Lifshitz point (LP, ◇).

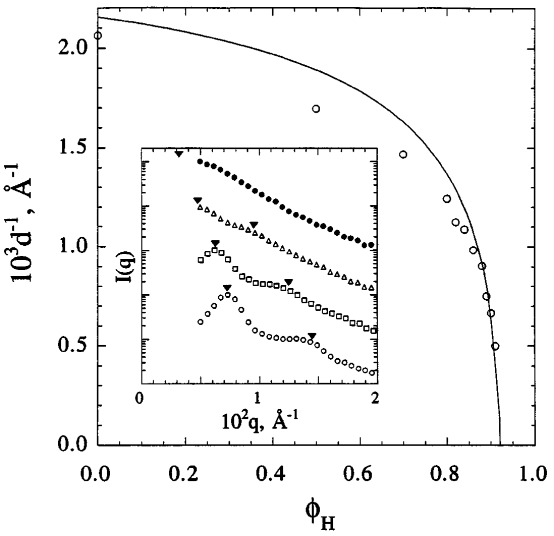

FIG. 2. Lamellar spacing d as a fucntion of the volume fraction of homopolymer ϕ_{H} near the order-disorder transition. The solid curve was obtained using the mean-field theory [11]. Representative SANS date obtained at 120 °C from $\phi_{\mathrm{H}} = 0.82$ (○), 0.86 (□), 0.89 (△), and 0.91 (●) mixtures are shown in the inset. $I(q)$ and q represent the intensity and scattering wave vector, respectively. First- and second-order reflections are identified by arrows. The principal peak position for the $0.88 \leq \phi_{\mathrm{H}} \leq 0.91$ mixtures was established using higher resolution measurements (not shown here).

($\phi_H = 0.916$ form [4,7,11]. Mean-field behavior was obtained at all compositions and temperatures within experimental resolution (1 °C) of the critical points (solid symbols, Fig. 1); mean-field Lifshitz behavior was documented in a previous report [11] for the $\phi_H = 0.916$ mixture. The line of second-order transitions for $\phi_H \geq 0.916$ is closely anticipated by the mean-field theory (solid curve, inset of Fig. 1).

The morphological characterization of soft materials is rarely conclusive without real-space images. Because the deuterated PE component (both the homopolymer and block) crystallizes below about 105 °C we were able to freeze structures present in the melt state by rapid immersion in liquid nitrogen. This technique is described in a recent publication [16] that includes a transmission electron microscopy (TEM) image of the pure PE-PEP ($\phi_H = 0$) lamellar phase. Following equilibration at 150 °C mixture specimens were cooled to 119 °C and held at this temperature for about 30 minutes [17], then quenced in liquid nitorgen, warmed to room temperature, and cryoultramicrotomed into thin (ca. 80 nm) sections. Exposure to ruthenium tetraoxide vapor selectively stained the amorphous PEP component, thereby producing TEM contrast. Four representative TEM images, obtained from specimens with $\phi_H = 0.86$, 0.90, 0.91, and 0.92 are shown in Fig. 3.

At $\phi_H = 0.86$ a (highly defective) lamellar morphology is observed consistent with the SANS results (Fig. 2). However, the unmistakable (local) translational order present at $0 \leq \phi_H \leq 0.89$ is destroyed at higher homopolymer contents. Images obtained from the $\phi_H = 0.90$ and 0.91 specimens bear a striking resemblance to freeze-fracture electron micrographs of the bicontinuous microemulsion phase (and the related sponge or L_3 phase), found in low molecular weight amphiphilic mixtures [18]. Increasing ϕ_H to 0.92 induces another dramatic transition, to a 2-phase morphology that appears to be composed of complementary droplet microemulsions; the micron-scale phases would coarsen if the specimen were annealed for longer times. These morphological changes are consistent with the phase diagram presented in Fig. 1.

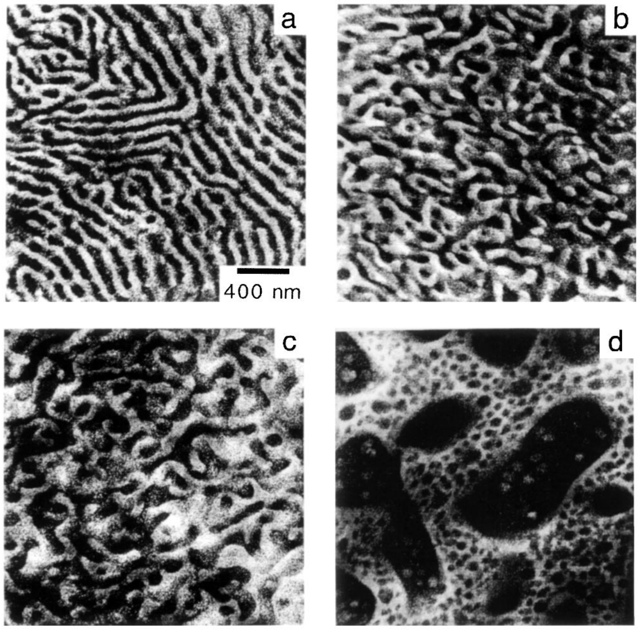

FIG. 3. Transmission electron micrographs from symmetric PE-PEP/PE/PEP mixtures that were annealed at 119 °C, then frozen, sectioned, and stained; (a) $\phi_H = 0.86$, (b) 0.90, (c) 0.91, and (d) 0.92. These images are consistent with (a) defective lamellae; (b),(c) bicontinuous microemulsion; and (d) a two-phase state.

The results shown in Fig. 3 Support the notion that lamellar fluctuations drive the formation of a bicontinuous microemulsion as $d \to \infty$, a primary ingredient in several approaches to modeling self-assembled soft materials [1,4]. We find a direct correlation between the density of lamellar defects near the disordering transition [Fig. 3(a)] and proximity to the microemulsion state. This effect is anticipated by the Monte Carlo simulations of a Ginzburg-Landau model by Gompper and Kraus [19], who also find fluctuation-induced passages between layers in the vicinity of the lamellar-microemulsion transition. Their simulated lamellar and microemulsion configurations are remarkably similar to the structures found in Fig. 3.

Perhaps the most striking aspect of these results is the catastrophic effect of fluctuations so narrowly focused about the Lifshitz composition. Along the liquid-liquid Ising branch of the critical curve $\phi_H \geq 0.916$, mean-field theory accurately locates the transition temperature and nonclassical scaling behavior is localized within a small region of order N^{-1} (Ginzburg parameter) in reduced temperature about the transition (<1 °C in the present experiment) [20]. The universality class to which this critical branch belongs is characterized by upper and lower critical dimensions of $d_u = 4$ and $d_l = 1$, respectively. Fluctuations in a three-dimensional realization of such a system, while producing a small nonclassical region, do not alter the continuous nature of the phase transition.

In contrast, fluctuations play a more significant role along the order-disorder branch of the critical curve $\phi_H \leq 0.89$. Mean-field theory [11] anticipates that this branch consists of second-order, continuous transitions, while fluctuation treatments [14] based on a self-consistent Hartree approximation yield weak first-order transitions between the disordered and lamellar phases at reduced temperatures. In contrast with the Ising branch, the appropriate Ginzburg parameter is of order $N^{-1/3}$, so fluctuation effects extend significantly farther from the transition. Experiments on undiluted, symmetric block copolymer melts have confirmed this scenario of a fluctuation-induced first-order transition and semiquantitative agreement has been obtained with the Hartree predictions [9,15].

We have determined that the self-consistent Hartree approximation breaks down as the theoretical Lifshitz composition is approached along the order-disorder branch.

The effects of fluctuations weaken as $\phi_{\rm H} \rightarrow \phi_{\rm H,LP}$ leading to a predicted Lifshitz point at 124.8 °C, just slightly lower than the mean-field value (see inset, Fig. 1). The experimental observation of a microemulsion (a continuous, but strongly fluctuating, extension of the disordered phase) beyond $\phi_{\rm H} = 0.89$ suggests that fluctuations destroy the lamellar phase and the Hartree predictions are spurious beyond this point. Indeed, the Hartree approximation is well known [21] to incorrectly induce a first-order transition when applied to a continuous transition such as the Ising branch. Apparently it is also incapable of dealing with the strong long-wavelength critical fluctuations in the vicinity of the Lifshitz composition.

The upper critical dimension of an isotropic Lifshitz point for a scalar field ($n = 1$) is $d_u = 8$ [13,22], and while not conclusively proven, there is theoretical evidence [23] that the lower critical dimension is $d_l = 4$. Thus, fluctuations would be expected to suppress the transition temperature to zero in a three-dimensional system at the Lifshitz composition. That this composition is actually extremely close to that predicted by mean-field theory is undoubtedly related to the polymeric nature of the system, as is the abrupt onset of the fluctuation-induced microemulsion channel as the Lifshitz composition is approached from either side. The asymmetry in shape and position of the channel relative to $\phi_{\rm H,LP} = 0.92$ is also consistent with the higher susceptibility of the lamellar phase to fluctuations (i.e., Ginzburg parameter of $N^{-1/3}$ versus N^{-1}).

Finally, we comment on the relationship of these observations to the low-temperature picture used to rationalize the appearance of conventional (nonpolymeric) microemulsions [4]. From such a perspective, the right boundary of the microemulsion channel in Fig. 1 is associated with saturation of the A/B interfaces with A-B diblock copolymer and a vanishing interfacial tension γ. The left boundary coincides with the bending modulus K of an isolated copolymer-laden interface attaining a value that is comparable to k_BT. Indeed, we have determined that estimates of γ and K following the approach of Ref. [18] are consistent with the width of the channel shown in Fig. 1. However, K grows with decreasing T, so the channel should eventually narrow, although this is preempted by a crystallization at 105 °C, where $K \approx 2k_BT$.

On a fundamental level, blends of high molecular weight block copolymers and homopolymers appear to provide one of the best opportunities for uniting microscopic [6,11] and phenomenological [19] approaches to bicontinuous mircoemulsion and isotropic Lifshitz phenomena. Molecular parameters such as block compositions and degrees of polymerization can be tuned nearly continuously to position features of interest in a convenient experimental window. On a more practical level, our work shows that bicontinuous microemulsions can be designed from commercially relevant polymers by using simple mean-field theory to locate Lifshitz compositions. We are optimistic that such mesoscopically structured, yet macroscopically homogenous, materials could possess unique and useful mechanical, electrical, optical, or barrier properties.

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