Effect of Hydrogen Bonding on the Melting Point Depression in Polymer Blends Where One Component Crystallizes

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ABSTRACT: The Nishi-Wang equation has been modified to account for the effect of strong specific interactions through the application of an associated model. The modified equation is then applied to blends of poly(ethylene oxide) with first, an amorphous polyurethane, second, a poly(vinylphenol), and finally, an ethylene-*co*-methacrylic acid copolymer. All of these systems have been previously studied by infrared spectroscopy, and equilibrium constants describing the distribution of hydrogen-bonded species as a function of composition were taken from this work. By assuming that χ, which in this model describes nonspecific interactions only, can be obtained from solubility parameters, the melting point depression of poly(ethylene oxide) crystal can be calculated. There is excellent agreement between theoretical prediction and experimental measurements, and the strong composition dependence of specific interactions is clearly demonstrated.

Introduction

The depression of the melting point of the crystalline component of a mixture where the amorphous phase is a miscible blend has been widely used to study interactions between polymer segments (see refs 1-14, for example). The data obtained in these studies are usually analyzed in terms of the equation derived by Nishi and Wang,[1] which, in turn, is based on using the Flory-Huggins equation[15] to obtain the chemical potential of the crystallizable component in the amorphous phase:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R}{\Delta H_f}\frac{V_A}{V_B}\left[\frac{\ln \phi_A}{m_A} + \left(\frac{1}{m_A} - \frac{1}{m_B}\right)\phi_B + \phi_B^2\chi\right] \tag{1}$$

where A is the crystallizable polymer, V_A and V_B are the molar volumes of the repeating unit of the polymers A and B, V_B is used to define the lattice cell size (and hence χ), m_A and m_B are the degrees of polymerization, ϕ_i is the volume fraction of the *i*th component, and T_m and T_m° are the equilibrium melting temperatures in the blend and in pure A, respectively. When m_A and m_B are both large, then the left-hand side of eq 1 is a linear function of ϕ_B^2. The line should (just about) go through the origin and have a slope equal to χ, and therefore be a useful method for measuring this interaction parameter.

There are problems, of course. Alfonso and Russell[8] determined that at least in blends of poly(ethylene oxide) (PEO) with poly(methyl methacrylate) (PMMA) the accuracy to which the equilibrium melting points can be determined is comparable to the depression of the melting point, so that an interaction parameter cannot be determined with any degree of certainty. In this system, however, the maximum melting point depression observed was only 2.5 °C. In other blends, particularly those involving strong(er) specific interactions, such as hydrogen bonds, the melting point depression can be larger, sometimes 5-10 °C or more,[1-14] but obviously errors are still a significant factor, casting doubts on the accuracy of any value of χ so determined. In many of these systems there is also a clear composition dependence of the interaction parameter or parameters. Even in some systems where the data have been fit to a straight line, the intercept at zero concentration ($\phi_B = 0$) is finite (after accounting for the molecular weight terms in eq 1). The limited composition range employed in some of these studies suggests that the relationship here might also be nonlinear, but over a narrow range the resulting curve appears flat.

Although in some studies the interaction parameters determined from measurements of melting point depression have been equated to a heat of mixing, in general, it is more appropriate to regard χ as a free energy term which could be composition dependent. Our various studies of hydrogen bonding in polymer blends[16] suggest that there is indeed a strong dependence of such specific interactions on concentration. We will demonstrate this more explicitly here and also experimentally test the ability of the model to *predict* the melting point depression and its variation with composition in three binary blend systems, all of which contain the same crystallizable component, PEO, mixed with three polymers that hydrogen bond: poly(vinylphenol) (PVPh), an amorphous polyurethane (APU), and ethylene-*co*-methacrylic acid copolymer (55% methacrylic acid, EMMA[55]).

Experimental Section

The polymers employed in this study, PEO, APU, EMMA[55], and PVPh, and the preparation of the PEO-APU, PEO-EMAA[55], and PEO-PVPh blends have been fully described previously.[17-23] The characteristics of these polymers are listed in Table I.

Blend compositions of 80:20, 75:25, 70:30, 63:35, and 60:40% by weight of PEO:APU, 90:10, 85:15, 80:20, 75:25, 70:30, and 65:35% by weight of PEO:EMAA[55], and 95.2:4.8, 90.0:9.1, 87:13, 83.33:16.67, and 80:20% by weight of PEO:PVPh were prepared by solution casting from THF. Care was taken to obtain uniform films, and the PEO-EMAA[55] and PEO-APU samples were kept in a vacuum oven overnight at 80 °C to remove residual solvent and to minimize the "$\Delta\chi$" effect,[24] which can cause phase separation and hence errors in the determination of experimental melting points. In the case of the PEO-PVPh blend, the samples were heated to 140 °C for 3-4 h, as the glass transition of the PVPh we used is ~140 °C (longer annealing times can lead to degradation of PEO). Also, prior to each run, each sample was heated to 75 °C for 8-10 min to melt the crystalline residue formed during the preparation procedure.

Melting point measurements were conducted on a Mettler FP80 hot stage using an Olympus polarizing microscope. A heating rate of 3 °C/min was employed for all blends. The melting point was taken as the temperature at which the last birefringent entity vanished. However, it should be noted that the crystallization times vary for different compositions and blends, due to the wide range of undercoolings employed.

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Table I

	PEO	APU	PVPh	EMAA[55] (28.5% mole basis)
source of polymer	Aldrich	Du Pont[a]	Polysciences	Du Pont
T_g, °C	−65	98	140	32
mol wt	$M_w = 100\,000$	$M_n = 15\,000$	$M_n = 1500–7000$	

[a] Synthesized from butanediol and a mixture of the 2,4 and 2,6 isomers of tolyl isocyanate by Dr. T. Krizan of E. I. du Pont de Nemours and Co.[20]

Modification of the Nishi–Wang Equation To Account for Specific Interactions

The association model we have used to describe strong, specific interactions in polymer blends essentially starts with the randomly mixed covalent chains as a reference state. The free energy changes corresponding to the formation of specific interactions are then accounted for as an excess free energy term by determining the probability that the mixture would spontaneously occur in a configuration equivalent to that of, in this case, the hydrogen-bonded system.[16,21] The associated species are allowed random contacts with one another, so that a final equation of the form

$$\frac{\Delta G_m}{RT} = \frac{\phi_A}{m_A}\ln\phi_A + \frac{\phi_B}{m_B}\ln\phi_B + \phi_A\phi_B\chi + \frac{\Delta G_H}{RT} \qquad (2)$$

is obtained. Accordingly, in a polymer mixture phase behavior is largely determined by a balance between favorable (to mixing) hydrogen-bonding interactions and an unfavorable χ term, which is assumed to represent (largely) nonpolar interactions. All the parameters in the ΔG_H term can be determined from spectroscopic measurements[16,25–27] and we assume that χ can be determined from the solubility parameters of the polymers, calculated from group contributions defined so as to exclude association effects (which are separately accounted for in the ΔG_H term).[28] Accordingly, as defined here χ is independent of composition, but, in general, ΔG_H has a strong composition dependence.

The Nishi–Wang[1] equation is thus easily modified to account for hydrogen bonding by simply including the contribution of ΔG_H to the partial molar free energy. We employ a convention where the subscript A refers to the non-self-associating component, in this case PEO, while B refers to the self-associating polymers (EMAA[55], APU, and PVPh). Accordingly, we can now rewrite eq 1:

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{Rr}{\Delta H_f^\circ}[\chi\phi_B^{\,2} + (\Delta\bar{G}_H)_A] \qquad (3)$$

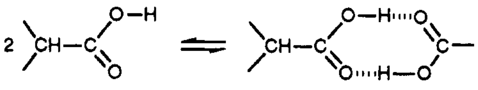
where r is the ratio of the molar volumes of the chemical repeat units, V_A/V_B, and V_B is used to define the lattice cell size, so that χ is calculated from

$$\chi = \frac{V_B}{RT}(\delta_A - \delta_B)^2 \qquad (4)$$

The hydrogen-bonding interactions of APU, PVPh, and EMAA[55] in the pure state (self-association) are described in different ways; hence $(\Delta\bar{G}_H)_A$, has different forms. The urethane functional groups of APU form chains in such a manner that the equilibrium constant describing self-association, K_B

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1} \qquad (5)$$

can be assumed to be independent of h.[20] In contrast, hydrogen bonds between the OH group of PVPh are such that the stoichiometry of hydrogen bonding is more accurately described by using an equilibrium constant for the formation of dimers, K_2, that is different from that of subsequent h-mers, K_B.[27] Finally, the carboxylic acid groups of EMAA[55] form strongly hydrogen-bonded cyclic dimers:[23]



carboxylic acid dimer

which we will also describe by an equilibrium constant K_B, although only dimers are formed.

Equations for the free energy and chemical potentials have been derived elsewhere.[16,21,23] The general result is

$$(\Delta\bar{G}_H)_A = \frac{1}{r}\ln\left(\frac{\phi_{A_1}}{\phi_A}\right) + \frac{V_B}{V}[n_B(p_{BB} - p_{BB}^\circ) + n_A p_{BA}] \qquad (6)$$

where $(p_{BB} - p_{BB}^\circ)$ is the difference in the fraction of B---B hydrogen bonds found in the mixture relative to that found in pure B, while p_{BA} is the fraction of A segments hydrogen bonded to B.[16] To calculate these quantities we rewrite the nonlogarithmic terms as functions of the equilibrium constants (K_B and K_A) and the volume fractions of the B and A segments that are *not* hydrogen bonded, ϕ_{B_1} and ϕ_{A_1}, respectively, as these are the quantities that are directly computed. For the PEO–APU blend

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{Rr}{\Delta H_f}\left\{\chi\phi_B^{\,2} + \frac{1}{r}\ln\frac{\phi_{A_1}}{\phi_A} + \phi_B K_B(\phi_{B_1} - \phi_{B_1}^\circ) + \frac{\phi_B(1 - K_B\phi_{B_1})}{1 + K_A\phi_{A_1}/r}(K_A\phi_{A_1}/r)\right\} \qquad (7)$$

For the PEO–PVPh blend

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{Rr}{\Delta H_f}\left\{\chi\phi_B^{\,2} + \frac{1}{r}\ln\frac{\phi_{A_1}}{\phi_A} + \phi_B\left[\frac{\Gamma_1^\circ}{\Gamma_2^\circ}\right] - \phi_{B_1}\Gamma_1\right\} \qquad (8)$$

where

$$\Gamma_1 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{1 - K_B\phi_{B_1}}\right) \qquad (9)$$

$$\Gamma_2 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 - K_B\phi_{B1})^2}\right) \qquad (10)$$

and Γ_1° and Γ_2° refer to the quantities in pure B. Finally, for the PEO–EMAA[55] blend

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{Rr}{\Delta H_f}\left\{\chi\phi_B^{\,2} + \frac{1}{r}\ln\frac{\phi_{A_1}}{\phi_A} - \phi_{B_1}(1 + K_B\phi_{B_1}) + \phi_B\frac{1 + K_B\phi_{B_1}^\circ}{1 + 2K_B\phi_{B_1}^\circ}\right\} \qquad (11)$$

Specific Interactions and the Composition Dependence of Interaction Parameters

Most models that have been used to describe interactions in polymer blends assume random contacts and include a term of the form $\phi_A\phi_B\chi$, where χ is now an overall or effective parameter and can be a free energy rather than a simple enthalpy term. It is well-known that χ is composition dependent even in mixtures of relatively nonpolar molecules, however, and this can be accounted for by expressing χ as a series in powers of the volume fraction

$$\chi = \chi_1 + \chi_2\phi_B + \chi_3\phi_B^2 + ... \qquad (12)$$

The higher order terms can be relatively small so for blends of nonpolar or weakly polar molecules it is perhaps reasonable to neglect composition dependence. If strong, specific interactions are present, however, there is a strong composition dependence, and before proceeding to a discussion of our result, it is useful to illustrate this explicitly using an association model.

Flory[29,30] considered the statistical mechanics of mixing chains that form by reversible associations (e.g., hydrogen bonds) with "inert" (non-hydrogen-bonding) solvents and obtained for the partial molar free energy of the solvent (A)

$$\frac{\Delta\bar{G}_A}{RT} = \ln \phi_A + \phi_B p_{BB} + \phi_B^2\chi \qquad (13)$$

(where for purposes of simple illustration Flory used the disoriented molecules as the reference state, so that terms in z and σ do not appear). The term p_{BB} is, as above, the fraction of B molecules that are hydrogen bonded and can be related to the average degree of "polymerization" (association), $\bar{h}$, by

$$\bar{h} = 1/(1 - p_{BB}) \qquad (14)$$

Substituting for p_{BB} gives the usual form of the Flory–Huggins partial molar free energy. Hildebrand and Scott[31] elaborated on this treatment to demonstrate the composition dependence of the interactions. If the association has the form

$$B_h + B_1 \overset{K_B}{\rightleftharpoons} B_{h+1} \qquad (15)$$

and, for simplicity, it is assumed that K_B is independent of h, then it can be shown that

$$K_B\phi_B = p_{BB}/(1 - p_{BB})^2 \qquad (16)$$

Because $p_{BB} < 1$ we can use

$$1/(1 - p_{BB})^2 = 1 + 2p_{BB} + 3p_{BB}^2 + 4p_{BB}^3 + ... \qquad (17)$$

to obtain

$$K_B\phi_B = p_{BB} + 2p_{BB}^2 + 3p_{BB}^3 + 4p_{BB}^4 + ... \qquad (18)$$

Using the usual equations for the reversion of a series

$$p_{BB} = K_B\phi_B - 2(K_B\phi_B)^2 + 5(K_B\phi_B)^3 - 14(K_B\phi_B)^4 + ... \qquad (19)$$

The equation for the partial molar free energy can now be written

$$\frac{\Delta\bar{G}_A}{RT} = \ln \phi_A + (\chi + K_B)\phi_B^2 - 2K_B^2\phi_B^3 + 5K_B^3\phi_B^4 - 14K_B^4\phi_B^5 + ... \qquad (20)$$

Clearly, if K_B is small (i.e., self-association is weak), then only the first term is important and an average χ term can be used. For hydrogen bonding between groups such as amide, urethane, hydroxyl, etc., K_B is of the order 50–100 (at 25 °C, expressed in terms of volume fractions, as defined by Flory[29]), and hence there is a very strong concentration dependence. One of the most interesting questions that this analysis raises is the extent of association in polymers such as poly(vinyl chloride) and polyacrylonitrile, where there is spectroscopic evidence for association, but (presently) it does not appear definitive enough to obtain equilibrium constants.

The expansion used by Hildebrand and Scott[31] is an illuminating way of demonstrating composition dependence, but it neglects self-association in pure B and does not consider the modifying effect of a competing association as in, for example, a mixture of urethanes and ethers or phenols with esters. The competing equilibrium complicates the problem enormously, but a solution can still be obtained.

Table II

expansion terms	$K_B = 100$ $K_A = 30$	$K_B = 100$ $K_A = 300$
$T_1 = -\frac{2K_R - 1}{K_R^2K_B} + \frac{1}{2K_R}(2 - 3K_R)$	1.9	-1.2
$T_2 = -\frac{(1 - K_R)(1 - 4K_R) + 1}{K_BK_R^3} - \frac{1}{3K_R^2}[6(1 - K_R^2) + K_R^2]$	-11.5	-1.2
$T_3 = -\frac{2(1 - K_R)(3 - 5K_R + 4K_R^2) + 1}{K_BK_R^4} + \frac{1}{4K_R^3}[-15K_R^3 + 48K_R^2 - 54K_R + 20]$	73.4	-1.1

The method we devised follows the general lines outlined above but is more involved and we have therefore relegated the algebra to an appendix. Furthermore, in our use of association models[16] we use the quantity ϕ_{B_1}, the volume fraction of B molecules (or segments) that are not hydrogen bonded, as this provides an easily computable link between the stoichiometry of hydrogen bonding, the free energy of mixing, and infrared spectroscopic measurement. The quantity p_{BB} is equal to $K_B\phi_{B_1}$ and for the mixing of two polymers that hydrogen bond we have obtained the following expression for the partial molar free energy of the non-self-associating (A) segments:[16,24]

$$\frac{\Delta\bar{G}_A}{RT} = \left[\frac{\ln \phi_A}{m_A} - \phi_B\left(\frac{1}{m_B} + \frac{1}{m_A}\right) + \phi_B^2\chi\right] + \left[\ln\frac{\phi_{A_1}}{\phi_A} + r\left\{\phi_BK_B(\phi_{B_1} - \phi_{B_1}{}^\circ) + \frac{\phi_B(1 - K_B\phi_{B_1})(K_A\phi_{A_1}/r)}{1 + K_A\phi_{A_1}/r}\right\}\right] \qquad (21)$$

where again r is the ratio of the segment molar volumes V_A/V_B, ϕ_{A_1} is the volume fraction of A units that are not hydrogen bonded, and m_A and m_B are the degrees of polymerization of the covalent chains. The terms in the first set of parentheses are the usual Flory–Huggins terms, while those in the second set of parentheses can be rewritten[16] as

$$\ln\left(\frac{\phi_{A_1}}{\phi_A}\right) + \frac{V_A}{V}\{n_B(p_{BB} - p_{BB}{}^\circ) + n_Ap_{BA}\} \qquad (22)$$

which has the simpler form of the usual Flory lattice model and is how we account for the free energy of specific interactions through a determination of the modification of the number of configurations available to the covalent chains as a result of specific interactions. To simplify the presentation we assume that $r = 1$ and K_B and K_A are of the order of 30 dimensionless units or greater (see appendix) to obtain

$$\frac{\Delta\bar{G}_A}{RT} = \left[\frac{\ln \phi_A}{m_A} - \phi_B\left(\frac{1}{m_B} - \frac{1}{m_A}\right)\right] + \phi_B\left[(1 - K_B\phi_{B_1}{}^\circ) + \frac{1}{K_A} - 1\right] + \phi_B^2(\chi + T_1) + \phi_B^3(T_2) + \phi_4^4(T_3) + ... \qquad (23)$$

The terms T_1, T_2, and T_3 are listed in Table II, where the quantitity K_R is equal to the ratio of the equilibrium

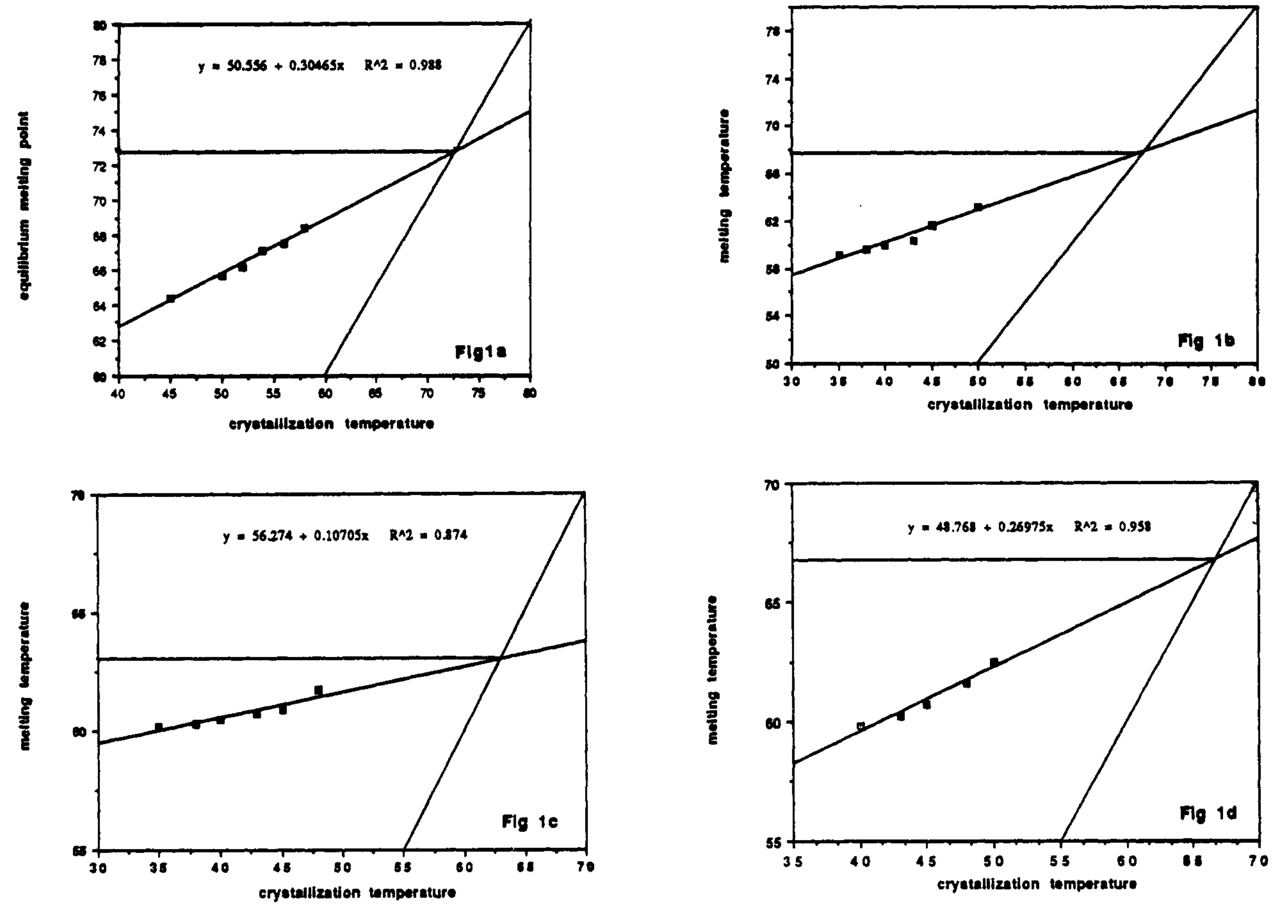


Figure 1. (a) Hoffman–Weeks plot for the calculation of the equilibrium melting temperature ($T_m°$) of pure PEO. (b) Hoffman–Weeks plot for PEO melting points in a 60:40 (weight/fraction) PEO–APU blend. (c) Hoffman–Weeks plot for PEO melting points in an 83.3:16.7 (weight fraction) PEO–PVPh blend. (d) Hoffman–Weeks plot for PEO melting points in a 70:30 (weight fraction) PEO–EMAA[55] blend.

constants K_A/K_B. For the most frequently encountered cases where K_B is of the order of 50–100 and K_R ($=K_A/K_B$) about 0.3 (see below), higher order terms are very significant. For the less usual case of $K_R > 1$, the composition dependence appears less severe (perhaps because the mixture is dominated by AB "dimers"), but the composition dependence of the self-association terms remains large, as in the simpler result obtained by Hildebrand and Scott[31] (eq 19). The terms increase in magnitude but oscillate in sign as the series is ascended. It would presumably be possible to define a composition dependence with interaction terms that are defined differently (i.e., not in terms of equilibrium constants), such that at some point higher order terms become negligible, but that there is indeed a strong composition dependence for systems that interact strongly appears inescapable. Accordingly, the use of simple overall or effective Flory–Huggins parameters to describe such interactions would lead to significant error. With this in mind we now turn to an examination of the melting point depression in mixtures where hydrogen bonds occur.

Results and Discussion

Representative plots of the observed melting point plotted as a function of crystallization temperature for PEO and PEO–APU, PEO–PVPh, and PEO–EMAA[55] blends are shown in Figure 1a–d, respectively. The data are extrapolated, following Hoffman and Weeks,[32] to give the equilibrium melting temperatures, $T_m°$.

For the PEO–APU blends crystals of PEO could be observed at APU weight fractions as high as 0.5. The observed melting point depressions are plotted as a function of ϕ_B, the volume fraction of APU in the blend, in Figure 2. Also shown in Figure 2 is the melting point depression calculated from eq 7. The entire composition range is shown to illustrate the predicted trend. The parameters used in this calculation are those determined in our previous spectroscopic studies of this system[20] and from our recently determined group contributions to cohesive energy densities[28] and molar volumes. These are listed in Tables III and IV. No attempt was made to obtain a better fit between theoretical predictions and experimental observations by adjusting any of these parameters. The agreement between the predictions of the association model and experimental results is very good, as can be more clearly seen in Figure 3, which focuses on that portion

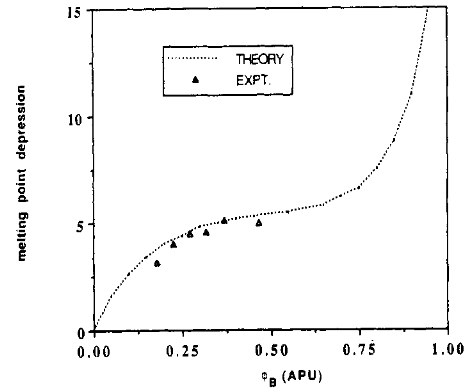


Figure 2. Comparison of predicted versus experimentally measured melting point depressions for PEO–APU blends.

Table III

	PEO(A)	APU(B)	PVPh(B)	EMMA[55](B)
molar vol (V), cm^3 mol^{-1}	41.4	108.3	100	163.7
T_m°, K	345.7			
ΔH_f, cal mol^{-1} of repeat unit	1980			
δ, (cal cm^{-3})$^{0.5}$	9.4	11.2	10.6	10.5

Table IV

	APU	PVPh	EMMA[55]
K_B	229.0	66.0	85 800
K_2		21.0	
K_A	10.7	85	160
h_A, kcal mol^{-1}	5.0	5.4	6.0
h_B, kcal mol^{-1}	5.0	5.2	7.2 14.4 (for dimer)
h_2, kcal mol^{-1}		5.6	
χ	0.59	0.24	0.33

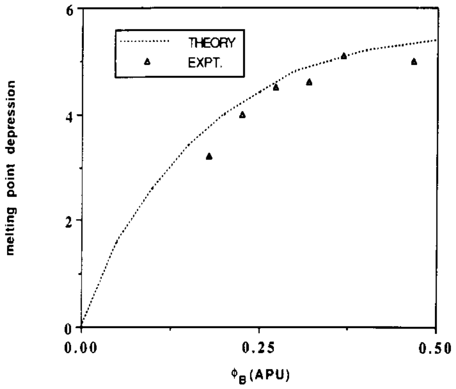


Figure 3. A closer view of the data shown in Figure 2.

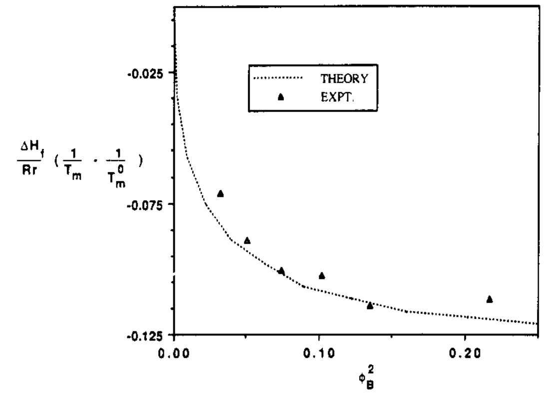


Figure 4. Plot of $(\Delta H_f/Rr)(1/T_m - 1/T_m°)$ vs ϕ_B^2 for the PEO–APU blends.

of the composition plot where experimental data were obtained. Figure 4 shows a plot of the left-hand side of eq 7, multiplied by $\Delta H_f/Rr$, against ϕ_B^2. The data points do not fall on a straight line, but the association model predicts the composition dependence of the interactions very well.

Similar results were obtained for the PEO–PVPh blends, but over a narrower composition range (crystallization rates were extremely slow at weight fractions of PVPh greater than 0.2). Figure 5 shows the experimental melting point depressions as a function of ϕ_B (volume fraction of PVPh), while Figure 6 shows a plot of the values of the left-hand side of eq 7, multiplied by $\Delta H_f/Rr$, as a function of ϕ_B^2. Also shown on both plots are the theoretical predictions of the association model (the parameters used are again listed in Table IV and were taken without alteration from refs 27 and 28). A small and systematic deviation of theory from experiment is revealed in both plots, possibly due to small inaccuracies in the value chosen for the solubility parameter of PVPh.[27] Nevertheless, the model clearly reproduces the nonlinear dependence on ϕ_B^2.

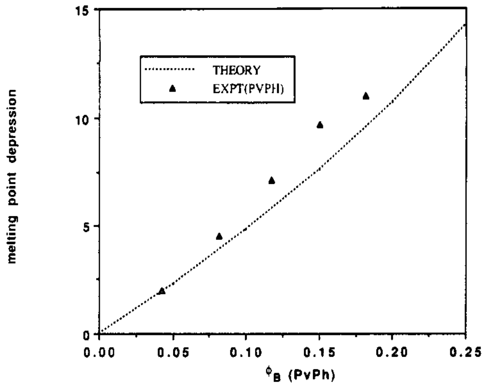


Figure 5. Comparison of the predicted and experimentally measured melting point depressions for PEO–PVPh blends.

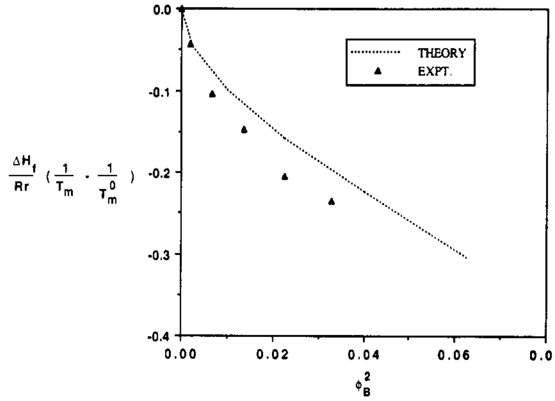


Figure 6. Plot of $(\Delta H_f/Rr)(1/T_m - 1/T_m°)$ vs ϕ_B^2 for the PEO–PVPh blends.

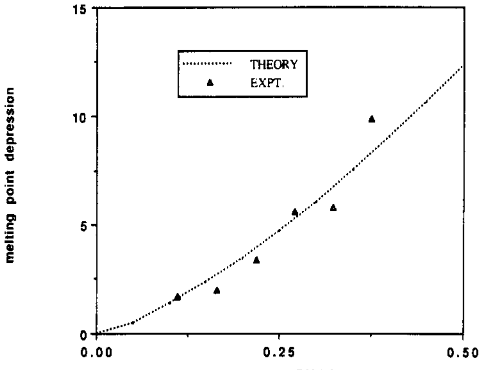


Figure 7. Theoretical predictions compared with the experimentally measured melting point depressions of PEO in PEO–EMAA[55] blends.

Finally, a corresponding comparison of theory and experiment is presented in Figures 7 and 8 for the PEO–EMAA[55] blend. There is excellent agreement, but in this case it is possible to also fit the experimental data points shown in Figure 8 to a linear plot, albeit one that does not intercept the y axis at any value close to the origin, as also shown in Figure 8. This results corresponds closely to those obtained by Jo and Lee[13] for blends of PEO with poly(styrene-*co*-acrylic acid). The apparent rectilinear relationship that can be obtained is a consequence of the narrow concentration range for which observable PEO crystals can be obtained and the fairly flat nature of the curve over this range. Unlike PVPh and

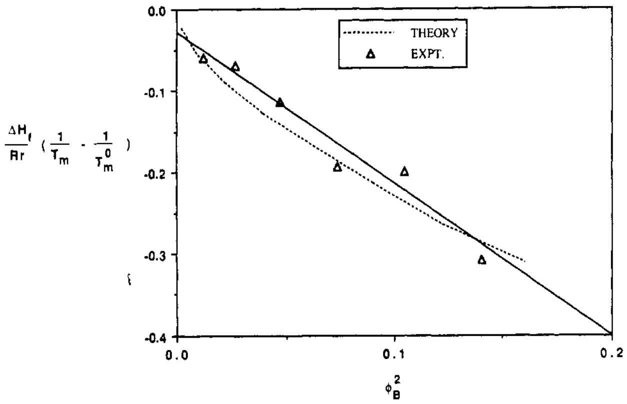


Figure 8. Plot of $(\Delta H_f/Rr)(1/T_m - 1/T_m^\circ)$ versus ϕ_B^2 for the PEO–EMAA[55] blends.

APU, where self-association results in the formation of chains, only like (acid–acid) and unlike (acid–ether) dimers appear to be formed in this system, and it is possible that in the narrow composition range used in this study a change in the distribution of such paired species does not result in as great an overall composition dependence of the interaction parameters.

Conclusions

1. In blends where the components interact strongly there is a strong composition dependence of the interaction parameters that is reflected in observed melting point depressions.

2. The association model predicts the observed experimental behavior very well. This, in turn, suggests that, in systems where there are strong interactions, these dominate the overall composition dependence, as in this model specific interactions are treated separately from those that are nonspecific (dispersion forces etc.) and these latter interactions are assumed to be independent of composition.

3. The results indicate that the apparently rectilinear relationships that do not pass through the origin (see eq 7) that have been obtained in other studies are a consequence of ignoring the composition dependence of the interactions. Applying interaction parameters obtained from the slopes of these plots to the entire composition range could then result in serious error.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation, Polymers Program.

Appendix. Series Expansion of the Hydrogen-Bonding Terms in the Expressions for the Chemical Potentials

The terms in the expression for the partial molar free energy (eq 21) that we are concerned with is

$$\ln\frac{\phi_{A_1}}{\phi_A} + r\left\{\phi_B K_B(\phi_{B_1} - \phi_{B_1}{}^\circ) + \frac{\phi_B(1 - K_B\phi_{B_1})(K_A\phi_{A_1}/r)}{1 + K_A\phi_{A_1}/r}\right\} \tag{A1}$$

which can be rewritten as

$$\ln\frac{\phi_{A_1}}{\phi_A} + r\left\{\phi_B(1 - K_B\phi_{B_1}{}^\circ) - \frac{\phi_{B_1}}{1 - K_B\phi_{B_1}}\right\} \tag{A2}$$

by using the equations for the stoichiometry of hydrogen bonding (see ref 16). We will concentrate initial attention on the final term $\phi_{B_1}/(1 - K_B\phi_{B_1})$. Because $K_B\phi_{B_1} < 1$

$$\frac{1}{1 - K_B\phi_{B_1}} = 1 + K_B\phi_{B_1} + (K_B\phi_{B_1})^2 + (K_B\phi_{B_1})^3 + \ldots \tag{A3}$$

so that

$$\frac{\phi_{B_1}}{1 - K_B\phi_{B_1}} = \frac{1}{K_B}\{K_B\phi_{B_1} + (K_B\phi_{B_1})^2 + (K_B\phi_{B_1})^3 + \ldots\} \tag{A4}$$

Our aim is to obtain a series of the form

$$K_B\phi_{B_1} = A\phi_B{}^2 + B\phi_B{}^3 + C\phi_B{}^4 + \ldots \tag{A5}$$

From the equations describing the stoichiometry of hydrogen bonding[16] we can write

$$\phi_B\left[1 - K_B\phi_{B_1} + K_A\phi_{B_1} + \frac{K_A\phi_{B_1}/r}{1 - K_B\phi_{B_1}}\right] = \left[1 + \frac{K_A\phi_{B_1}/r + \phi_{B_1}}{1 - K_B\phi_{B_1}} + \frac{K_A\phi_{B_1}{}^2}{(1 - K_B\phi_{B_1})^2}\right] - 1 \tag{A6}$$

We have added +1 and −1 to the right-hand side of this expression because each term in parentheses can now be expressed as a series of the form

$$1 + a_1x + a_2x^2 + a_3x^3 + \ldots$$

By substituting for $1/(1 - K_B\phi_{B_1})$ from eq A3, eq A6 can be written

$$\phi_B S_1 = S_2 - 1 \tag{A7}$$

or

$$\phi_B = \frac{S_2}{S_1} - \frac{1}{S_1} \tag{A8}$$

where

$$S_1 = 1 + \frac{1}{K_B}\left[(K_A - K_B) + \frac{K_A}{r}\right]K_B\phi_{B_1} + \left(\frac{K_A}{K_B r}\right)(K_B\phi_{B_1})^2 + \left(\frac{K_A}{K_B r}\right)(K_B\phi_{B_1})^3 + \left(\frac{K_A}{K_B r}\right)(K_B\phi_{B_1})^4 + \ldots \tag{A9}$$

and

$$S_2 = 1 + \left[\left(\frac{K_A}{r} + 1\right)\frac{1}{K_B}\right](K_B\phi_{B_1}) + \left[\left(\frac{K_A}{r} + 1\right)\frac{1}{K_B} + \frac{K_A}{K_B{}^2}\right](K_B\phi_{B_1})^2 + \left[\left(\frac{K_A}{r} + 1\right)\frac{1}{K_B} + \frac{2K_A}{K_B{}^2}\right](K_B\phi_{B_1})^3 + \left[\left(\frac{K_A}{r} + 1\right)\frac{1}{K_B} + \frac{3K_A}{K_B{}^2}\right](K_B\phi_{B_1})^4 + \ldots \tag{A10}$$

We can now use well-known expressions for the reciprocal of a series and ratio of two series to obtain a series in powers of $(K_B\phi_{B_1})$.

To simplify the algebra we consider the case where $r = 1$ and we assume relatively strong interactions, such that we can neglect $1/K_B$ and $K_A/K_B{}^2$ relative to K_A/K_B (for many hydrogen-bonded systems K_A is in the range 30–300, while K_B is of the order of 60–200. Most often, $K_B > K_A$). We have carried through the complete expansions and this approximation has little effect, except that we end up with a term in $1/K_A$ instead of $1/(K_A + 1)$, so that the final series does not reduce correctly to the expansion for pure self-association when $K_A = 0$.

The series S_2 now has the simpler form

$$S_2 = 1 + \frac{K_A}{K_B}[(K_B\phi_{B_1}) + (K_B\phi_{B_1})^2 + (K_B\phi_{B_1})^3 + \ldots] \tag{A11}$$

Substituting into

$$K_B\phi_B = K_B\left[\frac{S_2}{S_1} - \frac{1}{S_1}\right]$$

and using the appropriate expressions for $[S_2/S_1 - 1/S_1]$ (note the general form of $1/S_1$ should be subtracted term by term from S_2/S_1 first, as this simplifies the result *before* substitution), we obtain

$$K_B\phi_B = K_A(K_B\phi_{B_1}) + 2K_A(1 - K_R)(K_B\phi_{B_1})^2 + K_A(1 - K_R)(3 - 4K_R)(K_B\phi_{B_1})^3 + 4K_A(1 - K_R)^2(1 - 2K_R)(K_B\phi_{B_1})^4 + \ldots \quad \text{(A12)}$$

where $K_R = K_A/K_B$. Upon series reversion

$$K_B\phi_{B_1} = \phi_B/K_R - 2(1 - K_R)(\phi_B/K_R)^2 + (1 - K_R)(5 - 4K_R)(\phi_B/K_R)^3 - (1 - K_R)^2(14 - 8K_R)(\phi_B/K_R)^4 + \ldots \quad \text{(A13)}$$

Substituting, the term for $\phi_{B_1}/(1 - K_B\phi_{B_1})$ is now given by

$$\frac{\phi_B}{K_A} - \frac{2K_R - 1}{{K_R}^2K_B}{\phi_B}^2 - \frac{(1 - K_R)(1 - 4K_R) + 1}{K_B{K_R}^3}{\phi_B}^3 - \left\{\frac{2(1 - K_R)(3 - 5K_R + 4{K_R}^2)}{K_B{K_B}^4} + 1\right\}{\phi_B}^4 + \ldots \quad \text{(A14)}$$

Expansion of Other Terms. In the body of the text (eq 23) we illustrate the composition dependence of specific interactions using eq A14 as an example. The $\phi_B(1 - K_B\phi_{B_1}{}^0)$ term is trivial, in that $(1 - K_B\phi_{B_1}{}^0)$ is a constant ($\phi_{B_1}{}^0$ is the volume fraction of non-hydrogen-bonded B units in pure B).

The term in ln (ϕ_{A_1}/ϕ_A) can also be expanded by first noting that from the equations for the stoichiometry of hydrogen bonding

$$\frac{\phi_{A_1}}{\phi_A} = \frac{1}{1 + K_A\phi_{B_1}/(1 - K_B\phi_B1)} = S_3 \quad \text{(A15)}$$

We have already expressed the term in parentheses in the denominator in terms of a series and can therefore obtain ϕ_{A_1}/ϕ_A as a series in ϕ_B using equations for expressing the reciprocal of a series as a new series. Similarly, the natural logarithm of a series can be expressed as a new series, S_4, using

$$S_4 = 1 + \ln S_3 \quad \text{(A16)}$$

We obtain

$$S_3 = 1 - \phi_B + \frac{1 - K_R}{K_R}{\phi_B}^2 - \frac{1}{{K_R}^2}(1 - K_R)(2 - K_R){\phi_B}^3 + \frac{1}{{K_R}^3}[-{K_R}^3 + 7{K_R}^2 - 11K_R + 5]{\phi_B}^4 + \ldots \quad \text{(A17)}$$

and

$$\ln\frac{\phi_{A_1}}{\phi_A} = S_4 - 1 = -\phi_B + \frac{1}{2K_R}(2 - 3K_R){\phi_B}^2 - \frac{1}{3{K_R}^2}[6(1 - K_R)^2 + {K_R}^2]{\phi_B}^3 + \frac{1}{4{K_R}^3}[-15{K_R}^3 + 48{K_R}^2 - 54K_R + 20]{\phi_B}^4 + \ldots \quad \text{(A18)}$$

References and Notes

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