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Phase Diagrams for the Blends of a Styrene-Butadiene Diblock Copolymer and a Styrene-Butadiene Random Copolymer: Theory

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ABSTRACT: The phase diagram of the blends of a diblock copolymer (A−B) and a random copolymer (ABR) is constructed by the modified confined-chain model developed earlier where the morphology of A−B block copolymer is lamellae and the composition of ABR random copolymer is close to that of A−B. These theoretical results predict a relatively simple phase behavior for the A−B/ABR blends in comparison to the A−B/A blends, A being a homopolymer, studied previously. Unlike in A−B/A blends, the order−disorder transition temperature in A−B/ABR blends is lowered by the addition of the random copolymer regardless of its molecular weight. It is also found that the fraction of ABR solubilized into the A−B is very limited due to the endothermic mixing interaction between ABR and each block of A−B.

1. Introduction

It is well-known that block copolymer forms several types of morphologies such as lamellae, cylinder, sphere, etc. depending on the volume ratio of different blocks separated into microdomains.[1−13] Block copolymers also exhibit the order−disorder transition (ODT) phenomenon. When a diblock copolymer is mixed with a homopolymer, the microscopic phase transition occurring in the block copolymer itself and the macroscopic phase separation occurring between the block copolymer and the homopolymer give rise to a more complex phase behavior than can be seen with a block copolymer alone. The blend of a diblock copolymer and a homopolymer can be classified into two categories based on the type of the added homopolymer, that is, A−B/A blend system[14−26] or A−B/C blend system.[27−32] Here A−B denotes a diblock copolymer, A a homopolymer with segments that are chemically identical to those of A blocks in A−B, and C a homopolymer with segments that are chemically different from those of any blocks but may have some specific interaction with A blocks. In the case of the A−B/C blends, it was found that a specific interaction existing between the A block and the homopolymer affects the phase behavior of the blend appreciably.

Until now, only a few works[33−39] have been reported about blends of a block copolymer with a copolymer, random or block copolymer. The main objectives of these studies are the elucidation of the effect of the added copolymer on (1) the miscibility between the two polymers and (2) the morphology of the block copolymer. The phase behavior of the blends of two monodisperse diblock copolymers consisting of A and B monomer units (A−B/A−B) has been investigated by Shi and Noolandi[33−35] using self-consistent mean-field theory, in which several particularly interesting structures, such as bilayer and inverted spherical phases, were found in addition to the conventional lamellar, cylindrical, and spherical structures. Kressler et al.[36] have studied the miscibility in blends of random copolymers of styrene−acrylonitrile, P(S-*ran*-AN), with block copolymers of styrene and methyl methacrylate, PS-*block*-PMMA, and found that the addition of block copolymer increased the miscibility markedly in comparison to the blends containing random copolymers of styrene and methyl methacrylate. In the present paper, we theoretically predict the phase behavior of the blends of a block copolymer (A−B) and a random copolymer having the same monomer components as A−B. This random copolymer is denoted by ABR. In the A−B/ABR blend system, it is expected that, at temperatures below the order−disorder temperature (T_{ODT}) of the block copolymer itself, the added ABR could dissolve into the periodic microdomain of the A−B or be macroscopically separated from the A−B depending on the relative molecular weights of the copolymers and the composition of the ABR. In the case of the ABR composition being not largely different from 0.5, the addition of ABR molecules of higher molecular weight than the A−B molecules gives rise to a macroscopic phase segregation of random copolymers from block copolymers, due to the large, positive interaction between the random copolymers and each block in the ordered state. However, in the case where the molecular weight of the added ABR is very low, it could occur that the effect of the mixing entropy is larger than the effect of the unfavorable enthalpy on mixing. This makes it possible for the added ABR to dissolve into the microdomains of the A−B. It is also expected that, at temperatures above T_{ODT}, the blend forms a homogeneous phase as a result of the very small interaction between the random copolymers and the block copolymers in the disordered state. A similar behavior is not expected with previous A−B/C (or A−B/A) blends studied before, and this expectation encourages us to explore the blends of a block copolymer and a random copolymer. In this study, the phase diagram of A−B/ABR mixtures will be constructed by the use of the modified confined chain model reported earlier.[20,31]

2. Model for Phase Equilibrium

A general approach to determining the phase separation behavior of a blend is to examine the relative stabilities (i.e., the chemical potential of each component in the blend) of all possible phases that can be realized under the given condition. It is assumed at the outset that a blend system containing a block copolymer and a random copolymer is in either one of two different states, an ordered or a disordered state. The ordered state is the so-called “mesophase”, where the ordered microdomains of the block copolymer are swollen with

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the added random copolymer. The disordered state is a liquid state, in which the disordered block copolymer is randomly mixed with the random copolymer. In trying to construct a concentration−temperature phase diagram of A−B/ABR blend, it is necessary to compare the free energy of the ordered phase (mesophase) with that of the liquid phase at various temperatures. The mesophase has a regular microdomain structure and its free energy is evaluated by the modified confined chain model.[31] In the liquid phase, the block copolymer is assumed to behave like a random copolymer and its free energy is evaluated by the Flory−Huggins theory.

2-1. Free Energy of the Liquid Phase. The free energy of mixing per unit volume to form the liquid phase by blending the ordered block copolymer with the random copolymer is given by

$$\Delta G_{\mathrm{liq}} = \Delta G_{\mathrm{random}} + \Delta G_{\mathrm{mst}}\phi_{\mathrm{A-B}} \tag{1}$$

where $\Delta G_{\mathrm{random}}$ is the free energy change of mixing of a random copolymer with a disordered block copolymer and ΔG_{mst} is the free energy change per unit volume associated with microdomain dissolution, i.e., the transition from ordered to the disordered state of the pure block copolymer. The composition of the blend is expressed by ϕ_{ABR} and $\phi_{\mathrm{A-B}}$, the volume fractions of the two polymers. $\Delta G_{\mathrm{random}}$ is estimated by the Flory−Huggins equation:[40]

$$\Delta G_{\mathrm{random}} = RT[(\phi_{\mathrm{A-B}}/V_{\mathrm{A-B}}) \ln \phi_{\mathrm{A-B}} + (\phi_{\mathrm{ABR}}/V_{\mathrm{ABR}}) \ln \phi_{\mathrm{ABR}}] + B_{\mathrm{A-B/ABR}}\phi_{\mathrm{ABR}}\phi_{\mathrm{A-B}} \tag{2}$$

with

$$B_{\mathrm{A-B/ABR}} = (f_{\mathrm{A}} - f_{\mathrm{A}}')^2 B_{\mathrm{A/B}} \tag{3}$$

Here, $B_{\mathrm{A/B}}$ is the interaction energy density between A and B, and f_{A} and f_{A}' are the fractions of component A in the block copolymer and the random copolymer, respectively. In eq 2, $V_{\mathrm{A-B}}$ and V_{ABR} are the molar volumes of the block copolymer and the random copolymer, respectively. ΔG_{mst} in eq 1 can be calculated by the same method as developed previously.[41] It has a positive value below the microphase separation transition (MST) (or order−disorder transition (ODT)) temperature of the block copolymer. As the temperature is raised, ΔG_{mst} gradually decreases in magnitude and eventually becomes zero at the MST temperature of the block copolymer.

2-2. Free Energy of the Mesophase. No general theory for the free energy of mixing a random copolymer and a block copolymer in the ordered state is available to date. It is, however, possible to obtain an approximate estimate of the free energy by the use of a simplified model incorporating some reasonable assumptions. The change in the free energy per unit volume in forming the blend in the ordered state, starting from the random copolymer and the pure block copolymer in the ordered state, can be written as follows:

$$\Delta G_{\mathrm{meso}} = \Delta H_{\mathrm{mix}} - T(\Delta S_{\mathrm{comb}} + \Delta S_{\mathrm{confA-B}} + \Delta S_{\mathrm{confABR}} + \Delta S_{\mathrm{elas}}) \tag{4}$$

The first term on the right-hand side of eq 4, ΔH_{mix}, denotes the heat of mixing the random copolymer and the block copolymer. The first term within the parentheses is the combinatorial entropy change on mixing, and the second and the third terms give the conformational entropy losses associated with the confinement of the blocks of the block copolymer within their microdomains and the compression of the random copolymer necessary to accommodate them within the block copolymer microdomains, respectively. The fourth term in parentheses is the elastic entropy change resulting from the alteration in the dimensions of the two blocks from those in the pure block copolymer.

In writing, eq 4 we have assumed that contributions to the free energy of the mesophase from the interfacial regions between microdomains are small and can be neglected. The approach used in eq 4, which divides the total entropy change into separate elements, has been adopted by Meier[1,41] in his confined chain model, with which he calculated the solubility limit of a homopolymer in an ordered block copolymer. Tucker and Paul[42] have also used this approach in their model to estimate the free energy of blends of homopolymer and block copolymer. We believe that this equation, although approximate, makes the contributions to the free energy change by various thermodynamic factors more intuitively visible.

2-3. Solubilization of ABR into A−B. As previously reported,[31] in the A−B/C blend system, the localization of added homopolymer into the central region of the A domain of block copolymer is found to be an important factor in the stabilization of the mesophase. We, therefore, incorporate the same localization phenomenon in our attempt to evaluate the stability of the mesophase of blends of a random copolymer and a block copolymer. (For more details about the localized solubilization, please refer to our previous paper.[20]) Consider the block copolymer in the ordered state with the random copolymer added. Figure 1 gives a schematic diagram of such a state. Figure 1a presents the density distribution of polymer segments in the microdomains before ABR is solubilized into the block copolymer, and Figure 1b presents the density distribution of polymer segments with the ABR solubilized into the block copolymer, where ζ denotes the fraction of ABR solubilized into the A domains. Figure 1b shows the case of $\zeta > 0.5$. Although the actual distribution of the polymer segments may be more complex, here it is approximated that the distribution varies linearly as shown in Figure 1.[43] To simplify the derivation we here treat only the case where the volume fraction of A block in the block copolymer is 0.5, so that A−B adopts only a lamellar morphology. In Figure 1, the vertical axis denotes the normalized density of segments, while the horizontal axis denotes distance in the lamellar thickness direction. D_0 is the interdomain distance of A−B before the addition of ABR, and D is the interdomain distance after the addition. d_{A0} (or d_{B0}) and d_{A} (or d_{B}) are the domain thicknesses of A (or B) within which A blocks (or B blocks) are confined before and after the addition of ABR, respectively. It is assumed that the interface thickness is very narrow compared with the domain thickness, so the interfacial region is not explicitly represented in Figure 1.

An ABR molecule added to A−B could be solubilized either into the A domain or into the B domain causing the domain sizes of A and B blocks to increase. If a fraction ζ of the random copolymer is solubilized into the A domain and a fraction $1 - \zeta$ is solubilized into the B domain, the thicknesses, D_{A} and D_{B}, of the two

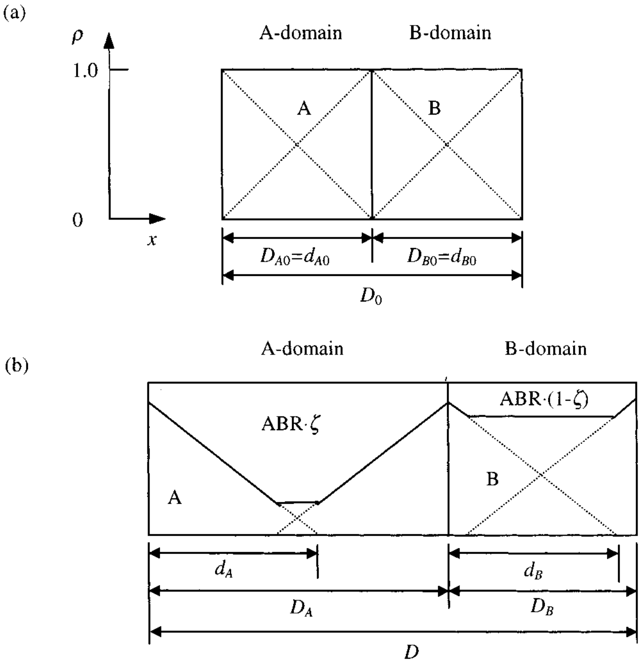

Figure 1. Schematic diagram of the spatial segmental distribution in the microdomain space of A–B/ABR blends. The total density is normalized to be unity. Key: (a) pure block copolymer (A–B); (b) block copolymer + random copolymer (A–B/ABR); the thick solid line denotes density profile of A–B with the A block segments within the A domain and the B block segments within the B domain. It should be noted that it is possible for the block chain in each domain to extend itself for the sake of entropy, which results in the variation of the density profile manifested by the change of its slope.

domains after the addition of the ABR are given as follows:

$$D_{\mathrm{A}} = \frac{f_{\mathrm{A}}\phi_{\mathrm{A-B}} + \zeta\phi_{\mathrm{ABR}}}{f_{\mathrm{A}}\phi_{\mathrm{A-B}}} D_{\mathrm{A0}} \qquad (5)$$

$$D_{\mathrm{B}} = \frac{(1 - f_{\mathrm{A}})\phi_{\mathrm{A-B}} + (1 - \zeta)\phi_{\mathrm{ABR}}}{(1 - f_{\mathrm{A}})\phi_{\mathrm{A-B}}} D_{\mathrm{B0}} \qquad (6)$$

Here, D_{A0} and D_{B0} are the thicknesses of the A and B domains of the pure block copolymer, respectively.

It should be noted that, in this model, there could exist a particular interface region no longer occupied by either A block or B block, through which the freely moving ABR chain may go to the A domain from the B domain or vice versa. This makes the amount of ABR confined within the microdomain decreased. To see it more clearly, Figure 2 is drawn with the point of stress on the amount of ABR confined within the microdomain. In Figure 2a, the parameter z indicates the fraction of interface area occupied by the block copolymer, A–B. Therefore, the case of $z = 1$ means the interface is blocked off by A–B molecules, so that the ABR molecules cannot penetrate into the interface and are confined within the microdomain. With z decreasing, the interface region through which the ABR molecule moves freely to and fro is developed and enlarges its domain among the total interface region. As shown in parts a and b of Figure 2, with $z \neq 1$, the amount of the freely moving ABR molecules is obtained so as to be $(1 - z)$ times the total amount of polymers, and it is not affected by ζ. However, with the same amount of ABR solubilized into A–B, the amount of ABR confined within each domain is varied as ζ varies from 0 to 1. As you can see in parts a and b of Figure 2, a greater amount of ABR is confined within the A domain with $\zeta > 0.5$ than with $\zeta = 0.5$, which indicates that the free energy of the system depends on the inclination of ABR being dissolved into one of two domains. In principle, the addition of ABR induces an environmental change around A–B molecules as well as ABR ones, which then arouses a conformational change of the molecules to minimize the total free energy. The variation of the molecular conformation is closely related to the density profile which is a function of three variables, d_{A}, d_{B}, and ζ in this modified confined chain model as shown in Figure 1b. With d_{A} and d_{B}, one can determine the conformation of the A–B chain, and with ζ, and hence D_{A} and D_{B}, one can determine the conformation of the ABR chain. At a given value of ζ, the values of d_{A} and d_{B} are determined to give the lowest ΔG_{meso} in eq 4, which means that ΔG_{meso} is a function of only one variable ζ, $\Delta G_{\mathrm{meso}}(\zeta)$. In conclusion, the minimum $\Delta G_{\mathrm{meso}}(\zeta^*)$ with $0 \le \zeta^* \le 1$ is what proves to be the free energy change of the mesophase at a given ϕ_{ABR}. In this way, we can now obtain all the requested ΔG_{meso}s needed to construct the complete concentration–temperature phase diagram for A–B/ABR blend system.

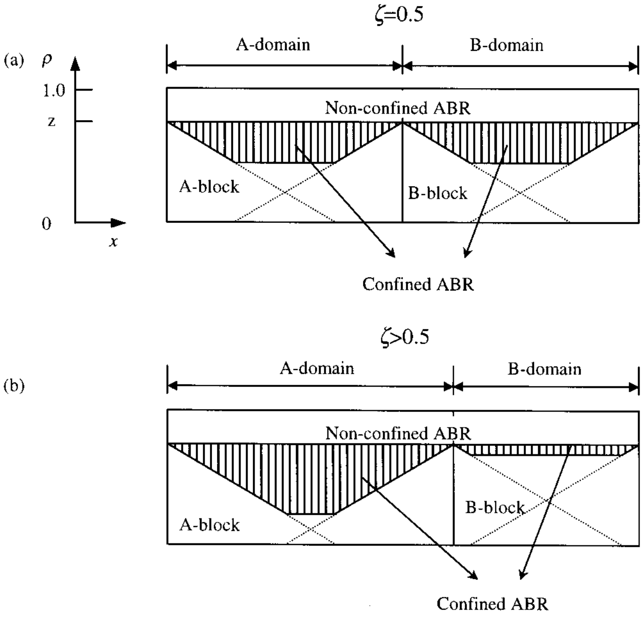

Figure 2. Schematic diagram of the spatial segmental distribution in the microdomain space of A–B/ABR blends, especially focusing on the variation of the amount of ABR chains confined in each domain with ζ at a fixed $\phi_{\mathrm{ABR}}(\neq 0)$. The case of $\zeta = 0.5$ is shown in part a) and the case of $\zeta > 0.5$ in part b, in which the amount of the confined ABR within the microdomains is represented by the patterned area. We should note that there exists an interesting region through which some of the added ABR chains are able to move freely without being confined within each domain. In this figure, the amount of the ABR chains belonging to such free-moving ABR chains is given by the $(1 - z)$ fraction of the total amount of the polymers.

3. Modified Confined Chain Model

On the basis of the density distribution shown in Figure 1, each of the four terms contributing to the free energy of the mesophase (eq 4) is evaluated as follows.

3-1. Conformational Entropy of the A–B Block Copolymer. From the diffusion equation with absorbing boundary condition,[41] we write the conformational probability of an A−B chain in the ordered state, $P_{A-B}(d_A,d_B;d_I)$, as

$$P_{A-B}(d_A,d_B;d_I) = \frac{16}{\pi^3}\frac{d_A d_B}{d_I}\sum_{m,p=1,3,...}^{\infty}\frac{1}{mp}\left(\frac{m d_B \sin\frac{p\pi d_I}{d_B} - p d_A \sin\frac{m\pi d_I}{d_A}}{m^2 {d_B}^2 - p^2 {d_A}^2}\right) \times \exp\left[-\frac{\pi^2}{6}\left(\frac{m^2 n_A {l_A}^2}{{d_A}^2} + \frac{p^2 n_B {l_B}^2}{{d_B}^2}\right)\right] \quad (7)$$

Here, d_I is the interfacial thickness, which is assumed to be small, compared to the domain thickness d_A or d_B and remains fixed regardless of the amount of ABR added. Then, the difference in the conformational entropy of the A−B chain per unit volume in the ordered state before and after the addition of ABR can be obtained by

$$\Delta S_{confA-B} = S_{after} - S_{before} = R\frac{\phi_{A-B}}{V_{A-B}}[\ln P_{A-B}(d_A,d_B;d_I) - \ln P^0_{A-B}(d_{A0},d_{B0};d_I)] \quad (8)$$

where $P^0_{A-B}(d_{A0},d_{B0};d_I)$ is the conformational probability of an A−B chain in the mesophase before the addition of ABR.

3-2. Combinatorial Entropy of Mixing. Since in the ordered microdomain structure, the block copolymers form a kind of network on mixing with ABR, there is no combinatorial entropy change associated with the block copolymer, and only the combinatorial entropy change associated with the random copolymer need be considered.

Because the density distribution of the random copolymer, as shown in Figure 1, is not uniform, the combinatorial entropy change per unit volume of the random copolymer is obtained by the integral

$$\Delta S_{comb} = \frac{R}{V_{ABR}}\int_0^{D_A+D_B}\rho_{ABR}(x)\ln\frac{\rho_{ABR}(x) + \rho_{A-B}(x)}{\rho_{ABR}(x)}\,dx \quad (9)$$

where $\rho_{ABR}(x)$ is the density distribution of ABR segments scaled to satisfy $\int_0^{D_A+D_B}\rho_{ABR}(x)\,dx = \phi_{ABR}$, and $\rho_{A-B}(x)$ is the density distribution of A−B segments scaled similarly.

3-3. Heat of Mixing. In terms of the reduced density distributions, $\rho_{A-B}(x)$ and $\rho_{ABR}(x)$, the heat of mixing per unit volume, ΔH_{mix}, is given by

$$\Delta H_{mix} = (D_A + D_B)\int_0^{D_A+D_B}B_{A-B/ABR}(x)\rho_{A-B}(x)\rho_{ABR}(x)\,dx \quad (10)$$

where $B_{A-B/ABR}(x)$ is the interaction energy density between the segments of the block copolymer A−B and of the random copolymer ABR. Note that $B_{A-B/ABR}(x)$ acquires a value equal to the interaction energy density between the A block and the ABR, $B_{A/ABR}$ $(=(1 - f_A')B_{A/B})$, while x is in the A domain, and a value equal to the interaction energy density between the B block and the ABR, $B_{B/ABR}$ $(= f_A' B_{A/B})$, while x is in the B domain.

3-4. Elastic Entropy Difference. As the density profile of the A or B segments is altered, as seen in Figure 1, with the addition of the ABR, the dimension of the A or B block is changed. The degree of shrinking or stretching of the chain can be characterized by the change in its end-to-end distance. In analogy with the result obtained by Meier,[1] this elasticity entropy change is written as follows:

$$\Delta S_{elas} = -\frac{1}{2}R\frac{\phi_{A-B}}{V_{A-B}}[({W_1}^2 - 2\ln W_1) - ({W_0}^2 - 2\ln W_0)] \quad (11)$$

Here, W_1 and W_0 are the ratios of perturbed to unperturbed end-to-end distance of block copolymer after and before mixing with the random copolymer, respectively.

3-5. Conformational Entropy Change of Random Copolymer Chains. When the ABR is added, it may be solubilized into either the A domain or the B domain or it may be present in both domains at the same time. It should be noted that, as seen in Figure 2, there could exist ABR chains moving freely across the interface in the ordered microdomain structure and not suffering any other restrictions on their conformations compared to those not solubilized into the A−B domain. Therefore, it should be kept in mind that the amount of such ABR chains moving freely in the domain structure must be excluded when we calculate the conformational entropy change of ABR. The fraction of the amounts of the free ABR chains is represented in terms of $(1 - z)$ in Figure 2. The conformational entropy change of the added ABR, $\Delta S_{confABR}$, can be evaluated as follows:

$$\Delta S_{confABR} = R\frac{\zeta\phi_{ABR}}{V_{ABR}}\ln\left[\int_0^{D_A}dx\,\frac{\rho_{ABR}(x)\cdot z}{\phi_{ABR}}\frac{4}{\pi}\sum_{p=1,3,...}^{\infty}\frac{1}{p}\sin\left(p\pi\frac{x}{D_A}\right)\exp\left(\frac{-p^2\pi^2 n_{ABR}{l_{ABR}}^2}{6{D_A}^2}\right)\right] + R\frac{(1-\zeta)\phi_{ABR}}{V_{ABR}}\ln\left[\int_{D_A}^{D_A+D_B}dx\,\frac{\rho_{ABR}(x)\cdot z}{\phi_{ABR}}\frac{4}{\pi}\sum_{p=1,3,...}^{\infty}\frac{1}{p}\times\sin\left(p\pi\frac{x}{D_B}\right)\exp\left(\frac{-p^2\pi^2 n_{ABR}{l_{ABR}}^2}{6{D_B}^2}\right)\right] \quad (12)$$

D_K is the K-domain thickness (K = A and B) and n_{ABR} and l_{ABR} are the number of monomer units and the statistical length of the monomer unit in ABR, respectively.

4. Free Energy of the Mesophase

To simplify the calculation of the free energy of the mesophase, it has been assumed that the statistical lengths l_A and l_B are equal to each other and the densities of A and B polymers are both 1 g/cm^3, allowing $M_K = V_K$ (K = A and B) in eqs 7−12. The unperturbed chain dimension is estimated from $M_K {C_K}^2$, C_K being the characteristic length of the monomeric unit (or segment). The length of the monomeric unit is assumed to be 0.7 Å for all the polymers. The domain thickness D_{A0}

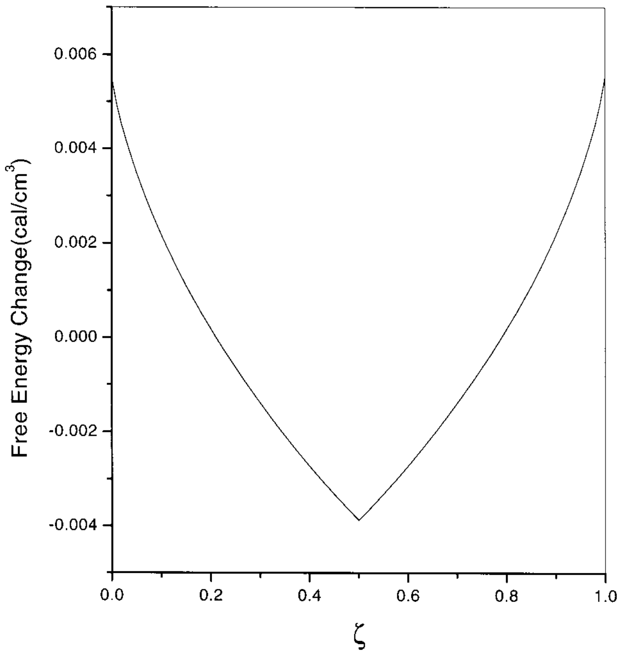

Figure 3. Free energy change of the mesophase as a function of ζ at 340 K with $\phi_{ABR} = 0.1$, $M_{A-B} = 25000$, $M_{ABR} = 6250$, $f_A = f_A' = 0.5$, and $B_{A/B} = 1.6 - 0.002T$ (cal/cm^3) (for PS/PBd blends). The critical value of ζ, ζ^*, is determined from the minimization of the free energy.

of the A block is obtained by using $D_{A0} \cong 1.4(M_A C_A{}^2)^{1/2}$, and D_{B0} is also obtained in a similar way.

For the interaction energy density $B_{A/B}$, we used the experimental value determined from the polystyrene (PS)−polybutadiene (PBd) pair

$$B_{A/B} = 1.6 - 0.002T\ (\text{cal/cm}^3) \tag{13}$$

where T is the temperature in kelvin. The molecular weight of A−B is fixed to be 25 000 ($M_{A-B} = 25\,000$), and the volume fraction of the A block in A−B, f_A, is also fixed to be 0.5, which ascertains the lamellar microdomain structure of A−B.

Recall that in obtaining ΔG_{meso} at a given ϕ_{ABR} and T, we have to determine ζ^*, so that $\Delta G_{meso}(\zeta)$ has the lowest value. Figure 3 shows the variation of $\Delta G_{meso}(\zeta)$ with ζ, where $M_{ABR} = 6250$, $T = 340$ K, and $f_A' = 0.5$. In Figure 3, we should note that $\Delta G_{meso}(\zeta)$ has a left-right symmetry on the minimum point of $\zeta = 0.5$, which is a natural result from the symmetric property of the system, $f_A = f_A' = 0.5$. In this way, one can determine the lowest ΔG_{meso} at given ϕ_{ABR} and T.

Figure 4 shows ΔG_{meso} as a function of ϕ_{ABR}, where ΔG_{meso} has a negative value in a narrow ϕ_{ABR}-region, $0 < \phi_{ABR} < 0.17$, and a positive value in the other ϕ_{ABR} region. The molecular parameters used in this figure is as follows: $M_{ABR} = 6250$, $f_A' = 0.5$, and $T = 340$ K. The block copolymer containing a very small amount of random copolymer is more stabilized than the pure block copolymer without the random copolymer, which goes against the previous result of the A−B/A blend system in which the addition of A reduces the free energy of mesophase greatly in most of the A region. (As for the case of A−B/A with $f_A' = 1$, ΔG_{meso} has a negative value in all the ϕ_A region.) This low solubilization of random copolymer into the block copolymer seems to be a typical phase behavior of this blend system.

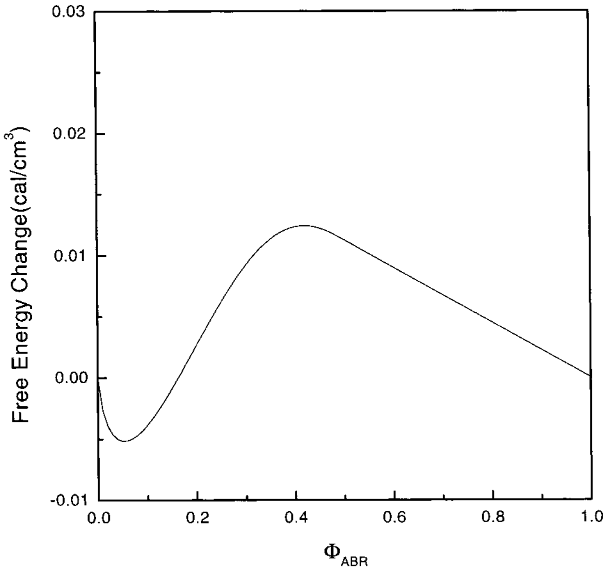

Figure 4. Free energy change of the mesophase as a function of the volume fraction of random copolymer, ϕ_{ABR}, calculated at 340 K. The other numerical values are the same as those used in Figure 3.

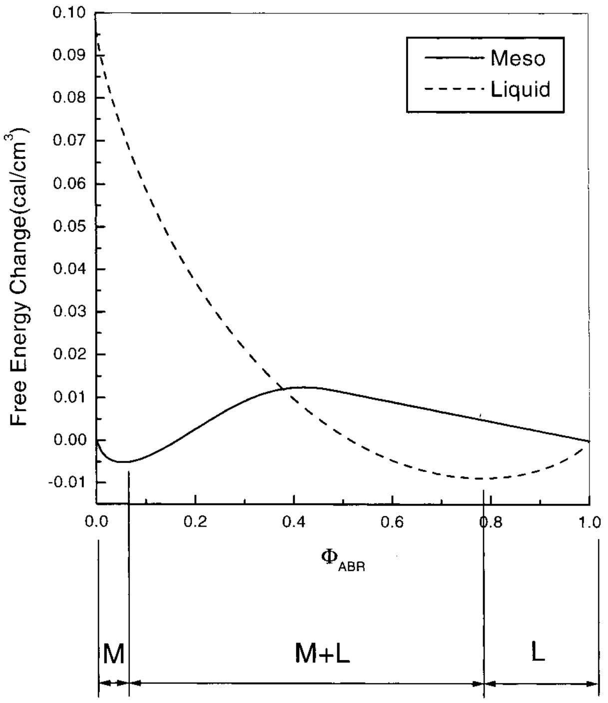

Figure 5. Example for determining the coexistent phases using the tangent line method from the calculated free energy changes of the mesophase (M) and the liquid phase (L). The temperature is 340 K and $M_{A-B} = 25\,000$, $M_{ABR} = 6250$, $f_A = f_A' = 0.5$, and $B_{A/B} = 1.6 - 0.002T$ (cal/cm^3).

5. Examples of Phase Diagrams

In trying to construct phase diagram of A−B/ABR (for example, S−B block copolymer/SB random copolymer) blends, the free energy change of the mesophase should be compared to that of the liquid one at various temperatures. Figure 5 is plotted as an example for determining the coexistent phases under a given temperature. The following numerical data are used: $M_{ABR} = 6250$ and $T = 340$ K. The free energy change of the mesophase (denoted by M) is expressed by a solid line and that of the liquid phase (denoted by L) by a dashed line. The determination of the coexisting phase under

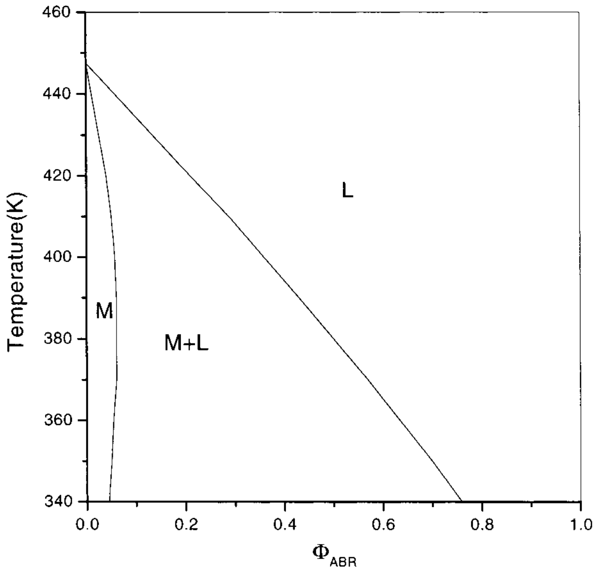

Figure 6. Calculated concentration−temperature phase diagram of A−B/ABR blend, which is obtained by comparing the free energy change of the mesophase with that of the liquid phase at various temperatures. For the calculation, the numerical values assumed in Figure 5 are used. The state of M + L denotes that the mesophase of the ordered microdomain coexists with the liquid phase.

a given temperature is done graphically by constructing the common tangent line. In the same way, we can determine the coexisting phases at various temperatures, from which the complete concentration−temperature phase diagram is obtained.

The resultant phase diagram is shown in Figure 6 where $M_{ABR} = 6250$ and $f_A' = 0.5$. As ϕ_{ABR} increases, the temperature at which the phase transition from M+L to L takes place, gradually decreases. The mesophase M is existent only over a small range of ϕ_{ABR} near $\phi_{ABR} = 0$ for the temperatures below the T_{ODT} of the pure block copolymer. This indicates that ABR is hardly dissolved into the microdomain of A−B, which is due to the increased ΔH_{mix} when ABR is mixed with A−B. In contrast to ΔH_{mix} in the A−B/ABR blend system, ΔH_{mix} in the A−B/A blend system is equal to zero, which encourages the mixing of the homopolymer into the corresponding domain of A−B.

The effect of the molecular weight of ABR on the phase behavior is shown in Figure 7 where only the transition from M + L phase to L phase is highlighted. Three molecular weights of ABR are used; $M_{ABR} = 6250$, 25 000, and 50 000. As M_{ABR} decreases, T_{ODT} at a given ϕ_{ABR} decreases. When the same amount of ABR with different molecular weight is mixed with the common A−B to form the mixtures, the mixture having small random copolymer gains more translational freedom in liquid phase than that having large random copolymer, which makes the liquid phase more stable. Thus, the mixture having small random copolymer favors the liquid phase to the mesophase as shown in Figure 7. It should be noted that in A−B/ABR blend system, the solubility of ABR into A−B is very low compared with that in A−B/A blend system, so that the effect of the random copolymer on the solubilization of mesophase is negligibly small, which makes it acceptable to consider only the free energy change of the liquid phase in order to examine the molecular weight effect of the added random copolymer on the phase behavior of A−B/ABR blends. This low solubilization at mesophase together with low enthalpy increase on mixing in liquid phase give rise to a difference in the phase behavior between A−B/A blends and A−B/ABR blends; in A−B/A blends, the addition of the homopolymer of $M_A > 0.25M_{A-B}$ invokes the elevation of T_{ODT}, whereas as shown in Figure 7, in A−B/ABR blends, the addition of even larger molecules ($M_{ABR} = 50\,000$), whose molecular weight is 4 times as large as that of the A block of the A−B of $M_{A-B} = 25\,000$, cannot increase T_{ODT}.

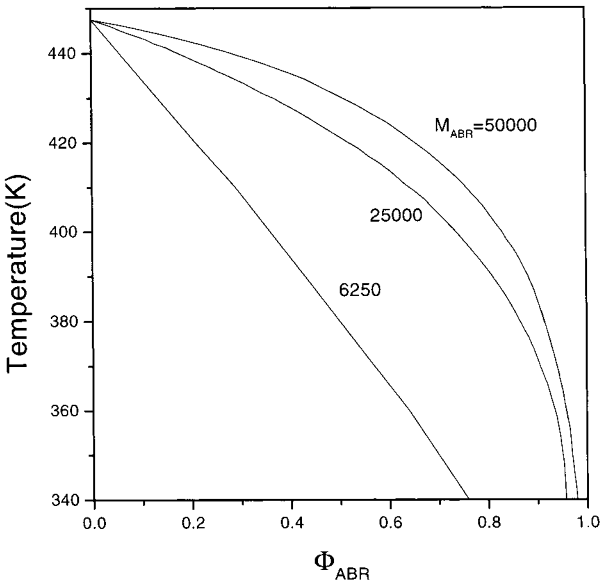

Figure 7. Effect of the molecular weight of the ABR on the phase behavior of the A−B/ABR blends, in which only the transition from the M + L phase to the L phase is highlighted. The highest line denotes the result for $M_{ABR} = 50\,000$, the middle one the result for $M_{ABR} = 25\,000$, and the lowest one the result for $M_{ABR} = 6250$. The same numerical data as used in Figure 5 are also used.

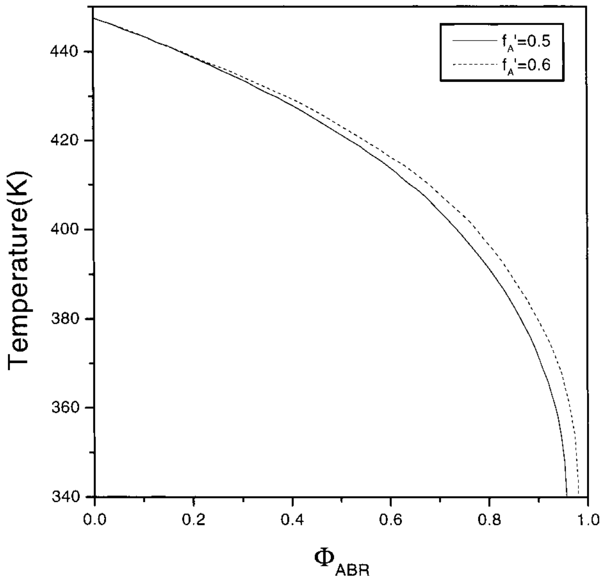

Figure 8. Effect of the component A of the ABR, f_A', on the phase behavior of the A−B/ABR blends, in which only the transition from the M + L phase to the L phase is highlighted. The solid line denotes the result of $f_A' = 0.5$ and the dashed line the result of $f_A' = 0.6$. The same numerical values as those used in Figure 5 are also used.

In Figure 8, we examine the effect of the A component fraction of ABR, f_A', on the phase behavior of A−B/ABR blends with $M_{ABR} = 25000$. The solid line denotes the result of $f_A' = 0.5$ and the dashed line the result of $f_A' =$

0.6. As in the case of Figure 7, the transition point from the M + L phase to the L phase (T_{ODT}) is highlighted. The mixture of $f_A' = 0.6$ shows a higher T_{ODT} than that of $f_A' = 0.5$, which is due to the increase of the interaction energy in ΔG_{liq} shown in eqs 1 and 2. As in the case of Figure 6, here, the free energy change of liquid phase is more important in determining the phase behavior of A−B/ABR blends than that of the mesophase. However, we should notice that as f_A' approaches unity, that is, as the ABR resembles more and more the homopolymer A, the effect of the free energy change of mesophase on the phase behavior of A−B/ABR blends will be augmented.

6. Conclusions

By modification of the confined chain model originated by Meier, the complete concentration−temperature phase diagram for A−B/ABR blends was constructed. From such a constructed phase diagram, it was found that the A−B/ABR blend system showed a relatively simple phase behavior compared with the A−B/A blend system: In the A−B/ABR blends, as ϕ_{ABR} increased, T_{ODT}, the order−disorder transition temperature, merely decreased, not showing any sign of increment at all. It was also found that the added ABR is hardly dissolved into the microdomains of the A−B due to the energetically unfavorable interaction between the ABR and each block of A−B where the fraction of A monomer in ABR is 0.5. The depression of T_{ODT} appeared in A−B/ABR mixture system seems to be similar to the very well-known melting point depression observed in crystal/solvent mixture system, in which the principal driving force of that phenomenon is the very large increase of mixing entropy acquired when the crystal melts and mixes with the solvent. This large mixing entropy increase was also found to be a main factor controlling the phase behavior in A−B/ABR mixtures, which showed another good correspondence found in nature between different material systems.

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