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# Effect of Sequence Distribution on the Miscibility of Polymer/Copolymer Blends

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ABSTRACT: Previous theories describing the phase behavior of copolymer blends have ignored the sequence distribution of monomer units in the copolymer. We introduce a parameter, $\theta$, that describes the binary sequence distribution of the monomers in a copolymer chain. By varying $\theta$, we can describe a block, random, or alternating copolymer. It is assumed that the interaction energy between a monomer of homopolymer C and the monomer A (or B) in the copolymer AB is mediated by the nearest neighbors chemically bonded to the A (or B) structural unit. It is found that the sequence distribution may significantly affect the degree of compatibility between the polymers AB and C. For a fixed composition, there is an optimal range of $\theta$ values (or sequence distributions) for which the C/AB system is miscible.

## Introduction

By mixing compatible polymers, it is possible to create a blend having more desirable properties and a greater variety of applicability than those of the individual components. Much current research has centered on searching for such pairs of mutually miscible polymers. Consequently, understanding the factors that effect miscibility is of great interest. Recent studies[1-3] have extended the formalism of the Flory–Huggins[4,5] theory for mixtures to explicitly include interactions between the covalently bonded monomers of copolymers. Specifically, for a polymer/copolymer system, miscibility can be caused by a "repulsive" interaction between the monomeric units of the copolymer being diluted by the homopolymer.

A major drawback common to all Flory–Huggins type theories for mixtures involving copolymers is that no distinction is made between copolymer types (random, block, etc.). Herein, we present a theory that lifts this restrictive aspect of describing systems of copolymer blends. For a copolymer of fixed composition, we examine the effect of sequence distribution on copolymer/polymer miscibility. This is done by introducing an order parameter $\theta$ that allows us to distinguish between block, random, or alternating copolymers. Further, we assume that the interaction energy between a monomer of the homopolymer C and the monomer A (or B) in the copolymer chain is mediated by the nearest neighbors chemically bonded to the A (or B) structural unit. This intuitive notion seems particularly appropriate if one or both units of the copolymer are polar molecules. We fit these ideas into the framework outlined by ten Brinke, Karasz, and MacKnight[3] (to be described in more detail below) and investigate the effect of varying $\theta$ on the window of miscibility for polymer/copolymer systems.

## Theoretical Model

The free energy of mixing for a binary mixture of a homopolymer and copolymer is given by[1-3]

$$\Delta G/RT = (\phi_1/N_1)\ln\phi_1 + (\phi_2/N_2)\ln\phi_2 + \phi_1\phi_2\{f\chi_{AC} + (1-f)\chi_{BC} - f(1-f)\chi_{AB}\} \quad (1)$$

where $\chi$ is the parameter that expresses the strength of the polymer–polymer interaction, $f$ and $(1-f)$ denote the composition of the copolymer $(A_fB_{1-f})_n$ with volume fraction $\phi_1$ and degree of polymerization $N_1$, and the homopolymer C has a volume fraction $\phi_2$ and degree of polymerization $N_2$. This free energy is identical with the usual Flory–Huggins one when the following identification is made:

$$\chi_{blend} = f\chi_{AC} + (1-f)\chi_{BC} - f(1-f)\chi_{AB} \quad (2)$$

Thus, the single $\chi$ parameter has been decomposed into the three separate $\chi$'s that are associated with each type of interacting pair.

Table I
Interactions of a C Unit with an A-Centered Triplet

| terms | configuration | probability |
|---|---|---|
| $\chi_{BAB;C}$ | B<br>$A \longleftrightarrow C$<br>B | $\frac{f_{AB}^2}{f_A^2}\phi_A\phi_C = \frac{f_{AB}^2}{f_A}\phi_{AB}\phi_C$ |
| $\chi_{BAA;C}$ | B<br>$A \longleftrightarrow C$<br>A | $2\frac{f_{BA}f_{AA}}{f_A^2}\phi_A\phi_C = 2\frac{f_{BA}f_{AA}}{f_A}\phi_{AB}\phi_C$ |
| $\chi_{AAB;C}$ | A<br>$A \longleftrightarrow C$<br>B | |
| $\chi_{AAA;C}$ | A<br>$A \longleftrightarrow C$<br>A | $\frac{f_{AA}^2}{f_A^2}\phi_A\phi_C = \frac{f_{AA}^2}{f_A}\phi_{AB}\phi_C$ |

Here we will also consider a binary mixture of a homopolymer consisting of monomers C and a copolymer composed of monomers A and B, but in addition we assume that the interaction energy for the C–A pair is influenced by the units that are chemically bonded to A. This idea is understandable in terms of the polarizability of a group. The $\chi_{ij}$ parameters are related to the product of the electronic polarizabilities ($\alpha$) for each unit $i$ and $j$.[6] Since it is well-known that $\alpha$ of an atom in a molecule is influenced by the neighbors to which it is chemically bonded (e.g., electron-withdrawing or -donating groups), it seems reasonable to expect that $\chi_{AC}$ will depend on the local sequence distribution.

In order to consider all the possible homopolymer–copolymer interactions, or C–A and C–B interactions, all the possible triplets with A or B occupying the central site must be enumerated. Next, the probability of occurrence for each specific triplet is calculated. Then, an energy value is assigned to each C–triplet interaction. Table I illustrates this procedure for C–A interactions. In the first column is the energy assigned to the configuration found in the second column, whose probability of occurrence is given in column 3. A similar scheme can be constructed for the C–B interactions.

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In column 1, the interaction energies have been identified with the Flory interaction parameter $\chi$. The probabilities in column 3 are expressed in terms of $f_A$ and $f_B$, the fraction of A and B molecules, respectively, in a single copolymer chain. Furthermore, $f_{AB}$, $f_{BB}$, and $f_{AA}$ are the pair probabilities of AB, BB, and AA pairs in a single chain. Finally, $\phi_A$, $\phi_B$, $\phi_{AB}$, and $\phi_C$ are the volume fractions of the A, B, AB, and C species, respectively. The variables listed above are related through the following equations:

$$\begin{gathered} f_A = f_{AA} + f_{AB} \\ f_B = f_{BB} + f_{BA} \\ f_{AB} = f_{BA} \\ f_A + f_B = 1 \\ \phi_A + \phi_B = \phi_{AB} \\ f_A\phi_{AB} = \phi_A \\ f_B\phi_{AB} = \phi_B \\ \phi_{AB} + \phi_C = 1 \end{gathered} \tag{3}$$

For example, consider the probability of the A–C interaction involving the triplet BAA. The probability of a BAA triplet is equal to $f_{BA}$ times $f_{AA}/f_A$; the latter is the conditional probability that an A will follow another A. There are four distinct triplets involving an A central comonomer unit, and the sum of these four triplet probabilities must equal $f_A$. This implies that the properly normalized BAA triplet probability equals $f_{AB}f_{AA}/f_A^2$. Now the mean field pair probability of an A–C interaction is $\phi_A\phi_C$, and thus the probability of an A–C interaction involving the BAA triplet is equal to $(f_{AB}f_{AA}/f_A)\phi_{AB}\phi_C$.

As can be seen a large number of $\chi$ parameters are required to properly describe the energetics. To reduce the number of parameters, the following simplifications are introduced: It will be assumed that all A–A and B–B interactions are equivalent and equal zero. Although there are 16 possible A–B interactions, all will be assumed equivalent with average interaction parameter $\bar{\chi}_{AB}$. (This assumption will be relaxed later when AB/A mixtures are considered.) Additionally, in Table I it will be assumed for A–C interactions that $\bar{\chi}_{AC} \equiv \chi_{BAB;C} = \chi_{AAB;C} = \chi_{BAA;C} \neq \chi_{AAA;C}$ are similarly for the B–C interactions $\bar{\chi}_{BC} \equiv \chi_{ABA;C} = \chi_{ABB;C} = \chi_{BBA;C} \neq \chi_{BBB;C}$. With these approximations the free energy of the AB/C binary mixture contains the term $\phi_{AB}\phi_C\chi_{blend}$, where

$$\chi_{blend} = \chi_{comp} + \chi_{dist} \tag{4}$$

$$\chi_{comp} = f_A\bar{\chi}_{AC} + f_B\bar{\chi}_{BC} - f_Af_B\bar{\chi}_{AB} \tag{5}$$

$$\chi_{dist} = (f_{AA}^2/f_A)\Delta\chi_A + (f_{BB}^2/f_B)\Delta\chi_B \tag{6}$$

$$\Delta\chi_A \equiv \chi_{AAA;C} - \bar{\chi}_{AC} \tag{7}$$

$$\Delta\chi_B \equiv \chi_{BBB;C} - \bar{\chi}_{BC} \tag{8}$$

Note that the composition dependence of $\chi_{blend}$ is just eq 2 and that consideration of the comonomer sequence distribution results in a zeroth-order correction to eq 2 that is denoted as $\chi_{dist}$. A negative $\Delta\chi_A$ implies that AAA–C interactions are energetically more favorable than any other A–C interactions, and conversely, a positive $\Delta\chi_A$ implies that AAA–C interactions are less favorable than all other A–C interactions. Similar comments apply to $\Delta\chi_B$.

It is convenient to introduce the parameters $\theta$ and $\delta$ defined by

$$f_{AB} = 2\theta f_Af_B \tag{9}$$

$$f_A = \tfrac{1}{2}(1 + \delta) \qquad f_B = \tfrac{1}{2}(1 - \delta) \qquad -1 \le \delta \le 1 \tag{10}$$

All other probabilities can be expressed as functions of $\theta$ and $\delta$ by eq 3. A block copolymer corresponds to $\theta$ approaching zero. Since $f_{AB}$ assumes its mean field value at $\theta = {}^1/_2$, this value of $\theta$ describes a random copolymer. If $f_B \le f_A$, then the maximum value of $f_{AB}$ equals $f_B$, which corresponds to the situation where every B unit is bonded to two A units. Thus the maximum value of $\theta$ is

$$\theta_{max} = (1 + |\delta|)^{-1} \tag{11}$$

For a symmetric copolymer ($\delta = 0$), $\theta_{max} = 1$; this describes an alternating copolymer. More generally $0 \le \theta < {}^1/_2$ describes a "blocky" copolymer, $\theta = {}^1/_2$ describes a random copolymer, and ${}^1/_2 < \theta \le \theta_{max}$ describes a copolymer containing "alternating" patterns.

It is easy to show that the average run (or block) lengths $\langle n\rangle_A$ and $\langle n\rangle_B$ of A and B units are given by

$$\begin{gathered} \langle n\rangle_A = f_A/f_{AB} = 1/[\theta(1 - \delta)] \\ \langle n\rangle_B = 1/[\theta(1 + \delta)] \end{gathered} \tag{12}$$

Thus, for a symmetric copolymer

$$\langle n\rangle_A = \langle n\rangle_B = 1 \qquad \theta = 1 \tag{13a}$$

$$\langle n\rangle_A = \langle n\rangle_B = 2 \qquad \theta = \tfrac{1}{2} \tag{13b}$$

$$\langle n\rangle_A = \langle n\rangle_B \rightarrow \infty \qquad \theta \rightarrow 0 \tag{13c}$$

Now with the help of eq 3, $\chi_{dist}$ can be rewritten in terms of $\theta$ and $\delta$

$$\chi_{dist} = \tfrac{1}{2}(1 + \delta)[1 - \theta(1 - \delta)]^2\Delta\chi_A + \tfrac{1}{2}(1 - \delta)[1 - \theta(1 + \delta)]^2\Delta\chi_B \tag{14}$$

Since $\chi_{dist}$ is quadratic in $\theta$, it will have an extremum at $\theta_c$ defined by $\partial\chi_{dist}/\partial\theta = 0$. This yields

$$\theta_c = \frac{\Delta\chi_A + \Delta\chi_B}{(1 + \delta)\Delta\chi_B + (1 - \delta)\Delta\chi_A} = \frac{1}{1 + \delta(1 - R)/(1 + R)} \tag{15}$$

with

$$R \equiv \Delta\chi_A/\Delta\chi_B \tag{16}$$

Note that for a symmetric copolymer $\theta_c = 1$ for all $R$. Either the purely alternating or the block copolymer is most stable. For asymmetric copolymers ($\delta \neq 0$) the analysis is aided by adopting *the convention that component B is always chosen to be the minor component* ($f_B \le f_A$) *and* $\delta$ *is always positive*. Now note that if $R > 0$ and $\delta \neq 0$, $\theta_c$ is not in the allowed interval $[0,\theta_{max}]$. If $R < 0$, then $\theta_c$ can be rewritten as

$$\theta_c = \frac{1}{1 + \delta(1 + |R|)/(1 - |R|)} \qquad R < 0 \tag{17}$$

and an extremum always appears in $\chi_{dist}$ in $[0,\theta_{max}]$ if $|R| < 1$. This is the most interesting case because the possibility exists for a "window" of miscibility or immiscibility. To decide which is the case, $\chi_{dist}$ is evaluated at $\theta_c$

$$\chi_{dist}(\theta_c) = \frac{2\theta_c\Delta\chi_A\Delta\chi_B}{\Delta\chi_A + \Delta\chi_B}\delta^2 \tag{18}$$

If $R$ is negative and $|R| < 1$, then

$$\chi_{dist}(\theta_c) < 0 \qquad \Delta\chi_A + \Delta\chi_B > 0 \qquad \text{(miscibility window)} \tag{19a}$$

$$\chi_{dist}(\theta_c) > 0 \qquad \Delta\chi_A + \Delta\chi_B < 0 \qquad \text{(immiscibility window)} \tag{19b}$$

When there is no extremum in $[0,\theta_{max}]$, i.e., when $R > 0$ or when $R < 0$ but $|R| > 1$, $\chi_{dist}$ is a monotonic function of $\theta$ on $[0,\theta_{max}]$. Either the block copolymer ($\theta = 0$) or the alternating copolymer ($\theta = \theta_{max}$) will have the smallest, or most stable, value of $\chi_{\mathrm{dist}}$. A criterion can easily be developed to determine the most stable distribution by examining the sign of $\partial\chi_{\mathrm{dist}}/\partial\theta$ at $\theta = {}^1/_2$. This yields the result that for $f_B \le f_A$

$$f_A\Delta\chi_A + f_B\Delta\chi_B > 0 \quad \text{alternating copolymer most stable} \tag{20a}$$

$$f_A\Delta\chi_A + f_B\Delta\chi_B < 0 \quad \text{block copolymer most stable} \tag{20b}$$

Of course, the above criterion is invalid for $R < 0$, $|R| < 1$ because $\chi_{\mathrm{dist}}$ has an extremum in $[0,\theta_{\max}]$.

A special case of interest is the AB/C blend where C is either A or B because it may be an experimentally more accessible system. 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 probability of the homopolymer A interacting with the copolymer triplet BBB is given by $\phi_A'$, the volume fraction of homopolymer A times the probability of the BBB configuration, which is $\phi_B f_{BB}^2/f_B^2$. The probability of an AAA copolymer triplet interacting with the BBB copolymer triplet is given by $\phi_A\phi_B(f_{AA}^2/f_A^2)(f_{BB}^2/f_B^2)$, while the probability of an (ABA) segment interacting with a (BAB) species is $\phi_A\phi_B(f_{AB}^2/f_A^2)(f_{AB}^2/f_B^2)$. Now the $\phi_A\phi_B$ factor multiplying the copolymer–copolymer interactions is rewritten as

$$\phi_A\phi_B = f_A f_B\phi_{AB} - f_A f_B\phi_A'\phi_{AB} \tag{21}$$

It is important to note that the term linear in the volume fraction variable ($\phi_{AB}$) is not important in determining phase stability or equilibria and is ignored. Hence the terms in $\chi_{\mathrm{blend}}$ arising from copolymer–copolymer interactions enter with a minus sign.

The remaining 14 pairs of A–B interacting triplets are assigned an average value of $\bar{\chi}_{AB}$. In what follows, all A–A and B–B interactions are assigned a zero interaction parameter as before. When all terms are collected, the total expression for the energy of interaction can be written as $\phi_A'\phi_{AB}\chi_{\mathrm{blend}}$, where

$$\chi_{\mathrm{blend}} = \chi_{\mathrm{comp}} + \chi_{\mathrm{dist}} \tag{22}$$

$$\chi_{\mathrm{comp}} = \bar{\chi}_{AB}(f_B^2) \tag{23}$$

$$\chi_{\mathrm{dist}} = \Delta\chi^b(f_{BB}^2/f_B)\left(1 - \frac{f_{AA}^2}{f_A}\right) + \Delta\chi^a\frac{f_{AB}^4}{f_A f_B} \tag{24}$$

$$\Delta\chi^b = \chi_{\mathrm{AAA;BBB}} - \bar{\chi}_{AB} \tag{25}$$

$$\Delta\chi^a = \bar{\chi}_{AB} - \chi_{\mathrm{BAB;ABA}} \tag{26}$$

The "a" and "b" superscripts on $\Delta\chi$ refer to alternating and block sequences, respectively. The analogous equations for the AB/B system are obtained by interchanging the indicies A and B.

Since the AAA–BBB and ABA–BAB interactions are extremes (pure block–block and alternating–alternating triplet interactions), we expect that in most systems $\Delta\chi^a$ and $\Delta\chi^b$ will have the same sign. Notice that the positive coefficient on $\Delta\chi^a$ varies monotonically as $\theta^4$, whereas the positive coefficient on $\Delta\chi^b$, which is a more complicated quartic function of $\theta$, may exhibit an extremum (or extrema) on $[0,\theta_{\max}]$. Thus, "windows" of miscibility and immiscibility can potentially be observed with AB/A blends as a function of sequence distribution.

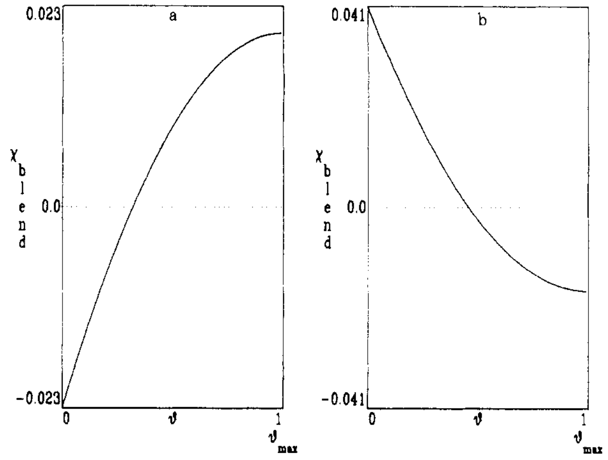

**Figure 1.** $\chi_{\mathrm{blend}}$ vs. $\theta$. Since $f_A = f_B = 0.5$, $\theta_{\max} = 1$. The following values were picked for the relevant parameters: (a) $\Delta\chi_A = -0.022$ and $\Delta\chi_B = -0.063$, with $\chi_{\mathrm{comp}} = 0.0198$; (b) $\Delta\chi_A = 0.025$ and $\Delta\chi_B = 0.092$, with $\chi_{\mathrm{comp}} = -0.0173$.

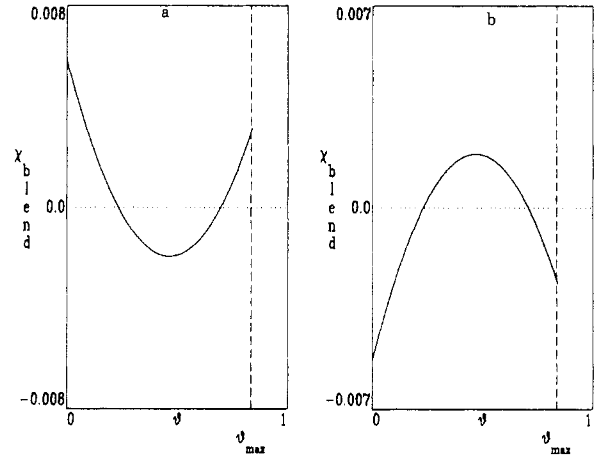

**Figure 2.** $\chi_{\mathrm{blend}}$ vs. $\theta$. Here $f_A = 0.6$, $f_B = 0.4$, and $\theta_{\max} = 0.833$. In both (a) and (b), $R < 0$ and $|R| < 1$. In (a), where $\Delta\chi_A = -0.088$ and $\Delta\chi_B = 0.125$ (thus the sum is positive), this results in a window of miscibility ($\chi_{\mathrm{comp}} = 0.0117$). In (b), $\Delta\chi_A = 0.070$ and $\Delta\chi_B = -0.100$ (a negative sum) and an immiscibility window appears ($\chi_{\mathrm{comp}} = -0.0070$).

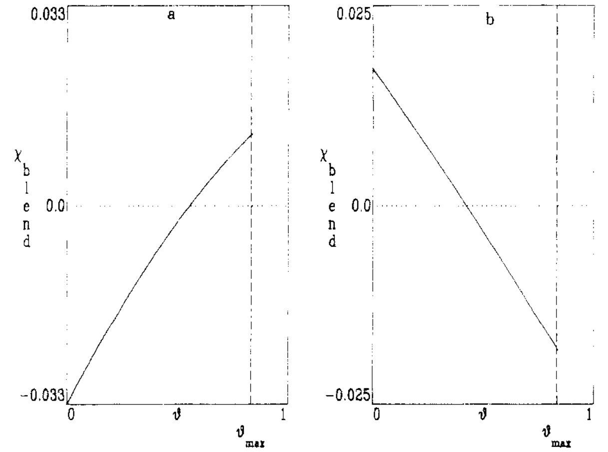

**Figure 3.** $\chi_{\mathrm{blend}}$ vs. $\theta$ ($f_A = 0.6$, $f_B = 0.4$, and $\theta_{\max} = 0.833$). Here, $R < 0$ but $|R| > 1$ and $\chi_{\mathrm{blend}}$ is a monotonic function of $\theta$. In (a), $\Delta\chi_A = -0.1140$ and $\Delta\chi_B = 0.0390$; thus the blocky copolymer is most stable (see eq 20) ($\chi_{\mathrm{comp}} = 0.0194$). For (b), $\Delta\chi_A = 0.1440$ and $\Delta\chi_B = -0.1030$; consequently, the alternating copolymer is most stable ($\chi_{\mathrm{comp}} = -0.0277$).

## Results and Discussion

Figures 1–4 show plots of $\chi_{\mathrm{blend}}$ vs. $\theta$ for various values of $f_A$ and $f_B$. ($\chi_{\mathrm{comp}}$ is a constant that when added to $\chi_{\mathrm{dist}}$ to yield $\chi_{\mathrm{blend}}$ will just shift this figure either up or down with respect to the $\chi_{\mathrm{dist}} = 0$ axis.) In what follows, it is assumed that the polymers involved are of high molecular

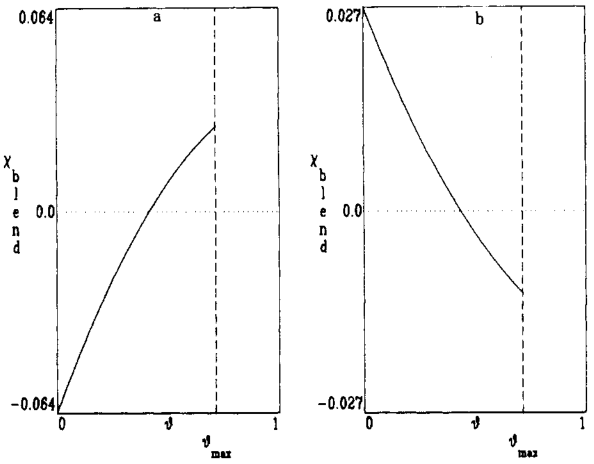

**Figure 4.** $\chi_{\text{blend}}$ vs. $\theta$ ($f_A = 0.7$, $f_B = 0.3$, and $\theta_{\max} = 0.714$). Now, $R > 0$, and again $\chi_{\text{blend}}$ is a monotonic function of $\theta$. In (a), $\Delta\chi_A = -0.1320$ and $\Delta\chi_B = -0.0950$ ($\chi_{\text{comp}} = 0.0572$), while in (b), $\Delta\chi_A = 0.066$ and $\Delta\chi_B = 0.0240$ ($\chi_{\text{comp}} = -0.0262$).

weight; thus a negative $\chi_{\text{blend}}$ indicates blend miscibility, whereas a positive $\chi_{\text{blend}}$ describes immiscibility. Overall, the plots show that copolymer/polymer systems can be made miscible by varying $\theta$. By examining the values of $\Delta\chi_A$ and $\Delta\chi_B$ we see that the curves are intuitively correct. For example, in the case where $f_A = f_B = 0.5$ and $\Delta\chi_A$ and $\Delta\chi_B$ are both negative, we see in Figure 1a that the C/AB system is more miscible for a "blocky" ($0 \leq \theta < {}^1/_2$) copolymer. Likewise, if $\Delta\chi_A$ and $\Delta\chi_B$ are positive, we would expect the opposite trend to occur: $\chi_{\text{blend}}$ is negative for ${}^1/_2 < \theta \leq 1$. This situation can be seen in Figure 1b.

The convex parabolic form of $\chi_{\text{blend}}$ in Figure 2 corresponds to a window of miscibility: for the range of $\theta$ values that yield a negative $\chi$, the polymers are miscible and form a single phase. On the other hand, the concave form of $\chi_{\text{blend}}$ corresponds to an immisicibility window: for the range of values that result in a positive $\chi_{\text{blend}}$, the polymers are immiscible and separate into two phases.

To summarize, previous calculations[1-3] have shown that for the copolymer $(A_fB_{1-f})_n$, there is an optimal range of values for the composition variable $f$ such that the C/AB system is miscible. When $\chi_{\text{blend}}$ is further expanded in terms of $\theta$ and the energy parameters for the various triplet interactions, there exist optimal sequential arrangements of the A and B monomers for miscibility.

Finally, we comment on the experimental availability of the parameters used in the equations above. As yet, there has been no investigation on high molecular weight, polymer/copolymer systems where the sequence distribution has been systematically varied. As can be seen in eq 4-8, there are five $\chi$ parameters to be determined for the AB/C blend. In principle, two of these parameters, $\chi_{\text{AAA;C}}$ and $\chi_{\text{BBB;C}}$, can be determined from A/C and B/C homopolymer blend data. The remaining three parameters could be determined from AB/C blend data involving at least three random ($\theta = {}^1/_2$) AB copolymers varying in composition, or equivalently, at least three copolymers with different sequence distributions. In the special case of a symmetric alternating copolymer ($\delta = 0$ and $\theta = 1$), $\chi_{\text{dist}} = 0$ and there are only three $\chi$ parameters to be determined: $\chi_{\text{BAB;C}} \equiv \bar{\chi}_{\text{AC}}$, $\chi_{\text{ABA;C}} \equiv \bar{\chi}_{\text{BC}}$, and $\bar{\chi}_{\text{AB}}$.

For AB/A systems, there are in general three $\chi$ parameters to be determined. However, for a symmetric block copolymer ($\delta = 0$ and $\theta = 0$) there is only one $\chi$ parameter: $\chi_{\text{AAA;BBB}} = \bar{\chi}_{\text{AB}} = 4\chi_{\text{blend}}$. For the symmetric alternating copolymer ($\delta = 0$ and $\theta = 1$), there are only two $\chi$ parameters: $\chi_{\text{ABA;BAB}}$ and $\chi_{\text{ABA;AAA}} = \bar{\chi}_{\text{AB}}$.

Diad probabilities, or equivalently $\theta$, can be determined by using $^1$H and $^{13}$C NMR or can be estimated from known reactivity ratios.[7] Deuteration of homopolymer C would allow $\chi_{\text{blend}}$ to be determined for any miscible AB/C blend by small-angle neutron scattering (SANS).[8] SANS can also be used to determine $\chi_{\text{AAA;BBB}}$ for disordered block copolymers.[9]

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