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Miscibility in Poly(vinylethylene) Isotopic Mixtures by Carbon-13 NMR

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ABSTRACT: A solid-state NMR dipolar dephasing experiment is constructed to probe the phase morphology of isotopic blends of poly(vinylethylene). The strong dependence on the relevant spin separation distances of both the ^1H–^{13}C cross-polarization intensity and the extent of dipolar dephasing enables carbons from the components to be distinguished from one another. Using this method we demonstrate that the blend is segmentally mixed for component molecular weights at which the critical value of the interaction parameter, as calculated using the Flory–Huggins lattice model, is less than the actual interaction parameter of the blend.

Introduction

Isotopic Mixtures. There has been much interest over the last decade in mixtures of polymer isotopes.[1-17] Although much of this attention arises from the extensive use of isotopic labeling to enhance small-angle neutron scattering (SANS) contrast, the near ideality of such mixtures makes them of interest in their own right. The thermodynamics of mixtures of chemically dissimilar polymers invariably deviate from predictions of lattice models such as the Flory–Huggins theory; however, since isotopic substitution exerts a minor influence on chemical behavior, isotope blends are expected to be more accurately described by simple theory. New theoretical developments,[18-24] however, have indicated that correlation effects and chain connectivity will alter the excess free energy from that calculated using mean-field theories such as Flory–Huggins. Even in athermal mixtures the unlike contacts are diminished in favor of like contacts and this nonrandom mixing broadens the homogeneous region of the phase diagram.[19,20]

The deviation of polymer–polymer interaction parameters from an inverse temperature dependence and from a concentration invariance evidences their nonadherence to simple mixing theory. Experimental demonstration that polymer isotope mixtures are not simple mixtures has already been obtained from small-angle neutron scattering measurements on poly(vinylethylene) (PVE) isotopic blends.[15,16] The interaction parameter, χ, extracted from the SANS data exceeded the Flory–Huggins critical value, indicating that polymer isotopic blends exhibit greater miscibility than predictions based on the assumption of random mixing. The present study was intended to corroborate that polymer isotopes do not behave as Flory–Huggins mixtures.

^{13}C Cross Polarization and Dipolar Dephasing. Solid-state nuclear magnetic resonance (NMR) dipolar dephasing experiments[25] were used to probe the intimacy of mixing in blends of hydrogenous PVE with its deuterated isomer. This method exploits the distance dependence of the magnetic dipole interaction between hydrogen and ^{13}C nuclei. The efficiency of magnetization transfer from ^1H to ^{13}C nuclei is in part dependent on the inverse sixth power of their separation distance,[26,27] and, hence, substantial transfer of magnetization between heteronuclei occurs only when they are separated by no more than approximately 0.5–1.0 nm.[28,29] In the isotope blend, cross polarization from protons of the hydrogenous PVE to carbons on the deuterated component requires the spatial intimacy associated with thermodynamic miscibility. A phase-segregated morphology would preclude significant cross polarization of the deuterated carbons.

In an isotope blend the determination of miscibility is complicated by the absence of distinct chemical shifts for the various carbons of the components. The strong distance dependence of the static dipolar interaction, however, will diminish the magnitude of the dipolar interaction of hydrogen with deuterated carbons relative to that between carbons and directly bonded hydrogen. Moreover, the extent of the reduction in the former is determined by the phase morphology.

The NMR dipolar dephasing technique[30] consists of transient exposure of the ^{13}C spins to the proton dipolar interaction after an appropriate cross-polarization contact time. The extent of the consequent dephasing (broadening) of the ^{13}C resonances is dependent on the proximity of the nuclei to protons. The duration of the dephasing period can be limited such that carbons more distant from protons than those with directly bonded protons (i.e., the deuterated carbons) remain essentially unperturbed. The presence of carbon intensity in this experiment must then be attributed to carbons which lack directly bound protons but are spatially close to protons. Such a result would provide an unambiguous determination of segmental mixing.

Experimental Section

The poly(vinylethylenes) were synthesized in vacuo using a modifier that yields primarily 1,2-addition.[31,32] According to the manufacturer (MSD Isotopes), the deuterated butadiene had 0.6% residual protons randomly situated. Molecular weights were determined both by gel permeation chromatography and from measurement of the terminal melt viscosity.[15] The results (Table I) were consistent with the initiator levels employed during polymerization.

PVE mixtures containing the critical concentration of components were prepared from carbon disulfide solutions, followed by vacuum drying at 313 K for several days. The critical composition is given by[3]

$$\phi_i^* = N_j^{1/2}/(N_i^{1/2} + N_j^{1/2}) \qquad (1)$$

where ϕ_i represents the volume fraction of the ith component with the degree of polymerization equal to N_i. The resulting film was packed into the magic angle spinning (MAS) rotor under pressure at 313 K. After filling the tube, the samples were annealed for at least 1 week. The two blends used in this study are listed in Table I.

All NMR spectra were run on a Bruker MSL 300 spectrometer in a static magnetic field of 7.0 T, using a double-tuned MAS probe equipped for 7-mm-o.d. sample rotors. The ^1H and ^{13}C Larmor frequencies were 300.1 and 75.5 MHz, respectively. The temperature was maintained at 260 K, approximately 15 K below

Table I
Blend Compositions

blend	^{1}H component N_w[a]	^{2}H component N_w[a]	^{2}H component vol fraction	χ_{cr}[b]
B1	2570	3170	0.48	7.1×10^{-4}
B2	5200	3170	0.56	5.1×10^{-4}

[a] Weight-average degree of polymerization; polydispersities equal 1.2. [b] Using eq 2.

the glass transition temperature of the samples, in order to maintain a strong dipole reservoir. ^{1}H and ^{13}C radio-frequency fields during cross polarization and decoupling were maintained at 50 kHz, and the MAS frequency was 4.0 kHz ● 5 Hz.

The NMR cross polarization/dipolar dephasing experimental conditions were designed to allow an unambiguous determination of the phase morphology of the blends. The Hartmann–Hahn cross polarization/magic angle spinning method was employed[33-35] using a contact time experimentally determined to provide maximal cross polarization of deuterated carbons in a miscible blend. Carbons in the deuterated component of an immiscible blend would not undergo cross polarization because of their greater distance from protons. This was experimentally verified by cross polarizing for 8 ms an intimate physical mixture of equal parts of deuterated and hydrogenous polystyrene, whereby no carbon magnetization was in evidence after 50 μs of dipolar dephasing. In addition, cross-polarization experiments on pure deuterated PVE with no dipolar dephasing showed no observable evidence of cross-polarized carbon magnetization. An appropriate dipolar dephasing time was determined such that magnetization of carbons with directly bonded hydrogen would be dephased; hence, any subsequently existing magnetization can be ascribed to deuterated carbons not bonded, but in proximity, to protons.

Results

Two PVE blends were examined whose compositions were chosen to represent miscible and immiscible blends as predicted by Flory–Huggins theory. The critical value of the Flory–Huggins interaction parameter is given by[3]

$$\chi_{cr} = [N_i^{-1/2} + N_j^{-1/2}]^2/2 \qquad (2)$$

For the deuterated PVE mixed with the lower molecular weight protonated isomer (the blend designated B1 in Table I), χ_{cr} is calculated to be 7.1×10^{-4}. This is greater than the interaction parameter determined for PVE isotopic mixtures ($\chi = 6.8 \times 10^{-4} \pm 0.2 \times 10^{-4}$ at room temperature,[14-16] and hence sample B1 is expected to be miscible. Sample B2 is comprised of higher molecular weight PVE (Table I), such that $\chi_{cr} = 5.1 \times 10^{-4}$ according to eq 2. The expectation is that composition B2 will be thermodynamically immiscible, since $\chi > \chi_{cr}$.

The effect of cross-polarization contact times on the intensity of the carbon resonances (chemical shift = 40 ppm) in the ^{13}C NMR spectrum is shown in Figure 1 for B1 and B2, as well as for pure hydrogenous PVE. In all spectra there is a rapid buildup of magnetization over the first 1 ms due to facile cross polarization of the carbons with directly bonded hydrogen. At longer cross-polarization times the curves are characterized by a loss in magnetization as governed in part by the proton rotating-frame spin–lattice relaxation time constant, $T_{1\rho}$.[36] The measured proton $T_{1\rho}$ for pure hydrogenous PVE was 13 ms, compared with 17 ms for blend B1. Differences in the cross-relaxation time constant, T_{CH}, for deuterated and hydrogenous carbons may also contribute to the differences in carbon intensity among these samples at long cross-polarization times. The pure hydrogenous sample exhibits the fastest rate of magnetization loss. The isotope blends relax significantly more slowly and are apparently characterized by nearly identical proton $T_{1\rho}$'s. Obviously the proton environment is more dilute in the miscible blend B1 than in the neat hydrogenous PVE. In addition, since the magnitude of the proton $T_{1\rho}$ varies inversely with the second moment of the homonuclear ^{1}H–^{1}H dipolar interaction,[37] we expect $T_{1\rho}$ to increase as the proton density is decreased by dilution with deuterated polymer. The nearly identical apparent proton $T_{1\rho}$ behavior of blend B2 with that of miscible blend B1 suggests that the proton environment must be similar in these mixtures, implying a similarity in their phase morphologies. Furthermore, since both blends apparently exhibit proton $T_{1\rho}$'s substantially longer than that of the neat hydrogenous compound, we infer that both mixtures are miscible. Dipolar dephasing experiments were carried out to further examine this aspect.

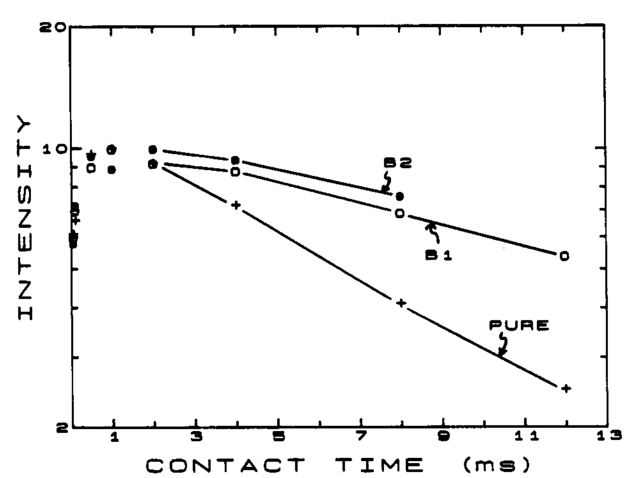

Figure 1. Semilogarithmic plot of the intensity of the ^{13}C resonance (chemical shift = 40 ppm) as a function of contact time for B1, B2, and pure ^{1}H PVE. Note that both B1 and B2 exhibit significantly lower rates of magnetization loss at long contact times relative to pure ^{1}H PVE. This result is consistent with dilution of the hydrogenous component by the deuterated component and indicates segmental mixing in both blends.

A contact time for cross polarization was determined such that the deuterated carbons in a miscible blend would acquire a maximum amount of magnetization. As will be subsequently shown, this optimal contact time was 8 ms. An appropriate dipolar dephasing time must then be utilized, whereby the resonances of carbons with directly bonded protons are broadened by dipole coupling to the hydrogen; however, this dephasing time must be sufficiently short that deuterated carbons, being more distant from protons, are not significantly dephased by the heteronuclear dipolar interaction. The spectra in Figure 2 show the change in the normalized ^{13}C signal intensities for pure hydrogenous PVE as the dipolar dephasing time is varied up to 100 μs. Since all of the carbons in this sample have at least one directly bonded hydrogen, the strong static dipolar field present at each carbon nucleus effects rapid dephasing of the resonances. As seen in Figure 2, a loss of signal intensity and complete broadening of the saturated carbon resonances (chemical shift = 40 ppm) occurs after 50 μs of dipolar dephasing.

The above results were obtained using a cross-polarization contact time of 8 ms, which gives maximal magnetization transfer to deuterated carbons in miscible blend B1. This value was determined by using a 50-μs dipolar dephasing time for sample B1 and varying the contact time to achieve the largest ^{13}C intensity. Since the carbons with directly bonded hydrogens will be substantially broadened after 50 μs of dipolar dephasing, the remaining intensity is primarily attributable to the deuterated carbons which are in intimate contact with the

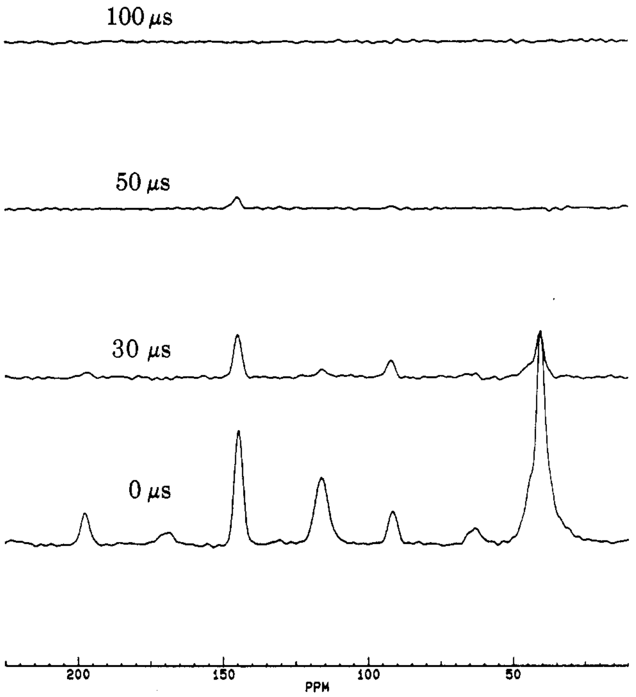

Figure 2. Effect of varying dipolar dephasing time on the ^{13}C spectrum of pure ^1H PVE. The overlapping peaks at 40 ppm correspond to the two saturated carbons of PVE while the peaks at 117 and 145 ppm correspond to the two unsaturated carbons; remaining peaks are spinning sidebands displaced in multiples of 4000 Hz from the unsaturated resonances. Note that essentially complete broadening of all peaks occurs after 50 μs of dipolar dephasing, attesting to the strong heteronuclear dipolar interaction at these carbons, which all have directly bonded protons.

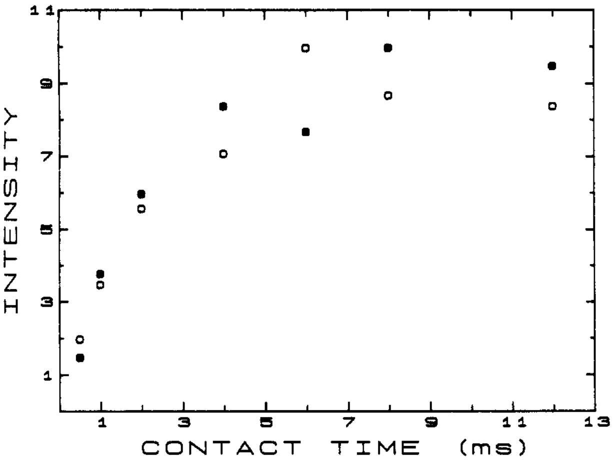

Figure 3. Intensity of the ^{13}C resonance (chemical shift = 40 ppm) as a function of contact time using a fixed dipolar dephasing time of 50 μs for B1 (○) and B2 (●). Since a 50-μs dipolar dephasing time was shown to result in complete broadening of the carbons with directly bonded protons, the intensities in this plot are attributed primarily to deuterated carbons. Note that the maximum in the deuterated ^{13}C intensity occurs after approximately 8 ms of contact time. The origin of the apparent oscillatory nature of these plots is unclear; similar behavior has been observed by other workers.[40]

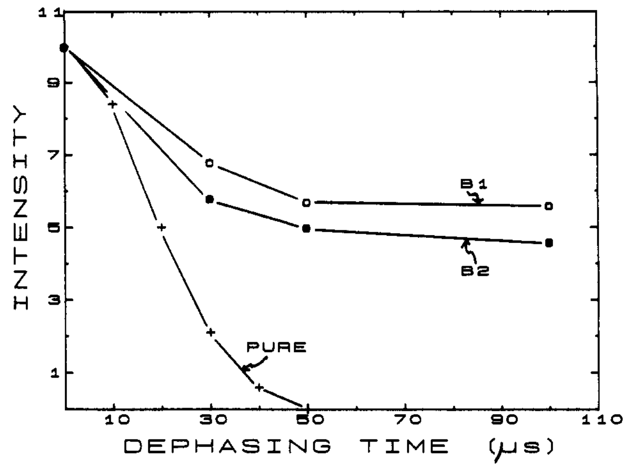

Figure 4. Intensity of the ^{13}C resonance (chemical shift = 40 ppm) as a function of dipolar dephasing time using a fixed contact time of 8 ms for B1, B2, and pure ^1H PVE. The carbons of the pure ^1H PVE are completely dephased after 50 μs of dipolar dephasing because of the strong heteronuclear dipolar interaction of each carbon in this sample. Both blends exhibit a rapid initial loss in carbon intensity as a result of the dephasing of the hydrogenous component, followed by a modest rate of magnetization loss between 50 and 100 μs of dipolar dephasing. This result affirms the sequential mixing, and hence thermodynamic miscibility, of both blends. The intimate contact between the two components allows cross polarization of the deuterated carbons, while the increased distance of deuterated carbons from hydrogen results in a longer dipolar dephasing time constant.

hydrogenous component. In a miscible blend, dilution with a deuterated component will result in a reduction of the heteronuclear dipolar interaction at carbons from the hydrogenous component, although this effect can reasonably be expected to be small compared to the interaction resulting from bonded hydrogens. Figure 3 shows a plot of normalized ^{13}C intensity (chemical shift = 40 ppm) for blends B1 and B2 as the cross-polarization contact time is varied up through 12 ms with a constant 50-μs dipolar dephase time. It is observed that a maximum intensity from the deuterated carbons in B1 and B2 occurs at approximately 6–8 ms of contact time. This result is in accord with the expectation that the deuterated carbons, by virtue of their greater distance from protons, will exhibit a substantially longer cross-relaxation time constant.[26,27] For a phase-separated blend, cross polarization of deuterated carbons could only substantially occur at the phase boundary. Since cross polarization is effective over distances less than approximately 1.0 nm,[28,29] the observance of a significant signal intensity from deuterated carbons is limited to blends which are miscible.

The foregoing results can be used to construct an experiment that allows direct observation of cross polarization and dipolar dephasing sensitivity of the deuterated carbons in the blends. The data for B1 indicate that a contact time of 8 ms will effect the maximum intensity from the deuterated carbons of a miscible blend. In Figure 4 the measured normalized carbon intensity is displayed as a function of dipolar dephasing time for the neat hydrogenous PVE and for both blends. There occurs a rapid, almost identical, loss in carbon intensity in both blends over the first 50 μs of dipolar dephasing time. This can be attributed to dephasing of the carbons directly bonded to protons. When all carbons are bound to protons (the situation seen Figure 2), a complete dephasing of the carbon resonances is effected by a 50-μs dipolar dephasing period. In Figure 4, however, it is seen that about half of the magnetization remains, even when the dipolar dephasing time is extended to 100 μs. This magnetization arises primarily from the deuterated carbons.

The data in Figure 4 directly demonstrate that substantial cross polarization of the deuterated carbons in both B1 and B2 has occurred. Such cross polarization indicates that the deuterated chains must be spatially close to protons, consistent with the miscibility in both blends. This conclusion is also consistent with the longer proton $T_{1\rho}$ behavior reflected in the data of Figure 1.

Conclusions

The results of solid-state ^{13}C cross-polarization and dipolar dephasing NMR experiments demonstrate the intimate contact existing between the components in both of the two blends. The SANS result[15,16] suggesting that the morphology of isotope mixtures remains homogeneous for values of the interaction parameter beyond the Flory–Huggins critical value is thus corroborated. Consistent with theoretical developments,[18–24] the thermodynamics of polymer mixtures diverge from predictions based on the assumption of random mixing. Polymer isotopic mixtures are neither ideal nor simple mixtures. The latter fact is not made apparent from measurements executed well away from critical conditions, the situation prevailing in much of the published literature on polymer isotope blends. A result of this extended miscibility is that deductions of mixing free energies based on the degree of polymerization required to effect phase separation[16,38,39] (an approach only feasible when $\chi > 0$) will tend to underestimate the magnitude of the excess free energy.

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