Thermodynamics of Hydrogen Bonding in Polymer Blends. 2. Phase Behavior

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ABSTRACT: The equation for the spinodal is derived from expressions describing the free energy of mixing polymers that interact through the formation of hydrogen bonds. The temperature dependencies of the hydrogen bonding the physical interactions in the mixture are such that a rich variety of intriguing phase behaviors is predicted.

Introduction

In the preceding paper we used an association model to obtain an expression for the free energy of mixing polymer molecules that can hydrogen bond in a specific but very common manner (one polymer self-associates through formation of "chains" of hydrogen bonds; the second does not, but is capable of forming hydrogen bonds with units of the first). The obvious next step is to apply this model to a quantitative description of phase behavior in these systems, so that the model can be experimentally tested. Binodal curves are, of course, calculated by equating the chemical potentials of each component in each phase and solving by numerical methods. In contrast, analytical expressions can usually be determined for the spinodal, so curves defining the stability limit are more easily obtained. This remains true when hydrogen-bonding interactions are accounted for by an association model, as we will demonstrate in this paper. Before proceeding with the derivation, however, we will present a brief qualitative description of the effect of hydrogen bonding on the phase behavior of binary mixtures, as this will provide a useful conceptual basis for interpreting our results.

Mixtures of molecules that hydrogen bond are characterized by unusual phase behavior, often including the phenomenon of reappearing phases, a consequence of closed-loop coexistence curves in the phase diagram. The factors controlling these properties in small molecules have recently been discussed in a splendid review by Walker and Vause.[1] According to these authors, at high temperatures entropy of mixing contributions dominate the free energy and a binary mixture is miscible. As the temperature is lowered, the positive contribution of an exchange energy term describing van der Waals interactions becomes increasingly significant, and the mixture becomes immiscible. A lower temperatures still, hydrogen-bonding interactions start to dominate, a temperature-dependent negative enthalpy contribution to the free energy finally offsetting the unfavorable entropy of forming a specific directional bond (and the positive contribution of physical forces), so that the system again becomes miscible. If hydrogen bonding between like as well as unlike molecules occurs, than the balance of forces can change yet again at still lower temperatures, resulting in a reappearing immiscible phase.

The competing factors involved in this type of phase behavior have also been quantitatively described by Walker and Vause.[2] Their description is in the Ising model language of magnetic phase transitions, but essentially consists of the usual exchange interaction energy term for van der Waals forces coupled to orientation-dependent potentials that account for the attractive energy of hydrogen bonding. Only bonds between unlike molecules are considered, and systems are characterized in terms of parameters that are a measure of hydrogen-bond strength and the orientational specificity of the bond. Observed phase behavior is then reproduced by fitting to these two parameters.

Our approach to the description of hydrogen bonds is somewhat different and is formulated in terms of the concepts of classical physical chemistry. The free energy of forming a hydrogen bond is not separated into enthalpic and entropic contributions (indeed, the work of Pimental[3] and Prigogine[4] demonstrates that these are dependent variables) but expressed in terms of an equilibrium constant. The constants describing the competitive equilibria between hydrogen bonds in a polymer blend can often be determined by infrared spectroscopy and are thus not variables that have to be determined by a fit to thermodynamic data.[5–7] Furthermore, the strength of the hydrogen bond between many of the functional groups found in polymers (e.g. amides, urethanes, hydroxyls) is roughly the same, so that the type of model suggested by Walker and Vause,[2] where this is the prime variable for modeling the observed phase behavior, would be of only limited value. In our view of much more significant factor is the *number* of interactions that can form. In a urethane of the form R–OCONH, for example, the size of the group R can be varied by introducing greater or lesser numbers of CH_2 or other non-hydrogen-bonding linkages. Providing that no unusual electronic or steric factors are involved, the strength of the urethane–urethane hydrogen bonds should remain largely unaffected, except, perhaps, at high dilution. The number of hydrogen bonds that form will vary systematically with the size of R, however, due to simple concentration effects, and we developed equations for the description of this situation in the preceding paper.[7] Naturally, this also makes the model amenable to experimental verification, in that there are many types of polymers (urethanes, ethers, acrylates, etc.) that contain hydrogen-bonding functional groups, but that vary in the constitution of the remaining non-hydrogen-bonding repeat unit. Accordingly, the equations for the spinodal will be described here and a comparison to experimental data presented in the following paper.

Notation

The symbols used in this paper are identical with those used in the preceding paper and are summarized in the glossary.

Spinodal Equation

The equation for the free energy of mixing a self-associating polymer B with one that does not self-associate, A, but is capable of forming a hydrogen bond with B, is given by[6,7]

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$$\frac{\Delta G_M}{RT} = \left[\frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B + \Phi_A\Phi_B\chi\right] + \left[\Phi_B \ln\left(\frac{\Phi_{B_1}}{{\Phi_{B_1}}^0}\right) + \frac{\Phi_A}{r}\ln\Phi_{0A} + K_B\Phi_B(\Phi_{B_1} - {\Phi_{B_1}}^0) + \Phi_B(1 - K_B\Phi_{B_1})\frac{X}{1+X}\right] - \left[\frac{\Phi_B}{{\bar{n}_H}^0}\ln\Phi_B + \frac{\Phi_A}{r}\ln\Phi_A\right] \quad (1)$$

Note that here ΔG_M is defined in terms of a reference volume V_B. In our initial derivation we will consider the simplest case of the interacting units A and B being identical with the chemical repeat units. The resulting equations are then easily modified to account for the usual situation where these functional groups are a fraction of the size of their respective chemical repeat units by appropriate adjustment of the values of the equilibrium constants K_B and K_A.

Equation 1 has been split into three parts: a Flory combinational entropy of mixing and physical interaction term in the first set of brackets; terms in the second brackets that describe the free energy associated with the change in the pattern of hydrogen bonding upon mixing A and B units, but which because of the way it is derived also contains an extraneous combinatorial entropy of mixing A and B components; a third set of terms that converts the second to an excess function, i.e., one that expresses the free energy change associated with the hydrogen-bonding interactions alone.

The spinodal equation is given by the condition

$$\partial^2(\Delta G/RT)/\partial{\Phi_B}^2 = 0 \quad (2)$$

The second derivatives of the terms in the first and last set of brackets in eq 1 have the familiar form

$$\left[\frac{1}{N_A\Phi_A} + \frac{1}{N_B\Phi_B} - 2\chi\right] - \left[\frac{1}{{\bar{n}_H}^0\Phi_B} + \frac{1}{r\Phi_A}\right] \quad (3)$$

The second derivative of the second set of terms in brackets in eq 1 is not so easily obtained, however, and requires some manipulation. The first derivative is given by

$$\ln\left(\frac{\Phi_{B_1}}{{\Phi_{B_1}}^0}\right) + \Phi_B\left(\frac{1}{\Phi_{B_1}}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} - \frac{1}{{\Phi_{B_1}}^0}\frac{\partial{\Phi_{B_1}}^0}{\partial\Phi_B}\right) + \frac{\Phi_A}{r\Phi_{0A}}\frac{\partial\Phi_{0A}}{\partial\Phi_B} - \frac{1}{r}\ln\Phi_{0A} + K_B\Phi_B\left[\frac{\partial\Phi_{B_1}}{\partial\Phi_B} - \frac{\partial{\Phi_{B_1}}^0}{\partial\Phi_B}\right] + K_B(\Phi_{B_1} - {\Phi_{B_1}}^0) - K_B\Phi_B\left[\frac{X}{1+X}\right]\frac{\partial\Phi_{B_1}}{\partial\Phi_B} + \left[\frac{X}{1+X}\right](1 - K_B\Phi_{B_1}) + \frac{\Phi_B(1 - K_B\Phi_{B_1})}{(1+X)^2}\frac{\partial X}{\partial\Phi_B} \quad (4)$$

Of course ${\Phi_{B_1}}^0$, the concentration of non-hydrogen-bonded species in pure B ($\Phi_B = 1$) is a constant, so that

$$\partial{\Phi_{B_1}}^0/\partial\Phi_B = 0 \quad (5)$$

Also

$$X = K_A\Phi_{0A}/r \quad (6)$$

so, from the stoichiometric relationship

$$\Phi_{0A} = (1 - \Phi_B)\left[1 + \frac{K_A\Phi_{B_1}}{1 - K_B\Phi_{B_1}}\right]^{-1} \quad (7)$$

the last term in eq 4 is given by

$$\frac{\Phi_B(1 - K_B\Phi_{B_1})^3}{(1+X)^2\Phi_{B_1}} - \frac{\Phi_B(1 - K_B\Phi_{B_1})}{\Phi_{B_1}(1+X)}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} \quad (8)$$

The equation can be further simplified by using

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B\Phi_{B_1})^2}(1 + X) \quad (9)$$

From eq 7 we can also express $\partial\Phi_{0A}/\partial\Phi_B$ in the terms of $\partial\Phi_{B_1}/\partial\Phi_B$:

$$\frac{\partial\Phi_{0A}}{\partial\Phi_B} = -\frac{\Phi_{0A}}{\Phi_A}\left[\frac{\Phi_{0A}K_A}{(1 - K_B\Phi_{B_1})^2}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} + 1\right] \quad (10)$$

By substituting (8) and (10) into (4) it can be shown that terms in $\partial\Phi_{B_1}/\partial\Phi_B$ cancel, so the first derivative of the hydrogen-bonding terms is given by

$$\ln\left(\frac{\Phi_{B_1}}{{\Phi_{B_1}}^0}\right) - \frac{1}{r}\ln\Phi_{0A} - \frac{1}{r} + (1 - K_B{\Phi_{B_1}}^0) \quad (11)$$

The second derivative of this equation is then

$$\frac{1}{\Phi_{B_1}}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} - \frac{1}{r\Phi_{0A}}\frac{\partial\Phi_{0A}}{\partial\Phi_B} \quad (12)$$

This is a beautifully simple and intuitively pleasing result. The free energy associated with hydrogen-bonding interactions in the blend is derived in terms of the concentrations of "monomers", i.e., those units that have no hydrogen-bonded partners whatsoever, through substitution of the condition of equality of the chemical potentials of these "monomers" and their stoichiometric counterparts[5-7]

$$\mu_{B_1} = \mu_B; \quad \mu_{0A} = \mu_A \quad (13)$$

a relationship demonstrated by Prigogine[4] for a system in equilibrium. Accordingly, the stability limit should depend upon the balance between the variation of the concentration of these units with composition, a relationship expressed by eq 12. Furthermore, on this basis we would also expect the spinodal equation to have the same form if we now characterize the self-association of the B units by two equilibrium constants, one describing the formation of dimers and the second the formation of n-mers ($n > 2$). It is a conceptually straightforward (but algebraically complicated) matter to demonstrate that this is indeed so, and the derivation is reproduced in the Appendix.

The derivative terms in eq 12 can be determined numerically (as can the spinodal directly from the second derivative of eq 1), but for simple systems this is unnecessary (and inelegant) in that analytical expressions for $\partial\Phi_{B_1}/\partial\Phi_B$ and $\partial\Phi_{0A}/\partial\Phi_B$ are readily obtained by taking derivatives of eq 7 and 9 and solving the two simultaneous equations in $\partial\Phi_{B_1}/\partial\Phi_B$ and $\partial\Phi_{0A}/\partial\Phi_B$ to give

$$\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\left[-\frac{X}{1+X}\frac{r}{\Phi_{B_1}}\frac{\Phi_B}{\Phi_A} + \frac{1+X}{X\Phi_{B_1}}\left(\frac{1 + K_B\Phi_{B_1}}{1 - K_B\Phi_{B_1}}\right)\right] = \frac{1}{X\Phi_B} + \frac{1}{\Phi_B\Phi_A} \quad (14)$$

Values for $\partial\Phi_{0A}/\partial\Phi_B$ are then obtained by substitution in eq 10. These equations have a clumsy appearance, however, and eq 12 remains the simpler and more illuminating form. We therefore write the equation for the spinodal as

$$2\chi - \left[\frac{1}{\Phi_{B_1}}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} - \frac{1}{r\Phi_{0A}}\frac{\partial\Phi_{0A}}{\partial\Phi_B}\right] + \left[\frac{1}{\bar{n}_H{}^0\Phi_B} + \frac{1}{r\Phi_A}\right] = \frac{1}{\Phi_B N_B} + \frac{1}{\Phi_A N_A} \quad (15)$$

In this derivation we have assumed that the interacting unit and chemical repeat are identical, i.e., $V_B = V_\beta$. The terms in brackets strictly apply to the interacting functional groups, entities that are not always easily defined. The equation can be simply transformed into parameters defined in terms of chemical repeat as in the preceding paper[7] by defining the number of segments in each repeat unit as

$$s_B = V_B/V_\beta \qquad s_A = V_A/V_\alpha \quad (16)$$

and adjusting the values of the equilibrium constants accordingly, i.e.

$$K_B = K_\beta/s_B \qquad K_A = K_\alpha/s_B \quad (17)$$

It is the quantities K_B and K_A that are determined experimentally, so a knowledge of s_B is not required.

Temperature Dependence

Phase behavior as a function of temperature and composition is simply obtained for this model. We let χ have the conventional $1/T$ dependence and note that the equilibrium constants K_B and K_A describing B–B and B–A hydrogen bonds depend upon the enthalpy of these bonds, h_B and h_{BA}, through the usual thermodynamic relationships:

$$\partial \ln K_B/\partial(1/T) = -h_B/R \quad (18)$$

$$\partial \ln K_A/\partial(1/T) = -h_{BA}/R \quad (19)$$

Hence

$$K_B = K_B{}^0 \exp\left\{-\frac{h_B}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right\} \quad (20)$$

$$K_A = K_A{}^0 \exp\left\{-\frac{h_{BA}}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)\right\} \quad (21)$$

where $K_B{}^0$ and $K_A{}^0$ are the values of the equilibrium constants at the absolute temperature T^0. Of course, this assumes that the enthalpy of hydrogen-bond formation remains a constant with temperature. We have noted infrared frequency shifts in the NH (and OH) stretching region of the spectra of various polymers that indicate that this is not so.[8-10] Accordingly, we can include a linear dependence of enthalpy upon temperature as

$$h_B = h_B{}^0 + h_B{}^1(1 - T^0/T) \quad (22)$$

where T^0 is a reference temperature and $h_B{}^1$ is an enthalpy correction term. In the usual range of temperatures accessible to polymers the infrared frequency shifts are of the order 20–40 cm^{-1}, however, which indicates only small changes in enthalpy.[3,11] Accordingly, the refinement offered by eq 22 seems unwarranted at this stage, where we are interested in predicting broad trends. it may become significant when we consider more precise quantitative predictions or the phase behavior of high-temperature polymers.

Calculations

The balance between the favorable (to mixing) hydrogen-bonding forces and unfavorable physical interactions results in a rich variety of phase behavior. To illustrate this, we will consider a general situation where the equilibrium constant describing self-association, K_B, has a value of 40, while competing interactions are characterized by a value of $K_A = 4$ (at 300 K). These values are similar to those determined experimentally for an amorphous polyurethane blended with a polyether ($K_B = 31.5$ and $K_A = 0.315$ at 110 °C[5,6]).

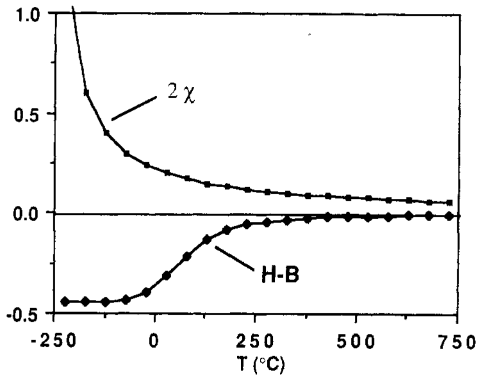

Figure 1. Plot of values of 2χ and the hydrogen-bonding terms of eq 15 as a function of temperature with values of $K_B = 40$, $K_A = 4$, $\chi = 0.1$, $r = 0.5$, $\Phi_B = 0.5$, and $N_A = N_B = 100$.

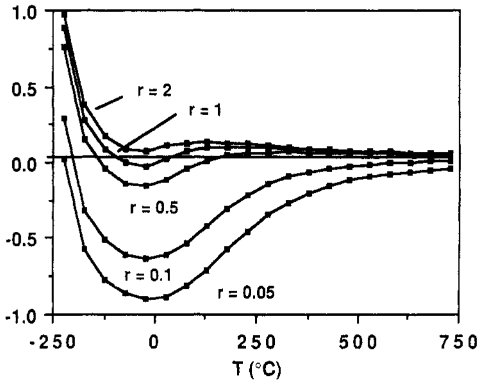

Figure 2. Sum of the curves shown in Figure 1 as a function of r, the ratio of the molar volumes of the chemical repeat units. All other parameters are the same as in Figure 1. The line parallel to the temperature axis is calculated from $(1/\Phi_A N_A + 1/\Phi_B N_B)$.

The factors in eq 15 that vary with temperature are χ and the two terms in brackets, which represent the contribution of the hydrogen-bonding interactions. The simple χ parameter used here has a $1/T$ dependence, and the variation of the factor 2χ with temperature is plotted in Figure 1 (a value of $\chi = 0.1$ at 300 K was assumed as a reference point). The hydrogen-bonding terms vary through the dependence of the equilibrium constants upon temperature. We assume the enthalpies of hydrogen-bond formation h_B and h_{BA} are equal, $h_B = h_{BA} = -5$ kcal/mol (infrared frequency shifts[5] indicate that this is true to a first approximation). The terms in parentheses in eq 15 are then evaluated as a function of temperature, using the relationships of eq 14 and 10 for the derivative terms and the equations defining the stoichiometry of the system, eq 7 and 9. The resulting curve is also shown in Figure 1 (for a composition of $\Phi_A = \Phi_B = 0.5$).

Points on the spinodal are obtained when the sum of the contributions illustrated in Figure 1 cross a line defined by $(1/\Phi_A N_A + 1/\Phi_B N_B)$, the right-hand side of eq 15. The curves obtained for various values of r, the ratio of the molar volumes of the chemical repeat units, are illustrated in Figure 2. For small values of r, the second derivative of the free energy changes sign only once, at low temperature, the curves asymptotically approaching the line defined by the right-hand side of eq 15 at high temperature. At larger values of r the curves can cross this line (or the

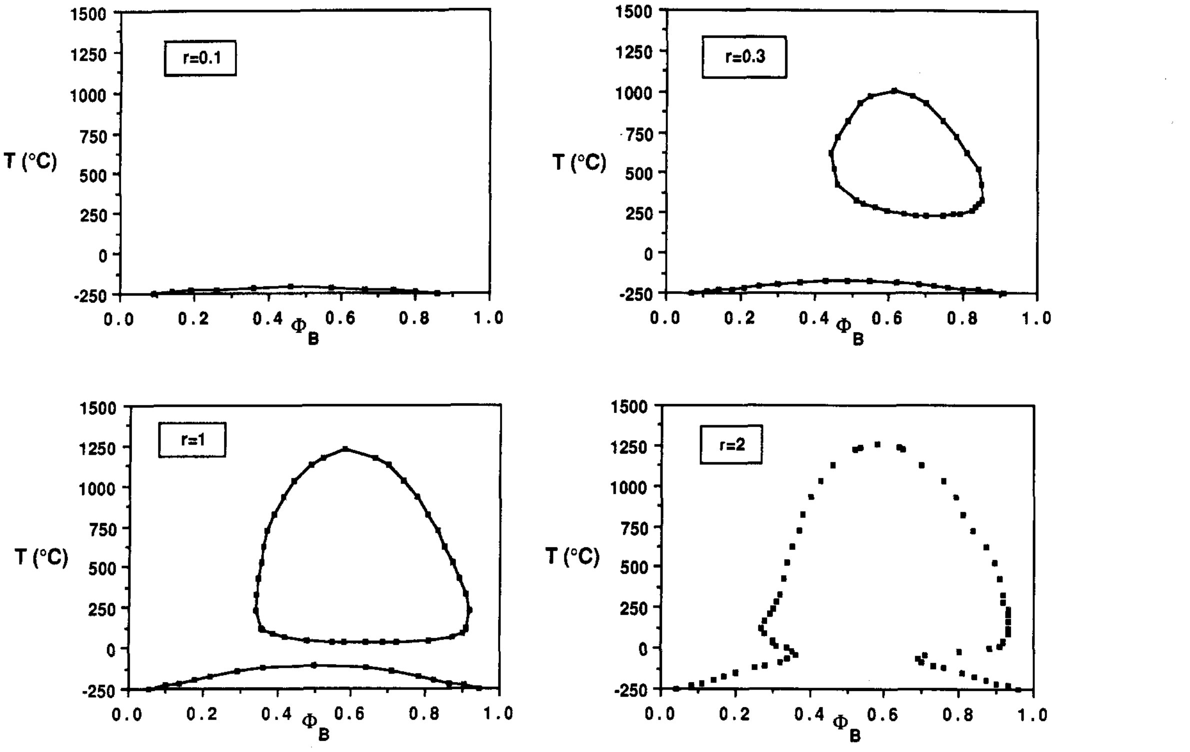

Figure 3. Spinodal curves calculated as a function of r for a hypothetical blend with values of $K_B = 40$, $K_A = 4$, $\chi = 0.1$, and $N_A = N_B = 100$.

second derivative can change sign) two more times, however (some of the crossover points are off the temperature scale of Figure 2). This results in the type of closed-loop spinodal curves characteristic of hydrogen-bonding mixtures.[1,2] Note that the change in sign of the curves in Figure 2 is opposite the change in sign of the second derivative, because of the way eq 15 is arranged. Accordingly, the first crossover point at low temperature indicates a transition from an unstable to a miscible mixture.

An enormous range of phase behavior is predicted by this model, the specifics obviously depending upon the values of the various parameters. To illustrate this, we will use the equilibrium constants given above, which as we noted are typical order of magnitude values for urethanes and ethers, and consider the effect of varying r, the ratio of the molar volumes of the chemical repeat units, χ, and the molecular weight of the polymers. We now assume that the urethane interacting unit is one-quarter the size of the chemical repeat unit, so that the number of segments s_B equals 4. (A fraction that can be determined by assuming that the -OCONH- group is the interacting unit and calculating the ratio of the molar volume of this segment to that of the chemical repeat. The value of 0.25 is approximately that calculated for the amorphous polyuretane characterized in a recent study.[5]) Equation 17 together with the appropriate equations describing the stoichiometry given in the preceding paper are used to calculate the spinodals.

Figure 3 illustrates the effect of changing the relative size of the chemical repeat units through the parameter r. If, for example, we consider mixing a particular amorphous polyurethane with a range of different polyethers, then the values of the equilibrium constants are unaltered, the difference in the size of the species affecting the phase behavior of the blends through the factor K_A/r. Values of $\chi = 0.1$ and $N_A = N_B = 100$ were assumed. Ignoring for the moment the clearly ridiculous (for polymers) range of temperatures in these particular plots, we note that at values of r equal to 0.3 (top right-hand plot) a closed loop characterized by an upper and lower critical solution temperature is obtained. As r is decreased this loop decreases in size and disappears at a double critical point. For $r = 0.1$ (top left-hand plot) all that is observed is an upper critical solution temperature on the bottom curve. Conversely, as r increases, this curve rises to meet the closed-loop stability curve, which also gets larger with r. For this system the lower lying upper critical solution temperature (i.e., on the bottom curve) meets the lower critical solution temperature of the closed loop at a value of r between 1 and 2. At higher values of r the phase diagram then takes on an increasingly hourglass shape.

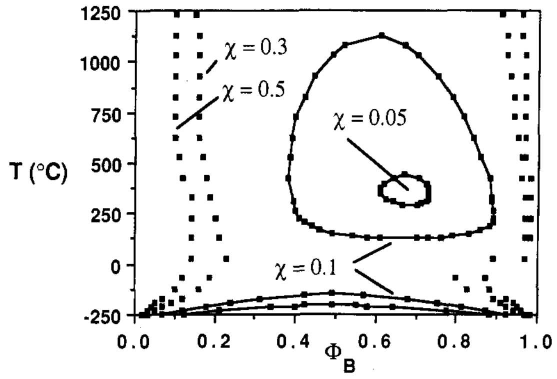

Figure 4. Spinodal curves calculated as a function of χ for a hypothetical blend with values of $K_B = 40$, $K_A = 4$, $r = 0.5$, and $N_A = N_B = 100$.

Clearly this model predicts the type of reappearing phases considered characteristic of mixtures involving hydrogen-bonding components. In the example presented above, however, the closed-loop region of immiscibility is calculated to be at experimentally unattainable temperatures. But, the precise position of the curves is a sensitive function of, on one hand χ and on the other the molecular weight of the blend components and the parameters that define ΔG_H, the equilibrium constants, K, and the ratio of the molar volumes of the chemical repeat units, r. Accordingly, we predict on the basis of this model that we should be able to experimentally observe a rich variety of

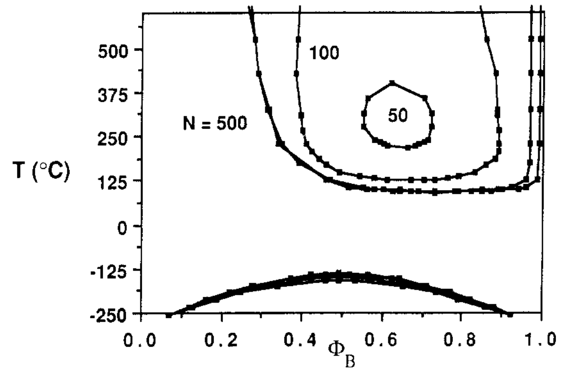

Figure 5. Spinodal curves calculated as a function of degree of polymerization ($N_A = N_B$) for a hypothetical blend with values of $K_B = 40$, $K_A = 4$, $r = 0.5$, and $\chi = 0.1$.

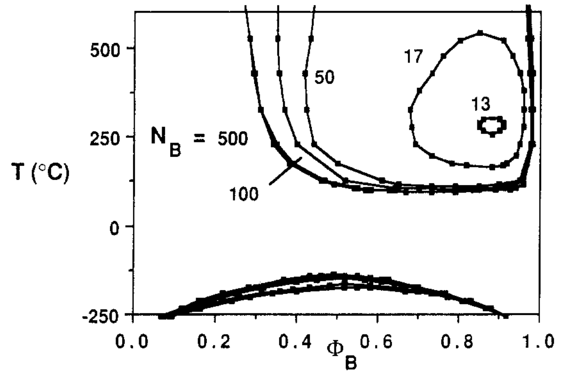

Figure 6. Spinodal curves calculated as a function of degree of polymerization ($N_A = 500$, N_B variable) for a hypothetical blend with values of $K_B = 40$, $K_A = 4$, $r = 0.5$, and $\chi = 0.1$.

phase behaviors through the systematic variation of controllable parameters. This is illustrated in Figures 4–6, where the effect of varying χ and the degrees of polymerization of the polymer components of a blend are illustrated.

Varying the size of the chemical repeat units by the introduction of "inert" (non-hydrogen-bonding units) not only changes ΔG_H through the factors r and the equilibrium constants K_A and K_B but also results in a change of the value of χ. In the following paper we will estimate this parameter through the use of solubility parameters. Here we simply illustrate the effect of varying χ at a constant r, as shown in Figure 4. At small values of χ (<0.1) we calculate a small immiscibility loop that at least for a polyurethane–polyether blend would be above the degradation temperature. For systems with larger values of χ this loop is also larger, finally taking on the appearance of an hourglass shape in this temperature range.

The effect of varying molecular weight is shown in Figures 5 and 6, the former displaying the effect of mixing polymers of equal degrees of polymerization while the latter considers the effect of systematically altering the self-associating component while the degree of polymerization of the other polymer is held constant. These phase diagrams were calculated for a hypothetical mixture, and we will turn our attention in the following paper to polymer blends that are particularly amenable to experimental investigation.

Acknowledgment. The theoretical work described here is aimed at providing a general framework for a range of problems involving the description of hydrogen bonding. Accordingly, we gratefully acknowledge the support of the National Science Foundation, Polymers Program, the Office of Basic Energy Sciences, Department of Energy, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are grateful to Dr. Stephen Howe for many intense and illuminating discussions.

Appendix

Assuming that the chemical repeat units are identical with the interacting units, the free energy of mixing polymers containing interacting units B and A is given by

$$\frac{\Delta G^M}{RT} = \frac{\Phi_A}{N_A}\ln\Phi_A + \frac{\Phi_B}{N_B}\ln\Phi_B + \Phi_A\Phi_B\chi + \left[\Phi_B\ln\left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0}\right] + \frac{\Phi_A}{r}\ln\Phi_{0A} + \Phi_B\left[\frac{\Gamma_1{}^0}{\Gamma_2{}^0} - \frac{\Gamma_1}{\Gamma_2}\right] + \Phi_B\left[\frac{\Gamma_1}{\Gamma_2}\right]\left[\frac{X}{1+X}\right]\right] - \left[\frac{\Phi_B}{\bar{n}_H{}^0}\ln\Phi_B + \frac{\Phi_A}{r}\ln\Phi_A\right] \quad (A1)$$

This follows directly from the derivation given in the preceding paper,[7] where Γ_1 and Γ_2 are defined as

$$\Gamma_1 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{1 - K_B\Phi_{B_1}}\right) \quad (A2)$$

$$\Gamma_2 = \left(1 - \frac{K_2}{K_B}\right) + \frac{K_2}{K_B}\left(\frac{1}{(1 - K_B\Phi_{B_1})^2}\right) \quad (A3)$$

and $\Gamma_1{}^0$ and $\Gamma_2{}^0$ are defined for solutions of pure B where $\Phi_{B_1} = \Phi_{B_1}{}^0$.

The second derivative of the first three Flory–Huggins type terms and the terms in the final parentheses are the same as in the body of the text. The second derivative of the four terms in the first set of parentheses are the required quantities. The first derivative is given by

$$\ln\left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0}\right] - \frac{1}{r}\ln\Phi_{0A} + \frac{\Phi_B}{\Phi_{B_1}}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} + \frac{\Phi_A}{r\Phi_{0A}}\frac{\partial\Phi_{0A}}{\partial\Phi_B} + \frac{\Gamma_1{}^0}{\Gamma_2{}^0} - \frac{\Gamma_1}{\Gamma_2} - \Phi_B\frac{\partial}{\partial\Phi_B}\left[\frac{\Gamma_1}{\Gamma_2}\right] + \frac{\Gamma_1}{\Gamma_2}\left[\frac{X}{1+X}\right] + \Phi_B\frac{\Gamma_1}{\Gamma_2}\left[\frac{1}{(1+X)^2}\right]\frac{\partial X}{\partial\Phi_B} + \Phi_B\left[\frac{X}{1+X}\right]\frac{\partial}{\partial\Phi_B}\left[\frac{\Gamma_1}{\Gamma_2}\right] \quad (A4)$$

We note that

$$\frac{\partial\Gamma_1}{\partial\Phi_B} = \frac{K_2}{(1 - K_B\Phi_{B_1})^2}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} = \Gamma'_1\frac{\partial\Phi_{B_1}}{\partial\Phi_B} \quad (A5)$$

$$\frac{\partial\Gamma_2}{\partial\Phi_B} = \frac{2K_2}{(1 - K_B\Phi_{B_1})^3}\frac{\partial\Phi_{B_1}}{\partial\Phi_B} = \Gamma'_2\frac{\partial\Phi_{B_1}}{\partial\Phi_B} \quad (A6)$$

and substitute for $\partial X/\partial\Phi_B$ and $\partial\Phi_{0A}/\partial\Phi_B$ as in the main text. Gathering terms in $\partial\Phi_{B_1}/\partial\Phi_B$, we obtain

$$\frac{\partial\Phi_{B_1}}{\partial\Phi_B}\frac{\Phi_B}{\Phi_{B_1}} - X[\Gamma_1 + \Phi_{B_1}\Gamma'_1] - \Phi_B\left[\frac{\Gamma'_1}{\Gamma_2} - \frac{\Gamma_1}{\Gamma_2{}^2}\Gamma'_2\right] + \frac{X\Phi_B}{1+X}\left[\frac{\Gamma'_1}{\Gamma_2} - \frac{\Gamma_1}{\Gamma_2{}^2}\Gamma'_2\right] - \frac{\Phi_B}{1+X}\frac{\Gamma_1}{\Gamma_2}\left[\frac{1}{\Phi_{B_1}} + \frac{\Gamma'_2}{\Gamma_2}\right] \quad (A7)$$

which can be simplified to

$$\frac{\Phi_B}{\Gamma_2\Phi_{B_1}}[\Gamma_2 - \Gamma_1 - \Gamma'_1\Phi_{B_1}] \quad (A8)$$

Substituting for Γ_2, Γ_1, and Γ'_1 we obtain for the terms in parentheses

$$\frac{K_2}{K_B}\left(\frac{1}{(1-K_B\Phi_{B_1})^2}\right)-\frac{K_2}{K_B}\left(\frac{1}{1-K_B\Phi_{B_1}}\right)-\frac{K_2\Phi_{B_1}}{(1-K_B\Phi_{B_1})^2}=$$

$$\frac{1}{(1-K_B\Phi_{B_1})^2}\left[\frac{K_2}{K_B}-\frac{K_2}{K_B}(1-K_B\Phi_{B_1})-K_2\Phi_{B_1}\right]=0 \quad \text{(A9)}$$

The remaining terms reduce to

$$\ln\left[\frac{\Phi_{B_1}}{\Phi_{B_1}{}^0}\right]-\frac{1}{r}\ln\Phi_{0A}+\frac{\Gamma_1{}^0}{\Gamma_2{}^0}-\frac{1}{r} \quad \text{(A10)}$$

Hence, the second derivative is simply

$$\frac{1}{\Phi_{B_1}}\frac{\partial\Phi_{B_1}}{\partial\Phi_B}-\frac{1}{r\Phi_{0A}}\frac{\partial\Phi_{0A}}{\partial\Phi_B} \quad \text{(A11)}$$

List of Symbols

A	chemical repeat unit of non-self-associating molecule
B	chemical repeat unit of self-associating molecule
C	concentration defined as n/V, mol m^{-3}
G	Gibbs free energy
G^M	Gibbs free energy of mixing
G_H	component of Gibbs free energy associated with hydrogen bonding
H	enthalpy
h_B	enthalpy of formation of a hydrogen bond between B units
h_{BA}	enthalpy of formation of a hydrogen bond between B and A units
K_A	association equilibrium constant for formation of a hydrogen bond between B and A units
K_B	self-association equilibrium constant between B units
K_α	association equilibrium constant for formation of a hydrogen bond between the "true" interacting units of the B and A chemical repeat units
K_β	self-association equilibrium constant for that part of the B chemical repeat that can be defined as the interacting unit
N_A	degree of polymerization of A covalent polymer molecules
N_B	degree of polymerization of B covalent polymer molecules
n	n-mer
$\bar{n}_H{}^0$	number-average hydrogen-bonded chain length of self-associated B units in pure B
r	ratio of molar volumes of A and B chemical repeat units, V_A/V_B
r_i	ratio of molar volumes of α and β chemical repeat units, V_α/V_β
s_A	number of segments in chemical repeat unit A, V_A/V_α
s_B	number of segments in chemical repeat unit B, V_B/V_β
T	temperature
V	volume of 1 true mole of solution
V_A	molar volume of chemical repeat unit A
V_B	molar volume of chemical repeat unit B
V_α	molar volume of interacting unit of A chemical repeat
B_β	molar volume of interacting unit of B chemical repeat
X	a parameter defined equal to $K_A\Phi_{0A}/r$
α	interacting unit of A chemical repeat
β	interacting unit of B chemical repeat
γ	lattice coordination number
σ	symmetry number
Φ	volume fraction
Φ_{B_n}	volume fraction of a hydrogen-bonded chain of n B units
Φ_{B_nA}	volume fraction of a hydrogen-bonded chain of n B units and one A unit
χ	Flory–Huggins interaction parameter
μ	chemical potential

Subscripts and Superscripts

i	interacting unit
0	property of pure component
A, B, β, α, etc.	as defined above

References and Notes

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