Phase diagrams for block copolymer/homopolymer blends exhibiting *LCST* behaviour

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We present phase diagrams of binary blends (or mixtures) of a homopolymer H, with a block copolymer, A–B, in which there is an exothermic interaction between two types of segments, H and A. In trying to construct phase diagrams, we extend the approach of predicting phase separation behaviour in such binary blends where H is chemically identical with one of the blocks of the copolymer, e.g. A. A binary blend of a homopolymer with a block copolymer is divided into two distinct states, i.e. an ordered state and a disordered state. On the assumption that the block copolymer in the disordered state acts as a random copolymer, the free-energy change in the disordered state can be estimated by a model including the localized solubilization of added homopolymers, which is a modification of the confined-chain model originated by Meier. To determine coexisting phases under a given temperature, we examine the relative stabilities (i.e. the chemical potential of each component in the blend) of the two states. As a result, the concentration–temperature phase diagrams of blends of H and A–B can be obtained. From the predicted phase diagrams, it is found that the exothermic interaction of this system greatly increases the solubility of H into the A domains and affects the shape of the phase diagram.

(Keywords: polymer blends; block copolymer; phase diagram)

INTRODUCTION

Binary blends of a homopolymer, H, with a block copolymer of the type AB, A–B, can exhibit complex phase behaviour arising from coupling of two kinds of phase transitions, i.e. a microscopic phase-separation of the copolymer itself and a macroscopic segregation between the two polymeric species. A number of experimental and theoretical studies on this problem have been reported in recent literature[1-17]. However, these investigations have focused mainly on the special case where H is chemically identical with one of the blocks of the copolymer, e.g. A. Only a few studies[18-21] have dealt with the phase relations and miscibility in blends of H with A–B in which there is an exothermic interaction between the two kinds of segments, i.e. H and A. (Binary blends of H with A–B are hereafter denoted as H/A–B or A–B/H blends.) The main purpose here is to present phase diagrams of H/A–B blends.

For homopolymer/homopolymer blends exhibiting lower critical solution temperature (*LCST*) behaviour, an exothermic interaction between the two types of segments is one of the most important factors driving their mutual miscibility. From thermal analysis of the blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with styrene-based block copolymers[18,19] it was found

that the favourable energetic interaction between PPO and the styrene blocks has a critical effect on the solubilization of PPO into the styrene domains of the block copolymer. On the basis of the experimental results, Tucker and Paul[20] presented a simple model for the enthalpic effect in H/A–B blends. Blends of PPO with styrene–isoprene diblock copolymers were also investigated by Hashimoto et al.[21]. They provided experimental evidence for the complex phase behaviour in H/A–B blends.

Because a blend of a homopolymer with a block copolymer having a segregated microdomain structure has an inhomogeneity of concentration, the free energy of the blend cannot be estimated by the typical Flory–Huggins treatment[22] which is a mean-field model of predicting liquid–liquid phase separation in polymer systems. In an attempt to estimate thermodynamic factors which contribute to the free energy change arising from the inhomogeneity of concentration in this type of system, Noolandi and co-workers[3-5] have developed a different formulation of a mean-field theory. The phase separation behaviour in A/A–B blends near the spinodal for microphase separation has been satisfactorily described by their theoretical formulations. However, it is difficult to extend their theory to H/A–B blends.

In a previous article[23], we developed an alternative approach to predicting phase separation behaviour in binary blends of a homopolymer with a block copolymer, and predicted a complete concentration–temperature phase diagram of A/A–B blend which was

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consistent with experimental results[1,2]. It was concluded that phase diagrams of A/A–B blends could be constructed by comparing the free-energy change on mixing homopolymers and ordered block copolymers with the free-energy change on mixing homopolymers and disordered block copolymers. In this article, we extend this approach to the case of H/A–B blends. The significant thermodynamic factors governing miscibility are also discussed.

PHASE EQUILIBRIA IN H/A–B BLENDS

The order–disorder transition (or the microphase separation transition) of block copolymers should be a first-order phase transition according to the theory of Leibler[24], but experimentally its character has not yet been established clearly. Then a blend system containing a homopolymer and a block copolymer can be 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 added homopolymer. The disordered state is a 'liquid phase' in which the disordered block copolymer is randomly mixed with the homopolymer. A general approach to determine phase separation behaviour in the blend is to examine the relative stabilities (i.e. the chemical potential of each component in the blend) of all possible phases present under a given condition. In trying to construct a concentration–temperature phase diagram of H/A–B blend, it is necessary to compare the free energy of the mesophase with that of the liquid phase at various temperatures.

Free energy change for the liquid phase

By assuming that the block copolymer in the disordered state acts as a random copolymer, the free-energy change per unit volume for the liquid phase (i.e. the mixed phase of a homopolymer with a disordered block copolymer) is given by[23]:

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

where ΔG_{random} is the free-energy change of mixing of a homopolymer with a random copolymer having the corresponding composition and molecular weight of the block copolymer and is estimated by the typical Flory–Huggins equation[22]:

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

with

$$B_{\text{H/AB}} = f_{\text{A}}B_{\text{H/A}} + (1 - f_{\text{A}})B_{\text{H/B}} - f_{\text{A}}(1 - f_{\text{A}})B_{\text{A/B}} \tag{3}$$

where $B_{K/K'}$s are the interaction energy densities of K polymer and K' polymer, and f_{A} is the composition of the A block in the copolymer. In equation (2), R is the gas constant, T is the absolute temperature (K), V_{H} and V_{AB} are the molar volumes of the homopolymer and the block copolymer, respectively, and Φ_{H} and Φ_{AB} are the volume fractions of the two polymers in the blend with the condition $\Phi_{\text{H}} + \Phi_{\text{AB}} = 1$.

In equation (1), ΔG_{mst} is the free-energy change per unit volume associated with microdomain dissolution, i.e. a phase transition from the ordered state to the

disordered state of the pure block copolymer (A–B), and can be calculated by using the same formulations developed in Meier's theory[25]. The free energy ΔG_{mst} has a positive value below the microphase separation transition (*MST*) temperature of the pure block copolymer, A–B; when the temperature is raised ΔG_{mst} gradually decreases in magnitude, so that from equation (1) the free energy change for the liquid phase ΔG_{liq} decreases, to become zero at the *MST* temperature of the pure block copolymer.

Free energy change for the mesophase

No general theory is yet available that deals with the free-energy change on mixing of H and A–B in the ordered state having a segregated microdomain structure. However, it may be possible to estimate the free-energy change by the use of a simple model based on reasonable assumptions.

When the H segments have a favourable interaction with the A segments, the H molecules may be preferentially dissolved into the A domains. On the assumption that the H molecules can be dissolved only into the A domains and any contributions from the B domains or the interfacial regions between the two coexisting domains to the free-energy change for the mesophase can be ignored, the free-energy change per unit volume for the mesophase is given by[26]:

$$\Delta G_{\text{meso}} = \Delta H_{\text{mix}} - T(\Delta S_{\text{comb}} + \Delta S_{\text{confAB}} + \Delta S_{\text{confH}}$$
$$+ \Delta S_{\text{p}} + \Delta S_{\text{elas}}) \tag{4}$$

Here, the subscript 'meso' signifies that the ordered microdomain structure of the block copolymer remains on the addition of H. The first term on the right-hand side in equation (4), ΔH_{mix}, indicates the heat of mixing of H and A. The first term in the bracket is the combinatorial entropy of mixing and the second and third terms are the conformational entropy losses due to the confinement of the A block chain in the A domain and the compression of the H chain in the same domain, respectively. The fourth term in the bracket is the placement entropy change involved in the volume change of the interface to which the A–B junction is restricted, and the last term is the elastic entropy change of the A block chain resulting from the variation of its dimension, if any, compared to that of the pure block copolymer.

The approach used in equation (4), which divides the total entropy change into separate elements, has been used earlier by Meier[26] in his confined-chain model with which he calculated the solubility limit of a homopolymer into an ordered block copolymer. Tucker and Paul[20] have also used this approach in their simple model of estimating the free-energy change in H/A–B blends. We believe that this equation, although approximate, makes the contributions to the free-energy change more intuitively visible by various thermodynamic factors.

LOCALIZED SOLUBILIZATION OF ADDED HOMOPOLYMER

According to experimental results[11–15] for systems having lamellar morphology, the solubilized homopolymer may swell the A domains of the block copolymer axially, laterally or both, as a function of the molecular

weight ratio of the homopolymer to the A block and the interaction energy between them. It is known that the lateral expansion of the microdomain (i.e. the increase in the distance between the neighbouring covalent junctions of the block copolymer at the interface) may change the microdomain morphology. Recently, using small-angle X-ray scattering experiments on blends of styrene–isoprene (S–I) diblock copolymers with polystyrene (PS), Hashimoto and co-workers[11,12] and Winey et al.[14] provided some results on the solubilization behaviour of the added homopolymer. They found that PS was not distributed uniformly throughout the styrene domains but was localized in the centre of the microdomain space. (The possibility of the localized solubilization of the added homopolymer has also been suggested in other experimental investigations[2,9,10].) They also reported that the lateral expansion decreases with increasing the molecular weight of the added homopolymer. These results imply that as the molecular weight ratio of the homopolymer to the corresponding block decreases, the uniform solubilization is more favourable than localized solubilization.

We believe that 'localized solubilization' may be a more critical factor in the stabilization of the mesophase than 'morphological transition' arising from the lateral expansion of the domain, and may be more easily treated by simple modelling. Thus it is assumed that the domain shape of the block copolymer is lamellar and there is no morphological transition induced by the addition of homopolymer. In the previous paper[23], we proposed a simple model including the localized solubilization of the added homopolymer in A/A–B blends. In this localized solubilization model, which was a modification of Meier's original model, the density distribution of the localized homopolymer was assumed to be a step function for the simplicity of computational problems. It should be mentioned that the step function in representing the density distribution is replaced by a gradient function in this paper. We give here a brief summary of our model and provide mathematical formulations of the contributions to the free-energy change for the mesophase (equation (4)) in the next section.

Although the actual distribution of polymer segments may be complex, it is assumed that the distribution has a simple linear function as shown in *Figure 1*. *Figure 1a* shows the density distribution of the A and B segments in the A and B domains and the interface in the case of the pure copolymer, A–B, where d_{A0} is the thickness of the domain (including both the A domain and the interface) containing the A segments, and d_B is the thickness of the domain (including both the B domain and the interface) containing the B segments. *Figures 1b* and *c* show the density distribution for the block copolymer mixed with homopolymer, H, where d_A indicates the thickness of the domain which contains both the A and H segments without the B segments, and d_C the thickness of the domain to which the A segments are confined. In particular, *Figure 1c* visualizes the localization of the added homopolymer in the central part of the A domain. The horizontal axis denoted by x indicates the distance across the domains and the vertical axis denoted by $Q_A(x)$ the segmental density of A in the domains. The total density, $Q_t(x)$, normalized to unity, is composed of the A, B and H segmental densities, as shown in *Figure 1*: $Q_t(x) = Q_A(x) + Q_B(x) + Q_H(x) = 1$. In *Figures 1a–c*,
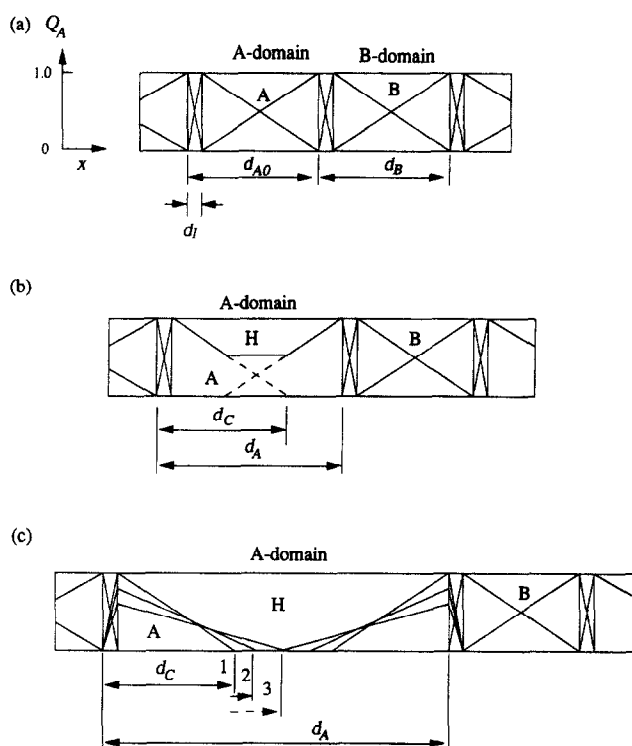

Figure 1 Schematic representation of the spatial segmental distribution in the microdomain space of H/A–B blends. The total density is normalized to be unity. (a) Pure block copolymer (A–B); (b) block copolymer + homopolymer (H/A–B) ($d_A < 2 \times d_C$); (c) block copolymer + homopolymer (H/A–B) ($d_A > 2 \times d_C$). In *Figure c* there are three forms of density distributions denoted by numbers 1, 2 and 3. In the sequence of increasing number, d_C increases

d_I indicates the thickness of the interface to which the A–B junctions are confined.

To determine the thicknesses d_{A0} and d_I in *Figure 1a*, we use the method developed previously by Meier. Then the domain thickness is related to the size of the A block by:

$$d_{A0} \cong 1.4 \sqrt{n_A l_A^2} \qquad (5)$$

where $\sqrt{n_A l_A^2}$ is the root mean square end-to-end distance of the A blocks, with number of segments n_A and length of segment l_A. The appropriate interfacial thickness d_I is determined by minimizing, while keeping the domain thickness constant, a free energy associated with the microphase separation from a homogeneous state to the mesophase state at room temperature. On the assumption that the added homopolymer is only dissolved into the A domain, and the interfacial area between the two coexisting domains (A and B domains) remains unchanged, the increment of the interdomain distance induced by the addition of H can be calculated from a geometrical consideration of the ordered domain structure. For lamella-shaped microdomains, d_A is given by:

$$d_A = \frac{(1 - \Phi_H) f_A + \Phi_H}{(1 - \Phi_H) f_A} d_{A0} \qquad (6)$$

where d_{A0} is the domain thickness of the pure block copolymer as described in *Figure 1a*.

Figure 1c also shows the variation of the density profile in the A domain which is a function of d_C. When H is

mixed with the A segments, the density distribution of the A segments may be different from that in the non-mixed state and therefore d_C can have a different value at a given Φ_H, as marked by 1, 2 and 3. It should be noted that ΔG_{meso} is greatly dependent on the density distribution (or d_C). Hence the equilibrium density profile which gives the lowest ΔG_{meso} should always be determined at a given Φ_H.

MODIFIED CONFINED CHAIN MODEL

On the basis of the density distributions shown in *Figure 1*, the contribution of each of six terms to the free-energy change for the mesophase (equation (4)) can be formulated.

Conformational entropy change of homopolymer chains

The probability that the H chain obeying random-flight statistics will be confined within the A domain of the block copolymer can be obtained from the diffusion equation:

$$\frac{\partial P_H(x_H; x_H')}{\partial n} = \frac{l^2}{6} \frac{\partial^2 P_H(x_H; x_H')}{\partial x^2} \tag{7}$$

where n is the number of statistical elements (or monomer units) of length l, and x_H and x_H' are positions of the chain ends. The appropriate boundary condition for the H chain is $P_H(0, x_H') = P_H(d_A, x_H') = 0$ (absorbing boundary conditions). Then one can see that the solution is given by:

$$P_H(x_H; x_H') = \frac{2}{d_A} \sum_{p=1}^{\infty} \sin\frac{p\pi x_H}{d_A} \sin\frac{p\pi x_H'}{d_A}$$
$$\times \exp\left(-\frac{p^2\pi^2 nl^2}{6d_A^2}\right) dx_H \tag{8}$$

Since both ends of the H chain can be anywhere within the A domain, we first integrate equation (8) over x_H', and then over x_H, to obtain the probability $P_H(d_A)$ with all segments constrained to stay within the domain space of thickness d_A.

This double integration gives the conformational entropy change per unit volume of the H chain confined within the A domains of the mesophase by[25]:

$$\Delta S_{confH} = R\frac{\Phi_H}{V_H}\ln\left[\frac{8}{\pi^2}\sum_{p=1,3,...}^{\infty}\frac{1}{p^2}\exp\left(\frac{-p^2\pi^2 n_H l_H^2}{6d_A^2}\right)\right] \tag{9}$$

where d_A is the domain thickness as shown in *Figure 1* (see equation (6)), and n_H and l_H are the number of monomer units and the statistical length of the monomer unit of H, respectively.

Conformational entropy change of A–B block chains

In the original confined-chain model[26], Meier assumes that the density of the solubilized homopolymer is essentially uniform over the A domain, and suggests that the free end of the A block chain, 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 uniform density requirement. However, in this model, the requirement of maintaining uniform density can be satisfied easily by localizing the

homopolymer molecules in the central part of the A domain, which otherwise has to be filled by highly stretched A block chains. As a result, the conformational entropy loss of the A block chain can now be effectively lowered by releasing the extension of the A block chain.

With the consideration that the A–B chain must have the junction point confined within the narrow interfacial region, the probability (which is a function of variables x_A and x_B, the position vectors of free ends of the A–B chain) that the A–B chain should obey can be written as $P_{AB}(x_A, x_B; x_I)$ where x_I is the position vector of the junction point within the interfacial region. If it is properly taken into account that both segments must be in their respective domains, the probability $P_{AB}(x_A, x_B; x_I)$ can be written as the product of two probabilities for the A and B blocks, that is, $P_{AB}(x_A, x_B; x_I) = P_A(x_A, x_A') P_B(x_B, x_B')$, where the primed vector indicates the position of the junction end of each block within the interfacial region.

As for the A block, the conformational entropy change is equivalent to that from Meier's original model, except that the thickness of the confined region is d_C instead of d_{A0} as shown in *Figure 1*. But for the B block, no conformational entropy change is assumed on the addition of H. Referring to equation (8), the probability $P_A(x_A, x_A')$ that the A blocks are confined within the domain of thickness d_C, with both ends at x_A and x_A', can be obtained by solving the diffusion equation. The boundary condition is $P_A(0, x_A') = P_A(d_C, x_A') = 0$ (absorbing boundary conditions). Then the probability for the A block is given by:

$$P_A(x_A, x_A') = \frac{2}{d_C} \sum_{m=1}^{\infty} \sin\frac{m\pi x_A}{d_C} \sin\frac{m\pi x_A'}{d_C}$$
$$\times \exp\left(-\frac{m^2\pi^2 n_A l_A^2}{6d_C^2}\right) dx_A \tag{10}$$

and similarly, the probability for the B block with domain thickness d_B is given by:

$$P_B(x_B, x_B') = \frac{2}{d_B} \sum_{p=1}^{\infty} \sin\frac{p\pi x_B}{d_B} \sin\frac{p\pi x_B'}{d_B}$$
$$\times \exp\left(-\frac{p^2\pi^2 n_B l_B^2}{6d_B^2}\right) dx_B \tag{11}$$

In equations (10) and (11), n_K is the number of statistical elements of K chain and l_K is the statistical length. It should be noted that x_A' and x_B' indicate the same point in the interfacial region, for they are the position vectors as seen from different points of view, A or B, of the same A–B junction point. Thus the following condition must be satisfied: $x_A' + x_B' = d_I$, where d_I is the interfacial thickness. Then from equations (10), (11) and

$$P_{AB}(x_A, x_B; x_I) = P_A(x_A, x_A') P_B(x_B, x_B'),$$

$P_{AB}(x_A, x_B; x_A')$ is given by:

$$P_{AB}(x_A, x_B; x_A') = P_A(x_A, x_A') P_B(x_B, d_I - x_A') \tag{12}$$

where x_B' is replaced by $d_I - x_A'$.

Since the junction point can be anywhere within the interface, equation (12) is integrated over x_A' from zero

to d_I to give the probability $P_{AB}(x_A, x_B; d_I)$ that allows the junction point to be anywhere within the interface. The integration gives:

$$
\begin{aligned}
P_{AB}(x_A, x_B; d_I) = \frac{4}{\pi d_I} \sum_{m, p=1}^{\infty} & \frac{m d_B \sin \dfrac{p \pi d_I}{d_B} - p d_C \sin \dfrac{m \pi d_I}{d_C}}{m^2 d_B^2 - p^2 d_C^2} \\
& \times \sin \frac{m \pi x_A}{d_C} \sin \frac{p \pi x_B}{d_B} \\
& \times \exp\left[\frac{-\pi^2}{6}\left(\frac{m^2 n_A l_A^2}{d_C^2} + \frac{p^2 n_B^2 l_B^2}{d_B^2}\right)\right] \\
& \times dx_A \, dx_B
\end{aligned}
\tag{13}
$$

As for the two free end points whose coordinates are expressed by x_A and x_B, they can be anywhere in their respective domains, i.e. the A and B domains, respectively. Hence in order to obtain the probability of the A–B chain in the ordered mesophase, equation (13) is integrated over x_A and x_B as follows:

$$
\begin{aligned}
P_{AB}(d_C, d_B; d_I) &= \int_0^{d_C} \int_0^{d_B} P_{AB}(x_A, x_B; d_I) \, dx_B \, dx_A \\
&= \frac{16}{\pi^3} \frac{d_C d_B}{d_I} \sum_{m, p=1,3,\ldots}^{\infty} \frac{1}{mp} \\
&\quad \times \left(\frac{m d_B \sin \dfrac{p \pi d_I}{d_B} - p d_C \sin \dfrac{m \pi d_I}{d_C}}{m^2 d_B^2 - p^2 d_C^2}\right) \\
&\quad \times \exp\left[-\frac{\pi^2}{6}\left(\frac{m^2 n_A l_A^2}{d_C^2} + \frac{p^2 n_B l_B^2}{d_B^2}\right)\right]
\end{aligned}
\tag{14}
$$

From equation (14), the conformational entropy change per unit volume of the A–B chain in the mesophase associated with the addition of H can be obtained by:

$$
\begin{aligned}
\Delta S_{confAB} &= S_{after} - S_{before} = R \frac{\Phi_{AB}}{V_{AB}} \ln P_{AB}(d_C, d_B; d_I) \\
&\quad - R \frac{\Phi_{AB}}{V_{AB}} \ln P_{AB}^0(d_A^0, d_B; d_I)
\end{aligned}
\tag{15}
$$

where P_{AB}^0 is the probability of the A–B chain in the mesophase without H. It should be noted that only d_C is variable in equation (15).

Combinatorial entropy change on mixing

Since the ordered domain structure in the mesophase can be thought to be a kind of network, the combinatorial entropy change on mixing for the copolymer seems to be negligible, and hence in our study only the entropy change for the homopolymer is considered. In order to calculate the combinatorial entropy change, the density profile as shown in *Figure 1* should be considered.

Because the density distribution is not uniform, the combinatorial entropy change per unit volume for the homopolymer is obtained by integration process:

$$
\Delta S_{comb} = \frac{R}{V_H} \int_0^{d_A + d_B} \rho_H(x) \ln \frac{\rho_H(x) + \rho_A(x)}{\rho_H(x)} \, dx
\tag{16}
$$

where $\rho_H(x)$ is the reduced density of the H segments

defined as $\int_0^{d_A + d_B} \rho_H(x) \, dx = \Phi_H$, and $\rho_A(x)$ is the reduced density of the A segments defined similarly.

Heat of mixing

When there is a specific interaction between two types of segments, A and H, it can be assumed that the added H molecules are preferably dissolved only into the A domains. As in the previous section, if the reduced densities, $\rho_A(x)$ and $\rho_H(x)$, are introduced, the heat of mixing per unit volume, ΔH_{mix}, is given by:

$$
\Delta H_{mix} = B_{H/A}(d_A + d_B) \int_0^{d_A + d_B} \rho_A(x) \rho_H(x) \, dx
\tag{17}
$$

where $B_{H/A}$ is the interaction energy density between the segments of H and A. In equation (17), we omit the term involving the gradient of the spatial composition of the H (or A) segments to account for 'non-local interactions', that is, the term $l^2/6(\partial \rho / \partial x)^2$, where l is a measure of intermolecular forces (usually used as the root-mean square length of one segment). For most block copolymer systems the slope $\partial \rho / \partial x$ is very small because the domain size is of the order of 10^3 or more, and hence the influence of the additional gradient term is negligibly small and therefore the gradient term will not be included.

Elasticity entropy difference

In the mesophase the density profile of the A segments is variable, as shown in *Figure 1c*, which brings about the change of the A block's dimension. The degree of shrinkage or stretch of the A chain can be characterized by its end-to-end distance. On the grounds of the work done by Meier[27], this elasticity entropy change can be formulated as follows (for one dimension):

$$
\begin{aligned}
\Delta S_{elas} &= -\tfrac{1}{2} R \frac{\Phi_{AB}}{V_{AB}}(W_1^2 - 1 - 2 \ln W_1) \\
&\quad + \tfrac{1}{2} R \frac{\Phi_{AB}}{V_{AB}}(W_0^2 - 1 - 2 \ln W_0)
\end{aligned}
\tag{18}
$$

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

Placement entropy change

The placement entropy change ΔS_P equals zero because the A–B junctions have not been influenced at all by the added H, and therefore the volume occupied by the junctions is not changed. Hence in obtaining ΔG_{meso}, the contribution of ΔS_P was left out in this study.

FREE ENERGY CHANGE FOR THE MESOPHASE

In order to calculate the free-energy change for the mesophase, it is assumed that physical parameters of each molecule are the same and therefore the statistical lengths l_A, l_B and l_H are equal and the densities of A, B and H polymers are of the same value (density = $1 \, g \, cm^{-3}$), so that $M_K = V_K$ ($K = A$, B and H) in equations (9), (15), (16), (17) and (18). The unperturbed chain dimension $n_K l_K^2$ is estimated from $M_K C_K^2$, where C_K is a characteristic length of monomeric unit (or segment) and the length of the monomeric unit is assumed to be $0.7 \, Å$ for all the polymers. The domain

thickness d_{A0} of the copolymer corresponding to the molecular weight of the A block is obtained by using

$$d_{A0} \cong 1.4\sqrt{M_A C_A^2}.$$

For the interaction energy densities, $B_{A/B}$ and $B_{H/B}$, we used the experimental value determined from the polystyrene (PS)–polybutadiene pair[28]:

$$B_{A/B} = B_{H/B} = 1.60 - 0.002T \qquad (19)$$

where T is the absolute temperature and $B_{K/K'}$ is in cal cm^{-3}. The molecular weight of the A–B block copolymer has the fixed value of 25 000 ($M_{AB} = 25000$) and the volume fraction of the A block in the block copolymer, f_A, is also fixed at 0.5 ($f_A = 0.5$) which ascertains that the microdomain structure of the block copolymer in the mesophase is lamellar.

Recall that in obtaining ΔG_{meso} at fixed Φ_H and T, the only variable is the thickness of the domain confining the A segments, d_C. *Figure 2* shows the contribution of each of five terms (ΔS_{comb}, ΔS_{confAB}, ΔS_{confH}, ΔS_{elas} and ΔH_{mix}) to the free-energy change for the mesophase, as a function of d_C/d_{A0} at 300 K with $\Phi_H = 0.5$, where $B_{H/A}$ ($= -0.2 + 0.0005T$ (cal cm^{-3})) was determined by a light-scattering experiment for PS/poly(vinylmethyl-ether) (PVME) blend in our laboratory. As d_C increases, $-T\Delta S_{comb}$, $-T\Delta S_{confAB}$ and ΔH_{mix} decrease, but $-T\Delta S_{elas}$ increases, and $-T\Delta S_{confH}$ is unchanged. The total free energy, ΔG_{meso} has a minimum. Thus the critical domain thickness, which gives the lowest ΔG_{meso}, can be determined from the minimization of ΔG_{meso}

$$\left. \frac{\partial \Delta G_{meso}}{\partial d_C} \right|_{d_C=d_C^c} = 0$$

Figure 3 shows the molecular weight dependence of H on d_C^c. As M_H increases, d_C^c decreases, indicating that the H molecule, having lower molecular weight, swells more the A block chain.
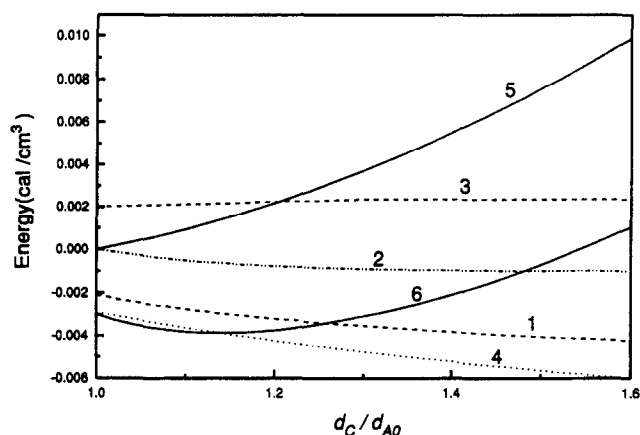

Figure 3 Similar plot to *Figure 2* with various molecular weights of homopolymer, $M_H = 5000$, 10000 and 25000. The critical value, d_C^c, decreases and the energy of the mesophase increases as M_H increases

Figure 4 The free-energy change for the mesophase as a function of the volume fraction of homopolymer, Φ_H, calculated at 380 K. The other numerical values are the same as those used in *Figure 3*. Curve 1, the energy change by the combinatorial entropy change; curve 2, the energy change by the conformational entropy change of A–B; curve 3, the energy change by the conformational entropy change of H; curve 4, the heat of mixing; curve 5, the energy change by the elastic entropy change of A–B; curve 6, the total mesophase free-energy change

Figure 2 The free-energy change for the mesophase as a function of d_C/d_{A0} at 300 K with $\Phi_H = 0.5$, $d_1 = 22$ Å, $M_{AB} = M_H = 25000$, $f_A = 0.5$, $H_{H/A} = -0.2 + 0.0005T$ (cal cm^{-3}) (for PS/PVME blend), and $B_{H/B} = B_{A/B} = 1.6 - 0.002T$ (cal cm^{-3}) (for PS/PBd blends)[26]. Curve 1, the energy change by the combinatorial entropy change; curve 2, the energy change by the conformational entropy change of A–B; curve 3, the energy change by the conformational entropy change of H; curve 4, the heat of mixing; curve 5, the energy change by the elastic entropy change of A–B; curve 6, the total mesophase free-energy change. The variation of d_C is shown in *Figure 1c*. The critical value of d_C/d_{A0}, d_C^c/d_{A0} is determined from the minimization of the free energy where d_{A0} is the thickness of the pure block copolymer
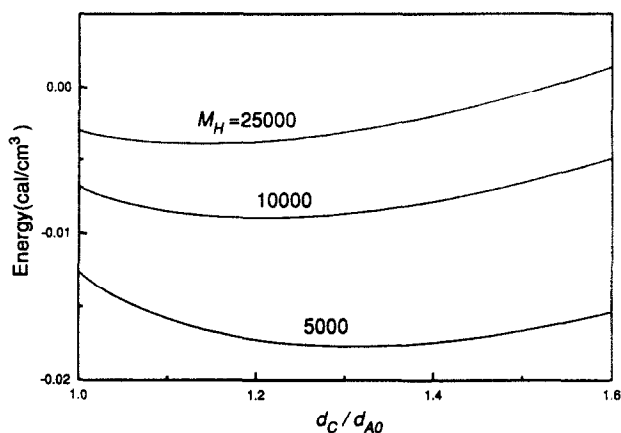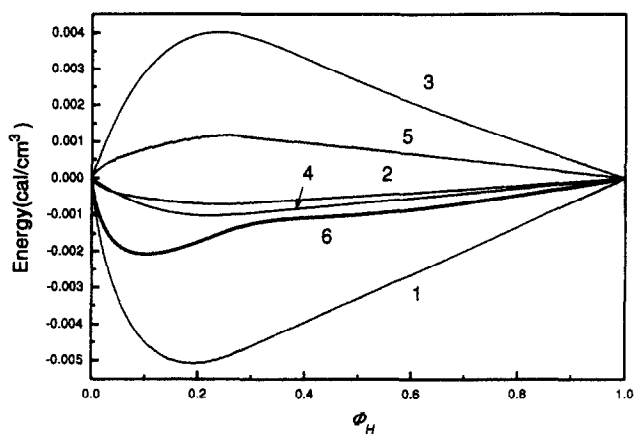
Figure 4 shows the contribution of each of the five terms to the free-energy change for the mesophase as a function of Φ_H at 380 K with $B_{H/A} = -0.2 + 0.0005T$ (cal cm^{-3}). The individual contributions are calculated by using equations (9), (15), (16), (17) and (18), respectively. As seen from *Figure 4*, the conformational entropy change of A–B, the heat of mixing, and the combinatorial entropy change tend to make the meso-phase stable, whereas the conformational entropy of H and the elastic entropy change tend to make it unstable. *Figure 5* shows the free-energy change for the mesophase at temperatures from 250 to 400 K, where the molecular weight of H is 25 000 and $B_{H/A} = -0.2 + 0.0005T$ (cal cm^{-3}). With decreasing T, the mesophase becomes more stable and the two phases which exist at higher T are combined into one phase at lower T, which is an analogy of the *LCST* phenomenon shown in PS/PVME blends. In *Figure 6* the molecular weight effect of H on ΔG_{meso} is shown. With lowering M_H, ΔG_{meso} decreases and the coexistence region disappears at $M_H = 6250$.
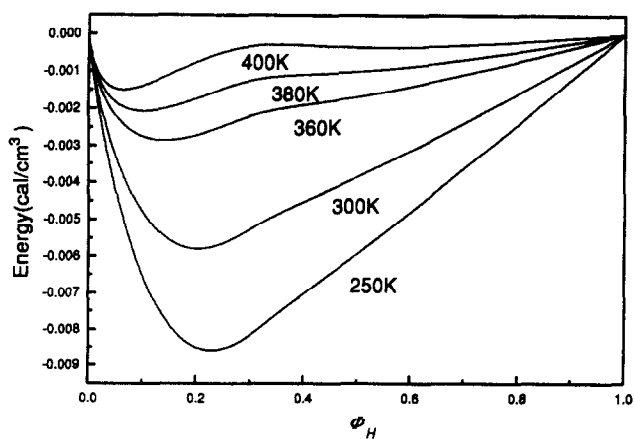
Figure 5 Similar plot to *Figure 4* with various temperatures: 250, 300, 360, 380 and 400 K. Only the total free-energy changes for the mesophase appear. The two-phase region at 400 K becomes narrower with decreasing temperature, and eventually the two phases are united into one phase at 250 K
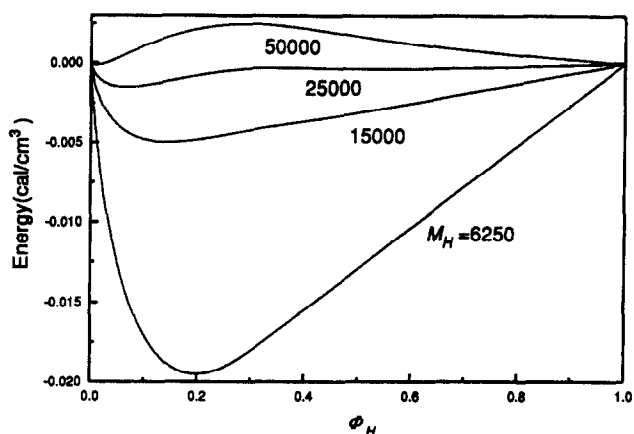

Figure 6 Similar plot to *Figure 4* with various molecular weights of homopolymer: 6250, 15000, 25000 and 50000. Only the total free-energy changes for the mesophase appear. With decreasing M_H, the two-phase region becomes narrower, disappearing at $M_H = 6250$; this is similar to the effect of decreasing T in *Figure 5*

EXAMPLES OF PHASE DIAGRAMS AND SOLUBILITY LIMITS

In trying to construct phase diagrams of H/A–B (for example PVME/S–B diblock copolymer) blends, the free-energy change for the mesophase should be compared with that for the liquid phase at various temperatures. *Figure 7* is given as an example for determining the coexistent phases under a given temperature. The following numerical data are used: $B_{H/A} = 0$, $M_{AB} = 25000$, $M_H = 6250$ and $T = 390$ K. The free-energy change for the mesophase (denoted as M) is expressed by a solid line and that for the liquid phase (denoted as L) by a dashed line. The determination of the coexisting phases under a given temperature is done graphically by constructing the common tangent line. In the same way, one can obtain the complete composition–temperature phase diagram of H/A–B blends.

Before constructing the phase diagram of H/A–B blends, some comparison for the solubility limit of the added H, $(\Phi_H)_s$ is given between experimental[29] and theoretical results[20,26] in *Figure 8*. Although for A/A–B
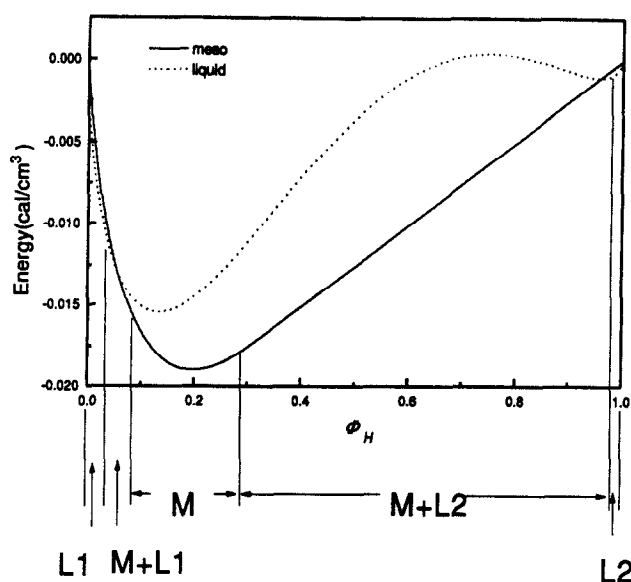

Figure 7 An example for determining the coexistent phases using the tangent line method from the calculated free-energy changes for the mesophase (M) and the liquid phase (L). The temperature is 390 K and $f_A = 0.5$, $V_H = M_H = 6250$, and $V_{AB} = M_{AB} = 25000$. It is assumed that $B_{H/A} = 0$, $B_{H/B} = B_{A/B} = 1.6 - 0.002T$ (cal cm^{-3})
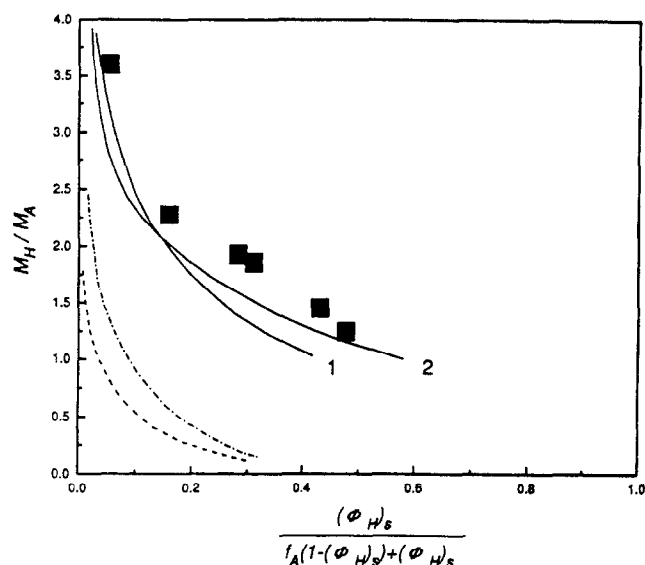

Figure 8 Comparison of theoretical and experimental results for the solubility limit. The horizontal axis represents relative volumes of homopolymer solubilized in the A domain $(\Phi_H)_s/\{f_A[1 - (\Phi_H)_s] + (\Phi_H)_s\}$. The symbols denote experimental results for the symmetric case and the curves denote calculated results: lowest curve (- - - - -) is that of Meier; the middle curve (- - - -) Tucker and Paul; highest two curves (———) are this model (1, $M_A = 12500$; 2, $M_A = 25000$)

systems, it gives some indirect evidence on applying our model to H/A–B systems. The symbols used in the figure indicate the experimental data, from which we see that for the symmetric case with $M_A/M_H \geq 1$, the infinite solubility limit is reached. The curves show theoretical predictions of $(\Phi_H)_s$: the lowest one is that of Meier, the middle one Tucker and Paul, and the highest two are our model (one for $M_A = 12500$ and the other for $M_A = 25000$). From the comparison of ours with the other two, it is found that our model predicts the experimental results more closely than the other two

models. This improvement in predicting the solubility limit can be explained by the adoption of the localization of the homopolymer. The models of Meier, and Tucker and Paul have assumed the uniform solubilization which induces a great increase of the elastic energy, expressed by ΔS_{elas} in equation (18), giving rise to a very low solubility limit. As a result, we concluded that the localization of the homopolymer, which decreases the elastic energy of block chains, has a governing effect on the solubility limit of the homopolymer and the resultant feature of phase diagrams.

Eastmond and co-workers[16,17] have made extensive studies of morphologies and phase separation in A/A–B and A/B/A–B blends, where A–B is a controlled graft copolymer. They found that the molecular weight ratio, M_A/M_H, is a critical factor in determining the solubilization of the homopolymer in the graft copolymer domain. They also suggested that the incompatibility of chemically identical blocks and homopolymers arises from a loss of conformational entropy (i.e. an increase of elastic energy) of block chains in the vicinity of microphase interfaces.

The complete phase diagram of H/A–B blends (with $B_{H/A} = -0.2 + 0.0005T$ and $M_{AB} = M_H = 25\,000$) is constructed as shown in *Figure 9*. In the calculated phase diagram, the different phase regions are indicated by M (homogeneous and ordered phase), M1 + M2 (separated and ordered phase), and L1 + L2 (separated and disordered phase). One can see that there is only one mesophase M at lower T. It resembles the *LCST* phenomenon shown in blends of PS/PVME. This interesting phenomenon was also observed in PPO/S–I blend[21] which shows no macroscopic phase separation at room temperature. As shown in *Figure 9*, the evaluated *MST* temperature of the pure block copolymer is about 387 K and it slightly increases as Φ_H increases up to about 0.12. This increment in the *MST* temperature is opposite to the melting-point depression appearing in solid–liquid systems. Experimentally, even if not in
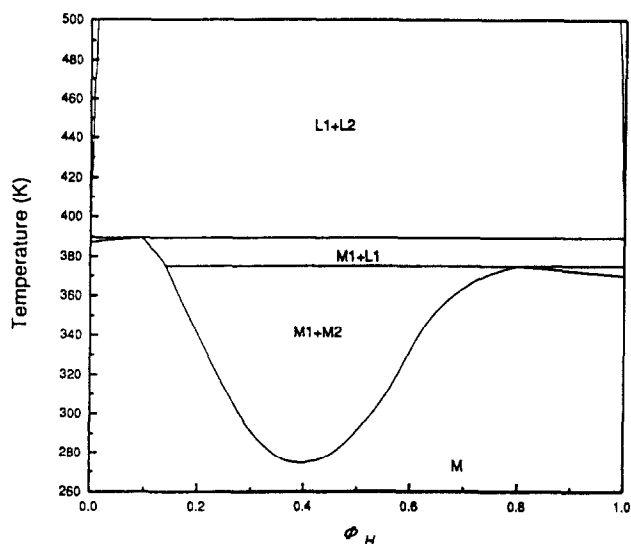

Figure 10 Calculated composition–temperature phase diagram of H/ A–B blend, which is calculated with the same numerical values assumed in *Figure 9* except that $M_H = 12\,500$ instead of $25\,000$

H/A–B systems, Roe and Zin[2] previously showed the increase of the *MST* temperature by the addition of homopolymer in the phase diagram for PS/S–B blends in the asymmetric case. (A detailed description of the *MST* temperature in H/A–B blends will be provided in a subsequent paper.) The phase diagram with lower molecular weight of H (= 12 500) is shown in *Figure 10*, where there exists only one mesophase (denoted by M) instead of the two mesophases (M1 and M2) in the blend with $M_H = 25\,000$. This indicates that lowering the molecular weight of H has a favourable effect on mixing of H into the A domains.

When a different interaction energy density between segments of H and A ($B_{H/A}$) is assumed, the shape of the phase diagram is expected to change. For this purpose, we have used $B_{H/A}$ estimated from PPO/PS blends in place of that for PS/PVME blends used in *Figure 9*. The resultant phase diagram is shown in *Figure 11*, which is

Figure 9 Calculated composition–temperature phase diagram of H/ A–B blend, which is obtained by comparing the free-energy change for the mesophase with that for the liquid phase at various temperatures. For the calculation, the numerical values assumed in *Figure 2* are used. The mesophase (M1 and M2) consists of ordered microdomains of the block copolymer swollen with homopolymer. The liquid phase (L1 and L2) consists of disordered block copolymer and homopolymer
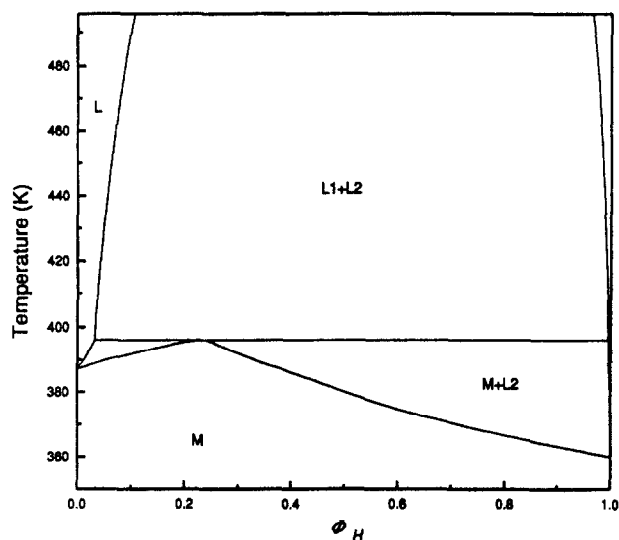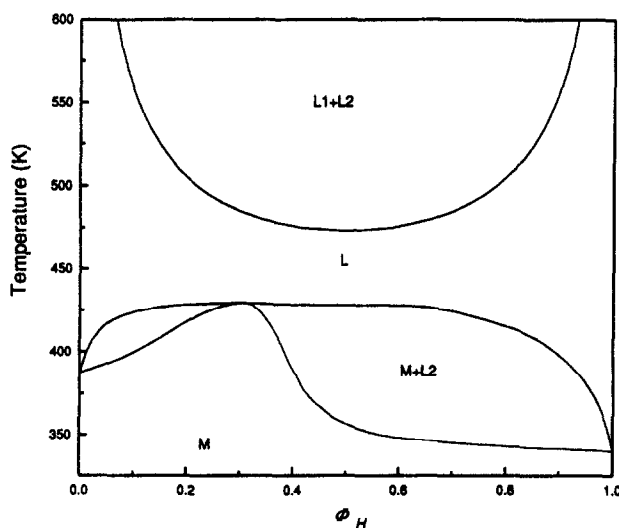

Figure 11 Calculated composition–temperature phase diagram of H/ A–B blend, which is calculated with the same numerical values assumed in *Figure 9* except for the interaction energy density between segments of H and A: $B_{H/A} = -1.17 + 0.0021T$ (cal cm^{-3}) for PS/PPO blends

similar in mesophase to *Figure 10*. However, in *Figure 10* the appearance of only one mesophase is induced by lowering M_H, whereas in *Figure 11* the appearance of one mesophase is induced by more exothermic interaction between the segments of H and A. It should be emphasized that the enthalpic effect also provokes the *LCST* phenomenon in the liquid phase, which indicates the importance of the interaction energy between H/A in examining the phase behaviour for H/A–B blends.

From the predicted phase diagram of A/A–B blend (Figure 9 in ref. 23), it was found that the concentration of the homopolymer that reaches the solubility limit has a constant value even when the temperature is raised. The reason is that the free-energy change for the mesophase is composed entirely of entropic contributions (i.e. $\Delta H_{mix} = 0$ in A/A–B blends). From the calculated phase diagrams of H/A–B blends (*Figures 9–11*), on the other hand, one can notice that the solubility limit of homopolymer into the A domains is very much dependent on $B_{H/A}$. Thus the shapes of the phase diagrams of H/A–B blends are strongly dependent on the functions for $B_{H/A}$ used to generate the diagrams. This fact leads us to believe that the energetic interaction between the segments of H and A has a considerable effect on the solubilization of H into the A domains of the block copolymer. It should be noted that when the enthalpic effect is more favourable to mutual miscibility of the two polymers at relatively lower temperatures, a complete solubilization of the homopolymer can be attained (see *Figure 9*). From experimental work on blends of PPO with styrene-based block copolymers, Tucker *et al.*[18,19] found no macroscopic segregation between PPO and the block copolymers, PPO being completely dissolved in the styrene domains. Their observations can also be explained by the fact that the favourable energetic interaction between PPO and the styrene blocks is dominant in a lower temperature region.

The modified version of Meier's model, although with many limitations such as no morphological transitions, no evidence for density uniformity, etc., not only describes satisfactorily the solubility limit behaviour for A/A–B systems, in the symmetric case, but also gives some information, not yet proved experimentally, on the phase behaviour of H/A–B systems with lamellar morphology. We hope that this paper will be useful for understanding the basic phenomena behind the real phase behaviour of H/A–B systems.

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