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Phase Diagrams for Block Copolymer/Homopolymer Blends

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ABSTRACT: A method is proposed for predicting the phase behaviors of blends of homopolymer A with block copolymer A–B. We assume that the mixtures are divided into two distinct states depending on their concentration and temperature. One state is a mesophase having ordered microdomains of the block copolymer, while the other is a liquid phase which consists of the disordered block copolymer and the homopolymer. On the assumption that the block copolymer in the liquid phase acts as a random copolymer, the free energy of mixing for the phase is evaluated by simply applying the Flory–Huggins equation to it. The free energy of mixing for the mesophase can be estimated by modifying the confined chain model originated by Meier. Then the relative stabilities of the two states, the mesophase and the liquid phase, are compared at various temperatures in order to construct a phase diagram. Consequently, by this method, we can obtain the composition–temperature phase diagrams for A/A–B blends, which are consistent with the results of previous experimental investigations.

1. Introduction

Blends of a block copolymer with a homopolymer exhibit a variety of phase transition and separation behavior that depends on temperature, the concentration of the added homopolymer, and the compositional structure of the copolymer molecule. The composition–temperature phase diagrams of blends of homopolymer (A) with block copolymer (A–B) were previously constructed by using small-angle X-ray and light scattering techniques.[1,2] Noolandi and co-workers[3,4] undertook theoretical studies of this type of system by means of the functional integral formalism for multicomponent polymeric systems, which is a mean-field theory first developed by Helfand et al.[5,6] for homopolymer interfaces and pure block copolymers. They expressed the free energy of the mixture as a series expansion in powers of the concentration fluctuation, in a manner analogous to Leibler's block copolymer theory.[7] By solving modified mean-field diffusion equations for the polymer distribution functions, they calculated a contribution to the free energy of mixing arising from the inhomogeneity of concentration in the blend system. The thermodynamic factors governing the mixing of block copolymer with homopolymer near the spinodal for microphase separation were described by their theoretical formulations.

Using his confined-chain model for block copolymer theory,[8] Meier[9] earlier treated the solubility limit of homopolymer (A) in the microdomains of ordered block copolymer (A–B) phase. He suggested that the total free energy change associated with adding homopolymer (A) to A-blocks of block copolymer (A–B) is

$$\Delta G_{\mathrm{meso}} = -T[\Delta S_{\mathrm{comb}} + \Delta S_{\mathrm{conf\ A}} + \Delta S_{\mathrm{conf\ H}}] \qquad (1)$$

The subscript "meso" signifies that the segregated microdomain structure of the block copolymer remains on addition of homopolymer. The first term in the brackets of eq 1 is the combinatorial entropy of mixing. The second and third terms are conformational entropy losses due to extension of the A-block and compression of the homopolymer molecules, respectively, which arise from a need to maintain a uniform density of the A-domain. We believe that this equation, although approximate, makes the contributions to the free energy change by various physical factors more intuitively visible.

In this paper, by minor modification of Meier's approach, we present a method of predicting the complete composition–temperature phase diagrams of blends of homopolymer (A) with block copolymer (A–B). The results obtained from this method are compared with those of earlier theoretical and experimental investigations,[1–4] and the significant thermodynamic factors governing the phase behaviors are also discussed.

2. Model and Assumptions

To construct the phase diagram of a mixture, one must examine the relative stabilities of all possible phases present under a given condition. The order–disorder transition (or microphase separation transition) of a block copolymer is generally known to be a thermodynamic transition, although its character has not yet been established clearly. A blend system containing a block copolymer is thus divided into two distinct states, i.e., an ordered state and a disordered state. The ordered state is the so-called "mesophase", where the ordered microdomains of the block copolymer are swollen with the homopolymer. The disordered state is a "liquid phase" in which the disordered block copolymer is randomly mixed with the homopolymer. The relative stabilities of these states can be determined by comparing the free energy of each phase.

The theories dealing with the ordered state of a block copolymer were extensively reported in the literature.[5,6,8,10] According to these theoretical analyses, the free energy change associated with microphase separation, i.e., a transformation from a homogeneous state to a domain-structured state of A–B block copolymer, ΔG_f, can be expressed by

$$\Delta G_f = \Delta H_{\mathrm{int}} - T\{\Delta S_p + \Delta S_{c,A} + \Delta S_{c,B}\} \qquad (2)$$

where ΔH_{int} is the interfacial energy change due to domain formation, ΔS_p is the entropy loss due to confinement of joints within the interface between two coexisting domains, and $\Delta S_{c,A}$ and $\Delta S_{c,B}$ are the entropy losses arising from the distortion of conformations to achieve uniform density in the A- and B-block, respectively.

When homopolymer (A) molecules are dissolved into A-domains of the copolymer, they perturb the conformations of A-block chains. Thus, the addition of homopolymer gives rise to a change in $\Delta S_{c,A}$ of eq 2. The

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conformations of the added homopolymer molecules are also disturbed, because they are to be confined within A-domains. The changes in the conformations of the two polymers (i.e., A-block and homopolymer A) give rise to an entropic loss on mixing the homopolymer with the ordered block copolymer. On the assumption that the homopolymer can be dissolved only into the A-block and any contributions from the B-block or the interface between two coexisting domains can be ignored, the free energy of mixing for the mesophase, ΔG_{meso}, is thus described by eq 1. To evaluate the two terms of the conformational entropy change in eq 1, we use the confined-chain model treated by Meier[8] in his earlier theories of pure block copolymer. The three contributions to the total free energy change on mixing, for the mesophase, in eq 1 will be formulated in the next section.

Above the microphase separation transition (MST) temperature of block copolymer, the segregated microdomain structure is not attained if the corresponding homopolymer pair exhibits an upper critical solution temperature behavior. The structure of such disordered block copolymer is essentially liquid-like, forming a single homogeneous phase lacking any long-range order. By means of the random phase approximation introduced by de Gennes,[10,11] Leibler[7] evaluated the scattering properties of a block copolymer in the disordered state. According to his approach, it is known that a strong correlation, whose length is related to the wavelength of spatial concentration fluctuations, remains even in the disordered state. The correlation arises from the covalent linkage between two coexisting blocks.

The length of the correlation arising from the connectivity is independent of the concentration of the added homopolymer as well as temperature. (When homopolymer molecules are dissolved into a domain of block copolymer in the "ordered" state, however, the correlation length corresponding to the interdomain distance must change with increasing concentration of homopolymer.) This implies that the excess free energy due to the concentration fluctuations has no effect on the free energy of mixing homopolymer with block copolymer in the disordered state. Thus we believe that the thermodynamic variables governing miscibility in the disordered state can be determined by the typical Flory–Huggins treatment[13] for mixing the homopolymer with a random copolymer having the same molecular weight and the same composition of the block copolymer, although they may be affected by the sequence distribution of monomeric unit in the copolymer.[14] Then for the liquid phase the free energy change on mixing can be given by

$$\Delta G_{\mathrm{liq}} = \Delta G_{\mathrm{random}} - \Delta G_{\mathrm{f}} \Phi_{\mathrm{AB}} \tag{3}$$

where Φ_{AB} is the volume fraction of the block copolymer in the mixture, ΔG_{f} is the free energy change associated with microphase separation of the block copolymer given by eq 2, and $\Delta G_{\mathrm{random}}$ is the free energy of mixing the homopolymer with a random copolymer (AB) having the same composition and molecular weight of the block copolymer (A–B). $\Delta G_{\mathrm{random}}$ can be estimated by the typical Flory–Huggins equation. The value of ΔG_{f} used as a reference value is a negative one below the microphase separation transition (MST) temperature of the block copolymer A–B. When the temperature is raised, the magnitude of ΔG_{f} will decrease and become zero at the MST temperature of the block copolymer.

3. Mathematical Formulation

(a) Conformational Entropy Change of Homopolymer Chains. For simplicity, we assume that the domain shape of the block copolymer (A–B) is lamellar and there is no morphological transition on addition of homopolymer (A). The conformational entropy change per unit volume of the homopolymer confined with A-domains of the block copolymer can be calculated by using the random-flight chain model for a chain confined in a box[15] given by

$$\Delta S_{\mathrm{conf\ H}} = \frac{R\Phi_{\mathrm{H}}}{V_{\mathrm{H}}} \ln \left[\frac{8}{\pi^2} \sum_{p=1,3...} \frac{1}{p^2} \exp\left\{ \frac{-\pi^2 N_{\mathrm{H}} b_{\mathrm{H}}{}^2 p^2}{6 d_{\mathrm{A}}{}^2} \right\} \right] \tag{4}$$

where R is the gas constant, Φ_{H} and V_{H} are the volume fraction and the molar volume of the homopolymer, respectively, d_{A} is the thickness of the A-domain, and N_{H} and b_{H} are the number of monomer units and the statistical length of the monomer of the homopolymer, respectively.

(b) Conformational Entropy Change of A-Block Chains. Similarly, the conformational entropy change of A-block chains can also be estimated by applying the confined-chain model to it. Meier[8,9] suggests that the free end of the A-block having the other junction end confined within the interfacial region should be on the average located at the middle of the A-domain to achieve the uniform density requirement. The conformational entropy change per unit volume of the A-block chains is given by eq 5, which is equivalent to the change of $\Delta S_{\mathrm{c,A}}$ in eq 2 on mixing.

$$\Delta S_{\mathrm{conf\ A}} = (\Delta S_{\mathrm{c,A}})_{\mathrm{after}} - (\Delta S_{\mathrm{c,A}})_{\mathrm{before}} \tag{5}$$

$$\begin{aligned} \Delta S_{\mathrm{conf\ A}} = {} & \frac{R\varphi_{\mathrm{AB}}}{V_{\mathrm{AB}}} \ln \left[\frac{1}{d_{\mathrm{A}}} \sum_{p=1,3...} \frac{1}{p\pi} \left(1 - \cos \frac{p\pi T_{\mathrm{i}}}{d_{\mathrm{A}}} \right) \times \right. \\ & \left. \exp\left(\frac{-p^2 \pi^2 N_{\mathrm{A}} b_{\mathrm{A}}{}^2}{6 d_{\mathrm{A}}{}^2} \right) \right] - \frac{R\varphi_{\mathrm{AB}}}{V_{\mathrm{AB}}} \ln \left[\frac{1}{d_{\mathrm{A0}}} \sum_{p=1,3...} \frac{1}{p\pi} \times \right. \\ & \left. \left(1 - \cos \frac{p\pi T_{\mathrm{i}}}{d_{\mathrm{A0}}} \right) \exp\left(\frac{-p^2 \pi^2 N_{\mathrm{A}} b_{\mathrm{A}}{}^2}{6 d_{\mathrm{A0}}{}^2} \right) \right] \end{aligned} \tag{6}$$

In eq 6, Φ_{AB} and V_{AB} are the volume fraction and the molar volume of the block copolymer, respectively, d_{A0} is the thickness of the A-domain in the pure block copolymer, and T_{i} is the interfacial thickness between two coexisting domains, and N_{A} and b_{A} are the number of monomer units and the statistical length of the monomer unit of the A-block chain, respectively.

As the added homopolymer is assumed to be dissolved into only A-domains of the block copolymer, the increment of interdomain distance due to volume change can be calculated from a geometrical consideration of the ordered domain structure.[16] For lamella-shaped microdomains, the interdomain distance increased by addition of homopolymer is given by

$$d_{\mathrm{A}} = \frac{(1 - \Phi_{\mathrm{H}}) f_{\mathrm{A}} + \Phi_{\mathrm{H}}}{(1 - \Phi_{\mathrm{H}})(1 - f_{\mathrm{A}})} d_{\mathrm{B}} \tag{7}$$

where f_{A} is the composition of the A-block in the copolymer and d_{B} is the thickness of the B-domain in the pure block copolymer. Then it is possible to describe the conformational entropy changes of eqs 4 and 6 with the volume fraction of homopolymer (Φ_{H}).

(c) Combinatorial Entropy Change on Mixing. In this method, we assumed that the added homopolymer molecules are uniformly distributed within the A-domains of the block copolymer. The change in spatial degree of

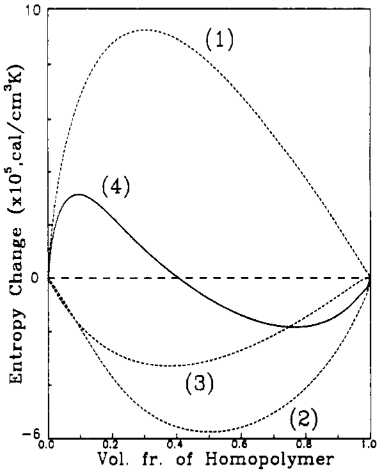

Figure 1. Three contributions to entropy change on mixing for the mesophase, calculated for the system in which block copolymer A–B ($f_A = 0.5$, $V_{AB} = M_{AB} = 25\,000$) is mixed with homopolymer A ($V_H = M_H = 5000$). Equations 4, 6, and 8 are used for the calculation. N_D in eq 8 is assumed to be infinite. It is assumed that the characteristic length of homopolymer A is 0.7 Å and the interphase thickness in the copolymer (T_i) is 20 Å. An empirical equation is used for the interdomain distance: $d = 0.24M^{2/3}$ (in Å), where M is molecular weight. Curve 1 is for the combinatorial entropy of mixing, curves 2 and 3 are for the conformational entropy losses of the A-block and the homopolymer, respectively, and curve 4 is for the total entropy change on mixing.

freedom per homopolymer molecule is given by

$$\frac{n_{AB}V_{AB}f_A + n_H V_H}{n_H V_H} \quad \text{(for a single homopolymer molecule)}$$

where n_{AB} and n_H are the number of moles for the homopolymer and the block copolymer, respectively. For the block copolymer, on the other hand, its spatial freedom is greatly restricted by the covalent joints between two coexisting blocks. Since the ordered domain structure of block copolymers is a kind of network, each chain in the domain tends to restrict the translational degree of freedom for the others. Hence, the block copolymer suffers a change in the spatial degree of freedom per domain (not per chain) given by

$$\frac{n_{AB}V_{AB}f_A + n_H V_H}{n_{AB}V_{AB}f_A} \quad \text{(for a single domain)}$$

Thus, the combinatorial entropy change per unit volume for the mesophase is given by

$$\Delta S_{\text{comb}} = -R\left\{\frac{\Phi_H}{V_H}\ln\frac{\Phi_H}{f_A + (1 - f_A)\Phi_H} + \frac{\Phi_{AB}}{N_D V_{AB}}\ln\frac{f_A\Phi_{AB}}{1 - (1 - f_A)\Phi_{AB}}\right\} \quad (8)$$

where N_D is the number of block copolymer molecules in a single B-domain. It is considered that the contribution of the second term is negligible when N_D is large.

4. Entropy Change on Mixing for the Mesophase

On addition of homopolymer (A) into the A-domains of the block copolymer (A–B), the contributions of each of three terms to the total entropy change per unit volume are shown in Figure 1, where eqs 4, 6, and 8 are used for the calculation. (The value of N_D in eq 8 is assumed to be infinite.) The terms of Nb^2 in these equations are estimated from unperturbed chain dimensions and molecular weights: $Nb^2 = MC^2$, where M is the molecular weight and C is the characteristic length of the chain. The interdomain distance (i.e., $d = d_A + d_B$) corresponding to the molecular weight of the block copolymer (M_{AB}) can be calculated by using the empirical relationship for styrene–isoprene and styrene–butadiene di- and triblock copolymers: $d = 0.24M^{2/3}$, where d is the interdomain thickness of the lamellae in angstroms.[8] We assume that the characteristic length of homopolymer A is 0.7 Å and the interfacial thickness of the block copolymer (T_i) is 20 Å for the calculation. The composition of the A-block in the copolymer (f_A) is assumed to be 0.5. The molecular weights of the copolymer (M_{AB}) and the homopolymer (M_H) are taken to be 25 000 and 5000, respectively.

From Figure 1, it is found that the contribution of the favorable combinatorial entropy of mixing competes against those of the two conformational entropy losses opposing the mixing. Note that the total entropy change on mixing has a negative value in the region of higher Φ_H (volume fraction of the homopolymer) and still has a negative value even near $\Phi_H = 1$. (In light of the thermodynamic principles governing phase diagrams, the entropy change on mixing must be positive as the volume fraction approaches unity.) This implies that the estimation of total entropy change from the confined-chain model has a limitation which makes it impossible to provide exact phase diagrams satisfying the phase rule. It is thought that the limitation arises from the fact that several thermodynamic consequences are neglected in trying to simplify our formulations. Two of the thermodynamic consequences may be the morphological transition induced by addition of the homopolymer and the localized solubilization of the added homopolymer molecules, both being factors that lower the free energy of mixing, especially in higher Φ_H, for the mesophase. We believe the latter may be a more critical factor in the stabilization of the mesophase and be more easily treated by a simple modeling. In the next section, the physical effects due to the "localized solubilization" will be considered for the purpose of estimating the free energy of mixing for the mesophase.

5. Modified Confined-Chain Model: Effects of Localized Solubilization

According to the original confined-chain model, the free end of the A-block having the other junction end confined within the interfacial region should be on the average located at the center of the A-domain to keep its density uniform. As the A-domains become swollen with solubilized homopolymer molecules, the A-block chains become more stretched. However, the requirement of maintaining a uniform density can now be satisfied more easily by placing more of the homopolymer molecules toward the central part of the lamellae which otherwise had to be filled by highly stretched A-block chains. As a result, the free energy can be effectively lowered by releasing the extension of the A-block chains, although it may give rise to some disadvantageous consequences such as a decrease in the translational degree of freedom of the homopolymer molecule. The possibility of "localized solubilization" has already been suggested in the experimental investigation for blends of styrene–butadiene diblock copolymer (S–B) with polystyrene (PS), and it could account for the observed solubility of PS into S–B much greater than predicted by the confined-chain model.[2] Recently, using small-angle X-ray scattering (SAXS) on blends of styrene–isoprene diblock copolymer (S–I) with PS, Hashimoto et al.[17] also provided evidence for this phenomenon.

Now we propose a simple model describing the effects due to the localized solubilization of the added homopolymer molecules. Although the actual distribution must be a gradual one, it may assumed that the density distribution of the solubilized homopolymer has a step function as shown in Figure 2. In this figure, the densities of the A-block and the homopolymer molecule are assumed to be unity. The A-domain is thus divided into three regions: two mixed regions (A-block + homopolymer) and one localized homopolymer region. In the mixed regions, the solubilized homopolymer molecules are assumed to be randomly mixed with A-block chains. To evaluate the density function of the solubilized homopolymer, we introduce a volume ratio, X_{SH}, which is termed the "fraction of intermixed homopolymer", defined as

$$X_{SH} \equiv \frac{\text{volume of homopolymer in mixed regions}}{\text{total volume of homopolymer}} \tag{9}$$

$$= 1 - X_{LH} \quad (0 < X_{SH} < 1) \tag{10}$$

where X_{LH} is the fraction of the localized homopolymer. Hence, the density of the homopolymer in the mixed regions, ρ_{SH}, and the thickness of the mixed region, d_{SH}, are described by X_{SH}.

$$\rho_{SH} = \frac{X_{SH}\Phi_H}{f_A\Phi_{AB} + X_{SH}\Phi_H} \tag{11}$$

$$d_{SH} = \frac{d_{A0}}{2}\frac{f_A\Phi_{AB} + X_{SH}\Phi_H}{f_A\Phi_{AB}} \tag{12}$$

where d_{A0} is the thickness of the A-domain of the pure block copolymer.

On the basis of this model, we can now reformulate the three components of the free energy change for the mesophase as follows.

(i) Conformational entropy change of the homopolymer chains: this component is independent of X_{SH}, and it is equivalent to that of the original confined-chain model given by eq 4.

(ii) Conformational entropy change of the A-block chains: this component can be, in an approximation, calculated from the original confined-chain model in which the thickness of the A-domain is $2d_{SH}$.

$$\Delta S_{\text{conf A}} = R\frac{\Phi_{AB}}{V_{AB}}\ln\left[\frac{1}{2d_{SH}}\sum_{p=1,3,\ldots}\frac{1}{p\pi}\left(1-\cos\frac{p\pi T_i}{2d_{SH}}\right)\times \exp\left\{\frac{-p^2\pi^2N_Ab_A{}^2}{6(2d_{SH})^2}\right\}\right] - R\frac{\Phi_{AB}}{V_{AB}}\ln\left[\frac{1}{d_{A0}}\sum_{p=1,3\ldots}\frac{1}{p\pi}\times \left(1-\cos\frac{p\pi T_i}{d_{A0}}\right)\exp\left(\frac{-p^2\pi^2N_Ab_A{}^2}{6d_{A0}{}^2}\right)\right] \tag{13}$$

(iii) Combinatorial entropy change on mixing: the number of homopolymer molecules solubilized in the mixed regions is $X_{SH}\Phi_H$, and the value of N_D (the number of block copolymer molecules in a B-domain) is assumed to be infinite.

$$\Delta S_{\text{comb}} = -RX_{SH}\frac{\Phi_H}{V_H}\ln\frac{\Phi_H}{f_A + (X_{SH} - f_A)\Phi_H} \tag{14}$$

In Figure 3, each of the three contributions to the total entropy change for the mesophase, ΔS_{tot} $(=\Delta S_{\text{comb}} + \Delta S_{\text{conf A}} + \Delta S_{\text{conf H}})$, as a function of the fraction of intermixed homopolymer, X_{SH}, is evaluated at $\Phi_H = 0.5$. For the calculation, it was assumed that the composition of the A-block in the copolymer (f_A) is 0.5, and the molecular weights of the homopolymer (M_H) and the block copolymer (M_{AB}) are 5000 and 25 000, respectively. Note that the conformational entropy loss of the A-block decreases with increasing X_{SH}, whereas the combinatorial entropy of mixing increases with increasing X_{SH}. (The conformational entropy loss of the homopolymer is independent of X_{SH}.) The equilibrium value of the fraction of intermixed homopolymer, X_{SH}, is obtained from a condition of minimization of free energy, i.e., $(\partial\Delta G_{\text{meso}}/\partial X_{SH}) = (\partial\Delta S_{\text{tot}}/\partial X_{SH}) = 0$.

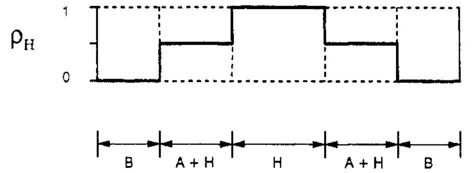

Figure 2. Schematic diagram of density profile for the solubilized homopolymer. B, A + H, and H denote B-domain, mixed region, and localized homopolymer region, respectively. The density of the intermixed homopolymer in the mixed regions (ρ_{SH}) is given by $\rho_{SH} = X_{SH}/(f_A\Phi_{AB} + X_{SH}\Phi_H)$. ($X_{SH}$ is the ratio of the volume of the intermixed homopolymer in the mixed regions of the total volume of the homopolymer defined as eq 9.)

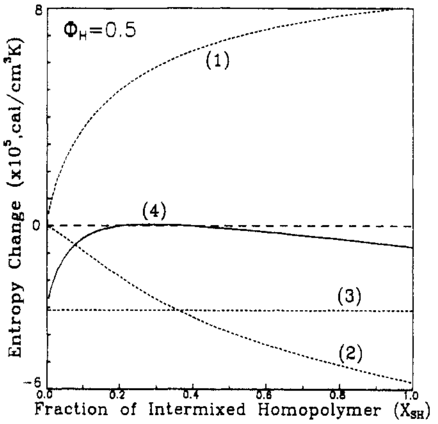

Figure 3. Total entropy change for the mesophase as a function of the fraction of intermixed homopolymer (X_{SH}). (X_{SH} is defined by eq 9.) Assumed numerical values used are $f_A = 0.5$, $V_H = M_H = 5000$, $V_{AB} = M_{AB} = 25\,000$, and $\Phi_{AB} = \Phi_H = 0.5$. Equations 4, 6, and 8 are used for the calculation. Curve 1 is for the combinatorial entropy change on mixing and curves 2 and 3 are for the conformational entropy losses of the A-block and the homopolymer, respectively.

Then the total entropy change corresponding to the equilibrium value of X_{SH} could be evaluated for the whole range of Φ_H, and it is shown in Figure 4. In this figure, it is found that the shape of the entropy curve obtained from the modified model in the region of higher Φ_H differs from that of the original confined-chain model. The difference between curve 1 (from the original confined-chain model) and curve 2 (from the modified model) results from the consideration of the thermodynamic consequences due to the localized solubilization of the homopolymer. From Figure 5, which shows the equilibrium value of X_{SH} as a function of Φ_H, it is found that the added homopolymer molecules start to be localized when the concentration of homopolymer (Φ_H) reaches a certain critical value.

In Figures 6 and 7, the equilibrium value of the fraction of intermixed homopolymer and the corresponding total entropy change for the mesophase are calculated at various molecular weights of homopolymer, respectively. From Figure 6, it is found that the critical concentration which is a starting point for localized solubilization increases with decreasing molecular weight of the added homopolymer (M_H). From Figure 7, it is also seen that the total entropy change increases with decreasing molecular weight of homopolymer (M_H). This means that the solubility

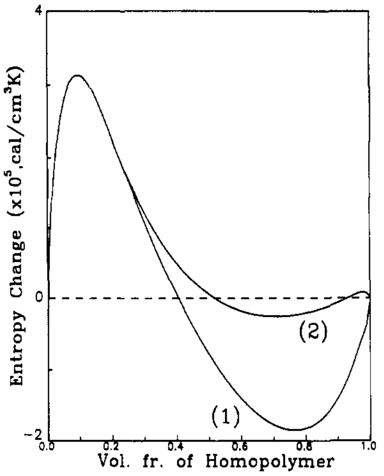

Figure 4. Total entropy change on mixing for the mesophase, calculated for the system in which block copolymer A-B (f_A = 0.5, $V_{AB} = M_{AB}$ = 25 000) is mixed with homopolymer A ($V_H = M_H$ = 5000). Curve 1, which is equivalent to the result of Figure 1, is obtained from the original confined-chain model, while curve 2 is from the modified model where eqs 4, 13, and 14 are used for the calculation. The difference between curves 1 and 2 results from the consideration of the thermodynamic consequences due to the localized solubilization of the homopolymer.

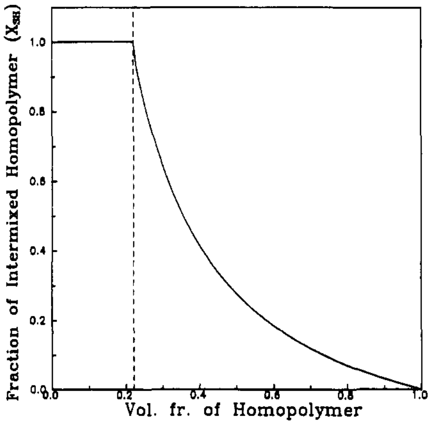

Figure 5. Equilibrium value of the fraction of intermixed homopolymer (X_{SH}) as a function of the volume fraction of the homopolymer (Φ_H). It is assumed that $f_A = 0.5$, $V_H = M_H = 5000$, and $V_{AB} = M_{AB}$ = 25 000. The values are obtained from the condition that $(\partial \Delta G_{meso}/\partial X_{SH}) = (\partial \Delta S_{tot}/\partial X_{SH}) = 0$.

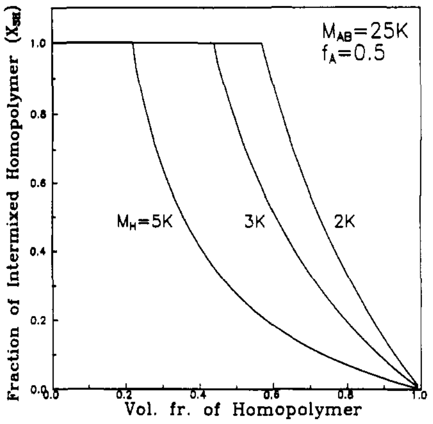

Figure 6. Equilibrium value of the fraction of intermixed homopolymer (X_{SH}) with respect to the molecular weight of the homopolymer (M_H). For the calculation, it is assumed that f_A = 0.5 and $V_{AB} = M_{AB}$ = 25 000.

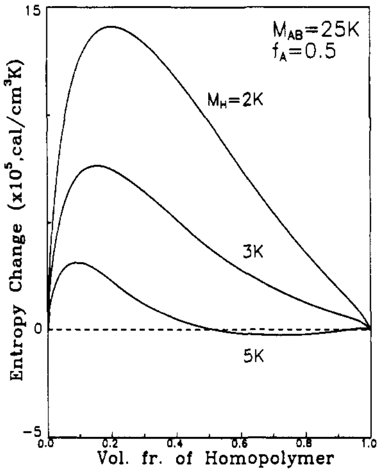

Figure 7. Total entropy change for the mesophase with respect to the molecular weight of the homopolymer (M_H). The total entropy changes are calculated at the equilibrium values of the fraction of intermixed homopolymer as shown in Figure 6. For the calculation, it is assumed that f_A = 0.5 and $V_{AB} = M_{AB}$ = 25 000.

limit of the homopolymer increases with decreasing molecular weight of the added homopolymer.

6. Phase Diagrams of Homopolymer/Block Copolymer Blends

In trying to construct the phase diagram, the free energy change in the mesophase is to be compared with that in the liquid phase at various temperatures. In Figure 8, each pair of the two curves (M for the mesophase and L for the liquid phase) is calculated at various temperatures (T1–T8). For both curves, it was assumed that the composition of the A-block in the copolymer (f_A) is 0.5, and the molecular weights of the homopolymer (M_H) and the block copolymer (M_{AB}) are 5000 and 25 000, respectively. For the L curve, we assume that the interaction energy density[18] for the A/B blend ($B_{A/B}$) and the free energy of domain formation (ΔG_f) are given by

$$B_{A/B} = 1.6 - 0.002T \quad (15)$$

$$\Delta G_f = -0.4 + 0.001T \quad (\text{for } M_{AB} = 25\,000, f_A = 0.5) \quad (16)$$

where T is the Kelvin temperature and B_{12} and ΔG_f are in cal/cm^3. (In eq 16, in consideration of the molecular weight and the composition of the block copolymer, we take the MST temperature to be 400 K. The zeroth coefficient (=−0.4) of the equation is given by $B_{A/B}f_A(1 - f_A)$, which approximates the heat of mixing released by the microphase dissolution. The first coefficient, in a first approximation, is given by 0.001 = 0.4/400, where 0.4 is the zeroth coefficient and 400 is the MST temperature.) Since the free energy change on mixing for M is composed entirely of entropic contributions, the shape (i.e., the relative magnitude as a function of the volume fraction of the homopolymer) of the curve is independent of temperature. In the case of L, on the other hand, the enthalpic effect due to the unfavorable interaction between the homopolymer and the B-block of the disordered block copolymer has to be additionally considered for the estimation of the free energy change. Hence, the L curve changes its shape with temperature as shown in the figures, since the interaction energy between the homopolymer and the disordered block copolymer depends on temperature.

As a result, the composition–temperature phase diagram of the A/A–B blend shown in Figure 9 could be obtained by comparing each pair of the two curves (M and L) at various temperatures as shown in Figure 8. In the phase diagram, the different phase regions are indicated by M1 or M2 (homogeneous and ordered phase), M1 + M2 (separated and ordered phase), L1 or L2 (homogeneous

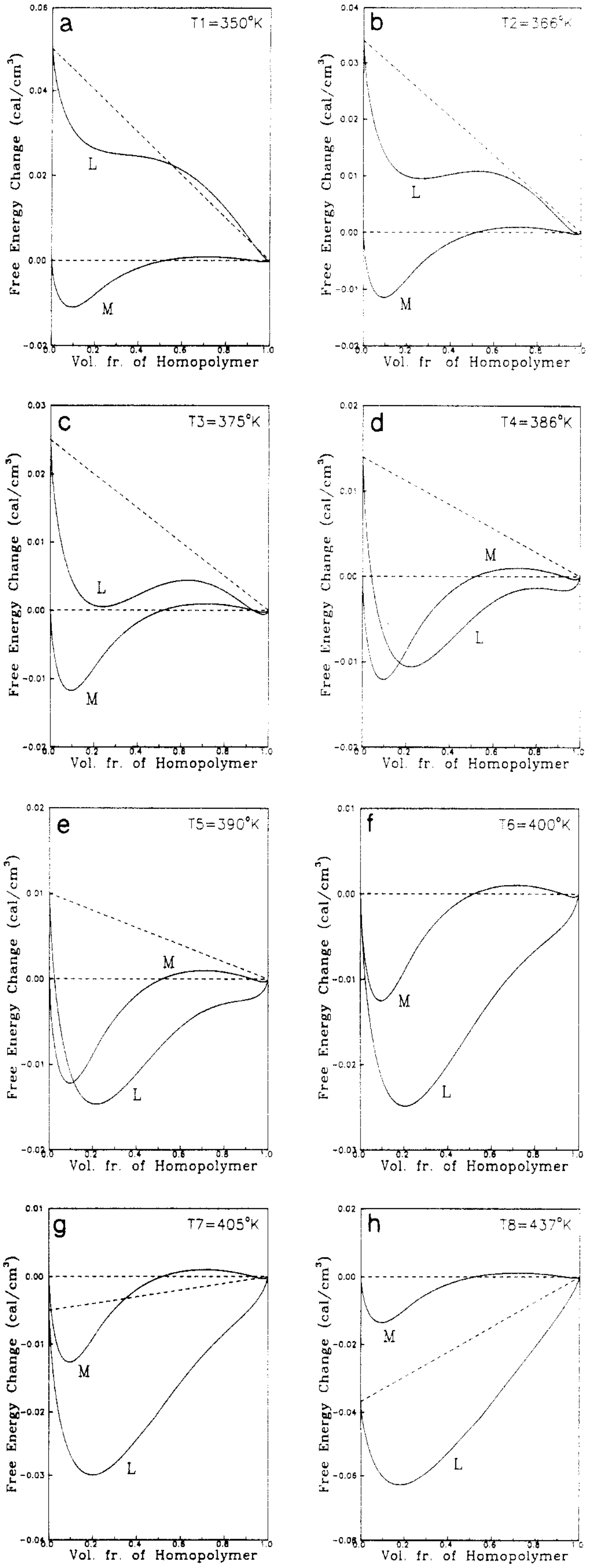

Figure 8. Comparison of the free energy change for the mesophase (M) with the liquid phase (L) at various temperatures. It is assumed that $f_A = 0.5$, $V_H = M_H = 5000$, and $V_{AB} = M_{AB} = 25\,000$. For the L curve, it is assumed that $B_{A/B} = 1.6 - 0.002T$ (cal/cm³) and $\Delta G_f = -0.4 + 0.001T$ (cal/cm³). (T is the Kelvin temperature.)

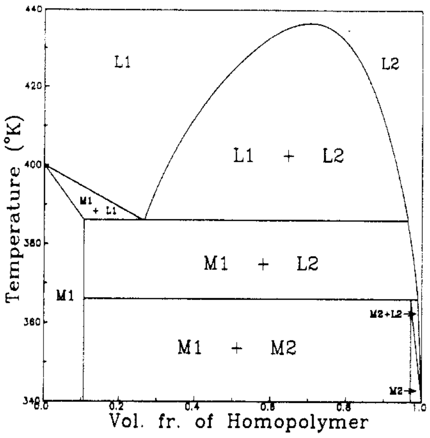

Figure 9. Calculated composition–temperature phase diagram for the A/A–B blend, which is obtained by comparing the free energy change for the mesophase against that for the liquid phase at various temperatures as shown in Figure 8. T4 is the pseudoeutectic temperature, T6 is the MST temperature of the pure block copolymer A–B, and T8 is the critical solution temperature for the blend of homopolymer A with the disordered block copolymer. Mesophase (M1 and M2) consists of ordered microdomains of the copolymer swollen with homopolymer. Liquid phase (L1 and L2) consists of disordered block copolymer and homopolymer.

and disordered phase), and L1 + L2 (separated and disordered phase). One notices that the shape of the diagram predicted by this method is almost identical with the results of previous experimental investigations.[1-2] As for block copolymer micelle, in the context of our approach, it is a type of the mesophase where microdomains are segregated from the homopolymer matrix. Thus, the region of M2 + L2 is to be regarded as the phase including micelles.

There are three noticeable observations in the diagram. First, the boundary lines between M1 and M1 + M2 and between M1 + M2 and M2 are independent of temperature. The reason is that the free energy change for M is composed entirely of entropic contributions. The concentration of the homopolymer to reach the solubility limit should, therefore, have a constant value even though the temperature is raised.

Second, in the calculated phase diagram, the upper critical solution temperature (UCST, T8) is higher than the MST temperature of the pure block copolymer (T6). The interaction energy density ($B_{A/B}$) governs the UCST, while the free energy change on domain formation (ΔG_f) governs the MST temperature. A different value of $B_{A/B}$ or ΔG_f would result in a different shape of the phase diagram.

Finally, it is shown that the MST temperature of the blend, which is located on the line between M1 + L1 and L1, decreases with increasing Φ_H. According to the previous theoretical and experimental investigations,[19-21] the direction of the change in the MST temperature induced by the addition of the homopolymer is determined by the length of the added homopolymer in relation to the length of the block copolymer and the overall composition of the monomers in the mixture.

In our method, the direction of change in the transition temperature can be predicted by comparing the free energy change for the mesophase with that for the liquid phase at the MST temperature of the pure block copolymer (i.e., $\Delta G_f = 0$ at the temperature). As an example, we now consider the condition for which the MST temperature is lowered by addition of the homopolymer. As one can see from the calculated phase diagram, the equilibrium phase regions which exist above T6 are L1, L1 + L2, and L2. This implies that there is no phase region containing M1 (i.e., M1, M1 + L1, and M1 + L2) at equilibrium when the temperature is above T6. Hence, a necessary condition for a decrease in the MST temperature is that at T6 the free energy of mixing for L (ΔG_{liq}) must be lower than that of M (ΔG_{meso}) at all concentrations. (See the curves at T6 in Figure 8f.) Thus the necessary condition for a decrease in the MST temperature induced by addition of the homopolymer is given by

$$\Delta G_{\mathrm{meso}} > \Delta G_{\mathrm{liq}} \quad (\text{at T6}, \Delta G_f = 0) \tag{17}$$

where

$$\Delta G_{\mathrm{meso}} = -T[\Delta S_{\mathrm{comb}} + \Delta S_{\mathrm{conf\ A}} + \Delta S_{\mathrm{conf\ H}}] = -T\Delta S_{\mathrm{tot}} \tag{1}$$

and

$$\Delta G_{\mathrm{liq}} = B_{\mathrm{A/B}}(1 - f_{\mathrm{A}})^2\Phi_{\mathrm{H}}\Phi_{\mathrm{AB}} + RT\{(\Phi_{\mathrm{AB}}/V_{\mathrm{AB}}) \ln \Phi_{\mathrm{AB}} + (\Phi_{\mathrm{H}}/V_{\mathrm{H}}) \ln \Phi_{\mathrm{H}}\} \tag{18}$$

Equation 17 can now be written as

$$-T\Delta S_{\mathrm{loss}} > B_{\mathrm{A/B}}(1 - f_{\mathrm{A}})^2\Phi_{\mathrm{A}}\Phi_{\mathrm{AB}} \tag{19}$$

where

$$\Delta S_{\mathrm{loss}} = -R\{(\Phi_{\mathrm{AB}}/V_{\mathrm{AB}}) \ln \Phi_{\mathrm{AB}} + (\Phi_{\mathrm{H}}/V_{\mathrm{H}}) \ln \Phi_{\mathrm{H}}\} - \Delta S_{\mathrm{tot}} \tag{20}$$

When eq 19 is satisfied, a decrease in the MST temperature would arise as shown in the calculated phase diagram.

7. Concluding Remarks

To construct the phase diagrams for blends of a homopolymer and a block copolymer, we examined the relative stabilities of the two phases, i.e., the mesophase and the liquid phase. It was shown that, if the thermodynamic consequences due to the localized solubilization of the added homopolymer are properly taken into account, the simple confined-chain model can be used to estimate the free energy change for the mesophase. It is thus concluded that our simple approach satisfactorily explains the phase behaviors as well as the thermodynamic factors governing miscibility for the blend system containing a block copolymer. The following companion paper[22] will provide the phase diagrams for homopolymer/block copolymer blends exhibiting an LCST behavior.

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