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Registry No. (BIS)·(MAPTAC)·(acrylamide) (copolymer), 98587-56-5; (BIS)·(SSS) (copolymer), 91293-65-1; acetone, 67-64-1; water, 7732-18-5.

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Copolymer/Copolymer Blends: Effect of Sequence Distribution on Miscibility

In a previous paper,[1] we have discussed the effect of the sequence distribution of monomer units in a copolymer on the phase behavior of copolymer/homopolymer blends. Our model yielded an improvement to Flory–Huggins type theories for mixturs involving copolymers in that it was possible to make a distinction between the copolymer types (random, block, etc.) participating in the mixture. This was accomplished by introducing a parameter, Θ, which described the binary sequence distribution of the monomers in the copolymer. By varying Θ, we could describe a block, random, or alternating copolymer. Further, we 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. We showed that for a fixed composition, there is an optimal range of Θ values (or sequence distributions) for which the AB/C system may be miscible.

In this communication, we apply the above model to the mixture of two copolymers that differ only in composition, one containing f_A units of A comonomer and f_B units of B comonomer ($f_A + f_B = 1$) and the other g_A units of A and g_B units of B ($g_A + g_B = 1$). A special case of interest is where both copolymers have the same composition ($f_A = g_A$) and differ only in the sequence distribution of their monomers. An interesting question is: Are there circumstances under which these polymers are immiscible? Experimentally it is known that blends of PVC and chlorinated polyethylene (CPE) are immiscible even when the CPE has the same Cl content as PVC.[2] In this context, CPE may be considered as a random copolymer of CH_2 ($\equiv$A) and CHCl ($\equiv$B), while PVC is the alternating copolymer composed of these units.

The theoretical formulations presented below will be compared to recent experimental observations of the phase behavior of blends of CPE.[2] It will be shown that these data allow the determination of the various interaction parameters required by theory.

The Model. The free energy of mixing for a mixture of two copolymers that differ only in polymer composition is given by[3]

$$\Delta G/RT = (\phi_{AB}/N)\ln\phi_{AB} + (\phi_{AB}'/N')\ln\phi_{AB}' + \phi_{AB}\phi_{AB}'(f_A - g_A)^2\chi_{AB} \quad (1)$$

where ϕ_{AB} is the volume fraction of one copolymer with degree of polymerization N and composition f_A, while ϕ_{AB}' is the volume fraction of the other copolymer with degree of polymerization N' and composition $g_A(\phi_{AB} + \phi_{AB}' = 1)$. This free energy is identical with the usual Flory–Huggins one, when the following identification is made:

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

Here, we will consider a binary mixture of two copolymers with compositions f_A and g_A but assume that the interaction energy for an A–B pair is influenced by the units that are chemically bound to A (and B). This requires that all the possible pairs of triplets, with A or B occupying the central site, be enumerated. Next, the probability of occurrence for each specific triplet is calculated and an energy is assigned to each A–B interaction. To reduce the large number of χ parameters required to properly describe the energetics, the following simplifications are introduced: 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 $\bar{\chi}_{AB}$. 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. These variables are related as follows:

$$\begin{gathered} f_A = f_{AA} + f_{AB}; \qquad f_B = f_{BB} + f_{BA}; \qquad f_{AB} = f_{BA} \\ f_A + f_B = 1; \qquad \phi_A + \phi_B = \phi_{AB} \qquad (3) \\ f_A\phi_{AB} = \phi_A; \qquad f_B\phi_{AB} = \phi_B \end{gathered}$$

An identical set of relationships apply to the g_A and g_B variables with $\phi_A' + \phi_B' = \phi_{AB}'$.

The probability of the AAA triplet of the f_A copolymer interacting with the BBB triplet of the g_A copolymer is given by the probability of the AAA configuration, $\phi_A(f_{AA}/f_A)^2$, times the probability of the BBB configuration, $\phi_B'(g_{BB}/g_B)^2$, which yields

$$\phi_{AB}\phi_{AB}'(f_{AA}g_{BB})^2/f_Ag_B \quad (4)$$

Similarly, the probability of a BAB triplet interacting with an ABA triplet is

$$\phi_{AB}\phi_{AB}'(f_{AB}g_{AB})^2/f_Ag_B \quad (5)$$

On the other hand, an AAA–BBB triplet interaction involving the same f_A copolymer is given by

$$(1 - \phi_{AB}')\phi_{AB}(f_{AA}f_{BB})^2/f_Af_B \quad (6)$$

and a BAB–ABA triplet interaction is given by

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$$(1 - \phi_{AB}')\phi_{AB}f_{AB}^4/f_Af_B \tag{7}$$

Of course, relations identical with (6) and (7) apply for triplet interactions involving the g_A copolymer (replace f by g).

As previously stated,[1] it is important to note that the term linear in the volume fraction variable ϕ_{AB} is not important in determining phase stability or equilibria and is ignored. Hence the terms in χ_{blend} arising from the copolymer self-interactions, relations 6 and 7, enter with a minus sign.

Collecting all terms, the total expression for the energy of interaction can be written as $\phi_{AB}\phi_{AB}'\chi_{blend}$, where

$$\chi_{blend} = \chi_{comp} + \chi_{dist} \tag{8}$$

$$\chi_{comp} = \bar{\chi}_{AB}(f_A - g_A)^2 \tag{9}$$

$$\chi_{dist} = \left[\left(\frac{g_{AB}^2}{g_B} - \frac{f_{AB}^2}{f_B}\right)\left(\frac{g_{AB}^2}{g_A} - \frac{f_{AB}^2}{f_A}\right)\right]\Delta\chi^a + \left[\left(\frac{g_{BB}^2}{g_B} - \frac{f_{BB}^2}{f_B}\right)\left(\frac{f_{AA}^2}{f_A} - \frac{g_{AA}^2}{g_A}\right)\right]\Delta\chi^b \tag{10}$$

where

$$\Delta\chi^a \equiv \bar{\chi}_{AB} - \chi_{BAB;ABA} \tag{11}$$

and

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

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

As in the previous calculation,[1] we introduce the parameters Θ and δ defined by

$$f_{AB} = 2\Theta f_Af_B \tag{13}$$

$$f_A = \tfrac{1}{2}(1 + \delta); \qquad f_B = \tfrac{1}{2}(1 - \delta); \qquad -1 \le \delta \le 1 \tag{14}$$

A block copolymer corresponds to $\Theta = 0$, a random copolymer is described by $\Theta = {}^1/_2$, and $\Theta = 1$ describes a purely alternating copolymer. The maximum value of Θ is given by[1]

$$\Theta_{max} = (1 + |\delta|)^{-1} \tag{15}$$

Using eq 3, 13, and 14, one can express as functions of Θ and δ all pair probabilities such as f_{AA}, f_{BB}, etc.

Results and Discussion. A special case of the above equations is a blend of a 50:50 alternating copolymer ($\delta = 0$ and $\Theta = 1$) with a 50:50 random copolymer ($\delta' = 0$ and $\Theta' = {}^1/_2$). For this system $\chi_{comp} = 0$, but

$$\chi_{dist} = (9\Delta\chi^a - \Delta\chi^b)/64 \tag{16}$$

There are no AAA–BBB interactions possible between the alternating and random copolymers; they are only possible when a random copolymer interacts with another random copolymer. On the other hand, BAB–ABA interactions are possible among all of the copolymers. This preference for interactions involving alternating over blocky ones is reflected in eq 16; the coefficient of the $\Delta\chi^a$ term is 9 times larger than that of the $\Delta\chi^b$ term. It is also obvious that χ_{dist} (and thus χ_{blend}) may be positive, which suggests that it is possible for alternating and random copolymers with the same composition ($f_A = g_A$) to be immiscible.

Two specific cases of eq 16 yield further insight into the physics described by this equation. In the first case, $\Delta\chi^a = 0$, $\Delta\chi^b$ is positive, and χ_{blend} is negative, which implies that the blend is miscible. Here, $\chi_{AAA;BBB} > \bar{\chi}_{AB}$ and the presence of the alternating copolymer dilutes the energetically unfavorable "blocky" interactions. In the second case, we set $\Delta\chi^b = 0$ and let $\Delta\chi^a$ be positive, which yields an immiscible mixture. Here, $\bar{\chi}_{AB} > \chi_{BAB;ABA}$ and the presence of the random copolymer acts to dilute the favorable interactions among alternating triplets. As previously reported,[3-5] we again see how the presence of a second component can mediate between unfavorable or favorable interactions.

Another special case of interest is a mixture of two random copolymers ($\Theta = \Theta' = {}^1/_2$) that only differ in composition ($\delta \neq \delta'$). In this case, $f_{AA} = f_A^2$, $f_{BB} = f_B^2$, $f_{AB} = f_Af_B$, etc. and eq 10 becomes

$$\chi_{dist} = (g_Bg_A^2 - f_Bf_A^2)(g_Ag_B^2 - f_Af_B^2)\Delta\chi^a + (f_A^3 - g_A^3)(g_B^3 - f_B^3)\Delta\chi^b \tag{17}$$

Notice that χ_{dist} is invariant under the interchange $f \leftrightarrow g$, as it should be.

The values of $\Delta\chi^a$ and $\Delta\chi^b$ can be obtained directly by applying our model to recent experimental observations. For mixtures of two polymers of CPE with different compositions, experiments[2] have yielded the critical compositions at 150 °C for which $\chi_{blend} = \chi_{crit}$. Knowing these critical values of f_A, f_B, g_A, and g_B, we can calculate the critical values of f_{AB}, f_{AA}, f_{BB}, g_{AB}, g_{AA}, and g_{BB}. (We have ignored the small fraction of CCl_2 moieties in the mixture, which is an order of magnitude smaller than the CHCl content.) Consequently, the only remaining unknowns are $\bar{\chi}_{AB}$, $\chi_{AAA;BBB}$, and $\chi_{BAB;ABA}$. These are easily obtained from a linear least-squares fit of the "apparent", observed values of $\chi_{CH_2;CHCl}$ through the following equations:

$$\chi_{blend}(\text{exptl}) = (f_A - g_A)^2\chi_{CH_2;CHCl}(\text{apparent}) \tag{18a}$$

$$= (f_A - g_A)^2\bar{\chi}_{CH_2;CHCl} + \chi_{dist} \tag{18b}$$

$$\chi_{CH_2;CHCl}(\text{apparent}) = \bar{\chi}_{CH_2;CHCl} + \chi_{dist}/(f_A - g_A)^2 \tag{18c}$$

In the initial regression of the data, $\bar{\chi}_{AB}$ ($A \equiv CH_2$, $B \equiv CHCl$) was found not to be significantly different from zero; therefore, a subsequent regression was performed with $\bar{\chi}_{AB}$ set identically equal to zero. This yielded the following values for the remaining variables: $\chi_{AAA;BBB} = 0.37 \pm 0.03$ and $\chi_{BAB;ABA} = -4.34 \pm 0.40$. The large negative value of $\chi_{BAB;ABA}$ implies that an alternating pattern of CH_2, CHCl is energetically more favorable than a random distribution of these substituents. Considering the hydrogen bonds that are encountered in PVC, this result seems intuitively correct. With these numbers for the χ's, Table I shows the predicted values for $\chi_{CH_2;CHCl}$, which can be compared to the experimental data in the adjacent column. The overall agreement between the predicted and observed values is within ±0.05.

We now have an insight into the fact that the "apparent" $\chi_{CH_2;CHCl}$ varies with the degree of chlorination.[2] More than one χ parameter is required to describe the CH_2–CHCl interaction. It can be seen from eq 8–12 and the calculation just performed that while the values of these χ's remain constant, it is the factors mulitptying the χ's that change as the copolymer compositions in the mixutre are altered. Specifically, the factors multiplying $\Delta\chi^a$ and $\Delta\chi^b$ (f_{AB}, f_{BB}, f_{AA}, etc.) vary with varying f_A, f_B, g_A, and g_B. The variation in these factors contributes to the variation of the observed χ with the degree of chlorination even though $\bar{\chi}_{AB}$, $\chi_{AAA;BBB}$, and $\chi_{BAB;ABA}$ are constants.

Having obtained these χ values, we can substitute the numbers into eq 16 to arrive at χ_{blend} for PVC and CPE of equivalent composition ($f_A = g_A = 0.5$). We calculate that χ_{blend} is 0.60, which indicates that the mixture is im-

Table I
Values of $\chi_{CH_2;CHCl}$ at Various Values of f_A and g_A and 150 °C

f_A	g_A	experimentally obsd	theoretically[a] calcd
0.690	0.766	0.42	0.32
0.678	0.759	0.36	0.30
0.665	0.754	0.30	0.27
0.652	0.749	0.25	0.25
0.639	0.743	0.22	0.23
0.625	0.737	0.19	0.20
0.595	0.727	0.14	0.16
0.564	0.721	0.10	0.12
0.530	0.715	0.069	0.085
0.493	0.711	0.050	0.056
0.453	0.707	0.037	0.033
0.410	0.703	0.028	0.020
0.363	0.685	0.023	0.0089
0.338	0.644	0.025	−0.0018
0.312	0.473	0.091	0.053
0.285	0.416	0.14	0.13
0.257	0.384	0.15	0.20
0.227	0.360	0.14	0.27

[a] These quantities are calculated by using eq 18c. The overall agreement between the calculated and observed values is within ±0.05.

miscible, as experimentally observed.[2]

Summary. Applying our previous model of the effect of sequence distribution in AB/C systems to AB/AB blends, we have shown that even in mixtures where the copolymers differ only in chain microstructure, the effect of sequence distribution may be sufficiently large as to make the polymers incompatible. Comparing our formulas to recent experimental data has allowed us to obtain values for the relevant χ parameters. Using these two χ parameters, we have been able to obtain a good correlation between our predictions and experimental observations that vary over an order of magnitude in value. This gives us confidence that these χ values may be further used to predict other trends.

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Registry No. PVC (homopolymer), 9002-86-2.

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CORRECTIONS

Matthew T. Bishop, Frank E. Karasz,* Paul S. Russo, and Kenneth H. Langley: Solubility and Properties of a Poly(aryl ether ketone) in Strong Acids. Volume 18, Number 1, January 1985, p 86.

We wish to amend results reported in ref 1 for the interpretation of Zimm plots (Figure 3). The correct relations for molecular weights ($\bar{M}_w$) and second virial coefficients (A_2) of the sulfonated and unsulfonated (subscripts s and u, respectively) polymers relative to the apparent (subscript a) results are $(\bar{M}_w)_s = \beta(\bar{M}_w)_a$, $(\bar{M}_w)_u = (\bar{M}_w)_a$, and $(A_2)_s = \beta^{-2}(A_2)_a$, where $\beta = c_s/c_u$. The corrected values should be used in place of those given in lines 3, 4, and 6 in Table I.

The revised estimate of the persistence length of protonated, sulfonated PEEK is ~32 Å and that of expansion relative to freely rotating unmodified PEEK is ~1.6–1.9. This expansion of PEEK in concentrated H_2SO_4, which we still attribute primarily to relatively short-range steric and electrostatic interactions, is seen to be even *less* than previously estimated and further strengthens our essential conclusions.

We are grateful to Dr. E. Nield for sending us a preprint of ref 2, which drew our attention to the error.

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