Screening versus Hydrogen Bonding in the Poly(vinylpyridine) + Poly(vinylbutyral) System

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Received January 20, 1995
Revised Manuscript Received April 28, 1995

Introduction

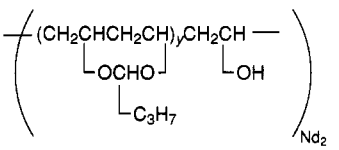
The study of polymer blends and alloys has been an active area of research for many years. As reviewed by Coleman et al.,[1] the relatively small entropy of mixing in polymer blends is generally insufficient to overcome the pure-component energetic preferences unless there are some strong specific interaction energies between the two components. The blend of poly(vinylpyridine) (PVP) + poly(vinylbutyral) (PVB) is an excellent example of such a system with strong hydrogen-bonding energies between the constituents and relatively negligible hydrogen bonding within the pure components. PVP provides strong proton acceptor sites on the nitrogen of the pyridine ring, while PVB provides proton donors from the hydroxyl groups remaining after the polymerization.

Considerable progress have been made recently in the theoretical analysis of hydrogen-bonding polymeric fluids. Panayiotou and Sanchez[2] have explored applications of the Perram–Veytsmann theory (cf. Veytsmann)[3] to polymer blends, and McHugh and co-workers[4] have applied Wertheim's thermodynamic perturbation theory (TPT)[5] to polymers in supercritical solvents. Suresh et al.[6] have shown that these two theories are nearly identical and that the entropy of bonding which appears in the Perram–Veytsmann theory is given by Wertheim's bonding volume. Chapman et al.[7] have shown that Wertheim's bonding volume can be approximated in terms of a well-defined volume integral and the radial distribution function at contact between the two sites that are hydrogen bonding. Furthermore, Ghonasgi and Chapman[8] have demonstrated that the value of the radial distribution function at contact can be approximated by equivalent isolated spheres (EIS) as long as the bonding sites protrude from the end of the molecule. Examples of this kind of protrusion are given by sites located at the end of a polyatomic chain, or even from the middle site of a molecule like propane as long as the other atoms on that molecule are pinned back away from the bonding site. The nitrogen on *p*-PVP is a prime example of an acceptor site that protrudes, and the hydroxyl group on PVB protrudes from the chain backbone. In this context, one would expect the *p*-PVP + PVB system to be readily approximated by the EIS approximation. When the nitrogen on *o*-PVP is located in the ortho position, however, there is little guidance as to how to proceed. One can visualize that the ortho site should be less accessible and that this should show up as a reduction in the radial distribution function at contact. Nevertheless, the magnitude of the screening effect might be large or small. It is possible to estimate the magnitude of the screening effect by molecular simulation,[9] but there has been no experimental evidence which can clearly indicate the magnitude of the screening effect, or whether it indeed exists.

In this paper we use the ortho and para isomers of PVP as a probe of the screening effect. It is reasonable to expect that the energy of bonding between PVP and PVB is roughly the same regardless of the isomer. Thus, by measuring the phase diagrams experimentally and correlating them in terms of thermodynamic perturbation theory (TPT), we can obtain a quantitative estimate of the reduction in the radial distribution function at constant resulting from intramolecular screening.

Experimental Section

Samples of PVP and PVB were purchased from Scientific Polymer Products, Inc. The values for the weight-average molecular weights (M_w) are listed in Table 1. The synthesis of poly(vinylbutyral) (PVB) usually encounters an incomplete conversion of vinyl alcohol to butyraldehyde; therefore, PVB may be viewed as a random copolymer of vinylbutyral and vinyl alcohol P(VB–VA) containing 10–20% of vinyl alcohol repeat units.[10] The copolymer utilized here, which is designated as PVB by the manufacturer, consists of 80 mol % vinylbutyral, 19% vinyl alcohol, and 1% unconverted vinyl acetate segments. For purposes of calculation, we have neglected the vinyl acetate content in the theoretical treatment described below; i.e., the structure of the PVB has been represented as:[10]



where y is the ratio of the number of vinylbutyral repeat units to that of vinyl alcohol repeat units and Nd_2 is the degree of polymerization of component 2 (PVB). We reserve the symbol "N_i" to designate the number of molecules as described later.

The mixtures of *o*-PVP + PVB and *p*-PVP + PVB were prepared in various proportions by codissolving in chloroform at ambient temperature. The solutions were stirred rigorously until the polymers were completely dissolved. The polymer concentration was approximately 20 wt % of the solution. An aliquot of the transparent solutions was placed on individual glass slides, and solvent was allowed to evaporate in a fume hood to form a blend film. The average film thickness was approximately 10 μm. The blend films were dried in a vacuum oven at 80 °C overnight and stored in a desiccator prior to use.

The details of the small-angle light scattering (SALS) apparatus for the cloud-point determination were described elsewhere.[11] The original SALS apparatus was slightly modified by using a photodiode detector to monitor the scattered intensity at various scattering angles, but the angle of observation was fixed at 20° in the present study. A 2-mW He–Ne laser light source (LSR2R, Aerotech) having a wavelength of 632.8 nm was utilized. A programmable temperature controller (Omega CN-2012) was interlinked with a computer (IBM PC2/30) for data acquisition and display, e.g., scattering intensity vs temperature. In the homogeneous state, the scattered intensity was low, but it increased substantially when the system phase separated into the inhomogeneous two-phase state during the course of heating. The temperature where the scattered intensity changed abruptly was designated as the cloud point. The 50/50 composition was measured twice at various heating rates (2.0, 1.0, and 0.5 °C/min), and the data were extrapolated to the zero heating rate. It turned out that the equilibrium point was very close to the value obtained at the heating rate of 0.5 °C/min (within a couple of degrees); thus, the cloud point measurements were made on other compositions only at the heating rate of 0.5 °C/min. The results obtained at the heating rate of 0.5 °C/min were used

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0024-9297/95/2228-5147$09.00/0

Table 1. Characteristic Parameters for PVP + PVB Blends[a]

	o-PVP	*p*-PVP	PVB
M_w	40 000	50 000	88 000
Nd	377	472	473
δ (cal/cm^3)$^{1/2}$	10.35	10.35	9.14
V (cm^3/mol)	37 500	45 000	64 900
ϵ_{HB}/k (K)	4000	4000	see acceptor
K_{AD} (cm^3/mol)	0.0014	0.0028	see acceptor

[a] Estimates of δ and V were determined by the procedure of Coleman et al.[1]

to compare with theoretical predictions as will be discussed in a subsequent section.

Theory

Wertheim's thermodynamic perturbation theory (TPT) was derived from a fundamental application of statistical mechanics via cluster series expansions. The derivation is complicated, but the final formulas have been summarized by Jackson et al.[12] in fairly simple fashion:

$$\frac{A^{assoc}}{NkT} = \sum_i x_i \sum_{B_j=\{A,D\}} \frac{M_i^{B_j}}{2} + \ln(X_i^{B_j}) - \frac{X_i^{B_j}}{2} \qquad (1)$$

where A^{assoc} is the Helmholtz free energy of bonding, N the total number of molecules in the system, k Boltzmann's constant x_i the mole fraction of the ith component, $M_i^{B_j}$ the number of bonding sites of type B_j (acceptor or donor) on the jth segment of the ith component, and $X_i^{B_j}$ the mole fraction of bonding sites of type B_j of the ith component which are not hydrogen bonded. Equation 1 represents a straightforward extension to mixtures of the formula given by Jackson et al.[12] for pure fluids. Wertheim's theory is closely related to methods of analyzing hydrogen bonding that have been available for some time. The previously available methods include the traditional chemical theory of writing numerous collections of explicit bonding mechanisms and the lattice method of counting hydrogen bonds originally developed in the 1960s. For some restricted cases, Wertheim's theory can be shown to be equivalent to the linear association model of chemical theory.[13] Wertheim's method offers a self-consistent and rational basis for extending to polysegmented and branched networks, however, where chemical theory has proved cumbersome in the past. With regard to the bond counting method, Wertheim's formulas are extremely similar with respect to the nature of the networks that can form. On the other hand, a characteristic quantity appears in the bond counting method, viz., the entropy of bonding, which is difficult to relate to the physics of the fluid. In Wertheim's theory, the analogous quantity has a very specific geometrical identity, given by an integral of the volume available for the donor and acceptor sites to overlap averaged over all orientations of the bonding home sites. The terms in Wertheim's theory can be directly represented in molecular simulations and the validity of the theory tested with no adjustable parameter. The molecular simulations to date have proved the guidance of Wertheim's theory to be highly reliable, even when extended substantially beyond the scope originally constructed by Wertheim himself (cf. Ghonasgi and Chapman[8] and Liu et al.[14]).

The material balances between acceptors, donors, and acceptor–donor complexes give a relation between the fractions of acceptors and donors that remain unbonded. For the problem at hand, it is convenient to write the balance for the first acceptor site on molecule 1:

$$X_1^{A_1} = [1 + \sum_j x_j \sum_{D_k} X_j^{D_k} \varrho \Delta_{A_1 D_k}]^{-1} \qquad (2)$$

where $\Delta_{A_1D_k} = K_{AD}[\exp(\epsilon_{HB}/kT) - 1]$ is Wertheim's bonding volume and $K_{AD} = g(\sigma_{12})V_{AD}$ is the volumetric factor. ϵ_{HB}/k is the energy of hydrogen bonding over Boltzmann's constant in degrees Kelvin and ϱ is the molar density (mol/cm^3).

The equations become much simpler if one allows a few approximate assumptions. First, one may assume that the acceptor and donor sites located all along each polyatomic chain form a collection of sites which are very similar and each may be approximated by the average for the entire collection. In other words,

$$X_1^{A_1} = X_1^{A_2} = \ldots = X_1^{A_j} \quad \text{and} \quad X_2^{D_1} = X_2^{D_2} = \ldots = X_2^{D_j} \qquad (3)$$

Another convenient assumption is that the self-association of each component may be neglected relative to the cross-association between the pyridine and the hydroxyl group. Then acceptors appear only on component 1, and donors appear only on component 2. With these two assumptions the equations simplify to:

$$\frac{A^{assoc}}{NkT} = x_1 Nd_1\left(\ln(X_1^{A_1}) + \frac{1 - X_1^{A_1}}{2}\right) + x_2 Nd_2\left(\ln(X_2^{D_1}) + \frac{1 - X_2^{D_1}}{2}\right) \qquad (4)$$

where Nd_i is the degree of polymerization of the ith component

$$X_1^{A_1} = [1 + x_2 Nd_2 X_2^{D_1} \varrho \Delta_{12}]^{-1} \qquad (5)$$

$$X_1^{D_1} = [1 + x_1 Nd_1 X_1^{A_1} \varrho \Delta_{12}]^{-1} \qquad (6)$$

Substitution of the right-hand side of eq 6 into eq 5 gives a quadratic equation that may be solved for $X_1^{A_1}$, and this result may be substituted into eq 6 for the complete solution.

To apply this result to polymer blends, one must also include a representation of the nonassociative thermodynamics. Here we simply apply the Flory–Huggins equation. We estimate the χ-parameter from solubility parameters and molar volumes as described by Coleman et al.[1] The final set of characteristic parameters is given in Table 1. The values for the enthalpy of bonding, ϵ_{HB}, have been set *a priori* based on the generally accepted value of about 2 kcal/mol. By setting the molar density equal to the reciprocal of the molar volume of the mixture, all terms are completely defined. This means that a single adjustable parameter, K_{AD}, was regressed from the experimental data for each blend. The final equations for the activity coefficients are given in the appendix, along with a sample calculation for complete clarification.

Results and Discussion

The experimental results are presented along with the results of the theory in Figure 1. Clearly, there is a significant effect of the position of the acceptor group on the phase diagram. While both blends exhibit lower critical solution behavior, the temperature must be

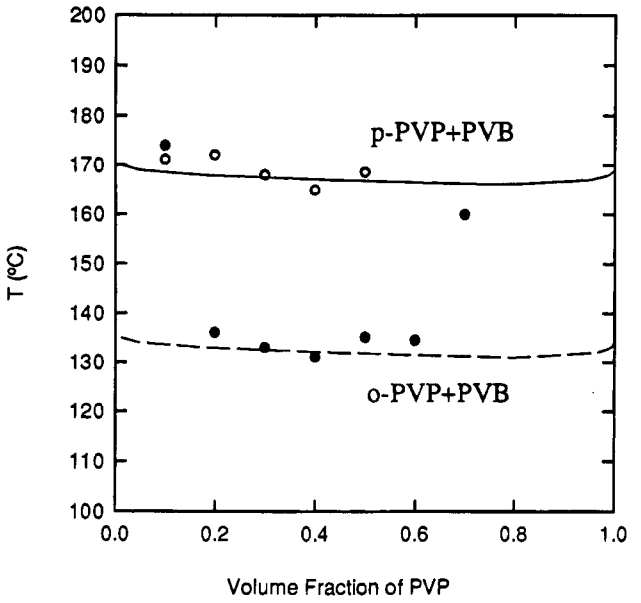

Figure 1. Cloud-point phase diagrams for the *p*-PVP + PVB (open circle) and *o*-PVP + PVB (filled circle) systems. The solid and dashed lines represent the theoretical predictions for *p*-PVP + PVB and *o*-PVP + PVB, respectively, based on Wertheim's thermodynamic perturbation theory. The greater extent of hydrogen bonding in the *p*-PVP + PVB system causes an elevation in the LCST relative to the *o*-PVP + PVB system.

elevated by an additional 40 °C to induce phase separation in the *p*-PVP + PVB blend. This is consistent with the notion that hydrogen bonding is stronger in the *p*-PVP blend such that higher temperatures (or thermal energies) must be provided to break the H-bonded newtwork and to revert to nonassociative behavior. To reproduce this effect, the theory suggests that the parameter K_{AD} must be increased from a value of 0.0014 for *o*-PVP to 0.0028 for *p*-PVP. Since the volume integral V_{AD} may be expected to be the same for both isomers, this result indicates that the radial distribution function at contact $g(\sigma_{12})$ must be reduced by a factor of 2 relative to the unscreened value when the acceptor group is moved to the ortho position.

There are a couple of significant deviations between the theory and the experiments at the lowest and highest compositions for the *o*-PVP blend. It is possible that these may be attributed to oversimplications of Flory–Huggins theory in the estimation of a constant χ-parameter. In other words compressibility effects have been neglected as well as any possible composition dependence in the physical contribution to χ. Additionally, some assumptions applied to Wertheim's TPT may be at fault; notably, the self-association of PVP may not be entirely negligible, as assumed above. Including the self-association for PVB would make the equations much less comprehensible than the current presentation. Furthermore, the substantially greater strength of the cross-association implies that whatever self-association may exist should be overwhelmed by the cross-association. Despite the specific details of the theoretical treatment, the explanation of the vertical shift in the phase diagrams seems to be accurately described in terms of the phenomenology of a screening effect. This is the principal objective of the present investigation, and further analysis of the details of the phase diagrams is left to the scope of future investigations.

In conclusion, we have presented a simple but definitive demonstration of the accuracy of the concepts underlying Wertheim's TPT as applied to strongly interacting polymer blends. The experimental system is simple enough to provide a clear indication of the specific role of screening of the hydrogen-bonding site relative to the extent of hydrogen bonding. By applying TPT, this system permits a quantitative characterization of the magnitude of the screening effect according to the position of the pyridine nitrogen in the aromatic ring. Further similar studies, coupled with molecular simulations and other statistical mechanical theories, can be expected to lead to a general theory of hydrogen bonding in polyatomic systems that covers a very broad range of applications.

Acknowledgment. This research was supported in part by the National Science Foundation through Grant No. GTS-911085.

Appendix: Activity Coefficient Expressions

$$\ln(\gamma_k) = \ln(\gamma_k^{FH}) + \ln(\gamma_k^{assoc}) = \ln(\gamma_k^{FH}) + \frac{\partial(A^{assoc}/_kT)}{\partial N_k}$$

$$\ln(\gamma_1^{assoc}) = \mathrm{Nd}_1\left[\ln(X_1^{A_1}) + \left(\frac{1 - X_1^{A_1}}{2}\right)\right] + \mathrm{Nd}_1 x_1 \frac{N\partial X_1^{A_1}}{\partial N_1}\left(\frac{1}{X_1^{A_1}} - \frac{1}{2}\right) + \mathrm{Nd}_2 x_2 \frac{N\partial X_2^{D_1}}{\partial N_1}\left(\frac{1}{X_2^{D_1}} - \frac{1}{2}\right)$$

Differentiating the quadratic equations for $X_1^{A_1}$ and X_2^{D} implicitly,

$$\frac{N}{-X_1^{A_1}}\frac{\partial X_1^{A_1}}{\partial N_1} = \frac{X_1^{A_1}\frac{N\partial a_1}{\partial N_1} + \left(\frac{N\partial a_2}{\partial N_1} - \frac{N\partial a_1}{\partial N_1}\right)}{2X_1^{A_1}a_1 + (1 + a_2 - a_1)} \quad \text{and}$$

$$\frac{N}{-X_2^{D_1}}\frac{\partial X_2^{D_1}}{\partial N_1} = \frac{X_2^{D_1}\frac{N\partial a_2}{\partial N_1} + \left(\frac{N\partial a_1}{\partial N_1} - \frac{N\partial a_2}{\partial N_1}\right)}{2X_2^{D_1}a_2 + (1 + a_1 - a_2)}$$

where

$$a_i = x_i \mathrm{Nd}_i \Delta_{12}/V \rightarrow \frac{N\partial_{aj}}{\partial N_i} = \mathrm{Nd}_j(\delta_{ij} - \Phi_j)\frac{V_i}{V_j}\frac{\Delta_{12}}{V}$$

and Φ_i is volume fraction of the ith component. The derivation for γ_2 is analogous.

Sample Calculation. Taking the parameters from Table 1 for *o*-PVP at 406 K and $x_1 = 0.3255$, we have $\Phi_1 = 0.2181$, $\Delta_{12}/V = 4.7514 \times 10^{-4}$, $X_1^{A_1} = 0.873\,956$, $X_2^{D_1} = 0.951\,513$,

$$\frac{N\partial X_1^{A_1}}{\partial N_1} = 0.08718; \quad \frac{N\partial X_2^{D_1}}{\partial N_1} = -0.11542; \quad A^{assoc}/NkT = -16.92$$

$$\ln(\gamma_1^{assoc}) = 377[\ln(0.874) + (1 - 0.874)/2 + 0.01828] + 473(-0.04289) = -40.42$$

The interesting feature regarding the present calculation is that any single acceptor site is predominately unbonded (the mole fraction unbonded is near unity),

and the related derivatives are also small. Nevertheless, the role of association is quite significant when multiplied by the degree of polymerization.

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MA950068C