Macromolecules **2005,** *38,* 3703−3707

The Miscibility of Hydrogen-Bonded Polymer Blends: Two Self-Associating Polymers

Yung Park,[†] Boris Veytsman,[‡] Mike Coleman, and Paul Painter*

Materials Science and Engineering Department, Penn State University,
University Park, Pennsylvania 16802, Department of Polymer Science and Engineering,
Sunchon National University, 315 Maegokdong Sunchon, Jeonnam, Korea, and ITT Industries,
Advanced Engineering & Sciences, 1761 Business Center Drive, Reston, Virginia 20190-5337

Received December 28, 2004; Revised Manuscript Received February 21, 2005

ABSTRACT: The factors that determine the miscibility of two polymers, each of which hydrogen bonds (self-associates) to itself in the pure state, is discussed. Equations describing the contributions of hydrogen bonding to the free energy of mixing are presented. It is shown that mixtures of this type are much less likely to be miscible than those where only one of the components self-associates, while the other has hydrogen-bonding acceptor groups. In addition, for mixtures of two self-associating polymers, the volume fraction of the hydrogen-bonding functional group relative to the volume of the polymer repeat unit is an important factor in determining miscibility. If this quantity differs significantly in the two polymers being mixed, even if they have identical hydrogen-bonding functional groups, the mixture will phase separate.

Introduction

Over the course of the last twenty years or so, work in this laboratory has focused on the development of an association model and its application to the study of hydrogen bonding in polymer blends.[1−3] This approach essentially rests on an analysis of the statistical mechanics of reversible association that can be found in an appendix to a paper by Flory on the mixing of heterogeneous polymers.[4] The model is particularly suited to the description of systems where one component self-associates in the form of chains or cyclic dimers (e.g., systems containing hydroxyl groups, amides, carboxylic acids, etc.), while the second component contains only hydrogen-bonding “acceptor” groups (such as an ester or ether). It has been shown that the contribution of hydrogen bonding to the free energy of mixing depends on the number of hydrogen bonds of each type present in the mixture at a given composition and temperature. The enthalpy and entropy changes that accompany the formation of each type of hydrogen bond determines this number and can be calculated from equilibrium constants that can, in turn, be determined spectroscopically and used to describe the stoichiometry of hydrogen bonding.[1−3]

Miscibility in these types of hydrogen-bonded blends then depends (for the most part) on two balances. The first balance is between self-association and interassociation. (By the latter, we mean hydrogen bonds between different types of functional groups on different chains.) If, for example, the amide groups in a particular polymer, such as a nylon, hydrogen bond to one another more strongly than to an acceptor group in a different polymer, say an ether oxygen, then the contribution of hydrogen bonding to the free energy of mixing would be expected to be unfavorable. The second balance is between the often-favorable contribution of specific interactions such as hydrogen bonds to the free energy of mixing and the unfavorable contributions of dispersion and weak polar forces.

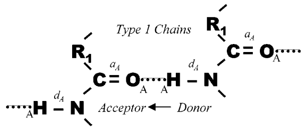
One type of system that we have been unable to describe with the use of simple self-association models involves mixtures of two self-associating polymers. This can be done,[5] but the algebra is complicated and does not lend itself as easily to the type of intuitive understanding of the important factors involved in mixing that can be obtained from applying this approach to simpler mixtures. We also felt that there would be few systems of interest because it would be more difficult to obtain a favorable free-energy balance when both components self-associate. However, in a systematic study of polyamide blends, Ellis[6−12] showed that miscible mixtures can indeed be obtained but interpreted his results in terms of the repulsion model. Brisson et al.[13,14] examined similar systems but found that this model gave poor results and emphasized the formation of hydrogen bonds as a driving force for miscibility in these blends. An interesting correlation between the fraction of the polymer repeat unit occupied by the hydrogen-bonded functional group and miscibility was observed.[13] More recently, it has been shown that a polyamide (nylon 66) can form miscible mixtures with an oligomeric phenolic resin as a result of the formation of strong hydrogen bonds between phenolic and amide groups.[15] The interaction strength of this hydrogen bond was calculated to be significantly larger than that of self-association of the two components.

The association model that we have used deals with the equilibrium distribution of hydrogen-bonded species, which is simply described when only one component self-associates in the form of chains. There is a different approach, originally described by Veytsman[16] and further developed by Panayioutou and Sanchez.[17] This counts how hydrogen bonds are distributed between “donor” and “acceptor” groups. The two models can be shown to be equivalent, as one might expect,[2,3] but this latter model is much more easily applied to the problem of describing mixtures where both components self-associate. Accordingly, in this paper, we will apply this model and show how it can be used to obtain at least a qualitative understanding of the factors that determine the phase behavior of these types of blends.

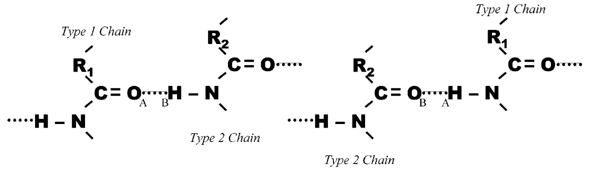
---

* Author to whom correspondence should be addressed. E-mail: painter@matse.psu.edu.
[†] Sunchon National University.
[‡] ITT Industries.

10.1021/ma0473115 CCC: $30.25



Self-Association: A - - A Hydrogen Bonds



Inter-Association: B - - A and A - -B Hydrogen Bonds

Figure 1. Illustration of the hydrogen-bonding donor and acceptor groups present in polyamides.

Equations

For clarity of presentation, we will consider the mixing of polyamides, but the equations will describe hydrogen bonding in any blend where the functional groups have both donor and acceptor properties (e.g., phenols and amides). The donor (d) and acceptor (a) parts of amide groups are illustrated in Figure 1, as are the types of hydrogen bonds we will be considering and the characteristics of the chains. Essentially, the N−H part of each amide linkage is the donor (d) group, while the C=O part is the acceptor (a) group.

We will describe mixtures where the non-hydrogen-bonding portion of the chain can be altered systematically. In the aliphatic nylons, for example, this would involve changing the number of CH_2 groups separating the amide linkages. We will let ϕ_1 and ϕ_2 represent the volume fraction of components 1 and 2 in a blend. We will identify the amide groups on polymer chains of type 1 with the letter A, while the amide groups on polymer chains of type 2 will be designated with the letter B. If the volume fraction of the amide functional group in the repeat unit of polymer 1 is f_A, the volume fraction of A amide groups present in the mixture is then

$$\phi_A = \phi_1 f_A \tag{1}$$

Similarly, if the hydrogen-bonding functional groups in chain 2 occupy a volume fraction f_B of the repeat unit, their volume fraction in the mixture is given by

$$\phi_B = \phi_2 f_B \tag{2}$$

We will use the terms d_A and d_B to designate the number of donor units per unit volume of type A and type B, respectively. Both donor groups are the N−H parts of amide linkages in the polyamide mixtures considered here, with the A donor groups designating N−H groups on chains of type 1, while the B donor groups designate N−H groups on chains of type 2. Similarly, a_A and a_B are the number of acceptor groups (C=O groups) of each type per unit volume (see Figure 1). For polyamide mixtures it follows that $a_A = d_A$ and $a_B = d_B$. We will use the molar volume of the amide group as an arbitrary reference volume for both donor and acceptor groups on each chain.

Proceeding directly from the partition function derived from Veytsman,[16] we then obtain the following expression for the free energy of hydrogen bonding (F_{HB}) the components of the mixture

$$\frac{G_{HB}}{kT} = V\left\{\sum_{i,j} m_{ij} + d_A \ln\left(1 - \frac{m_{AA} + m_{AB}}{d_A}\right) + a_A \ln\left(1 - \frac{m_{AA} + m_{BA}}{a_A}\right) + d_B \ln\left(1 - \frac{m_{BA} + m_{BB}}{d_B}\right) + a_B \ln\left(1 - \frac{m_{AB} + m_{BB}}{a_B}\right)\right\} \tag{3}$$

In this equation, V is the total volume of the mixture, m_{AA}, m_{BB}, m_{AB}, and m_{BA} are the number of hydrogen bonds of type AA, AB, etc., per unit volume, as illustrated in Figure 1. The m_{ij} term is simply the total number of hydrogen bonds per unit volume

$$\sum_{i,j} m_{ij} = m_{AA} + m_{AB} + m_{BB} + m_{BA} \tag{4}$$

The number of hydrogen-bonded donor groups (per unit volume) of type A is equal to $m_{AA} + m_{AB}$ because each of these hydrogen-bonded N−H groups is either linked to a carbonyl group in chains of type 1 (m_{AA}, H bonds between donors in chains of type 1 and acceptors in other chains of type 1) or to a carbonyl group in chains of type 2 (m_{AB}, H bonds between donors in chains of type 1 and acceptor group chains of type 2). Similarly, the number of hydrogen-bonded acceptor groups of type A is given by $m_{AA} + m_{BA}$, and so on. Note that there are also a certain number of non-hydrogen-bonded or "free" groups of each type in the mixture at a given temperature and composition. The logarithmic terms in eq 3 are actually the fractions of free donor and acceptor groups of each type present in the mixture. (Those readers familiar with the association model will no doubt recognize a correspondence in the form of the results.)

The number of hydrogen bonds of each type can be calculated from the equations describing the stoichiometry of hydrogen bonding,[1−3,16,17] which in this case can be written

$$m_{AA} = \left[\frac{\phi_1 f_A}{V_A} - (m_{AA} + m_{AB})\right]\left[\frac{\phi_1 f_A}{V_A} - (m_{AA} + m_{BA})\right]\frac{K_{AA} p_{AA}}{f_A \phi_1} \tag{5}$$

$$m_{BB} = \left[\frac{\phi_2 f_B}{V_B} - (m_{BA} + m_{BB})\right]\left[\frac{\phi_2 f_B}{V_B} - (m_{AB} + m_{BB})\right]\frac{K_{BB} p_{BB}}{f_B \phi_2} \tag{6}$$

$$m_{AB} = \left[\frac{\phi_1 f_A}{V_A} - (m_{AA} + m_{AB})\right]\left[\frac{\phi_2 f_B}{V_B} - (m_{AB} + m_{BB})\right]\frac{K_{AB} p_{BA}}{f_B \phi_2} \tag{7}$$

$$m_{BA} = \left[\frac{\phi_2 f_B}{V_B} - (m_{BA} + m_{BB})\right]\left[\frac{\phi_1 f_A}{V_A} - (m_{AA} + m_{BA})\right]\frac{K_{BA} p_{AB}}{f_A \phi_1} \tag{8}$$

Note that $a_A = d_A = \phi_1 f_A / V_A$, etc. The quantities K_{AA}, K_{BB}, etc., are the equilibrium constants describing the formation of hydrogen bonds of each type. The equilibrium constants are given by

$$K_{AA} = \frac{m_{AA}}{\nu_A^d\, \nu_A^a} \tag{9}$$

$$K_{BB} = \frac{m_{BB}}{\nu_B^d\, \nu_B^a} \tag{10}$$

$$K_{AB} = \frac{m_{AB}}{\nu_A^d\, \nu_B^a} \tag{11}$$

$$K_{BA} = \frac{m_{BA}}{\nu_B^d\, \nu_A^a} \tag{12}$$

In these equations, ν_A^d is the number of free (non-hydrogen-bonded) donor groups of type A per unit volume, ν_A^a is the number of free acceptor groups of type B per unit volume, etc. These are chemical equilibrium constants and are not the same as the dimensionless equilibrium constants that we used in our previous work.[1-3] These quantities are simply related, however. For K_{AA}, for example,

$$K_{AA} = \frac{m_{AA}}{\nu_A^d\, \nu_A^a} = K_{AA}'V_A \tag{13}$$

where K_{AA}' is a dimensionless equilibrium constant describing A–A hydrogen bonds.

Both the lattice model we employed in our initial work[1-3] and the treatment of hydrogen bonds by Veytsman[16] and Panayioutou and Sanchez[17] employ a mean field approximation to describe the probability that two segments are adjacent and, thus, capable of hydrogen bonding. In fairly recent work (see refs 2, 3, 18, 19, and citations therein), we have shown that chain connectivity results in a larger number of self-contacts than one would anticipate on the basis of a random mixing of segments. We account for this with the factor p in the above equations. The term p_{AB}, for example, is the probability of an A segment being next to a B segment. In the mean field approximation, $p_{AB} = \phi_A$ and the term $p_{AB}/\phi_A = p_{AB}/f_A\, \phi_1 = 1$. We use a simple approximation for these probabilities by introducing a parameter γ that is equal to the fraction of same-chain contacts.[18,19] For simplicity, here we will assume that this quantity is the same for both polymers in the blend, and we then have

$$p_{AA} = \gamma f_A + (1 - \gamma)f_A\phi_1 \tag{14}$$

$$p_{BA} = (1 - \gamma)f_B\phi_2 \tag{15}$$

$$p_{AB} = (1 - \gamma)f_A\phi_1 \tag{16}$$

$$p_{BB} = \gamma f_B + (1 - \gamma)f_B\phi_2 \tag{17}$$

In calculating the free energy of mixing, we assume that the contributions of hydrogen bonding can be simply added to the Flory–Huggins equation, where the χ term now describes dispersion and weak polar forces only and is also modified to account for same-chain contacts

$$\frac{\Delta G}{RT} = \frac{\phi_1}{M_1} \ln \phi_1 + \frac{\phi_2}{M_2} \ln \phi_2 + \phi_1\phi_2(1 - \gamma)\chi + \frac{\Delta G_H}{RT} \tag{18}$$

Note that the contribution of hydrogen-bond formation to the change in free energy of mixing is given by subtracting an expression for the free energy of hydrogen bonding of the polymers in the pure state, calculated by putting $m_{AB} = m_{BA} = 0$ in eq 3 above, from the free energy of hydrogen bonding in the mixture.

Results and Discussion

In our initial calculations, we assumed that we were mixing polyamides. In previous experimental work, we have determined that the self-association of aromatic nylons (amide/amide hydrogen bonds) are characterized by a value of a dimensionless equilibrium constant, K', of about 100.[20] Given a molar volume of close to 20 cm^3/mol for the amide group (calculated from group contributions[1]), this means that the equilibrium constants for amide/amide hydrogen bonds (eqs 9–12 above) would all have a value of about 2000 cm^3/mol. Although the local structure of the chain might affect this equilibrium constant (through steric hindrance or delocalization of electrons, for example), much of the work on nylon blends involved chemically similar polymers, so this assumption is reasonable and allows us to illustrate the factors that affect miscibility. In addition, we initially put $\chi = 0$ to determine the effect of hydrogen bonding alone on the phase behavior of two self-associating polymers. The degree of polymerization of each of the chains was assumed to be 100, so there is only a small contribution from the combinatorial entropy of mixing to the overall free energy. Finally, both simulations and experimental work[18,19] indicate that in the concentrated regime γ has a value between about 0.25 and 0.35. We used $\gamma = 0.30$.

If the volume fraction of the amide group in each of the polymers being mixed is the same, say $f_A = f_B = 0.2$, then, as one might expect, the free energy of mixing is negative, the second derivative of the free energy with respect to composition is positive, and the polymers are miscible over the entire composition range. In effect, the amide groups on chains of polymer 1 are just as likely to form hydrogen bonds with amide groups on chains of type 2 as they are to self-associate (i.e., chain type 1/chain type 1 hydrogen bonds). However, the favorable contributions of hydrogen bonding to the free energy of mixing is now much less than what we determined in previous work when only one of the polymers self-associated.[1-3] In such systems, fairly large values of χ, describing dispersion and weak polar forces, could be accommodated ($\chi \approx 0.5$ and sometimes more, depending on the strength of the hydrogen bonds between the different types of chains). Here, the overall contribution of hydrogen bonds to the free energy of mixing is much less because both components in a binary mixture self-associate in the pure state. This is illustrated in Figure 2, which shows spinodals calculated for two hypothetical polyamides, each with $f_A = f_B = 0.2$ as a function of χ. (The spinodals were determined numerically from calculated values of the free energy, so there appears to be some minor fluctuations in the curves from round-off errors.) It can be seen that values of χ of the order of 0.006 now result in phase separation at room temperature (~25 °C). In other words, the polyamides being mixed must have very similar chemical structures if mixing is to occur. Of course, larger values of χ can be accommodated if hydrogen bonding between groups on different polymers is for some reason larger than the hydrogen bonds involved in self-association. We will

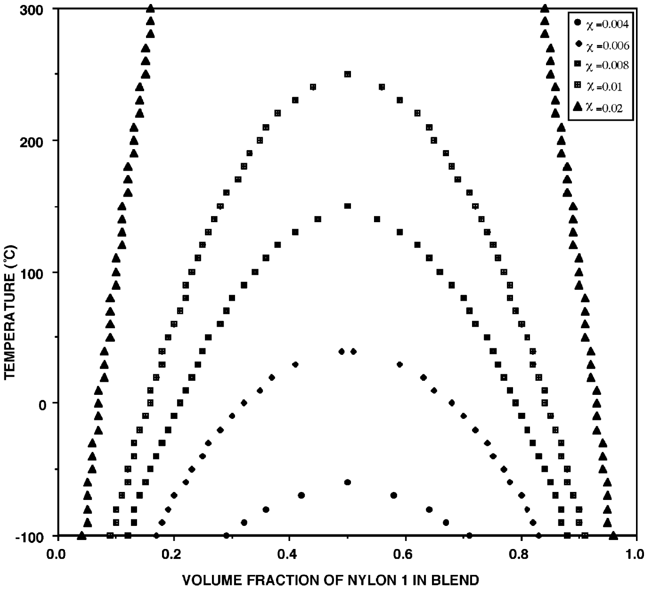


Figure 2. Plot of spinodals calculated for two hypothetical polyamides as a function of χ. The volume occupied by the amide group in the repeat unit of these nylons is the same ($f_A = f_B = 0.2$).

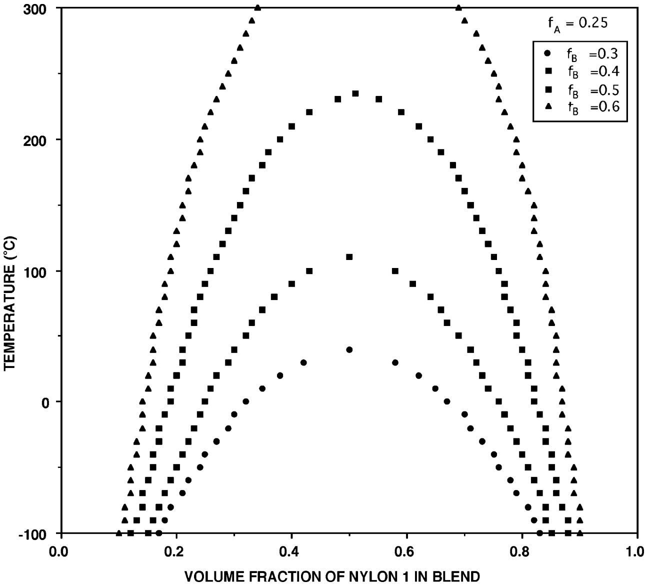


Figure 3. Plot of spinodals calculated for two hypothetical polyamides. The volume fraction occupied by the amide group in the segments of one component of the blend is held constant, ($f_A = 0.25$), while the structure of the second component (hence f_B) is allowed to vary.

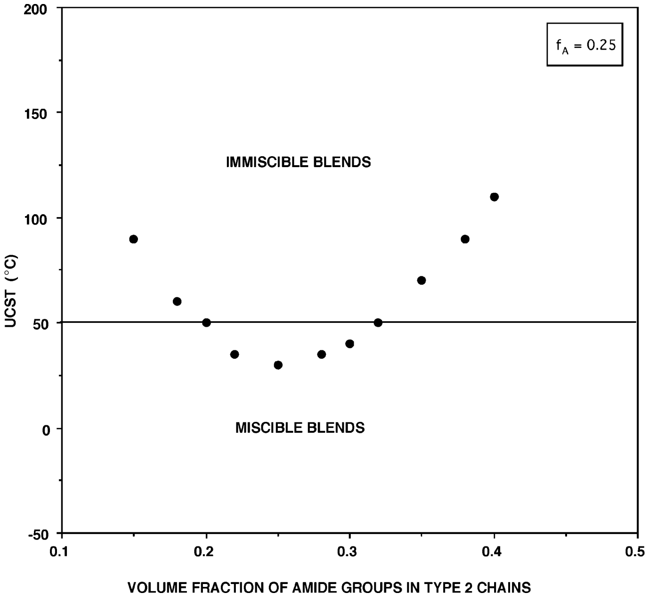


Figure 4. Calculation of the upper critical solution temperature for two hypothetical polyamides. The volume fraction occupied by the amide group in the segments of one component of the blend is held constant, ($f_A = 0.25$), while the structure of the second component (hence f_B) is allowed to vary.

address this point below. First, we wish to illustrate the effect of a second important factor.

Figure 3 shows the effect of holding the volume fraction occupied by the amide group in the segments of one component of the blend constant (polymer 1, $f_A = 0.25$), while the structure of the second component (hence f_B) is allowed to vary. As in Figure 2, we have plotted calculated spinodals. It can be seen that as the volume occupied by the amide group in the segments of one component of the blend increases with respect to the volume occupied by the amide group in the segments of the second component, the polymers become less likely to mix. This is because the probability of forming hydrogen bonds with chains of the same type relative to chains with a different structure changes systematically with this factor. If the volume occupied by the amide group in segments of polymer 1 is much greater than the volume occupied by equivalent amide groups in segments of polymer 2, for example, then segments of type 1 have a much higher probability of finding one another and forming hydrogen bonds. The balance between self-association and interassociation (hydrogen bonds between chains of type 1 and type 2) becomes unfavorable and phase separation occurs. There is a complication here, however. We have found that increasing the spacing between hydrogen-bonding functional groups along a chain increases their accessibility and, hence, ability to form hydrogen bonds. This would change the equilibrium constants describing both self- and interassociation and shift the position and width of the miscible range.

This calculation helps explain some of the results of Ellis[9] and Brisson et al.[13,14] For example, the latter authors studied blends of poly(*m*-phenylene isophthalamide) with poly(*n*-methylene isophthalamides) or *n*I nylons, with $n = 3-9$.[13] They found that miscibility depended on the spacing of amide groups. The *n*I nylons with $n = 6$ and 7 were determined to be miscible over the entire composition range, while the other blends phase separated to one degree or another. (Some were miscible at certain compositions.). The same authors determined a similar dependence of miscibility on composition for blends of poly(hexamethylene isophthalamide) with a series of nylons 6,*m*.[14] We cannot model these mixtures precisely because we do not have values of the equilibrium constants involved (which could be affected by different degrees of steric accessibility), but the balance between self-association and interassociation would change systematically in blends of this type. Calculations for a model system are shown in Figure 4, which shows the value of the upper critical solution temperature (UCST) for the blend systems where, again, the volume fraction occupied by the amide group in the segments of one component of the blend is held constant (polymer 1, $f_A = 0.25$), while the structure of the second component (hence f_B) is allowed to vary. This illustrates that there is a range of segment size relative

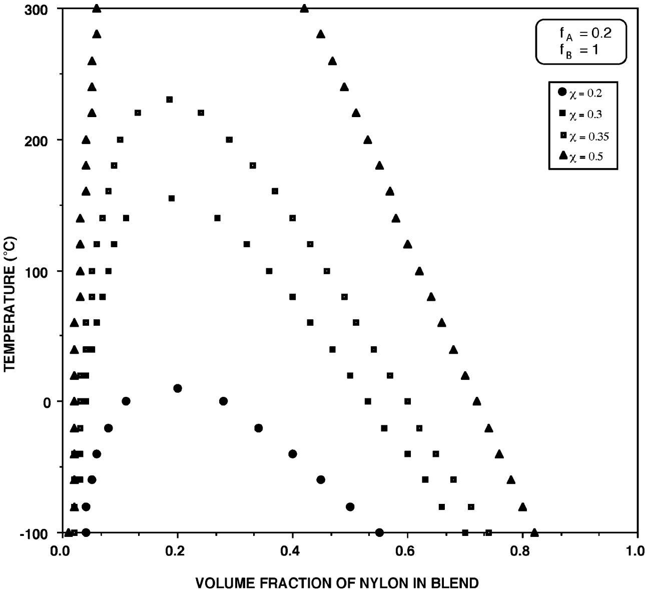


Figure 5. Plot of spinodals calculated for a blend of an oligomeric phenolic material and a polyamide.

to the volume occupied by the amide group that allows an optimum number of interassociation hydrogen bonds to form. If we neglect spacing and steric effects, such that all the equilibrium constants have the same values, then, for a value of $f_A = 0.25$, we calculate that miscibility would be determined for values of f_B between about 0.20 and 0.32 (with $\chi = 0.0058$). (We assumed that the blends have a Tg of about 50 °C, the lowest value found in the poly(hexamethylene isophthalamide)/nylon 6,*m* system,[14] so that mixtures with a UCST below this value would be determined to be miscible.) This range will naturally be shifted (and broadened or narrowed) by any dissimilarity in the relative strength of the hydrogen bonds that can be formed, but the overall trends would be similar.

Finally, we have examined the situation where interassociation equilibrium constants differ significantly from self-association equilibrium constants. Hartikainen et al. have recently found that nylon 66 can form miscible mixtures with oligomeric phenolic resins.[15] They calculated that the interaction energy for hydrogen-bond formation between amide and phenol groups is about 1.5 times the self-association energy of amide groups and nearly twice that of phenol/phenol hydrogen bonds. This would not translate directly into values of equilibrium constants, of course, but we can make some crude assumptions to show trends. The self-association equilibrium constant for amide/amide hydrogen bonds is about 2000 cm^3/mol, as noted above, while our previous work on phenolics indicates an equilibrium constant of 6000 cm^3/mol is appropriate for a phenolic segment occupying 100 cm^3/mol ($f_B = 1$, K' about 60).[1-3] If we arbitrarily assume $K_{AB} = 9000$ while $K_{AB} = 2000$, the results shown in Figure 5 are obtained. (We are essentially assuming that one interassociation hydrogen bond, the phenolic $-$OH to carbonyl C=O, for example, involves a much larger free-energy change than other donor/acceptor hydrogen bonds in this system). It can be seen that miscibility at ambient temperatures is predicted for these mixtures. In addition, because the phenolic component is oligomeric (we assumed degrees of polymerization of $N_1 = 100$ (nylon) and $N_2 = 5$ (phenolic oligomer)), a greater dissimilarity in chemical structure, hence χ, can be accommodated. Phase separation is predicted to occur for values of χ larger than about 0.2 given the equilibrium constants for hydrogen bonding described above. Using group frequencies, we calculate values of the solubility parameters of these two polymers of about 10.5 (nylon 66) and 10.9 (phenolic resin), respectively. (These are calculated on the basis of dispersion and weak polar forces only, see ref 1.) This suggests that materials of this type can form miscible mixtures with relatively small contributions of hydrogen bonding to the free energy of mixing.

Conclusions

The contribution of hydrogen bonding to the free energy of mixing two polymers that self-associate in the pure state is significantly smaller than that determined for mixtures where only one polymer self-associates, while the second has an acceptor group. As a result, those polymers that hydrogen bond to themselves in the pure state are much less likely to form miscible mixtures with one another. In addition, for mixtures of two self-associating polymers, the volume fraction of the hydrogen-bonding functional group relative to the volume of the polymer repeat unit is an important factor in determining miscibility. If this quantity differs in the two polymers being mixed, even if they have identical hydrogen-bonding functional groups, the mixture will phase separate.

Acknowledgment. Yung Park was supported by a grant from the Korea Research Foundation (KRF−2003−013−D00023).

References and Notes

(1) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA, 1991.
(2) Coleman, M. M.; Painter, P. C. *Prog. Polym. Sci.* **1995**, *20*, 1.
(3) Painter, P. C.; Coleman, M. M. In *Polymer Blends, Volume 1: Fundamentals*; Paul, D. R., Bucknall, C. B., Eds.; John Wiley and Sons: New York, 2000; Vol. 1, Chapter 6.
(4) Flory, P. J. *J. Chem. Phys.* **1944**, *12*, 425.
(5) Graf, J. F. Personal Communication.
(6) Ellis, T. S. *Macromolecules* **1989**, *22*, 742.
(7) Ellis, T. S. *Polymer* **1988**, *29*, 2016.
(8) Ellis, T. S. *Polym. Eng. Sci.* **1990**, *30*, 998.
(9) Ellis, T. S. *Polymer* **1990**, *31*, 1058.
(10) Ellis, T. S. *Macromolecules* **1990**, *23*, 1494.
(11) Ellis, T. S. *Polym. Commun.* **1991**, *32*, 489.
(12) Ellis, T. S. *Macromolecules* **1991**, *24*, 3845.
(13) Brisson, J.; Breault, B. *Macromolecules* **1991**, *24*, 495.
(14) Cote, P.; Brisson, J. *Macromolecules* **1994**, *27*, 7329.
(15) Hartikainen, J.; Lehtonen, O.; Harmia, T.; Lindner, M.; Valkama, S.; Ruokolainen, J.; Friedrich, K. *Chem. Mater.* **2004**, *16*, 3032.
(16) Veytsman, B. A. *J. Phys. Chem.* **1990**, *94*, 8499.
(17) Panayiotou, C.; Sanchez, I. C. *J. Phys. Chem.* **1991**, *95*, 10090.
(18) Painter, P. C.; Veytsman, B.; Kumar, S.; Shenoy, S.; Graf, J. F.; Xu, Y.; Coleman, M. M. *Macromolecules* **1997**, *30*, 932.
(19) (a) Coleman, M. M.; Pehlert, G. J.; Painter, P. C. *Macromolecules* **1996**, *29*, 6820. (b) Pehlert, G. J.; Painter, P. C.; Veytsman, B.; Coleman, M. M. *Macromolecules* **1997**, *30*, 3671. (c) Pehlert, G. J.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1998**, *31*, 8423.
(20) Hu, J.; Painter, P. C.; Coleman, M. M.; Krizan, T. D. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 149.

MA0473115