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On the Distribution of Specific Intermolecular Interactions in Miscible Polymer Mixtures: An Equilibrium Model

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ABSTRACT: An equilibrium model is proposed which describes the distribution of specific intermolecular interactions in miscible polymer mixtures. The main premise of this model is that rather than obeying mean field statistics, intermolecular interactions in miscible polymer blends assume an equilibrium distribution, where the relative probability of an interaction is dependent upon its energy. Comparison with the experimental results obtained from Fourier transform infrared studies of several polymer blends capable of forming hydrogen bonds between the components shows that the model satisfactorily predicts the distribution of hydrogen bonds observed as a function of composition and temperature.

Introduction

A polymer blend is simply a physical mixture of two or more distinguishable polymeric species which may or may not form a single homogeneous phase. If a single phase is formed the blend is termed miscible. The conceptual model most frequently used to describe polymer mixing is the lattice theory developed independently by Flory[1,2] and Huggins.[3] The approach of this theory is essentially identical with regular solution theory, the differentiating factor for polymer mixtures being that the usual driving forces for mixing, thermal motion and probability, are abnormally low, at least on a volume basis. As a consequence, miscibility can only be anticipated in systems where the interactional energy of the mixed state outweighs the combined energy of the pure components, in other words, systems where ΔH_m is negative. In practice such systems are encountered infrequently. This is because the total intermolecular energy is usually dominated by dispersive interactions, where the energy of an unlike contact pair (w_{ij}) is approximately the geometric mean of the self-association energies of the pure components. In general, ΔH_m can be negative only if there exist strong, nondispersive interactions such as hydrogen bonds between the blend components. This led Kraus[4] to emphasize that: "It is best to expect odd instances of compatibility between polymers, outside the scope of the Flory–Huggins theory, whenever hydrogen bonding is possible".

The above discussion, of course, is simplistic for two major reasons. First, it ignores the equation of state contributions,[5] which most certainly exert a strong influence on phase behavior. However, since in most cases the equation of state contributions are unfavorable to mixing,[6] the premise that specific interactions are still a prerequisite for miscibility appears justified. Second, as several authors have recently noted,[7-10] the overall interaction parameter (X_{12}) for a blend containing a copolymer, is actually a statistically weighted combination of X_{ij}'s representing all possible segment–segment contacts in the system; incidentally, some 4 decades ago Simha arrived at a similar conclusion for a copolymer solution.[11] This simply accounts for the fact that there are more than two different types of units in the mixture and, consequently, more than one interaction of the type ij is possible. Provided that the X value representing interactions internal to the copolymer is large (unfavorable) compared to the intermolecular values, the overall energy change can be negative, promoting miscibility. Accordingly, a blend containing at least one copolymer may be miscible even if blends of the parent homopolymers are not. ten Brinke and Karasz[9] have pointed out that miscibility in polymer blends is influenced by many factors, including the strength of the directional specific interaction, the difference in solubility parameters, and the amount of entropy lost due to the formation of a favorable interaction.

The majority of the studies performed on polymer blends have been with those systems in which the interactions have been relatively weak. In contrast, our more recent studies have been on systems in which there exists the potential for relatively strong intermolecular interactions (hydrogen bonds). This, in large part, has been because these systems are particularly amenable to infrared analysis. A number of miscible or partially miscible polymer blends have been recently reported where the presence of obvious, relatively strong, intermolecular interactions have been identified.[12]

In this paper, we present a model which attempts to describe the behavior of specific interactions in polymer blends. Predictions based upon this model will then be compared to experimental results obtained from Fourier transform infrared spectroscopic studies of a number of polymer blends which are capable of forming intermolecular hydrogen-bonding interactions between the blend components. Of primary interest will be the distribution of interactions and how this varies as a function of intrinsic parameters such as interaction strength, composition, and chemical structure. It should be emphasized that the proposed model takes a different perspective from both the Flory–Huggins and equation of state theories. These latter theories explicitly assume that the blend components and the intermolecular contacts obey mean field statistics. In contrast, we will assume that the distribution of intermolecular contacts is not necessarily random but is a direct function of interaction strengths (a situation not unlike that described by Orr in 1944 for polymer solutions[13]).

Model Development

According to the Flory–Huggins free energy expression,[14] the enthalpic contributions may be separated into two terms: Δw, which expresses the energy change upon formation of an unlike contact pair, and $zn_1x_1\phi_2$, which expresses the total number of unlike contact pairs in the mixture. In the latter, z is the number of nearest neighbors per lattice site, n_1 is the number of moles of species 1, x_1 is the number of segments per molecule, and ϕ_2 is the volume fraction of species 2. The energy change Δw can be further subdivided into terms representing the strengths of the individual interactions involved in the formation of an unlike contact pair (i.e., $\Delta w = w_{12} - {}^1/_2(w_{11} + w_{22})$). Similarly, the term $zn_1x_1\phi_2$ can also be subdivided into a

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term expressing the total number of interactions in the mixture, $zN/2$, where $N = \sum n_i x_i$ is the total number of segments in the mixture, and a term expressing the probability of forming an unlike contact pair, $\phi_1\phi_2$. The probability term can be thought of simply as the probability of having a segment of type 1 being in contact with a segment of type 2. In other words, $P_{ij} = P_i P_{j/i}$, where $P_i = \phi_i$, the probability of having a type-i segment, and $P_{j/i} = \phi_j$, the probability of a type-i segment interacting with a type-j segment (the conditional probability of a j given an i).

The conceptual view here, as described by Flory,[14] is that the energy of the mixture may be approximated by considering only first-order interactions among nearest neighbors and that the components of the mixture follow a random distribution. In the case of strong, specific interactions, however, the distribution of intermolecular contacts can no longer be expected to be random. In order to develop a more realistic model we will make the following assumptions:

1. The polymer chains in the mixture are assumed to consist of two distinct parts, one containing the functional groups which are directly involved in major intermolecular interactions and the other one containing parts of the molecules which are not. A segment is defined as a portion of the molecule equal in size to the functional group. In other words, the polymer chains are subdivided into segments of equal size based upon the size of the functional group. Each segment of the mixture experiences an environment in which the relative amounts of each type of species present, on a time-averaged basis, are equal to their respective volume or site fractions. This is equivalent to assuming that the segments are distributed randomly within the mixture. For nondilute mixtures of amorphous polymers this appears intuitively satisfying; moreover, any other distribution would be hard to justify, a priori.
2. Each segment is assumed to be involved in only one interaction at a time. Other contacts that a segment may form, those not involving specific interactions, are assumed to contribute negligibly to the overall energy of the system. Segments which contain no functional group are also considered to be able to form one contact, even though the contact energy may be negligible.
3. The probability of forming an i–j contact is assumed to be equal to $\phi_i'\phi_j'$, where ϕ_i' and ϕ_j' are effective site fractions, meaning the site fractions of nonbonded, or free, i and j segments.
4. Different contacts are assumed to have characteristic energies, w_{ij}, which depend primarily upon the the chemical structure of the functional groups involved.
5. Contacts of different energies are assumed to exist, on average, for different lengths of time. Energetically more favorable contacts last longer.

One side effect of the above assumptions is to decrease the number of recognized interactions by a factor of z over the Flory–Huggins case. In other words, $z = 1$ in our model. The possible error brought about by this assumption is clear. Since dispersive interactions generally far outnumber specific interactions they may collectively contribute significantly to ΔH_m, an aspect largely ignored by our model.

The primary effect of the above assumptions, however, is to change the distribution of interactions. The probability of finding an i–j interaction (P_{ij}) is simply the time-averaged fraction of i–j interactions in the blend:

$$P_{ij} = P_i P_{j/i} = N_{ij}/N_\mathrm{T} \qquad \text{(I)}$$

Here, N_{ij} is the number of i–j interactions and $N_\mathrm{T} = \sum_i\sum_{j=i} N_{ij}$, the total number of interactions in the mixture. This is analogous to the Flory–Huggins case but with the following distinction. In accordance with assumption 3, P_{ij} is now dependent not on the overall site fractions ϕ_i and ϕ_2 but on the *effective* site fractions ϕ_i' and ϕ_j'. These in turn are dependent upon factors r_{ij}, which express the relative rates at which i and j are made available. Given the dependence of r_{ij} on the relative length of time an i–j contact exists, it is convenient to treat this relationship on a kinetic basis.

According to our model, a polymer mixture exists in a dynamic state with intermolecular interactions being formed and broken continuously. By definition, equilibrium is reached when the distribution of interactions comes to rest, i.e., when, simultaneously for all contact pairs i–j, the rate of formation equals the rate of dissociation and both are constant. This condition may be expressed as

$$\sum_i\sum_{j=i} |R_{\mathrm{F}_{ij}} - R_{\mathrm{D}_{ij}}| = Q = 0; \qquad \partial Q/\partial T = 0 \qquad \text{(II)}$$

where $R_{\mathrm{F}_{ij}}$ and $R_{\mathrm{D}_{ij}}$ are the relative rates of formation and dissociation for each contact, respectively.

$R_{\mathrm{D}_{ij}}$ is simply the number of i–j contacts, N_{ij}, multiplied by the relative frequency at which i–j contacts are broken:

$$R_{\mathrm{D}_{ij}} = N_{ij} r_{ij} \Big/ \sum_i\sum_{j=i} (N_{ij} r_{ij}) \qquad \text{(III)}$$

Assuming that the relative rate of formation of an i–j contact is equal to the probability of forming an i–j contact and invoking assumption 3 yield

$$R_{\mathrm{F}_{ij}} = \phi_i'\phi_j' \Big/ \sum_i\sum_{j=i} \phi_i'\phi_j' \qquad \text{(IV)}$$

ϕ_i' and ϕ_j' are the effective site fractions of unbonded species and they must be related to the rate of dissociation. Since the equivalent of one free i segment is generated upon the dissociation of every nondegenerate i–j contact, this may be expressed as

$$\phi_i' = \sum_j R_{\mathrm{D}_{ij}} \Big/ \sum_i\sum_{j=i} R_{\mathrm{D}_{ij}} \qquad \text{(V)}$$

We now need to evaluate r_{ij}. An expression is required which relates the relative length of time a contact has, at any point in time, gained sufficient energy to dissociate. This is implied by the Boltzmann distribution:

$$P_s = g_s \exp(-u_s/RT) \Big/ \sum_s g_s \exp(-u_s/RT) \qquad \text{(VI)}$$

where g_s is a degeneracy factor.

The factors r_{ij} are thus simply the Boltzmann factors $\exp(-u/RT)$, where in our case $u = w_{ij}$. Equation III therefore becomes

$$R_{\mathrm{D}_{ij}} = N_{ij} \exp(-w_{ij}/RT) \Big/ \sum_i\sum_{j=i} N_{ij} \exp(-w_{ij}/RT) \qquad \text{(VII)}$$

Substituting eq IV and VII into eq II yields for the condition at equilibrium

$$\Big|\Big(\phi_i'\phi_j' \Big/ \sum_i\sum_{j=i}\phi_i'\phi_j'\Big) - \Big(N_{ij} \exp(-w_{ij}/RT) \Big/ \sum_i\sum_{j=i} N_{ij} \exp(-w_{ij}/RT)\Big)\Big| = Q = 0 \qquad \text{(VIII)}$$

where

$$\phi_i' = N_{ij} \exp(-w_{ij}/RT) \Big/ \sum_i\sum_{j=i} N_{ij} \exp(-w_{ij}/RT)$$

and

$$\partial Q/\partial T = 0$$

If the values for all w_{ij}'s are known, then this equation may be solved for N_{ij}, or since it is the distribution of interactions that is of primary interest, $N_{ij}/\sum_i\sum_{j=i} N_{ij}$.

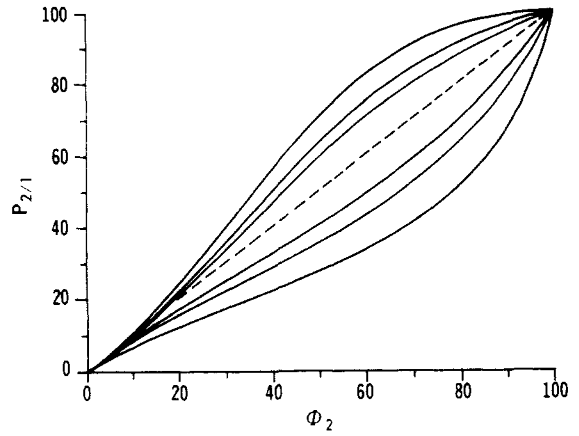

Figure 1. Fraction of 1–2 contacts ($P_{2/1}$) calculated for a binary mixture as a function of composition with various interaction strengths. The curves from top to bottom represent interaction energies (Δw_{12}) of −1000, −600, −400, 0, +400, +600, and +1000 cal/mol, respectively.

In the case of a true binary mixture ($i = 2$) it is possible to solve for the equilibrium condition directly. However, since the functional groups generally constitute only a fraction of the total volume of a molecule, most mixtures (and certainly all conceivable polymer mixtures), involve more than just two distinguishable segments. When $i \geq 3$, it can be awkward to solve for the equilibrium condition directly. Accordingly, we chose to take a simple, "brute force" approach to the problem by using an iterative computer technique. The computer program is designed to simulate the actual molecular process. An initial contact distribution is assumed where only like contacts exist. A constant fraction of the total number of contacts is then repeatedly broken and re-formed using VII and IV until eq VIII approaches zero. Input to the program includes the energies of all possible contacts in the mixture, the temperature, the molar composition of the various segments, and a dissociation factor (the fraction of the total number of contacts dissociated and re-formed during each iteration). A more complete description of the program is given in the Ph.D. Thesis of Howe.[15]

Simulations

Before comparing predictions from the above model with experimental results, it is pedagogically useful to examine the behavior of the model in general. From eq VIII it is evident that there are three sets of variables which affect the distribution of interactions: interaction strengths, temperature, and the concentration of the components in the mixture. In addition, the effects of chemical structure will be considered with respect to both the structure of the chemical repeat units and copolymer composition. In both cases, excess segments are effectively added to the mixture which are considered nonfunctional.

A. Composition and Interaction Strengths. Figure 1 shows the dependence of the number of 1–2-type interactions upon the blend composition and interaction strength for a binary mixture. The number of interactions is represented by the fraction of type-1 segments involved in 1–2 contacts, which gives a direct measure of the conditional probability $P_{2/1}$. For the athermal case ($\Delta w_{12} = 0$), the relationship between the fraction of 1–2 contacts and composition is linear; i.e., the fraction of 1–2 contacts $P_{2/1} = \phi_2$. This is equivalent to the Flory–Huggins case. Since the interactional energies all cancel, the distribution of interactions is random.

When $\Delta w_{12} < 0$ (favorable to mixing), positive deviations from randomness occur and the curve bows upward. Conversely, the opposite occurs when $\Delta w_{12} > 0$ (unfavorable to mixing). In either case, however, the magnitude of the deviation from random mixing increases with the magnitude of Δw_{12}. Furthermore, $P_{2/1}$ is always an increasing function of ϕ_2. It should be noted that, at any particular composition, $P_{2/1}$ is dependent only on Δw_{12} and not on the individual interaction strengths, w_{ij}.

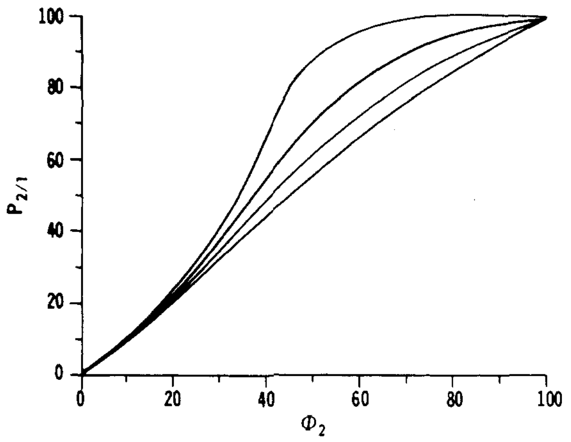

Figure 2. Fraction of 1–2 contacts as a function of composition for a binary mixture at various temperatures. The curves from Top to bottom represent blends at −200, −100, +100, and +400 °C, respectively.

B. Temperature. Since the exponential term of eq VIII is inversely dependent upon temperature, increasing the temperature tends to minimize the effects of nonzero interaction strengths. This is illustrated in Figure 2 for a binary mixture where Δw_{12} is assumed to be −300 cal/mol. At very low temperatures the fraction of 1–2 contacts is very high. (We must caution that the model does not take into account factors such as the glass transition temperature, which severely restricts mobility and would reduce the ability of the system to attain equilibrium.) As the temperature is raised, the distribution of interactions becomes increasingly more random, eventually approaching the athermal distribution. This naturally assumes that the segmental distribution remains random. In practice, a lower critical solution temperature is often reached where the mixture phase separates. This would be observed in a drastic reduction in $P_{2/1}$ to below the value of ϕ_2 over a narrow temperature range.

C. Chemical Structure. Excess segments can be added to the mixture in two ways: by making one or both of the components copolymers (for example, ethylene–vinyl acetate copolymers containing an increasing concentration of ethylene) or by making the repeat unit of the component polymers larger (for example, in a series of polylactones with an increasing number of methylene groups). In either case, the major effect is to dilute the mixture, making it harder for 1–2-type interactions to form.

In cases where the interaction strengths are all equal, the relationship between $P_{2/1}$ and ϕ_2 remains the same; i.e., for any copolymer composition, $P_{2/1} = \phi_2$. It is important to recognize, however, that since ϕ_2 decreases upon addition of excess segments to the mixture, the number of 1–2 contacts decreases. This is illustrated in Figure 3, where $P_{2/1}$ is plotted against the mole fraction of the *effective* repeat units of polymer 2, θ_2. Note that the shape of the curve depends upon which of the parent species, polymer 1 or polymer 2, contributes the excess segments.

Similar behavior is observed when the interaction strengths are not all equal. As more nonfunctional segments are added to the mixture, the number of 1–2 contacts still decreases. In contrast to the athermal case, however, the decrease depends not only upon concentra-

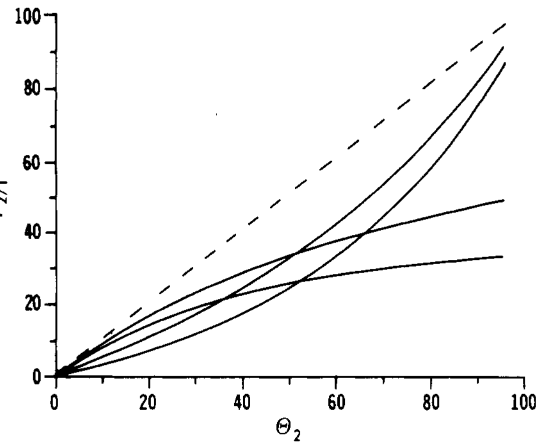

Figure 3. Fraction of 1–2 contacts vs. mole fraction of type-2 repeat units for athermal copolymer mixtures. The dashed line represents a binary blend. The concave curves from top to bottom represent mixtures where the copolymer consists of type-1 and type-3 segments in the ratio of 1:1 and 1:2, respectively. The convex curves from top to bottom represent mixtures where the copolymer consists of type-2 and type-3 segments in the ratio of 1:1 and 1:3, respectively.

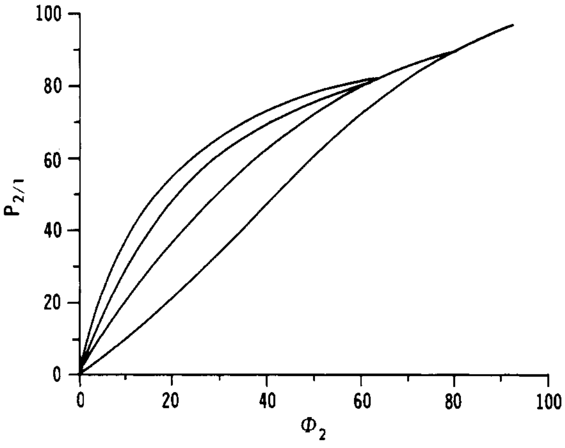

Figure 4. Fraction of 1–2 contacts plotted against the site fraction of type-2 segments for a series of copolymer blends. The curves from top to bottom represent mixtures in which the copolymer ratios of type-3 to type-1 segments are 5:1, 3:1, 1:1, and 0:1, respectively. The interaction energies employed were $w_{11} = -1000$, $w_{12} = -3000$, $w_{22} = -4500$, and $w_{13} = w_{23} = w_{33} = 0$ cal/mol.

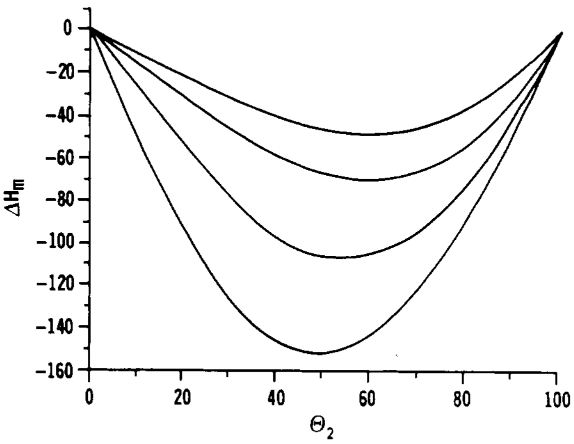

Figure 5. Enthalpy of mixing (ΔH_m) vs. θ_2 for a series of mixtures in which component 1 is a copolymer. The curves from top to bottom represent type-3 to type-1 ratios of 5:1, 3:1, 1:1, and 0:1, respectively. The interaction energies are the same as in Figure 4.

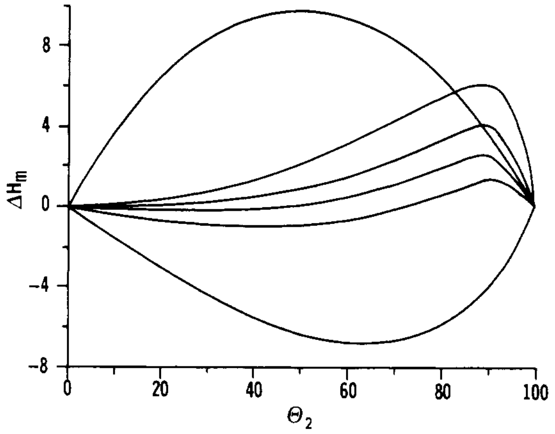

Figure 6. ΔH_m vs. θ_2 for a series of mixtures in which component 1 is a copolymer. The curves from top to bottom represent copolymer segment ratios (type 3 to type 1) of 0:1, 3:=1, 2.5:1, 2.25:1, 2:1, and 1:1, respectively. The contact energies employed were $w_{11} = -1000$, $w_{12} = -580$, $w_{22} = -200$, and $w_{13} = w_{23} = w_{33} = 0$ cal/mol.

tion of excess segments but also on the relative values of the w_{ij}'s. For exammple, keeping $\Delta w_{13} = \Delta w_{23}$, as we increase$\Delta w_{12}$, the number of 1–2 contacts at any given composition increases, approaching the binary mixture value. On a site fraction basis, $P_{2/1}$ can actually exceed the binary mixture value, making the copolymer mixture appear more miscible than the homopolymer mixture. An example is given in Figure 4. It must be emphasized, however, that on a molar basis the number of 1–2 contacts still decreases. As a consequence, the enthalpy change upon mixing, ΔH_m, decreases as shown in Figure 5. Thus in systems where $\Delta w_{13} = \Delta w_{23} < \Delta w_{12}$, addition of excess segments actually tends to decrease the driving force for miscibility.

In cases where Δw_{13} is not equal to Δw_{23}, the addition of excess tertiary segments tends to have the opposite effect; i.e., the driving force toward miscibility is increased. In such systems, unfavorable interactions which exist between the cosegments of the copolymer in the pure state are diluted upon mixing, resulting in an overall favorable energy change. For this to occur, Δw_{13}, the interaction energy between copolymer segments, must be greater than Δw_{23}. An example of this is shown in Figure 6, where ΔH_m is plotted against θ_2. In this particular case, $\Delta w_{12} > 0$. Assuming that $\Delta s_m \simeq 0$, and neglecting equation of state contributions, this makes the homopolymers of all three types of segments immiscible with one another. As shown in Figure 6, however, addition of excess seegments to component 1 decreases ΔH_m, allowing some of the copolymer mixtures to become miscible.

The above is analogous to the model developed by Kambour et al.[7] The difference in our work is that interactions are not restricted to a random distribution. This has two effects, both of which may be appreciated by comparing the results shown in Figure 6 with those calculated for the same system assuming a random distribution given in Figure 7. The first is to lower ΔH_m. This not only lowers the the driving force for mixing, it also lowers the upper copolymer composition limit of the miscibility window. According to the random model, these mixtures would be miscible up to a copolymer ratio of type-3 to type-1 segments of 4:1. In our model, the ratio is about 3:1.

The second effect is to induce partial phase separation in mixtures involving copolymers near the upper limit of the miscibility window. This can be seen in Figure 6 for mixtures where the copolymer ratios are 1:2, 1:2.25, and 1:2.5. Immiscibility is predicted at blend compositions rich in the homopolymer. Since in each of these blends com-

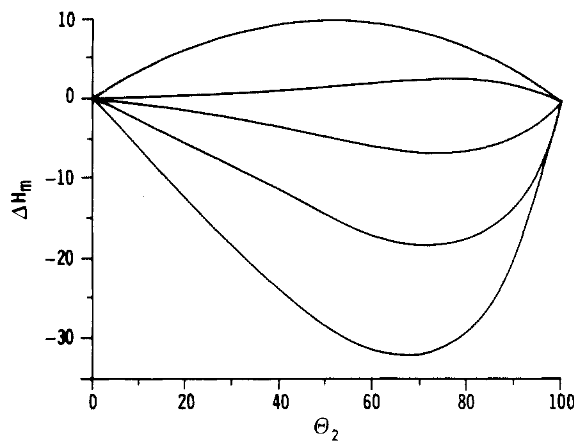

Figure 7. ΔH_m vs. θ_2 for a series of copolymer mixtures where the distribution of interactions is random. The curves from top to bottom represent copolymer segment ratios (type 3 to type 1) of 0:1, 4:1, 3:1, 2:1, and 1:1, respectively. The interaction energies are the same as for Figure 6.

positions exist where ΔH_m is negative, only partial phase separation should occur. In fact, the immiscible compositions would separate into an essentially pure polymer-2 phase and mixed phases with higher copolymer concentrations. (Evidence for such systems has been seen recently in poly(vinyl chloride) and poly(vinylphenol) blends with an ethylene–vinyl acetate copolymer containing 45% vinyl acetate.[16,17]) This phenomenon is not predicted when the interactions are distributed randomly. As can be seen from Figure 7, all of the random mixtures have ΔH_m either greater than or less than zero over the entire composition range. Some of the curves, however, do exhibit a slight concave character at compositions rich in the copolymer, suggesting that some of them may be metastable.

Comparison with Experimental Results

In order to compare the predictions of our model with experimental results, we require miscible polymer blend systems in which the distribution of intermolecular interactions can be determined as a function of composition, temperature, and chemical structure (i.e., the variation of the concentration of excess segments). Fortunately, we have recently obtained precisely this type of information from Fourier transform infrared (FT-IR) spectroscopic studies of poly(4-vinylphenol) (PVPh) blends.[18,19] Specifically, in PVPh blends containing poly(vinyl acetate) (PVAc) and three ethylene–vinyl acetate copolymers (designated EVA[70], EVA[45], and EVA[25] for the copolymers containing 70, 45, and 25 wt % vinyl acetate, respectively) we were able to quantitatively measure the fraction of hydrogen-bonded carbonyl groups as a function of temperature and composition.[18] As the concentration of methylene groups varies in PVAc and the series of EVA's the effect of excess segments can also be tested. Furthermore, we have similar data on PVPh blends with the homopolymers poly(ϵ-caprolactone) (PCL) and poly(β-propiolactone) (PPL).[19,20] In this case, excess segments are introduced by the larger chemical repeat unit of PCL compared to PPL.

PVPh Blends with PVAc, EVA[70], and EVA[45]. Before theoretical values for the degree of hydrogen bonding in the blends of PVPh with PVAc and the EVA's can be calculated, values for the segment fractions, ϕ_i, and the contact energies must be obtained.

According to assumption 1 (see Model Development), the blend components should be divided into segments equal in size to the average size of the functional groups involved in the primary intermolecular interaction. For the PVPh blends with PVAc and EVA, the functional groups are simply assumed to be the acetate carbonyl and the phenolic hydroxyl groups. Defining the segment size as equal to the average of the van der Waals volumes of the carbonyl and hydroxyl groups (9.87 cm^3/mol),[21] the "excess" volumes (i.e., total volume minus volume of the functional group) of the vinyl acetate, ethylene, and vinylphenol chemical repeat units can each be divided into the following number of segments: vinyl acetate, 3.65; ethylene, 2.07; vinylphenol, 6.11. Although the EVA copolymers are thought to be essentially random copolymers, an average value of the number of ethylene units to the vinyl acetate units has been assumed. For the EVA[70] and EVA[45] copolymers the ratio of ethylene units to vinyl acetate units is approximately 1:1 and 4:1, respectively. Designating the acetate carbonyl groups as type-1 segments, the aromatic hydroxyl groups as type-2 segments, and the nonfunctional groups (the remainder) as type-3 segments yields the following segment distribution for each of the effective repeat units:

	segment type		
repeat unit	1	2	3
PVAc	1	0	3.65
EVA[70]	1	0	5.72
EVA[45]	1	0	11.93
PVPh	0	1	6.11

The segment fractions can now be readily calculated from the mole fractions of the parent species in the blends of different compositions.

In principle, the contact energies can be obtained from infrared data. It has been previously demonstrated, both theoretically[22] and empirically,[23,24] that a linear relationship exists between wavenumber shift and bond energy for chemical groups involved in hydrogen bond formation. Purcell and Drago[22] suggested the following relationship:

$$\Delta H = (hcN/4X_c)\nu + E_{HB} \qquad \text{(IX)}$$

where ΔH is the enthalpy of bond formation, E_{HB} is the bond energy, X_c is the anharmonicity constant for the oscillator, and ν is the wavenumber shift.

Three points concerning the applicibility of these relationships bear mentioning. First, they apply only to groups that can be approximated as diatomic oscillators (not a severe problem for studies such as ours where we are considering essentially isolated stretching vibrations). Secondly, we have recently pointed out that the absorption coefficient is a very strong function of the relative strength of the hydrogen bond.[25] For very broad bands, such as those observed for self-associated hydroxyl groups in PVPh[18] and Phenoxy,[26] it is possible for the slope of the absorption coefficient vs. wavenumber to be steep enough in the region around the true band center to cause a significant distortion in the observed band position. In such a case, the measured wavenumber shift (i.e., the frequency difference between the "free" and the hydrogen-bonded bands) would be in error and the relationship depicted in eq IX would break down. Finally, it should be noted that ΔH in eq IX is the partial enthalpy of formation of the hydrogen bond. The total enthalpy change is the sum of the partial enthalpies of both chemical groups and consequently does not necessarily scale with ν. Note also that this is ΔH_f and not ΔH_m.

Keeping the above reservations in mind, we have employed the information obtained from infrared shifts observed in the hydroxyl and carbonyl stretching regions of the spectrum to estimate the values of w_{11}, w_{12}, and w_{22}. (All contacts involving type-3 segments have been assumed

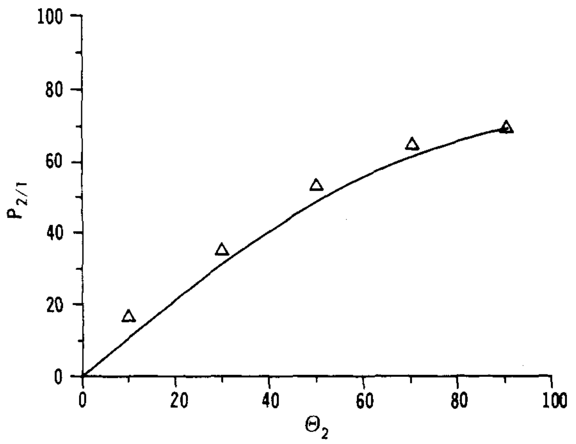

Figure 8. Comparison of the theoretically calculated (solid line) and experimentally determined (△) $P_{2/1}$ values plotted against θ_2 for PVPh–PVAc blends.

to have zero energy.) There is an abundance of information available for phenol mixtures. Data published by Purcell and Drago[22] suggest the following relationship between the hydrogen bond formation energy E_{HB} and the wavenumber shift of the hydroxyl stretching vibration:

$$E_{HB} = 0.0458\nu_{OH} + 1.0117 \qquad \text{(X)}$$

where E_{HB} is in kcal/mol. Substituting the wavenumber shift associated with the 1–2 contact in the PVPh–PVAc blend ($\simeq$95 cm^{-1})[18] into this equation gives $w_{12} = -5.36$ kcal/mol. This is in good agreement with the result estimated from temperature studies of the PVPh–EVA[45] blend.[18] For self-associated hydroxyl groups the frequency shift is $\simeq$165 cm^{-1}, yielding a value of −8.57 kcal/mol for w_{22}.

As we now have a value of w_{12}, the value of w_{11} may be obtained from the corresponding frequency shifts observed in the carbonyl stretching region of the spectrum. We initially need the frequency of the "free" carbonyl group. This may be estimated by extrapolation of the band positions corresponding to known energy to zero contact energy. In practice, this is achieved by measuring the frequency of the carbonyl band in 1% solutions of solvents of varying acceptor numbers.[23] Details are presented in the Ph.D. thesis of Howe[15] and a summary of the results is presented in Table I. In any event, the "free" carbonyl stretching vibrations for PVAc, EVA[70], and EVA[45] were determined to be 1749.8, 1745,9, and 1745.2 cm^{-1}, respectively. For PVAc the band shift corresponding to the 1–2 contact is 35.5 cm^{-1}. Remembering that w_{12} (calculated earlier from the hydroxyl stretching region) is −5.36 kcal/mol, we can simply estimate the value of w_{11} by linear extrapolation. A 10.5-cm^{-1} shift estimated for the self-associated PVAc in the amorphous solid state yields a value of −1.59 kcal/mol. The frequency shifts corresponding to 1–2 contacts in the PVPh–EVA[70] and PVPh–EVA[45] blends are also approximately 35.5 cm^{-1}, strongly suggesting that the strength of the 1–2 contacts are essentially identical with that of PVAc. On the other hand, the shifts corresponding to 1–1 contacts in EVA[70] and EVA[45] are measurably less (~9.5 and 7.0 cm^{-1}, respectively) than in PVAc. Frankly, we do not have much confidence in the values of these shifts. Unlike the O–H stretching region of the spectrum where the "free" and hydrogen-bonded O–H frequencies of pure PVPh in the amorphous solid state are well resolved and readily identified, the corresponding "free" and self-associated carbonyl bands of PVAc and the EVA's are not. As a result, the "true" positions of the self-associated carbonyl groups cannot be directly measured. For the purposes of this work we will make the assumption that w_1 for PVAc and the two EVA's are identical at −1.59 kcal/mol.

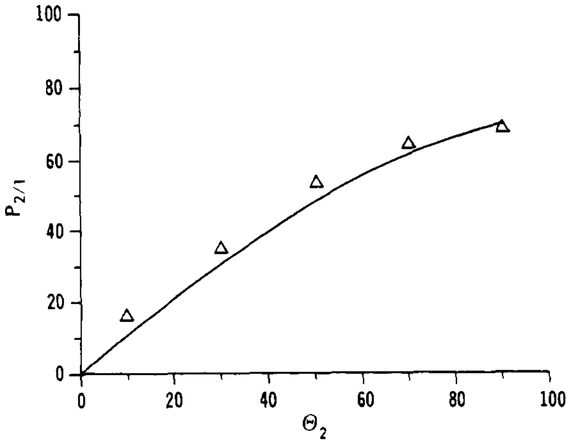

Figure 9. Comparison of the theoretically calculated (solid line) and experimentally determined (△) $P_{2/1}$ values plotted against θ_2 for PVPh–EVA[70] blends.

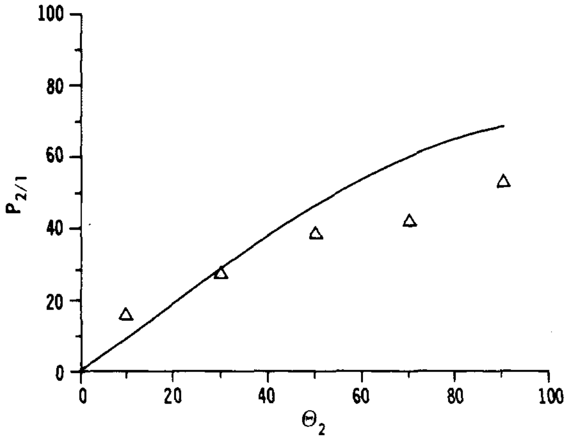

Figure 10. Comparison of the theoretically calculated (solid line) and experimentally determined (△) $P_{2/1}$ values plotted against θ_2 for PVPh–EVA[45] blends.

In summary, the values of w_{ij} which we will use in our theoretical model are $w_{11} = -1.59$ kcal/mol, $w_{22} = -8.57$ kcal/mol, $w_{12} = -5.36$ kcal/mol, and $w_{i3} = w_{3i} = 0$ for $i =$ 1–3.

Theoretical values for the fraction of 1–2 contacts ($P_{2/1}$) as a function of mole fraction of vinylphenol units, θ_2, in blends of PVPh with PVAc, EVA[70], and EVA[45] are compared with the experimental FT-IR values obtained by Moskala in Figures 8–10. The theoretical and experimental curves for the PVPh blends with PVAc and EVA[70] are in excellent agreement.

The agreement between the theoretical and experimental curves for the PVPh–EVA[45] blends is not nearly as satisfying. As can be seen in Figure 10, the curves become increasingly dirvergent as θ_2 increases. Evidence has recently been presented, however, that strongly suggests that the PVPh–EVA[45] system is only partially miscible.[16] In light of these results, disparity between the theoretical and experimental curves is to be expected. For example, if the system was only miscible at compositions below $\theta_2 = 0.5$, blends with a composition above this value would tend to separate into a rich PVPh phase and a second phase where $\theta_2 < 0.5$. The experimental $P_{2/1}$ curve in such a case would tend to level off above $\theta_2 = 0.5$ whereas the theoretical curve, calculated assuming a single phase, would continue to increase.

Theoretical values for the fraction of hydrogen-bonded

Table I

A. Frequency of the Carbonyl Stretching Vibration of the Polymers in Solution with Solvents of Varying Acceptor Numbers (AN)

		frequency of carbonyl band, cm^{-1}				
solvent	AN[a]	PVAc	EVA[70]	EVA[45]	PPL	PCL
tetrahydrofuran	8.0	1743.5	1739.5	1738	1745	1738
benzene	8.2	1742.5	1738.5	1737		
carbon tetrachloride	8.6	1743	1739	1738	1744	1738
pyridine	14.2	1739	1735.5	1735	1741	
acrylonitrile	15.3	1739	1734.5		1742	1731
dichloromethane	20.4	1739	1734	1735	1735	1728
chloroform	23.1	1736	1731	1730	1737	1727.5
ethanol	37.1	1724	1718	1717		1719
methanol	41.3	1723	1718	1715	1727	1717

B. Least-Squares Fit of the Acceptor Number Data Listed Above

			frequency of carbonyl band, cm^{-1}		
polymer	slope	SD	"free" (extrap)	H bonded	self-associated
PVAc	-1.54	12.3	1749.8	1714.5	1739.5
EVA[70]	-1.44	12.3	1745.9	1710.5	1736.5
EVA[45]	-1.39	13.1	1745.2	1710	1738
PPL	-1.7	11.2	1749.9	1721	1741
PCL	-1.54	12.8	1743.0	1707.5	1735

[a] Reference 31.

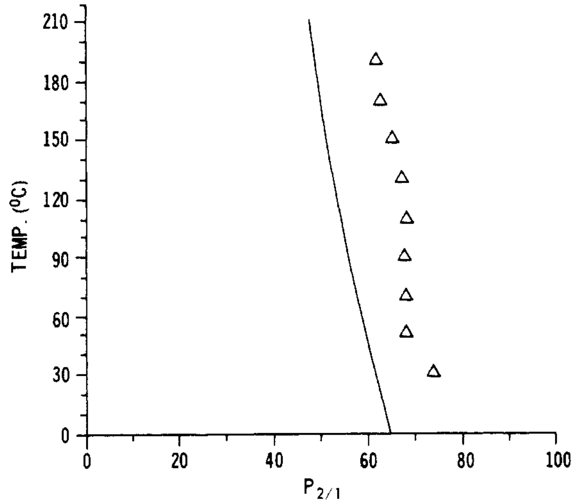

Figure 11. Comparison of the theoretically calculated (solid line) and experimentally determined (Δ) $P_{2/1}$ values plotted against temperature for PVPh-PVAc blends.

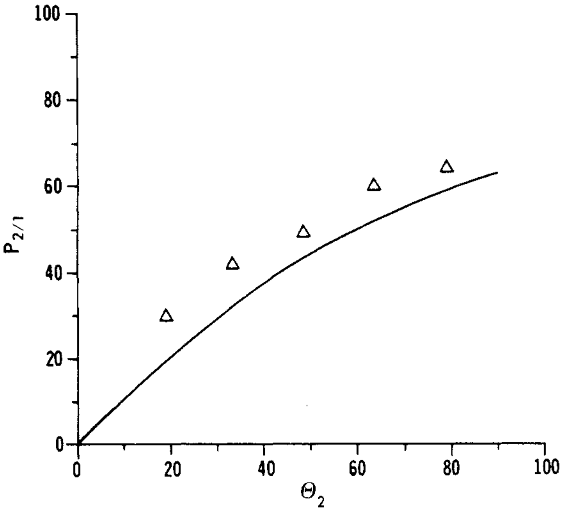

Figure 12. Comparison of the theoretically calculated (solid line) and experimentally determined (Δ) $P_{2/1}$ values plotted against θ_2 for PVPh-PCL blends.

carbonyl groups, $P_{2/1}$, have also been calculated for the PVPh blends as a function of temperature. Experimental FT-IR temperature data have previously been presented for 80:20 wt % PVPh blends with PVAc, EVA[70], and EVA[45].[18] Accordingly, calculations were performed on these blend compositions in order that a direct comparison could be made. Figure 11 shows the experimental and theoretical curves for the PVPh-PVAc blend. Although there is a discrepancy between the absolute values of $P_{2/1}$ at any given temperature, it is consistent and the temperature dependence of $P_{2/1}$ is in satisfactory agreement. The corresponding results obtained for the PVPh-EVA-[70] blend are very similar to those of the PVPh-PVAc blend.[15] However, in the case of the PVPh-EVA[45], the agreement is much less favorable. Again, this may be rationalized on the basis that the system is only partially miscible.[16,17]

PVPh Blends with PCL and PPL. The chemical repeat units of PCL and PPL may be represented by $-[(CH_2CH_2)_xCOO-$, where $x = 1$ for PPL and $x = 2.5$ for PCL. The functional segment contained in each polymer is, again, the carbonyl group. Dividing the "excess" volume of each repeat unit into segments of volume 9.87 cm^3/mol, as was done for the previous set of blends, yields the following segment distribution:

	segment type		
polymer	1	2	3
PPL	1	0	2.61
PCL	1	0	5.72

The contact energies w_{11}, w_{12}, and w_{22} are assumed to be identical with those used previously (i.e., -1.59, -5.36, and -8.57 kcal/mol, respectively). This appears reasonable as there is no significant difference in the FT-IR frequency shifts observed in the PVPh blends with acetate-containing polymers and those containing ester groups.[18,20]

Experimental $P_{2/1}$ values for PVPh blends with PPL and PCL were obtained from the elevated-temperature data of Moskala[19] using the same procedure described in our recent publication.[18] It should be noted that the $P_{2/1}$ values were measured at 75 °C for PCL and 90 °C for PPL, which is above the respective melting points of the pure polymers, to ensure that crystallization of a fraction of the polymers in the blends did not occur. The theoretical calculations were performed at the same temperatures.

Figures 12 and 13 compare the experimental and theo-

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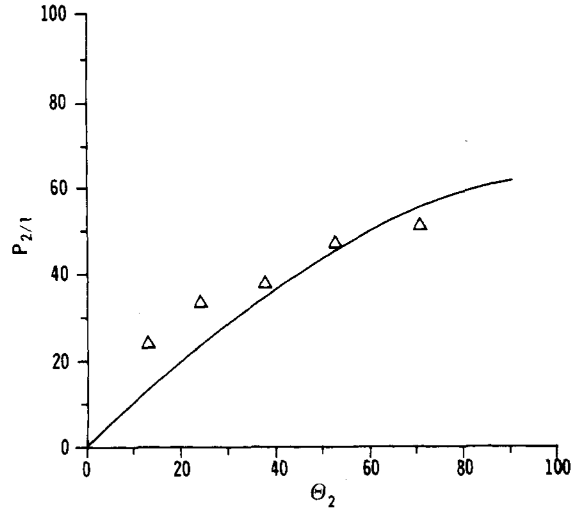

Figure 13. Comparison of the theoretically calculated (solid line) and experimentally determined (Δ) $P_{2/1}$ values plotted against θ_2 for PVPh–PPL blends.

retical results for the PVPh–PCL and PVPh–PPL blends, respectively. The results, while not as obviously pleasing as those of the PVPh blends with PVAc and EVA[70], are in satisfactory agreement. Again, we would emphasize the overall shape of the curves rather than the absolute values, which are subject to significant error.

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Registry No. PVPh (homopolymer), 24979-70-2; PVAc (homopolymer), 9003-20-7; EVA (copolymer), 24937-78-8; PCL (homopolymer), 24980-41-4; PCL (SRU), 25248-42-4; PPL (homopolymer), 25037-58-5; PPL (SRU), 24938-43-0.

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Polymers at a Liquid–Liquid Interface

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ABSTRACT: We study the behavior of homopolymers at the liquid–liquid interface of a biphasic regular binary solution. We find that the polymers are attracted to the interface, with the polymer concentration profile having a maximum near the interface, on the side of the better solvent. Expressions for interfacial width and the surface tension are derived.

I. Introduction

Comparatively little attention has been paid to the behavior of polymers at liquid–liquid interfaces. Most of the research in this area has been confined to binary systems (phase-separated solution of a single solvent and a monodisperse polymer.[1–4] In the following we will address the theory of the behavior of homopolymers at the liquid–liquid interface of a biphasic regular binary solution (i.e., a system consisting of a monodisperse polymer and two simple solvents). Surprisingly, we find that homopolymers may be attracted to the interface, even though they are not assumed to be amphiphilic. This predicted facet of homopolymer behavior may be relevant to wetting behavior, emulsion stabilization, etc.

Understanding of these systems may be developed by considering the various interactions between the polymer monomeric units (M) and the two types of solvent molecules (1 and 2): (i) the interaction energy between solvent 1 and the monomer (M–1) as compared with the interaction energy between solvent 2 and the monomer (M–2) (when the energy associated with the M–1 interaction is lower than the energy associated with the M–2 interaction, we will say that "solvent 1 is the preferred solvent"); (ii) the interaction energy between solvent 1 molecule and solvent 2 molecule (1–2) relative to the energy associated with the configuration where the two different solvent

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