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Nuclear Magnetic Resonance Study of Polyisoprene/ Poly(vinylethylene) Miscible Blends

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ABSTRACT: In accord with their thermodynamic miscibility, blends of 1,4-polyisoprene and poly(vinylethylene) exhibit a single glass transition. In compositions with a relative abundance of poly(vinylethylene) that is very high in 1,2-microstructure, the glass transition, as observed in calorimetry, thermal expansivity measurements, and dynamic mechanical spectra, is extremely broad. ^{1}H NMR results are presented, which corroborate the intimate nature of the mixing in this system, notwithstanding the breadth of the glass transition. Solid-state ^{13}C NMR measurements indicate that molecular motions of the components have different temperature dependencies. Despite the morphological homogeneity and thus equivalence in free volumes, carbons on the respective components exhibit distinct "glass transitions". It is this phenomenon that underlies the broad glass transitions observed by conventional methods. Such breadth, or in principle even distinct glass transition temperatures, is not inconsistent with thermodynamic miscibility.

Introduction

Characterization of glass transition behavior is the usual means to assess the extent of morphological homogeneity in polymer mixtures. The popularity of this approach is due primarily to its convenience. The basis for utilizing T_g is the expectation that since only in a segmentally mixed blend will the various chain units experience equivalent free volumes, a single T_g, intermediate between the glass transition temperatures of the pure components, can be taken to evidence thermodynamic miscibility. The smallest structural heterogeneity resolvable through glass transition measurements are on the order of 10 nm;[1-3] consequently, the observation of a single glass transition is consistent with, but not an unambiguous confirmation of, an absence of phase heterogeneity.

Blends of polyisoprene (PIP) with poly(vinylethylene) (PVE) exhibit one glass transition.[4-7] The thermodynamic miscibility of the mixtures has been confirmed by diffusion and small-angle neutron-scattering experiments.[6,8-10] There is no specific (chemical) interaction in the blends; miscibility is a consequence of the similarities in the polarizability and liquid structure of PIP and PVE.[9-11] A single T_g is expected for these mixtures given their miscibility; what is unexpected is the broad nature of the transition under particular circumstances. Glass transitions in polymer blends are typically no more than several degrees in breadth. However, in calorimetry measurements, blends of PIP with a high concentration of PVE (the latter high (>90%) in 1,2-microstructure) convert from the glassy to a rubbery state over roughly 30 K.[9,10,12,13] Similarly, the change in dynamic mechanical behavior associated with the glass transition extends over very many decades of frequency.[12,13] The observation of such breadth is suggestive of phase heterogeneity, notwithstanding the experimental evidence to the contrary.[6,8-10] An intent of the present study is to provide corroboration of miscibility in PIP/PVE mixtures. Should the existence of morphological homogeneity be confirmed, it is of interest to explore the origin of the anomalous transition breadths. This report describes ^{1}H and ^{13}C NMR experiments directed toward these objectives.

Experimental Section

The polymer blends were prepared by dissolution of the components in carbon disulfide, followed by vacuum drying. For ^{1}H NMR studies the samples were placed into short lengths of 5-mm-o.d. glass tubing. For ^{13}C NMR, the dried films were packed into the magic angle spinning (MAS) rotors with a weighted plunger at 45 °C in vacuo. The plunger was maintained in contact with the material for several days to provide the uniform mass distribution necessary for subsequent spinning of the rotors at 3000 Hz.

Four samples were studied by NMR: a pure PIP sample (96% *cis*-polyisoprene), a pure PVE sample containing 3% 1,4-butadiene monomeric units, and two PVE/PIP blends. (The chemical structures of the three-component polymers are shown in Figure 1.) The blend referred to as B1 (which exhibits a broad glass transition[9,10,12,13]) was 32% PIP and 68% PVE, the latter containing 3% 1,4-butadiene monomeric units. The blend labeled B2, exhibiting a normal glass transition breadth,[6,8] was 32% PIP mixed with 68% PVE containing 15% 1,4-butadiene monomeric units.

All NMR spectra were run on a Bruker MSL 300 spectrometer (reference to a particular product is made for identification purposes only and is not meant to imply that other products would not serve equally well in this application) in a static magnetic field of 7.0 T. The corresponding proton and carbon-13 Larmor frequencies were 300.1 and 75.5 MHz, respectively. Proton spectra were obtained by using a static, high-power solid-state probe equipped with a 5-mm transverse solenoid, with a 90° pulse length of 3.5 μs (71-kHz B_1 field) and a relaxation delay of 2 s.

^{13}C experiments were carried out with a double-tuned magic angle spinning probe equipped for 7-mm-o.d. sample rotors. Cross-polarization spectra[14] were acquired by using the Hartmann–Hahn cross-polarization technique.[15,16] Other spectra were obtained with a single carbon 90° pulse of 5 μs. All ^{13}C spectra were obtained with magic angle spinning[17,18] and high-power proton decoupling[19] throughout acquisition of the free induction decay. A B_1 ($=B_2$) field of 50 kHz was utilized for cross polarization and decoupling. The cross-polarization contact time was 1 ms. The MAS rotor frequency was maintained at 3 kHz ± 5 Hz throughout each experiment. The relaxation delay was 2 s.

Results and Discussion

^{1}H NMR. A variety of NMR techniques exist for investigating domain sizes and miscibility in polymer systems. These techniques generally rely on observation of some spin interaction between spins on different molecules or in different domains and in some cases measurement of the rate of interaction. In order to observe

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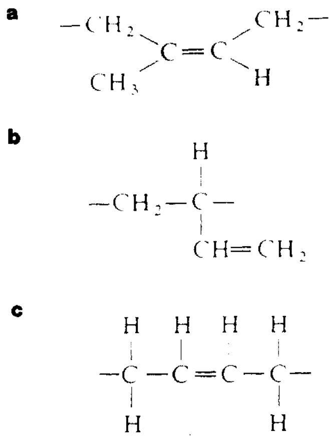

Figure 1. Chemical structure of the polymers: (a) polyisoprene; (b) poly(vinylethylene); (c) 1,4-polybutadiene.

and measure the rates of these interactions, spins in different environments must be differentiated by the NMR experiment; isotopic substitution,[20,21] chemical shift,[21-23] or differences in relaxation rates[24,25] or line widths may allow spins in different environments to be distinguished. For spin -$^1/_2$ nuclei in solids, the dipole–dipole interaction provides a coupling between different domains or molecules that gives rise to spin diffusion or polarization transfer.

Below the glass transition the ^{1}H NMR spectrum of polymers generally consists of a broad, featureless line due to static magnetic dipolar interactions between the protons. Near the glass transition, the line starts to narrow as molecular motions modulate the dipolar interactions. The line continues to narrow until the frequency of the molecular motions exceeds the static dipolar line width. Thus the NMR line width is sensitive to the glass transition temperature. PVE and PIP have very different T_g's, approximately 270 and 200 K, respectively, as measured by calorimetric techniques.[6-8] The T_g's are approximately 25 K higher as observed by NMR due to its sensitivity to higher frequency motions. The differences in the polymers' local mobility over a certain temperature range are expected to give rise to very different ^{1}H NMR line widths, thus providing a mechanism to distinguish between the polymers. This expectation is borne out by the data presented in Figure 2. The room-temperature proton line width of the PVE sample is 20 kHz (Figure 2a) and that of the PIP sample is about 600 Hz (Figure 2b). The latter resonance shows some structure due to the isotropic chemical shifts. This structure is lost in the PVE spectrum because strong dipolar interactions broaden the line.

If PIP and PVE are immiscible, the ^{1}H NMR spectrum would consist of the superposition of the resonances of the pure polymers. Interaction between the PIP and PVE spin systems across the phase boundary via spin diffusion processes[26] will cause the protons in the interfacial region to have a common T_2. As the domain sizes of the two phases decrease, the amount of interfacial region increases. When the domain sizes are less than 0.5–1 nm, all protons in the sample will have a common T_2, and the wide-line spectrum will exhibit a single resonance of line width intermediate to the line widths of the pure components. A long-chain molecule pervades a distance much beyond this 1 nm (for example, the PVE used herein, with M_w = 414 000, has a radius of gyration of over 20 nm under Θ conditions[27]). Figure 2c is the room-temperature ^{1}H NMR spectrum of the PVE/PIP blend B1. A single resonance is observed with a line width of 2 kHz, intermediate to that of the pure components. This confirms that PIP and PVE are segmentally mixed.

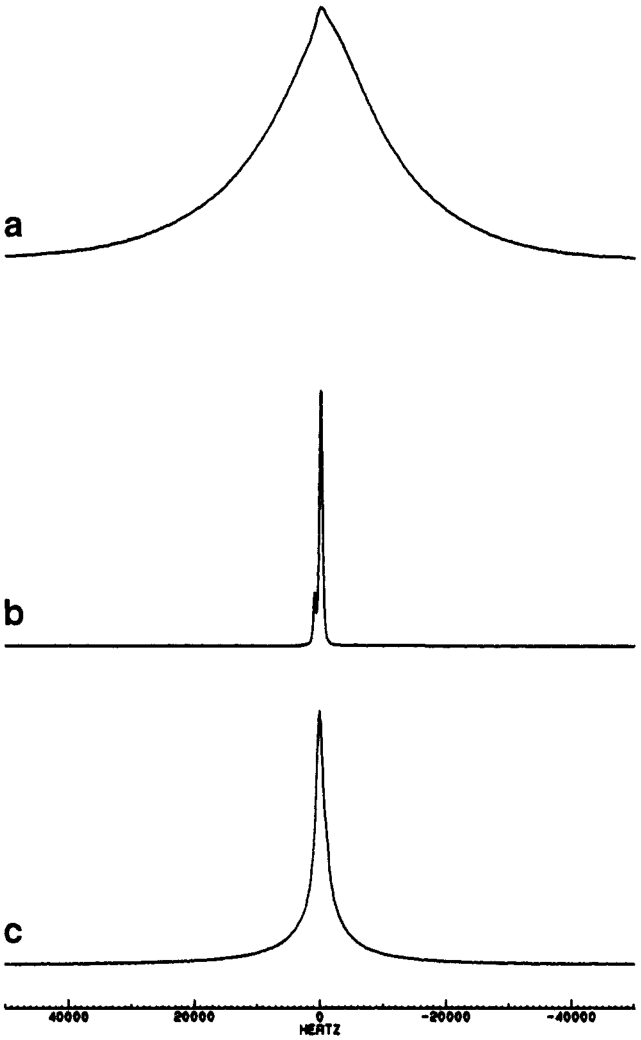

Figure 2. ^{1}H NMR spectra obtained at 296 K: (a) pure PVE; (b) pure PIP; (c) blend B1.

The ^{1}H NMR results do not give any indication of a broad glass transition range for sample B1. The transition from broad to narrow line occurs over approximately the same temperature range for the pure polymers and both the blends. There is no clear evidence of a two-component line for the blend B1 at any temperature, although at intermediate temperatures the free induction decays (FID) cannot be fit to either a single-exponential or Gaussian function. This simply reflects the transition from hindered (Gaussian line shape) to liquidlike (exponential line shape) motions.

^{13}C Magic Angle Spinning. ^{13}C MAS NMR studies allow the components of polymer blends to be differentiated by their isotropic chemical shifts. Specifically, each polymer has two peaks in the vinyl region of the ^{13}C spectrum, which can be easily resolved in the spectrum of the polymer blend B1 as shown in Figure 3. ^{13}C chemical shift anisotropy (CSA) is sensitive to local motions of the polymers, as are ^{1}H–^{13}C dipolar couplings, the latter manifested in the intensities of cross-polarization spectra and the ability to decouple the protons from the carbons. ^{13}C spectra may therefore provide information on local motions and any changes thereof associated with blending.

^{13}C MAS NMR spectra of PVE, PIP, and the polymer blends exhibit temperature-dependent line widths, as shown in Figure 4. Quantitative measurements of line width have been made (by fitting the lines to Lorentzian functions) only on the carbon resonances in the vinyl region (90–140 ppm in Figure 3) of the spectrum. Overlap of

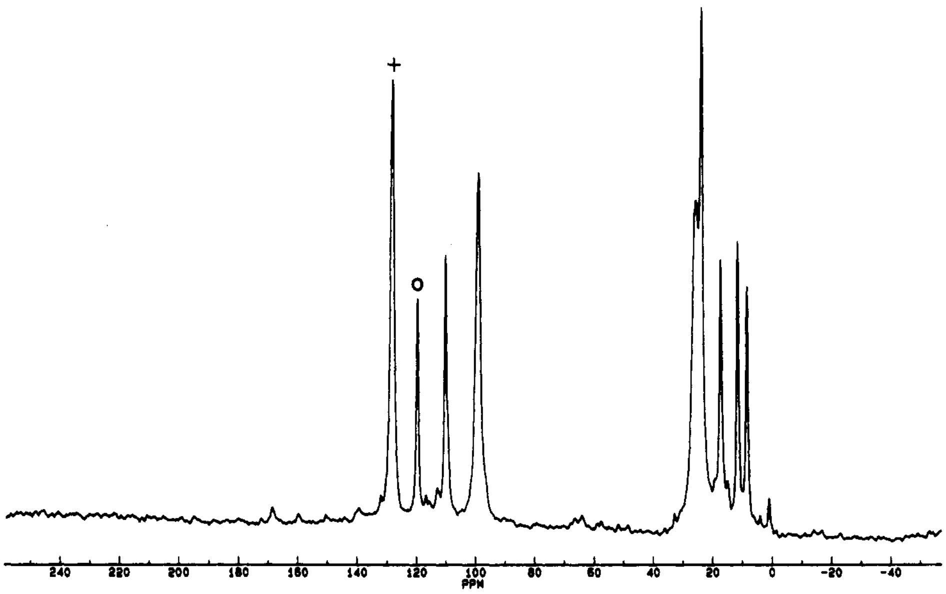

Figure 3. ^{13}C one-pulse MAS spectrum of blend B1 obtained at 340 K. The peaks at approximately 100 and 130 ppm are due to the pendant vinyl carbons of PVE, and the peaks at 110 and 120 ppm are due to the backbone vinyl carbons of PIP. Weak peaks between 110 and 120 ppm are due to the 3% abundant 1,4-butadiene monomeric units in the PVE. The + and o denote the PVE and PIP peaks, respectively, from which the line-width data used in Figure 5 were obtained. The weak spinning sidebands discussed in the text can be seen in the region of 135–175 ppm.

resonances in the aliphatic region does not allow adequate measurement of individual line widths. For the molecular motions governing the vinyl carbons, transition temperatures are obtained from semilogarithmic plots of line width versus inverse temperature by calculating the centers of mass of the plots (the temperature about which the first moment of the curve is zero). For the pure polymers, the vinyl carbon transition temperatures occur near the glass transitions observed by ^1H NMR; however, chemically distinct carbons on the same chain appear to pass through their line-width maxima at slightly different temperatures. For example, the transition temperatures of the two PIP vinyl peaks differ by approximately 4 K while the difference for the two PVE peaks is less than 2 K. Similar results are obtained for the blends.

Dynamical Heterogeneity. Although the ^1H NMR indicates that there is a single transition temperature for the polymer blends, different transition temperatures are observed in the ^{13}C NMR. Figure 5 is a plot of line width as a function of inverse temperature for the PVE and PIP vinyl carbons marked with a + and o, respectively, in Figure 3. Figure 5a is the plot for the pure polymers and Figure 5b is that for blend B1. These plots show that the transition temperatures for both polymers have been shifted closer together upon blending; however, they do not occur at the same temperature. It is generally inferred from the phase homogeneity associated with thermodynamic miscibility that mixtures possessed of the latter will exhibit a single glass transition temperature. The only strict requirement of miscibility, however, is that the components experience the same average free volume. Such free-volume equivalency does not imply equivalent glass transition temperatures. As noted in regard to Figure 3, different carbons on the same molecule can undergo the transition to liquidlike mobility at different temperatures. Relevant in this regard is the well-established variation in the fractional free volume among polymers at their respective glass transition temperatures.[28] Differing free-volume requirements for liquidlike mobility can evidently result in different "glass transitions" within a single-phase mixture. Miscible blends can thus exhibit dynamical heterogeneity, notwithstanding their morphological homogeneity.

Blend B2 does not exhibit a broad glass transition in calorimetry measurements.[6,8] Figure 5c is a plot of vinyl carbon line width as a function of inverse temperature for sample B2. The line widths are from the same vinyl carbons as used for the plots in parts a and b of Figure 5. The shifts of the transition temperatures relative to the T_g for the pure components are somewhat greater for B2 than for B1; the difference in transition temperatures between the components of B2 is about 16 K. The pure polymers differ in their vinyl carbon transition temperatures by 57 K, while this difference is approximately 22 K in blend B1. It may also be noted from the plots in Figure 5 that the breadth of the transition region (defined, somewhat arbitrarily, as the region over which the line width changes by more than 50% with a 10 K change in temperature) for the PVE vinyl peak in blend B1 is about 25% greater than that in blend B2. These observations are qualitatively consistent with the notion that the breadths of these glass transitions as measured by calorimetry are related to the spread in transition temperatures as observed by ^{13}C NMR.

The dynamical heterogeneity reflected in Figure 4b is most prominent in blends containing a high proportion of poly(vinylethylene) that is very high (>90%) in 1,2-microstructure.[9,10,12,13] The reason this aspect of the blends' behavior should be accentuated in particular compositions is presently unknown.

Line-Broadening Mechanisms and Cross-Polarization NMR. There are two possible origins for the temperature dependence of the line widths observed in the MAS (with proton decoupling) spectra. Molecular motions that modulate the CSA can interfere with the MAS modulation of CSA.[29] Also molecular motions that modulate the ^1H–^{13}C dipolar interaction can interfere with the proton decoupling modulation of the dipolar interaction.[30] Molecular motions that interfere with MAS must have spectral components at the MAS spinning rate (i.e., in the kilohertz range), whereas interference with proton decoupling requires spectral components in the tens of kilohertz range. A determination of the origin of the line broadening would reveal the rates of the molecular motions prevalent at the temperature of maximum line broadening. Previous observations of this temperature-dependent line-

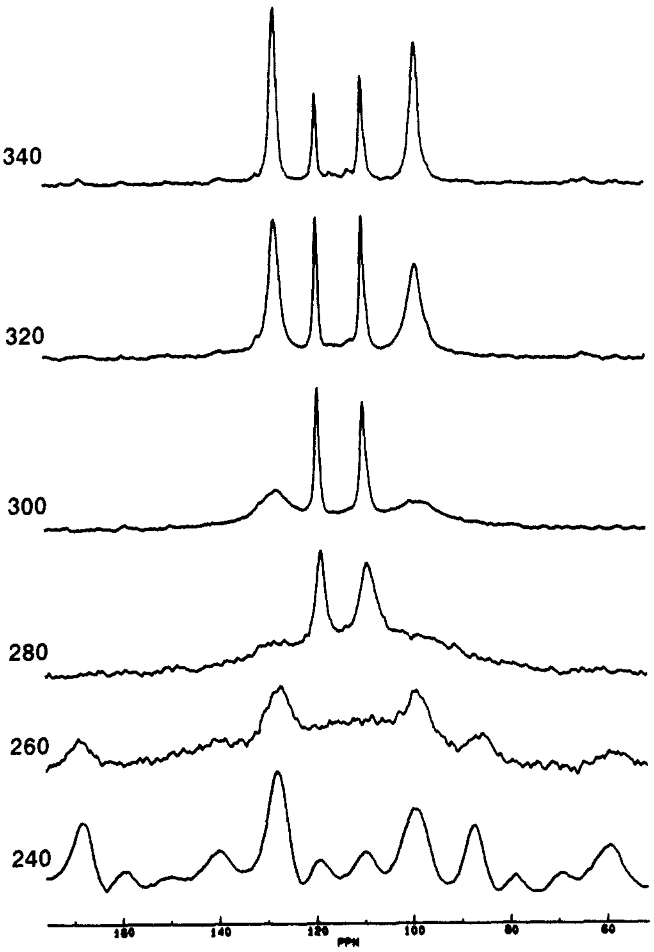

Figure 4. Vinyl region of the ^{13}C spectrum of blend B1 obtained at 20 K temperature intervals from 240 to 340 K. All spectra were measured with one-pulse excitation, proton decoupling, and MAS except at 240 K, for which cross polarization was used to enhance the sensitivity. At low temperatures strong spinning sidebands are observed for all resonances. As the temperature is increased, the resonances broaden and then narrow again. The PIP resonances broaden at lower temperatures than do those of the PVE. Note that resonances of carbons on the same molecule appear to narrow at different rates on the high-temperature side of the line broadening (280 and 320 K).

broadening effect in polymers have attributed it to interference with proton decoupling.[31]

The spectra in Figure 4 give some hint as to the mechanism of the temperature-dependent line widths. Below the transition temperature many spinning sidebands associated with the vinyl resonances are observed. Above the transition temperature the spinning sidebands are not observed, indicating the onset of molecular motions that modulate the chemical shift anisotropy. Interference with MAS must therefore contribute at least in part to the line broadening.

Cross polarization refers to the process whereby magnetization is transferred between two dipolar coupled spin systems.[15,16] The cross-polarization spectra (not shown) of both PIP and PVE show that dipolar couplings among carbons and protons are still present above the transition temperatures. The peak intensities in the cross-polarization spectra are weak above the glass transition. One-pulse spectra obtained at temperatures above the transition show no additional broadening or decreased signal intensity with increasing temperature, which would be evidence of interference with proton decoupling. The weak cross-polarization signals are likely due to decreased dipolar coupling strength. The observed line broadening may therefore be an effect of interference with both MAS and proton decoupling. This is not unreasonable given that the motions required are separated by only a decade in frequency, the transition range observed in the ^{13}C NMR (20–40 K) is very broad, and the motional correlation times of polymers are in general very broad.[32]

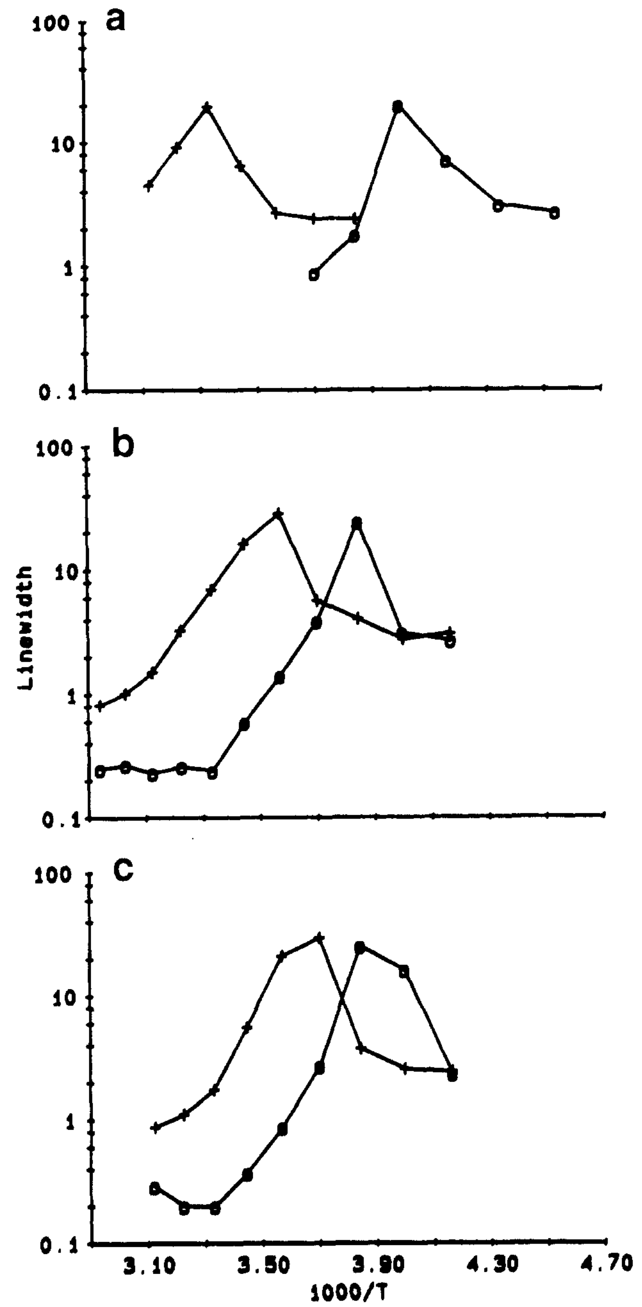

Figure 5. Semilogarithmic plots of line width as a function of inverse temperature for the PVE (+) and PIP (O) peaks denoted in Figure 3: (a) pure PVE and PIP; (b) blend B1; (c) blend B2. The lines connecting data points are only a visual aid and do not represent any fit to the data. The maximum line widths (determined by using the first moments of the curves) for PVE and PIP occur, respectively, at: (a) 302 and 250 K; (b) 288 and 266 K; (c) 277 and 261 K. Note that the breadth of the transition region is greater for PVE in blend B1 than in either the pure material or blend B2, qualitatively consistent with calorimetric determinations.

The behaviors of the pure polymers and the blends have several characteristics in common. The most notable is that below the transition temperature spinning sidebands associated with the vinyl carbons are in evidence. Above the transition temperature only extremely weak spinning sidebands 3 kHz downfield from the vinyl centerbands are observed (Figure 3). The sidebands are most likely due to incomplete averaging of the chemical shift anisotropy caused by anisotropic motion of the polymers; however, the absence of the expected upfield sidebands[33] cannot presently be explained. The anisotropy is a consequence of the retarded chain mobility over the time scale of the NMR experiment (tens of microseconds). Magnetic field inhomogeneity and bulk magnetic susceptibility can also cause spinning sidebands; however, these effects are expected to be too small to account for the observed sideband intensity.

As with the pure polymers, signal intensity of cross-polarization spectra of the blends above the transition temperature is very weak. Signals due to PIP disappear completely 20–30 K above its transition temperature, while weak signals due to PVE persist to the highest temperatures measured (340 K), decreasing in intensity with increasing temperature. In addition, anomalous peak intensities, which change with temperature, are observed for PVE; the downfield vinyl peak is approximately half the intensity of the upfield vinyl peak at 340 K. As with the pure components, one-pulse spectra with decoupling show no increase in line width in this temperature range.

The observation of cross-polarization spectra above the transition temperatures indicates that molecular motions have not averaged the dipolar interaction to zero. If the weak spinning sidebands present above the transition temperatures do arise from anisotropic molecular motions, which do not average the chemical shift interaction to its isotropic value, then nonzero dipolar couplings are not unexpected. In the case of PIP the disappearance of signals from cross-polarization spectra even when molecular motions are anisotropic may be due to slow cross polarization through the small dipolar couplings. In fact, if the dipolar couplings are sufficiently small, MAS may average them to zero. The one-pulse spectrum (at 340 K) of blend B1 without decoupling shows no increase in line broadening over the decoupled spectrum, other than the presence of J coupling,[26] providing evidence of the weakness of the dipolar couplings. In principle, a short proton $T_{1\rho}$ can also account for the low intensity of the cross-polarization spectra above the transition temperatures. Such short $T_{1\rho}$'s require molecular motions, which would also lead to interference with proton decoupling. This in turn would lead to broad lines; experimentally we observe narrow lines; therefore, a short $T_{1\rho}$ is inconsistent with the data.

The anomalous intensities of the PVE vinyl peaks observed in the high-temperature cross-polarization spectra may also be explained by small dipolar couplings. The cross-polarization rate is dependent upon the strength of the C–H dipolar couplings. If the molecular motions do not average the couplings from directly bonded protons to zero, in the absence of proton spin diffusion the cross-polarization rate will depend on the number of attached protons.[34] We would therefore expect the intensity of the upfield peak, with two attached protons, to be greater than the intensity of the downfield peak, with one attached proton, for short cross-polarization times. The difference in intensity of the two peaks increases with increasing temperature (decreasing dipolar coupling), supporting this postulate.

Summary

^{13}C NMR demonstrates that the molecular motions of the two components in the blends have different temperature dependencies; therefore, the single line width observed in the ^{1}H NMR spectra must be the result of spin diffusion between nearby polymer chains. At higher temperatures where the dipolar couplings are weak, MAS quenches spin diffusion in the ^{13}C spectra, producing the results discussed above. The shifts in transition temperature observed in both the ^{1}H and ^{13}C NMR attest to the miscibility of these polymer blends. The differences in transition temperature observed in the ^{13}C NMR for different components of the blends are in agreement with no chemical interaction between PIP and PVE and provide an explanation for the varying breadths of the glass transitions measured by calorimetry. It is thus demonstrated that very broad glass transitions, or in principle even distinct glass transition temperatures, are not inconsistent with thermodynamic miscibility.

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