

# Phase separation in polymer blends comprising copolymers: 7. Statistical theory of block copolymer–homopolymer systems

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The miscibility of a homopolymer in corresponding domains of a copolymer predicted by Meier's theory is far less than found experimentally. In this paper, a density gradient model is suggested for describing the segment distribution of the bound and free chains in block copolymer–homopolymer systems. Using this model, Helfand's theory, which has been successful in explaining microphase separation of block copolymers, is extended to polymer blends of homopolymer and corresponding block copolymer with lamellar structure. The calculated free energy of mixing of the system shows that the predicted miscibility is much larger than that obtained by Meier's theory and is in good agreement with the main known experimental results. In particular, on the basis of the present theory, homopolymer can be expected to be solubilized by corresponding blocks in the whole composition range provided that the molecular weight of the former is less than that of the latter.

**(Keywords: phase separation; block copolymers; polymer blend; statistical theory; miscibility; density gradient model)**

## INTRODUCTION

In this series of research papers dealing with the miscibility of blocks of a copolymer and corresponding homopolymers, based on systematic studies of blends of various copolymers and polymers, it has been shown that the molecular weight ratio of the homopolymer to that of the corresponding block chains of the copolymer and molecular architecture of the copolymer have a considerable effect on homopolymer–copolymer miscibility<sup>1–3</sup>. However, concerning the relevant statistical theory, even for the simplest case of diblock copolymer with lamellar structure, the miscibility predicted by Meier's unique theory<sup>4</sup> differs greatly from experimental results. A new theoretical project to explore the nature of miscibility in polymer blends comprising copolymers and predict the basic relations between miscibility and molecular parameters as well as structures of the component polymers has been started and initial results are reported here.

As an extension of his theory of microphase separation<sup>5</sup>, Meier first developed a theory for the miscibility of blends of block copolymer AB and homopolymer (A or B). The free energy change associated with the solubilization is considered to be composed of the following terms: changes of interfacial energy; placement entropy; constraints and perturbations of both homopolymers and block copolymers; and entropy of mixing. Meier concluded that miscibility depends considerably on the molecular weight ratio of homopolymer to copolymer; and that the larger is the

ratio, the less is the miscibility. This is in conformity with experimental results. However, the predicted miscibility is very limited. For example, only 5% homopolymer A is expected to be solubilized in the domains of block A when the molecular weight of homopolymer A ( $M_H$ ) is equal to that of block A ( $M_A$ ) in the copolymer. This predicted miscibility is about one order of magnitude less than that found by electron microscope and SAXS studies. Meier<sup>4</sup> attributed this discrepancy to the nonequilibrium nature of the solvent-cast films used for the experimental observations. This explanation is not convincing since the theoretical result is in conflict with the data from various laboratories<sup>7–10</sup> and some of the micrographs reported in the literature show regular arrangement of the domain structure, which indicates that the films are at least close to equilibrium. In fact, in the authors' opinion, the reason for this discrepancy can lie only in defects of the physical model used in the theory.

In recent years, Helfand<sup>11–14</sup> has developed a statistical theory of block copolymers in which the mean-field theory, the modified diffusion equation and narrow-interface approximation were used for calculating the free energy change during microphase separation and then the equilibrium shape and dimensions of the domains were evaluated. The theory has been found to be in accordance with experimental results. Helfand's theory provides a suitable theoretical base for exploring the problem of miscibility of homopolymer–block copolymer systems. In this paper a density gradient model is suggested. Based on Helfand's theory and using this model, the free energy change is calculated for a homopolymer–copolymer system in which the copolymer has a lamellar structure. The results predict much higher

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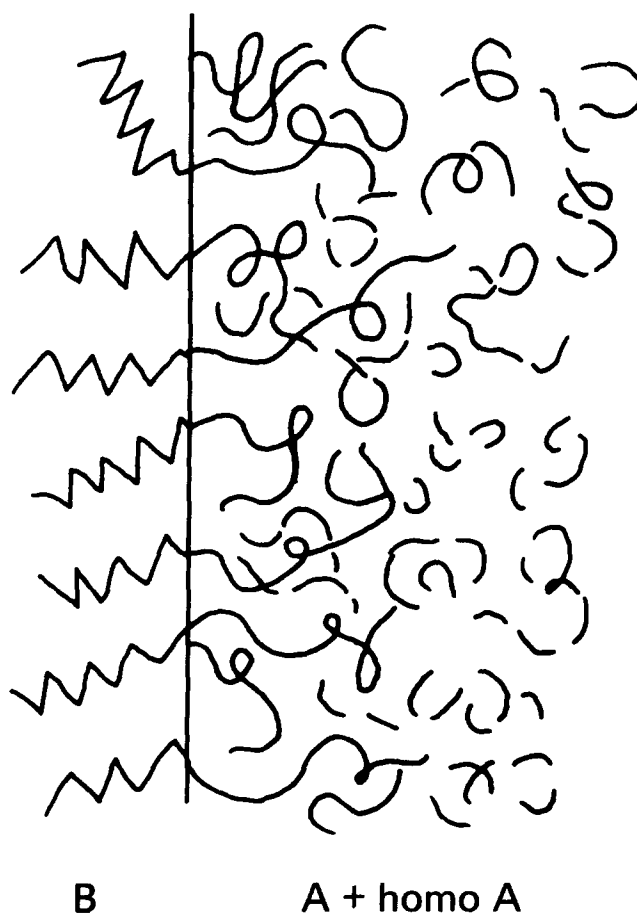
miscibility than that of Meier's theory and explain the most relevant experimental results reported in literature.

#### DENSITY GRADIENT MODEL

Meier formulated a statistical theory of microphase separation of block copolymers. In the theory, the density nonuniformity of the segments in domains caused by the requirement of the A–B junctions to be localized at the interface region is compensated by homogeneous extension of the blocks with accompanying loss of conformation entropy. However, in his theory dealing with the miscibility of homopolymer and corresponding chains of related block copolymers, Meier assumed that in the whole block domains where the homopolymer is solubilized the segment densities of both the free and homo chains are constant. This assumption can be realized only if the bound chains adopt some very improbable conformations for filling the domain centres that entail high entropy loss, which may exceed the driving force of the solubilization, namely the combinatorial entropy increment in the solubilization. Thus, this assumption is likely to be one of the main factors resulting in the prediction of low miscibility.

A close inspection of some published micrographs of homopolymer–block copolymer blends reveals that Meier's assumption is to some extent unrealistic. For example, *Figure 2* of ref. 7 shows, for a blend of diblock copolymer of styrene and isoprene with lamellar structure and a large quantity of polystyrene, that the lamellar microdomains of PB are randomly diluted by homo PS. In the micrograph, the distance between some neighbouring PB domains reaches the order of  $10^4$  Å. In addition, *Figure 9* of ref. 1 also shows that the distance between the neighbouring rod-like polybutadiene domains may be as large as  $10^4$  Å. However, in these examples, the molecular weights of PS blocks are only  $23 \times 10^4$  and  $9.5 \times 10^4$  and the corresponding unperturbed chain dimensions are only  $\sim 321$  Å and  $\sim 206$  Å respectively<sup>15</sup>. Apparently, it is almost impossible for such PS blocks to extend to the centre of the enlarged PS domains. This virtually implies that the region near the centre of the domains is filled only by homopolymer chains.

In the case of pure block copolymer, the requirement of uniformity of total density of the segments in the domains can be fulfilled only by adjusting the conformations of the blocks of the copolymer. However, for blends of homopolymer and copolymer, obviously this requirement can be satisfied by changing the conformations of both the bound and free chains. In particular, by contrast with block chains, homopolymer chains with two free ends are able to assume suitable spatial distributions to compensate partially for nonuniformity of segments caused by the localization of the A–B junctions. Based on these considerations, in this paper a density gradient model in copolymer–homopolymer systems is assumed: maintaining a constant total reduced density of the segments in the whole domains solubilized with homopolymer chains, the blocks form a distribution of segment density decreasing from the boundary to the centre of the domains while the segment density of homopolymer decreases from the centre to the interface of the domains. For the case of lamellar-structure block copolymer, the model is shown schematically in *Figure 1*.



**Figure 1** Schematic representation of lamellar domains of block copolymer swollen by homopolymer without details of the interface region. Broken and solid lines denote homo and block chains respectively

In this paper, for simplifying the calculation the gradients of both the bound and free chains are assumed to be constant; that is, the density profile gradients are linear. Although this is only a rough description of the distributions of the segment densities, as will be seen later, the results based on this model are in good agreement with experimental data.

#### THEORY OF MISCIBILITY IN HOMOPOLYMER–BLOCK COPOLYMER SYSTEMS

This initial research dealing with the miscibility theory of copolymer–homopolymer systems will concentrate on the case in which the block copolymer has characteristic lamellar structure. First, the relevant parameters and symbols characterizing the system are as follows:

1. For convenience, in this paper A, B and H are used to denote block A and block B in the copolymer and homopolymer A respectively.

2. The density (the segment number per unit volume) of the polymer of type  $k$  (A or B) when pure is designated as  $\rho_{0k}$ . We will often express the density of  $k$  segments in the blends in reduced units:

$$\tilde{\rho}_k(\bar{y}) = \rho_k(\bar{y}) / \rho_{0k}$$

(note that Helfand uses  $\bar{r}$  instead of  $\bar{y}$ ).

3. The Kuhn statistical length of a segment of  $k$  is  $b_k$ .

4. The degree of polymerization of a homopolymer or block is  $Z_k$ .

5. The total number of block copolymer molecules is  $N$  and that of the dissolved homopolymer A is  $N_H$ .

6. The molecular weight of block A is  $M_A$  while that of homopolymer A is  $M_H$ .

7. The volume ratio of dissolved homopolymer A to block A chains is  $q$ .

8.  $d_A$  and  $d_B$  denote the width of A and B domains respectively while  $d$  denotes the periodicity distance, i.e. the sum of A domain and B domain widths,

$$d = d_A + d_B$$

$d_A$  and  $d_B$  are related by

$$\frac{d_A \rho_{0A}}{Z_A} = \frac{d_B \rho_{0B}}{Z_B} \quad (1)$$

when no homopolymer is dissolved. However, after solubilization, the A domain width will become  $d_A(1+q)$  while B domain width will remain unchanged.

With regard to the theoretical treatment of the miscibility between homopolymer A and block A of the copolymer, the main point is to calculate the free energy change of the system during solubilization. Clearly, before solubilization, the system is made up of two independent subsystems, i.e. the block copolymer AB and homopolymer A. If the free energies of the subsystems are denoted by  $F_{C_0}$  and  $F_{H_0}$  respectively, we have

$$F_0 = F_{C_0} + F_{H_0} \quad (2)$$

where  $F_0$  is the total free energy of the system.

After solubilization, the total free energy becomes

$$F_1 = F_{C_1} + F_{H_1} + F_{\text{mix}} \quad (3)$$

where  $F_{C_1}$  and  $F_{H_1}$  are the free energies of the block copolymer AB and the homopolymer A after solubilization respectively while  $F_{\text{mix}}$  is the free energy of mixing. Therefore, the free energy change of the system due to solubilization is given by

$$\begin{aligned} \Delta F = F_1 - F_0 &= (F_{C_1} - F_{C_0}) + (F_{H_1} - F_{H_0}) + F_{\text{mix}} \\ &= \Delta F_C + \Delta F_H + F_{\text{mix}} \end{aligned} \quad (4)$$

The contributions of each term in equation (4) are now discussed.

#### Free energy change of block copolymer AB, $\Delta F_C$

According to Helfand's theory, based on the narrow-interface approximation, the free energy change of block copolymers of lamellar structure during microphase separation is given by

$$\begin{aligned} \frac{F}{NKT} &= \frac{2\gamma}{K_B T} \left( \frac{Z_A}{\rho_{0A}} + \frac{Z_B}{\rho_{0B}} \right) \frac{1}{d} + \ln \left( \frac{d}{2a_j} \right) \\ &\quad - \alpha \left( \frac{Z_A}{\rho_{0A}} \right) \left( \frac{Z_B}{\rho_{0B}} \right) \left/ \left( \frac{Z_A}{\rho_{0A}} + \frac{Z_B}{\rho_{0B}} \right) \right. - \ln \Omega_A - \ln \Omega_B \end{aligned} \quad (5)$$

Here  $\gamma$  is the interfacial tension,  $\alpha$  is a parameter that measures the degree of repulsion between A and B and relates to AA and BB interactions,  $a_j$  is the interfacial width,  $K_B$  is Boltzmann's constant and  $T$  is absolute temperature. The possible changes of the terms in

equation (5) caused by solubilization of homopolymer A are now examined.

The first term is associated with the contribution of the interfacial energy. In accordance with the density gradient model, the probability that the solubilized homopolymer A chains will reach the interfacial region between A and B domains is almost zero. Hence, it is reasonable to assume that solubilization hardly affects the interfacial term.

The second term is so-called placement entropy, accounting for the entropy loss of the block copolymer due to the restriction of A-B junctions to the interfacial region. This is a function of the ratio of the volume of the interfacial region to that occupied by the block chains. Note that dissolution of homopolymer A will bring about only variation of the density profile of the block A chains but not of the virtually occupied volume of the blocks. In addition, as just mentioned, the interfacial region is not affected by solubilization of homopolymer A. Therefore, there is reason to think that solubilization has no effect on the placement entropy term.

The third term assigns the zero of free energy to a homogeneous phase of block copolymer. It is merely a constant and is unrelated to solubilization of homopolymer.

The fourth and fifth terms represent the contributions of the change of the conformational entropy of blocks A and B respectively. For the block copolymer AB, with A-B junctions lying in the interfacial region,  $\Omega_k$  represents the probability that chains of type  $k$  assume the conformations that keep density homogeneity in domain  $k$ . Clearly, when homopolymer is solubilized in the A domains, the B domains remain unchanged as does  $\Omega_B$ , so that the only term affected by solubilization is the fourth term,  $\ln \Omega_A$ . If the conformational entropy of block A before and after solubilization is denoted by  $K \ln \Omega_A^{(0)}$  and  $K \ln \Omega_A^{(1)}$  respectively, the corresponding change in free energy is given by

$$\frac{\Delta F}{NKT} = -(\ln \Omega_A^{(1)} - \ln \Omega_A^{(0)}) \quad (6)$$

Thus, it is clear that, in the investigation of the miscibility between block copolymer and corresponding homopolymer, one of the key points lies in the calculation of the conformational entropy change of the block A chains.

Since Helfand's theory<sup>11-14</sup> of block copolymers is the basis of the argument in this paper, the main points of the theory are mentioned here very briefly. In polymer conformational statistics, attention has been paid to a function  $Q_k(\vec{r}, t; \vec{r}_0)$ , which is proportional to the probability density that a chain of type  $k$  with number of segments (degree of polymerization)  $t$  has one end at  $\vec{r}$  and the other at  $\vec{r}_0$ . For the random coil model, in a uniform system of type  $k$ ,  $Q_k$  is the familiar Gaussian satisfying the simple diffusion equation. Employing mean field theory, Helfand has shown that for the system of block copolymer AB,  $Q_k$  satisfies a modified diffusion equation

$$\begin{aligned} \frac{\partial Q_k}{\partial t} &= \frac{b_k^2}{6} \nabla^2 Q_k \frac{1}{\rho_{0k}} \left\{ \alpha \left[ \frac{\tilde{\rho}_k(\vec{r})}{\tilde{\rho}_A(\vec{r}) + \tilde{\rho}_B(\vec{r})} \right]^2 \right. \\ &\quad \left. + \frac{1}{\kappa K_B T} [\tilde{\rho}_A(\vec{r}) + \tilde{\rho}_B(\vec{r}) - 1] \right\} Q_k \end{aligned} \quad (7)$$

where  $\kappa$  is the compressibility. In addition, in equation (7), if  $k$  is A then  $k'$  is B and vice versa. The term in braces represents  $(1/K_B T)$  times the chemical potential change of bringing a segment of type  $k$  from pure  $k$  into the region with the densities  $\tilde{\rho}_A(\vec{y})$  and  $\tilde{\rho}_B(\vec{y})$ .

Helfand successfully used this equation to calculate the conformational entropy of block copolymer in resolving the microphase separation problem. Later, he considerably simplified the equation by adopting the so-called narrow-interface approximation (NIA). Under NIA condition, the equations determining the properties of the block copolymers with lamellar domain structure in the A domain and into interface are as follows:

$$R_A^2 \frac{\partial Q}{\partial t} = -\mathcal{L} Q \quad (8)$$

$$\mathcal{L} = -\frac{\partial^2}{\partial y^2} + u(y) \quad (9)$$

$$R_A = 6^{1/2} d_A / 2b_A \quad (10)$$

$$\tilde{\rho}_A(x) = \tilde{\rho}(y) \rho_A^1(x - x_G) \quad (11)$$

$$\tilde{\rho}(y) = \frac{1}{\Omega_A Z_A} \int_0^{Z_A} dt \int_0^1 dy_A Q(y_A, Z_A - t; y) Q(y, t; 1) \quad (12)$$

$$\Omega_A = \int dy_A Q(y_A, Z_A; 1) \quad (13)$$

with boundary conditions

$$\left. \frac{\partial Q}{\partial y} \right|_{y=0} = \left. \frac{\partial Q}{\partial y} \right|_{y=1} = 0 \quad (14)$$

and initial condition

$$Q(y, t=0; y_0) = \delta(y - y_0) \quad (15)$$

where  $Q(y, t; y_0)$  is the probability function and  $y = 2x/d_A$  is the reduced distance. The function  $u(y)$  is to be selected for maintaining uniform density in the domain, i.e.,

$$\tilde{\rho}(y) = 1 \quad (0 \leq y \leq 1) \quad (16)$$

Equations (8)–(16) can also be applied to B domains.

The solution of these equations is quite complex. In achieving the numerical solutions, Helfand adopted a piecewise constant function  $\{u_i(y)\}$  for  $u(y)$ . To solve equations (8) to (16), a function  $u(y)$  is selected as a first approximation.  $Q$ ,  $\tilde{\rho}$  and  $\Omega_A$  can then be written in terms of the spectrum of  $\mathcal{L}$ . The eigenvalues of the  $\mathcal{L}$  operator are determined by the boundary conditions while the coefficients of the eigenfunctions are determined by the initial condition. If  $\tilde{\rho}(y)$  is not everywhere equal to unity then  $u(y)$  is readjusted by a Newtonian iteration technique. In fact,  $\tilde{\rho}(y)$  cannot be equal to unity in the whole range of  $y$ , therefore it is  $\tilde{\rho}_i$  ( $i = 1, 2, \dots$ ), the mean values of  $\tilde{\rho}(y)$  over small intervals, that will be unity by repeated iteration and the final  $k \ln \Omega_A^{(0)}$  will be the desired conformational entropy.

Helfand has fitted his evaluated data to a formula

$$-\ln \Omega_k = 0.085 (R_k / Z_k^{1/2})^{2.5}$$

Furthermore, Helfand obtained the domain size at equilibrium by minimization of the free energy. For the case of  $\chi Z = 37$ , where  $\chi$  is the Flory–Huggins interaction constant, the equilibrium domain width satisfies the relationship  $d/bZ^{1/2} = 3.1$  while for  $\chi Z = 10$  the corresponding equation is  $d/bZ^{1/2} = 2.4$ . For styrene and isoprene of diblock copolymer, according to the results of the SAXS measurements<sup>16</sup>, the conditions of  $d/bZ^{1/2} = 2.4$  and  $d/bZ^{1/2} = 3.1$  approximately correspond to the block copolymers with molecular weights of  $2 \times 10^4$  and  $1 \times 10^5$  respectively.

Now the conformational entropy of block A chains in A domain swollen by homo A is considered. In the density gradient model, a basic requirement is that for a miscible homopolymer A–copolymer system, the total density of the system is maintained constant throughout microdomains, i.e. the reduced density of block A chains plus that of homo A chains must equal unity in A domain in a sense of piecewise average over small intervals. The corresponding density profiles of homo A and block A are shown in Figure 2.

Under the constraint of this type of  $\tilde{\rho}_1(y)$ , the probability function  $Q_A(\vec{y}, t; \vec{y}_0)$ , may still be obtained by solving the diffusion equation (7) with the subsidiary equations (9) to (15). However, owing to the dissolution of the homopolymer, the size of A domain has to extend to  $d_A(1+q)$  and correspondingly, equation (12) should be replaced by

$$\tilde{\rho}(y) = \frac{1}{(1+q)\Omega_A Z_A} \int_0^{Z_A} dt \int_0^1 dy_A Q(y_A, Z_A - t; y) Q(y, t; 1) \quad (17)$$

whereas the reduced distance is redefined as

$$y = \frac{2x}{d_A(1+q)}$$

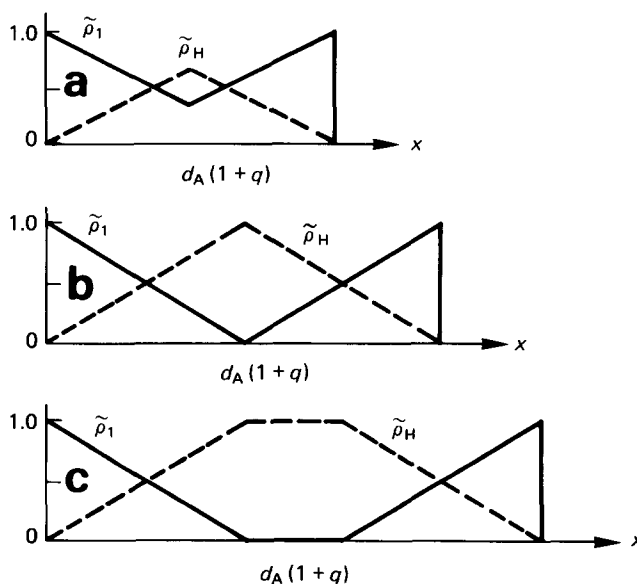


Figure 2 Profiles of the reduced densities of block chains (—), and homopolymer chains (---). (a)  $q = 1/2$ ; (b)  $q = 1$ ; (c)  $q = 3/2$

Using procedures similar to those mentioned above for the pure block copolymer,  $\Omega_A^{(1)}$  was obtained by repeated iteration and the result is shown in Figure 3. The contribution of the conformational entropy change of the A chains of the block copolymer is then easily calculated by equation (6). The relevant mathematical formulas can be found in more detail in the appendix of ref. 6.

*The free energy change of homopolymer  $\Delta F_H$*

The conformational entropy change of a homopolymer during solubilization may be evaluated by employing Helfand's theory of inhomogeneous polymers<sup>17</sup>. The key point still lies in the calculation of  $Q(\vec{y}, t; \vec{y}_0)$ , which satisfies the diffusion equation

$$\frac{\partial Q_k}{\partial t} = \frac{b_k^2}{6} \nabla^2 Q_k - \left[ \frac{u_k(\vec{y})}{K_B T} \right] Q_k \quad (18)$$

Under the mean field approximation,  $u_k(\vec{y})/K_B T$  may be replaced by the chemical potential  $\mu_k(\vec{y})$ . For the case that homopolymer A is solubilized in the A domain of block copolymer AB,  $\mu_A(\vec{y})$  has the form

$$\mu_A(\vec{y}) = \frac{1}{\kappa K_B T} [\tilde{\rho}_A(\vec{y}) + \tilde{\rho}_H(\vec{y}) - 1] \quad (19)$$

Substitution of equation (19) into (18) yields an equation that is very similar to but somewhat simpler than equation (7). Obviously, the same procedure may be used to solve the problem as in the case of block copolymer. Since in homopolymer there are no junctions, the equations determining  $Q_k$  can be simplified as follows

$$R_A^2 \frac{\partial Q}{\partial t} = -\mathcal{L}Q \quad (20)$$

$$\mathcal{L} = -\frac{\partial^2}{\partial y^2} + u(y) \quad (21)$$

$$R_A = 6^{1/2} \frac{d_A(1+q)}{2b_A} \quad (22)$$

$$\tilde{\rho}_H(y) = \frac{q}{(1+q)\Omega_H Z_H} \int_0^{Z_H} dt \int_0^1 dy_1 dy_0 Q(y_1, Z_H - t; y) Q(y, t; y_0) \quad (23)$$

$$\Omega_H = \int_0^1 Q(y_1, Z_H; y_0) dy_1 dy_0 \quad (24)$$

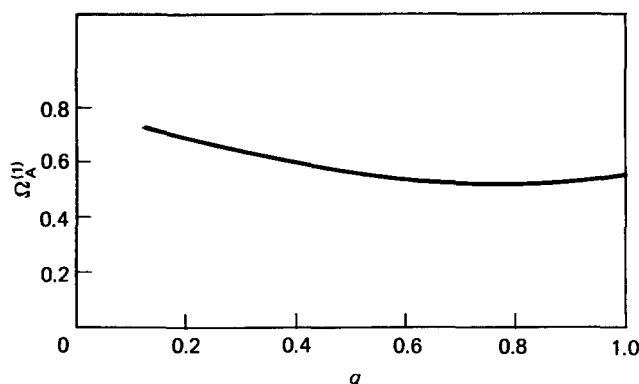


Figure 3 Variation of  $\Omega_A^{(1)}$  of block A chains with  $q$

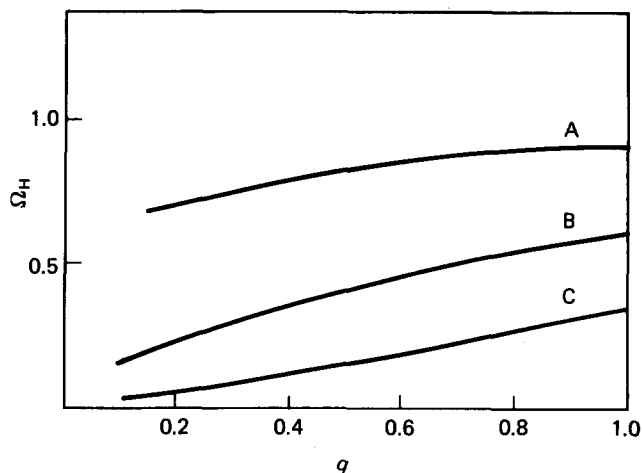


Figure 4 Variations of  $\Omega_H$  of homopolymer A chains with  $q$  for different values of  $M_H/M_A$ : A, 0.33; B, 1.0; C, 2.0

with boundary conditions

$$\left. \frac{\partial Q}{\partial y} \right|_{y=0} = \left. \frac{\partial Q}{\partial y} \right|_{y=1} = 0 \quad (25)$$

and initial condition

$$Q(y, t=0; y_0) = \delta(y - y_0) \quad (26)$$

where the reduced distance  $y$  is still defined as  $y = 2x/d_A(1+q)$ .

In a way similar to that for the case of block copolymer, by repeated iteration, a group of  $\{u_i(y)\}$  fulfilling the requirement of keeping the total density constant was found and thus the corresponding  $\Omega_H$  can be calculated. Since for the case of pure homo A,  $\tilde{\rho}_H$  is equal to unity everywhere so that  $\Omega_H^{(0)} = 1$ ,  $\ln \Omega_H^{(0)} = 0$ , the calculated  $K \ln \Omega_H$  is just the conformational entropy change of homopolymer A.

In Figure 4  $\Omega_H$  is plotted as a function of  $q$  for three different values of  $M_H/M_A$  (0.33, 1.0 and 2.0). The curves clearly reveal the dependence of  $\Omega_H$  on the relative molecular weight. It is quite understandable since the homopolymer molecule of larger molecular weight might suffer larger conformation restriction during solubilization in domains in which the copolymer blocks assume unfavourable conformations. It is of interest to note that  $\Omega_H$  always increases with  $q$ . Considering that the environment of the domain for dissolving homopolymer chains might become less unfavourable when more homopolymer chains are solubilized, the decrease of entropy loss for pure homo A molecule with  $q$  becomes understandable. However, the contribution of the conformational entropy of homo A to the free energy change is

$$\frac{\Delta F}{NKT} = q \frac{M_A}{M_H} \ln \Omega_H \quad (27)$$

showing that  $\Delta F_H$  is dependent on both  $q$  and  $\Omega_H$  and is no longer a monotonic function of  $q$ .

*Entropy of mixing*

Since the homo A and block A chains can be regarded as being chemically identical, no enthalpy change occurs

in the mixing process. Therefore, the only term that must be considered for  $\Delta F_{\text{mix}}$  is the entropy of mixing or the combinatorial entropy.

Considering the density inhomogeneity of both homo and block A chains in the swollen domain, the domain is divided into several small regions and the average densities of the bound and free A chains are evaluated in each region. Using Flory-Huggins theory<sup>18</sup> it is possible to calculate the entropy of mixing for each small region and then obtain the total entropy of mixing by summing the values of all the regions. The final expression is

$$\frac{\Delta S_{\text{mix}}}{K} = - \sum_i \left[ N_H \left( \frac{1+q}{q} \right) h_i (1-\tilde{\rho}_i) \ln(1-\tilde{\rho}_i) + N(1+q) h_i \tilde{\rho}_i \ln \tilde{\rho}_i \right] \quad (28)$$

where  $(1-\tilde{\rho}_i)$  and  $\tilde{\rho}_i$  are the volume fractions of homo A and block A segments in  $i$ -th region respectively. The factors ahead of  $\ln(1-\tilde{\rho}_i)$  and  $\ln \tilde{\rho}_i$  are the number of molecules of homo and block A in the  $i$ -th region and  $h_i$  is the width of the region. Using the relation between  $N_H$  and  $N$ , equation (28) can be simplified to

$$\frac{\Delta S_{\text{mix}}}{NK} = -(1+q) \sum_i h_i \left[ \frac{M_A}{M_H} (1-\tilde{\rho}_i) \ln(1-\tilde{\rho}_i) + \tilde{\rho}_i \ln \tilde{\rho}_i \right] \quad (29)$$

The corresponding change of the free energy is then

$$\frac{F_{\text{mix}}}{NKT} = - \frac{\Delta S_{\text{mix}}}{NK} = (1+q) \sum_i h_i \left[ \frac{M_A}{M_H} (1-\tilde{\rho}_i) \ln(1-\tilde{\rho}_i) + \tilde{\rho}_i \ln \tilde{\rho}_i \right] \quad (30)$$

The calculated results based on equation (29) are shown in Figure 5 for three different values of  $M_H/M_A$ . The curves show saturation as  $q$  approaches unity.

## DISCUSSION

The calculated results for the case  $d/bZ^{1/2} = 2.4$  are

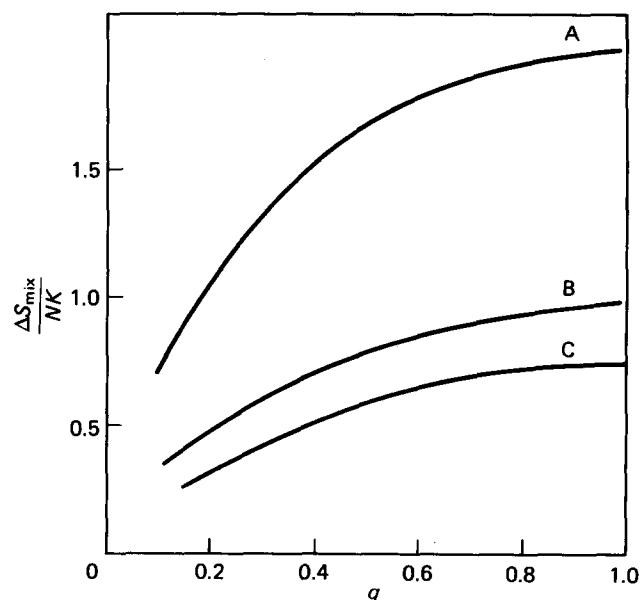


Figure 5 Variations of the changes of the entropies of mixing with  $q$  for different values of  $M_H/M_A$ : A, 0.33; B, 1.0; C, 2.0

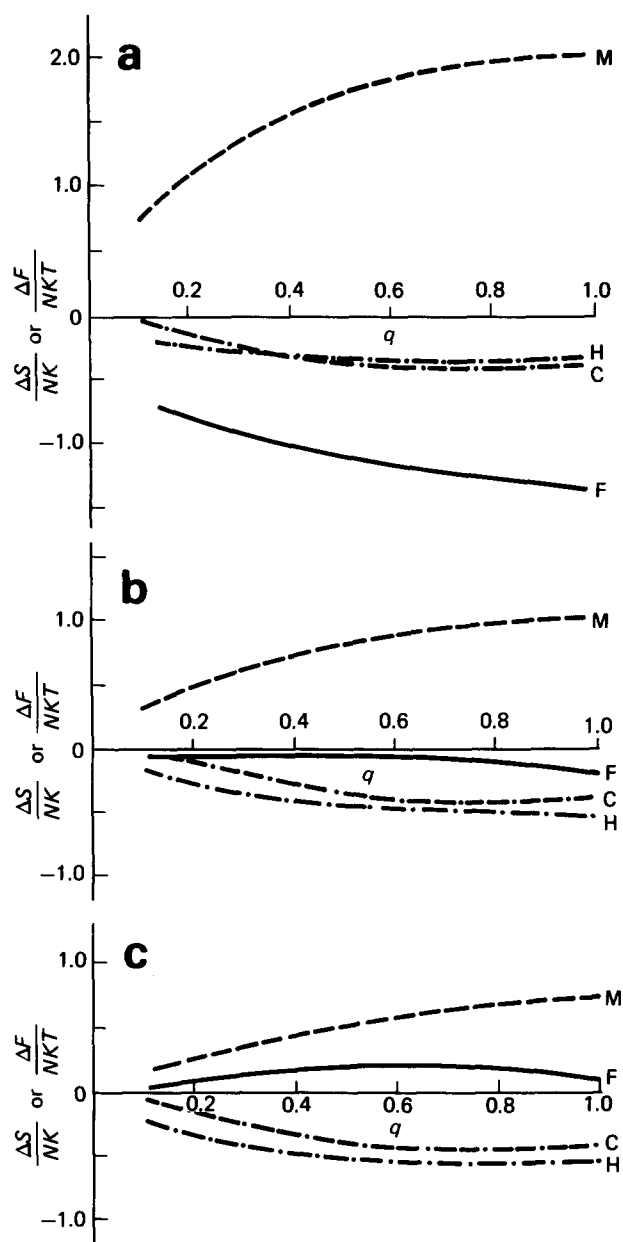


Figure 6 Plots of the entropy change of homo chains ( $\Delta S_H/NK$ , curve H), the entropy change of block chains ( $\Delta S_C/NK$ , curve C), the entropy change of mixing ( $\Delta S_{\text{mix}}/NK$ , curve M) and the free energy change ( $\Delta F/NKT$ , curve F) as functions of  $q$  for various values of  $M_H/M_A$ : (a), 0.33; (b), 1.0; (c) 2.0

summarized in Figure 6, which presents three typical cases, in which the molecular weight of the homopolymer is far less than ( $M_H/M_A = 0.33$ ), is equal to ( $M_H/M_A = 1$ ) and is considerably larger than ( $M_H/M_A = 2.0$ ) that of the corresponding blocks of the copolymer.

An inspection of the cases leads to the conclusion that the solubilization behaviour of a homopolymer in domains of corresponding blocks of copolymer predicted by the extended Helfand theory for the density gradient model has the following characteristics:

1. The miscibility strongly depends on the molecular weight ratio of the homopolymer to the corresponding blocks.
2. Homopolymer can be substantially solubilized in the corresponding domains if  $M_H$  is equal to or less than  $M_A$ .

Figure 6(a) represents the case of homopolymer of low relative molecular weight. It is clear that the solubilization of homopolymer in the domains results in some entropy loss for both homo A and block A chains. However, since the molecular weight ratio is low, the entropy of mixing is relatively large and increases monotonically with  $q$ ; in the whole range  $0 < q \leq 1$  the favourable entropy of mixing will exceed the entropy loss and then the free energy change in the whole range will be negative, i.e. no macrophase separation between the homopolymer and copolymer can be found for the blends with this molecular weight ratio.

The results for the more interesting case,  $M_H = M_A$ , is shown in Figure 6(b). By comparison with the case  $M_H/M_A = 0.33$ , the mixing entropy is less while the entropy losses are larger. This variation results in negative but very small free energy in the range  $0 < q \leq 1$ , which means that blends of homopolymer and copolymer with the molecular weight ratio  $M_H/M_A = 1$  should be miscible in the range  $0 < q \leq 1$  at equilibrium but that the driving force for the solubilization is limited. In fact, several examples can be found in the literature that indicate miscibility of homo A and block A at high  $q$  values. For example, Figure 1 in ref. 9, which represents a blend of SB diblock and PS of molecular weight ratio  $M_H/M_A = 0.95$ , shows homogeneous morphology on the macroscopic scale. According to the relevant data presented in ref. 9, the calculated  $q$  value for the blend reaches  $\sim 3$ . Similarly, in ref. 7, a series of blends of diblock copolymer SI and various amounts of PS with  $M_H/M_A = 0.78$  exhibit a homogeneous morphology that includes the case where the  $q$  value is as large as 5.2. Besides, Selb *et al.*<sup>19</sup> reported that 6.5–10 wt% copolymer can be homogeneously dispersed in a matrix of large proportion (90–93.5%) of low-molecular-weight polybutadiene. This experimental phenomenon of a block copolymer being able to solubilize a large quantity of the homopolymer is understandable in the light of the present model. For a system with negative free energy change at  $q=1$ , which means the system exhibits homogeneous morphology according to the present model, the reduced density of homo A at the centre of the swollen domain A by the homo A should reach 1, which means that in this part of the domain almost no block chains exist and that the homopolymer chains will assume the conformations of the homo chains in pure state. Thus, it is reasonable to assume that if more homo A is added to the system, this kind of swollen A domain will be randomly diluted by homo A since this process will not cause any more conformational entropy loss but will increase the total entropy of the system. In fact this argument anticipates that if a blend of a homopolymer and the relevant copolymer has negative free energy change in the whole range of  $0 < q \leq 1$ , it is likely that the blend will show homogeneous morphology on the macroscopic scale for any composition of the component polymers.

Since the free energy change is very close to zero for  $M_H/M_A = 1$ , it is expected that the free energy change will become positive and macrophase separation between the homopolymer and copolymer will occur as  $M_H/M_A$  increases further. The results shown in Figure 6(c) clearly demonstrate that the free energy change for  $M_H/M_A = 2.0$  turns out to be positive as a result of the decrease of the

mixing entropy and increase of the conformational entropy loss of homo chains as  $M_H/M_A$  increases. Inoue *et al.*<sup>7</sup> came to the important conclusion based on systematic electron microscopy studies of polymer blends of diblock copolymer and homopolymers that homopolymer can be solubilized in the domains of corresponding blocks if the molecular weight of the former is less than that of the latter; otherwise they are immiscible. Later, much experimental data were published<sup>8–10</sup> that supports this conclusion. In this paper, the extended Helfand theory based on the density gradient model clearly explains the nature of the miscibility of homopolymer and copolymer with lamellar structure and is generally in agreement with the experimental results.

The calculated results just discussed are for the case of  $d/bZ^{1/2} = 2.4$ . Calculations were also carried out for another typical case of  $d/bZ^{1/2} = 3.1$ , indicative of much higher molecular weight. The results show the same characteristic features as that for  $d/bZ^{1/2} = 2.4$ . However, since the entropy losses of both homo and block chains increase with  $M_H$  and  $M_A$ , for the same molecular weight ratio, the driving force for mixing of the system with higher value of  $d/bZ^{1/2}$ , i.e. higher molecular weight, will be less than that of the low  $d/bZ^{1/2}$  system.

Finally, it is emphasized that the theoretical results in this paper were obtained only for diblock copolymer of lamellar structure. The preliminary success suggests using the extended Helfand theory and the density gradient model to handle the miscibility of homopolymer and copolymers with different microphase structures or complicated architectures, provided the architectural difference is fully taken into account.

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