Origin of the Negative Excess Enthalpy in Poly(vinylethylene)/*cis*-1,4-Polyisoprene Blends

C. M. Roland, J. B. Miller, and K. J. McGrath*

Chemistry Division, Code 6120, Naval Research Laboratory, Washington, D.C. 20375-5342

Introduction

Poly(vinylethylene) (PVE) and *cis*-1,4-polyisoprene (PIP) form thermodynamically miscible,[1,2] albeit dynamically heterogeneous,[3-5] blends. There are no specific interactions between the components;[6] the intermolecular forces are strictly dispersion (van der Waals) interactions. Although this implies a positive excess enthalpy and miscibility that is solely a consequence of the combinatorial entropy gain, the miscibility extends to infinite molecular weight of the components.[7] Miscibility also persists upon isotopic substitution,[5] even though the latter significantly alters the van der Waals energy of PVE.[8,9] These facts are inconsistent with a positive heat of mixing. Recently small-angle neutron scattering measurements on this blend demonstrated that the interaction parameter, χ, which provides a measure of all noncombinatorial entropy contributions to the mixing free energy, is in fact negative.[10] The temperature dependence of χ suggested that the negative sign has an enthalpic origin. This is surprising, since van der Waals mixtures are expected to exhibit endothermic heats of mixing.[11-14] A negative excess enthalpy in a van der Waals mixture indicates that the dispersion forces between dissimilar units are stronger than those between like contacts. It was suggested[10] that such an enhancement of the van der Waals bonding in the PIP/PVE blend might be due to closer intermolecular contact between the components relative to the neat polymers. Congruent with this hypothesis, a very slight densification (ca. 0.1%) has been reported in PVE/PIP blends.[15] Of course, because of the nonlinear distance dependence of the van der Waals interaction energy,[16] enhanced van der Waals bonding need not necessarily be accompanied by any bulk densification and may, for example, occur as a result of packing variations associated with molecular structure.

This study focuses on the proposed mechanism for the negative excess enthalpy in PIP/PVE blends. In order to directly probe the interactions in the PIP/PVE mixture, a cross polarization solid-state NMR experiment was carried out. The NMR technique of cross polarization is a useful probe of spatial intimacy in materials, due to the strong dependence of the magnetization transfer rate on the internuclear separation.[17,18] The inverse time constant for this process, the cross relaxation rate T_{IS}^{-1}, is directly proportional to the second moment, $M_{(2)SI}$, of the S spin (carbon) resonance line through dipolar coupling with the I spins (protons)[17] for the high-effective-field spin-lock cross-polarization NMR experiment. The second moment is directly proportional to the inverse sixth power (r^{-6}) of the distance separating the carbon and proton nuclei[19] and thus significant cross polarization among ^{13}C and ^1H nuclei occurs only at distances less than 0.5–1.0 nm.[20,21] In the following experiments, the measured cross-polarization rates (using dipolar dephasing) reflect the distance r separating the chain units, potentially providing a quantitative comparison of interchain separations in the blend versus the pure components. In this context, the rate of cross polarization from protonated poly(vinyleth-

ylene) (^1H PVE) or protonated polyisoprene (^1H PIP) to perdeuterated poly(vinylethylene) was examined.

Experimental Section

Samples of a protonated and a perdeuterated PVE, both 97% 1,2-polybutadiene, were used; their weight-average degrees of polymerization were 2570 and 3170, respectively (polydispersities equal to 1.2). The 1,4-polyisoprene (70% *cis*) specimen was monodisperse, with a degree of polymerization = 1690. Two blends were utilized, an isotopic mixture of the PVE's and a blend of the perdeuterated PVE with the PIP. Each composition, containing about 50% by weight of the components, had the same proton concentration, 0.050 mol/cm³. The blends were prepared by dissolution of the polymers in cyclohexane, followed by vacuum drying for 1 day at 40 °C. The dried films were packed into the magic angle spinning tubes with a weighted plunger, the latter left in contact for 1 week at room temperature in order to achieve the uniform mass distribution necessary for spinning.

All NMR experiments were run on a Bruker MSL spectrometer with a static magnetic field of 7.04 T, corresponding to Larmor frequencies of 75.5 and 300.1 MHz for ^{13}C and ^1H, respectively. The Hartmann–Hahn technique of cross polarization[22-24] was employed using proton and carbon radio-frequency fields of 50 kHz (5-μs $\pi/2$ pulsewidth) and a magic angle spinning rate of 3.0 kHz ± 5 Hz. The NMR dipolar dephasing technique[25] was used in conjunction with cross polarization to rapidly dephase (broaden) resonances arising from carbons with directly bonded hydrogen and thereby allow observation of cross-polarized deuterated carbons only. A fixed dipolar dephasing time of 100 μs was used in all experiments; this is sufficient to induce complete dephasing of the carbon NMR peaks from the hydrogenous component. The cross-polarized deuterated carbon resonances are essentially unaffected by the 100-μs dephasing, since those carbons are more distant from the protons. Hence, the intensity of the deuterated carbon resonances could be monitored as a function of the cross-polarization contact time.

Results and Discussion

Each of the carbon resonances of PVE was used to assess the extent of cross polarization of the deuterated component. Figure 1A is a plot of the carbon-13 NMR signal intensity of the downfield vinyl resonance ($-CH=$, $\delta = 143$ ppm) as a function of cross-polarization contact time measured for the ^2H PVE/^1H PVE isotopic blend at 245 K and the ^2H PVE/^1H PIP isotopic blend at 220 K. These temperatures are 25 K below the respective glass transition temperatures (as determined calorimetrically) and therefore the two samples will exhibit approximately equal segmental relaxation spectral densities. Thus, the factors affecting ^{13}C spectral resolution[26,27] were carefully controlled so that differences in the rate of cross relaxation between the blends could be primarily ascribed to the relative spatial proximity of the components. The ^2H PVE/^1H PVE blend was measured at 220 K as well. Note that the intensities in Figure 1 represent magnetization from cross-polarized *deuterated* carbons only, since 100-μs dipolar dephasing was used to eliminate contributions from carbons with directly bonded protons.

The cross-relaxation time constants T_{IS} were determined from the data at short ($\leq$4-ms) cross-polarization contact times. At such short times, the signal decay due to proton $T_{1\rho}$ relaxation is not too severe, since proton $T_{1\rho}$ values are typically substantially longer than 4 ms in organic glasses. For the downfield vinyl resonance, the calculated values of T_{IS} for the ^2H PVE/^1H PVE blend at 220 and 245 K were nearly identical, corresponding to 2.4 ± 0.2 and 2.5 ± 0.2 ms, respectively. In contrast, T_{IS} for the ^2H PVE/^1H PIP blend at 220 K was 1.8 ± 0.2 ms. This difference represents a 25% decrease in the cross-relaxation time
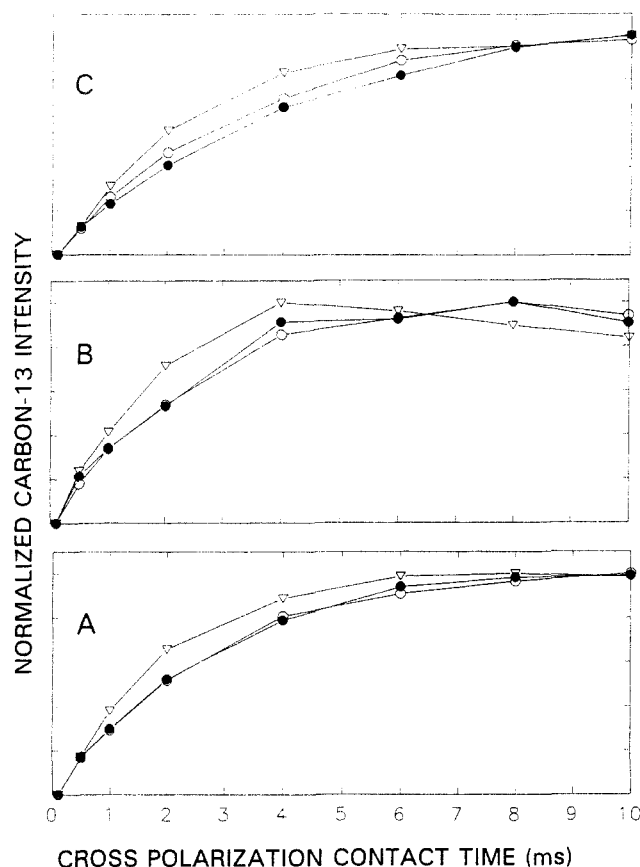
Figure 1. Plot of normalized PVE downfield vinyl (A), upfield vinyl (B), and saturated (C) NMR carbon resonance intensity versus cross-polarization contact time with a fixed 100-μs dipolar dephasing time: ^{2}H PVE/^{1}H PVE at 220 K (O), ^{2}H PVE/^{1}H PVE at 245 K (●), ^{2}H PVE/^{1}H PIP at 220 K (▽). Note that the cross-relaxation time T_{IS} for the ^{2}H PVE/^{1}H PIP blend is reduced significantly at each carbon site relative to the ^{2}H PVE/^{1}H PVE blend.

constant for the ^{2}H PVE/^{1}H PIP blend relative to the ^{2}H PVE/^{1}H PVE isotope blend at 220 and 245 K. A decrease of this magnitude would require an approximate 7% densification in the PIP/PVE blend (after taking into account the expected variation in density upon blending) over and above the 0.1% densification actually reported.[15] As noted previously, the cross-relaxation time constant is proportional to the sixth power of the distance separating the hydrogens of the hydrogenous component and the carbons of the deuterated component. The diminution in the T_{IS} value for the PVE/PIP blend thus suggests greater spatial intimacy of the two components in this blend relative to the PVE/PVE blend; the exact mechanism for this enhanced local density in PVE/PIP is not presently understood although a wider *distribution* of packing densities in the PVE/PIP blend would give such a result. Even larger decreases in the cross-relaxation time constant are observed for the cross polarization of the PVE upfield vinyl carbon resonance (=CH$_2$, δ = 114 ppm), 1.5 ± 0.2 ms for PVE/PIP (220 K) vs 2.6 ± 0.3 ms (220 K) and 2.9 ± 0.3 ms (245 K) for PVE/PVE, and the two overlapping PVE saturated carbon resonances (δ = 40 ppm), 2.1 ± 0.1 ms for PVE/PIP (220 K) vs 3.1 ± 0.2 ms (220 K) and 3.6 ± 0.2 ms (245 K) for PVE/PVE (parts B and C of Figure 1 respectively).

The cross-relaxation rate T_{IS}^{-1} is also directly proportional to the cross-polarization spectral density function J_x of the I spins.[17] It is therefore possible that the observed differences in the cross-relaxation rates could be attributed to differences in this cross-polarization spectral density

function. However, based upon the high-effective-field spin-lock experimental procedure used, in which the deviation from the Hartmann–Hahn condition is negligible, a Gaussian correlation function for the proton spins can be assumed, and the spectral density function J_x can be approximated as being directly proportional to the correlation time τ_c of the proton–proton dipolar fluctuations.[17,20] The proton dipolar fluctuation time τ_c in the blends will in turn be largely dependent upon the *local* proton density at the temperatures (below T_g) where the cross-relaxation time constants T_{IS} were measured. As noted, the PVE/PIP and PVE/PVE compositions were chosen to give equivalent *bulk* proton densities. However, the local proton density of PIP is approximately 8% *higher* than that of PVE; closer packing results in stronger proton–proton dipolar couplings and hence will result in a shorter proton–proton dipolar fluctuation time in the PVE/PIP blend (at 220 K) relative to the PVE/PVE blend. The shorter proton fluctuation time would have the effect of *reducing* J_x in the ^{2}H PVE/^{1}H PIP blend (at 220 K) and thus reducing the rate of cross relaxation. Contrarily, the cross-relaxation rate is *faster* for the ^{2}H PVE/^{1}H PIP blend at 220 K compared to the ^{2}H PVE/^{1}H PVE blend at both 220 and 245K; therefore, the differences in the cross-relaxation rates observed for the two blends cannot be attributed to differences in the proton–proton spectral density functions. The significantly shorter cross-relaxation time constant observed in the ^{2}H PVE/^{1}H PIP blend reflects a shorter average internuclear distance between the protons of ^{1}H PIP and the carbons of ^{2}H PVE than in the isotopic blend of PVE.

Summary

Blends of PIP/PVE exhibit a negative interaction parameter despite the absence of specific interactions. The NMR results presented herein demonstrate that the exothermic mixing enthalpy arises from enhancement of the van der Waals dispersion forces engendered by closer spatial contact between the components. This unusual phenomenon is made possible in this particular mixture because of the remarkable equivalence of the cohesive energy densities of PIP and PVE.[2,28] In most blends, a mismatch in cohesive energy densities results in a large positive excess enthalpy; thus, in the absence of specific interactions, phase separation results. Since the miscibility of PIP and PVE has an enthalpic origin, a lower critical solution temperature (LCST) is anticipated (though at a temperature well beyond the polymers' decomposition temperatures);[10] however, contrary to the norm, in this blend the LCST is not due to specific interactions or equation of state effects.[29,30] When the former are sufficiently strong, local ordering may be induced.[31-33] This is not anticipated in the present van der Waals blend.

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