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

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Introduction

Poly(vinylethylene) (PVE) and cis-1,4-polyisoprene (PIP) form thermodynamically miscible, albeit dynamically heterogeneous, blends. There are no specific interactions between the components; 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. Miscibility also persists upon isotopic substitution, even though the latter significantly alters the van der Waals energy of PVE. These facts are inconsistent with a positive heat of mixing. Recently small-angle neutron scattering measurements on this blend demonstrated that the interaction parameter, $\chi$, which provides a measure of all noncombinatorial entropy contributions to the mixing free energy, is in fact negative. The temperature dependence of $\chi$ 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. 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 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. Of course, because of the nonlinear distance dependence of the van der Waals interaction energy, 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. The inverse time constant for this process, the cross relaxation rate $T_{1s}$, is directly proportional to the second moment, $M_{DSS}^{(2,5)}$, of the S spin (carbon) resonance line through dipolar coupling with the I spins (protons) 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 and thus significant cross polarization among $^{13}$C and $^1$H nuclei occurs only at distances less than 0.5–1.0 nm. 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 polyvinylethylene ($^1$H PVE) or 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/cm$^3$. 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 $^1$H, respectively. The Hartmann-Hahn technique of cross polarization was employed using proton and carbon radio-frequency fields of 50 kHz ($\pi$-2/2 pulsewidth) and a magic angle spinning rate of 3.0 kHz ± 5 Hz. The NMR dipolar dephasing technique 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 depopulation 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 ($^{1}$H CH=, $\delta$ = 143 ppm) as a function of cross-polarization contact time measured for the $^2$H PVE/$^1$H PVE isotopic blend at 245 K and the $^2$H PVE/$^1$H 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 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 $^2$H PVE/$^1$H 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 $T_{1s}$ were determined from the data at short (<4 ms) cross-polarization contact times. At such short times, the signal decay due to proton $T_{1s}$ relaxation is not too severe, since proton $T_{1s}$ values are typically substantially longer than 4 ms in organic glasses. For the downfield vinyl resonance, the calculated values of $T_{1s}$ for the $^2$H PVE/$^1$H 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, $T_{1s}$ for the $^2$H PVE/ $^1$H PIP blend at 220 K was 1.8 ± 0.2 ms. This difference represents a 25% decrease in the cross-relaxation time.
It is therefore possible that the observed differences in this cross-polarization spectral density function are attributed to differences in the cross-polarization spectral density of the hydrogenous component and the hydrogens of the hydrogenous component and the hydrogens of the deuterated component. The diminution in relative to the PVE/PVE blend; the exact mechanism for the LCST in this blend must be the spatial intimacy of the two components in this blend. This unusual phenomenon is made possible in this particular mixture 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); however, contrary to the norm, in this blend the LCST is not due to specific interactions or equation of state effects. When the former are sufficient, 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); however, contrary to the norm, in this blend the LCST is not due to specific interactions or equation of state effects. When the former are sufficiently strong, local ordering may be induced. This work was supported by the Office of Naval Research. We thank Dr. A. N. Garroway for helpful comments on the manuscript.

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 1.00-μs dipolar dephasing time: 2H PVE/1H PVE at 220 K (O), 2H PVE/1H PVE at 245 K (∗), 2H PVE/1H PIP at 220 K (v). Note that the cross-relaxation time constant for the 2H PVE/1H PIP blend is reduced significantly at each carbon site relative to the 2H PVE/1H PVE blend.