Effect of Hydrogen Bonding on the Enthalpy of Mixing and the Composition Dependence of the Glass Transition Temperature in Polymer Blends

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ABSTRACT: A classical thermodynamic theory is presented for the composition dependence of the glass transition temperature for miscible polymer blends that involve strong specific interactions, such as hydrogen bonds. The derived T_g equation is separated into three terms, a nonspecific interaction component, a heat of mixing in the liquid-state term, and a term that accounts for that part of the temperature dependence of the specific heat that is due to self-association. This third term is assumed to dominate the overall temperature dependence of the specific heat, so that the nonspecific interaction component is assumed independent of temperature. We also argue that the heat of mixing in systems with strong specific interactions can be positive, depending upon the balance between self-association and association between segments of the different components of the blend (interassociation). Using parameters reported in previous studies, we find the predicted mixtures' T_g's are in good agreement with experiment, allowing an understanding of the unusual variations of T_g with composition that are observed for some blends that have strong specific interactions.

Introduction

The most commonly used criterion for establishing the miscibility of the components of a polymer blend is the detection of a single glass transition temperature (T_g), usually at a point between the T_g's of the homopolymer constituents. There are various relationships describing the composition dependence of the blend T_g,[1-14] the most general of which appear to be those originally derived by Couchman and Karasz[1] and Couchman,[2,3] in the sense that various other equations can be derived from these by making simplifying assumptions. Couchman's equations follow from thermodynamic arguments and have the advantage of being formulated in terms of pure component properties, so that the blend T_g can, in principle, be predicted from known or experimentally determined parameters.

Although successfully applied to certain blends, there are a number of systems where the deviations of observed T_g's from Couchman's equations are significant.[11,15-23] Some of the largest and most intriguing differences have been observed in those systems where the interactions between the different components are strong and specific, through the formation of either electron donor–acceptor complexes[19,20] or hydrogen bonds.[11,15-18,21-23] Kwei,[11] for example, observed large positive deviations of T_g's from the calculated weight-average values for blends of novolac resins with isotactic poly(methyl methacrylate), but S-shaped curves for blends with syndiotactic poly(methyl methacrylate), where the blend T_g's were lower than those calculated from the weight-average values at high concentrations of this polymer but higher than the weight-average values at low concentrations. Similarly, in this laboratory we have observed a T_g for a blend of poly(vinylphenol) (PVPh) with poly(vinylpyridine) (PVPy) that is higher than either of the homopolymer T_g's,[21] as did Meftahi and Fréchet in a more extensive and systematic study of mixture of these polymers.[22]

There have been a number of attempts to rationalize such deviations by the use of equations similar in form to those described by Couchman, but with added terms, some of which have been derived from fundamental arguments[12-14] while others are largely empirical with parameters that are obtained by a fit to the data.[7-11] Although it is often stated that these quantities are related to the strength of the interactions between the different components, parameters with very different signs have been determined for blends where the type and number of interactions appear to be very similar.[11,17,19,20] On more fundamental grounds, Goldstein[24] has argued that the proposed thermodynamic basis for Couchman's equations is not valid and proposed an alternative definition of mixing terms.

In this paper we will first make some observations concerning the enthalpy and entropy of mixing polymers that hydrogen bond and then proceed to demonstrate how these provide an explanation for the unusual results described above.

Specific Interactions, Self-Association, and the Enthalpy of Mixing

It appears to be accepted wisdom to state that because the combinatorial entropy of mixing polymers is small an exothermic heat of mixing (ΔH_m) is necessary for miscibility and that specific interactions are one source of a negative ΔH_m. In systems that hydrogen bond, however, there is the possibility of an endothermic heat of mixing in a miscible mixture. The origin of this positive ΔH_m is self-association of at least one of the pure components and mixing then occurs because of a gain in *entropy* upon mixing. These characteristics of systems with specific interactions are sometimes assumed to be negligible or apparently unaccounted for in treatments of polymer mixtures and we will consider them here. Although our arguments will center on systems that clearly hydrogen bond, the points we will make are general and apply to mixtures where, for example, a specific interaction, hence association, has its origin in ionic or strong dipole forces.

It is often the case that miscible binary mixtures of polymers that hydrogen bond have as one component a polymer that "self-associates" (i.e., is hydrogen bonded in the pure state), while the second does not, but has a functional group capable of hydrogen bonding to segments of the first.[25] Examples of the former include polyamides, polyurethanes, polymers containing carboxylic acid functional groups, and polymers containing phenolic OH groups, such as poly(vinylphenol). Examples of the second class of polymers include polyethers, polymers containing ester functional groups, and those with a basic nitrogen

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atom, such as poly(vinylpyridine). This list can be extended to include polymers that associate less strongly, perhaps through weak hydrogen bonds or dipole interactions, such as poly(vinyl chloride) or polyacrylonitrile, often mixed with polymers of copolymers that contain ester groups. Although the enthalpy of formation of *individual* hydrogen bonds (or other types of associated complexes) is always negative, the overall enthalpy of mixing will depend upon the balance between three contributions: (a) a *positive* contribution to the enthalpy of mixing that is a result of "breaking" hydrogen bonds in the self-associating polymer as it is mixed and diluted with the second component of the mixture; (b) a *negative* contribution to the enthalpy of mixing that is a result of *forming* hydrogen bonds between the self-associating polymer and second component; (c) contributions from other interactions (dispersion forces, dipole forces, etc.).

Although the heats of mixing of polymers cannot be measured directly, Paul and co-workers have used analog calorimetry to determine the heats of mixing of a number of model compounds as, for example, in their recent study of mixtures of molecules containing carboxylic acids with those containing esters,[26] where a positive heat of mixing was determined over most of the composition range. The enthalpy of formation of specific types of hydrogen bonds can be fairly accurately determined by spectroscopic methods, however, as can the number of hydrogen bonds of each type that are present. This allows us to calculate the contributions of hydrogen bonds to the heat of mixing with a reasonable degree of confidence. The enthalpy of mixing can be simply written as[25]

$$\Delta H_m = n_B(p_{BB} - p^\circ_{BB})h_B + n_A p_{BA} h_{BA} + RT(V/V_B)\phi_A\phi_B\chi \quad (1)$$

where n_B and n_A are the number of moles of segments of the self-associating and non-self-associating species, respectively, where a segment is defined so as to contain just one functional group capable of forming a hydrogen bond; p_{BB} is the fraction of functional groups of type B that are hydrogen bonded to other B segments in the mixture (equal to the probability that a B group, taken at random, is hydrogen bonded in this fashion); p°_{BB} is the fraction of hydrogen-bonded B segments in pure B; p_{BA} is the fraction of A segments that are hydrogen bonded to a B segment; h_B and h_{BA} are the enthalpies of individual B- - -B and B- - -A hydrogen bonds, respectively; and V is the molar volume of the mixture, while V_B is the molar volume of the B segments, which we use as a reference volume to define χ. We will use poly(vinylphenol) (PVPh) as an example of a self-associating polymer and consider mixtures with poly(n-butyl methacrylate) (PBMA) and poly(vinylpyridine) (PVPy). We have studied systems of the first type in considerable depth[25,27-30] and determined equilibrium constants that accurately reproduce the experimentally measured fraction of hydrogen-bonded species of each type and the enthalpies of hydrogen bond formation that define the variation of these quantities with temperature. The relationship between the quantities p_{BB} and p_{BA} in eq 1 and these equilibrium constants are given in ref 25, and the parameters used in the calculations are listed in Table I.

Figure 1 shows the calculated heats of mixing (at 25 °C) as a function of composition for blends of PVPh with PBMA. They are positive throughout the composition range. Also shown in this figure are the separate contributions of the χ term, calculated from the values of the solubility parameters given previously,[25] and the contribution of the hydrogen-bonding interactions. This latter term is positive over *most* of the composition range, because of the balance of the terms in eq 1. This may, at first, appear to be a surprising and perhaps even unlikely result, so we will explore it in a little more detail.

Table I
Hydrogen-Bonding Association Constants[a]

interaction	V_{ref}, mL/mol	K	Δh, cal/mol	ref
OH- - -OH (phenolic dimer formation)	100.0	21.0	-5600	32
OH- - -OH (phenolic self-association)	100.0	68.0	-5200	32
OH- - -N (phenolic–pyridine)	100.0	598.0	-7000	39
OH- - -OCO (phenolic–methacrylate)	100.0	37.1	-3750	29
OCONH- - -O (urethane–ether)	108.3	9.6	-5000	41
OCONH- - -OCONH (urethane self-association)	108.3	205.0	-5000	41

[a] V_{ref} = reference volume of equilibrium constant, K = association equilibrium constant at 25 °C, Δh = enthalpy of hydrogen bond formation.

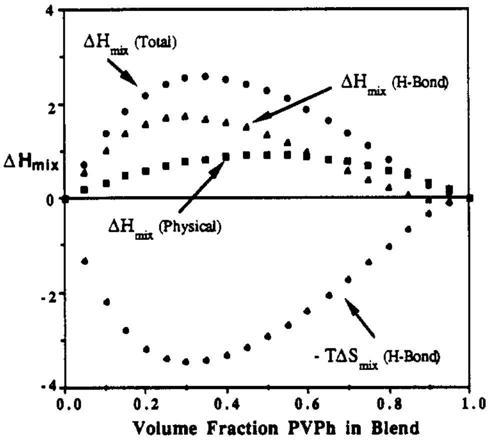


Figure 1. Plot of the calculated heat of mixing of PVPh–PBMA blends as a function of composition. Also shown are the separate contributions of the hydrogen bonding and nonspecific interaction terms to ΔH_{mix} and the calculated contribution of the change in entropy of the system due to the change in hydrogen bonding with composition.

The first term in eq 1 represents the change in the number of like, B- - -B, hydrogen bonds upon mixing. The fraction of such bonds in pure B is always greater than in the mixture, $p^\circ_{BB} > p_{BB}$, so that this term is always positive (h_B is, of course, negative). Accordingly, if a simple molecule such as phenol is diluted with a non-hydrogen-bonding solvent such as cyclohexane, there is a positive heat of mixing.[31] We have used eq 1 (with $h_{BA} = 0$) to calculate heats of mixing for such mixtures, and the results are compared to experiment in Figure 2. Equilibrium constants etc. describing the self-association of phenol in cyclohexane have been reported by Whetsel and Lady,[32] and we used values of 10.3 and 8.4 for the solubility parameters of phenol and cyclohexane, the former representing a value obtained so as to *exclude* the effects of hydrogen bonding.[25] Given the limits of using solubility parameters, the agreement is good, but the crucial point here is the positive contribution to the heat of mixing that is a consequence of self-association in the pure state. Clearly, if instead of cyclohexane we use a solvent that could hydrogen bond to phenolic OH groups, we could then obtain a negative contribution to the heat of mixing, *but this will depend upon the values of* p_{BA} *and* h_{BA}, i.e., the relative strength of the like (B- - -B) and unlike (B- - -A) hydrogen bonds. For the PVPh–PBMA system we calculate that the negative contribution to the free energy

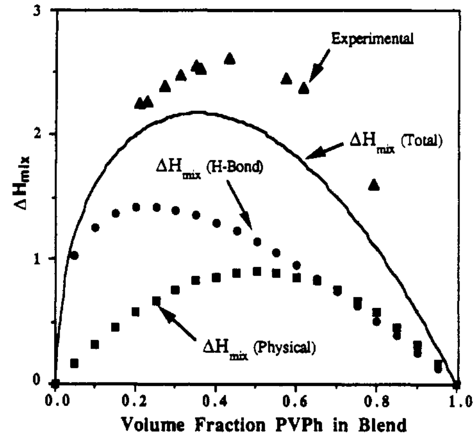


Figure 2. Comparison of experimental heat of mixing data[31] for phenol-cyclohexane mixtures to calculated values.

from the formation of OH- - -ester (B- - -A) hydrogen bonds is not large enough to overcome the effect of self-association, except at low concentrations of the ester-containing polymer (i.e., more ester/OH hydrogen bonds are formed than OH/OH hydrogen bonds are broken at these concentrations). This is because both K_A and h_A, the equilibrium constant describing B- - -A interactions and the enthalpy of such interactions, are both smaller than the equivalent quantities that describe self-association. [Note that the equilibrium constant K_A and enthalpy of hydrogen bond formation h_A were determined *experimentally* for the polymer repeat units. For low molecular weight analogues of equivalent molar volume, there could be different values of K_A, h_A, etc., as these quantities may depend upon chain stiffness.[25]]

Given this result, one might at first conclude that there is no reason for these two polymers to mix; but they are theoretically predicted to be miscible over the entire composition range, using the same parameters for the calculations of the free energy and spinodal, and experiments confirm these predictions[29] (up to temperatures of ~160 °C, where an LCST occurs). This is because there are significant entropic in addition to enthalpic changes as a result of hydrogen bond formation, or for that matter the formation of any associated complex. This remains true in polymers, even though the *combinatorial* entropy of mixing is negligible, because the number of configurations available to the polymer changes with concentration (i.e., the number and type of hydrogen bonds that are present). This can be perceived by considering the entropy of mixing two polymers, relative to a reference state of the separate and oriented species, as the sum of two parts:

$$\Delta S_m = \Delta S_{comb} + \Delta S_{dis} \qquad (2)$$

the first term involving the usual combinatorial entropy, negligible for mixing two polymers, while the second describes an entropy of disorienting these molecules. For weak nonpolar forces ΔS_{dis} is assumed independent of composition and is eliminated when converting to a reference state of the pure disoriented polymers. The formation of hydrogen-bonding complexes limits the number of configurations available to the chain at any instant of time, however, and this forms the basis for applying association models to these systems.[25,33] The distribution of hydrogen-bonded species in a mixture is usually very different from that in the pure components, and this results in a significant change in the entropy of the system (for small molecules, the formation of an A- - -B hydrogen bond leads to a loss of rotational freedom of the molecules; for a polymer, entropy changes will be related to loss of degrees of internal rotational freedom of segments of the chain). It is interesting to note that 21 years ago Flory[34] pointed out that specific local interactions could affect the configurations in this manner (footnote on p 12 of ref 34).

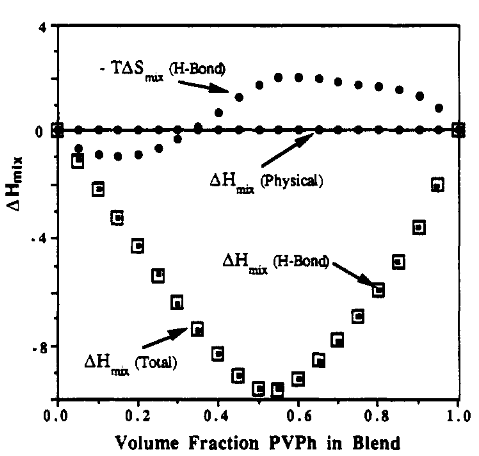


Figure 3. As in Figure 1, but for the blend PVPh-PVPy.

As might be expected, the entropy changes associated with specific interactions are usually opposite in sign and effect to the heat of mixing (although these also depend upon the balance between the changes corresponding to breaking "like" hydrogen bonds and forming "unlike" ones). Using equations given in complete form in refs 25 and 33, we calculated the $-T\Delta S$ component of the hydrogen-bonding interactions by subtracting the heat of mixing from the free energy changes (due to hydrogen bonding), and this result is also presented in Figure 1. It can be seen that the calculated increase in entropy corresponding to the "breaking" of B- - -B hydrogen bonds, less the entropy loss from forming A- - -B bonds, gives a larger negative contribution to the free energy than the positive heat of mixing, so that these polymers are miscible at ambient temperatures.[29] Accordingly, it appears that it may not be necessary to have an exothermic heat of mixing to obtain polymer miscibility; the entropy changes corresponding to the change in the number of self-association interactions is also crucial. It follows that the assumption that self-association can be ignored in theories of specific interactions in polymers neglects what could be an important factor in determining the miscibility of many systems. Furthermore, heat of mixing measurements on model systems are not necessarily good guides to the miscibility of these blends. We appreciate that these observations might be viewed skeptically, and it is unfortunate that we cannot experimentally test these conclusions by direct heat of mixing measurements on blends. However, we will demonstrate here that calculated heats of mixing can be used to predict the composition dependence of the glass transition with some success.

Finally, for completeness and later use in our discussion of blend T_g, we present an example of a system where the enthalpy of mixing is negative and the entropic changes corresponding to the change in the distribution of hydrogen-bonded species are now unfavorable to mixing over most of the composition range. Again using the parameters presented in Table I, we calculate a large exothermic heat of mixing for blends of PVPh with poly(vinylpyridine) (PVPy) as shown in Figure 3. The "strength" of the hydrogen bond formed between the phenolic OH groups and the basic nitrogen of the pyridine ring is much stronger than the forces of self-association between the phenolic OH groups, and this is reflected in both the experimentally determined enthalpy of hydrogen bond formation and the equilibrium constant given in Table I. In this case the favorable enthalpic terms are larger than the unfavorable entropic changes, and this system should therefore be miscible. That this is indeed so has been demonstrated by Meftahi and Fréchet.[35]

Equations for the Composition Dependence of the Glass Transition

From the condition that S, H, and V are continuous at T_g and the assumption that the entropy, enthalpy, and volume of mixing, ΔS_{mix}, ΔH_{mix}, and ΔV_{mix}, are also continuous, the following equations are obtained:[1-3]

Entropy, S

$$\ln T_{g_m} = \frac{X_A \Delta C_{p_A} \ln T_{g_A} + X_B \Delta C_{p_B} \ln T_{g_B}}{X_A \Delta C_{p_A} + X_B \Delta C_{p_B}} \qquad (3)$$

Volume, V

$$T_{g_m} = \frac{X_A V^\circ_A \Delta\alpha_A T_{g_A} + X_B V^\circ_B \Delta\alpha_B T_{g_B}}{X_A V^\circ_A \Delta\alpha_A + X_B V^\circ_B \Delta\alpha_B} \qquad (4)$$

Enthalpy, H

$$T_{g_m} = \frac{X_A \Delta C_{p_A} T_{g_A} + X_B \Delta C_{p_B} T_{g_B}}{X_A \Delta C_{p_A} + X_B \Delta C_{p_B}} \qquad (5)$$

where X is the mole fraction, V° is the volume of the pure polymer, ΔC_p and $\Delta\alpha$ are the discontinuities in the specific heat and thermal expansion coefficient at the respective T_g's, and subscripts A, B, and m denote the pure polymers and the mixture, respectively. Goldstein notes that eqs 1 and 3 cannot simultaneously be true except in the limiting condition of $T_{g_A} = T_{g_B}$. His major criticisms are on more fundamental grounds, however, and predominantly involve the possibility of discontinuities in the entropy of mixing, ΔS_m, together with ΔH_m and ΔV_m, at the glass transition.[24]

Couchman and Karasz[1] and Couchman[2,3] obtained eq 1 by letting the entropy of the mixture be equal to the weighted sum of the entropies of the pure components plus an entropy of mixing term, ΔS_m, that includes *all* contributions from mixing

$$S = X_A S_A + X_B S_B + \Delta S_m \qquad (6)$$

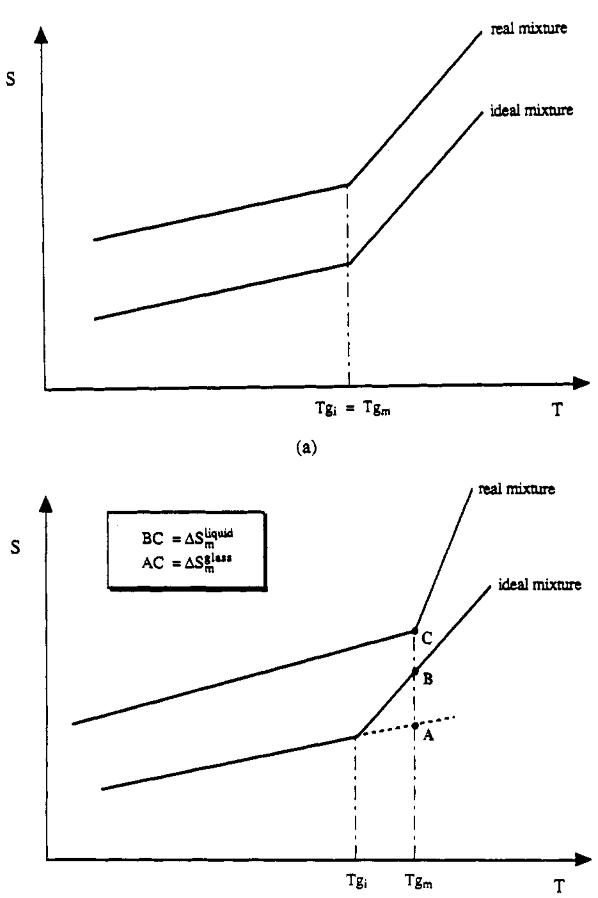
S_A and S_B are then defined relative to their pure component glass transition temperatures T_{g_A} and T_{g_B} to obtain

$$S = X_A\left[S^\circ_A + \int_{T_{gA}}^{T_{gm}} C_{p_A}\, d(\ln T)\right] + X_B\left[S^\circ_B + \int_{T_{gB}}^{T_{gm}} C_{p_B}\, d(\ln T)\right] + \Delta S_m \qquad (7)$$

Equation 5 can be written for both the liquid and glassy states (superscripts l and g), and from the condition that $S^l = S^g$ at T_{g_m}, the following equation can be obtained:

$$X_A \int_{T_{gA}}^{T_{gm}} (C_{p_A}{}^{l} - C_{p_A}{}^{g})\, d(\ln T) + X_B \int_{T_{gB}}^{T_{gm}} (C_{p_B}{}^{l} - C_{p_B}{}^{g}) \times d(\ln T) + \Delta S_m{}^{l} - \Delta S_m{}^{g} = 0 \qquad (8)$$

If it is now assumed that the heat capacity increments are independent of temperature and that $\Delta S_m{}^l = \Delta S_m{}^g$, then eq 3 is obtained. Goldstein[24] points out, however, that ΔS_m, *as defined by Couchman*, can be discontinuous at T_{g_m}, and his arguments are illustrated by Figure 4. Figure 4a compares a schematic entropy/temperature plot for an "ideal" ($\Delta S_m = 0$) mixture (with a glass transition temperature T_{g_i}) to that of a "real" mixture (T_{g_m}). Couchman[2] argues that for polymer mixtures ΔS_m is very small, so that any difference between $\Delta S_m{}^l$ and $\Delta S_m{}^g$ can be neglected and $T_{g_i} = T_{g_m}$. For blends where the interactions are relatively weak, such as the poly(2,6-dimethyl-1,4-phenylene oxide)–polystyrene system, this is apparently a good assumption and eq 1 works well.[2] For blends where the components interact strongly, there are significant contributions to ΔS_m from noncombinational terms, however, as we noted above. The entropy of mixing in the liquid state $\Delta S_m{}^l$ is now appreciable due to this contribution from specific interactions, and any difference between $\Delta S_m{}^l$ and $\Delta S_m{}^g$, which will depend on how the latter is defined, can no longer be neglected. Goldstein argues that (in effect) T_{g_m} determines $\Delta S_m{}^g$, and this situation is illustrated schematically in Figure 4b for $T_{g_m} > T_{g_i}$, a situation experimentally observed in the PVPh–PVPy blends mentioned in the Introduction. Now $\Delta S_m{}^g$, as defined by Couchman, is no longer equal to $\Delta S_m{}^l$ and would only be equal to $\Delta S_m{}^l$ when $T_{g_i} = T_{g_m}$ (but, to reiterate, this is apparently a good assumption in mixtures where the interactions are relatively weak).



(a)

(b)

Figure 4. Entropy vs temperature curves for "ideal" and "real" mixtures where the enthalpies of mixing in the liquid and glassy states are equal (top plot) and discrete (bottom plot).

Clearly, there can be no conceptual difficulty in using any of the thermodynamic variables, S, H, or V, to obtain equations describing the composition dependence of T_{g_i}; discrepancies arise from the nature of the assumptions used to obtain various solutions, such as the dependence of ΔC_p upon temperature and the nature of $\Delta S_m{}^g$, $\Delta H_m{}^g$, etc. In our view the central problem is the assignment of a working definition to the concept of an entropy or enthalpy of mixing in the glassy state. Angell et al.[36] considered the issue to be "too close to metaphysical" to be considered but proposed that the only sort of mixing that can be conceptually compatible with the glassy state is ideal mixing in a process where labels are changed but positions remain inviolate. Goldstein proposed that ΔS_m at any temperature be defined as the mixing of the polymer components in whatever state they happen to be, glassy or liquid, at that temperature. This issue is crucial in systems where hydrogen bonds (or other strong, specific interactions) occur, in that the number of hydrogen-bonded species is a strong function of temperature in the liquid state, but the distribution of species becomes frozen at or just below the T_g. To proceed, therefore, we need to make some assumptions concerning mixing in the glassy state. The validity of these assumptions can then be tested by how well we can *predict* experimental observations of composition dependence (i.e., without the use of empirical parameters obtained by a fit to the data).

We will use enthalpy as our thermodynamic variable, for two reasons. First, we can obtain parameters (equilibrium constants) describing the distribution of hydrogen-bonded species and the enthalpy changes that occur upon mixing from infrared spectroscopic measurements, as discussed above. Second, the result we then obtain is comparable in form to those derived by Kwei[11] and Braun and Kovacs.[5]

The enthalpy of mixing in the glassy state, ΔH_m^g can be taken to mean one of two things. It can be the difference in enthalpy between a real mixture and an ideal one at the temperature where it becomes frozen into a particular configuration. This would be equal to ΔH_m^l at this temperature (although one could presumably freeze a configuration characteristic of a higher temperature by quenching the sample from this temperature to one well below T_g, thus freezing a distribution of hydrogen-bonded species (or other types of complexes) that is different from the one found at T_{g_m}). Alternatively, it could be taken to mean the hypothetical mixing of the glassy polymers mentioned above. These processes lead to distinctly different mixtures for polymers that interact strongly, such as the PVPh–PVPy blends that we have used as an example. In the glassy state the hydrogen bonds between the hydroxyl groups of poly(vinylphenol) are frozen in the distribution found at or just below the T_g of this polymer (assuming slow cooling). We presume mixing in the glassy state to mean that this distribution remains unchanged upon blending with poly(vinylpyridine), so that O–H- - -O–H hydrogen bonds are not broken and O–H- - -N hydrogen bonds are not formed in this process. In this case ΔH_m^l will be very different from ΔH_m^g. At this time we know of no fundamental theoretical justification for choosing one of these definitions over the other, and we have not been able to come up with one that is anything more than hand-waving. However, on the compelling grounds that in many strongly interacting systems it has been experimentally found that T_{g_m} is not equal to T_{g_l}, we will assume that the second definition is the appropriate one for this problem and see where that leads us. In effect, we will adopt aspects of the definitions given by Goldstein[24] and Angell et al.[36] We are not concerned with the conceptual problem of a discontinuity in ΔH_m at T_g, assuming it is an artifact of how we define ΔH_m^g, but we do not entirely accept the argument that (hypothetical) mixing in the glassy state is ideal. If we follow Angell et al.[36] and consider this process to be one where labels are changed but positions remain inviolate, then mixing requires exchanging labels in such a manner that the covalent connections of the polymers are maintained to give the molecular weight distribution found in the pure species, *as are the hydrogen bond connections between segments of the same type*, to give the distribution of hydrogen-bonded species also found in the pure components. Each of the configurations available to the system under these restrictions will have a different distribution of noncovalent and hydrogen-bonded contacts, however, which will presumably contribute to the enthalpy of the system in a manner that can be described, for example, by a χ parameter defined so as to describe weak (nonspecific) dispersive forces only. Accordingly, if we separate the enthalpy of mixing into two contributions, from specific (ΔH_m^H) and nonspecific or "physical" forces (ΔH_m^P), we can write

$$\Delta H_m^{\,l} = \Delta H_m^{\,H,l} + \Delta H_m^{\,P,l} \qquad (9)$$

$$\Delta H_m^{\,g} = \Delta H_m^{\,H,g} + \Delta H_m^{\,P,g} \qquad (10)$$

where $\Delta H_m^{H,g} = 0$ (because the distribution of hydrogen bonds, in the examples we are using, is not allowed to change) and $\Delta H_m^{P,g} = \Delta H_m^{P,l}$, where we assume changing labels in the glassy state gives an equivalent contribution to the enthaply as allowing the molecules to mix in the liquid state (with no changes in the distribution of associated species). It follows that $\Delta H_m^l - \Delta H_m^g$ is equal to $\Delta H_m^{H,l}$, the contribution of specific interactions to the heat of mixing in the liquid state.

We can now follow the procedure of Couchman and Karasz[1] and Couchman[2,3] to obtain equations for the composition dependence of T_g by first writing equations of the following form for both the glassy and liquid states:

$$H = X_A H_A + X_B H_B + \Delta H_m \qquad (11)$$

Defining H_A and H_B relative to their pure component glass transitions and using the continuity of H at T_g, we then obtain

$$X_A \int_{T_{g_A}}^{T_{g_m}} \left(\left[\frac{\partial H_A^{\,l}}{\partial T} \right] - \left[\frac{\partial H_A^{\,g}}{\partial T} \right] \right) dT + X_B \int_{T_{g_B}}^{T_{g_m}} \left(\left[\frac{\partial H_B^{\,l}}{\partial T} \right] - \left[\frac{\partial H_B^{\,g}}{\partial T} \right] \right) dT + \Delta H_m^{\,l} - \Delta H_m^{\,g} = 0 \qquad (12)$$

In hydrogen-bonding *liquids* there is a strong dependence of the specific heat on temperature, but as Costas and Patterson[37,38] have pointed out, this is dominated by the variation in the distribution of hydrogen-bonded species with temperature. It is a natural consequence of the Flory lattice model we have employed that strong specific interactions are separated from weaker dispersion and other "physical" forces.[25] Accordingly, we also express the specific heat of the liquid as the sum of these two contributions:

$$C_p^{\,l} = C_p^{\,P,l} + C_p^{\,H,l} \qquad (13)$$

We now make the assumption that over the temperature range of interest $C_p^{P,l}$ is constant, as is C_p^g (because there is no change in the distribution of hydrogen-bonded species in the glassy state) to obtain

$$T_{g_m} = \frac{X_A \Delta C_{p_A} T_{g_A} + X_B \Delta C_{p_B} T_{g_B}}{X_A \Delta C_{p_A} + X_B \Delta C_{p_B}} - \frac{1}{X_A \Delta C_{p_A} + X_B \Delta C_{p_B}} \left[X_A \int_{T_{g_A}}^{T_{g_m}} \left[\frac{\partial H_A^{\,H,l}}{\partial T} \right] dT + X_B \int_{T_{g_B}}^{T_{g_m}} \left[\frac{\partial H_B^{\,H,l}}{\partial T} \right] dT + \Delta H_m^{\,H,l} \right] \qquad (14)$$

where we have substituted $\Delta H_m^{H,l}$ for $\Delta H_m^l - \Delta H_m^g$, omitted the superscript P from the specific heat increments ΔC_p, and left C_p^H as $\partial H^H/\partial T$ terms for reasons that will soon be apparent.

It has been our experience that hydrogen-bonding interactions can result in miscibility in blends where one component self-associates (e.g., PVPh), but the second does not, but has a functional group capable of "accepting" the hydrogen-bonding proton of the first (e.g., PVPy).[25] We follow our usual convention and let the subscript B represent the self-associating polymer, and for these systems we can now write

$$\int_{T_{g_A}}^{T_{g_m}} \left[\frac{\partial H_A{}^{H,l}}{\partial T} \right] dT = 0 \tag{15}$$

$$\int_{T_{gB}}^{T_{g_m}} \left[\frac{\partial H_B{}^{H,l}}{\partial T} \right] dT = (H_B{}^{H,l})_{T_{gm}} - (H_B{}^{H,l})_{T_{gB}} = (H^\circ + n_B p^\circ{}_{BB} h_B)_{T_{gm}} - (H^\circ + n_B p^\circ{}_{BB} h_B)_{T_{gB}} = n_B h_B [(p^\circ{}_{BB})_{T_{gm}} - (p^\circ{}_{BB})_{T_{gB}}] \tag{16}$$

$$\Delta H_m{}^{H,l} = n_B h_B (p_{BB} - p^\circ{}_{BB})_{T_{gm}} + n_A h_A (p_{BA})_{T_{gm}} \tag{17}$$

where as above $p^\circ{}_{BB}$ is the fraction of B segments involved in B- - -B hydrogen bonds in pure B, p_{BB} is the fraction in the mixture, h_B is the enthalpy of formation of a B- - -B hydrogen bond, p_{BA} is the fraction of A segments hydrogen bonded to B segments, h_{BA} is the enthalpy of formation of a B- - -A hydrogen bond, and n_A and n_B are the numbers of moles of A and B segments, respectively, which are defined so that each contains just one hydrogen-bonding functional group. The heat of mixing $\Delta H_m{}^{H,l}$ is determined at T_{g_m}. To reiterate, the fractions of hydrogen-bonded species p_{BB}, $p^\circ{}_{BB}$, and p_{BA} can all (in principle) be determined from infrared spectroscopic measurements, as can h_B and h_{BA} from the variation of these quantities with temperature. We relate the quantities p_{BB}, p_{BA}, etc. to equilibrium constants and the important volume fraction quantities ϕ_{B1} and ϕ_{A1}, which represent the fraction of B and A segments which are *not* hydrogen bonded, as these parameters form an easily computable link between infrared spectroscopic measurements, the stoichiometry of hydrogen bonding, and thermodynamic quantities.

We can now write eq 14 in the following form:

$$T_{g_m} = \frac{X_A \Delta C_{p_A} T_{g_A} + X_B \Delta C_{p_B} T_{g_B}}{X_A \Delta C_{p_A} + X_B \Delta C_{p_B}} - \frac{X_B[(H_B{}^{H,l})_{T_{gm}} - (H_B{}^{H,l})_{T_{gB}}] + \Delta H_m{}^{H,l}}{X_A \Delta C_{p_A} + X_B \Delta C_{p_B}} \tag{18}$$

If we now make the following substitutions

$$k = \Delta C_{p_B} / \Delta C_{p_A} \tag{19}$$

$$q = -\frac{X_B[(H_B{}^{H,l})_{T_{gm}} - (H_B{}^{H,l})_{T_{gB}}] + \Delta H_m{}^{H,l}}{X_A X_B} \tag{20}$$

or

$$q' = -\frac{X_B[(H_B{}^{H,l})_{T_{gm}} - (H_B{}^{H,l})_{T_{gB}}] + \Delta H_m{}^{H,l}}{X_A X_B (X_A + k X_B)} \tag{21}$$

we can obtain the equation derived by Braun and Kovacs[5]

$$T_{g_m} = \frac{X_A T_{g_A} + k X_B T_{g_B}}{X_A + k X_B} + \frac{X_A X_B q}{X_A + k X_B} \tag{22}$$

or that given by Kwei[11]

$$T_{g_m} = \frac{X_A T_{g_A} + k X_B T_{g_B}}{X_A + k X_B} + X_A X_B q' \tag{23}$$

If we are correct in our analysis, the origin of the change is sign of q' in blends of similar polymers is now immediately apparent, as this parameter should not be considered as simply reflecting the strength of unlike interactions in systems with strong specific interactions. Instead, it depends upon the balance between self-association and association between unlike polymers, as expressed in the $\Delta H_m{}^{H,l}$ term. Furthermore, it also depends upon the temperature dependence of the specific heats of one or both components. The sign of this latter contribution will depend upon whether $T_{gB} > T_{g_m}$ or $T_{g_m} < T_{gB}$. (Also, the composition dependence of the interactions (when these are strong and specific) is more complex than the mean field $X_A X_B q$ form would suggest.) Accordingly, a more general form of the Kwei equation can be written as

$$T_{g_m} = \frac{X_A T_{g_A} + k X_B T_{g_B}}{X_A + k X_B} + X_A X_B (q'_m(X) + q'_B(T)) \tag{24}$$

where $q'_m(X)$ is a composition-dependent term that depends upon the balance of interactions (self-association vs interassociation) in the system while $q'_B(T)$ represents the contribution from the temperature dependence of the specific heat of the self-associating component (or components). To reiterate, the $q'_m(X)$ term can be either positive or negative, depending upon the balance of self-association and interassociation interactions, and in special cases the sign of this term can also change with composition. The sign of the $q'_B(T)$ term will depend upon whether or not $T_g > T_{gB}$. This all presumes, of course, that there is some validity to our assumptions. We will now turn our attention to a comparison of the results calculations based on eq 18 to experimentally determined values of T_{g_m}.

Table II
Pure-State Properties of Various Polymers

polymer	mol wt	V,[a] mL/mol	ΔC_p,[b] cal/(g·K)	T_g,[c] °C
poly(methyl methacrylate)	100.1	82.8	0.101	100.0
poly(*tert*-butyl acrylate)	128.2	119.3	0.036	30.0
poly(vinylphenol)	120.2	100.2	0.128[d]	138.0
poly([43%]VPh-*co*-styrene)	258.3	224.5	0.138[d]	147.0
poly(vinylpyridine)	105.2	84.9	0.156[d]	155.0
APU	132.2	108.3	0.104[d]	98.0
EPO [70% EO]	48.0	46.3	0.164	−65.0
PHMP	106.1	63.0	0.123	89.9

[a] V = repeat-unit volume, obtained by Penn State group contributions. [b] ΔC_p = liquid–glass Δ in heat capacity, experimental value at T_g. [c] T_g = glass transition temperature, experimental value. [d] Obtained by a van Krevelen heat capacity group contribution method.

Calculations and Discussion

To calculate the contribution of the enthalpic quantities $H_B{}^{H,l}$ and $\Delta H_m{}^{H,l}$ to T_{g_m} we require a knowledge of the equilibrium constants describing self-association and those describing association between unlike groups.[25] The systems that we have characterized most thoroughly are those involving PVPh,[25,28-30] so we have chosen blends involving this polymer for most our calculations. The first system we will consider involves mixtures of PVPh with PVPy, and we will use the experimental data of Meftahi and Fréchet[35] for purposes of comparison. Using the parameters listed in Tables I and II, we calculated values of T_{g_m} using eq 18 rearranged to the following form:

$$[X_A \Delta C_{p_A} (T_{g_m} - T_{g_A}) + X_B \Delta C_{p_B} (T_{g_m} - T_{g_B})] + X_B[(H_B{}^{H,l})_{T_{gm}} - (H_B{}^{H,l})_{T_{gB}}] + [\Delta H_m{}^{H,l}] = 0 \tag{25}$$

This was accomplished by an iterative process, as the equi-

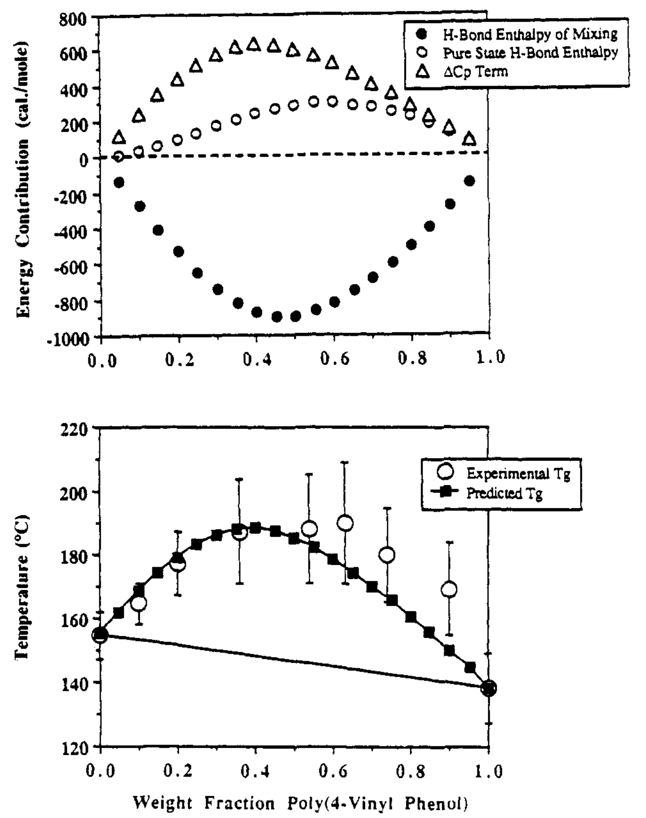


Figure 5. Energy contributions to the T_g equation (top) and the predicted blend T_g (bottom) for poly(vinylpyridine) mixed with poly(vinylphenol).

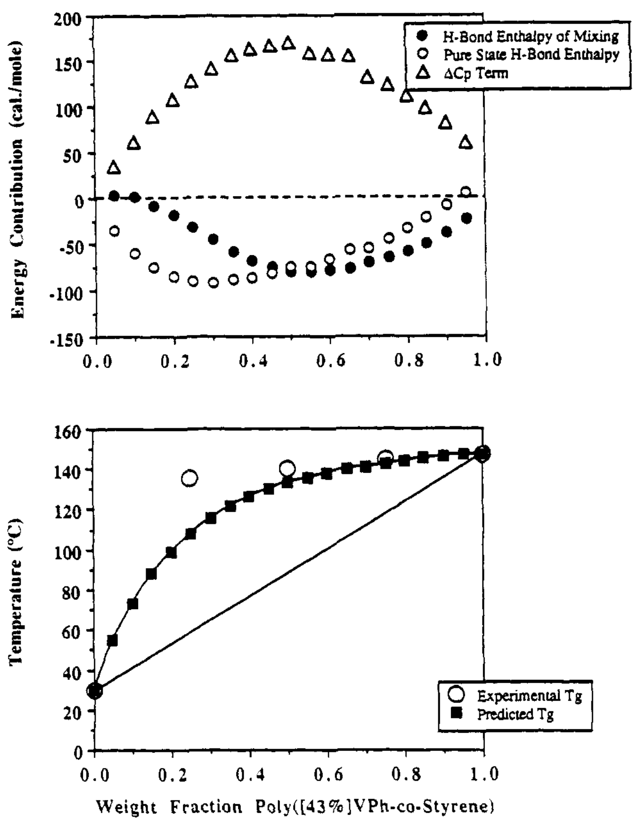


Figure 6. Energy contributions to the T_g equation (top) and the predicted blend T_g (bottom) for poly(styrene-*co*-vinylphenol[43 mol %]) and poly(*tert*-butyl acrylate).

librium constants vary according to the van't Hoff relationship, thus accounting for the variation of the enthalpic terms with temperature. Using eqs 16 and 17 and expressions for p_{BB} etc. given elsewhere,[25] we calculate values of T_{g_m} as a function of composition that are compared to the experimentally observed values in the plot shown at the bottom of Figure 5. It can be seen that the agreement is excellent over most of the composition range, showing some relatively minor deviations at high PVPh concentrations. We emphasize that this curve is not obtained by fitting any of the parameters. In fact, we did not have a value for the equilibrium constant K_A describing phenolic OH–pyridine hydrogen bonds, and so we simply used that reported by Gramstad[39] nearly 30 years ago.

The plot shown at the top of Figure 5 displays the contributions of the three different terms in square brackets on the left-hand side of eq 25. It can be seen that the heat of mixing, $\Delta H_m^{H,l}$, is large and negative, and this is only partly compensated by the term representing the contribution of hydrogen bonds to the change in enthalpy of pure PVPh on going from T_{g_B} to T_{g_m} (i.e., the $(H^{H,l})_{T_{g_m}} - (H^{H,l})_{T_{g_B}}$ term). Accordingly, we calculate large deviations of T_{g_m} from the weight fraction mean, which allows the ΔC_p term (i.e., the first term in eq 19) to become large enough to balance the difference in these two terms. In other words, the T_g's of the mixtures show large positive deviations from those which would be determined by Couchman's equations because of the large negative heat of mixing term.

Similar results are obtained for blends of a poly(styrene-*co*-vinylphenol [43 mol %]) copolymer with poly(*tert*-butyl acrylate), a system studied by Zhu et al.[40] In this system, however, there is a smaller negative enthalpy of mixing term, but because $T_{g_B} > T_{g_A}$, the pure-state enthalpy term also contributes to the positive deviation of the calculated value of T_{g_m} from the weight-average mean, as shown in Figure 6. The sum of the terms is such that the calculated value of T_{g_m} rises steeply with increasing concentration of the styrene-*co*-vinylphenol copolymer and then levels off at a value close to the T_g of this component in the pure state. The predictions are again in good agreement with the experimental values that have been reported.

In the first part of this paper we pointed out that a positive heat of mixing is possible for miscible blends that interact through strong, specific interactions. We calculate such a positive heat of mixing for blends of PVPh with poly(methyl methacrylate) as shown in Figure 7. For this blend we also calculate that the contributions of the pure PVPh enthalpic term (which, it will be recalled, represents the contribution of hydrogen bonds to the temperature variation of C_p^l) are negative. The balance of terms is such that the calculated values of T_{g_m} are close to the weight-average mean of the pure component T_g's. In this case the agreement between the calculated values and those determined experimentally by Gow and Siow[23] are not as spectacularly good, but, given the breadth of the glass transition observed in most blends, is still reasonable. In fact, relatively minor changes in just one parameter, the enthalpy of O–H- - -ester carbonyl hydrogen bonds, h_A, from 3.75 to 4.1 kcal/mol, within the range of experimental error for determining such parameters from spectroscopic measurements,[25] results in excellent agreement. We would emphasize that even without such minor adjustments we obtain relatively good agreement with experiment, however, and include the values of the "fitted" T_g here simply to illustrate that our calculated results are as close to the observed values as can be expected given the effect of experimental error. It should also be noted that in the first example we considered (PVPh–PVPy, Figure 5) the values of T_{g_m} were largely determined by the heat of mixing

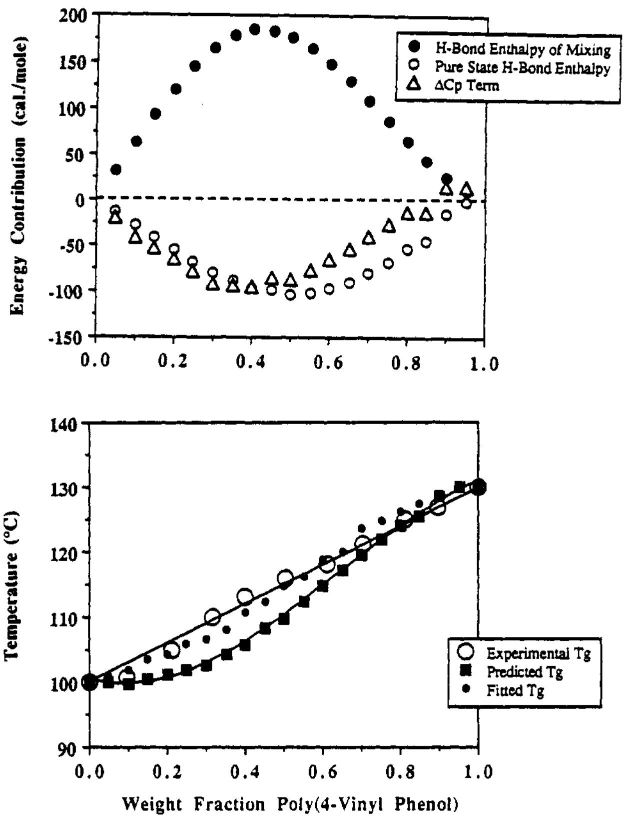


Figure 7. Energy contributions to the T_g equation (top) and the predicted blend T_g (bottom) for poly(vinylphenol) mixed with poly(methyl methacrylate).

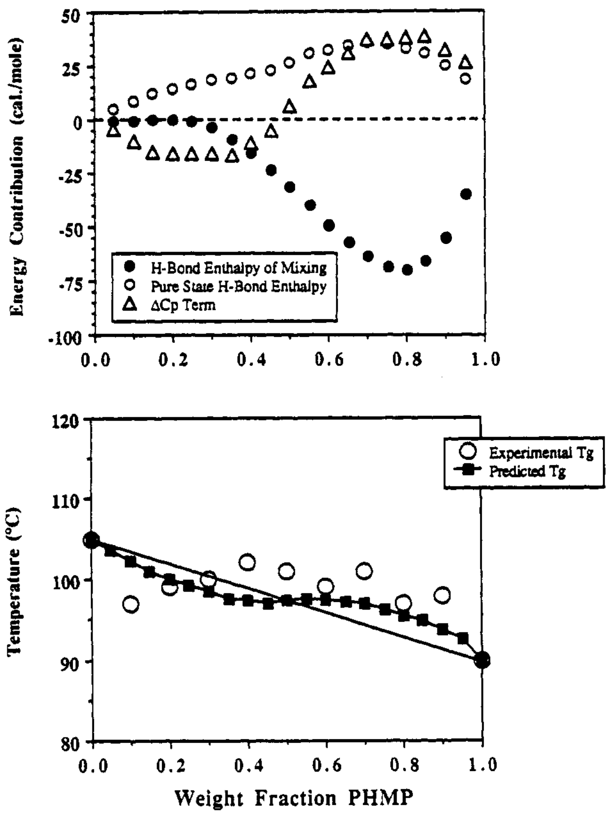


Figure 8. Energy contributions to the T_g equation (top) and the predicted blend T_g (bottom) for poly[(1-hydroxy-2,6-phenylene)methylene] mixed with poly(methyl methacrylate).

term, while in the second example (Figure 6) both this term and the term accounting for the temperature dependence of the specific heat due to self-association have the same sign, so both act to produce positive deviations of T_{g_m}. In the case of blends of PVPh with PMMA these two terms are of opposite sign and much more finely balanced, producing much smaller deviations of the calculated values of T_{g_m} from the weight-averaged mean. One would therefore expect that errors in each of these terms would have a greater effect in blends of this type.

Clearly, when the enthalpic terms are of opposite sign and asymmetric in their composition dependence, it would be possible to obtain the unusual S-shaped T_g curves observed by Pennacchia et al.[18] and Kwei[11] in blends involving novolacs. Unfortunately, we do not have equilibrium constants for many of the polymers used in this work, some of which contain polar substituents that can dramatically alter the strength of the hydrogen bonds in the system.[18] The simplest polymer used, a poly[(1-hydroxy-2,6-phenylene)methylene] (PHMP), should have interactions that are similar to PVPh, however, and we employed equilibrium constants from this latter system, adjusted so as to account for the difference in molar volume of the repeat units of these polymers[25] (see Table II). We used a value of h_A = 5.06 kcal for the enthalpy of OH- - -ester hydrogen bonds (compared to the value of 3.75 kcal used for the PVPh–PMMA blend), as this corresponds to the value experimentally determined by Pennacchia et al.[18] by spectroscopic measurements. The results are shown in Figure 8, where it can be seen that we calculate an S-shaped curve for T_{g_m} that is in good agreement with experimental values. The shape of this curve is determined by the asymmetry of the enthalpy of mixing term (which is slightly positive at low PHMP concentrations and negative at high concentrations) and the balance between this and the temperature dependence of the contribution of specific interactions to the enthalpy of the pure PHMP.

Finally, we have so far dealt only with blends where the self-associating component contains a phenolic OH group, because we are limited to studies of systems where we have obtained equilibrium constants by spectroscopic methods or where other investigators have reported such parameters. We have also characterized blends of an amorphous polyurethane with a poly(ethylene oxide-*co*-propylene oxide) (EPO) copolymer,[41] however, and using the parameters reported in this study (see Tables I and II), we can again compare predicted and experimental values of the values of T_{g_m}, as shown in Figure 9. Again there is good agreement, but because the enthalpy terms (i.e., second and third terms of eq 19) are of opposite sign and not much different in magnitude, their effect practically cancels, leaving a result that is close to that which would be obtained with Couchman's equation.

Summary and Conclusions

Our first observation is that in a miscible system where strong specific interactions occur it is possible to have an endothermic heat of mixing. This is because of favorable noncombinatorial entropic factors, usually ignored in simple theories of mixing, which have their origin in self-association of one of the blend components. It follows that in certain systems heat of mixing measurements are not a good guide to (free energy) interaction parameters.

Although this observation cannot be tested directly, it has certain ramifications concerning the composition dependence of the T_g of such mixtures. By making an assumption concerning the nature of mixing in the glassy state, or more precisely how we should define the difference in the enthalpy of a glassy real mixture relative to an ideal one, we have derived an equation similar in form to that

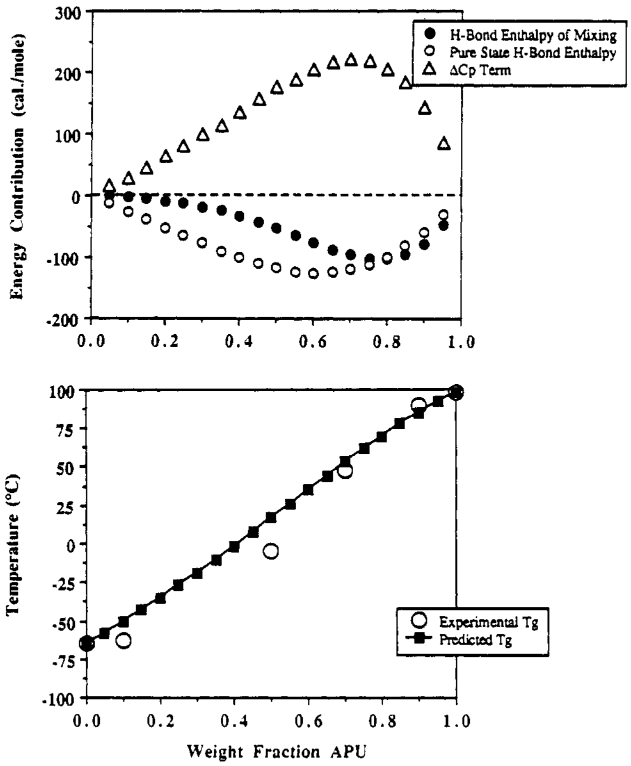


Figure 9. Energy contributions to the T_g equation (top) and the predicted blend T_g (bottom) for an amorphous polyurethane (APU) mixed with poly(ethylene oxide-*co*-propylene oxide) (EPO).

obtained by Braun and Kovacs[5] and Kwei.[11] This is equivalent to the result obtained by Couchman,[2,3] but with additional terms. For blends where there are strong specific interactions, such as hydrogen bonds, these terms have two components, a heat of mixing in the liquid state and a term that accounts for that part of the temperature dependence of the specific heat that is due to self-association. We assume that this term dominates the overall temperature dependence of this quantity, so that the nonspecific interaction component is assumed independent of temperature. Using parameters reported in previous studies, we have calculated values for the T_g's of mixtures that are in good agreement with experiment, allowing an understanding of the unusual variations of T_g with composition that are observed for some blends that have strong specific interactions.

In spite of this success, we remain uneasy about the assumptions we have made or, more fundamentally, the entire concept of mixing in the glassy state. We conclude this article with an observation that could ultimately provide a more satisfactory explanation for the success of the equations we have derived, but which will require more work to establish its validity. Wunderlich and Jones[42] have pointed out that differences in conformation, crystallinity, and intermolecular forces are of only minor importance in determining the heat capacity of linear polymers between about 60 K and their glass transitions. Differences in heat capacity between polymers in this temperature range appear to be largely governed by differences in mass per carbon backbone atom and differences in the molecular vibrations characteristic of the isolated chains. If this is so, then we would expect that the enthalpy or entropy vs temperature curves of a "real" mixture below T_{g_m} would be close to that of an ideal mixture; i.e., the "ideal" and "real" S vs T lines for the glassy state shown in Figure 4b would, to a first approximation, superimpose. Accordingly, ΔS_m^{glass}, defined as the separation in these curves, would be small or zero. If this can be shown to be a good assumption, we could obtain the same result as above (eq 18), with the exception that the contribution of "physical" interactions to the heat of mixing term, ΔH_m^{liquid}, should now also be included.

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Registry No. PVPh (homopolymer), 59269-51-1; PBMA (homopolymer), 9003-63-8; PVPy (homopolymer), 9003-47-8; (St)(VPh) (copolymer), 72317-19-2; (APU)(EPO) (copolymer), 9003-11-6; $H_2C{=}CHCO_2Bu$-*t* (homopolymer), 25232-27-3; $H_2C{=}C(CH_3)CO_2Me$ (homopolymer), 9011-14-7; poly[(2-hydroxy-1,3-phenylene)methylene], 77222-49-2.