Miscibility limits in poly(vinylethylene) isotopic mixtures

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Summary
      The interaction parameter for isotopic mixtures of poly(vinylethylene) was determined from small angle neutron scattering measurements to vary from 6.6×10^{-4} to 5.7×10^{-4} over a temperature range of from just above T_g to 71°C. The phase behavior of these blends differs significantly from the predictions of Flory-Huggins theory, indicating that, in addition to their non-ideality, polymer isotopes do not form simple mixtures. This phase behavior, however, was found to be congruent with the symmetrical model of mixtures.

Introduction
      The influence of isotopic substitution on molar volume often gives rise to an appreciable excess free energy in polymer mixtures containing such isotopes [1-8]. This importance of this effect is the frequent use of deuterium substitution to obtain enhanced contrast in small angle neutron scattering measurements. This scattering intensity is

$$I(Q) = (b_i - b_j)^2 S(Q)/V_o \qquad (1)$$

where b is the neutron scattering length, Q the momentum transfer and V_o the irradiated volume. The structure factor for an incompressible two component mixture in the random phase approximation is given by [3]

$$S(Q)^{-1} = S_i{}^o(Q)^{-1} + S_2{}^o(Q)^{-1} - 2X \qquad (2)$$

with

$$S_i{}^o = 2N_i o_i \, [\, R_i{}^2 Q^2 + \exp(-R_i{}^2 Q^2) - 1 \,] \, / \, R_i{}^4 Q^4 \quad (3)$$

for a coil of radius of gyration equal to

$$R_i = l_i (N_i/6)^{1/2} \qquad (4)$$

The Flory-Huggins parameter, X, characterizes the non-combinatory portion of the free energy of mixing [3,9]

$$\Delta G_M/kT = N_i{}^{-1} \phi_i \ln \phi_i + N_j{}^{-1} \phi_j \ln \phi_j + X \phi_i \phi_j \qquad (5)$$

and for "simple mixtures" is independent of concentration. In these expressions ϕ_i represents the volume fraction of

component i, consisting of N_i segments of volume V_i, l_i is the segment length consistent with equation 4, and kT has its usual significance.

The contribution to X from isotopic substitution usually represents an unwanted complication in attempts to measure the mixing energy of a blend. The molar volume isotope effect can be directly measured in binary isotope blends however, and consequently it provides a means to probe the thermodynamics of polymer mixtures near their critical point. The present report describes neutron scattering measurements on poly(vinylethylene) isotope mixtures carried out in order to assess the extent to which their miscibility conforms to theoretical predictions.

<u>Experimental</u>

The poly(vinylethylenes) (PVE) were synthesized as described elsewhere [10], with blend compositions shown in Table 1. Molecular weights of the component polymers were determined both by gel permeation chromatography and from measurement of the terminal viscosity in compression (employing a Perkin-Elmer TMA 7 for this purpose). It was ascertained that this viscosity (in units of Pa-sec) varied at room temperature according to

$$n_O = 3.0 \times 10^{-3} N^{3.4} \tag{6}$$

where N is the weight average degree of polymerization. Noting that small changes in molecular weight introduce a large variation in the Newtonian viscosity, it can be appreciated that n_O provides a reliable corroboration of GPC results. The molecular weights determined in this fashion were consistent with the initiator levels employed during polymerization.

Small angle neutron scattering measurements were performed at the National Bureau of Standards at temperatures from below the glass transition temperature up to 74^OC. An incident neutron wavelength of 6Å and a sample to detector distance of 3.6m in conjunction with a converging collimation system yielded measurements down to 0.01 Å^{-1}. The details of the experimental apparatus can be found elsewhere [11].

TABLE 1
Blend Compositions

Blend	Hydrogenous Component N	Deuteriated Component N	Deuteriated Component ϕ
B1	2570	3170	0.53
B2	5200	3170	0.47

<u>Molar Volume Isotope Effect</u>

Displayed in Figure 1 are representative SANS measurements for the PVE isotope blends. In order to extract
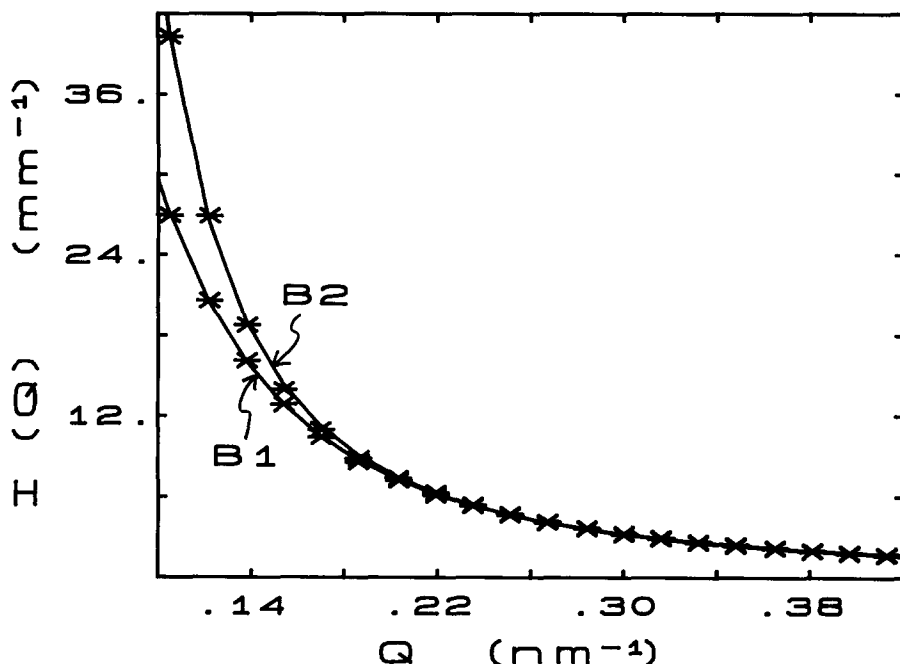
Figure 1. The neutron differential scattering cross sections measured at 24°C, along with fitted curves from equation 1.

a value of the interaction parameter for the mixture, non-linear least squares fitting of equation 1 to the experimental data was accomplished by an iterative procedure using the complimentary DFP algorithm [12]. In addition to the coherent scattering described by equation 1, a weak incoherent scattering will also be included in the measured intensities. This was corrected for by fitting the high angle data ($Q > 0.06$ Å^{-1}) to provide the magnitude of this angle independent background (which was consistent with the independently measured scattering from PVE samples containing only one isotopic species). The uncertainty in the component molecular weights obviates to some extent uncertainty in the statistical segment length, and herein $l_i = l_j = 5.9$ Å is utilized consistent with the characteristic ratio under Theta conditions [13]. The total uncertainty in the obtained values of X_{isot} arising from these factors is judged to be about 15%.

In large polyatomic molecules this molar volume isotope effect primarily reflects differences in the vibrational motions arising from their dependence on mass and mass distribution [14-16]. The effect is dominated by the C-H symmetric stretching mode, the anharmonicity of which results in a slightly greater bond length for C-H bonds (which occupy a higher position in the potential well) than for C-D bonds. Mixing of the isotopes causes an increase in molar volume of the deuteriated species and a corresponding contraction of the

hydrogenous component. The free energy change resulting from the mixing of isotopes can be considered as consisting of a contribution from the compression (dilation) of each species to its volume in the mixture, and from the ensuing mixing at constant volume of the two components [17,18]. For large molecules the latter contribution is negligible relative to the excess free energy arising from the molar volume change; therefore, calculation of the free energy change associated with altering the molar volume of the pure components to that in the blend provides a direct estimate of the isotope effect in polymer mixtures. The excess free energy associated with bringing the components to their volume in the blend can be expressed as [17]

$$X_{vol} = (\Delta V)^2 / 2kTBV \qquad (7)$$

where B is the isothermal compressibility and

$$(\Delta V)^2/V = (\Delta V_i)^2/V_i = (\Delta V_j)^2/V_j \qquad (8)$$

Such volume changes calculated according to the equation of state for the liquid would alter the equilibrium structure (particle packing) of the components; the ensuing constant volume mixing would necessarily require a change in chemical potential so that X_{vol} can not be precisely equal to X_{isot}. The shape of the distribution functions describing atom-atom correlations are invariant to the isotopic molar volume changes [18]. The properly calculated compression or expansion over the isotopic volume difference gives the excess free energy for an equal volume fraction of the two isotopes resulting from the molar volume isotope effect as [19]

$$X_{isot} = (nu/2)(\Delta V/V)(h/kT)(v_i-v_j) \qquad (9)$$

where n is the number per monomer unit of carbon-hydrogen symmetric stretching modes, of frequency v, h is Planck's constant, and u (the Gruneisen coefficient [20]) gives the molar volume dependence of the vibrational frequency

$$u = -d \ln v / d \ln V \qquad (10)$$

which is assumed to be isotope independent.

The experimental results for X can be compared to the molar volume isotope effect calculated using equation 9. The difference between the stretching frequency of C-H and C-D is 800 cm^{-1}, and n is equal to 6. The other requisite parameters are not available for PVE, but can be estimated to provide for an approximate comparison with the experimental results. The isotopic molar volume change for 1,4-polybutadiene has been reported to be 4 x 10^{-3} [6]. With half the number of carbon-hydrogen bonds per main chain unit, $\Delta V/V$ for PVE is therefore taken to equal 2 x 10^{-3}. The value of the Gruneisen coefficient spectroscopically determined for benzene, u=0.035 [19,21], is also utilized. The resulting calculated X_{isot} equals 8 x 10^{-4} at room temperature. It is noted that the experimental values are about 20% lower, a difference that is well within the uncertainty of the calculation.
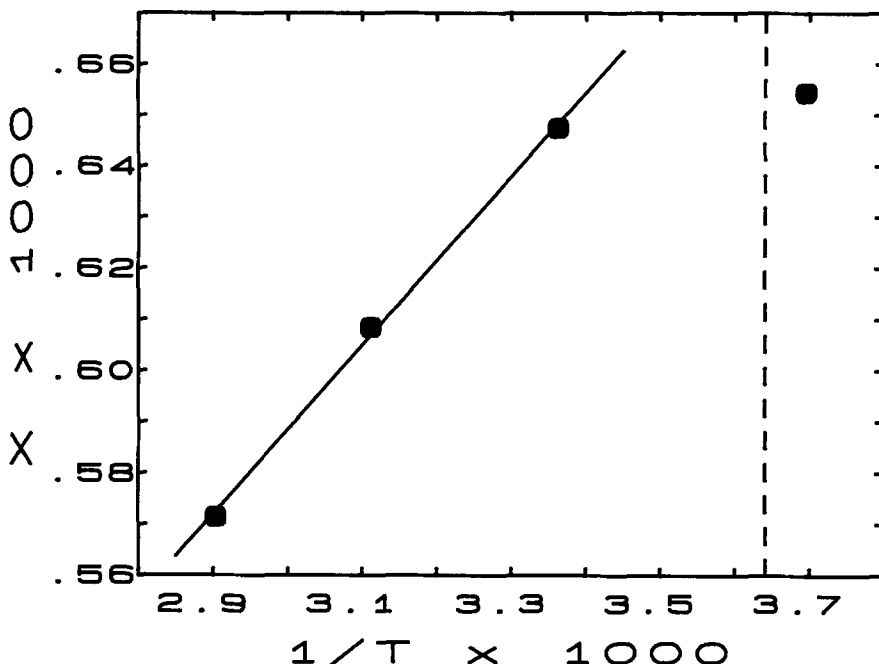
Figure 2. The interaction parameter for sample B2 displayed versus the inverse of the various SANS measurement temperatures (in Kelvin). The highest value was obtained when the sample was below its glass transition temperature (denoted by the vertical dashed line). Least squares fitting to the liquid state data yielded the indicated straight line with a slope and intercept of 0.17 degrees and 9.3 x 10^{-5} respectively.

The interaction parameters determined for blend B2 are displayed in Figure 2 as a function of the inverse of the measurement temperature. The data points corresponding to scattering from the sample in the liquid state are collinear. The lowest measurement temperature (-3.6° C) is about 5 degrees below the glass transition temperature of the PVE [10]. Extrapolation of the higher temperature data suggests that the structure at -3.6° C is not significantly different from that at room temperature.

Phase Behavior
According to the theory of simple mixtures the value of the interaction parameter above which phase segregation can be expected is given by the spinodal equation [3,21]

$$X_S = [(N_i \phi_i)^{-1} + (N_j \phi_j)^{-1}]/2 \qquad (11)$$

From the data in Table 1 it is found that $X_S = 7.1$ x 10^{-4} and 5.2 x 10^{-4} for blends B1 and B2 respectively, with the

uncertainty in N giving an error of less than 1×10^{-4}. Equation 11 is thus seen to predict phase heterogeneity in sample B2. This is in clear contradiction with the neutron scattering results, however, which are consistent only with miscibility. To wit:

- both the magnitude and angle dependence of the SANS measurements are well described by mean field theory.

- the fitting to equation 1 yielded values of the interaction parameter in good accord with sample B1 (X = 6.1×10^{-4}) and with an earlier determination [8] executed on a composition for which X_s (= 1.4×10^{-3}) was a factor of two larger than X, such that this composition lay well within the miscible region of the phase diagram.

- the SANS measurements on sample B2 were time invariant. When a mixture is immiscible, the equilibrium morphology (corresponding to total phase segregation) is never attained due to the high viscosity of the polymeric melt state; nevertheless, when the B2 blend was taken in temperature from ambient (where n_o is circa 100 gigapoise) to 50° higher, the neutron scattering did not exhibit the time dependence expected for a system in a nonequilibrium morphological state upon increase in its molecular mobility.

In addition, when films consisting of the pure components of sample B2 were maintained in contact at 50°C, spontaneous interdiffusion was observed. This direct observation of spontaneous _mixing_ of the deuterated and hydrogenous species provides unambiguous evidence of their thermodynamic miscibility [22,23].

Since the blend sample B2 is miscible, it is clear that the calculated X_s must be in error. It is emphasized that this error can not be attributed to experimental uncertainties in the molecular weights of the polymers, which could alter X_s less than 15%. It must therefore be inferred that the divergence of the experimental phase behavior from the expectations of the calculated spinodal reflects a divergence of the free energy from simple (Flory-Huggins) theory. The failure of equation 11 in describing the precise location of the spinodal is only made obvious when experiments are carried near the critical region. In most polymer blends, whereby specific interactions are responsible for the miscibility, the interaction parameter is negative, and hence the spinodal line can not be traversed by increases in the component molecular weights.

The inadequacies of simple mixing theory in the vicinity of criticality is well established for mixtures of small molecules [24]. A better description is provided by the symmetrical mixture model [19,20], which gives for the excess free energy

$$\Delta G_M/kT = N_i^{-1}\phi_i \ln o_i + N_j^{-1}\phi_j \ln \phi_j + \phi_i\phi_j (X' + X''(\phi_i - \phi_j)^2 + \dots) \qquad (12)$$

Note that retention of only the first enthalpy term yields the relation for simple mixtures (equation 5). In extending the excess enthalpy to higher powers of concentration equation 12 bears similarity to empirical expressions for the mixing free

energy that have been employed to account for a measured concentration dependence of the interaction parameter [25,26]. The spinodal equation for a symmetrical mixture can be obtained by setting the second derivative of the free energy with respect to concentration equal to zero, yielding to second order

$$[(N_i \phi_i)^{-1} + (N_j \phi_j)^{-1}] = 2[X' + X''(5(\phi_i-\phi_j)^2 - 4\phi_i\phi_j)] \qquad (13)$$

with

$$X_s = X' + X''(\phi_i-\phi_j)^2 \qquad (14)$$

For $o_i \sim o_j$ and taking $X''/X' = 0.2$ [19], the spinodal value for the symmetrical mixture is 25% greater than X_s for the simple mixture, which is the magnitude required to accommodate the experimental values. The important qualitative point revealed by equation 13 is that the miscible region of the phase diagram for the symmetrical mixture extends beyond that of a simple mixture, indicating that the former provides a better description of the behavior of the PVE mixtures.

The simple mixture model assumes no concentration dependence of the excess enthalpy, but for a symmetrical mixture the enthalpy only depends upon the difference in the component concentrations. For blends B1 and B2 (in which the quantity $(\phi_i-\phi_j)$ was invariant) no difference in X would be expected from either model. The observed small difference reflects only the experimental uncertainty that results from the use of a different hydrogenous species in each of these samples.

Conclusions

It has previously been recognized that isotopic polymer mixtures are non-ideal, with the excess enthalpy arising from the molar volume isotope effect. It is now apparent that these compositions are not simple mixtures either. From the observed phase behavior it can be inferred that the enthalpy change does not vary in direct proportion to the product of the component concentrations, but exhibits a magnitude that is consistent with the symmetrical model. Further study is warranted of the concentration dependence of the isotope interaction parameter suggested by the present results, particularly by investigating the phase behavior of samples in the vicinity of the critical point. It is interesting to note that the extent of non-ideality for the mixtures of hydrogenous PVE with its deuteriated isomer ($X = 6 \times 10^{-4}$) significantly exceeds that for blends of the former with the chemically distinct cis-1,4-polyisoprene (for which $X < 2 \times 10^{-4}$ [10]), even though both are regular mixtures (that is, characterized by an absence of specific interactions).

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