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Diblock Copolymer Blends as Mixtures of Surfactants and Cosurfactants

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ABSTRACT: The effects of short diblock copolymers on the phase behavior of long diblock copolymer melts are investigated theoretically. Due to the enthalpy gain, the short chains segregate to the interfaces and change the interfacial properties, behaving like cosurfactants in a surfactant system. It is shown that small amounts of short diblock copolymer chains at the interfaces are able to shift the phase boundaries of the system, thus providing a new method to modify the morphologis of long diblock copolymer melts.

Diblock copolymers are macromolecules composed of two covalently bonded sequences, or blocks, of chemically distinct repeat units (A and B).[1] The equilibrium phase behavior and morphological characteristics of a monodisperse A-B diblock copolymer melt are determined by the overall degree of polymerization N, the composition f (overall volume fraction of the A component), and the A-B segment-segment (Flory-Huggins) interaction parameter χ. For $\chi N \ll 10.5$, the copolymers form a spatially homogeneous or disordered phase. As χN is increased to be of order 10, a delicate balance between energetic and entropic factors produces a disorder-to-order phase transition.[2] In the strong segregation limit (SSL) region, corresponding to the situation of $\chi N \gg 10.5$, narrow interfaces of width $\Delta \sim \chi^{-1/2}$ separate well-developed, nearly pure A and B microdomains.[3] The interaction associated with the A-B contacts is localized in the interfacial regions, giving rise to an interfacial tension $\gamma \sim \chi^{1/2}$. The system would like to minimize the total area of such interfaces but must do so under the constraint of incompressibility and with an entropic penalty of extended chain configurations. The competition between these two factors results in a rich phase diagram for the system. For example, seven ordered phases have been identified in the polystyrene-polyisoprene (PS-PI) diblock copolymer system in the SSL region.[4] Four microstructures characterize these ordered phases of PS-PI melts: spherical microdomains arranged on a body-centered cubic (BCC) lattice, hexagonally packed cylinders, an ordered bicontinuous double-diamond (OBDD) structure, and lamellae. Varying the microstructure can be accomplished by changing f, thus the equilibrium morphology of monodisperse diblock copolymer melts in the SSL region is controlled by the copolymer composition. For a given f and in the strong segregation limit region, the equilibrium morphology of the diblock copolymer melts is determined.

The question we will address is, how can we modify the morphology of the system without significantly changing the bulk properties? In this paper we propose a method of modifying the *equilibrium* morphologies of a diblock copolymer melt by melt blending a small amount of shorter diblock copolymer chains of identical chemical structure into the system. In other words, heating an ordered structure of long diblock copolymers, melt blending a few volume percent of short diblock molecules, and allowing the ordered structure to re-form upon cooling is the process we will consider. In what follows we will demonstrate that these short chains segregate to the interfaces and thereby change the interfacial properties of the system. The phase boundaries between the different ordered phases are displaced by the addition of the short diblock copolymers, resulting in a change of the equilibrium phase behavior of the system.

The short diblock chains are characterized by their degree of polymerization N_s, composition f_s, and the Flory-Huggins parameter χ. There are a number of factors which determine the state of the short diblock copolymer (SDCP) chains in an ordered longer diblock copolymer (LDCP) system. First, the entropy of mixing of the SDCP's with the LDCP's favors a random distribution of the SDCP's. On the other hand, localization of the SDCP's at the interface with each block of the SDCP extending into its compatible domains lowers the enthalpy of mixing. We consider the cases where the SDCP at the interfaces is in equilibrium with the SDCP in the bulk phases; *i.e.*, the SDCP chemical potential μ_s is spatially uniform. In practice this chemical potential is limited by the formation of SDCP micelles in the system. We assume that the concentration of the SDCP's is very low and the blocks are short so that the formation of micelles can be ignored. We also choose SCDP chains so that $\chi N_s < 10.5$; thus the short chains do not form a separate ordered phase within or outside of the large domains.[2] The segregation of the SDCP chains to the interface can be understood by using the fact that, for $N_s \ll N$, the mesoscopic domains of the LDCP chains are much larger than the size of the SDCP chains; therefore, we can view these domains as "bulk" A or B phases. The situation is then similar to the system of diblock copolymer chains at an A-B homopolymer interface.[5] The chemical potential of an SDCP chain in these bulk phases can be estimated by using the standard Flory-Huggins free energy.[6] For an SDCP chain in the A (or B) domain, $\mu_s^{A,B} \approx \ln \phi^{A,B} + \chi N_s^{A,B}$, where $\phi^{A,B} \ll 1$ is the volume fraction of the SDCP chains in the A domain (B domain). On the other hand, the chemical potential of an SDCP chain at the interface is approximately $\mu_S^i \approx \ln \phi_i$,[6] where ϕ_i is an effective SDCP volume fraction at the interface and $N_s^{A,B}$ ($N_s^A = f_s N_s$, $N_s^B = (1 - f_s) N_s$) are the degrees of polymerization of the A and B blocks of the SDCP chains. The equilibrium condition, $\mu_s^{A,B} = \mu_s^i$ leads

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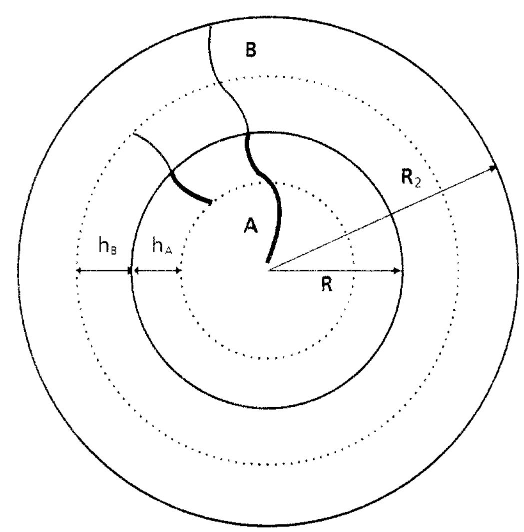

Figure 1. Schematic cross section of a spherical Wigner–Seitz cell composed of long and short diblock copolymer chains. The dashed curves represent the location of the boundaries of the free short chain ends. Strong segregation of the A and B blocks and the incompressibility condition relate the layer thickness of each "brush" to the radius R and the interface σ's: $h_A/R = 1 - (1 - dN_s^A\sigma/R)^{1/d}$, and $h_B/R = (1 + dN_s^B\sigma/R)^{1/d} - 1$. The two radii, R and R_2, are also determined by the incompressibility condition: $R = dN\sigma[(1 - \phi)f + n\phi f_s]$, and $R_2 = R\{(1 - \phi + n\phi)/[(1 - \phi)f + n\phi f_s]\}^{1/d}$.

to the relations $\phi_{A,B} = \phi_i \exp(-\chi N_s^{A,B})$. Therefore, for the case of not too short SDCP chains, $\chi N_s^{A,B} > 1$, the volume fraction of the SDCP in the LDCP domains is exponentially small compared with the effective interfacial volume fraction, resulting in the segregation of the SDCP chains to the interfaces. In what follows we will assume that the segregation is complete and thus neglect the short chains in the LDCP bulk domains.

The effect of the SDCP chains on the interfacial properties can be understood by considering the simplest case of a blend of symmetric ($f = 0.5$) LDCP chains and asymmetric ($f_s \neq 0.5$) SDCP chains. In the absence of the SDCP chains, the interface must be flat due to the symmetry of the LDCP chains. The addition of the asymmetric SDCP chains to the interface breaks this symmetry and thereby changes the interfacial properties. Therefore, we expect that the addition of the SDCP chains will also affect the morphologies of the system. The interfacial properties do not, however, give a complete picture of the effect of the short chains since for a diblock copolymer melt the polymer chains have to be stretched to fill up the whole volume: the size of a domain is determined by the incompressibility constraint.[3] To proceed, we have to consider models which deal with the interfacial free energy and the incompressibility constraint simultaneously. To this end, we make a spherical approximation for the Wigner–Seitz cell of the spherical, cyndrical, and lamellar structures and employ the method of Semenov[7] to estimate the free energies of these structures. Comparison of these free energies determines the phase diagram of the system. Semenov demonstrated that in the large χN limit, a simple analytic treatment of the polymer chains is possible. At the strong segregation limit, the free energy of the spherical Wigner–Seitz cell can be easily estimated by dividing the cell into four regions (Figure 1): an A "brush" region of height h_A, containing the A block of the shorter chains and an N_s^A long section of the longer chains grafted on the inside of the sphere at R; an A "core" region containing the remaining $N^A - N_s^A$ ends of the longer chains; a B "brush" region of height h_B, containing the B block of the shorter chains and an N_s^B long section of the longer chains grafted on the outside of the sphere at R; and a B "corona" region containing the remaining $N^B - N_s^B$ ends of the longer chains. The free energy per cell, F, can be decomposed into contributions from these four regions plus the interfacial tension:

$$F = F_{A1} + F_{A2} + F_{B1} + F_{B2} + F_I, \tag{1}$$

where F_{A1} and F_{B1} are the contributions from the two brushes of height h_A and h_B, F_{A2} is the contribution from the A core region, F_{B2} is the contribution from the B corona region, and F_I is the interfacial contribution. The interfacial contribution is simply the product of the effective interfacial tension, γ_{eff},[8] with the area of the interface of the cell, $A_d = S_dR^{d-1}$, where $S_d = 2\pi^{d/2}/\Gamma(d/2)$ and $d = 1$–3 denotes the lamellar, cyndrical, and spherical cases, respectively.

The contributions to the free energy from the different regions in Figure 1 can be estimated by using the strong stretching approximation of Semenov.[7] The key assumption in this theory is that at the strong segregation limit, each chain can be characterized by a definite trajectory. For a polymer "brush" grafted on the inside surface of a d-dimensional cell of radius R_c ($d = 1$–3 corresponds to lamellar, cyndrical, and spherical cases, respectively), the trajectory can be characterized by the distance from the surface $r(n)$. If the free end of the chain lies at r_0 then $r(N) = r_0$, where N is the length of the chain. The free energy of the polymer brush can be written in the form

$$U_d = \frac{1}{4}\int_0^h dr_0 \int_0^{r_0} dr\, E(r,r_0) g_d(r_0) \tag{2}$$

where h is the height of the brush, $E(r,r_0) = dr(n)/dn$ is the local extension of the chain, and $g_d(r_0)dr_0$ is the number of chains whose free ends lie in the interval dr_0. The functions $E(r,r_0)$ and $g_d(r_0)$ are obtained by minimizing the free energy (2) under the incompressibility constraints. A calculation similar to the one performed by Semenov[7] gives

$$E(r,r_0) = \frac{\pi}{2N}(r_0^2 - r^2)^{1/2} \tag{3}$$

$$g_1(r) = \frac{2}{N}\frac{r}{(h^2 - r^2)^{1/2}}$$

$$g_2(r) = \frac{2\pi r}{N}\left\{\frac{R_c - r}{(h^2 - r^2)^{1/2}\}} + \ln\frac{h + (h^2 - r^2)^{1/2}\}}{r}\right\}$$

$$g_3(r) = \frac{8\pi r}{N}\left\{R_c \ln\frac{h + (h^2 - r^2)^{1/2}}{r} - (h^2 - r^2)^{1/2} + \frac{(r - h)^2}{2(h^2 - r^2)^{1/2}}\right\} \tag{4}$$

Having obtained the functions $E(r,r_0)$ and $g_d(r_0)$, one can calculate the free energy of the polymer brush cell from eq 2,

$$U_d = f_0\frac{h^3}{N^2}A_d l_d\left(\frac{h}{R_c}\right) \tag{5}$$

where $f_0 = \pi^2/48$ is a constant, $A_d = S_dR_c^{d-1}$ is the total area of the brush, and the functions $l_d(x)$ are given by

$$l_1(x) = 1$$

$$l_2(x) = 1 - \frac{3}{4}x$$

$$l_3(x) = 1 - \frac{3}{2}x + \frac{3}{5}x^2$$

The contributions to the free energy from the two "brushes" can be calculated by setting $N = N_A$ ($N = N_B$), $h = h_A$ ($h = h_B$), and $R_c = R$ ($R_c = -R$) for the A or B brushes, respectively. It is then straightforward to show that these contributions are given by

$$F^d_{A1} = f_0 \frac{h_A^3}{(N_s^A)^2} A_d l_d \left(\frac{h_A}{R}\right)$$

$$F^d_{B1} = f_0 \frac{h_B^3}{(N_s^B)^2} A_d l_d \left(-\frac{h_B}{R}\right) \tag{6}$$

The free energies of the "core" can be calculated by setting $N = N^A - N_s^A$ and $h = R_c = R - h_A$. After some algebra we obtain

$$F^d_{A_2} = f_0 \frac{(R - h_A)^{d+2}}{(N^A - N_s^A)^2} \lambda_d \tag{7}$$

where $\lambda_1 = 2$, $\lambda_2 = \pi/2$, and $\lambda_3 = 2\pi/5$. For the "corona" region, we assume the existence of a dead zone and employ the approximation of Semenov.[7] That is, we constrain the long B block ends to lie at the outer surface at R_2. The results are

$$F^1_{B_2} = f_0 2 \frac{h_{B2}^3}{(N^B - N_s^B)^2}$$

$$F^2_{B2} = f_0 \frac{6}{\pi^3} Q^2 \ln \frac{R_2}{R + h_B}$$

$$F^3_{B2} = f_0 \frac{3}{\pi^3} Q^2 \left(\frac{1}{R + h_B} - \frac{1}{R_2}\right) \tag{8}$$

where $Q = A_d(\sigma - \sigma_s)$ is the number of long chains in the cell and R_2 is the size of the cell (Figure 1). Here σ is the diblock copolymer chains per unit area at the interface, among them σ_s are the shorter chains; $\phi = \sigma_s/\sigma$ is the fraction of shorter chains at the interface, and $n = N_s/N$. The incompressibility condition gives relations between the interface coverage σ, σ_s, and the variety of lengths,

$$h_A/R = 1 - (1 - \mathrm{d}N_s^A \sigma/R)^{1/d}$$

$$h_B/R = (1 + \mathrm{d}N_s^B \sigma/R)^{1/d} - 1$$

$$R = \mathrm{d}N\sigma[(1 - \phi)f + n\phi f_s]$$

$$R_2 = R\{(1 - \phi + n\phi)/[(1 - \phi)f + n\phi f_s]\}^{1/d}$$

By conversion of all the parameters in terms of σ, the free energy per unit volume, $f_d = F/V$, where $V = S_d R_2^d/d$ is the volume of the cell, can be minimized with respect to σ for a fixed value of ϕ. For a small value of $n\phi$, the minimized free energies of the different geometries are found to the lowest order of $n\phi$ as

$$f_d/f_1 = G_d(f) + n\phi\Delta_d(f,f_s)$$

where f_d/f_1 is the reduced free energy scaled by the minimized lamellar free energy density. The zeroth order results are identical to those given by Semenov[7]

$$G_1 = 1$$

$$G_2 = [f(2 - (12/\pi^2) \ln f)]^{1/3}$$

$$G_3 = [f(27/10 + (36/\pi^2)(1 - f^{1/3}))]^{1/3} \tag{9}$$

Comparison of these free energies demonstrates that the transition from a spherical structure to a cylindrical one occurs at $f_{c1} = 0.126$, and from a cylindrical structure to a lamellar one at $f_{c2} = 0.283$. The correction terms due the short chains at the interfaces, $\Delta_d(f,f_s)$, will shift these transition points. Therefore, we expect that the short chains will drive the system from one phase to the neighboring one if the parameters are chosen appropriately. To get an estimate of the shift of the phase boundaries, we need to calculate the correction terms. For the lamellar case, $\Delta_1(f,f_s) = 0$ by definition. For the cylindrical and the spherical cases, a detailed calculations gives

$$\Delta_2(f,f_2) = -\frac{(3f - f_s)G_2^3 - (12/\pi^2)f(f - f_s)}{3fG_2^2} \tag{10}$$

$$\Delta_3(f,f_s) = -\frac{(3f - f_s)G_3^3 + (9/5)f f_s - (12/\pi^2)f^{1/3}(f - f_s)}{3fG_3^2} \tag{11}$$

From these expression, we estimate that the phase boundary between the cylindrical phase and the lamellar shifts from $f^0_{c2} = 0.283$ to $f_{c2} \approx f^0_{c2} + (1.145 - f_s)n\phi$ and the phase boundary between the spherical phase and the cylindrical phase shifts from $f^0_{c1} = 0.126$ to $f_{c1} \approx f^0_{c1} + 8.94(f_s - 0.08)n\phi$. Quantitatively, for the case $n = 0.1$ and $\phi = 0.1$, we expect that the shifts of the phase boundaries will be on the order of 0.01. Larger shifts of the phase boundaries are expected for large values of n and ϕ. However, a quantitative estimate of the shift for large values of n and ϕ requires more accurate models for the system.

Several comments are in order at this point. (1) In the above simple model, the Wigner–Seitz cell is divided into several regions, and the free energy contributions from these regions are simply added to get the free energy per cell. A more complete theory would treat the long and short chains on an equal footing, as in the theory of polydisperse brushes.[10,11] This more sophisticated treatment will give a more accurate estimate of the free energy of cores. However, due to the existence of the dead zone,[7] the corona contribution has to be approximated in the same fashion given above. We expect that the more refined model will give a more accurate estimate of the free energies, but will not change our conclusion significantly. (2) We have also neglected the bulk concentration of the short chains. A complete treatment of the problem should consider the thermodynamics of the whole system and analyze the stability of the different phases.[9] This more complete calculation will determine the SDCP interface fractionϕ for a given amount of SDCP chains added into the system. (3) We have assumed that the SDCP chains distribute uniformly at the interface. For the case $\phi \ll 1$, a nonuniform distribution of the SDCP chains will not change the energy but will result in a loss of entropy. Therefore a nonuniform distribution of the SDCP chains at the interface is not favored for the model system considered in this paper. (4) More important, due to the lack of a theory for the OBDD structure, we have not included this interesting structure in our simple model. Since the short chains stabilize the structures with a larger interfacial area (cylindrical versa lamellar), we expect that the short chains will also increase the stability region of the OBDD structure.

In conclusion, a rather simple picture emerges from the above argument: when a small amount of short diblock copolymer is added to a longer diblock copolymer melt, the short chains segregate to the interfaces and change the interfacial properties. For a monodisperse LDCP melt near its phase boundaries, the short DCP chains are able to drive the system from one phase into the other phase, thus changing the equilibrium morphology of the system. In particular, for the case of PS–PI, the transition from the lamellar phase to the OBDD phase occurs at about $f = 0.34$.[4] We expect that for a melt of PS–PI with f close to 0.34, the addition of shorter PS–PI chains into the melt will also change the lamellar–OBDD phase boundary. It would be of great interest to carry out such an experiment to test our predictions. More important, a better understanding of the melt phase behavior of the long plus short diblock copolymer system will offer a new way to modify the equilibrium morphologies of the system in a controllable fashion.

Note Added in Proof

We have recently performed mean-field studies of the diblock copolymer mixtures by numerically solving the mean-field equations for the system (Shi, A.-C.; Noolandi, J. *Macromolecules* **1994**, *27*, 2936). These more accurate and detailed studies show large changes in the phase boundaries when the short diblocks are added, in accordance with the main predictions of this paper. The simple model used here cannot, however, account for the structural fixed points found in our detailed studies. We believe this is due to the fact that when f_s is not close to 0.5, a significant amount of the short diblocks is localized in their corresponding bulk domains, and the simple model used in this paper is only applicable for the cases where $f_s \sim 0.5$.

Methods for calculating the free energy of bicontinuous phases in the strong segregation limit have been developed recently in Olmsted, P. D.; Milner, S. T. *Phys. Rev. Lett.* **1994**, *72*, 936; and Likhtman, A. E.; Semenov, A. N. *Macromolecules* **1994**, *27*, 3103. These authors found that the ordered bicontinuous double-diamond structure is unstable in the strong segregation limit. Recent experiments by Thomas *et al.* (Hajuk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063) indicate that the observed bicontinuous cubic phases in diblock copolymer melts are most consistent with space group *Ia3d*, which is different from the OBDD structure.

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References and Notes

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