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Notes

Effect of Sequence Distribution on the Critical Composition Difference in Copolymer Blends

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Introduction

Since the early theoretical work of Scott,[1] it has been known that two statistical AB copolymers, which have the same chain length but differ in composition, are not necessarily miscible in all proportions. Scott predicted that binary copolymer mixtures would be characterized by a maximum tolerable difference in chemical composition (in the following denoted by Δ) beyond which they are only partly miscible. This conclusion was experimentally verified by Molau[2] and Locatelli and Riess[3] for copolymers of styrene and acrylonitrile (SAN) and by Kollinsky and Markert[4,5] for various acrylic copolymers. However, the latter work also revealed that Δ depends on the chemical composition of one of the two copolymers in the mixture. This feature cannot be explained by Scott's theoretical analysis. However, it can be dealt with in a qualitatively correct way if the different constitutional repeat units are assigned different interacting surface areas.[6] In this way, if the B unit in a given copolymer can make more nearest-neighbor contacts per site than its A unit, we expect Δ to decrease with increasing A content. If, however, less contacts per site are possible, then Δ will increase with increasing A content. Calculations for different interacting surface area ratios show Δ to depend almost linearly on the composition of one of the copolymers in the mixture.[7] However, from the work of Kollinsky and Markert, it is clear that large deviations from linearity are possible, a behavior that remains unexplained by previous theories. In this paper, we will show that it is possible to explain these deviations from linearity by introducing sequence distribution effects. The starting point is the model developed by Balazs et al.,[8,9] which, for a copolymer of fixed composition, can examine the effects of sequence distribution on both copolymer/homopolymer[8] and copolymer/copolymer[9] miscibility.

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Theory

Consider a mixture of two copolymers that differ in composition, one containing f_A units of comonomer A and f_B units of comonomer B ($f_A + f_B = 1$) and the other g_A units of A and g_B units of B ($g_A + g_B = 1$). The free energy of mixing for this mixture is given by

$$\Delta G/RT = (\phi_1/N_1) \ln \phi_1 + (\phi_2/N_2) \ln \phi_2 + \phi_1\phi_2\chi_{\mathrm{blend}} \tag{1}$$

where ϕ_1 is the volume fraction of one copolymer with degree of polymerization N_1 and composition f_A, while ϕ_2 is the volume fraction of the other copolymer with degree of polymerization N_2 and composition g_A ($\phi_1 + \phi_2 = 1$). This free energy is identical with the usual Flory–Huggins one if we identify χ_{blend} as

$$\chi_{\mathrm{blend}} \equiv (f_A - g_A)^2\chi_{AB}$$

However, in our model, we assume that the interaction energy for a given A–B pair is influenced by the units that are chemically bound to A (and B). As a consequence, all possible pairs of triplets with A or B occupying the central site have to be enumerated. The probability of occurrence of each specific triplet has to be calculated and an energy has to be assigned to each specific A–B interaction. To reduce the large number of χ parameters required to properly describe the energetics, some simplifications have to be introduced. First, it will be assumed that all A–A and B–B interactions are equivalent and equal to zero. Second, although there are 16 possible A–B interactions, a unique energy is assigned only to triplet pairs (AAA–BBB) and BAB–ABA): $\chi_{\mathrm{AAA;BBB}}$ and $\chi_{\mathrm{BAB;ABA}}$, respectively. The remaining 14 pairs of A–B interacting triplets are assigned an average value of $\bar{\chi}_{AB}$. The required pair probabilities f_{AB}, f_{BB}, and f_{AA} are the joint probabilities of AB, BB, and AA pairs. After enumerating all possible pairs of triplets and collecting all energy terms, we find that the energy of interaction can be written as $\phi_1\phi_2\chi_{\mathrm{blend}}$, where[9]

$$\chi_{\mathrm{blend}} = \chi_{\mathrm{comp}} + \chi_{\mathrm{dist}} \tag{2}$$

with

$$\chi_{\mathrm{comp}} = \bar{\chi}_{AB}(f_A - g_A)^2 \tag{3}$$

$$\chi_{\mathrm{dist}} = \left[\left(\frac{g_{AB}^2}{g_B} - \frac{f_{AB}^2}{f_B}\right)\left(\frac{g_{AB}^2}{g_A} - \frac{f_{AB}^2}{f_A}\right)\right]\Delta\chi^a + \left[\left(\frac{g_{BB}^2}{g_B} - \frac{f_{BB}^2}{f_B}\right)\left(\frac{f_{AA}^2}{f_A} - \frac{g_{AA}^2}{g_A}\right)\right]\Delta\chi^b \tag{4}$$

$$\Delta\chi^a = \bar{\chi}_{AB} - \chi_{\mathrm{BAB;ABA}} \tag{5}$$

$$\Delta\chi^b = \chi_{\mathrm{AAA;BBB}} - \bar{\chi}_{AB} \tag{6}$$

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

We note that when sequence distribution effects are ignored, all the χ's have the same value, namely, $\bar{\chi}_{AB}$, and thus, $\Delta\chi^a = \Delta\chi^b = 0$. In this limit, χ_{blend} reduces to χ_{comp} (eq 3), the expression previously derived by Scott[1] and more recently discussed by ten Brinke et al.[10]

Since we are interested in the critical composition difference, Δ, in a binary copolymer mixture, we must consider the spinodal condition, which is given by

$$\frac{\partial^2(\Delta G/NRT)}{\partial\phi_1\partial\phi_2} = \frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2} - 2\chi_{\mathrm{blend}} = 0 \tag{7}$$

Substituting eq 2 and 3 into eq 7 we find:

$$(f_A - g_A)^2 = \frac{1}{2\bar{\chi}_{AB}}\left(\frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2} - 2\chi_{\mathrm{dist}}\right) \tag{8}$$

If $\chi_{\mathrm{dist}} = 0$, eq 8 reduces to the equation obtained by Scott.[1]

As in our previous calculations,[9] we introduce the order parameter θ defined by

$$f_{AB} = 2\theta f_A f_B \tag{9}$$

The condition $0 \leq \theta < {}^1/_2$ describes a "blocky" copolymer, while $\theta = {}^1/_2$ describes a random copolymer and ${}^1/_2 < \theta \leq \theta_{\max}$ describes an "alternating" copolymer. Replacing all joint probabilities f_{AA}, f_{AB}, f_{BB}, etc. in χ_{dist} by use of eq 9, we find:

$$(f_A - g_A)^2 = \frac{1}{2\bar{\chi}_{AB}}\left(\frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2} - 32\Delta\chi^a(\theta_2^2 g_A^2 g_B - \theta_1^2 f_A^2 f_B)(\theta_2^2 g_A g_B^2 - \theta_1^2 f_A f_B^2) - 32\Delta\chi^b(\theta_2^2 g_B^3 - \theta_1^2 f_B^3)(\theta_1^2 f_A^3 - \theta_2^2 g_A^3)\right) \tag{10}$$

By solving this equation for a given set of values for ϕ_1, N_1, ϕ_2, N_2, θ_1, θ_2, $\bar{\chi}_{AB}$, $\Delta\chi^a$, and $\Delta\chi^b$, we can find for each input value f_A one or more critical values g_A at which phase separation will take place. This allows us to plot $|f_A - g_A|_{\mathrm{crit}} \equiv \Delta$ versus f_A or g_A.

Results and Discussions

In what follows, we only consider random (or statistical) copolymers ($\theta_1 = \theta_2 = {}^1/_2$) since only this case is of direct relevance to Scott's theoretical work, as well as to all available experimental data. In addition, this calculation emphasizes the importance of the sequence-dependent χ's, $\Delta\chi^a$ and $\Delta\chi^b$. We have solved eq 10 for different sets of values for the χ's. The values chosen for $\Delta\chi^a$ and $\Delta\chi^b$ are well within the range of values that were obtained for these variables when eq 2–4 were applied to recent experimental data.[9] Results for 1:1 mixtures of copolymers with equal degrees of polymerization $N_1 = N_2 = 1000$ are given in Figures 1 and 2. Both figures are symmetrical, which is to be expected with two random copolymers where χ_{dist} is invariant under the interchange $f \leftrightarrow g$. Figure 1 shows the normal Scott behavior: Δ assumes a constant value, which equals

$$\left(\frac{1}{2\bar{\chi}_{AB}}\right)^{1/2}\left(\frac{1}{N_1\phi_1} + \frac{1}{N_2\phi_2}\right)^{1/2} \tag{11}$$

Figure 2, however, shows a totally different behavior. Here, Δ is no longer a constant, nor is it a linear function of the composition of one of the copolymers. As can be seen in the figure, Δ passes through a minimum value. This behavior closely resembles experimental trends found by Kollinsky and Markert.[4] These preliminary results show that sequence distribution effects may be very important in understanding copolymer/copolymer miscibility. Specifically, by including the effects of sequence distribution on χ, the energy of interaction, our model has been able to reproduce the experimentally observed nonlinear behavior of Δ.

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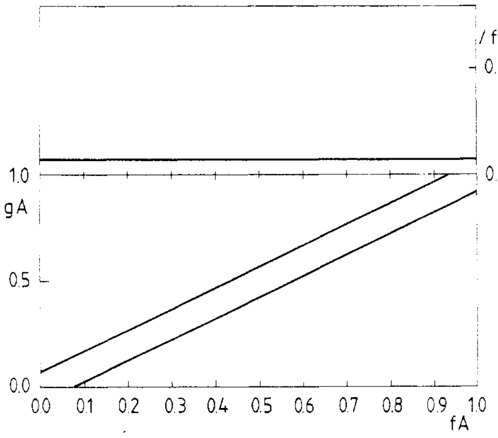

Figure 1. Critical composition difference, $|f_A - g_A|$, is plotted against f_A in the upper region of the figure. The lower region displays g_A versus f_A where the values of g_A are obtained from solving eq 10 for fixed values of the relevant χ's, ϕ_1, N_1, ϕ_2, N_2, θ_1, and θ_2 and f_A. In particular, we examined a 1:1 mixture ($\phi_1 = \phi_2 = 0.5$) of random copolymers ($\theta_1 = \theta_2 = 0.5$) with equal degrees of polymerization ($N_1 = N_2 = 1000$) and $\bar{\chi}_{AB} = 0.3$, $\Delta\chi^a = 1.1$, and $\Delta\chi^b = 0.1$.

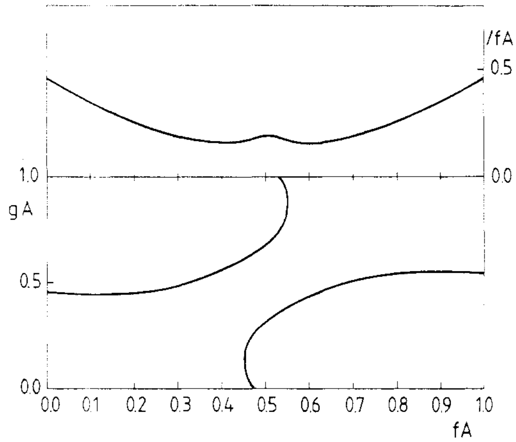

Figure 2. Same as for Figure 1, but with $\bar{\chi}_{AB} = -0.3$, $\Delta\chi^a = 0.5$, and $\Delta\chi^b = 0.7$.

Further work is necessary in order to describe copolymer/copolymer miscibility quantitatively. In particular, we plan to examine eq 10 for various values of the order parameter θ. However, it is now clear that sequence distribution effects may play a major role in determining the miscibility of copolymer mixtures.

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Convenient Synthesis of 2,4,6-Trichloroheptane, the Trimer Model of Poly(vinyl chloride)

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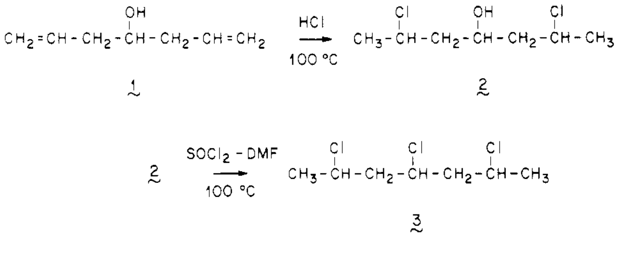
Introduction

For many years 2,4,6-trichloroheptane (**3**) has been employed as a model for poly(vinyl chloride) (PVC) in studies of physical properties. These investigations have included analyses of the vibrational spectra in order to examine the effect of stereochemical structure on conformation,[1-3] stereochemical equilibration to test the theory based on conformational energy calculations,[4-6] interpretations of the NMR spectra based on conformational calculations,[1,7] determinations of molar Kerr constants and dipole moments,[8] the study of transfer reactions involving secondary halogens,[9] and kinetic studies of the tri-*n*-butyltin hydride reductive dechlorination.[10]

The standard synthesis of **3** is a very cumbersome procedure with a yield of <10%.[9] This method involves the hydrogenation of 2,4,6-heptanetrione in the presence of Raney nickel catalyst at a pressure of 140–160 atm. and at 105 °C. The resultant triol is converted to the model trichloride by reaction with thionyl chloride. The combination of the poor yield and the necessity of using a pyrophoric catalyst under vigorous conditions makes this a less than desirable synthetic route.

Some improvements in the above synthesis have been reported. The use of sodium borohydride in the reduction step eliminates the need for high pressures but results in a triol yield of only ~12%.[11] The catalytic hydrogenation of the trione using a nonpyrophoric ruthenium catalyst has also been suggested.[7] In the chlorination of the triol the use of the Vilsmeier reagent, dimethylchloromethyleneammonium chloride, has been found to be more effective than is thionyl chloride.[3] Despite these improvements, the synthesis remains difficult and the yield is unsatisfactory. In order to obtain reasonable quantities of **3** for use in various investigations,[7,8,10] we have developed a new two-step synthetic route using a commercially available starting material, 1,6-heptadien-4-ol (**1**), which results in an acceptable yield of **3**.



Experimental Section

2,6-Dichloro-4-heptanol (2) was prepared by the hydrochlorination of 1,6-heptadien-4-ol (**1**) (Aldrich) with HCl. **1** (0.015 mol) was placed in a 200-mL Wheaton pressure bottle.[12] HCl (0.03 mol) was condensed into the pressure bottle at −98 °C. The rubber seal was closed and the mixture brought to room temperature. The bottle was then placed in an oil bath behind a shield and heated to 100 °C for 20 h with stirring. The pressure within the reaction vessel was calculated to be ~5 atm. After slow cooling to −98 °C to condense residual HCl, the bottle was opened and the dark brown solution poured into a collection flask. The hydrochlorination step was carried out several times due to the limited volume of the reaction vessel but could be scaled up for a larger vessel.

The combined product of several runs was diluted with a 5-fold volume of ether. The solution was then extracted 3 times with

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