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The Effect of Chain Microstructure on Polymer — Polymer Miscibility

A. C. Balazs, F. E. Karasz, and W. J. MacKnight

Polymer Science and Engineering Department, University of Massachusetts,
Amherst, MA 01003, USA

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A mean field model for the miscibility of binary polymer systems containing random copolymers has been extended to take into account the microstructure of the respective macromolecular constituents. The resulting model has been applied to the special case of mixtures of copolymers containing identical moieties but differing in microstructure and/or composition. An example of such a system is the mixture of polyvinyl chloride and chlorinated polyethylene.

INTRODUCTION

A major drawback common to all Flory-Huggins type theories for mixtures involving copolymers is that no account is taken of the copolymer microstructure: the ordering or sequence distribution of the monomers in the copolymer chain. Thus, there is no distinction between copolymer types (random, block, etc.). Below, we construct a model and present a series of equations that, for a copolymer of fixed composition, can examine the effect of microstructure on copolymer/polymer (or copolymer/copolymer) miscibility. This is done by introducing an order parameter Θ that allows us to distinguish between blocky, random or alternating copolymers. Further, we assume that the interaction energy between a monomer of 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 expression for the free energy of mixing of a homopolymer and copolymer and investigate the effect of varying Θ on the miscibility of copolymer/polymer systems. We then apply this model to a mixture of two copolymers that differ only in composition to derive an equation that allows us to investigate the effect of microstructure on copolymer/copolymer blends.

THEORETICAL MODEL

The free energy of mixing for a binary mixture of a homopolymer and copolymer is given by[1–6]

$$\Delta G/RT = (\Phi_1/N_1)\ln\Phi_1 + (\Phi_2/N_2)\ln\Phi_2 + \Phi_1\Phi_2\{f\chi_{AC} + (1-f)\chi_{BC} - f(1-f)\chi_{AB}\} \quad (1)$$

where χ is the Flory interaction parameter[7] and f and $(1\text{-}f)$ denote the compositions of the copolymer $(A_fB_{1-f})_n$ with volume fraction Φ_1, and degree of polymerization N_f, and the homopolymer C has a volume fraction Φ_2 and degree of polymerization N_2. This free energy is identical with the usual Flory-Huggins[7,8] one when the following identification is made:

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

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 nearest neighbors that are chemically bonded to A. We use this idea to reinterpret and calculate the interaction energies between polymer chains, as is illustrated in Table I. 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.

TABLE I

The Interactions of a C Unit with an A-centered Triplet

Terms	Configuration	Probability
$\chi_{BAB,C}$	B A ↔ C B	$\frac{f_{AB}^2}{f_A}\Phi_{AB}\Phi_C$
$\chi_{BAA,C}$	B A ↔ C A	$2\frac{f_{BA}f_{AA}}{f_A}\Phi_{AB}\Phi_C$
$\chi_{AAB,C}$	A A ↔ C B	
$\chi_{AAA,C}$	A A ↔ C A	$\frac{f_{AA}^2}{f_A}\Phi_{AB}\Phi_C$

In column 1, the interaction energies have been identified with the Flory interaction parameter χ. 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}, f_{AA} are the pair probabilities of AB, BB and AA pairs in a single chain. Finally, Φ_A, Φ_B, Φ_{AB} and Φ_C are the volume fractions of the A, B, AB and C species respectively. These variables are related through the equations in Table II.

TABLE II

$$f_A = f_{AA} + f_{AB}$$

$$f_B = f_{BB} + f_{BA}$$

$$f_{AB} = f_{BA}$$

$$f_A + f_B = 1$$

$$\Phi_A + \Phi_B = \Phi_{AB}$$

$$f_A \, \Phi_{AB} = \Phi_A$$

$$f_B \, \Phi_{AB} = \Phi_B$$

$$\Phi_{AB} + \Phi_C = 1$$

In order to reduce the number of parameters, we have introduced the following simplifications: 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 to the average interaction parameter $\bar{\chi}_{AB}$. Additionally, in Table I it will be assumed for A—C interactions that $\bar{\chi}_{AC} \equiv \chi_{BAB,C} = \chi_{AAB,C} = \chi_{BAA,C} \neq \chi_{BBA,C}$ and similarly for the B—C interactions $\bar{\chi}_{BC} \equiv \chi_{ABA,C} = \chi_{BBA,C} = \chi_{ABB,C} \neq \chi_{BBB,C}$. Using these approximations, we then sum up all the interaction energies to obtain the free energy of the AB/C binary mixture, which contains the term $\Phi_{AB} \, \Phi_C \, \chi_{blend}$ where

$$\begin{aligned}
\chi_{blend} &= \chi_{comp} + \chi_{dist} \\
\chi_{comp} &= f_A \, \bar{\chi}_{AC} + f_B \, \bar{\chi}_{BC} - f_A \, f_B \, \bar{\chi}_{AB} \\
\chi_{dist} &= (f_{AA}{}^2/f_A) \, \Delta \chi_A + (f_{BB}{}^2/f_B) \, \Delta \chi_B \qquad (3) \\
\Delta \chi_A &\equiv \chi_{AAA:C} - \bar{\chi}_{AC} \\
\Delta \chi_B &\equiv \chi_{BBB:C} - \bar{\chi}_{CB}
\end{aligned}$$

Note that the composition dependence of χ_{blend} is just Eq. (2) and that consideration of the comonomer sequence distribution results in a correction to Eq. (2) that is denoted as χ_{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 the AAA—C interaction is less than all other A—C interactions. Similar comments apply to $\Delta \chi_B$.

It is convenient to introduce the parameters Θ and δ defined by:

$$f_{AB} = 2 \, \Theta \, f_A \, f_B \qquad (4)$$

$$f_A = ½ \, (1 + \delta); \; f_B = ½ \, (1 - \delta); \; -1 \leq \delta \leq 1 \qquad (5)$$

If $f_B \leq f_A$, then the maximum value of f_{AB} equals f_B. Thus the maximum value of Θ is

$$\Theta_{max} = (1 + | \, \delta \, |)^{-1} \qquad (6)$$

For a symmetric copolymer ($\delta = 0$), $\Theta_{max} = 1$; this describes an alternating copolymer. More generally

$0 \leq \Theta < 1/2$ »blocky« copolymer

$\Theta = 1/2$ random copolymer

$1/2 < \Theta \leq \Theta_{\max}$ copolymer containing »alternating« patterns

Now, recalling that $f_{AA} = f_A - f_{AB}$ and $f_{BB} = f_B - f_{BA}$, $(f_{AB} = f_{BA})$, χ_{dist} can be rewritten in terms of Θ and δ:

$$\chi_{dist} = {}^1\!/_2\,(1 - \delta)\,[1 - \Theta\,(1 - \delta)]^2\,\Delta\chi_A + {}^1\!/_2\,(1 - \delta)\,[1 - \Theta\,(1 + \delta)]^2\,\Delta\chi_B \tag{7}$$

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

$$\Theta_c = \frac{\Delta\chi_A + \Delta\chi_B}{(1 + \delta)\,\Delta\chi_B + (1 - \delta)\,\Delta\chi_A} = \frac{1}{1 + \delta\left[\dfrac{1 - R}{1 + R}\right]} \tag{8}$$

with

$$R \equiv \Delta\chi_A/\Delta\chi_B$$

When $f_B \leq f_A$ (δ is positive), and R is negative and $|R| < 1$, then an extremum always appears in χ_{dist} in $[0, \Theta_{\max}]$ and there exists the possibility of a window of miscibility or immiscibility. When $R > 0$ or when $R < 0$ but $|R| > 1$, then χ_{dist} is a monotonic function of Θ on $[0, \Theta_{\max}]$.

A case of special interest for the AB/C system is where C is A or B. This mixture may prove to be a more experimentally accessible system. In this example, a unique energy is assigned only to the triplet pairs (AAA—BBB) and (ABA—BAB): $\chi_{AAA,BBB}$ for the former and $\chi_{BAB,ABA}$ for the latter. The remaining 14 pairs of A—B interactions are assumed to be equivalent to $\bar{\chi}_{AB}$ and as above, the A—A and B—B interactions are assumed to be zero. When all the triplet probabilities are calculated and the terms are collected, the total expression for the energy of interaction for the AB/A system can be expressed as $\Phi_A'\,\Phi_{AB}\,\chi_{blend}$ where:

$$\chi_{blend} = \chi_{comp} + \chi_{dist} \tag{9}$$

$$\chi_{comp} = \bar{\chi}_{AB}\,(f_B^2) \tag{10}$$

$$\chi_{dist} = \Delta\chi^b\,(f_{BB}/f_B)\,(1 - \frac{f_{AA}^2}{f_A}) + \Delta\chi^a\,\frac{f_{AB}^4}{f_A\,f_B} \tag{11}$$

$$\Delta\chi^b = \chi_{AAA,BBB} - \bar{\chi}_{AB} \tag{12}$$

$$\Delta\chi^a = \bar{\chi}_{AB} - \chi_{BAB,ABA} \tag{13}$$

The »a« and »b« superscripts on $\Delta\chi$ refer to alternating and block sequences, respectively. The variables Φ_A' and Φ_{AB} refer to the volume fractions of homopolymer A and copolymer AB, respectively.

We note that the positive coefficient multiplying $\Delta\chi^a$ varies monotonically as Θ^4, however, the positive coefficient multiplying $\Delta\chi^a$ is a more complicated quartic function of Θ and thus may exhibit an extremum or extrema on $[0, \Theta_{\max}]$. Consequently, we predict that windows of miscibility or immiscibility can potentially be observed with AB/A blends as a function of chain microstructure. Notice that an analogous set of equations are obtained for the AB/B system by interchanging the A and B indices.

This model may also be applied to a mixture of two copolymers that differ only in polymer composition. The free energy of mixing for a mixture of these two copolymers is given by[6]

$$\Delta G/RT = (\Phi_{AB}/N) \ln \Phi_{AB} + (\Phi_{AB}'/N') \ln \Phi_{AB}' + \Phi_{AB}\, \Phi_{AB}' (f_A - g_A)^2\, \chi_{AB} \tag{14}$$

where Φ_{AB} is the volume fraction of one copolymer with degree of polymerization N and composition f_A, while $\Phi_{AB'}$ is the volume fraction of the other copolymer with degree of polymerization N' and composition g_A. The free energy is again identical with the usual Flory-Huggins one, when we now make the following identification:

$$\chi_{\text{blend}} \equiv (f_A - g_A)^2\, \chi_{BA} \tag{15}$$

We will consider a binary mixture of two copolymers with compositions f_A and g_A but as in the previous example, we now assume that the interaction energy for an A—B pair is influenced by the units that are chemically bound to A (and B). Consequently, all the possible pairs of triplets, with A or B occupying the central site, must be enumerated. Again, the probability of occurrence for each specific triplet is calculated and an energy is assigned to each A—B interaction. As before, to reduce the large number of χ parameters required to properly describe the energetics, we make the following simplifications: it will be assumed that all A—A and B—B interactions are equivalent and equal to zero. Although there are 16 possible A—B interactions, a unique energy is assigned only to the triplet pairs (AAA—BBB) and (BAB——ABA): $\chi_{AAA;BBB}$ for the former and $\chi_{BAB;ABA}$ for the latter. The remaining 14 pairs of A—B interacting triplets are assigned an average value of $\bar{\chi}_{AB}$. As noted above, the required pair probabilities f_{AB}, f_{BB} and f_{AA} are the joint probabilities of AB, BB, and AA pairs; Φ_A and Φ_B are the volume fractions of A and B comonomers for the copolymer with composition f_A. The relation between these variables is identical to that given in Table II, however, now $\Phi_{AB} + \Phi_{AB'} = 1$. An identical set of relationships applies to the g_A and g_B variables with $\Phi_{A'} + \Phi_{B'} = \Phi_{AB'}$.

When we have calculated the probability of all the possible triplet interactions,[9] and have collected all the terms, the total expression for the energy of interaction can be written as $\Phi_{AB}\, \Phi_{AB'}\, \chi_{\text{blend}}$, where

$$\chi_{\text{blend}} = \chi_{\text{comp}} + \chi_{\text{dist}} \tag{16}$$

$$\chi_{\text{comp}} = \bar{\chi}_{AB} (f_A - g_A)^2 \tag{17}$$

$$\chi_{\text{dist}} = \frac{g_{AB}^2}{g_B} - \frac{f_{AB}^2}{f_B} \quad \frac{g_{AB}^2}{g_A} - \frac{f_{AB}^2}{f_A} \Delta\chi^a + \frac{g_{BB}^2}{g_B} - \frac{f_{BB}^2}{f_B} \quad \frac{f_{AA}^2}{f_A} - \frac{g_{AA}^2}{g_A} \Delta\chi^b \tag{18}$$

where

$$\Delta\chi^a \equiv \bar{\chi}_{AB} - \chi_{BAB,ABA} \tag{19}$$

and

$$\Delta\chi^b \equiv \chi_{AAA,BBB} - \chi_{AB} \tag{20}$$

The "a" and "b" superscripts on $\Delta\chi$ refer to "alternating" and "block" sequences, respectively. Since it is expected that $\chi_{AAA;BBB} > \overline{\chi}_{AB} > \chi_{BAB;ABA}$ or $\chi_{AAA;BBB} < \overline{\chi}_{AB} < \chi_{BAB;ABA}$, $\Delta\chi^a$ and $\Delta\chi^b$ should almost always have the same sign.

RESULTS AND DISCUSSION

Figures 1. and 2. show plots of χ_{blend} versus Θ (χ_{comp} is a constant that when added to χ_{dist} to yield χ_{blend} will just shift this figure up or down with respect to the $\chi_{dist} = 0$ axis). In what follows, it is assumed that the polymers involved are of high molecular weight, thus a negative χ_{blend} indicates blend miscibility, whereas a positive χ_{blend} describes immiscibility. The convex form of χ_{blend} in Figure 1. corresponds to a window of miscibility; for the range of Θ values which yield a negative χ, the polymers are miscible and form a single phase (here $\Delta\chi_A + \Delta\chi_B > 0$). The concave form of χ_{blend} corresponds to an immiscibility window: for the range of values which result in a positive χ_{blend}, the polymers are immiscible and separate into two phases (here $\Delta\chi_A + \Delta\chi_B < 0$). In Figure 2., χ_{blend} is a monotonic function of Θ; either the block (if $f_A\,\Delta\chi_A + f_B\,\Delta\chi_B < 0$) or the alternating of ($f_A\,\Delta\chi_A + f_B\,\Delta\chi_B > 0$) copolymer will have the most stable value of χ_{blend}.

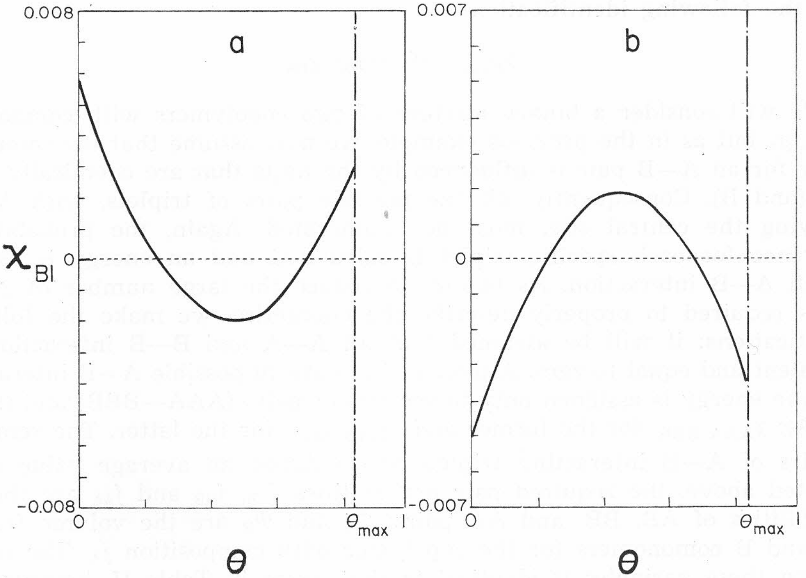

Figure 1. χ_{blend} versus Θ. Here $f_A = 0.6$, $f_B = 0.4$ and $\Theta_{max} = 0.833$. In both figures, $R < 0$ and $|R| < 1$. In (a), where $\Delta\chi_A = -0.088$ and $\Delta\chi_B = 0.125$ (thus the sum is positive), this results in a window of miscibility ($\chi_{comp} = 0.0117$). In (b), $\Delta\chi_A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

The general expression in equation (14) has been used to examine the following special cases: (1) a blend of a 50 : 50 alternating copolymer with a 50 : 50 random copolymer (same composition, different microstructure) and (2) two random copolymers (same microstructure) that differ only in compo-

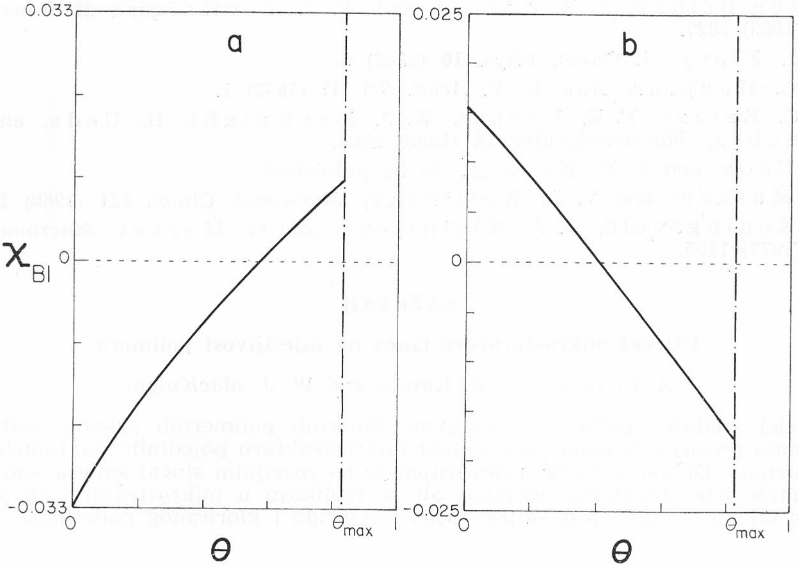

Figure 2. χ_{blend} versus Θ, $f_A = 0.6$, $f_B = 0.4$ and $\Theta_{\text{max}} = 0.833$. Here, $R < 0$ but $|R| > 1$ and χ_{blend} is a monotonic function of Θ. In Fig. (a), $\Delta\chi_A = -0.1140$ and $\Delta\chi_B = 0.0390$, thus the blocky copolymer is most stable ($\chi_{\text{comp}} = 0.0194$). For (b) $\Delta\chi_A = 0.1440$ and $\Delta\chi_B = 0.1030$, consequently, the alternating copolymer is most stable ($\chi_{\text{comp}} = -0.0277$).

siton.[9] Specifically, by comparing the equation obtained in case (1) to recent experimental observations on CPE and PVC,[10] we have been able to calculate $\Delta\chi^a$, $\Delta\chi^b$ and χ_{blend} for the CPE/PVC system.[9] In addition it should be noted that the CPE/PVC system is particularly appropriate for the present analysis because it contains repeat units with similar interacting surface areas. If in fact the repeat units were of differing molecular surface areas, a consideration of these differences might be necessary to quantitatively account for the observed effects.

In summary, we have theoretically shown that any immiscible copolymer/homopolymer system may be made miscible by varying the sequence distribution in the copolymer. Moreover, we have indicated[9] how this theory can be applied to experimental data to extract values for the important χ parameters.

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SAŽETAK

Utjecaj mikrosturkture lanca na mješljivost polimera

A. C. Balazs, F. E. Karasz and W. J. MacKnight

Model srednjeg polja za mješljivost binarnih polimernih sustava statističkih kopolimera proširen je uzimajući u obzir mikrostrukturu pojedinih makromolekulnih konstituenata. Dobiveni model primijenjen je na specijalni slučaj smjesa kopolimera koje sadrže iste strukturne jedinice, ali se razlikuju u mikrostrukturi ili sastavu. Primjer takvog sustava jest smjesa polivinilklorida i kloriranog polietilena.