Probing Miscibility and Intermolecular Interactions in Solid Polymer Blends Using the Nuclear Overhauser Effect

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ABSTRACT: We discuss a new strategy for probing polymer–polymer miscibility and detecting specific intermolecular interactions in polymer blends by exploiting nuclear Overhauser effects (NOE) in ^{13}C magic-angle spinning (MAS) NMR spectra of solid blends. In the comparison of deuterated polystyrene (PS)/poly(vinyl methyl ether) (PVME) blends cast from toluene versus chloroform, steady-state equilibrium NOE enhancements of the PS signals were observed for the toluene-cast films but not for the chloroform-cast films. Since cross-relaxation of the PS carbons may occur only through dipolar interactions with PVME protons (which have an inverse sixth power dependence on the internuclear distances), this demonstrates molecular level miscibility for the blends cast from toluene only. Below T_g, methyl group rotation about the C_3 axis is the only motion fast enough to stimulate dipolar cross-relaxation in the blend. Additional information concerning the molecular structure of the blend was obtained from the NOE growth rates for each type of carbon nucleus in the blend. The cross-relaxation rate constants for the PS aromatic ring carbons were several times greater than that of the PS main-chain carbons. This implies that the phenyl ring is much closer to the methyl group of PVME than to the main-chain carbons of PS. These results suggest that there exists a specific intermolecular interaction between the PS phenyl ring and the PVME methyl group in the solid state. Such an interaction has previously been suggested for polymer blend solutions.

Introduction

Polymer blends, mixtures, and composites are commercially important materials, and the increased interest in these materials is reflected by the variety of methods that have been developed to study polymer–polymer interfaces, to probe polymer miscibility, and to detect specific intermolecular interactions. Magnetic resonance methods have played an important role in evaluating the length scale of polymer mixing and for characterizing the intramolecular interactions. The ^{1}H spin diffusion measured via the T_1 and $T_{1\rho}$ relaxation times are frequently used to establish the length scale over which the blend is homogeneously mixed.[2,3] A single averaged value for the ^{1}H $T_{1\rho}$ is observed if the two constituents in a polymer blend are mixed on a length scale less than 20 Å, while a single T_1 is indicative of mixing on a length scale of ca. 200 Å. The mixing can be detected either indirectly using cross-polarization[4] or directly via one- and two-dimensional NMR.[5,6] Direct observation of ^{1}H–^{1}H spin diffusion using one- and two-dimensional exchange spectroscopy has also been used to establish mixing and domain sizes.[5,6] ^{13}C–^{13}C spin diffusion experiments in selectively labeled blends may be used to probe much smaller domain sizes, as these homonuclear dipole–dipole interactions are weaker than those for protons.[7,8] A particularly straightforward approach for establishing molecular level mixing in blends involves cross-polarization from the protons of one of the polymer constituents in the blend to the carbons of the other constituent, as in mixtures of protonated and deuterated polymers. Intermolecular cross-polarization is only observed for mixing on a length scale of less than 20 Å and has been reported for polystyrene/poly(vinyl methyl ether) (PS/PVME) and poly(methyl methacrylate)/poly(vinyl chloride) blends.[9,10]

Although the characteristics of the blend in the solid state are most desirable, few methods are available to measure internuclear distances in the solid state.[11,12] In strongly interacting polymer blends, such as hydrogen bonding or electron donor/acceptor complexes, the geometry of the blend can sometimes be inferred from the chemical shift changes.[13] However, for most blends, the chemical shift changes are too small to be observed by solid-state NMR. Two-dimensional nuclear Overhauser effect spectroscopy (NOESY) has been used to study the weak intermolecular interactions in mixtures that form miscible blends. In such high-resolution studies, the interacting groups can be identified and the forces that lead to molecular level miscibility can be determined.[14,15] While the nuclear Overhauser effect is routinely used in solution for structural and conformational analysis, it is rarely considered for true solid materials. Recently, however, there has been an increased interest in solid-state nuclear Overhauser enhancements (NOE). In general, most of these reports have focused on the deleterious effects of transient NOE's on the accurate determination of spin–lattice relaxation times. Findlay and Harris showed that transient NOE effects in polyester films necessitate the use of long recycle delays in gated decoupler experiments if accurate spectral intensities are desired.[16] Root and co-workers observed similar complications in saturation–recovery experiments on block copolymers with a mobile soft segment.[17] McDowell and co-workers established that mobile methyl groups control the relaxation and transient NOE's in crystalline alanine and that relaxation is anisotropic in accordance with the anisotropic motion of the rapidly rotating methyl group.[18,19] White and Haw measured steady-state NOE's and growth rates for several crystalline organic solids and suggested that for Bisphenol A, the NOE growth rates were a function of the distance from the rapidly rotating methyl group.[20] Douglass and McBrierty, in an earlier wideline study, included transient ^{1}H–^{19}F NOE measurements in their evaluation of polymer miscibility in poly(vinylidine fluoride)/poly(methyl methacrylate) blends.[21]

In this study, we report the use of steady-state and truncated driven ^{13}C magic-angle spinning (MAS) NOE experiments for probing polymer–polymer miscibility and intermolecular interactions in solid polymer blends at temperatures well below T_g. This work was motivated by our continuing effort to characterize solid polymer blends and the desire to extend NOE measurements to true solid polymer blends in a high-resolution magic-angle spinning

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mode for the first time. For our initial investigation, we have chosen the well-characterized PS/PVME blend which is compatible over the entire composition range. Experimental methods as well as the model used to interpret the results will be discussed in detail.

Experimental Section

Miscible blends of polystyrene (PS) and poly(vinyl methyl ether) (PVME) were prepared as films cast from 10 wt % toluene solutions in a nitrogen atmosphere for at least 24 h. The films were then either examined via NMR or further dried in a vacuum oven at 60 °C for 24 h (vide infra). Immiscible blends were prepared via solution casting from chloroform. Blends were prepared using both protonated (M_w = 95 800 and deuterated (d_8) polystyrene (M_w = 71 700). The molar ratio of the monomeric repeat units in the blend was 1:1 or 1:3 PS/PVME. Differential scanning calorimetry revealed a single T_g at ca. 50 °C for the 1:1 toluene blend dried in the oven at 60 °C. This agrees with previously reported results for blends of this composition.[22]

NMR measurements were carried out on a Varian Unity spectrometer at a carbon resonance frequency of 100 MHz. All spectra were obtained using 7-mm rotors and a Doty double-resonance probe with spinning speeds of ca. 6 kHz. NOE spectra were obtained by applying a variable length train of proton $\pi/2$ pulses separated by a 5-ms interpulse spacing. Immediately following the proton saturation time, a composite $\pi/2$ ^{13}C pulse was applied for carbon detection. The four-pulse composite $\pi/2$ pulse, of the type proposed by Bax and recently discussed by White and co-workers,[23,24] was used to suppress a carbon background signal from the spinning system. The $\pi/2$ pulse widths for carbons and protons were 4.9 μs, and the carbon T_1 measurements were made using the method of Torchia.[25]

Results

The miscibility of PS/PVME blends is critically dependent upon the casting solvent. Several years ago, Kwei and co-workers used the ^{1}H T_1 and $T_{1\rho}$ relaxation times to demonstrate that blends cast from toluene are homogeneously mixed while phase separation occurs for chloroform-cast blends.[26] More recent two-dimensional ^{1}H NMR experiments support these results in that intermolecular spin-diffusion cross-peaks are observed only in toluene-cast blends.[6] The measurement of polymer miscibility by ^{1}H spin diffusion relies on magnetization transfer mediated by static local dipolar interactions. However, polarization transfer may also occur via cross-relaxation stimulated by fluctuating local dipolar fields. This leads to nuclear Overhauser enhancements in one spin following perturbation of the spin transitions of the coupled spin system.

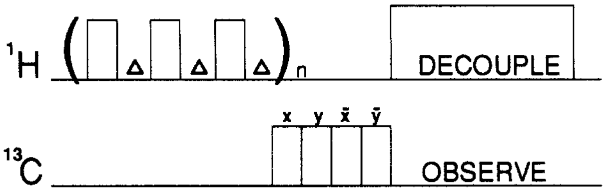

Figure 1. Pulse sequence for solid-state NOE measurement. $\pi/2$ pulses were used for both carbons and protons and the interpulse spacing (Δ) for the proton saturation pulse train is 5 ms. The composite $\pi/2$ pulse on the carbon side is used to suppress the background signal originating from the spinning system.[24]

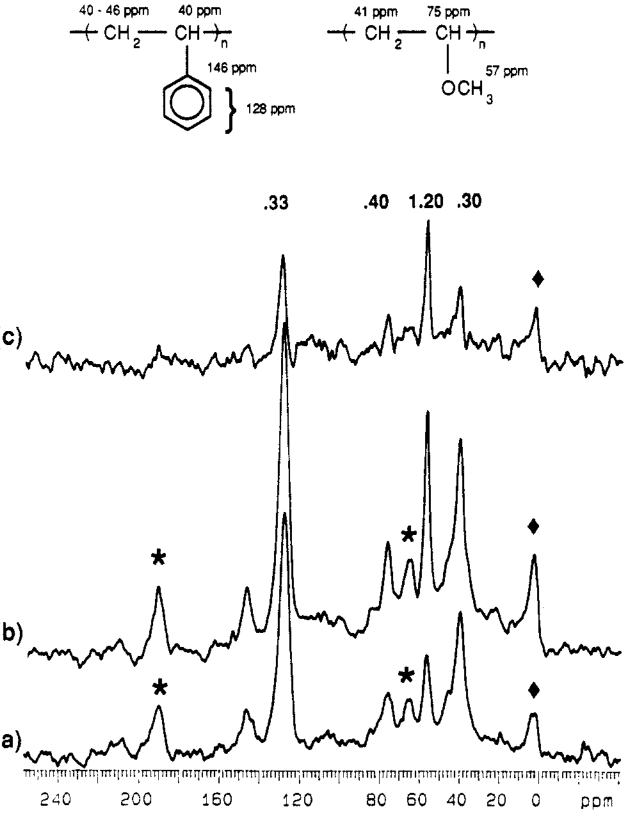

Figure 2. ^{13}C MAS spectra of a 1:1 molar PS-d_8/PVME blend cast from toluene obtained (a) without NOE and (b) with steady-state NOE. (c) is the difference spectrum. The steady-state NOE enhancements are listed above each peak, and the peak assignments are given by the appropriate carbon in the repeat unit structures shown. The symbol * denotes spinning sidebands, and ◆ denotes a spurious background signal from the probe which was not suppressed by the composite carbon pulse.

The theory of nuclear Overhauser effects has been reviewed in detail by Noggle and Neuhaus and will not be reviewed here.[27,28] Suffice it to say that for proton saturation and carbon observation, steady-state ^{13}C NOE's (η) range from 1.988 for fluctuating dipolar fields in the extreme narrowing motional regime ($\tau_c < 10^{-10}$ s) to 0.153 for motions characterized by infinitely long correlation times. Here, η is defined by

$$\eta = \frac{I(t) - I(0)}{I(0)} \tag{1}$$

where $I(t)$ is the ^{13}C signal following proton irradiation and $I(0)$ is the signal intensity at equilibrium, prior to proton irradiation. The steady-state enhancement is an equilibrium measure and provides no structural information. The distance-dependent cross-relaxation rate σ is a function of the difference between double and zero quantum transition probabilities ($W_2 - W_0$). Double, single, and zero quantum transition probabilities are proportional to the spectral densities $J(\omega_H + \omega_C)$, $J(\omega_C)$, and $J(\omega_H - \omega_C)$, respectively, where ω_H and ω_C are the proton and carbon Larmor frequencies. Using these definitions, the NOE enhancement may be expressed as

$$\eta = \frac{W_2 - W_0}{W_2 + W_1 + W_0} = \frac{\sigma}{\rho} \tag{2}$$

where σ is the cross-relaxation rate constant and ρ is the total spin–lattice relaxation rate constant. NOE's are maximized when the effective dipolar fields responsible for relaxation have correlation times $\tau_c < 10^{-10}$ s.

In theory, the relaxation rates and NOE's are anisotropic for solids, since the transition probabilities are a function of both the time-independent spin operator terms and the time-dependent geometrical terms relating the position of the dipolar vector. Waugh and co-workers demonstrated this for solid benzene in static experiments,[29] and more recent work by McDowell and co-workers has addressed the anisotropy of methyl group rotation in crystalline solids, its effects on relaxation rates and NOE's, and the effects of magic-angle spinning.[18,19] This anisotropy will not be considered explicitly here.

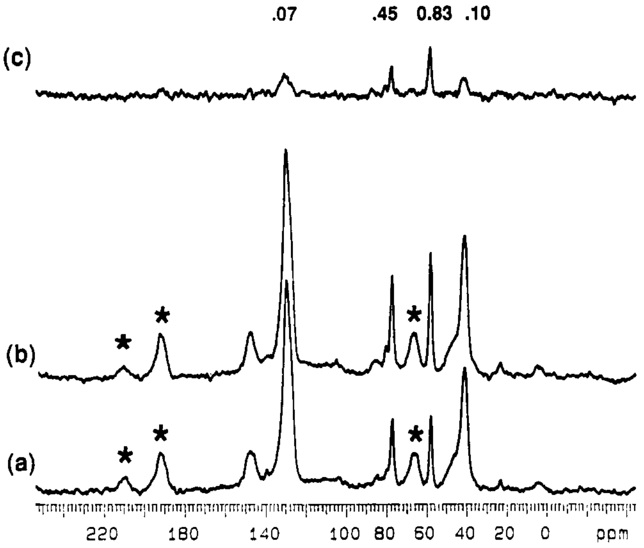

Figure 3. ^{13}C MAS spectra of a 1:1 molar PS-d_8/PVME blend cast from chloroform obtained (a) without NOE and (b) with NOE. (c) is the difference spectrum. The assignments are as in Figure 2.

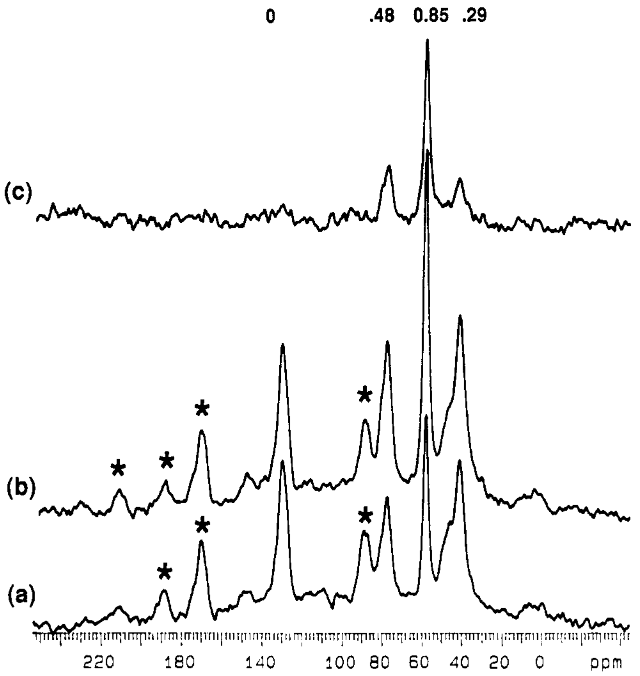

Figure 4. ^{13}C MAS spectra of a 1:3 molar PS-d_8/PVME blend cast from chloroform obtained (a) without NOE and (b) with NOE. (c) is the difference spectrum. The assignments are as in Figure 2.

Spectra obtained with and without NOE are shown in Figure 2 for a 1:1 molar PS-d_8/PVME blend cast from toluene. We chose the protonated/deuterated pair as a control sample for this initial study. Since the PS has no attached protons, cross-relaxation for the PS carbons may only occur via dipolar coupling to the PVME protons. Although it is not necessary to use a deuterated constituent, it was important in this first series of experiments to ensure that intramolecular effects were not attributed to intermolecular interactions. The steady-state NOE spectra shown in Figure 2 were acquired with a proton saturation pulse train of 163 s, and the total repetition delay between ^{13}C $\pi/2$ pulses was maintained in each experiment. The difference spectrum shows that in addition to the intramolecular enhancements observed for the methine (78 ppm) and methyl carbons (57 ppm) of PVME, significant intermolecular enhancements are observed for the PS resonances at 143, 128, and 40 ppm. The enhancement η is shown above each peak in the difference spectrum, and it should be remembered that for deuterated PS the minimum NOE is 0, not 0.153, since it contains no directly attached protons. The 40 ppm peak is actually the sum of three components, the PS methine and methylene backbone carbons and the main-chain methylene of PVME. However, most measurements were performed on 1:1 molar PS/PVME samples (ca. 67 wt % PS), in which the peak is dominated by the PS resonances. In contrast, spectra obtained for blends cast from chloroform exhibit essentially no enhancement, as shown in Figures 3 and 4 for 1:1 and 1:3 molar PS-d_8/PVME blends. The intermolecular PS enhancements range from 7% in the 1:1 blend to 0 in the 1:3 blend, far below the 30–40% consistently observed for the toluene blends. The residual enhancements observed for the chloroform blends most likely reflect dipolar interactions at the phase boundaries. The increased enhancement for the 40 ppm peak in the 1:3 PS/PVME chloroform-cast blend (Figure 4) relative to the 1:1 blend (Figure 3) is a result of the higher concentration of PVME methylene carbons. Since the solid-state NOE depends on the inverse sixth power of the internuclear separations, these spectra clearly demonstrate that the PS carbon nuclei have direct dipolar interactions with the PVME protons only for the toluene-cast blend.

These results demonstrate the utility and simplicity of using steady-state NOE's to probe miscibility in solid polymer blends below T_g. It is important to conduct these measurements below the glass transition temperature since we are interested in using the MAS NOE approach not only to establish molecular level miscibility in solid polymer blends but also to investigate specific intermolecular interactions. Above T_g, the main-chain motions could provide the necessary spectral density required for cross-relaxation. At temperatures well below the blend T_g, methyl group reorientation about the C_3 axis should be the only motion characterized by motions fast enough to promote cross-relaxation (vide infra). Since polarization of the PS carbons would occur via methyl rotation only, the opportunity exists to investigate specific interactions between the PS phenyl ring and the PVME methyl group. Evidence for such an interaction has been reported in concentrated solutions using two-dimensional NOESY experiments.[14] In the solid state, the resolution achieved using MAS allows NOE's to be measured for each type of carbon in the blend.

The sensitivity of the MAS NOE experiments to the molecular structure in the PS/PVME system is demonstrated by the NOE growth curves shown in Figure 5a,b for undried and dried toluene-cast PS-d_8/PVME films, respectively. The undried sample was cast in an N_2 drybox for 24 h, whereas the other sample was dried for an additional 24–48 h at 60 °C in vacuo. The sample preparation affects the physical characteristics of the blends, and the undried film exhibited much more elasticity than the brittle, dried film. Qualitatively, it is apparent that the initial intermolecular NOE growth rates decrease for each carbon in the dried versus undried samples. A similar, but more pronounced, change in the growth rates in dried vs undried samples was observed for the PS carbons in a protonated PS/PVME blend (Figure 6a,b). The sensitivity of the NOE growth rates to sample preparation suggests that a small amount of toluene left in the undried films acts as a plasticizer, lowering the T_g and increasing the motion of both the PVME and PS chains in the blend at room temperature. This would account for the increased growth rates observed for the PS aromatic carbons in the undried protonated blend versus the undried deuterated blend, as the carbons have directly attached protons in the former. However, the growth curves for

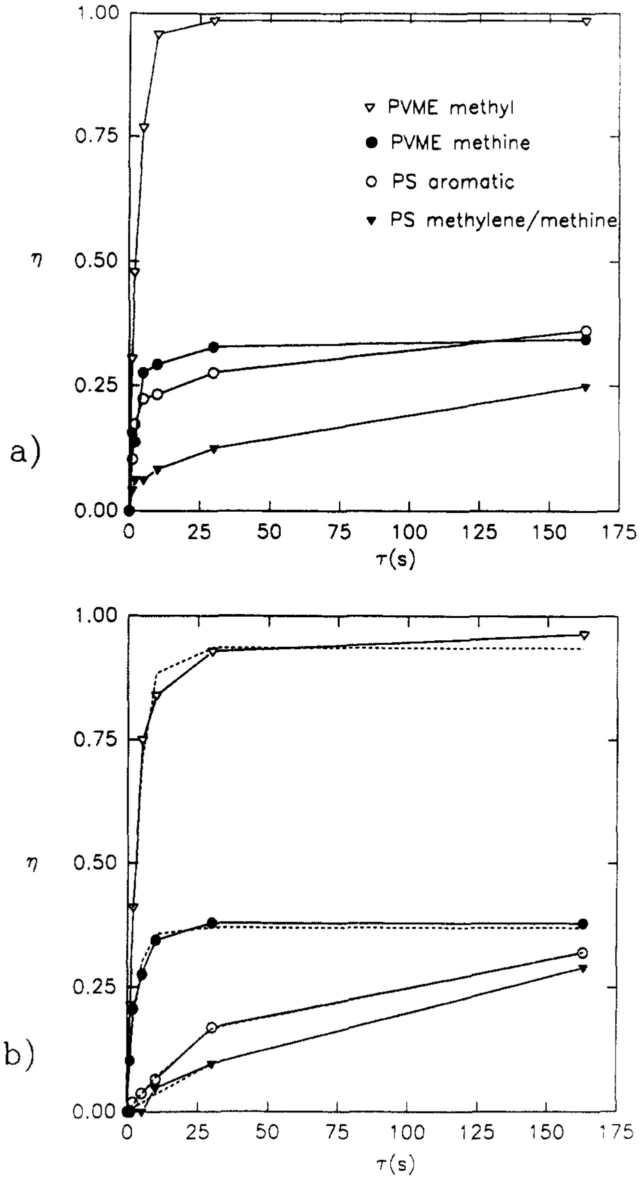

Figure 5. NOE growth curves measured at 23 °C for undried (a) and dried (b) 1:1 molar PS-d_8/PVME blends cast from toluene. The enhancement η is plotted as a function of the length of the proton saturation pulse train. Experimental data are given by the symbols with solid lines, and the simulations are shown by broken lines.

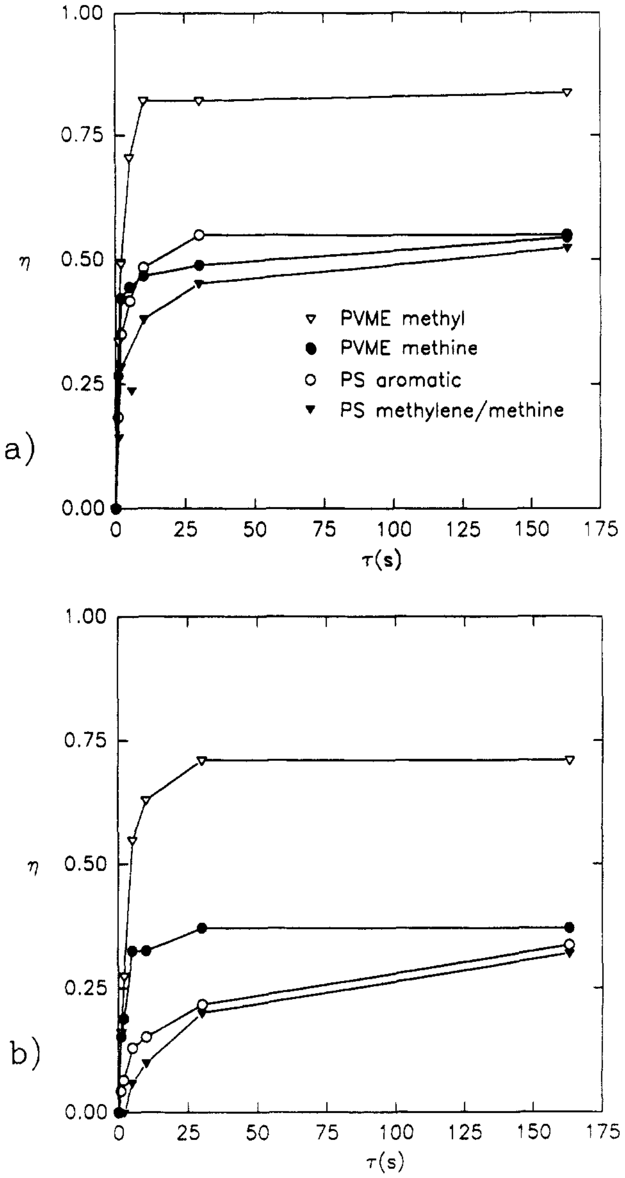

Figure 6. NOE growth curves measured at 23 °C for undried (a) and dried (b) 1:1 molar PS/PVME blends cast from toluene.

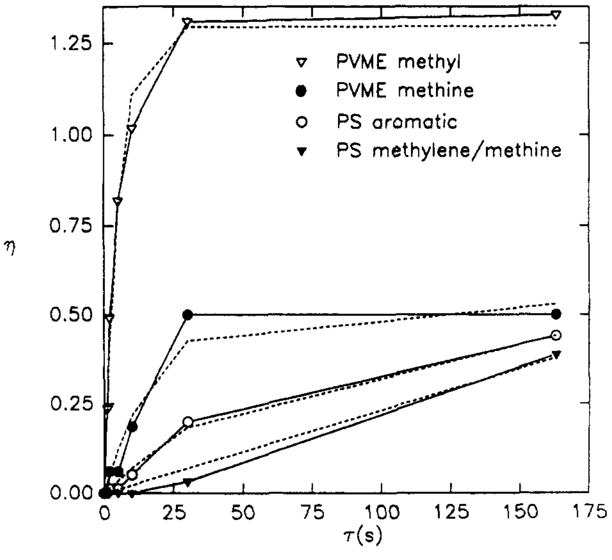

Figure 7. NOE growth curves for the sample in Figure 5b measured at −60 °C. The experimental data are given by the symbols with solid lines, and the simulations are shown by the broken lines.

the dried protonated blend (Figure 6b) were in every way similar to those for the dried deuterated blend (Figure 5b).

Figure 7 shows the NOE growth curve for the toluene-cast PS-d_8/PVME blend (i.e. the sample of Figure 5b) obtained at −60 °C. Quantitative analysis of such NOE growth curves should provide both cross-relaxation and spin–lattice relaxation rate constants. Assuming a single correlation function model, the NOE enhancement η at any time during saturation is given by

$$\eta = \frac{\sigma}{\rho}(1 - e^{-\rho t}) \qquad (3)$$

The values for σ and ρ may also be determined experimentally, σ by measuring the slopes in the linear region of the growth curves and ρ by T_1 experiments. Fits to the data are given by the broken lines in Figures 5b and 7, with the solid lines representing the experimental data. Rate constants obtained using both the experimental measurements and simulation are given in Table I for the experiments at +23 and −60 °C. The cross-relaxation rate constants fit using eq 3 are in excellent agreement with those calculated from the initial slopes. The PVME methyl carbons exhibit cross-relaxation rates several times greater

Table I. Experimental and Simulated Cross and Spin–Lattice Relaxation Rate Constants for Dried PS-d_8/PVME Blends at +23 and −60 °C

	σ_{fit} (s^{-1})	σ_{exp} (s^{-1})	$T_{1\mathrm{fit}}$ (s)
	23 °C		
PVME methyl	0.270	0.205	3.4
PVME methine	0.123	0.103	3.1
PS aromatic	0.008	0.006	41.8
PS main chain	0.004	0.002	92.5
	−60 °C		
PVME methyl	0.250	0.235	5
PVME methine	0.028	0.018	20
PS aromatic	0.008	0.007	62.5
PS main chain	0.002	0.002	>180

than other carbons and are essentially independent of temperature. In contrast, the PVME methine carbons exhibit significant temperature-dependent cross-relaxation behavior. The value for σ decreases by a factor of 5 upon cooling to −60 °C, suggesting that PVME main-chain motion contributes to dipolar cross-relaxation at room temperature. At −60 °C, well below the T_g of even pure PVME, these motions are frozen out and cross-relaxation is attributed exclusively to neighboring methyl group rotation.

The cross-relaxation rates for the PS aromatic carbons are several times greater than the rates for the main-chain PS carbons. In addition, the magnitude of the respective cross-relaxation rates are essentially independent of temperature, just as was observed for the methyl carbons. This implies that the aromatic ring is closer to the methyl group of PVME than to the methylene and methine carbons of PS, consistent with the presence of a specific intermolecular interaction between these two functional groups, as detected by other methods.[14]

Discussion

The molecular level characterization of polymer blends remains one of the important goals in polymer science, and we present here a new method to identify polymer blends that are miscible on the molecular level and for measuring specific intermolecular interactions. The experiments are simple to perform and are useful for the characterization of a wide variety of polymer blends. Due to the complicating effects of proton spin diffusion, there are no direct analogues of the two-dimensional NOESY experiment for solid samples. However, this work demonstrates that suitable one-dimensional experiments may be used for probing intermolecular distances in solids. For solid PS/PVME blends below T_g, we suggest that cross-relaxation of the PS carbons occurs only via dipolar interactions with the rapidly rotating PVME methyl group. This should especially hold true at −60 °C, below the glass transition of both the blend and pure PVME. We rule out other contributions to intermolecular NOE's, such as main-chain PVME motion or PS ring flips, on the basis of data reported in the literature as well as additional control experiments. In a recent examination of the temperature dependence of ^{13}C line widths in the MAS spectra of PS/PVME blends, Le Menestrel and co-workers identified the primary line-broadening mechanism as incoherent molecular motion of the PVME methine carbon that interfers with proton decoupling.[30] The maximum line width was recorded at 40 °C. Similarly, the maximum line width observed for the PS aromatic carbons was observed at 100 °C and was assigned to the interference between magic-angle spinning and molecular motions that occur on a similar time scale. The authors concluded that, although the components are mixed on a molecular length scale, the component chains have different molecular dynamics. In each case, the motions are in the kilohertz frequency regime, far below the 10^9–10^{10} Hz required to generate strong NOE's. As noted earlier, the cross-relaxation data in Table I indicate that only the PVME methine carbons are significantly affected as the temperature is lowered. Presumably, in agreement with the above mentioned results, there is some contribution from main-chain motion at room temperature, which is removed at −60 °C. This has no effect on the PS cross-relaxation.

We may also rule out PS ring flips as a source of dipolar interactions contributing to the NOE. Pure deuterated PS shows no NOE enhancement, while the protonated analogue exhibits only the theoretical minimum η of 0.153 (not shown). In order to assess the effects that blending has on PS ring dynamics, the ^2H spectra of pure PS-d_5 were compared to the spectra obtained for a PS-d_5/PVME blend (not shown). The spectra were identical in each case and similar to those previously reported by Spiess.[31] The Pake patterns were consistent with rigid C–D bonds, with only a small fraction of spectral intensity (ca. 10%) associated with motional averaging consistent with ring flips. Since the patterns were the same for the homopolymer and the blend and no NOE was observed for the homopolymer, we may rule out any contribution from ring flips in the blend. Indeed, Schaefer has shown that, although there exists a broad heterogeneity in the frequencies of ring flips in polycarbonate, there is essentially no contribution to the distribution at the higher frequencies required for NOE's to occur.[32]

The idea that methyl group rotation may dominate relaxation and cross-relaxation in polymers and polycrystalline solids is not a new one. Lyerla previously concluded, on the basis of variable-temperature proton and carbon relaxation measurements, that the methyl group dominates relaxation of all carbons in polypropylene.[33] As mentioned earlier, McDowell and co-workers found that methyl rotation was the primary mechanism for carbon relaxation and cross-relaxation in polycrystalline alanine.[18,19] We feel, therefore, that assigning intermolecular cross-relaxation of PS in PS/PVME blends to dipolar interactions with PVME methyl groups is consistent not only with our results, but also with the literature data. The observation that the cross-relaxation rate constant for the aromatic carbons of PS is several times larger than that for the main-chain PS carbons is strong evidence for specific intermolecular interactions between aromatic rings and methyl groups in the solid state.

In summary, we have presented a simple new method for the investigation of molecular level mixing in polymer blends and for identifying the specific intermolecular interactions that drive polymer blend formation. Our future efforts will be directed toward the study of new materials in which the driving forces for blend formation are not well characterized. We anticipate that these methods will be applicable to a wide variety of materials.

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