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Two-Dimensional NMR Studies of Molecular Weight and Concentration Effects on Polymer–Polymer Interactions

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ABSTRACT: Two-dimensional (2D) NMR experiments are used to measure the effects of molecular weight and concentration on polymer–polymer interaction for polystyrene–poly(vinyl methyl ether) mixtures in toluene. Through-space dipolar interactions lead to exchanges of magnetization that can be observed as cross peaks in a 2D nuclear Overhauser effect experiment. Concentration-dependent intrachain transfer is observed for both polymers, and specific polymer–polymer interchain transfer is observed between the polystyrene phenyl protons and the poly(vinyl methyl ether) methoxyl protons. For mixtures with poly(vinyl methyl ether) of 72 000 molecular weight, interchain transfer is similar for polystyrenes of 110 000 and 35 000 molecular weight. Transfer is diminished in 17 500 and 9000 molecular weight mixtures and disappears when the polystyrene molecular weight decreases below 4000. Interchain magnetization transfer is independent of polymer tacticity, and intrachain dipolar interactions are shown to be sensitive to chain entanglement.

Introduction

Polymers that form compatible blends are an exciting and interesting class of materials that can exhibit a wide variety of mechanical and chemical properties.[1] Chain mixing on a molecular level must result from short-range interactions, such as van der Waals, electrostatic, or hydrogen-bonding interactions, between the main-chain and side-chain atoms of neighboring polymers. However, there are relatively few techniques capable of probing the interactions between chains on a molecular level.[2–4] Among these, NMR[5–7] has great potential because the NMR parameters (chemical shift, line width, coupling constants, and relaxation rates) depend on the local magnetic environment. Chemical shifts are determined by both chemical structure and polymer conformation,[8] while the NMR relaxation[5] and nuclear Overhauser effects[9,10] (NOE) depend on the inverse sixth power of the internuclear separation between protons and on the segmental chain dynamics. In contrast to observations of the proton NMR spectrum in the solid state,[11,12] the lines in solution are relatively sharp and can be assigned to specific sites on the polymer chain.[7] By measuring spin exchange between these protons, one can identify the chemical nature of the interacting groups.[13–15]

In a previous study we examined the intra- and interchain interactions in concentrated solutions for two systems that form compatible polymer blends, polystyrene–poly(vinyl methyl ether) and polycaprolactone–poly(vinyl methyl ether).[14] Our initial purpose was to identify the chemical groups on neighboring chains that are close enough to undergo magnetization exchange. The correlation between our results and the limited results reported for solid polymer blends[2–4,16] shows that these solution experiments can accurately measure the interactions that are present in the solid samples. In the present paper we further explore the phenomenon of intermolecular spin transfer in the polystyrene–poly(vinyl methyl ether) system. We show that the intermolecular transfer depends strongly on molecular weight for low molecular weight samples and that intrachain interactions can be used to detect polymer chain entanglement even when the chains are too small to give rise to intermolecular nuclear Overhauser effects.

Experimental Section

Polystyrene and poly(vinyl methyl ether) were purchased from Polysciences Inc. The poly(vinyl methyl ether) was polydisperse and had an $\bar{M}_w$ of 72 000. Secondary polystyrene molecular weight standards of 110 000, 35 000, 17 500, 9000, 4000, and 800 ($\bar{M}_w/\bar{M}_n = 1.06$) were employed. The poly(vinyl methyl ether) was dried under vacuum at 85 °C overnight and mixed with polystyrene and deuterated toluene under a nitrogen atmosphere at 65 °C to give a 40 wt % mixture that was stirred for 12 h to ensure complete mixing.

NMR experiments were performed at 500 MHz on a JEOL GX-500 spectrometer, and the data were transferred to a MicroVax II computer for analysis using the program FTNMR (Hare Research Inc.). Hypercomplex[17] phase-sensitive 2D NOE spectra were acquired with the $(90°-t_1-90°-\tau_m-90°\text{-acquire})_n$ pulse sequence. A total of 512 complex spectra, each containing 1K complex points, were acquired for the 2D NOE experiments. Following zero filling once in the t_1 dimension, the final data matrix size was 1K × 1K (real points). Four-hertz apodization was used in both dimensions. The delay between acquisitions was long enough (5 s) to ensure that the system had returned to equilibrium between acquistions.

Results

Proton and carbon NMR have been extensively used to characterize synthetic polymers because of the chemical shift sensitivity to microenvironmental factors[6,8,18] (conformation, stereosequence, etc.) and the dependence of nuclear relaxation rates[5] on local polymer chain dynamics.[19] Spin-exchange experiments both in solution[13–15] and in the solid state[11,12] have recently been used to study the magnetic dipolar interactions between chains that form compatible blends. While extensive peak overlap, broad lines, and strong dipole–dipole interactions complicate the analysis of specific polymer–polymer interactions in the solid, this information can sometimes be extracted from two-dimensional NMR experiments in solution.

Figure 1 shows the 500-MHz proton spectra of several polystyrene–poly(vinyl methyl ether) mixtures that differ only in polystyrene molecular weight. All samples contain 20 wt % poly(vinyl methyl ether) of molecular weight 72 000 and 20 wt % polystyrene of molecular weights 110 000, 35 000, and 4000 in deuterated toluene. The part of the spectra between 6.0 and 7.0 ppm contains the polystyrene ortho and meta proton resonances while the peaks between 3.2 and 3.4 ppm are due to methine and methoxyl protons of poly(vinyl methyl ether). The highest field portion of the spectrum (1–2 ppm) contains the overlapping polystyrene methine and methylene protons and the poly(vinyl methyl ether) methylene protons. The

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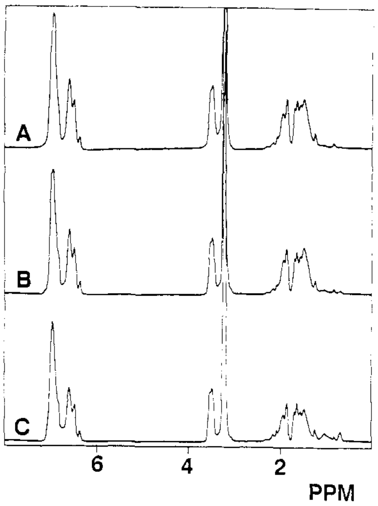

Figure 1. 500-MHz proton NMR spectra of polystyrene–poly(vinyl methyl ether) mixtures in deuterated toluene at 65 °C. The mixtures contained 20 wt % 72 000 molecular weight poly(vinyl methyl ether) and 20 wt % polystyrene of molecular weight (A) 110 000, (B) 35 000, and (C) 4000.

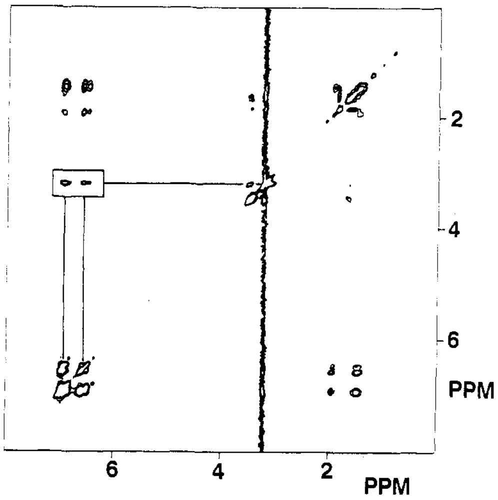

Figure 2. 2D NOE spectrum of the equal-weight polystyrene–poly(vinyl methyl ether) mixture (40 wt % total polymer) at 65 °C obtained with a mixing time of 0.75 s. The molecular weights of the polystyrene and poly(vinyl methyl ether) were 110 000 and 72 000, respectively. The boxed area shows the intermolecular cross peaks.

line widths in Figure 1 are determined by stereosequence effects on the chemical shift[18] (inhomogeneous broadening) and by local segmental dynamics.[19] The lines broaden slightly due to chain entanglement as the molecular weight of the polystyrene increases, but it is difficult to interpret such line broadening in the presence of the inhomogeneous broadening intrinsic to the polymer chains.

Figure 2 shows the 2D NOE[10] spectrum of a polystyrene–poly(vinyl methyl ether) mixture at 65 °C obtained with a mixing time of 0.75 s. The details of the interpretation of these types of spectra have been previously reported,[14,15] and only the salient points will be presented here. As in all 2D NOE spectra, the intense diagonal peaks contain the same information as the normal 1D spectrum, and the presence of off-diagonal (or cross) peaks shows the resonant frequency of those protons that are in close enough contact for the exchange of magnetization. For polymer systems such as those studied here, only protons within 4 Å give rise to observable cross peaks.[7,10,14] For polystyrene and poly(vinyl methyl ether), several intrachain cross peaks are expected from nearby protons, such as the ortho and meta protons of polystyrene. This cross peak appears as the off-diagonal intensity connecting the resonances at 6.5 and 7.0 ppm and illustrates the size of cross peak expected between protons separated by 2.4 Å. Intrachain phenyl to methine/methylene cross peaks are observed for polystyrene as are intrachain methoxyl, methine, and methylene cross peaks for poly(vinyl methyl ether). In addition, interchain cross peaks, shown in the box in Figure 2, reveal the molecular contact between the polystyrene phenyl and poly(vinyl methyl ether) methoxyl protons. This specific interchain interaction arises from the close contact (3.5 Å) between these two groups that results from extensive chain entanglement. A detailed discussion of the interaction for the polystyrene(110 000)–poly(vinyl methyl ether)(72 000) mixture has been presented previously.[14]

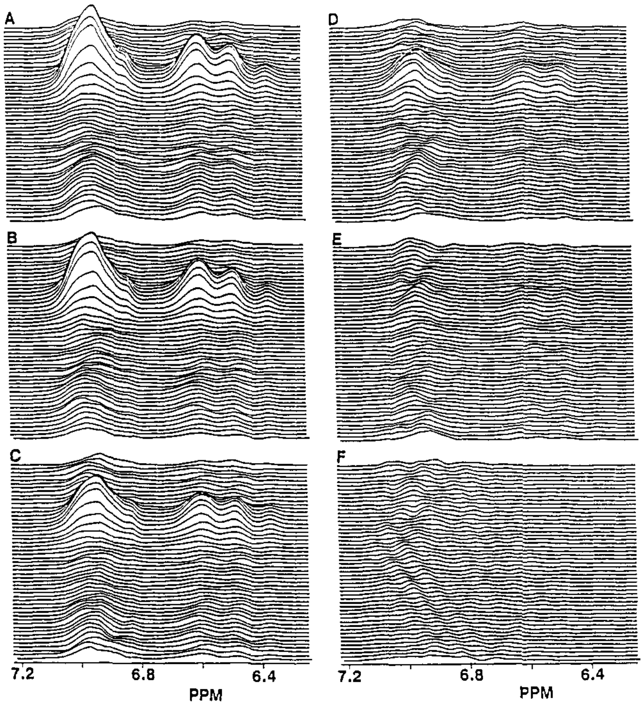

Figure 3. Stacked plots showing the intermolecular interaction between the polystyrene phenyl protons and the poly(vinyl methyl ether) methoxyl and methine protons as a function of polystyrene molecular weight. All conditions are the same as in Figure 2, and the stacked plot is of the boxed area in Figure 2. Spectra are shown for 72 000 molecular weight poly(vinyl methyl ether) mixed with (A) 110 000, (B) 35 000, (C) 17 500, (D) 9000, (E) 4000, and (F) 800 molecular weight polystyrene.

Figure 3 shows a stacked plot of a portion of the 2D NOE spectra for several mixtures that differ only in the molecular weight of the added polystyrene. This part of the spectra shows the interchain interaction between the polystyrene phenyl protons (bottom axis) and the poly(vinyl methyl ether) methine and methylene protons at 3.4 and 3.3 ppm that are enclosed in the box in Figure 2. The stacked-plot representation conveys the relative intensity of peaks more vividly than the contour plot. The most intense cross peak connects the poly(vinyl methyl ether) methoxyl and the overlapping meta/para polystyrene protons. A weaker peak connects the methoxyl and polystyrene ortho protons, and for the 110 000 molecular weight polystyrene, an even weaker peak between the overlapping meta/para cross peak to the methine protons can be seen. This peak may arise from indirect magnetization transfer.[20]

The intensity of the interchain cross peaks shows a strong dependence on molecular weight for mixtures with low molecular weight polystyrene. Little difference in cross peak intensity is found between the polystyrene mixtures of 110 000 molecular weight and 35 000 molecular weight. Thus, both the average distance separating the protons and the time scale for chain entanglement is unchanged as the molecular weight of the polystyrene changed by a factor of 3. However, when the molecular weight is decreased below 35 000, strong molecular weight effects on the intermolecular NOEs are observed. The cross peaks are reduced in intensity by 40% in the mixture with 17 500 polystyrene, are barely visible in the 9000 mixture, and completely disappear when the molecular weight of the polystyrene is reduced below 4000. There are two possible explanations for the decrease in cross peak intensity with molecular weight that can be distinguished upon closer examination of the 2D NOE spectrum. One possibility is that the interaction between lower molecular weight chains is not sufficiently strong to hold the two polymers in molecular contact long enough for the exchange of magnetization that generates observable cross peaks. The measured internuclear distance is an average of the entangled and nonentangled chains, and if the chains spend only a small fraction of time entangled, then the average internuclear distance will be greater than the 4-Å distances that can be measured in these 2D NOE spectra. A second possibility is that as the polystyrene molecular weight decreases, the intermolecular correlation time decreases to the point where the intermolecular cross relaxation rate becomes zero (vide infra). These two possibilities may be distinguished by observing the relative phases of the diagonal and cross peaks.

Ambiguities in the interpretation of nuclear Overhauser effects frequently arise because cross peak intensities depend on both internuclear separations and the local segmental dynamics.[7,9,10] The cross relaxation rate that generates cross peak intensity is given by[5,10]

$$\sigma_{ij} = \frac{\gamma^4 \hbar^2}{10 r_{ij}^6}\{-J_0(0) + 6J_2(2\omega)\} \qquad (1)$$

where γ is the gyromagnetic ratio and r_{ij} is the internuclear separation. The spectral density terms have the form $J_n(n\omega) = 2\tau_c/[1 + (n\omega)^2\tau_c^2]$, where ω is the spectrometer frequency and τ_c is the effective correlation time. Equation 1 shows that the cross relaxation rate can assume a variety of values depending on the internuclear distance and the segmental dynamics. However, the sign of the cross relaxation rate depends only on the relative magnitude of the $J_0(0)$ and $J_2(2\omega)$ spectral density terms. This results in positive NOEs in the fast-motion limit ($J_0(0) > 6J_2(2\omega)$), negative ones in the slow-motion limit ($J_0(0) < 6J_2(2\omega)$), and a disappearance of the NOE when the rate of molecular motion is such that $J_0(0) = 6J_2(2\omega)$. Characterization of the molecular dynamics follows directly from the phases of the cross peaks relative to the diagonals in the 2D NOE spectrum. In the fast-motion limit the cross peaks are opposite in phase to the diagonal peaks; they disappear when the cross relaxation rate is zero and are of the same phase as the diagonal in the slow-motion limit. This characterization of the segmental dynamics is independent of the internuclear distances.

The phase of the intrachain cross peaks can be used to determine if the rate of segmental motion for each polymer falls within the fast- or slow-motion regime. For poly(vinyl methyl ether) in all mixtures the methine–methoxyl cross peak has the same phase as the diagonal peaks, indicating that the intrachain dynamics are in the slow-motion regime. Similarly, the polystyrene ortho–meta cross peaks show that the intrachain motion for all polystyrene molecular weights is in the slow-motion limit. If both polymers are in the slow-motion limit, then it seems very unlikely that intermolecular interactions of the entangled chains could occur at a rate faster than the intramolecular molecular ones to cause the cross relaxation rate to approach zero. Furthermore, if the intermolecular dynamics depends on polystyrene molecular weight, then the intermolecular cross peaks would be positive for high molecular weights, disappear for intermediate ones, and appear as negative cross peaks for low molecular weight samples. This behavior is not observed; rather, the cross peaks disappear as the polystyrene molecular weight decreases and never appear with negative intensity. Therefore the more likely explanation is that the average distance between chains increases beyond the 4 Å that can be measured in these 2D NOE experiments. This presumably arises from the decrease in chain entanglement; the measured distance is the average of both the entangled (close) and nonentangled chains that have larger internuclear separations.

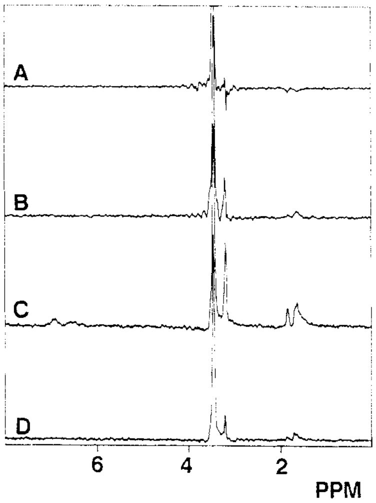

Figure 4. Cross sections through 2D NOE spectra at the frequency of the poly(vinyl methyl ether) methine protons for 72 000 molecular weight poly(vinyl methyl ether) at (A) 20 wt % and (B) 40 wt % and 20 wt % poly(vinyl methyl ether) mixed with 20 wt % polystyrene of (C) 110 000 and (D) 4000 molecular weight.

The phase of the intramolecular cross peaks also monitors chain entanglement. Figure 4 shows cross sections (slices) through the 2D NOE spectra at the frequency of the poly(vinyl methyl ether) methine protons for the polymer alone at 20 and 40 wt % concentrations and for the mixtures with 110 000 and 4000 molecular weight polystyrene. The intense positive peak corresponds to the diagonal methine resonance of poly(vinyl methyl ether), and the higher field peaks are due to the methoxyl (3.2 ppm) and methylene (1–2 ppm) intrachain cross peaks. Note that in Figure 4A (20 wt % poly(vinyl methyl ether)) the diagonal and cross peaks have opposite phases, indicating that the effective motion of the methine–methoxyl internuclear vector is within the fast-motion limit. As the concentration is increased to 40 wt % (Figure 4B) the phase of the methine–methoxyl cross peak becomes the same as the diagonal; the higher concentration leads to greater chain entanglements and alters the chain dynamics enough that the intrachain segmental motion is in the slow-motion regime. Parts C and D of Figure 4 show the cross sections through the same peak for the mixture containing 20 wt % poly(vinyl methyl ether) and 20 wt % polystyrene of molecular weight 35 000 and 4000. Even though the polystyrene was of too low molecular weight to generate an intermolecular cross peak in the 2D spectrum (Figure 3F), the chains entangle enough to slow

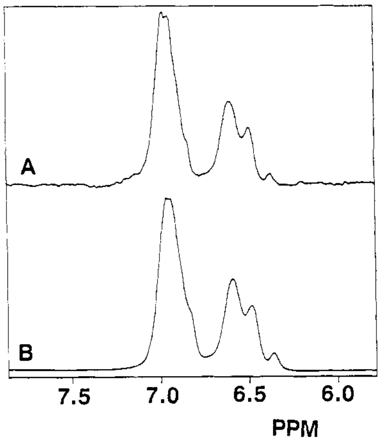

Figure 5. Comparison of the slice through the 2D NOE spectrum of the polystyrene–poly(vinyl methyl ether) showing the interchain interaction (A) with the 500-MHz 1D spectrum (B).

the poly(vinyl methyl ether) molecular motion.

In addition to the dynamic and structural information, the cross peaks in the 2D NOE spectrum provide information about the stereochemical preferences of the interacting groups on separate polymer chains. For example, if the *mm* diads had a stronger intermolecular interaction, its intensity in the 2D NOE spectrum would be enhanced relative to the other stereosequences. Figure 5 compares the 1D spectrum of polystyrene with a section of the 2D NOE spectrum for the polystyrene–poly(vinyl methyl ether) mixture (35 000). At 500 MHz the polystyrene ortho protons are resolved into three peaks corresponding to the *rr*, *mr*, and *mm* diads. We can determine if some stereosequences interact more than others by comparing the relative intensities of the peaks for the stereosequences in the 1D spectrum with the shape of the intermolecular cross peaks. Figure 5 shows that the same relative proportions of the diads are observed in the 1D spectrum and the slice through the 2D spectrum. This demonstrates a lack of stereochemical preference for the intermolecular phenyl to methoxyl interaction.

Discussion

The formation of compatible polymer blends is sometimes the result of specific chemical interactions between polymers. Specific interactions between the phenyl group of polystyrene and the ester group of poly(vinyl methyl ether) have been demonstrated both in the solid state[2-4] and in concentrated solutions.[14,15] IR studies of solid blends show that the oxygen lines of poly(vinyl methyl ether) differ between compatible blends cast from toluene and incompatible blends cast from chloroform solutions.[2,3] The polystyrene–poly(vinyl methyl ether) blend shows lower critical solution temperature behavior that is dependent on the degree to which the polystyrene phenyl ring is protonated or deuterated.[4] The NMR experiments in concentrated solutions show phenyl–methoxyl interchain cross peaks that result from a time-averaged internuclear separation of 3.5 Å.[14,15] These data demonstrate that the solution experiments measure the same interactions found in the solid blends.

The intermolecular interactions between the polystyrene phenyl and the poly(vinyl methyl ether) methoxyl group must be a van der Waals type of interaction with a free energy of association that is small compared to hydrogen-bonding and electrostatic interactions. The presence of many such weak interactions (one per monomer group) could account for the observed concentration[14,15] and molecular weight dependence of the intermolecular NOEs. For long chains, the polystyrene and poly(vinyl methyl ether) can entangle through many weak interchain interactions. The NMR data presented here do not place any specific limits on the geometry of the chains in solution other than the requirements that the poly(vinyl methyl ether) methoxyl protons be within 3.5 Å of the meta and para polystyrene protons. For the different molecular weights at the same concentrations, there are an equal number of possible monomer–monomer interactions. However, for short chains the concentration of chain end is increased relative to the longer polymer. These chain ends are expected to fray in solution and shift the equilibrium between the entangled and nonentangled states toward the nonentangled state. The internuclear distance measured in the 2D NOE studies is an average of the entangled (close) and nonentangled (distant) chains, and shifting the equilibrium toward the nonentangled state eventually increases the distance beyond that measurable in the 2D NOE experiments. In a similar way the equilibrium will be sensitive to temperature and polymer concentration.

The lack of intermolecular NOEs does not prove that the polymers are not interacting, rather that the geometry and time scale of any interaction is not sufficient for the exchange of magnetization. However, the intrachain dynamics are sensitive to both inter- and intrachain entanglements. This has previously been demonstrated in ^{13}C NMR relaxation studies of polymers as a function of temperature, concentration, and molecular weight.[21] Relaxation studies as a function of chain length show that the relaxation rate depends on molecular weight for short chains but becomes independent of molecular weight for chains longer than 100 monomer units.[22] For short chains the magnetic dipolar relaxation is caused by a combination of rotational Brownian motion and local segmental motion resulting from bond rotations in the main chain of the polymer. For long chains the rotational Brownian motion is too slow to cause relaxation, and the relaxation is governed only by the segmental dynamics. Thus, when chains entangle, the relaxation rates will be affected if the frequency of entanglements is greater than one per 100 monomer units. This type of relaxation information can also be extracted from the relative phases of the intramolecular cross peaks. This is illustrated for the methine–methoxyl proton interactions in poly(vinyl methyl ether), where increasing the polymer concentration leads to a change in the phase of the cross peak. The effects of chain entanglement in the polystyrene mixtures can be measured by the intrachain interactions even for low molecular weight mixtures where intermolecular NOEs are not observed.

In summary, we have used two-dimensional NMR to study the interactions between polymer chains in concentrated solutions. The results parallel those obtained for solid polystyrene–poly(vinyl methyl ether) blends, but because of the higher resolution of solution NMR, we can more precisely define the polymer–polymer interactions. The entanglement of chains in this system results from many weak interactions along the chain, and the NMR relaxation measured in the 2D experiments is sensitive to chain entanglements.

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