Mean-Field Studies of Block Copolymer/Homopolymers Blends

Hiroya Kodama[1,2] and Shigeyuki Komura[3,4]

[1] *Japan Chemical Innovation Institute, Nagoya University, Research and Education Center 1-4F, Nagoya 464-8601, Japan*
[2] *Yokohama Research Center, Mitsubishi Chemical Corporation, Yokohama 227-8502, Japan*
[3] *Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel*
[4] *Faculty of Computer Science and Systems Engineering, Kyushu Institute of Technology, Iizuka 820-8502, Japan*

Abstract. Equilibrium structure of ternary blends of A and B homopolymers and symmetric AB block copolymer is investigated using self-consistent field theory by means of computer simulations. We demonstrate that bicontinuous polymeric microemulsions (PME) can appear as a result of microphase separation without any long-range order.

Blends of homopolymers and copolymers have been stimulating considerable amount of experimental and theoretical studies [1]. Recently, bicontinuous polymeric microemulsions (PME) have been observed by Bates *et al.* in a ternary blends of A and B homopolymers of equal sizes and a symmetric AB diblock copolymer [2]. In addition to usual periodic ordered phases, the physical origin of such a new phase is of great interest and importance to understand.

In this paper, we show by means of computer simulations that the bicontinuous structure of PME can appear as a result of microphase separation into a strongly swollen lamellar phase whose stability is marginal. Our simulation method is based on the lattice self-consistent field theory (SCFT) [3]. In the SCFT, polymers are represented as random walks in a positional dependent segment potential, which depends in a self-consistent way on the distribution of segments. We have numerically solved the self-consistent set of equations [3] by employing the iteration scheme proposed by Hasegawa [4].

We consider a symmetric ternary system in the exchange of monomer types A and B. Such a system is characterized by two parameters; $\alpha = N_A/N_{AB} = N_B/N_{AB}$ and χN_{AB}, where N_A, N_B and N_{AB} are degrees of polymerization of A and B homopolymers and AB diblock copolymer, respectively, χ is the Flory-Huggins parameter between A and B monomers. Our simulations are done by using random initial conditions in pseudo-3D systems where any gradients along one specific axis are neglected. Independent runs are performed for different volume fraction of the
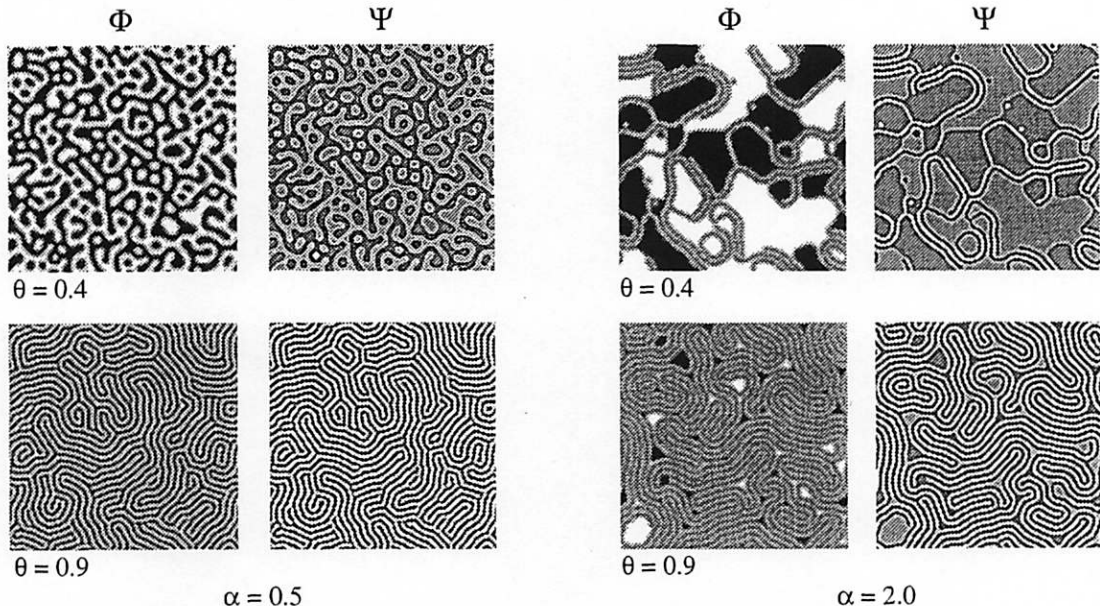
FIGURE 1. Typical pseudo-3D equilibrium patterns of the system with $\alpha = 0.5$ and 2.0 for different values of θ. $\Phi = \phi_A - \phi_B$ and $\Psi = \phi_a - \phi_b$. Dark area denotes the region of higher values.

copolymer θ. We also use 1-dimensionally periodic initial conditions, which produce lamellar structures with a well-defined periodicity. Throughout the simulations, the parameters are fixed to $\chi N_{AB} = 16$ corresponding to the intermediate-segregation regime of pure diblock copolymers.

First, we show the results of simulations with random initial distribution. Typical equilibrium patterns of the order parameters $\Phi = \phi_A - \phi_B$ and $\Psi = \phi_a - \phi_b$ are depicted in Fig. 1 for $\alpha = 0.5$ and 2.0 with $\theta = 0.4$ and 0.9. Here, ϕ_A and ϕ_B are the volume fractions of A and B homopolymers, and ϕ_a and ϕ_b represent the volume fractions of A and B blocks in the copolymer, respectively. For $\alpha = 0.25 \sim 1.0$, we find that the behavior of the system is qualitatively similar. For relatively small θ, the interfaces which are saturated with copolymer monolayers are formed without long-range order, resulting in the PME structures. The systems exhibit lamellar structures for large θ. On the other hand, the systems with $\alpha \sim 2.0$ undergoes macrophase separation, and we observe 3-phase coexistence between the lamellar phase and the A-rich and B-rich homogeneous phases.

In order to identify the equilibrium phase for given parameters, carefully controlled equilibration has been done. We started the simulations from 1-dimensional periodic distributions of the potential to obtain lamellar solutions, and calculated the canonical free energy F. Then, we plot the free energy of the lamellar phase with optimum periodicity as a function of θ as in Fig. 2. As θ is increased, we find that there are three different regions; Region (I) where the profile is flat, Region (II) where the curvature of the profile $(\partial^2 F/\partial \theta^2)$ is negative, and Region (III) where the curvature is positive. Only Region (III) is thermodynamically stable. Region (II) hardly exists for small α, whereas it is remarkable for $\alpha \sim 2$.
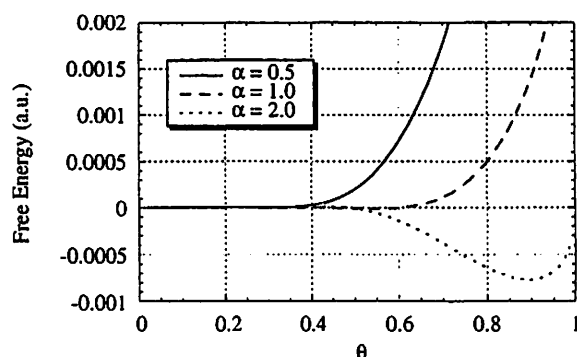
FIGURE 2. The free energy as a function of θ for various values of α.

The flat part of the free energy in Region (I) indicates the marginal stability of the lamellar phase. In this region, the saturated interfaces do not interact each other. Any separations between the interfaces are allowed without any free energy cost as far as the total amount of the interface is conserved. Negative curvature in Region (II) results from the attractive interactions between the monolayers [5]. In this region, the lamellar phase is thermodynamically unstable, and macrophase separation into the lamellar and the A-rich and B-rich phases should take place [6]. However, in spite of the existence of Region (II), we never observed 3-phase coexistence in the previous simulation except for large α such as $\alpha = 2$. This is because the difference in the free energy between the lamellar phase and the 3-phase coexisting state is quite small. Such delicate free energy balance should be comparable with fluctuation effects, which may play an important role for the creation of PME. The random initial condition in the previous simulation may mimic the fluctuation effects, giving rise to PME structures in the strongly swollen lamellar region.

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