Intramolecular Screening Effects in Polymer Mixtures. 1. Hydrogen-Bonded Polymer Blends

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Received June 4, 1996; Revised Manuscript Received October 11, 1996⊗

ABSTRACT: Spectroscopic evidence is presented to indicate that local screening effects are important in polymer mixtures. Essentially, a polymer segment has a locally higher concentration of like segments because of this factor. A simple modification to existing theories is presented to account for this local screening.

Introduction

Although the limitations of the Flory−Huggins treatment of polymer solutions and blends are well-known, because of its relative simplicity and ability to reproduce some of the major features of observed phase behavior it has remained the starting point for most treatment of thermodynamic data. Many attempts to obtain an improved fit between experimental observations and theoretical prediction have focused on the χ interaction term, which has often been made concentration, temperature, and sometimes molecular weight dependent. For example, Petri et al.[1] recently observed significant effects of both molecular weight and concentration on carefully measured values of χ in various systems. In this and a following communication we will suggest that these and many other results in the literature may be explained, at least in part, as arising from chain connectivity and correlation effects. We will approach the subject from a different perspective, however, by first considering hydrogen-bonded systems. This is because we have available to us a tool, infrared spectroscopy, that allows us to count certain types of contacts in systems that interact in this manner and thus explore directly some of the correlation effects that are involved in all types of contacts in polymer systems.

The mean-field Flory−Huggins treatment of polymer solutions and blends assumes that segments are randomly mixed. The presence of strong specific interactions such as hydrogen bonds introduces a network of nonrandom contacts, but these can also be treated in the context of a higher order mean-field approximation. In the approach used in our laboratory, the configurations of the equilibrium distribution of hydrogen-bonded chains are described by a Flory lattice model type of counting procedure.[2−4] The statistics include a term describing the probability that segments are adjacent and thus capable of hydrogen bonding. In the mean-field treatment this term is assumed to be proportional to the volume fraction of the segments involved. A similar assumption is used in the treatment of hydrogen bonds developed by Veytsman[5] and Panayioutou and Sanchez.[6] As we have noted before, these results give identical results when the same reference state is used.[4,7]

In recent work we have found that the usual assumption of *a mean field on the segments* in polymer blend systems may not be a good approximation. There are two lines of evidence that have led us to this view. The first involves the model we have developed that uses experimentally determined parameters to calculate the contribution of hydrogen bonds to the free energy of mixing. By using solubility parameters (carefully constructed so as to exclude association effects) to describe nonspecific interactions, a remarkable agreement between theoretical and observed phase behavior has been obtained.[3,4,8] However, the model includes what can be thought of as an empirical "correction term", constructed originally by an incorrect choice of reference states. Nevertheless, agreement between theory and experiment has been obtained on such a wide range of systems that we do not believe our results are simply fortuitous. Accordingly, our "correction term" must account for some factor we have neglected.

The second line of evidence is experimental and based on a detailed infrared spectroscopic study of blends of poly(4-vinylphenol) (PVPh) and poly(ethyl methacrylate) (PEMA), random copolymers of these units, mixtures of low molecular weight analogues, and mixtures of the polymers with the low molecular weight analogues.[9] The number of hydrogen bonds (at the same concentration of functional groups) formed in mixtures of the low molecular weight analogues was practically identical to those formed in mixtures of these analogues with polymers, but much larger than the number found in random copolymers of these units. In turn, there were far more hydrogen bonds formed in random copolymers than in homopolymer blends of the same units. Interpreting these results is not simple, in that factors such as steric accessibility, chain flexibility, etc., can affect the number of hydrogen bonds formed (and is accounted for by a term for the entropy of hydrogen bond formation). However, by comparing various types of mixtures we were led to the conclusion that in homopolymer blends the number of like contacts is much larger than would be expected (and, conversely, the number of unlike contacts far less). At first we thought that these differences, particularly those observed between random copolymers and blends of identical units, could be explained on the basis of compositional heterogeneities in the blends, but we could not detect any significant

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⊗ Abstract published in *Advance ACS Abstracts,* February 1, 1997.

S0024-9297(96)00815-7 CCC: $14.00

concentration fluctuations in neutron scattering experiments.[10]

The accumulating evidence, the most recent of which will be described below, has led us to the view that we are observing a "screening" or locally nonrandom mixing driven primarily by intramolecular connectivity effects. Essentially, the covalent linkages between homopolymer segments result in a number of same-chain contacts that enhances the number of like−like neighbors over what would be calculated on the basis of a random mixing of segments (in a homogeneous random copolymer, however, there would be no distinction in the types of contacts that are intrachain as opposed to interchain, thus explaining our previous spectroscopic observations). Our model may be thought of as being motivated primarily by the recent work of Szleifer[11] and Schweizer and Curro[12] who have both explicitly accounted for the effects of intramolecular connectivity in the calculation of the local packing around a chosen segment. It must be emphasized here that such local connectivity effects are usually introduced in the field theory description only through a semi-empirical ultraviolet cutoff. This does not account for the details of local packing effects which could be critically important in the context of this paper.

As mentioned above, it is the purpose of this and a following communication to explore the effect of chain connectivity on simple theories of mixing. Here we will focus our attention on hydrogen-bonded blends. A major advantage of studying this type of system is that we can "count" the number of contacts using infrared spectroscopy, providing that we choose our mixtures with care (the effect of experimental errors is such that meaningful distinctions can only be made in certain mixtures over certain composition ranges). In a following paper we will then consider non-hydrogen-bonded polymer solutions and show that a simple approach is capable of reproducing some of the major features of the composition and molecular weight dependence of χ.

Counting Contacts

It is useful to first consider segment−surface contacts before proceeding to the Flory approximation. Consider homopolymers of type A and type B, where M_A and M_B are the degrees of polymerization and N_A and N_B are the numbers of molecules of each type. Following Guggenheim,[13] we can use the quantities q_A and q_B to define the number of noncovalent contacts:

$$zq_A = M_A(z-2)+2 \tag{1}$$

$$zq_B + M_B(z-2)+2 \tag{2}$$

where z is the lattice coordination number. If n_{AA}, n_{BB}, and n_{AB} are the number of AA, BB, and AB contact pairs, respectively, then

$$2n_{AA} = N_A q_A z - n_{AB} \tag{3}$$

$$2n_{BB} = N_B q_B z - n_{AB} \tag{4}$$

We can also write

$$n_{AA} = \frac{1}{2}N_A q_A z p_{AA} \tag{5}$$

$$n_{BB} = \frac{1}{2}N_B q_B z p_{BB} \tag{6}$$

where p_{AA} is the probability that a site neighboring an A segment is occupied by an A segment (equal to the fraction of sites that are occupied in this manner) and an equivalent definition applies to p_{BB}. Note that p_{BA} is the probability that a site neighboring an A segment is a B. These probabilities must satisfy the criteria

$$p_{AA} = 1 - p_{BA} \tag{7}$$

$$p_{BB} = 1 - p_{AB} \tag{8}$$

However,

$$p_{AB} \neq p_{BA} \tag{9}$$

although we must have

$$n_{AB} = n_{BA} \tag{10}$$

It follows that

$$p_{AB} = p_{BA}\frac{\theta_A}{\theta_B} \approx p_{BA}\frac{\Phi_A}{\Phi_B} \tag{11}$$

where

$$\theta_A = \frac{N_A q_A}{N_A q_A + N_B q_B} \qquad \theta_B = \frac{N_B q_B}{N_A q_A + N_B q_B} \tag{12}$$

and for M_A, $M_B \gg 1$, $\theta_A \approx \Phi_A$ and $\theta_B \approx \Phi_B$, where Φ_A and Φ_B are the respective volume fractions (see eqs 1 and 2). A random mixing of the segments is usually assumed such that $p_{AB} = \theta_A$ and $p_{BA} = \theta_B$.

Now consider the effect of a chain bending back on itself, primarily through local effects but also through long range connectivity effects, such that there is an appreciable number of nearest-neighbor intrachain contacts. Let the fractions of such same chain contacts be γ_A and γ_B, respectively, for the two species in the blend. These quantities will depend upon chain conformation in a presumably complex manner, but in what follows we will assume that γ_A and γ_B are values that are averaged over the distribution of conformations characteristic of the unperturbed Gaussian state. In effect we treat γ_A and γ_B as constants characteristic of a given chain. We can now write for p_{AA}

$$p_{AA} = \gamma_A + (1-\gamma_A)\theta'_A \tag{13}$$

the factor $(1-\gamma_A)$ is obviously the fraction of interchain contacts made by A chains, while the factor θ'_A is the fraction of interchain contacts that are AA, i.e.

$$\theta'_A = \frac{N_A q_A(1-\gamma_A)}{N_A q_A(1-\gamma_A) + N_B q_B(1-\gamma_B)} \tag{14}$$

For M_A, $M_B \gg 1$

$$\theta'_A \approx \frac{\Phi_A(1-\gamma_A)}{\Phi_A(1-\gamma_A) + \Phi_B(1-\gamma_B)} \tag{15}$$

and for $\gamma_A \approx \gamma_B \approx \gamma$

$$p_{AA} = \gamma + (1-\gamma)\Phi_A \tag{16}$$

$$p_{BB} = \gamma + (1-\gamma)\Phi_B \tag{17}$$

We can now turn our attention to how interaction terms are modified by this adjustment to the random

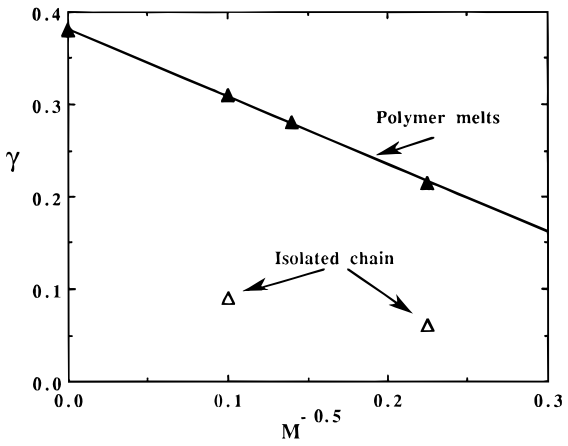

Figure 1. Plot of the calculated fraction of intramolecular contacts, γ vs $M^{-0.5}$, where M is the degree of polymerization.

mixing approximation. Before doing this, however, it is useful to obtain a rough idea of the relative size and hence importance of the γ term that we have introduced.

Lattice Simulations

We have argued in the preceding section that chains locally fold back on themselves, thus preventing segments of other chains from fully accessing the monomer of interest. This picture can be best visualized by considering a chain on a square lattice where a folded "U-like" configuration immediately allows only two sites to be a neighbor which could be accessed by a segment of another chain. Alternatively, from a local perspective one can argue that connectivity effects shield or screen a segment from contacts with segments of other chains. Since this effect is expected, on intuitive grounds, to be highly nonuniversal, it is not easily quantified through standard theoretical approaches. Consequently, we have utilized the device of Monte Carlo simulations for chains on a standard cubic lattice model to provide an estimate of this intramolecular contact effect.

We have considered cubic lattices [$z = 6$] which are typically composed of 100 sites on a side. Standard periodic boundary conditions were employed in all three spatial directions, and all segments interacted through pure excluded volume interactions. Polymer melts were simulated by filling a lattice with chains until an occupancy of 85% was achieved. We also simulated a few systems to densities as high as 99% and found essentially no difference in the computed results. In parallel, we also conducted simulations on isolated chains to understand the corresponding quantity for chains in a good solvent. The Monte Carlo simulations employed standard reptation moves and also employed the configurational bias move to achieve rapid equilibration of chain configurations. A variety of chain lengths ranging from 10 to 200 were considered in a range of simulations.

In the case of the melts we computed the average number of intramolecular and intermolecular contacts experienced by a single chain segment. These quantities then directly permitted the evaluation of γ, the fraction of intramolecular contacts. Values of γ are plotted as a function of $M^{-0.5}$ in Figure 1. It can be seen that for a melt γ is surprisingly large, approaching $\gamma = 0.38$ at infinite chain length. Similar calculations were performed for an isolated chain, but here there are only two calculated points and it is probable that in this case γ does not vary as $M^{-0.5}$.[14] However, the plot does illustrate that for swollen chains γ is much smaller, as would be expected. In this study we are confining our discussion to melts.

Interaction Terms

Our focus here is largely on hydrogen-bonding interactions, but for completeness we will also briefly consider the Flory χ term, which we use to describe dispersion and weak polar forces only. Hydrogen bonds and other specific interactions are described separately. We will also confine our attention to the mixing of polymers. For a polymer solution the modification introduced by connectivity effects has a sufficiently interesting form that we will consider it separately.

Flory χ Term. In his original treatment Flory expressed the enthalpy of mixing as

$$\Delta H_m = n_{AB}\Delta\omega_{AB} \tag{18}$$

where $\Delta\omega_{AB}$ is the energy change associated with the formation of an unlike pair of contacts:

$$\Delta\omega_{AB} = \omega_{AB} - \frac{1}{2}(\omega_{AA} + \omega_{BB}) \tag{19}$$

Using the surface contact relationships described in the preceding section, the Guggenheim approach yields

$$n_{AB} = N_B q_B z p_{AB} \tag{20}$$

but in the Flory approximation this is written

$$n_{AB} = N_B M_B z p_{AB} = N_B M_B z(1 - \gamma_B)\theta'_A \tag{21}$$

On a per mole of lattice site basis the interaction term then becomes

$$\Delta H_m\left(\frac{V_B}{V}\right) = \Phi_A\Phi_B\left(\frac{\theta'_A}{\Phi_A}(1 - \gamma_B)\right)\chi \tag{22}$$

and if M_A, $M_B \gg 1$ and $\gamma_A \approx \gamma_B \approx \gamma$

$$\Delta H_m\left(\frac{V_B}{V}\right) = \Phi_A\Phi_B(1 - \gamma)\chi \tag{23}$$

Thus for a blend of two flexible polymers the "effective" χ parameter is obtained by multiplying the Flory χ by a constant, $1 - \gamma$. However, if one chain is stiff, such that $\gamma_A > \gamma_B$, for example, then a composition dependent χ is obtained. Similarly, if chain expansion of the minor component is allowed at the composition extremes, such that γ_A and γ_B become very different, the effective value of χ assumes a parabolic form. We will explore these possibilities more thoroughly in future publications.

Hydrogen Bonding. A statistical mechanical approach to the description of hydrogen bonding (or any other reversible association) was first described in the work of Flory,[15,16] Tobolsky,[17] and Tobolsky and Blatz.[18] This approach treats the equilibrium distribution of hydrogen-bonded species, which may be chains, cyclic arrangements, etc., and has provided the basis for so-called association models. This is the approach we have adopted in our work, but its general validity has often been questioned (for example, see ref 19). However, if it is kept in mind that the identification of species is merely a convenient way of counting the distribution of hydrogen bonds, most of the difficulties disappear.

Furthermore, we have shown[4,7] that a more recently developed model by Veytsman[5] and Panayioutou and Sanchez[6] (VPS model), which counts how hydrogen bonds are distributed between donor and acceptor groups, gives identical results when the same reference state is used. As might therefore be expected, both models are modified in identical ways by the introduction of connectivity or intramolecular screening effects. Essentially, in the mean field approximation used previously the probability that a B segment is adjacent to another B segments is assumed to be proportional to Φ_B, the volume fraction of such segments. This term is now replaced by p_{BB}, which has the form given in eq 13. The equation for the free energy is not changed by this modification, although the equations for the chemical potentials and spinodal are. Because the treatment remains identical to that given previously, we will not reproduce it in the body of this paper, but a description is presented in the Appendix for the interested reader. Here we will focus on how the equations describing the stoichiometry of hydrogen bonding are changed, as this allows an experimental test of the model we are proposing.

We will consider the specific but very common case of a system where one component (B) self-associates, i.e., has both donor and acceptor groups and can thus hydrogen bond to itself in the pure state, while the second component (A) only has acceptor groups. For association in the form of linear chains the stoichiometry of hydrogen bonding can be defined in terms of dimensionless equilibrium constants K_B and K_A:

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1} \tag{24}$$

$$B_h + A \overset{K_A}{\rightleftharpoons} B_hA \tag{25}$$

Equation 24 assumes that the association is independent of chain length, which is not true for phenols and alcohols, where there are cooperative effects. However, the spectroscopically measured number of free and bonded groups can be accurately reproduced using just two self-association constants, K_2 describing dimer formation and K_B describing higher multimer formation, and this is all that is required for the model (the contribution of hydrogen bonding to the free energy of mixing depends only on the number of hydrogen bonds of each type; see the Appendix). For simplicity in this part of the development we will assume $K_2 = K_B$. Both constants are modified in an identical manner by intramolecular screening effects.

The constants K_B and K_A are usually defined in terms of volume fractions (see Flory[15] and the Appendix for a discussion of this point) as follows:

$$K_B = \frac{\Phi_{B_{h+1}}}{\Phi_{B_h}\Phi_{B_1}}\frac{h}{h+1} \tag{26}$$

$$K_A = \frac{\Phi_{B_hA}}{\Phi_{B_h}\Phi_{A_1}}\frac{hr}{h+r} \tag{27}$$

where Φ_{B_h} is the volume fraction of a hydrogen-bonded h-mer and r is the ratio of molar volumes, V_A/V_B. When screening effects are introduced, these equations become (see the Appendix)

$$K_B = \left[\frac{\Phi_{B_{h+1}}}{\Phi_{B_h}\Phi_{B_1}}\frac{h}{h+1}\right]\left[\frac{\Phi_B}{p}\right] = \tilde{K}_B\frac{\Phi_B}{p} \tag{28}$$

$$K_A = \left[\frac{\Phi_{B_hA}}{\Phi_{B_h}\Phi_{A_1}}\frac{hr}{h+r}\right]\left[\frac{\Phi_A}{(1-p)}\right] = \tilde{K}_A\frac{\Phi_A}{(1-p)} \tag{29}$$

where we have let $p = p_{BB}$. Using mass balance considerations, the equations for the stoichiometry of hydrogen bonding now become

$$\Phi_B = \frac{\Phi_{B_1}}{[1-\tilde{K}_B\Phi_{B_1}]^2}\left[1+\frac{\tilde{K}_A\Phi_{A_1}}{r}\right] \tag{30}$$

$$\Phi_A = \Phi_{A_1}\left[1+\frac{\tilde{K}_A\Phi_{B_1}}{(1-\tilde{K}_B\Phi_{B_1})}\right] \tag{31}$$

where Φ_B and Φ_A are the volume fraction of B and A units or segments present in the mixture, while Φ_{B_1} and Φ_{A_1} are the volume fractions of non-hydrogen-bonded species. These two equations are identical in form to those given previously; the only difference is that the constants K_B and K_A are replaced by the quantities $\tilde{K}_B$ and $\tilde{K}_A$. This remains true for all the other stoichiometric equations we have presented in our previous work, including those describing cooperative effects, where the quantities $\tilde{K}_2$, $\tilde{K}_B$, $\tilde{K}_A$, etc. are now used to describe the fractions of bonded and free species.

Infrared Spectroscopy and the Measurement of the Number of Hydrogen Bonds

In principle, infrared spectroscopy should be able to give a direct measurement of the number of hydrogen bonds present in many, if not most, hydrogen-bonded systems. Accordingly, by comparing the spectra of, e.g., ethyl methacrylate-*stat*-4-vinylphenol (EMAVPh) copolymers with analogous miscible blends of the two homopolymers that contain identical segment types, i.e. poly(ethyl methacrylate) (PEMA) and poly(4-vinylphenol) (PVPh), it should be possible to determine if the type of screening effects we have discussed here are important. Unfortunately, it is not that easy. Circumstantial evidence for a screening effect has been obtained from measurements of the fraction of hydrogen-bonded carbonyl groups (i.e. interassociation),[9] but it was not possible to quantitatively determine the corresponding fraction of hydrogen-bonded hydroxyl groups, for reasons that are discussed in detail elsewhere.[4]

What we really require in order to make meaningful distinctions between models is a quantitative probe of intramolecular contacts. To reiterate, the degree of hydrogen bonding of OH groups cannot be measured with any degree of precision in PVPh/PEMA blend systems. However, if we consider the case of miscible binary blends of random EMAVPh copolymers mixed with a polymer that has a different type of acceptor group, e.g., a polyether, then we can use the carbonyl band as a probe of intramolecular contacts. Now OH···O=C< contacts are unaffected by screening considerations, which only affect OH···ether contacts. This

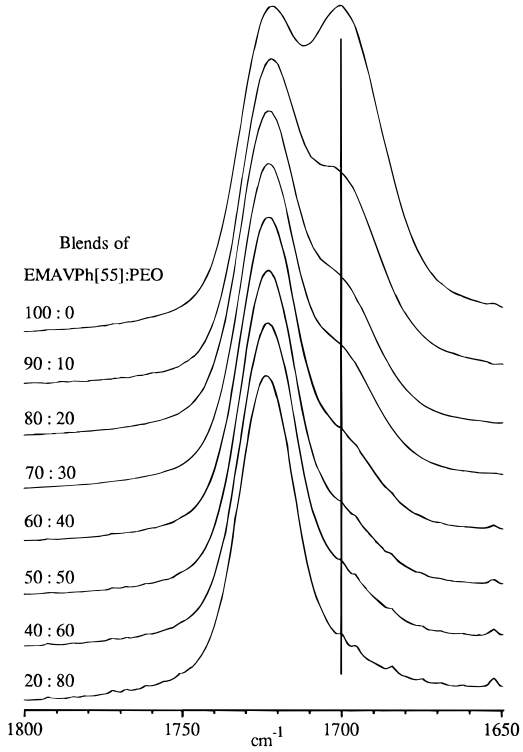

Figure 2. Infrared spectra recorded at 25 °C in the carbonyl stretching region of pure EMAVPh[55] and blends containing 10, 20 30, 40, 50, 60, and 80 volume % PEO.

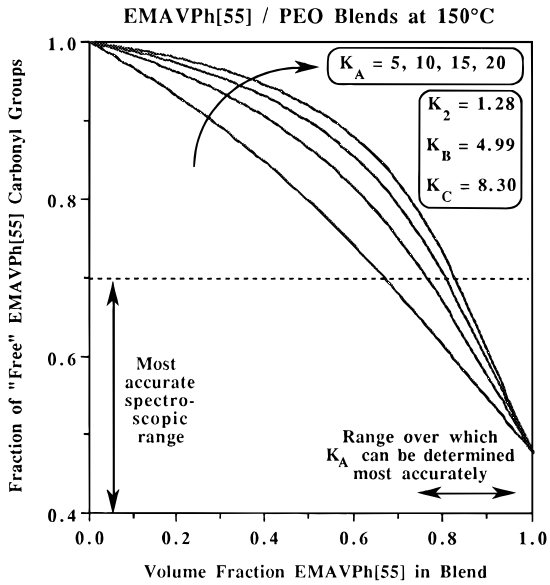

Figure 3. Simulations of the fraction of "free" carbonyl groups present at 150 °C in blends of EMAVPh[55] and PEO for K_A values of 5, 10, 15, and 20. The EMAVPh[55] self-association equilibrium constants K_2, K_B, and K_C were held constant at the values indicated.

leads us to a discussion of the infrared spectroscopic results that we have obtained from a study of poly(ethylene oxide) (PEO) blends with a random EMAVPh copolymer containing 55 weight % VPh (denoted EMAVPh[55]).

Figure 2 shows the carbonyl stretching region of typical infrared spectra obtained from films of pure EMAVPh[55] and blends containing 10, 20, 30, 40, 50, 60, and 80 weight % PEO, recorded at 150 °C (above the T_m of PEO and the T_g of the blend compositions). Note that in the spectrum of pure EMAVPh[55] two bands of approximately equal intensity are observed at ≈1725 and 1700 cm^{-1}. These bands are respectively attributed to carbonyl groups that are "free" (nonhydrogen bonded) and those that are hydrogen bonded to phenolic hydroxyl groups. By measuring the areas of these two bands the fraction of "free" carbonyl groups, $f_F^{C=O}$, may be determined, after due consideration is given to differences in the absorptivity coefficients.[3,4] From such data we have previously determined[9] values of the three dimensionless equilibrium constants (at 25 °C with a reference volume, $V_B = 100$ cm^3/mol) and enthalpies of hydrogen bond formation that describe the self-association of pure EMAVPh, i.e. $K_2 = 21.0$ and $h_2 = -5.6$ kcal/mol (OH···OH dimers), $K_B = 66.8$ and $h_B = -5.2$ kcal/mol (OH···OH "chainlike" multimers), and $K_C = 67.4$ and $h_C = -4.1$ kcal/mol (OH···O=C<).

When PEO is mixed with EMAVPh[55], the ether oxygen competes for the phenolic hydroxyl and $f_F^{C=O}$ inevitably decreases, as one can plainly see in the spectra shown in Figure 2. The extent of reduction in $f_F^{C=O}$ is of course a function of temperature, blend composition, and the value of the interassociation equilibrium constant that describes the OH···O< interaction, K_A. Armed with a set of experimentally determined equilibrium constants and the corresponding enthalpies of hydrogen bond formation, it is a relatively straightforward task to calculate the $f_F^{C=O}$ that will be present at a particular temperature in a mixture containing three different segments having phenolic hydroxyl, carbonyl, and ether oxygen groups.[4,21,22] At this stage we do not have experimental values of K_A or h_A, but we can easily calculate $f_F^{C=O}$ for different K_A values that are in the most probable range in which the experimental value of K_A might be anticipated to lie. Such calculations performed at 150 °C using K_A values of 5, 10, 15, and 20 (with $K_2 = 1.28$, $K_B = 4.99$, and $K_C = 8.30$, determined from the appropriate enthalpies of hydrogen bond formation—see above) are summarized in Figure 3. The most accurate range for determining $f_F^{C=O}$ spectroscopically is from ≈0.4 to 0.7, because this is where both the "free" and hydrogen-bonded carbonyl bands are well separated and have significant absorbances (for further details see ref 20). Accordingly, for the EMAVPh[55]/PEO system the optimum blend composition for quantitative analysis at 150 °C is between 0.05 and 0.2 volume fraction PEO.

For the sake of argument let us assume that the intramolecular screening effect discussed above does not exist. If this is so we can use the quantitative $f_F^{C=O}$ data derived from infrared spectra of EMAVPh[55]/PEO blends containing <0.2 volume fraction of PEO recorded at different temperatures (similar to those illustrated in Figure 2) to experimentally determine K_A and h_A. Using a curve-fitting methodology described in detail elsewhere[3,4] the "free" and hydrogen-bonded carbonyl band areas were determined and an experimental $f_F^{C=O}$ calculated using the appropriate absorptivity ratio ($a_R = 1.5$). These results are presented in Table 1. The interassociation equilibrium constant K_A can now be determined at a particular temperature by a least squares fit of the $f_F^{C=O}$ data to the appropriate equations describing the stoichiometry.[21,22] Table 2 lists the values of K_A determined between 140 and 190 °C. The enthalpy of hydrogen bond formation, h_A, may now be readily obtained from a van't Hoff plot of ln K_A versus inverse temperature. Using the six K_A values listed in Table 2, the following equation was determined by a

Table 1. Experimental Data

volume fraction			experimental fraction of "free" carbonyls					
EO	VPh	EMA	140 °C	150 °C	160 °C	170 °C	180 °C	190 °C
0.05	0.51	0.44	0.53	0.53	0.54	0.54	0.55	0.55
0.10	0.48	0.42	0.60	0.60	0.60	0.60	0.61	0.62
0.15	0.45	0.40	0.64	0.65	0.65	0.65	0.65	0.65
0.20	0.43	0.37	0.69	0.69	0.69	0.69	0.69	0.70
0.25	0.40	0.3		0.70				
0.30	0.37	0.33		0.71				
0.40	0.32	0.28		0.77				
0.50	0.27	0.23		0.81				
0.60	0.21	0.19		0.84				
0.80	0.11	0.09		0.89				

Table 2. Equilibrium Constants as a Function of Temperature

	equilibrium constants			
	self-association			interassociation
temp (°C)	K_2	K_B	K_C	K_A
140	1.51	5.79	9.35	16.6
150	1.28	4.99	8.30	14.2
160	1.10	4.32	7.38	12.3
170	0.95	3.77	6.61	10.4
180	0.83	3.31	5.59	9.05
190	0.72	2.92	5.38	8.05

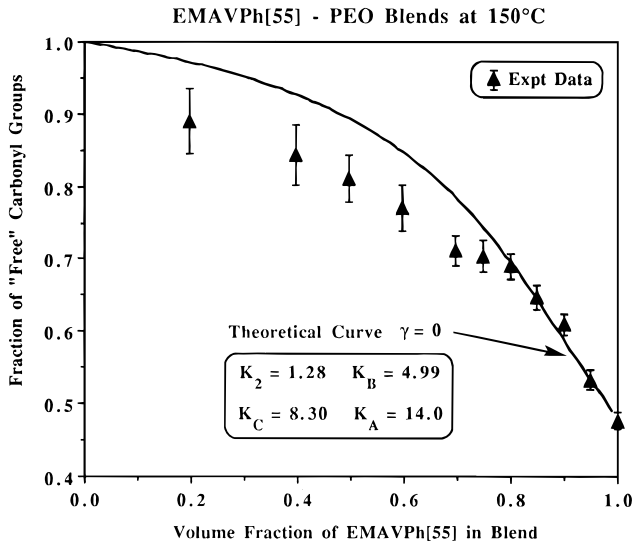

Figure 4. Plot of the calculated and experimental values of the fraction of free carbonyl groups in blends of EMAVPh[55] with PEO for the case of no intramolecular screening ($\gamma = 0$).

linear least squares fit ($R^2 = 0.998$):

$$\ln K_A = -4.00 + \frac{2814}{T} \qquad (32)$$

This corresponds to a h_A value of −5.6 kcal/mol and a value of $K_A = 231$ dimensionless units for the standard molar volume of 100 cm^3/mol at 25 °C.

Figure 4 shows the full theoretical curve of $f_F^{C=O}$ versus blend composition calculated at 150 °C, *in the absence of screening effects* (i.e. when $\gamma = 0$), together with experimental $f_F^{C=O}$ data covering the range from 0 to 80 volume % PEO. The agreement between the theoretical curve and the experimental data is excellent for the compositionally rich EMAVPh[55] blends, but it becomes progressively poorer with increasing concentration of PEO in the blend. While potential errors in the measurement of the $f_F^{C=O}$ also parallel this trend, the disparity between the theoretical curve and the experimental values is outside the limits of experimental error. It should also be mentioned that we have

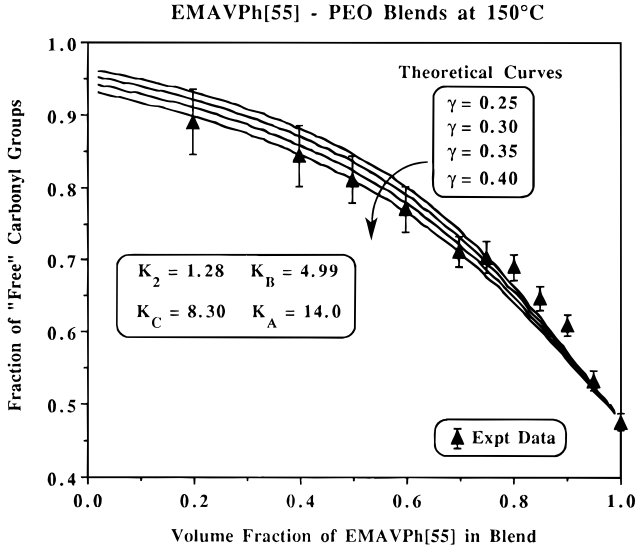

Figure 5. Plot of the calculated and experimental values of the fraction of free carbonyl groups in blends of EMAVPh[55] with PEO for the case with intramolecular screening ($\gamma = 0.25$, 0.30, 0.35, and 0.40).

obtained almost identical results from analogous EMAVPh blends with an ethylene oxide-co-propylene oxide copolymer.

Now let us recalculate the theoretical curves at 150 °C, using the same set of equilibrium constants, but with intramolecular screening introduced through the parameter γ (see eqs 13−17). Figure 5 shows a comparison of the experimental data to the theoretical curves calculated with γ values of 0.25, 0.30, 0.35, and 0.40. There are a number of aspects of these results that need to be thought about. First, and most important, the shape of the calculated curves reproduces the trend in the experimental data very well. The fit between calculated and experimental results at high concentrations of EMAVPh[55], i.e. at volume fractions greater than 0.8, is not quite as good as that shown in Figure 4, but there is a simple reason for this. These data points were used to calculate K_A in the "unscreened" system by a least squares fitting procedure, so the calculated curve was forced to fit these points. We then used this unmodified value of K_A to calculate the fraction of free carbonyls in a screened system, so that some small deviations at high concentrations will occur because of the inclusion of terms in γ. We could, of course, have used the experimental data to calculate both K_A and γ, but because these are dependent variables in the calculation of $f_F^{C=O}$, a wide range of pairs of values give practically equally good "fits". This would have defeated the purpose of the experiment, which was to demonstrate that at a given value of K_A calculations where screening is ignored cannot reproduce the overall trends in the data, but the inclusion of a screening effect does reproduce these trends. The crucial point is that at high concentrations of EMAVPh-[55] there is only a small difference in the calculated values of $f_F^{C=O}$, but as the concentration of this copolymer in the blend is decreased the difference becomes sufficient to distinguish by experiment, although one must keep in mind that the data points for the compositionally lean EMAVPh[55] are subject to the largest experimental error.

The second point that needs to be considered is that the curves calculated with γ values of 0.35 and 0.40, which are consistent with the predicted values deter-

mined from the lattice simulations, lie close to the experimental values. However, the value of γ determined from the simulations is probably too large, as they were performed on a cubic lattice and the average number of nearest neighbors in a real mixture is presumably larger than 6. Nevertheless, the calculated fraction of hydrogen-bonded carbonyls is not very sensitive to the assumed value of γ and values in the range 0.25−0.40 still result in a good agreement between calculation and experiment.

We believe that these observations are good evidence for the intrachain screening effect we have proposed. Nevertheless, we are presently devising additional, more precise, experimental checks that will be reported in future publications.

Calculations of Phase Behavior

In the final section of this paper we will note how the inclusion of an intramolecular screening effect modifies the equations for the binodal and spinodal and also indicate why the empirical correction term we have employed in previous work accounts for this effect.

The equations for the contributions of hydrogen bonding to the chemical potentials of a system that can be described with just two equilibrium constants are presented in the Appendix. Compared to the equations that do not include screening effects, they contain derivative terms. An equation for the contribution of hydrogen bonds to the spinodal becomes complex because of these terms but with the approximation $\gamma_A \approx \gamma_B \approx \gamma$ simplifies to

$$\frac{1}{\Phi_{B_1}}\left[\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\right] - \frac{1}{r\Phi_{A_1}}\left[\frac{\partial\Phi_{A_1}}{\partial\Phi_B}\right] - \left[\frac{1}{\Phi_B} + \frac{1}{r\Phi_A}\right] - \left\{\frac{\gamma\tilde{K}_B\Phi_{B_1}}{p\Phi_B}\left[1 - \frac{1}{\Phi_{B_1}}\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\right]\right\} = 0 \quad (33)$$

as also shown in the Appendix, together with expressions for the system where self-association is described with two equilibrium constants.

The first part of eq 33 is the same as that derived previously,[2,3] with the final term in parentheses arising from intramolecular screening effects. This brings us to the final question of why our previous (incorrect) choice of reference states works so well. Although the final term in eq 33 plays a role, there is a larger effect from another source. In our previous work on PVPh blends we used values of the self-association equilibrium constants (K_2, K_B) derived from 4-ethylphenol, but obtained interassociation constants directly from experimental measurements of the fraction of bonded groups in the blends. This means that the quantity Φ_{A1} and its derivatives were accurately reproduced in our calculations, at least over the bulk of the composition range. The quantity Φ_{B_1} and its derivatives were not accurately calculated, however. Nevertheless, the fraction of B···B hydrogen-bonded species, given simply by the quantity $K_B\Phi_{B_1}$ in a system where self-association is governed by a single equilibrium constant, is not greatly affected by large variations in K_B.[3,4] This is because as K_B increases, the fraction of "free" B groups, Φ_{B_1}, decreases and to a first approximation we have

$$\tilde{K}_B\Phi_{B_1} \approx K_B\Phi'_{B_1} \quad (34)$$

where it will be recalled that $K_B = (p/\Phi_B)K_B$.

What this means is that we used the calculated quantity Φ'_{B_1} in our calculations of phase behavior instead of the "correct" quantity Φ_{B_1} and its derivatives. However, we can write

$$\frac{1}{\Phi_{B_1}}\left[\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\right] = \frac{\tilde{K}_B}{\tilde{K}_B\Phi_{B_1}}\left[\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\right] \approx \frac{\tilde{K}_B}{\tilde{K}_B\Phi'_{B_1}}\left[\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\right] \quad (35)$$

and using

$$\Phi_{B_1} = \frac{K_B\Phi'_{B_1}}{\tilde{K}_B} = \frac{\Phi_B}{p}[\Phi'_{B_1}] \quad (36)$$

hence

$$\frac{\partial\Phi_{B_1}}{\partial\Phi_B} = \frac{\Phi'_{B_1}}{p} + \frac{\Phi_B}{p}\left[\frac{\partial\Phi'_{B_1}}{\partial\Phi_B}\right] \quad (37)$$

we obtain

$$\frac{1}{\Phi_{B_1}}\left[\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\right] = \frac{1}{\Phi'_{B_1}}\left[\frac{\partial\Phi'_{B_1}}{\partial\Phi_B}\right] + \frac{1}{\Phi_B} \quad (38)$$

This means that by calculating the quantity Φ'_{B_1} and its derivatives, we were introducing an error of the order of $1/\Phi_B$.

If eq 33 for the spinodal is examined, it will be seen that there is an equivalent factor $(-1/\Phi_B)$ in parentheses which cancels with the term that is in error. In other words, if we eliminate the term $1/\Phi_B$ in our old calculations, we compensate for connectivity effects. Our previous choice of reference states actually makes this term very small (see ref 3), thus compensating for intrachain screening.

Discussion

In this paper we have described various lines of evidence that have led us to the conclusion that intramolecular screening effects are important in polymer blends (and solutions). A significant driving force for this development was our inability to understand why our previous choice of reference states worked so well in allowing the prediction of phase behavior in hydrogen-bonded mixtures. We now believe our difficulties have been resolved. This may seem an esoteric and perhaps marginal point to those not interested in these types of systems, but the ramifications are actually much broader, affecting how we use simple models to describe interactions in all mixtures involving polymers. For example, the χ term used to describe nonspecific interactions has the form $\Phi_A\Phi_B(1 - \gamma)\chi$ (assuming $\gamma_A \approx \gamma_B \approx \gamma$) for blends of polymers consisting of A and B type segments, thus introducing a molecular weight dependence (through γ) into values of χ that are defined in terms of the Flory approximation ($\Phi_A\Phi_B\chi_F$, hence $\chi_F \approx (1 - \gamma)\chi$). For polymer solutions the introduction of screening effects also results in a very interesting composition dependence, but this we will consider in a separate publication.

Because of this potentially broad significance, we believe that it will be important to develop experimental probes of the number of contacts in polymer mixtures. In this regard hydrogen-bonded systems are presently unique, in that they can be probed by a spectroscopic technique that (in principle) allows the number of hydrogen bonds of each type to be counted. The initial

work presented in this paper indicates that intramolecular screening effects are indeed important and can be detected if we choose our systems carefully. We have also attempted to demonstrate the experimental difficulties in making these measurement and illustrate why the correct choice of system is crucial if various effects are to be distinguished in a reasonable manner. We will be exploring this topic and these problems in more depth in future publications.

Acknowledgment. The authors wish to acknowledge the assistance of Ms. L. Narvett in recording some of the spectra used in this study and gratefully acknowledge the financial support of the National Science Foundation, Polymers Program.

Appendix

In both the association model we have developed and the VPS treatment it is assumed that hydrogen bonds can be treated separately from other interactions, so that the partition function can be written

$$Z = Z_{FH} Z_H \tag{A-1}$$

where we use the Flory−Huggins approach to describe the mixing of chains and their "physical" (non-hydrogen bonded) interactions (Z_{FH} term), while the Z_H term imposes the constraints due to hydrogen bonding. This can be written

$$Z_H = \sum_i \Omega_i \exp(-F_i/kT) \tag{A-2}$$

where i represents a certain distribution of hydrogen-bonded species and F_i is a free energy term. For simplicity and ease of illustration we will consider a system where segments of type B have functional groups that have both donor and acceptor components (e.g., amides, urethanes, hydroxyls, etc.), while the second component, A, has only an acceptor functional group (e.g., ester, ether), as described in the body of this paper. This is typical of most of the blend systems we have studied. We will also assume that each of the hydrogen bonds in the chains (or cyclic species) formed by B is characterized by exactly the same free energy change or equilibrium constant. For many of the systems of interest this is not true, but it is easier to modify the equations later to account for cooperative effects. In fact, one remarkable aspect of the association model approach, which, to reiterate, describes the configurations available to the hydrogen bonds in terms of the equilibrium distribution of species formed, is that it actually does not require any assumption concerning the dependence of equilibrium constants on hydrogen bond chain length (or formation of cyclic species, etc.) in order to obtain an expression for the free energy. However, it is easier to follow the development if we use a concrete illustration.

The equilibrium distribution of hydrogen bonds can be described by two equilibrium constants, K_B and K_A, as also described in the main text:

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1} \tag{A-3}$$

$$B_h + A \overset{K_A}{\rightleftharpoons} B_hA \tag{A-4}$$

In the association model approach the quantity Ω_i describes the number of configurations available to the B_h, B_hA, and A_1 (non-hydrogen-bonded A units) mers characteristic of the ith distribution on a lattice whose cell size is defined by the molar volume of a B unit. Following the Flory counting procedure we used previously[2,3] we can obtain

$$\Omega_i = \frac{1}{\prod n^i_{B_h}! \prod n^i_{B_hA}! \prod n^i_{A_1}!} \times \left[\frac{n_B! n_A!}{n_B^{\sum n^i_{B_h}(h-1)} n_B^{\sum n^i_{B_hA}(h-1)} n_A^{\sum n^i_{B_hA}}}\right] \times [p_{BB}^{\sum n^i_{B_h}(h-1)+\sum n^i_{B_hA}(h-1)} p_{AB}^{\sum n^i_{B_hA}}] \frac{(z-1)^{\sum n^i_{B_h}(h-1)+\sum n^i_{B_h}h}}{\sigma^{\sum n^i_{B_h}+\sum n^i_{B_hA}}} \tag{A-5}$$

where the superscript i refers to the ith distribution.

This differs from our previous result in that we no longer assume that the probability of a B segment being adjacent to another B segment is given by Φ_B, but is equal to p_{BB}. Similarly, the probability of an A segment being adjacent to a B segment is given by p_{AB}. (In eq A-5 the quantities n_B and n_A are the numbers of segments of B and A units, respectively, the segment being defined in terms of a chemical unit containing a single hydrogen-bonding functional group. As usual, z is the coordination number and σ is a symmetry number. The products and sums are over all values of h, $1-\infty$).

The partition function is now

$$Z_H = \sum_i \Omega_i \exp(-n^{i,h}_{BB} \Delta f^\circ_{BB} - n^{i,h}_{AB} \Delta f^\circ_{BA}) \tag{A-6}$$

where $n^{i,h}_{BB}$ is the number of B···B hydrogen bonds and $n^{i,h}_{AB}$ is the number of AB hydrogen bonds in the ith distribution:

$$n^{i,h}_{BB} = \sum n^i_{B_h}(h-1) + \sum n^i_{B_hA}(h-1) \tag{A-7}$$

$$n^{i,h}_{AB} = \sum n^i_{B_hA} \tag{A-8}$$

The quantities Δf°_{BB} and Δf°_{AB} are the standard free energy changes for formation of BB and AB hydrogen bonds. In the usual development the sum in eq A-6 is replaced by the largest term, characteristic of the equilibrium distribution, which is found by differentiating with respect to n_{B_h} and n_{B_hA} and putting the results equal to zero. Performing the former operation, we obtain

$$\ln \frac{\Phi_{B_h}}{h} + 1 - \frac{h}{n_o}\left(\sum n_{B_h} + \sum n_{B_hA} + n_{A_1}\right) - (h-1)(\ln(z-1) - 1) + \ln \sigma - (h-1)\left(\ln \frac{p}{\Phi_B}\right) + (h-1)\frac{\Delta f^\circ_{BB}}{kT} = 0 \tag{A-9}$$

where for convenience we have simply replaced p_{BB} with p and n_o is the total number of lattice sites:

$$n_o = n_B + r n_A \tag{A-10}$$

where

$$r = \frac{V_A}{V_B} \tag{A-11}$$

It can be seen that eq A-9 has the Flory form of a partial molar free energy, $\bar{F}_h$, for mixing h-mers and other species with one another, together with terms in p/Φ_B and Δf°_{BB}. Flory[15] demonstrated that for the equilibrium defined by eq A-3 we have the relationship

$$-\Delta f^\circ_{BB} = \bar{F}_{h+1} - \bar{F}_h - \bar{F}_1 \tag{A-12}$$

which for $p = \Phi_B$ leads to

$$-\frac{\Delta f^\circ_{BB}}{kT} = \ln\left[\frac{\Phi_{B_{h+1}}}{\Phi_{B_h}\Phi_{B_1}}\frac{h}{h+1}\right] - \ln(z-1)\sigma \tag{A-13}$$

Because z and σ are constants, they can be included in an equilibrium constant defined as

$$K_B = \left[\frac{\Phi_{B_{h+1}}}{\Phi_{B_h}\Phi_{B_1}}\frac{h}{h+1}\right] \tag{A-14}$$

For $p \neq \Phi_B$ we have

$$K_B = \left[\frac{\Phi_{B_{h+1}}}{\Phi_{B_h}\Phi_{B_1}}\frac{h}{h+1}\right]\left[\frac{\Phi_B}{p}\right] = \tilde{K}_B\frac{\Phi_B}{p} \tag{A-15}$$

Similarly

$$K_A = \left[\frac{\Phi_{B_hA}}{\Phi_{B_h}\Phi_{A_1}}\frac{hr}{h+r}\right]\left[\frac{\Phi_A}{(1-p)}\right] = \tilde{K}_A\frac{\Phi_A}{(1-p)} \tag{A-16}$$

Flory[15,16] and Tobolsky and Blatz[18] used the method of undetermined multipliers to obtain equations for the stoichiometry of hydrogen bonding. These are much more easily constructed using mass balance considerations, however (see ref 3), and for systems where $p \neq \Phi_B$

$$\Phi_B = \frac{\Phi_{B_1}}{(1-\tilde{K}_B\Phi_{B_1})^2}\left(1 + \frac{\tilde{K}_A\Phi_{A_1}}{r}\right) \tag{A-17}$$

$$\Phi_A = \Phi_{A_1}\left(1 + \frac{\tilde{K}_A\Phi_{B_1}}{1-\tilde{K}_B\Phi_{B_1}}\right) \tag{A-18}$$

These equations are of exactly the same form as those given previously, except now $\tilde{K}_B$ and $\tilde{K}_A$ replace K_B and K_A. These equations, together with spectroscopic measurements of the equilibrium constants, are used to define the equilibrium distribution of species. However, the expression for the free energy that we obtain from eqs A-5 and A-6, which contains sums over all h,

$$\frac{\Delta F^*_H}{RT} = \sum n_{B_h}\ln\left[\frac{\Phi_{B_h}}{h}\right] + \sum n_{B_hA}\ln\left[\frac{\Phi_{B_hA}}{h+r}\right] + n_{A_1}\ln\left[\frac{\Phi_{A_1}}{r}\right] + n^h_{BB} + n^h_{AB} + (\text{terms in } z \text{ and } \sigma) - \left(n^h_{BB}\ln\frac{p}{\Phi_B} + n^h_{AB}\ln\frac{(1-p)}{\Phi_A}\right) - \left(n_B\ln\Phi_B + n_A\ln\frac{\Phi_A}{r}\right) + n^h_{BB}\Delta f_{BB} + n^h_{AB}\Delta f_{AB} \tag{A-19}$$

is not in a form that lends itself to a calculation of ΔF^*_H (note that this is a free energy with respect to Flory's reference state; to obtain the contribution of hydrogen bonds to free energy of mixing, we must subtract free energy terms corresponding to the distribution of hydrogen bonds in the pure components, which in this example involves just pure B). To obtain a useful expression, we use a result due to Prigogine, namely that the chemical potential of the components B and A are equal to the chemical potentials of the monomers

$$\mu^*_B = \mu_{B_1} \qquad \mu^*_A = \mu_{A_1} \tag{A-20}$$

The chemical potentials can be obtained by differentiating eq A-19 with respect to n_{B_1} and n_{A_1}, but before doing so, it is convenient to rearrange the expression for the free energy using eqs A-13 (and an equivalent expression for Δf°_{AB}), A-15, and A-16, to obtain

$$\frac{\Delta F^*_H}{RT} = \sum n_{B_h}\ln\left[\frac{\Phi_{B_h}}{h}\right] + \sum n_{B_hA}\ln\left[\frac{\Phi_{B_hA}}{h+r}\right] + n_{A_1}\ln\left[\frac{\Phi_{A_1}}{r}\right] + n^h_{BB} + n^h_{AB} + (\text{terms in } z \text{ and } \sigma) - n_B\ln\Phi_B - n_A\ln\Phi_A - n^h_{BB}\ln\tilde{K}_B - n^h_{AB}\ln\tilde{K}_A \tag{A-21}$$

The chemical potentials, with respect to Flory's reference state (where the species are initially separate and oriented) are then given by

$$\frac{\Delta\mu^h_B}{kT} = \ln\left[\frac{\Phi_{B_1}}{\Phi_B}\right] + M_{BB} + M_{AB} - \Phi_A M_{BB}\left[\frac{1}{\tilde{K}_B}\frac{\partial\tilde{K}_B}{\partial\Phi_B}\right] - \Phi_A M_{AB}\left[\frac{1}{\tilde{K}_A}\frac{\partial\tilde{K}_A}{\partial\Phi_B}\right] \tag{A-22}$$

$$\frac{\Delta\mu^h_A}{kT} = \ln\left[\frac{\Phi_{A_1}}{\Phi_A}\right] + r\left\{M_{BB} + M_{AB} + \Phi_B M_{BB}\left[\frac{1}{\tilde{K}_B}\frac{\partial\tilde{K}_B}{\partial\Phi_B}\right] + \Phi_B M_{AB}\left[\frac{1}{\tilde{K}_A}\frac{\partial\tilde{K}_A}{\partial\Phi_B}\right]\right\} \tag{A-23}$$

where for compactness we have defined a volume fraction of BB and AB hydrogen bonds as

$$M_{BB} = \Phi_B\left[\frac{n^h_{BB}}{n_B}\right] \tag{A-24}$$

$$M_{AB} = \frac{\Phi_A}{r}\left[\frac{n^h_{AB}}{n_A}\right] \tag{A-25}$$

and in the differentiation we used $\partial n_B/\partial n_{B_1} = 1$ and $\partial\Phi_B/\partial n_B = \Phi_A\Phi_B/n_B$.

A simple form of the free energy can now be reconstructed using

$$\Delta F^*_H = n_B\Delta\mu_B + n_A\Delta\mu_A \tag{A-26}$$

to give

$$\frac{\Delta F^*_H}{RT} = n_B\ln\left[\frac{\Phi_{B_1}}{\Phi_B}\right] + n_A\ln\left[\frac{\Phi_{A_1}}{\Phi_A}\right] + n^h_{BB} + n^h_{AB} \tag{A-27}$$

This is exactly the same form as given previously, except now the equilibrium distribution of species is defined by $\tilde{K}_B$ and $\tilde{K}_A$ instead of K_B and K_A.

The remarkable aspect of eq A-27 is that it only contains terms that describe the free energy of mixing the hydrogen-bonded species with one another. Terms in the free energy of forming individual types of hydrogen bonds (Δf_{BB} and Δf_{AB}) only enter implicitly, in that they define the equilibrium distribution. Furthermore, the free energy only depends upon the volume fraction of the non-hydrogen-bonded species, Φ_{B_1} and Φ_{A_1}, and the number of hydrogen bonds of each type, n^h_{BB} and n^h_{AB}. The form of the species is unimportant, and we could have started by considering cyclic or other species as well as linear ones.

The VPS model gives identical results when also modified to account for connectivity or correlation effects. For the example we are considering the partition function can be written

$$Z_H = \sum \Xi \exp\left(-\frac{n^h{}_{BB}\Delta f_{BB}}{kT} - \frac{n^h{}_{AB}\Delta f_{AB}}{kT}\right) \qquad \text{(A-28)}$$

where

$$\Xi = \Xi_o \hat{p}_{BB}^{n^h_{BB}} \hat{p}_{AB}^{n^h_{AB}} \qquad \text{(A-29)}$$

and Ξ_o counts the number of ways of distributing BB and AB hydrogen bonds between the donor and acceptor groups, no matter where they are located. A mean-field assumption is then introduced to impose the restriction that groups must be adjacent in order to bond, thus accounting for the $\hat{p}$ factors in eq A-29 (the definition of $\hat{p}_{BB}$ is slightly different from p_{BB}, being equivalent to V_B/V). The usual development leads to eq A-27 and also equations for the stoichiometry of hydrogen bonding.

A criticism that is often leveled at association models is that they require assumptions concerning the form of the transient species present. In the development of the equation for the free energy it does, but one always obtains eq A-27, which is essentially independent of the form of the species and only depends on the number of hydrogen bonds of each type that are present. It is thus perfectly valid to start from eq A-27, as most association models do, for any problem. The trick, however, is in the calculation of the distribution of the number of hydrogen bonds of each type and this often requires an assumption concerning the way groups hydrogen bond to one another (e.g., are there cooperative effects, etc.). This is also true of the VPS or any other model, however.

Finally, if we now include cooperative effects and use two equilibrium constants to describe self-association, we have

$$M_{BB} = \Phi_B\left[1 - \frac{\tilde{\Gamma}_1}{\tilde{\Gamma}_2}\right] \qquad \text{(A-30)}$$

where

$$\tilde{\Gamma}_2 = \left[1 - \frac{\tilde{K}_2}{\tilde{K}_B}\right] + \frac{\tilde{K}_2}{\tilde{K}_B}\left[\frac{1}{(1 - \tilde{K}_B\Phi_{B_1})^2}\right] \qquad \text{(A-31)}$$

$$\tilde{\Gamma}_1 = \left[1 - \frac{\tilde{K}_2}{\tilde{K}_B}\right] + \frac{\tilde{K}_2}{\tilde{K}_B}\left[\frac{1}{(1 - \tilde{K}_B\Phi_{B_1})}\right] \qquad \text{(A-32)}$$

The equation for the spinodal for both the simple self-association case ($\tilde{K}_2 = \tilde{K}_B$) and ($\tilde{K}_2 \neq \tilde{K}_B$) is

$$\frac{\partial^2(\Delta F^*_H/RT)}{\partial \Phi_B{}^2} = 0 = \frac{1}{\Phi_{B_1}}\left[\frac{\partial \Phi_{B_1}}{\partial \Phi_B}\right] - \frac{1}{r\Phi_{A_1}}\left[\frac{\partial \Phi_{A_1}}{\partial \Phi_B}\right] - \left[\frac{1}{\Phi_B} + \frac{1}{r\Phi_A}\right] - \frac{1}{\tilde{K}_B}\left[\frac{\partial \tilde{K}_B}{\partial \Phi_B}\right]\left[\frac{\partial M_{BB}}{\partial \Phi_B}\right] + \frac{M_{BB}}{\tilde{K}_B{}^2}\left[\frac{\partial \tilde{K}_B}{\partial \Phi_B}\right]^2 - \frac{M_{BB}}{\tilde{K}_B}\left[\frac{\partial^2 \tilde{K}_B}{\partial \Phi_B{}^2}\right] - \frac{1}{\tilde{K}_A}\left[\frac{\partial \tilde{K}_A}{\partial \Phi_B}\right]\left[\frac{\partial M_{AB}}{\partial \Phi_B}\right] + \frac{M_{AB}}{\tilde{K}_A{}^2}\left[\frac{\partial \tilde{K}_A}{\partial \Phi_B}\right]^2 - \frac{M_{AB}}{\tilde{K}_A}\left[\frac{\partial^2 \tilde{K}_A}{\partial \Phi_B{}^2}\right] \qquad \text{(A-33)}$$

where

$$\frac{\partial M_{BB}}{\partial \Phi_B} = \frac{M_{BB}}{\Phi_B} + \frac{M_{BB}}{\tilde{K}_B}\left[\frac{\partial \tilde{K}_B}{\partial \Phi_B}\right] + \frac{M_{BB}}{\Phi_{B_1}}\left[\frac{\partial \Phi_{B_1}}{\partial \Phi_B}\right] \qquad \text{(A-34)}$$

$$\frac{\partial M_{AB}}{\partial \Phi_B} = -\frac{1}{r}\left[1 + \frac{\partial \Phi_{A_1}}{\partial \Phi_B}\right] \qquad \text{(A-35)}$$

In terms of p, the derivatives of the terms $\tilde{K}_A$ and $\tilde{K}_B$ are

$$\frac{\partial \tilde{K}_B}{\partial \Phi_B} = \frac{\tilde{K}_B}{p}\left[\frac{\partial p}{\partial \Phi_B}\right] - \frac{\tilde{K}_B}{\Phi_B} \qquad \text{(A-36)}$$

$$\frac{\partial^2 \tilde{K}_B}{\partial \Phi_B{}^2} = \frac{2\tilde{K}_B}{\Phi_B}\left[\frac{1}{\Phi_B} - \frac{1}{p}\frac{\partial p}{\partial \Phi_B}\right] + \frac{\tilde{K}_B}{p}\left[\frac{\partial^2 p}{\partial \Phi_B{}^2}\right] \qquad \text{(A-37)}$$

$$\frac{\partial \tilde{K}_A}{\partial \Phi_B} = \frac{\tilde{K}_A}{\Phi_A} - \frac{\tilde{K}_A}{(1-p)}\left[\frac{\partial p}{\partial \Phi_B}\right] \qquad \text{(A-38)}$$

$$\frac{\partial^2 \tilde{K}_A}{\partial \Phi_B{}^2} = \frac{2\tilde{K}_A}{\Phi_A}\left[\frac{1}{\Phi_A} - \frac{1}{(1-p)}\frac{\partial p}{\partial \Phi_B}\right] - \frac{\tilde{K}_A}{(1-p)}\left[\frac{\partial^2 p}{\partial \Phi_B{}^2}\right] \qquad \text{(A-39)}$$

where

$$\frac{\partial p}{\partial \Phi_B} = (1 - \gamma_B)\left[\frac{\partial \theta_B}{\partial \Phi_B}\right] \qquad \text{(A-40)}$$

$$\frac{\partial^2 p}{\partial \Phi_B{}^2} = (1 - \gamma_B)\left[\frac{\partial^2 \theta_B}{\partial \Phi_B{}^2}\right] \qquad \text{(A-41)}$$

and

$$\frac{\partial \theta_B}{\partial \Phi_B} = \frac{\theta_A \theta_B}{\Phi_A \Phi_B} \qquad \text{(A-42)}$$

$$\frac{\partial^2 \theta_B}{\partial \Phi_B{}^2} = \frac{\theta_A \theta_B}{(\Phi_A \Phi_B)^2}[(\theta_A - \theta_B) + (\Phi_B - \Phi_A)] \qquad \text{(A-43)}$$

However, in the approximation $\gamma \approx \gamma_A \approx \gamma_B$

$$\frac{\partial p}{\partial \Phi_B} = (1 - \gamma) \tag{A-44}$$

$$\frac{\partial p^2}{\partial \Phi_B{}^2} = 0 \tag{A-45}$$

and the derivatives of $\tilde{K}_A$ with respect to composition are all zero, resulting in eq 33 given in the body of the paper for the simple self-association case ($\tilde{K}_2 = \tilde{K}_B$).

When ($\tilde{K}_2 \neq \tilde{K}_B$) we have

$$\frac{\partial^2(\Delta F_H^*/RT)}{\partial \Phi_B{}^2} = 0 = \frac{1}{\Phi_{B_1}}\left[\frac{\partial \Phi_{B_1}}{\partial \Phi_B}\right] - \frac{1}{r\Phi_{A_1}}\left[\frac{\partial \Phi_{A_1}}{\partial \Phi_B}\right] - \left[\frac{1}{\Phi_B} + \frac{1}{r\Phi_A}\right] - \frac{\gamma(1-\gamma)}{p^2}\left[1 - \frac{\tilde{\Gamma}_1}{\tilde{\Gamma}_2}\right] - \frac{\gamma}{p}\left[1 - \frac{\tilde{\Gamma}_1}{\tilde{\Gamma}_2}\right] \times \left[\frac{1}{\Phi_{B_1}}\frac{\partial \Phi_{B_1}}{\partial \Phi_B} - \frac{\gamma}{p\Phi_B}\right]\left[1 - \frac{2(\tilde{\Gamma}_1/\tilde{\Gamma}_2)}{(1 - \tilde{K}_B\Phi_{B_1})}\right] \tag{A-46}$$

References and Notes

(1) Petri, H. M.; Schuld, N.; Wolf, B. A. *Macromolecules* **1995**, *28*, 4975.
(2) Painter, P. C.; Graf, J. F.; Coleman, M. M. *J. Chem. Phys.* **1990**, *92*, 6166.
(3) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing, Inc.: Lancaster, PA, 1991.
(4) Coleman, M. M.; Painter, P. C. *Prog. Polym. Sci.* **1995**, *20*, 1.
(5) Veytsman, B. A. *J. Phys. Chem.* **1990**, *94*, 8499.
(6) Panayiotou, C.; Sanchez, I. C. *J. Phys. Chem.* **1991**, *95*, 10090.
(7) Painter, P. C.; Veytsman, B.; Coleman, M. M. *J. Pol. Sci. A. Polym. Chem.* **1994**, *32*, 1189.
(8) Bhagwagar, D. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1994**, *27*, 7139.
(9) Coleman, M. M.; Xu, Y.; Painter, P. C. *Macromolecules* **1994**, *27*, 127.
(10) Bhagwagar, D. E. Ph.D Thesis, The Pennsylvania State University, 1994.
(11) Szleifer, I. *J. Chem. Phys.* **1990**, *92*, 6940.
(12) Schweizer, K. S.; Curro, J. G. *Chem. Phys.* **1990**, *149*, 105.
(13) Guggenheim, E. A. *Mixtures*; Clarendon: Oxford, U.K., 1952.
(14) Victor, J. M.; Imbert, J.-B.; Lhuiller, D. *J. Chem. Phys.* **1994**, *100*, 5372.
(15) Flory, P. J. *J. Chem. Phys.* **1944**, *12*, 425.
(16) Flory, P. J. *J. Chem. Phys.* **1946**, *14*, 49.
(17) Tobolsky, A. V. *J. Chem. Phys.* **1944**, *12*, 402.
(18) Tobolsky, A. V.; Blatz, P. J. *J. Chem. Phys.* **1945**, *13*, 379.
(19) Huyskens, P. L.; Haulait-Pirson, M. C.; Siegel, G. G.; Kapuku, F. *J. Phys. Chem.* **1988**, *92*, 6841.
(20) Coleman, M. M.; Pehlert, G. J.; Painter, P. C. *Macromolecules* in press.
(21) Le Menesterel, C.; Bhagwagar, D. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1992**, *25*, 7101.
(22) Zhang, H.; Bhagwagar, D. E.; Graf, J. F.; Painter, P. C.; Coleman, M. M. *Polymer* **1994**, *35*, 5379.

MA960815L