

Origin of Polymeric Microemulsions

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Traditional microemulsions (ME) being mixture of oil, water, and surfactant are known to exhibit various interesting microstructures depending on the temperature or the composition. It has also been recognized that mixtures of high molecular weight homopolymers and block copolymer are analogous to ME. Very recently, an *equilibrium* bicontinuous structure with no long-range order has been found by Bates *et al.* in a ternary blends of *A* and *B* homopolymers and symmetric *AB* diblock copolymer [1]. If one focuses on the case where the volume fractions of the two homopolymers are equal, the thermodynamic variables reduce to temperature and the average volume fraction of the copolymer denoted by θ . Transmission electron microscopy images revealed that a lamellar (LAM) structure is observed for $\theta > \theta_L$, whereas a 2-phase (2P) structure appears for $\theta < \theta_L$, where θ_L is the Lifshitz volume fraction. These observations are consistent with the predictions from the previous mean-field theories [2,3]. Surprisingly, images obtained from the specimens close to θ_L bear a striking resemblance to the traditional ME. Such a new phase has been termed as "polymeric microemulsions" (PME) whose physical origin is of great interest and importance to understand.

So far the formation of a bicontinuous PME near the isotropic Lifshitz point has been regarded as a disordered phase (DIS) which is driven by fluctuations of lamellar phase [1]. To explain the existence of such a phase, they assumed a singular cusp in the phase transition temperature as θ is varied about θ_L , and DIS is considered to extend to very low temperatures within this cusp. As pointed out by the authors [1], however, this catastrophic failure of mean-field theory seems to be in contradiction to their previous report in which a clear mean-field Lifshitz behavior has been observed by small-angle neutron scattering.

In this paper, we show by means of computer simulations that the bicontinuous structure of PME can appear within mean-field theory (i.e., without any fluctuations) as a result of microphase separation. Contrary to the well known regularly ordered periodic structures in block copolymers, this bicontinuous structure does not possess any long-range order, but it is an ordered phase in the sense that it appears below the transition temperature. Our simulation method is based on the self-consistent field theory (SCFT) which is one of the most powerful tools in study-

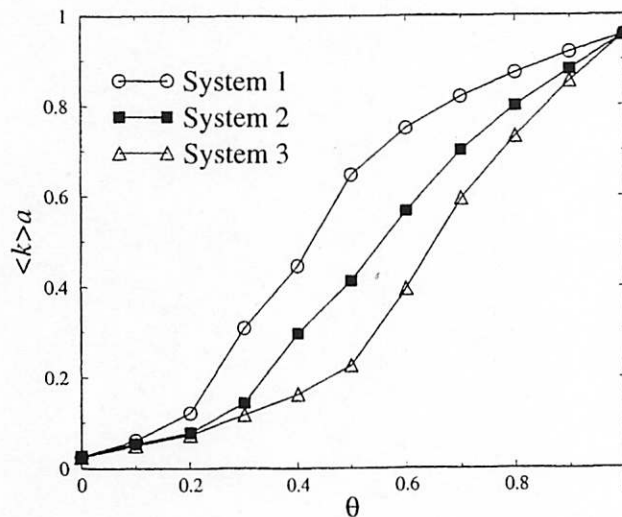
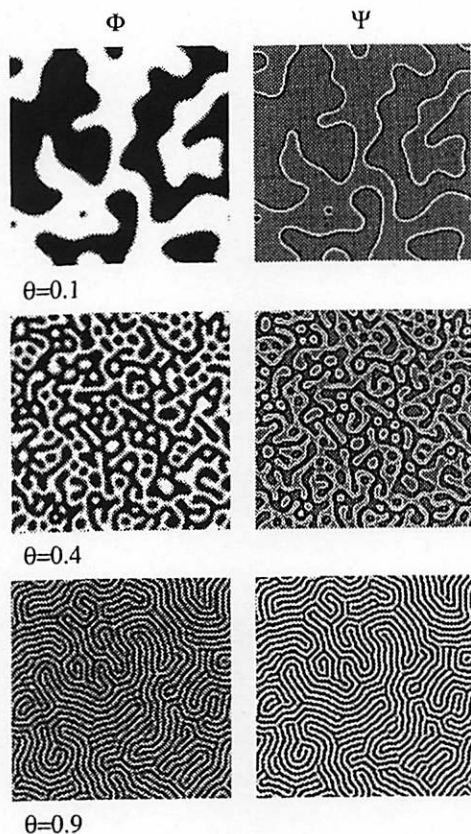


FIGURE 1. (left) Typical pseudo-3D equilibrium patterns for a blend of A4 and B4 homopolymers, and A4B4 block copolymer. θ is the average volume fraction of the copolymer. $\Phi = \phi_A - \phi_B$ where $\phi_{A(B)}$ is the volume fraction of A (B) homopolymer. $\Psi = \phi_a - \phi_b$ where $\phi_{a(b)}$ is the sum of the segment volume fraction of type A (B) which belongs to the AB copolymer. Dark area denotes the region of higher values. (right) The inverse characteristic length as a function of θ for different systems. System1: A2+B2+A4B4, System2: A4+B4+A4B4, System3: A8+B8+A4B4. The Flory-Huggins parameter is fixed to $\chi_{AB} = 2$. All the polymers are assumed to have the same bond length b , and $a = 0.78b$ is a unit length of the simulation.

ing complex fluid systems. Focusing on the symmetric polymeric ternary system, we obtained the sequence of the equilibrium morphology (2P \rightarrow PME \rightarrow LAM) as θ is increased (see Fig. 1 left). (However, copolymers are adsorbed at the interface for $\theta = 0.1$.) We also find that the copolymer becomes more efficient in the emulsification of homopolymers by choosing relatively longer copolymer chain (see Fig. 1 right). Details of our results will be published elsewhere.

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