Effect of added homopolymer on the microphase separation transition temperature of block copolymer

Hwan-Koo Lee [1], Chang-Kwon Kang [2], Wang-Cheol Zin [1]

[1] Department of Materials Science and Engineering, POSTECH,
P.O. Box 125, Pohang, 790-784, Korea
[2] Cheil Synthetics Inc. No. 14, Nongseo-Ri, Kiheung-Eub, Yongin-Gun,
Kyounggi-Do, 449-900, Korea

Summary

The change in the microphase separation transition temperature (T_{mst}) of a diblock copolymer (AB), induced by the addition of homopolymer (HA), is theoretically studied. The calculations based on the modified Meier's theory show that T_{mst} is dependent on both the volume fraction of added homopolymer and the molecular volume ratio of HA to AB, which is the same as the previous theoretical results and qualitatively in agreement with the experimental results. This theory also predicts that the molecular weight ratio at the crossover of T_{mst} from elevation to depression is affected by the molecular weight of AB.

Introduction

In a block copolymer having two types of blocks mutually immiscible, the blocks segregate out into their own microdomains forming an ordered macrolattice. When the temperature is raised, such an ordered phase may be transformed into a disordered phase which is a single homogeneous phase lacking any long range order. This order-disorder transition is often called the microphase separation transition (MST). The thermodynamic stability of the microdomains and hence T_{mst} may be affected by the addition of homopolymer. The purpose here is to explore the microphase separation behaviors in binary mixtures containing a block copolymer and a homopolymer.

Using the scattering theories (1-5), first developed by Leibler (1) who has used the random phase approximation (RPA) method, Nojima and Roe (6) have studied the molecular size effect of homopolymer on the change in the spinodal temperature (T_s) of the microphase separation in mixtures of a block copolymer and a homopolymer. They show that for a symmetrical copolymer if the molecular volume of homopolymer is larger than a quarter of that of copolymer, T_s goes up as the volume fraction of homopolymer Φ_{HA} increases, and the magnitude of the increment of T_s is larger with increasing the molecular volume of homopolymer. Of course, if the molecular volume ratio of HA to AB is below a quarter, T_s goes down with increasing Φ_{HA}. The scattering theory also predicts that the molecular volume ratio of HA to AB, which is at

the crossover from depression to elevation of T_s, depends on the composition f_A of the block copolymer. The other approach investigating the change in T_s is developed by Whitmore and Noolandi (7). The result of this approach is qualitatively in agreement with that of the scattering theory.

Several experimental studies (6,8-11) for binary mixtures containing a block copolymer have shown that as Φ_{HS} increases, T_{mst} (or T_s) decreases or increases depending on the molecular weight ratio of HA to AB, which were qualitatively in agreement with the above theoretical results (6,7).

In the previous work (12), we have developed a method of predicting phase separation behaviors in binary mixtures of a homopolymer and a block copolymer by modifying Meier's theory (13) and thus calculated complete concentration-temperature phase diagrams of the mixtures. In this study, we focus our attention on a particular boundary line in the phase diagrams dividing the ordered phase and the disordered one of the mixtures only to examine the change in the MST temperature induced by added homopolymer.

Free energy of Mixing of a Block Copolymer with a Homopolymer

The order-disorder transition (or the MST) of a block copolymer should be of "first order" according to the theory of Leibler (1), but experimentally its character has not yet been established clearly. It is assumed in this study that the MST is a first order phase transition.

A binary mixture of a block copolymer and a homopolymer is thus divided into two distinct states, i.e., an ordered state and a disordered one. 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. In trying to determine the change in the MST temperature, we now compare the chemical potential of the block copolymer in the mesophase against that in the liquid phase.

Free Energy change of the Liquid phase First, we consider the free energy of mixing of a homopolymer HA with a block copolymer AB in the disordered state. On the assumption that the block copolymer in the disordered state acts as a random copolymer, the free energy change on mixing per unit volume in the liquid phase (ΔG_{liq}) can be given by

$$\Delta G_{liq} = \Delta G_{random} + \Delta G_{mst} \cdot \Phi_{AB} \tag{1}$$

with

$$\Delta G_{random} = RT\{(\Phi_{HA}/V_{HA})\ln \Phi_{HA} + (\Phi_{AB}/V_{AB})\ln \Phi_{AB}\} + B_{HA/AB}\Phi_{HA}\Phi_{AB} \tag{2}$$

where R is the gas constant, Φ_{HA} and Φ_{AB} are the volume fractions of HA and AB in the mixture, V_{HA} and V_{AB} are the molar volumes of the two polymers, and $B_{HA/AB}$ is the energy interaction density between HA and AB. The free energy change per unit volume associated with microdomain dissolution, i.e., a transformation from the ordered

state to the disordered state of pure block copolymer, ΔG_{msi}, can be calculated by Meier's theory (13).

Free energy change of the mesophase No general theory is yet available that gives the free energy change on mixing of a homopolymer and a block copolymer in the ordered state having a segregated microdomain structure. However, it is possible to estimate the free energy change by using a simple model based on reasonable assumptions.

When HA is added to AB block copolymer, HA may be dissolved only into the A-domains and any contributions from the B-domains or the interfacial region between the two coexisting domains can be ignored, which results in the free energy change on mixing per unit volume in the mesophase formulated by

$$\Delta G_{meso} = \Delta H_{meso} - T\Delta S_{meso} \tag{3}$$

with

$$\Delta S_{meso} = \Delta S_{comb} + \Delta S_{conf\,AB} + \Delta S_{conf\,HA} + \Delta S_{elas} + \Delta S_{place} \tag{4}$$

In eq. (3), ΔH_{meso} is the heat of mixing per unit volume of HA with the A-block, which is equal to zero for AB/HA (or HA/AB) blend systems. In eq. (4), the total entropy change in the mesophase (ΔS_{meso}) is composed of five contributions. The first term is the combinatorial entropy of mixing. The second and third terms are the conformational entropy losses due to extension of the A-block and compression of the homopolymer molecules, respectively, which arise from a constraint to maintain a uniform density of the A-domain. The forth and fifth terms denote the elasticity entropy change reflecting the chain deformation from its random-coil state and the placement entropy change induced by the addition of homopolymer.

In trying to evaluate the contributions to the free energy change in the mesophase, we use in this study a simple model of describing the localized solubilization of added homopolymer, which is a modification of the confined-chain model originated by Meier (12). The density distribution profile of polymeric segments is shown in Figure 1 where d_A indicates the thickness of the domain which contains both the HA and A-block segments without the B segments, and d_C the thickness of the domain to which the A-block segments is confined. The horizontal axis denoted by x indicates the distance across the domains and the vertical one denoted by $P_A(x)$ the segmental density of the A-block in the domains. The total density, $P_t(x)$, normalized to one, is consisted of the A-block, B-block, and HA segments as shown in Figure 1 ; $P_t(x) = P_A(x) + P_B(x) + P_{HA}(x) = 1$. The combinatorial entropy change per unit volume for the homopolymer is obtained by

$$\Delta S_{comb} = \frac{R}{V_{HA}} \int_0^\infty \rho_{HA}(x) \ln \frac{\rho_{HA}(x) + \rho_A(x)}{\rho_{HA}}(x)\,dx \tag{5}$$

where $\rho_{HA}(x)$ is the reduced density of the HA segments defined as $\int_0^D \rho_{HA}(x)\,dx = \Phi_{HA}$ and $\rho_A(x)$ the reduced density of the A-block segments defined
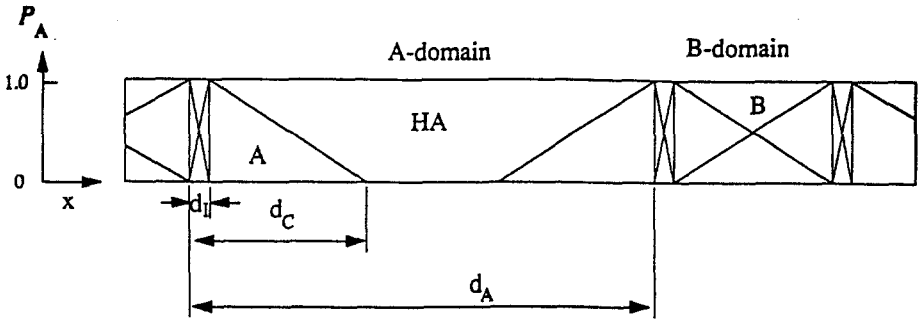
Figure 1. Normalized density distribution profile of AB/HA blend.

similarly, and D is the interdomain distance.

The conformational entropy change per unit volume of the AB chain in the mesophase associated with the addition of HA can be obtained by

$$\Delta S_{conf\,AB} = R\frac{\varPhi_{AB}}{V_{AB}} \ln P_{AB}(d_A, d_B; d_I) - R\frac{\varPhi_{AB}}{V_{AB}} \ln P^o_{AB}(d^o_A, d_B; d_I) \tag{6}$$

where $P_{AB}(d_A, d_B; d_I)$ is the probability of AB chain with A-block confined within the domain of thickness d_A and B-block confined within the domain of thickness d_B and the superscript o over P^o_{AB} denotes the reference state without homopolymers. The interfacial thickness is denoted by d_I.

The conformational entropy change per unit volume of the homopolymer confined within the A-domain is given by

$$\Delta S_{conf\,HA} = R\frac{\varPhi_{HA}}{V_{HA}} \ln\left[\frac{8}{\pi^2} \sum_{p=1,3,\dots}^{\infty} \frac{1}{p^2}\left(\frac{-p^2\pi^2 n_{HA} l^2_{HA}}{6 d^2_A}\right)\right] \tag{7}$$

where d_A is the domain thickness and n_{HA} is the number of the link of length l_{HA}.

The elasticity entropy change can be formulated as follows;

$$\Delta S_{elas} = -\frac{1}{2} R\frac{\varPhi_{AB}}{V_{AB}}(W_1^2 - 1 - 2\ln W_1)$$
$$+\frac{1}{2} R\frac{\varPhi_{AB}}{V_{AB}}(W_0^2 - 1 - 2\ln W_0) \tag{8}$$

where W_1 and W_0 are the ratios of perturbed to unperturbed A-block's end-to-end distance of mixed state with HA and non-mixed state, respectively.

The placement entropy change is equal to zero because the AB junction has not been influenced by the added HA at all and therefore the volume occupied by the junctions can not be changed, which excludes the contribution of the placement entropy change from obtaining ΔG_{meso}.

Results and Discussion

The procedure in obtaining the MST temperature of the blends is as follows; first to calculate the complete phase diagram and then to examine the specific part of the phase diagram suitable for our purpose. In trying to construct phase diagrams of AB/HA mixtures, the free energy change of the mesophase should be compared with that of the liquid phase at various temperatures. Once a temperature is given, the phase having lower energy than that of the other phase is determined to be the real phase. For the coexisting phases, they are determined graphically by constructing the common tangent line. In this way, one can obtain the complete composition-temperature phase diagram of AB/HA mixtures.

Since the change in T_{mst} induced by added homopolymer can go upward or downward, which was shown by experimental results (9-11) and predicted by theoretical ones (6,7), Figures 2-(a) and (b) are drawn to demonstrate the two situations. These diagrams are small parts of schematic phase diagrams constructed by the previous work (12). In these diagrams, M and L denote the mesophase and the liquid phase respectively. As one can see from Figure 2-(a), the MST temperature is located on the boundary line (which is highlighted by thick line) dividing the phase regions of M1+L1 and L. In the region denoted by M1+L1, the mesophase and the liquid phase coexist. One of the end points of the boundary line is linked with the binodal line of the liquid phase(L $\rightarrow$ L1+L2) at the pseudoeutectic temperature denoted as T_{eut}. On cooling a mixture Φ_1 from the single liquid phase denoted as L1, the MST (i.e., the microdomain formation) commences with the separation of the mesophase M from the liquid phase L1 at temperature T_1. On the other hand, when $\Phi_{HA} > \Phi_{eut}$, such as Φ_2, the MST occurs at the pseudoeutectic temperature (T_{eut}). At higher temperature than T_{eut}, there exist macroscopically separated liquid phases (L_1+L_2) without any microdomain structure. In Figure 2-(a), the MST temperature decreases with increasing Φ_{HA}, while in Figure 2-(b),

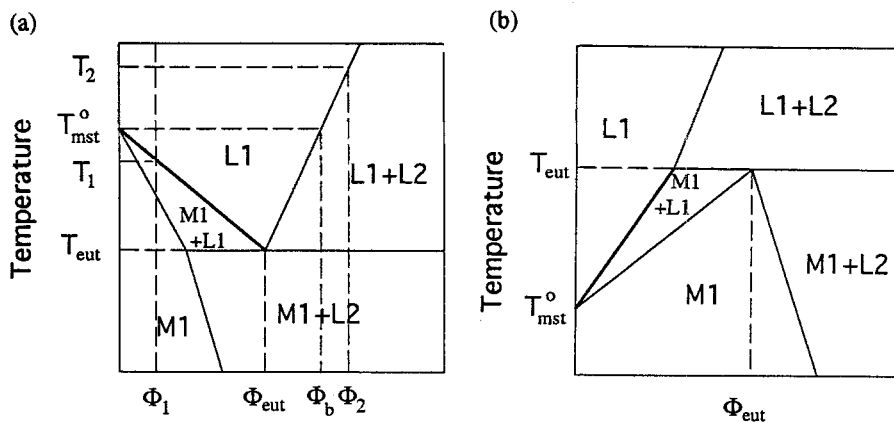(a)   (b)

Figure 2-(a), (b). Parts of schematic phase diagrams of AB/HA blend.

the MST temperature increases with increasing Φ_{HA}, and as it will be seen later, whether the MST temperature increases or decreases depends on the molecular weight ratio of the two polymers. The smaller molecular weight homopolymer has a more tendency to decrease the MST temperature compared to the higher molecular weight one.

In trying to investigate the effect of homopolymer molecular weight on the MST temperature, we construct the MST temperature lines of mixtures of a block copolymer (AB) with a homopolymer (HA) of various molecular weights. For simplicity, the densities of A and B segments are assumed to be 1g/cm³, and thus the molecular volume and the molecular weight will be used interchangeably in this paper, that is, $M_{HA(AB)}=V_{HA(AB)}$.

The results calculated by the modified Meier's theory are shown in Figure 3 where the molecular weight of copolymer is 25K and the volume fraction of A-block is 0.5, that is, the copolymer is symmetric. The x-axis is the volume fraction of homopolymer in the blend, Φ_{HA}, and the y-axis the temperature, and the interaction energy density of A and B blocks is assumed to be 0.8 cal/cm³, which is a comparable value with that for PS/PBd blend (11). As seen in Figure 3, the addition of small homopolymer molecules decreases T_{mst}, while the addition of large homopolymer molecules increases T_{mst}, and the molecular weight ratio M_{HA}/M_{AB} at the crossover from depression to elevation of T_{mst} is about 0.25, which is in agreement with the results of the other theories (6,7), although they have studied the change in the spinodal rather than the binodal. Experimental works (6,8-11) show that the change in T_{mst} or T_s is greatly dependent on M_{HA}/M_{AB}, which is qualitatively in agreement with this theoretical work. Our theory in the present form assumes lamellar microdomain structure for the block copolymer as well as its mixtures with a homopolymer. Thus, this theory is valid in a
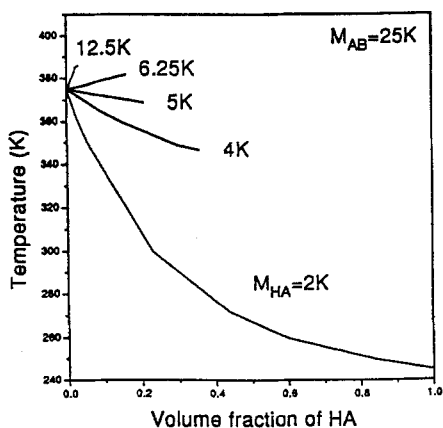

Figure 3. Calculated T_{mst} for blends of a block copolymer AB ($f_A=0.5$ and $M_{AB}=25K$) with various molecular weight homopolymers (HA).
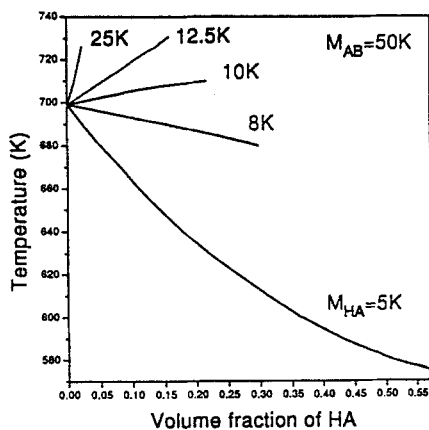
Figure 4. Calculated T_{mst} for blends of a block copolymer AB ($f_A=0.5$ and $M_{AB}=50K$) with various molecular weight homopolymers (HA).

limited range of ϕ_{HA} smaller than about 0.33 where the lamellar morphology is preserved (14). For the comparison of the experimental works with this theoretical results, it should be noted that in the case of most experimental studies, the copolymers used are not a symmetric copolymer, but a asymmetric one. This makes a direct quantitative comparison between the experimental results and this prediction not possible yet.

Figure 4 also shows the similar calculated results as Figure 3 except for M_{AB} being 50K. One can see the same trend that T_{mst} goes down with the addition of small homopolymer molecules while T_{mst} goes up with the addition of large ones. However, the crossover molecular weight ratio (M_{HA}/M_{AB}) is decreased from 0.25 to 0.18 as M_{AB} is increased from 25K to 50K, which is not expected from other theoretical results (6,7) that have shown the crossover molecular weight ratio to be 0.25 regardless of the molecular weight of copolymer. The main difference between this theoretical method and the others is that this method calculates the binodals for microphase separation and the others the spinodals.

In conclusion, the modified Meier's theory predicts quantitatively the binodal of the MST for mixtures of block copolymer and homopolymer by constructing the phase diagram, even though this theory has limitation that the morphology of ordered microdomains remains as lamellae even after a homopolymer is added. It is found that the change in the MST temperature is greatly dependent on the ratio M_{HA}/M_{AB}, which is consistent with the previous results. This theory also predicts that the molecular weight of block copolymer affects the ratio M_{HA}/M_{AB} at the crossover from depression to elevation of T_{mst}.

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