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Miscibility in Ternary Mixtures Containing a Copolymer and Two Homopolymers. Effect of Sequence Distribution

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ABSTRACT: We examine the effect of sequence distribution in copolymers on the miscibility of the ternary A/B/AB system. Using the formalism developed in an earlier model, we derive a new equation for the free energy of mixing that includes terms that depend on the sequence distribution in the AB copolymer. Through this equation, we calculate new phase diagrams for the A/B/AB mixture. The diagrams clearly show that miscibility in these systems is strongly dependent on the copolymer sequence distribution. It is also evident that block copolymers do not always act as the best bulk thermodynamic compatibilizers for creating a completely miscible A/B/AB blend. Finally, we obtain phase diagrams that could not be generated using the simpler Flory–Huggins model.

Introduction

It is generally agreed that miscibility in polymer blends arises from a negative heat of mixing, since the entropic term in these systems is negligibly small.[1-5] Consequently, examinations of and corrections to the enthalpy term are essential in understanding the phase behavior of polymer mixtures. With this rationale in mind, we modified the enthalpic term in the Flory–Huggins expression for ΔG, the free energy of mixing, to include the sequence distribution of monomer units in a copolymer.[6] Using this expression, we previously examined the effect of the sequence distribution of monomer units in a copolymer on the miscibility of various copolymer-containing blends.[6-8] Specifically, we investigated the phase behavior of binary mixtures composed of either a copolymer and a homopolymer or two copolymers.[7,8] In these calculations, we introduced an order parameter, θ, which describes the sequence distribution of the monomers in the copolymer. Further, we assumed that the interaction energy between a pair of monomers is influenced by the nearest neighbors chemically bound to these monomers. For example, the interaction energy between a monomer of homopolymer C and monomer A (or B) in copolymer AB is mediated by the nearest neighbors bonded to A (or B). Through these calculations, we showed that, for a copolymer of fixed composition, there is an optimal range of sequence distributions for which the C/AB system may be miscible.[6] In addition, we could predict an experimentally observed incompatibility between two AB copolymers having the same composition but differing only in sequence distribution.[7] Furthermore, we showed how this theory can be applied to experimental data to extract values for the relevant χ parameters. Most recently, the values of these sequence distribution dependent χ parameters have been used to successfully explain the experimentally observed phase behavior of a second system.[9]

In this article, we begin an investigation of the role of sequence distribution on the miscibility of ternary mixtures containing a copolymer and two homopolymers: the A/B/AB system. We focus our attention on the situation where the AB copolymer can act as a compatibilizer in the thermodynamic sense of the word:[10] the presence of this component can mediate unfavorable enthalpic interactions between the two homopolymers and thus produce a *single homogeneous phase*.

All previous calculations of equilibrium phase diagrams for such ternary systems were forced to assume that the AB copolymer was a random copolymer.[11,12] This is clearly insufficient, since copolymer sequence distribution effects have been experimentally shown to play an important role in polymer phase behavior.[7,9,13] The strength of our model is that we can examine the phase behavior as the copolymer sequence distribution deviates from this random value.

In the special case of block copolymers, microphase separation may occur before macroscopic phase separation. Our theory does not address the behavior of block copolymers in microphase-separated systems or examine their role in reducing the interfacial tension at the boundary of mixtures that remain macroscopically demixed. This represents a limitation of the model in the $\theta = 0$ or block copolymer limit.

The objective of the following discussion is to show how deviations from the random sequence distribution will affect the equilibrium phase diagrams for this ternary system. Thus, for a given set of interaction parameters, polymer volume fractions, and copolymer compositions, the equations can be used to determine which copolymer sequence distribution will yield the most effective bulk compatibilizing agent. Furthermore, we examine whether our correction terms to the Flory–Huggins expression will result in new phase diagrams. As shall be seen, by including the effects of sequence distribution, we can generate figures that could not be obtained via the earlier model. Such is the case even for copolymers near $\theta = {}^1/_2$ or the random sequence distribution.

The Model

The general expression for the free energy of mixing for a ternary mixture of two homopolymers, A and B, and copolymer AB is given by

$$\Delta G/RT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + (\phi_3/N_3)\ln\phi_3 + \chi_{AB}(\phi_1\phi_2 + f^2\phi_2\phi_3 + (1-f)^2\phi_1\phi_3) \quad (1)$$

where f and $1 - f$ denote the composition of copolymer $(A_fB_{1-f})_n$ with volume fraction ϕ_3 and degree of polymerization N_3 and homopolymers A and B have volume fractions ϕ_1 and ϕ_2, respectively, and degrees of polymerization N_1 and N_2, respectively. The volume fractions are related as follows:

$$\phi_1 + \phi_2 + \phi_3 = 1 \quad (2)$$

The interaction parameter χ_{AB} characterizes the strength of the polymer–polymer interaction.

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In a previous calculation,[6] we have derived the correction terms to the interaction energy that depend on the sequence distribution in the copolymer for the AB/A and AB/B systems. In order to consider all the possible homopolymer–copolymer interactions, as well as the copolymer self-interactions, all the possible triplets with A or B occupying the central site are enumerated. Then, the probability of occurrence for each specific triplet is calculated. Of the 16 possible A–B interactions, a unique energy is assigned only to the triplet pairs (AAA–BBB) and (ABA–BAB): $\chi_{\mathrm{AAA;BBB}}$ for the former and $\chi_{\mathrm{BAB;ABA}}$ for the latter. The remaining 14 pairs of A–B interacting triplets are assigned the average value $\bar{\chi}_{\mathrm{AB}}$. (All A–A and B–B interactions are assumed to be equal to zero.) These energies are multiplied by their probability of occurrence, and then all the terms are summed to obtain a new expression for the total energy of interaction. For the AB/A case, this energy is $\phi_1\phi_3\chi_{\mathrm{blend}}$, where

$$\chi_{\mathrm{blend}} = \chi_{\mathrm{comp}} + \chi_{\mathrm{dist}} \tag{3}$$

$$\chi_{\mathrm{comp}} = \bar{\chi}_{\mathrm{AB}} f_{\mathrm{B}}^2 \tag{4}$$

$$\chi_{\mathrm{dist}} = \Delta\chi^{\mathrm{b}}(f_{\mathrm{BB}}^2/f_{\mathrm{B}})\left(1 - \frac{f_{\mathrm{AA}}^2}{f_{\mathrm{A}}}\right) + \Delta\chi^{\mathrm{a}}\frac{f_{\mathrm{AB}}^4}{f_{\mathrm{A}}f_{\mathrm{B}}} \tag{5}$$

with $\Delta\chi^{\mathrm{b}} = \chi_{\mathrm{AAA;BBB}} - \bar{\chi}_{\mathrm{AB}}$ and $\Delta\chi^{\mathrm{a}} = \bar{\chi}_{\mathrm{AB}} - \chi_{\mathrm{BAB;ABA}}$. Equation 4 represents the composition dependence of χ_{blend}, while eq 5 is the correction term that depends on the sequence distribution in the AB copolymer. Here, f_{A} and f_{B} are the fraction of A and B molecules, respectively, in a single copolymer chain. The variables f_{AB}, f_{BB}, and f_{AA} are the pair probabilities of AB, BB, and AA pairs in a single chain. These parameters are related in the following way:

$$\begin{gathered} f_{\mathrm{A}} = f_{\mathrm{AA}} + f_{\mathrm{AB}} \\ f_{\mathrm{B}} = f_{\mathrm{BB}} + f_{\mathrm{BA}} \\ f_{\mathrm{AB}} = f_{\mathrm{BA}} \\ f_{\mathrm{A}} + f_{\mathrm{B}} = 1 \end{gathered} \tag{6}$$

In eq 5, the a and b superscripts on $\Delta\chi$ refer to alternating and block sequences, respectively. A negative $\Delta\chi^{\mathrm{b}}$ implies that AAA–BBB interactions are energetically more favorable than the other A–B interactions represented by $\bar{\chi}_{\mathrm{AB}}$ and, conversely, a positive $\Delta\chi^{\mathrm{b}}$ implies that AAA–BBB interactions are less favorable than the $\bar{\chi}_{\mathrm{AB}}$ type interactions. Similar comments apply to $\Delta\chi^{\mathrm{a}}$.

The total interaction energy for the AB/B case is $\phi_2\phi_3\chi_{\mathrm{blend}}$, where eq 3 again defines χ_{blend}, but now

$$\chi_{\mathrm{comp}} = \bar{\chi}_{\mathrm{AB}} f_{\mathrm{A}}^2 \tag{7}$$

$$\chi_{\mathrm{dist}} = \Delta\chi^{\mathrm{b}}(f_{\mathrm{AA}}^2/f_{\mathrm{A}})\left(1 - \frac{f_{\mathrm{BB}}}{f_{\mathrm{B}}}\right) + \Delta\chi^{\mathrm{a}}\frac{f_{\mathrm{AB}}^4}{f_{\mathrm{A}}f_{\mathrm{B}}} \tag{8}$$

By adding eq 4, 5, 7, and 8 to $\phi_1\phi_2\chi_{\mathrm{AB}}$, we can obtain a new expression for the interaction energy for the A/B/AB system:

$$\phi_1\phi_2\chi_{\mathrm{AB}} + \phi_3\bar{\chi}_{\mathrm{AB}}(\phi_1 f_{\mathrm{B}}^2 + \phi_2 f_{\mathrm{A}}^2) \tag{9}$$

$$+ \phi_1\phi_3\left\{\Delta\chi^{\mathrm{b}}\left(\frac{f_{\mathrm{BB}}^2}{f_{\mathrm{B}}}\right)\left[1 - \frac{f_{\mathrm{AA}}^2}{f_{\mathrm{A}}}\right] + \Delta\chi^{\mathrm{a}}\frac{f_{\mathrm{AB}}^4}{f_{\mathrm{A}}f_{\mathrm{B}}}\right\} + \phi_2\phi_3\left\{\Delta\chi^{\mathrm{b}}\left(\frac{f_{\mathrm{AA}}^2}{f_{\mathrm{A}}}\right)\left[1 - \frac{f_{\mathrm{BB}}^2}{f_{\mathrm{B}}}\right] + \Delta\chi^{\mathrm{a}}\frac{f_{\mathrm{AB}}^4}{f_{\mathrm{A}}f_{\mathrm{B}}}\right\} \tag{10}$$

Equation 9 now contains the terms that depend only on composition, while both terms in eq 10 depend on the sequence distribution in the copolymer. Note that if $\Delta\chi^{\mathrm{b}} = \Delta\chi^{\mathrm{a}} = 0$, eq 9 + 10 reduce to the enthalpic contribution to $\Delta G/RT$ in eq 1.

We now introduce the order parameter θ, which we define through the following equation:[6]

$$f_{\mathrm{AB}} = 2\theta f_{\mathrm{A}} f_{\mathrm{B}} \tag{11}$$

For convenience we also introduce the parameter δ, so that:

$$\begin{gathered} f_{\mathrm{A}} = \tfrac{1}{2}(1 + \delta) \\ f_{\mathrm{B}} = \tfrac{1}{2}(1 - \delta) \\ -1 \le \delta \le 1 \end{gathered} \tag{12}$$

A block copolymer corresponds to $\theta = 0$, a random copolymer is described by $\theta = {}^1/_2$ and $\theta = 1$ describes a purely alternating copolymer. This order parameter reaches a maximum value at:[6]

$$\theta_{\max} = (1 + |\delta|)^{-1} \tag{13}$$

It is easy to show that the average run (or block) lengths $\langle n_{\mathrm{A}}\rangle$ and $\langle n_{\mathrm{B}}\rangle$ of A and B units are given by:

$$\begin{gathered} \langle n_{\mathrm{A}}\rangle = f_{\mathrm{A}}/f_{\mathrm{AB}} = 1/[\theta(1 - \delta)] \\ \langle n_{\mathrm{B}}\rangle = 1/[\theta(1 + \delta)] \end{gathered} \tag{14}$$

Using eq 6, 11, and 12, we can rewrite eq 10, the expression dependent on sequence distribution, in terms of θ and δ:

$$\phi_1\phi_3\Delta\chi^{\mathrm{b}}(\tfrac{1}{2})(1 - \delta)[1 - \theta(1 + \delta)]^2\{1 - \tfrac{1}{2}(1 + \delta)[1 - \theta(1 - \delta)]^2\} + \Delta\chi^{\mathrm{a}}\frac{\theta^4}{4}(1 + \delta)^3(1 - \delta)^3 + \phi_2\phi_3\Delta\chi^{\mathrm{b}}(\tfrac{1}{2})(1 + \delta)[1 - \theta(1 - \delta)]^2\{1 - \tfrac{1}{2}(1 - \delta)[1 - \theta(1 + \delta)]^2\} + \Delta\chi^{\mathrm{a}}\frac{\theta^4}{4}(1 + \delta)^3(1 - \delta)^3 \tag{15}$$

For the sake of simplicity, we will study the case where $f_{\mathrm{A}} = f_{\mathrm{B}} = 0.5$ and thus $\delta = 0$. For this example, the total interaction energy, simplifies to:

$$\phi_1\phi_2\chi_{\mathrm{AB}} + \phi_3(1 - \phi_3)\chi_{\mathrm{blend}} \tag{16}$$

where

$$\chi_{\mathrm{blend}} = \chi_{\mathrm{comp}} + \chi_{\mathrm{dist}} \tag{17}$$

$$\chi_{\mathrm{comp}} = 0.25\bar{\chi}_{\mathrm{AB}} \tag{18}$$

$$\chi_{\mathrm{dist}} = \left[\Delta\chi^{\mathrm{b}}(\tfrac{1}{2})(1 - \theta)^2\{1 - \tfrac{1}{2}(1 - \theta)^2\} + \Delta\chi^{\mathrm{a}}\frac{\theta^4}{4}\right] \tag{19}$$

The first term in eq 16 refers to the homopolymer–homopolymer interaction energy, while the χ_{blend} term describes the energetics of the homopolymer–copolymer and copolymer–copolymer interactions.

From eq 19, it can be seen that if $\Delta\chi^{\mathrm{a}}$ and $\Delta\chi^{\mathrm{b}}$ are both positive, χ_{dist} is positive; if $\Delta\chi^{\mathrm{a}}$ and $\Delta\chi^{\mathrm{b}}$ are both negative, χ_{dist} is also negative. The extrema of this function can be determined by setting $\partial\chi_{\mathrm{dist}}/\partial\theta$ equal to zero. This yields:

$$\partial\chi_{\mathrm{dist}}/\partial\theta = \Delta\chi^{\mathrm{b}}\theta(1 - \theta)(\theta - 2) + \Delta\chi^{\mathrm{a}}\theta^3 = 0 \tag{20}$$

Note that, for the case $f_{\mathrm{A}} = f_{\mathrm{B}} = 0.5$, $\theta = 0$ (corresponding to the block copolymer) is always an extremum for this function. The other extrema are given by:

$$\theta_{\mathrm{c}} = \frac{-3 \pm (1 + 8R)^{1/2}}{2(R - 1)} \tag{21}$$

$$R = \frac{\Delta\chi^{\mathrm{a}}}{\Delta\chi^{\mathrm{b}}} \tag{22}$$

If $R \ge 0$, an extemum always appears in χ_{dist} in the interval [0,1]. This corresponds to the $\theta_{\mathrm{c}} = [-3 + (1 + 8R)^{1/2}]/[2(R$

$- 1)]$ solution. Evaluating the sign of $\partial^2\chi_{\text{dist}}/\partial\theta^2$ at $\theta_c = 0$ will also yield information about this second extremum:

$$\left.\partial^2\chi_{\text{dist}}/\partial\theta^2\right|_{\theta_c = 0} = -2\Delta\chi^{\text{b}} \tag{23}$$

Thus, if $\Delta\chi^{\text{b}}$ is positive, $\theta_c = 0$ is a local maximum and the other θ_c is a local minimum. If $\Delta\chi^{\text{b}}$ is negative, $\theta_c = 0$ corresponds to a local minimum and the second θ_c is a local maximum.

Two special cases are noteworthy. If $R = 0$, then eq 21 yields $\theta_c = 1$. Thus, one extremum corresponds to the block copolymer, while the other extremum is the alternating copolymer. When $R = 1$ ($\Delta\chi^{\text{a}} = \Delta\chi^{\text{b}}$), eq 20 must be used to calculate the second θ_c, which then equals $^2/_3$.

If $-^1/_8 < R < 0$, there is no extremum in [0,1] and χ_{dist} is a monotonic function of θ in this interval. Thus, if $\Delta\chi^{\text{b}}$ is positive, the curve decreases from a maximum at $\theta_c = 0$, whereas if $\Delta\chi^{\text{b}}$ is negative, the curve increases from a minimum at $\theta_c = 0$.

Phase Stability

In addressing the question of phase stability, we are only interested in examining the macroscopic phase behavior and do not consider the issue of microphase separation (as can be observed with block copolymers). By adding eq 1, the entropic contribution, to eq 16–19, we have a new free energy of mixing that includes the effects of sequence distribution for the case where

$$f_{\text{A}} = f_{\text{B}} = 0.5$$

$$\Delta G/RT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + (\phi_3/N_3)\ln\phi_3 + \phi_1\phi_2\chi_{\text{AB}} + \phi_3(1 - \phi_3)\chi_{\text{blend}} \tag{24}$$

For a ternary mixture at fixed temperature and pressure, a homogeneous phase is thermodynamically stable or metastable only if the following conditions are satisfied:[14]

$$\begin{bmatrix} G_{ii} & G_{ij} \\ G_{ji} & G_{jj} \end{bmatrix} > 0 \tag{25}$$

where

$$G_{ij} = \frac{\partial^2\Delta G/RT}{\partial\phi_i\partial\phi_j} \tag{26}$$

and

$$G_{ii} > 0 \qquad \text{for all } i \tag{27}$$

By substituting eq 24 into eq 25 and 27, we can find the bounds on the values the χ parameters must have in order for the A/B/AB mixture to form a stable, miscible phase. For the general case, we obtain the following three conditions

$$\chi_{\text{blend}} < \tfrac{1}{4}(Q_1 + Q_2 + 2Q_3) \tag{28}$$

$$\chi_{\text{AB}} < \tfrac{1}{2}(Q_1 + Q_2) \tag{29}$$

$$\chi_{\text{AB}}^2 + 2\chi_{\text{AB}}(Q_3 - 2\chi_{\text{blend}}) + 2\chi_{\text{blend}}(Q_1 + Q_2) - Q < 0 \tag{30}$$

where $Q_i = 1/(\phi_iN_i)$ and $Q = Q_1Q_2 + Q_2Q_3 + Q_1Q_3$. χ_{blend} is given by eq 17–19. Equation 30 can be rewritten as:

$$(2\chi_{\text{blend}} - Q_3) - [(Q_3 - 2\chi_{\text{blend}})^2 - 2\chi_{\text{blend}}(Q_1 + Q_2) + Q]^{1/2} < \chi_{\text{AB}} < (2\chi_{\text{blend}} - Q_3) + [(Q_3 - 2\chi_{\text{blend}})^2 - 2\chi_{\text{blend}}(Q_1 + Q_2) + Q]^{1/2} \tag{31}$$

This can be simplified to:

$$(2\chi_{\text{blend}} - Q_3) - [(Q_1 + Q_3 - 2\chi_{\text{blend}}) \times (Q_2 + Q_3 - 2\chi_{\text{blend}})]^{1/2} < \chi_{\text{AB}} < (2\chi_{\text{blend}} - Q_3) + [(Q_1 + Q_3 - 2\chi_{\text{blend}})(Q_2 + Q_3 - 2\chi_{\text{blend}})]^{1/2} \tag{32}$$

In the case where $N_1 = N_2 = N_3 = N$, the three conditions simplify to:

$$N\chi_{\text{blend}} < \tfrac{1}{4}\left(\frac{1}{\phi_1} + \frac{1}{\phi_2} + \frac{2}{\phi_3}\right) \tag{33}$$

$$N\chi_{\text{AB}} < \tfrac{1}{2}\left(\frac{1}{\phi_1} + \frac{1}{\phi_2}\right) \tag{34}$$

$$\left(2N\chi_{\text{blend}} - \frac{1}{\phi_3}\right) - \left[\left(\frac{1}{\phi_1} + \frac{1}{\phi_3} - 2N\chi_{\text{blend}}\right) \times \left(\frac{1}{\phi_2} + \frac{1}{\phi_3} - 2N\chi_{\text{blend}}\right)\right]^{1/2} < N\chi_{\text{AB}} < \left(2N\chi_{\text{blend}} - \frac{1}{\phi_3}\right) + \left[\left(\frac{1}{\phi_1} + \frac{1}{\phi_3} - 2N\chi_{\text{blend}}\right)\left(\frac{1}{\phi_2} + \frac{1}{\phi_3} - 2N\chi_{\text{blend}}\right)\right]^{1/2} \tag{35}$$

In order to form a miscible blend, *all* the specified conditions must be satisfied.

Finally, in the case where $N_1 = N_2 = N_3 = N$ *and* $\phi_1 = \phi_2 \neq \phi_3$, the conditions reduce to one requirement:

$$4N\chi_{\text{blend}} - \frac{2}{\phi_3(1 - \phi_3)} < N\chi_{\text{AB}} < \frac{2}{1 - \phi_3} \tag{36}$$

Note that this condition also implies:

$$N\chi_{\text{blend}} < \frac{\phi_3 + 1}{2\phi_3(1 - \phi_3)} \tag{37}$$

In the simplest case where $N_1 = N_2 = N_3 = N$ and $\phi_1 = \phi_2 = \phi_3 = {}^1/_3$, the above equations yield the requirement that

$$(4N\chi_{\text{blend}} - 9) < N\chi_{\text{AB}} < 3 \tag{38}$$

and this equation implies that

$$4N\chi_{\text{blend}} - 9 < 3 \qquad N\chi_{\text{blend}} < 3 \tag{39}$$

Phase Diagrams

Equations 28–37 also indicate how the phase behavior depends on the volume fraction variables ϕ_1, ϕ_2, and ϕ_3. To clarify this relationship, we have calculated ternary phase diagrams. Here, all the χ's, N's, and θ are held constant. At each point in the composition grid of a ternary diagram, we determine if any of the conditions expressed in eq 28–30 are violated. If a condition is violated, the blend is immiscible for this combination of ϕ_i's and a minus sign is drawn at that point. If all the conditions are satisfied, the blend is miscible at this point in composition and no symbol is printed. Thus, inside the dashed region, the polymers phase separate, while outside the region, the single homogeneous phase is stable or metastable.

Results and Discussion

Figures 1–4 show plots of χ_{blend} versus θ for various values of the specified χ parameters, volume fractions, and degrees of polymerization. (The parameter χ_{comp} is a constant that when added to χ_{dist} to yield χ_{blend}, will just shift the figure either up or down with respect to the $\chi_{\text{blend}} = 0$ axis.) As noted above, χ_{blend} describes the strength of the copolymer–homopolymer and copolymer–copolymer interactions. Of particular interest are the cases where χ_{AB} is positive: the homopolymer–homopolymer interactions are repulsive, and these two polymers are immiscible. It is in these cases that the role of the copolymer as a com-

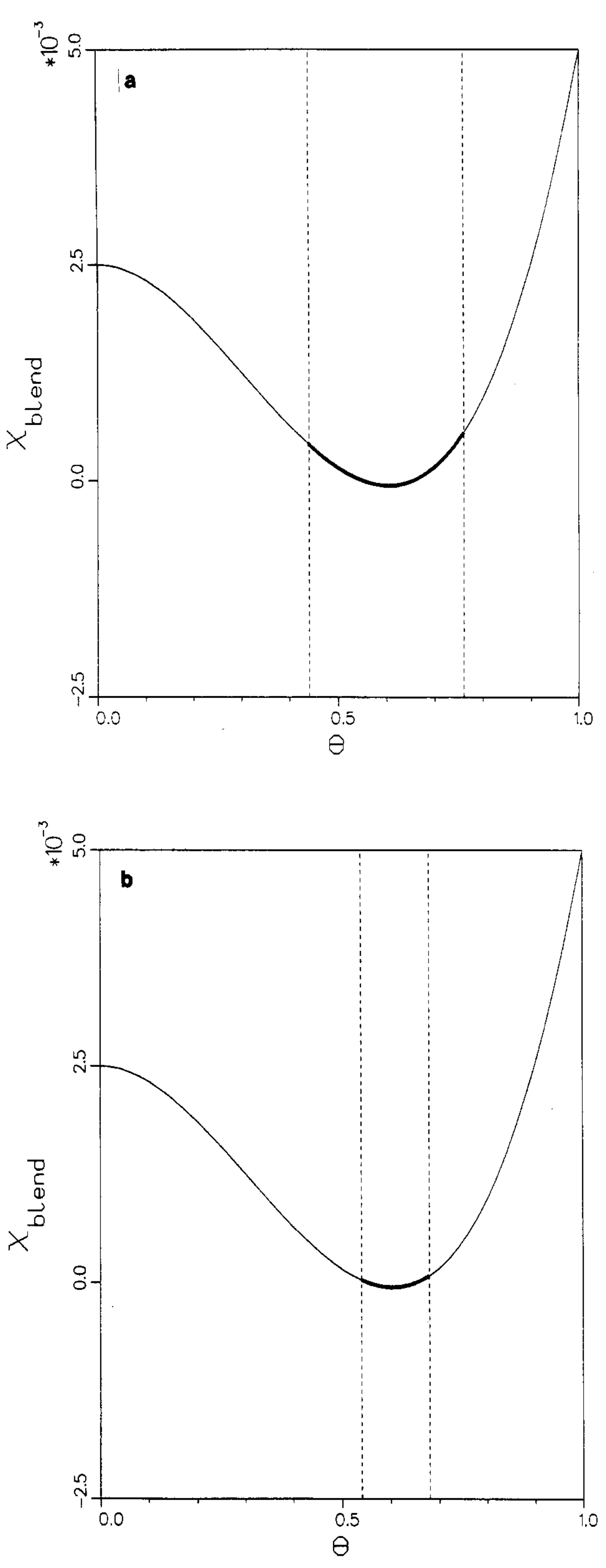


Figure 1. χ_{blend} vs θ. In all the figures, the sections of a curve drawn in the thick line indicate where the polymers are miscible and form a single, homogeneous phase. The dashed vertical lines separate the miscible region from the immiscible region (drawn in a thin line). In this case, $R > 0$. The following values were picked for the relevant parameters: $\Delta\chi^a = 0.03$, $\Delta\chi^b = 0.02$, $\chi_{AB} = 0.00004$, and $\bar{\chi}_{AB} = -0.01$. The volume fractions are fixed at $\phi_1 = \phi_2 = 0.2$ and $\phi_3 = 0.6$. In (a), $N = 5000$; thus, the product $N\chi_{AB} = 0.2$. In (b), N has been increased to 100000; thus, $N\chi_{AB}$ now equals 4. In the above, both $\Delta\chi^a$ and $\Delta\chi^b$ are positive and, thus, the figure shows a window of miscibility. Note that as N is increased this "window" becomes narrower.

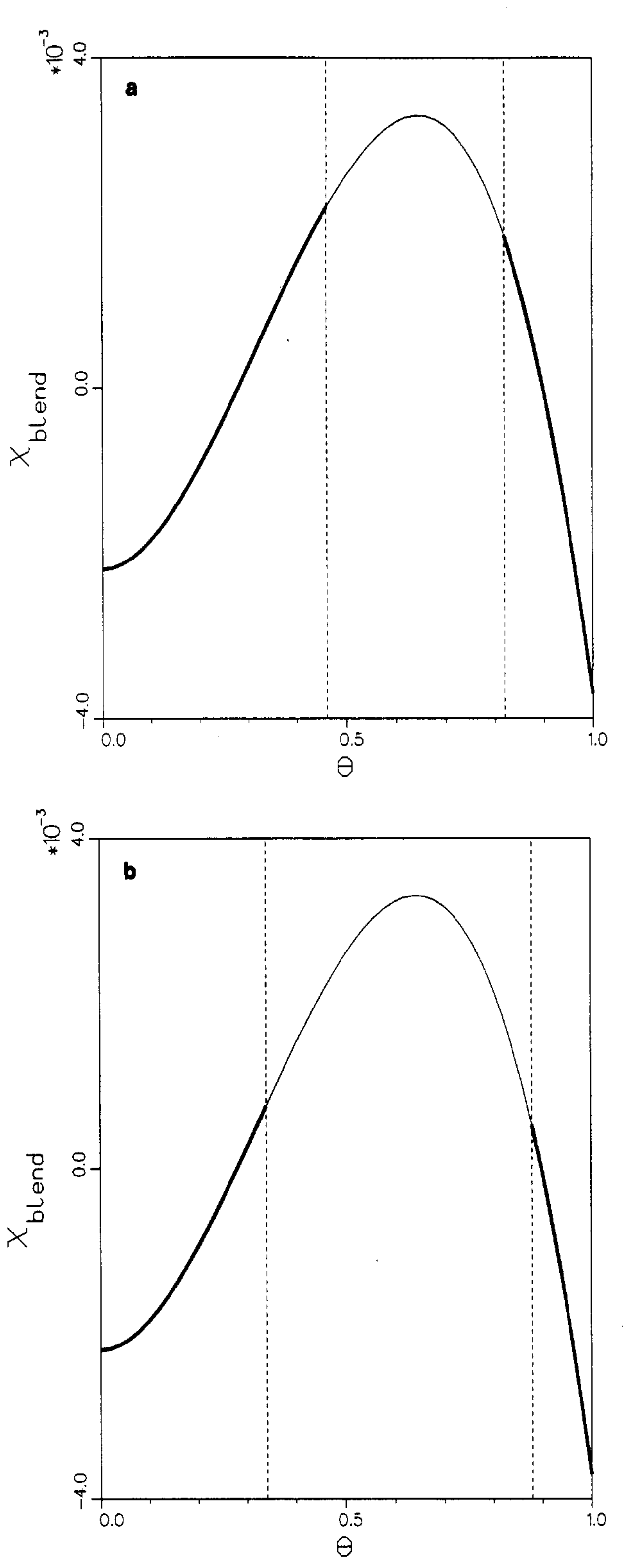


Figure 2. χ_{blend} vs θ. Here again, $R > 0$. The following values were picked for the relevant parameters: $\Delta\chi^a = -0.045$, $\Delta\chi^b = -0.039$, $\chi_{AB} = 0.0001$, and $\bar{\chi}_{AB} = 0.0302$. The volume fractions are fixed at $\phi_1 = \phi_2 = 0.2$ and $\phi_3 = 0.6$. In (a), $N = 1000$, thus $N\chi_{AB} = 0.1$. In (b), N has been increased to 3000, and $N\chi_{AB}$ now equals 0.3. Here $\Delta\chi^a$ and $\Delta\chi^b$ are both negative, and the plot reveals an immiscibility window. The region of immiscibility increases with increasing N.

patibilizing agent becomes apparent. (The specific values of these positive χ_{AB}'s are given in the figure captions. The numbers are all within the range of experimentally observed values.)

In the figures, the portions of a curve drawn in thick line are the regions where all the necessary conditions for

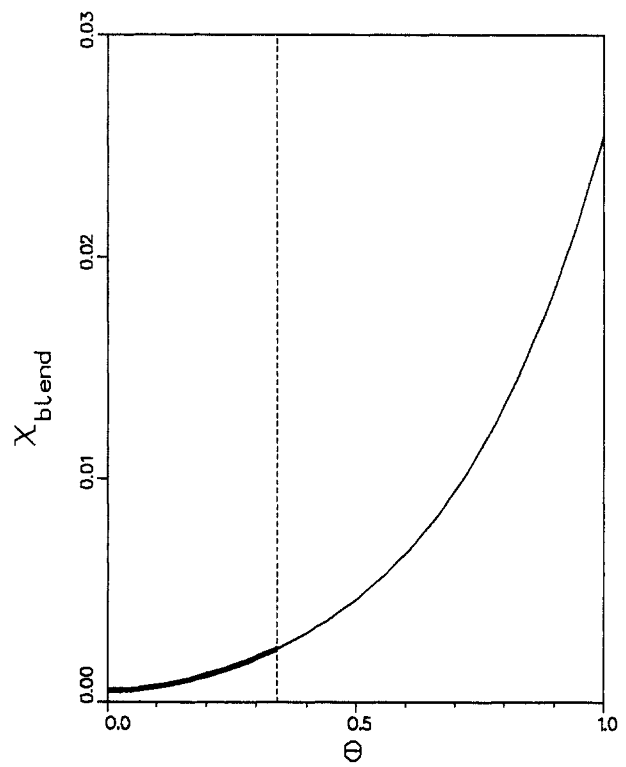


Figure 3. χ_{blend} vs θ. Here $-^1/_8 < R < 0$ and χ_{blend} is a monotonic function of θ. The following values were picked for the relevant parameters: $\Delta\chi^a = 0.08$, $\Delta\chi^b = -0.02$, $\chi_{AB} = 0.001$, and $\bar{\chi}_{AB} = 0.022$. The volume fractions are held constant at $\phi_1 = \phi_2 = 0.25$ and $\phi_3 = 0.5$. $N = 1000$; thus, $N\chi_{AB} = 1$. Since $\Delta\chi^b$ is negative, $\theta_c = 0$ is a local minimum, and $\chi_{AAA;BBB} < \bar{\chi}_{AB}$. Thus, a blocky copolymer is the best compatibilizer.

miscibility are satisfied. Here, the polymers form a single homogeneous phase. The thin line portion of the curve corresponds to the region where at least one of the necessary conditions is violated. In this region, the polymers are immiscible and phase separate. For further clarity, these two regions are separated by the dashed vertical lines.

Overall, the plots show that the A/B/AB systems can be made miscible by varying θ. By examining the values of $\Delta\chi^a$ and $\Delta\chi^b$, we see that the curves are intuitively correct. For the case $R > 0$, $\Delta\chi^a$ and $\Delta\chi^b$ have the same sign. If both terms are positive, then $\chi_{BAB;ABA} < \bar{\chi}_{AB} < \chi_{AAA;BBB}$. The relatively large value of $\chi_{AAA;BBB}$ implies a repulsive interaction between a "blocky" copolymer and a homopolymer. Thus, a blocky polymer would not promote copolymer–homopolymer miscibility. The relatively small value of $\chi_{BAB;ABA}$ indicates an attractive interaction between the segments of the copolymer. Adding an alternating copolymer would promote copolymer–copolymer interactions in favor of copolymer–homopolymer interactions. Consequently, a random-type copolymer, one with θ approximately equal to $^1/_2$, would provide the best compatibilizer in this case. This is seen in Figure 1. Here, the convex form of χ_{blend} displays a window of miscibility: for values of θ near $^1/_2$, all the necessary conditions are satisfied and the ternary system forms a homogeneous blend.

If both $\Delta\chi^a$ and $\Delta\chi^b$ are negative, $\chi_{AAA;BBB} < \bar{\chi}_{AB} < \chi_{BAB;ABA}$. Here, the relatively small value of $\chi_{AAA;BBB}$ implies an attractive interaction between a blocky copolymer and the homopolymer. Thus, the blocky copolymer now acts as a good compatibilizer. In addition, however, the large value of $\chi_{BAB;ABA}$ implies a copolymer–copolymer repulsion and, thus, promotes copolymer–homopolymer mixing. Consequently, the alternating copolymer also acts as a good compatibilizer. This situation is seen in Figure 2. The concave form of χ_{blend} displays a window of immiscibility: for a range of intermediate θ values, a least one of the specified conditions is violated and the polymers phase separate.

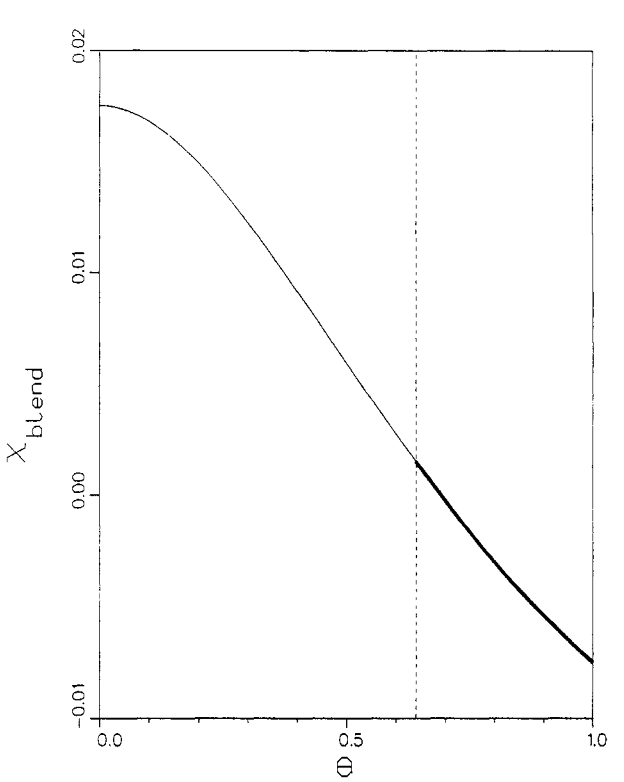
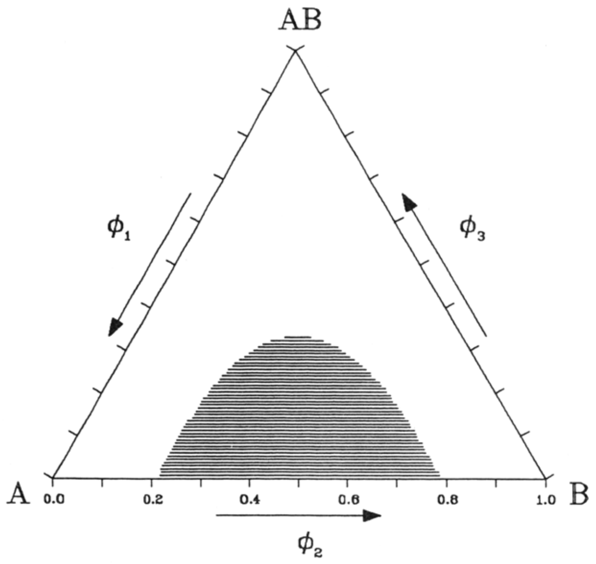


Figure 4. χ_{blend} vs θ. Here $-^1/_8 < R < 0$ and χ_{blend} is a monotonic function of θ. The following values were picked for the relevant parameters: $\Delta\chi^a = -0.02$, $\Delta\chi^b = 0.08$, $\chi_{AB} = 0.0001$, and $\bar{\chi}_{AB} = -0.01$. The volume fractions are held constant at $\phi_1 = \phi_2 = 0.250$ and $\phi_3 = 0.500$. $N = 1000$; thus, $N\chi_{AB} = 0.1$. Here $\Delta\chi^b$ is positive, $\theta_c = 0$ is a local maximum, and $\chi_{AAA;BBB} > \bar{\chi}_{AB}$. Thus, the best compatibilizer is the copolymer for which $^1/_2 \leq \theta \leq 1$.

In Figures 3 and 4, $-^1/_8 \leq R \leq 0$ and χ_{blend} is a monotonic function on [0,1]. In Figure 3, $\Delta\chi^b < 0$; consequently, $\theta_c = 0$ is a local minimum and $\chi_{AAA;BBB} < \bar{\chi}_{AB}$. Thus, a blocky copolymer is the best compatibilizer. In Figure 4, $\Delta\chi^b > 0$; thus, $\theta_c = 0$ is a local maximum and $\chi_{AAA;BBB} > \bar{\chi}_{AB}$. Thus, the best compatibilizer is the copolymer for which $^1/_2 \leq \theta \leq 1$.

As the degree of polymerization, N, is increased, the entropy of mixing becomes less favorable, and smaller values of all the χ parameters are needed in order to maintain miscibility (see eq 33–39). This can be seen in Figures 1b and 2b, where the χ's are held constant and the region of miscibility decreases as N is increased. In the limit that $N \rightarrow \infty$, the above equations show that both χ_{blend} and χ_{AB} must be negative. Thus, for significantly high molecular weight polymers, the only condition under which the A/B/AB system will be miscible is if the A–B homopolymers are miscible and the homopolymers/copolymer are also miscible.

Another way to view the effects of sequence distribution is to examine a series of ternary phase diagrams, where the values of the χ's and N's are held constant and the value of θ is varied from one diagram to another. In order to test our model, we initially set χ_{dist} equal to zero ($\Delta\chi^a = \Delta\chi^b = 0$) and $\chi_{AB} = \bar{\chi}_{AB}$. This choice of values eliminates sequence distribution effects and reduces our theory to the standard mean-field Flory–Huggins type model described by eq 1. Setting $N\chi_{AB}$ equal to values chosen by Leibler,[12] we recover the phase diagrams predicted by him for the simple mean-field model. (Figure 5 shows such a curve for $N\chi_{AB} = 3$.)



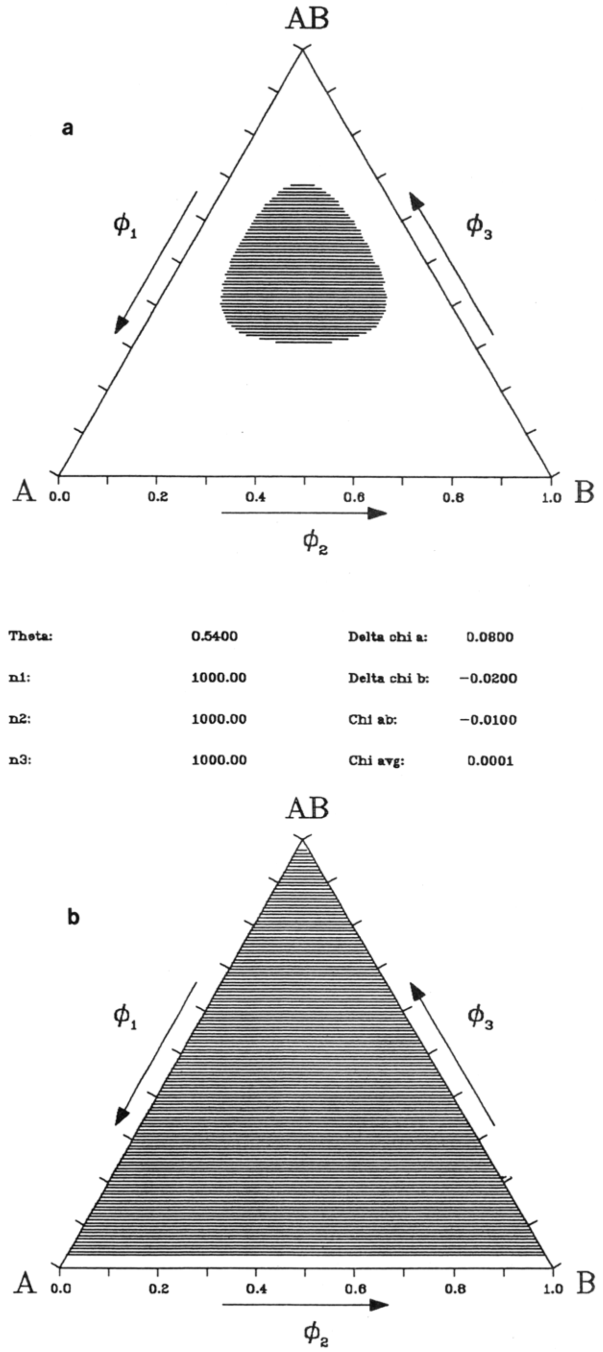
Theta:	0.5000	Delta chi a:	0.0000
n1:	1000.00	Delta chi b:	0.0000
n2:	1000.00	Chi ab:	0.0030
n3:	1000.00	Chi avg:	0.0030

Figure 5. Ternary phase diagram for the case where sequence distribution effects have been eliminated by setting $\Delta\chi^a = \Delta\chi^b = 0$ and $\chi_{AB} = \bar{\chi}_{AB}$. Here, $N = 1000$ and $\chi_{AB} = 0.003$. The dark shaded area encloses the region where the polymers are immiscible and, thus, phase separate. This diagram displays the same results as obtained by Leibler using the Flory–Huggins model given by eq 1 and setting the product $N\chi_{AB}$ equal to 3 (as we have done here). Specifically, the outline of the phase-separated region coincides with the spinodal curve calculated by Leibler.[12] Outside this region, the homogeneous phase is thermodynamically stable or metastable.

Figures 6 and 7, however, display the unique ternary phase diagrams that are predicted when sequence distribution effects are included. Specifically, Figure 6a shows a closed immiscibility loop in the center of the ternary phase diagram. The value of θ in the picture is 0.54. The immiscibility loop initially appears at $\theta = 0.53$; below this value, the blend is miscible over the entire composition range. As θ is increased beyond 0.54, the immiscible region broadens dramatically, leaving only two narrow regions of miscibility at $\theta = 1$ (see Figure 6b).

On the other hand, Figure 7c shows a miscibility loop near the center of the phase field. For this figure, θ equals 0.79. At $\theta = 0$, the blend is immiscible over almost all of the phase field, displaying only small regions of miscibility at each corner of the figure (see Figure 7a). As θ is increased to 0.68, the regions of miscibility expand and connect, leaving three distinct immiscible regions along each axis (see Figure 7b). Increasing θ to 0.79, however, decreases the degree of miscibility and exposes the closed loop diagram in 7c. Beyond $\theta = 0.79$, the degree of miscibility continues to decrease, so that, at $\theta = 1$, the phase diagram again resembles that at $\theta = 0$.

Closed-loop phase diagrams have been predicted[15] and observed[16] for binary polymer blends. Thus, the closed-loop phase diagrams displayed above can clearly be rationalized as experimental possibilities. They cannot, however, be predicted using the simpler Flory–Huggins expression given by eq 1. We await further experimental work to confirm the existence of such complicated phase behavior.



Theta:	0.5400	Delta chi a:	0.0800
n1:	1000.00	Delta chi b:	−0.0200
n2:	1000.00	Chi ab:	−0.0100
n3:	1000.00	Chi avg:	0.0001

Theta:	1.0000	Delta chi a:	0.0800
n1:	1000.00	Delta chi b:	−0.0200
n2:	1000.00	Chi ab:	−0.0100
n3:	1000.00	Chi avg:	0.0001

Figure 6. In (a), the ternary phase diagram displays a closed immiscibility loop (the shaded area). Here $\theta = 0.54$ and $\Delta\chi^a = 0.08$, $\Delta\chi^b = -0.02$, $\chi_{AB} = -0.01$, $\bar{\chi}_{AB} = 0.0001$, and $N = 1000$. In (b), θ has been increased to 1. The narrow region of miscibility along the A–B axis is attributable to the negative value of χ_{AB}. Note the small miscible region at the AB vertex.

Further insights into the phase behavior of the A/B/AB system can be obtained by examining eq 36–37. These expressions show the effect of ϕ_3, the volume fraction of copolymer, on the miscibility of A/B/AB blends. The right side of eq 36, $2/(1 - \phi_3)$, increases monotonically as ϕ_3 decreases. On the left side, however, for a fixed value

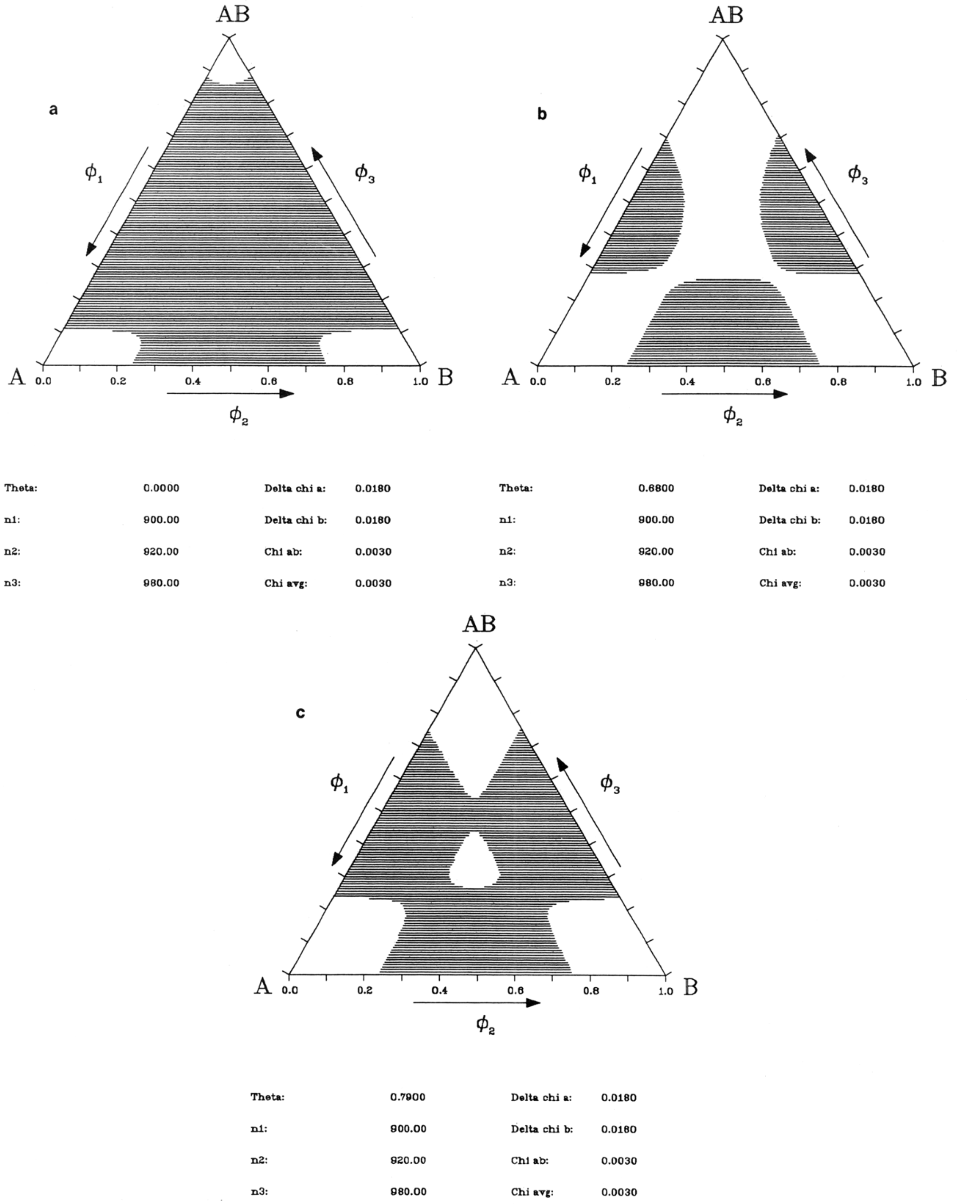


Figure 7. In this series of diagrams, a closed miscibility loop is seen to emerge. Here $\Delta\chi^a = \Delta\chi^b = 0.0180$, $\chi_{AB} = \bar{\chi}_{AB} = 0.003$, $N_1 = 900$, $N_2 = 920$, and $N_3 = 980$. At $\theta = 0$, small regions of miscibility are seen only at the corners of the phase diagram (a). As θ is increased to 0.68, the regions of miscibility increase in size and are connected (b). However, as θ is increased beyond this value, the region of miscibility begins to shrink, exposing a closed loop of miscibility in the center of the diagram for $\theta = 0.79$ (c).

of $N\chi_{\text{blend}}$, the function $\{4N\chi_{\text{blend}} - 2/[\phi_3(1 - \phi_3)]\}$ is a concave parabola with a maximum at $\phi_3 = 0.5$. Thus, for $\phi_3 < 0.5$, an increase in ϕ_3 will satisfy the right inequality but not necessarily satisfy the inequality on the left. In other words, for fixed values of $N\chi_{\text{blend}}$ and $N\chi_{AB}$ and for $\phi_3 < 0.5$, increasing ϕ_3 (decreasing $\phi_1 = \phi_2$) does not necessarily promote miscibility. However, if the system is miscible at $\phi_3 = 0.5$, the blend will remain miscible for increased values of ϕ_3 (and decreased $\phi_1 = \phi_2$).

This equation also indicates that as $N\chi_{AB}$ is increased (either through an increase in N or an increased incompatibility between the A and B homopolymers), larger amounts of copolymer are needed in order to make a miscible blend. Recently, Leibler[12] has reached similar conclusions concerning the effect of ϕ_3 on the A/B/AB system. (For $\phi_3 < 0.5$ an increase in ϕ_3 may require a decrease in $N\chi_{\text{blend}}$ in order to satisfy the inequality on the left side of eq 36, as well as the inequality in eq 37. Thus, as more copolymer is added, the compatibility between copolymer–homopolymer may also need to be increased.)

In summary, we have generated new phase diagrams for ternary blends of the type A/B/AB. The diagrams show that miscibility in these systems is extremely sensitive to the value of θ or the copolymer sequence distribution. Also evident is the fact that the block copolymer does not always act as the best bulk agent in creating a completely miscible A/B/AB blend. This observation concurs with recent experimental findings.[13] We hope our predictions concerning the complicated phase diagrams that can be obtained with this model will encourage new experimental efforts in this area. We conclude by noting that our future work will examine the compatibilizing efficiency of block copolymers in microphase-separated systems. In this regime, the entropy term in our model (ΔS) must be modified. Specifically, the theory must reflect the reduction in ΔS when block copolymers undergo microphase separation.

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Association Equilibria Theory of Preferential Adsorption in Systems with Solvent–Solvent and Solvent–Polymer Interactions

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ABSTRACT: The theory of association equilibria is used to derive the amount of preferential adsorption for polymer–mixed solvent systems in which one of the two liquids in the mixed solvent (B) autoassociates and interacts specifically with the polymer and with the other liquid (A). The model takes into account the constants for the association of one molecule of B to one site in A and of one molecule of B to one site in the polymer and also the corresponding constants for the multiple self-association of B for the case where the first B molecule is associated either with A or with the polymer or is free. The theoretical results are applied to the systems poly(alkyl methacrylate)s, alkyl = Me, Et, iBu, in the mixed solvent methanol (B) + 1,4-dioxane (A). The experimental results of these systems can be quantitatively well reproduced by the theory.

Introduction

Preferential or selective adsorption is a very common phenomenon in ternary systems composed of a polymer and a binary solvent mixture. There is a great variety of ternary systems that have been studied, mainly those containing at least one polar component.[1] In many cases, specific interactions between polar groups are important, and the formation of hydrogen bonds have to be taken into account. This is the case, especially, when alcohols are components of the system.

In systems with specific interactions random mixing cannot be assumed. Hence, the thermodynamic theories traditionally used to interpret ternary system properties, such as the Flory–Huggins formalism or the equation-of-state theory of Flory,[2] are expected not to apply to such systems.

For systems showing strong specific effects such as hydrogen bonding, Pouchlý et al.[3–5] have developed a theoretical framework that is based on the theory of association equilibria.[4] The existence of associated complexes formed by association of individual molecules is explicitly recognized in such theory, and the thermodynamic properties are derived from the equilibrium constants for association. This type of formalism is expected to be useful in the interpretation of systems having complexation by hydrogen bonding, such as those containing alcohols or water, which are liquids frequently found in studies of polymers in mixed solvents.

The treatment in such theory of association equilibria, although straightforward, is more difficult to develop in detail than the usual random thermodynamic treatment. As far as we know, the theory of association equilibria has