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Two-Dimensional NMR Studies of Polymer Mixtures

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ABSTRACT: Two-dimensional NMR has been used to study the inter- and intrachain interactions in concentrated polymer solutions and in the bulk for mixtures of polystyrene/poly(vinyl methyl ether) and poly(vinyl methyl ether)/polycaprolactone. These experiments measure proton–proton dipolar interactions that depend on the inverse sixth power of the internuclear distances and are a measure of both the local chain conformation and the interactions between chains. In solutions of less than 25% (w/v) concentration no interactions between the polymer chains are observed for polystyrene/poly(vinyl methyl ether) mixtures. Above 40% (w/v) concentration the interchain dipolar interactions are of the same magnitude as intrachain interactions and show a specific interaction between the polystyrene phenyl protons and the poly(vinyl methyl ether) methoxyl group. Bulk mixtures and 50% (w/v) solutions of polycaprolactone/poly(vinyl methyl ether) show less specific interchain interactions. In this case the interaction is observed between the poly(vinyl methyl ether) methoxyl group and all the polycaprolactone protons. These results show that 2D NMR can be used to measure the specific interchain interactions that lead to the formation of compatible polymer blends.

Introduction

Interactions between unlike polymer chains, whether in bulk or solution, are of great fundamental interest. They are generally discussed in thermodynamic terms without specific consideration of the nature of the groups and forces involved, although infrared studies of mixtures of polymers have been reported.[1-3] Two-dimensional nuclear Overhauser effect spectroscopy (2D NOE) permits one in principle to examine polymer–polymer interactions in some detail provided the chains are on average within ca. 4 Å of each other.[4] Caravatti et al.[5,6] have used solid-state proton 2D NMR to demonstrate such interactions in polystyrene/poly(vinyl methyl ether) mixtures laid down as films from certain solvents. Natansohn and Eisenberg[7] show similar evidence for specific interactions between methyl methacrylate–4-vinylpyridine copolymer and a partially sulfonated polystyrene in relatively dilute DMSO solution. In this situation the interaction was strongly favored by ionic attraction (i.e., salt formation) between the chains.

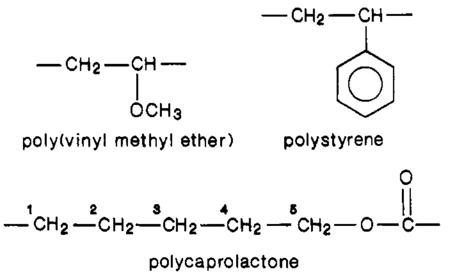
In this paper we use 2D NMR to study the interactions between polymer chains in concentrated solutions and in the bulk. There are several advantages to solution measurements and we show that the results are directly applicable to solid polymer blends. One advantage of the solution experiment is that the resonances are much narrower than in the solid because of the high chain mobility. The higher resolution enables us to measure more local and specific interactions. This is particularly important because NMR studies are limited to systems where the component polymers give different NMR spectra. In solid mixtures containing crystalline polymer components, it is difficult to separate out effects due to crystalline interactions, whereas in the melt or solution this question does not arise.

Here we report that polystyrene–poly(vinyl methyl ether) and polycaprolactone–poly(vinyl methyl ether) (Chart I) show intermolecular interactions in concentrated but not in dilute solution, and we further show that these interactions can be assigned to specific chemical groups. The results for solutions parallel the less detailed conclusion from solid-state studies of the two blends reported from FTIR data[1-3] and the effects of deuterium substitution on the lower critical solution temperature.[8,9] It appears from our study that 2D NMR can probe the chemical interactions that lead to the formation of compatible polymer blends.

Materials and Methods

Polystyrene, polycaprolactone, and poly(vinyl methyl ether) were obtained from Polymer Sciences; the number-average molecular weights were 110 000, 92 000, and 72 000, respectively.

Chart I



NMR measurements were made at 500 MHz on a JEOL GX-500 NMR spectrometer at 65 °C using the $(\pi/2-t_1-\pi/2-\tau_m-\pi/2\text{-acquire})_n$ pulse sequence. Phase-sensitive 2D NOE spectra were acquired by the method of States et al.[10] In a typical experiment, 256 spectra, each consisting of 1K complex data points, were acquired with a mixing time of 0.10 or 0.35 s. The data were transferred to a Micro Vax II computer and processed by using software written by D. Hare (Infinity Systems). The spectra were processed with 2-Hz line broadening, base-line correction, and zero filling to give a final data matrix of 1K × 1K real points.

Results

Concentration Dependent NMR Spectra. The NMR spectra of polymer solutions have been very extensively studied over the past 30 years and it is well-known that the apparent spectral resolution depends on the concentration, molecular weight, and the microstructure of the polymer chains.[11] Sharp lines are observed at low concentrations due to rapid segmental motion of the polymer chains, regardless of the macroscopic solution viscosity. However, for polymers characterized by differing stereochemical sequences, or other complex microstructures, the lines are frequently inhomogeneously broadened by chemical shift dispersion. At higher concentrations the polymer chains may entangle and alter the dynamics, leading to further broadening of the lines.[11,12]

Figure 1 shows the effect of polymer concentration on the appearance of the 500-MHz proton NMR spectra of 50:50 mixtures of polystyrene/poly(vinyl methyl ether) in toluene. Only minor spectral differences are observed between 1% and 25% (w/v) concentrations. As the concentration increases there is a loss of resolution in the methylene (1.5–2.5 ppm) and phenyl ring (6.5–7 ppm) proton resonances. Between 25 and 40% (w/v) the resolution decreases in the methylene region to a point where only two bands are observed. Figure 2 shows the bulk polycaprolactone spectrum, the bulk spectrum of a 90:10 polycaprolactone/poly(vinyl methyl ether) mixture, and an equal weight polycaprolactone/poly(vinyl methyl ether) mixture at 50% (w/v) in toluene at 65 °C, the melting

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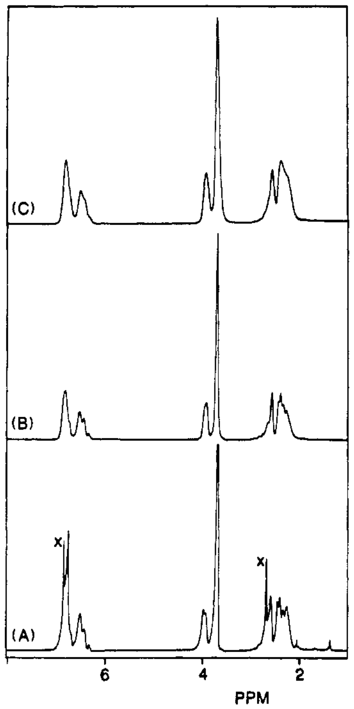

Figure 1. Concentration effects on the 500-MHz proton NMR spectrum of 50:50 mixtures of polystyrene and poly(vinyl methyl ether) at 65 °C. The solutions are (A) 1%, (B) 25%, and (C) 40% w/v in deuteriated toluene. The × in spectrum A shows the residual toluene resonances.

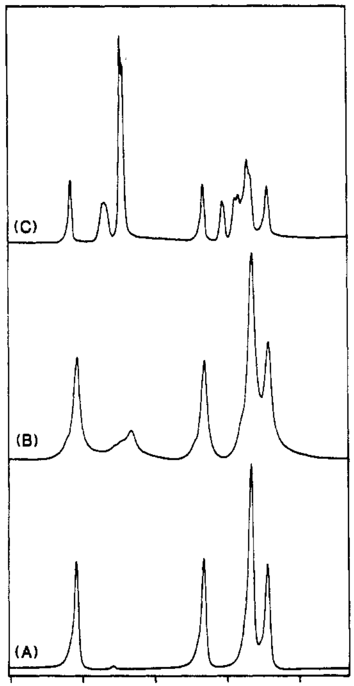

Figure 2. 500-MHz spectra of (A) polycaprolactone in the bulk, (B) a 90:10 bulk mixture of polycaprolactone and poly(vinyl methyl ether), and (C) a 50% w/v solution of a 50:50 mixture of polycaprolactone and poly(vinyl methyl ether) in deuteriated toluene at 65 °C, the melting point of polycaprolactone.

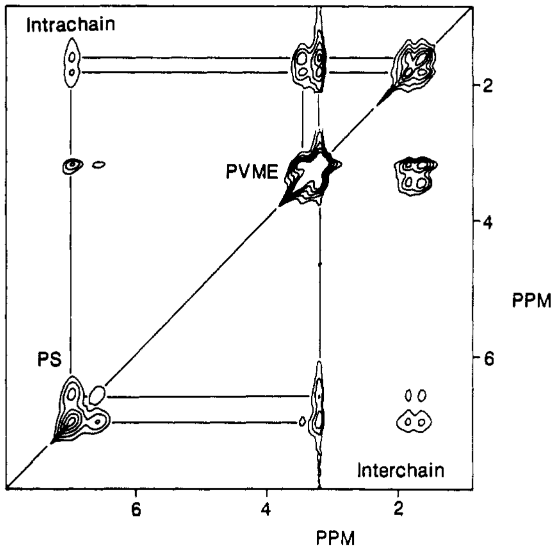

Figure 3. Two-dimensional nuclear Overhauser effect spectrum of a 40% (w/v) equal weight mixture of polystyrene/poly(vinyl methyl ether) at 65 °C. The phase-sensitive spectrum was recorded with a 0.1-s mixing time. The intrachain polystyrene and poly(vinyl methyl ether) connectivities are shown in the upper part of the spectrum and the interchain in the lower part. See Material and Methods for details.

point of polycaprolactone.[13] In the molten bulk state (Figures 2A,B) the resonances are broader than in solution, indicating that overall reorientation of the polymer chains is slow on the NMR time scale. However, the lines in the molten state are much sharper than for solid polymers. While the bulk spectra are less well resolved than the solution spectra, two of the polycaprolactone resonances (C1 and C5) and the poly(vinyl methyl ether) methoxy resonance are clearly resolved. Somewhat higher resolution is observed for the 50% (w/v) polycaprolactone/poly(vinyl methyl ether) solution relative to the polystyrene/poly(vinyl methyl ether) mixtures, indicating that these chains are less restricted. Assignments for the chemical shifts were made by analogy with the published spectra for the separate polymers and other 2D NMR studies (see below).

Two-Dimensional NMR Studies. Changes in the line widths that accompany increased concentrations are indicative of a change in the segmental dynamics of the polymer chains. However, these changes alone do not provide detailed information concerning the nature of the chain entanglements. Two-dimensional (2D) NMR has the potential to provide this information because the cross peaks in a 2D nuclear Overhauser effect (2D NOE) spectrum are related to the inverse sixth power of the internuclear distance.[4,14,15] Cross peaks between protons on different chains can provide a direct probe of those chemical units that are in close contact (<4 Å).

Figure 3 shows the 2D NOE spectrum of the 40% (w/v) mixture of polystyrene/poly(vinyl methyl ether) obtained with a mixing time of 0.1 s. The normal 1D spectrum appears along the diagonal, and the off-diagonal peaks connect the resonance of protons in close spatial proximity. The close spatial positioning of protons leads to through-space dipole–dipole interactions that cause the exchange of magnetization during the mixing time.[4,14,15] The transfer of magnetization is related to the cross-relaxation rate σ_{ij}

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

where γ is the proton gyromagnetic ratio, h is Planck's constant, r_{ij} is the internuclear distance, and the spectral density terms ($J_0(0)$ and $J_2(2\omega)$) depend on the spectrometer frequency and the effective correlation time. The intensities of the peaks depend on the strength of the dipolar interaction, (through the sixth power of the distance), the effective correlation time governing reorientation of the interproton vectors, and the mixing time. The longest reorientational correlation time establishes the distance scale that can be probed by NMR. For polymer

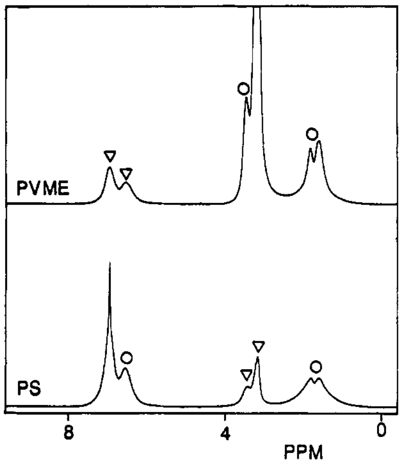

Figure 4. Cross sections through the 2D NOE spectrum of a 40% polystyrene/poly(vinyl methyl ether) mixture at the frequency of the (top) poly(vinyl methyl ether) methoxyl protons and (bottom) the polystyrene phenyl protons. Intrachain interactions are shown by circles and interchain interactions by triangles. The cross section was extracted from the experiment shown in Figure 3.

mixtures that have correlation times between 0.1 and 2 ns, internuclear separations greater than 4 Å result in cross peaks too small to be observed.

The spectrum of the polystyrene/poly(vinyl methyl ether) mixture shows both intra- and intermolecular cross peaks. The lowest field portion of the spectrum contains the ortho and meta phenyl proton resonances of polystyrene at 6.5 and 7.0 ppm, respectively. The strong cross peak connecting the ortho and meta protons show the size of a cross peak expected for interactions between protons separated by 2.48 Å. The phenyl protons also show a cross peak to protons at 3.4 ppm; these can be identified as the methoxy protons of poly(vinyl methyl ether). This is a clear example of an intermolecular NOE; the fact that a cross peak is observed at all indicates that the time-averaged distance between the polymer chains is on the order of 2.5–4 Å. At lower contour levels, and in the cross sections of Figure 4, a weaker peak can also be observed from the polystyrene meta–para protons to the poly(vinyl methyl ether) methine protons. At higher field (1.5–2.5 ppm) another group of cross peaks reveals an interaction between the polystyrene phenyl protons and the methylenes. Since the polystyrene methine and methylene protons overlap with the poly(vinyl methyl ether) methylene protons, it is not obvious from the contour plot if the cross peak is due to intra- or intermolecular interactions or a mixture of the two. Other notable cross peaks in the spectrum are observed between the poly(vinyl methyl ether) methine and methoxy protons (3.4–3.6 ppm) and the overlapping methylene protons (1.5–2.5 ppm). Unresolved cross peaks within the methylene region are also observed.

Additional information as to the origin of the interactions giving rise to the cross peak can be obtained by examination of cross sections through the 2D NOE spectrum, as shown in Figure 4. The bottom slice is a cross section through the polystyrene phenyl protons. The large peak at 7 ppm corresponds to the intense diagonal peak from the meta and para protons, while the peak at 6.5 ppm is the ortho–meta cross peak. Weaker interactions are visible to the poly(vinyl methyl ether) methine and methoxyl protons (3–4 ppm) and the overlapping polystyrene methine and polystyrene and poly(vinyl methyl ether) methylenes (2–3 ppm). The upper trace shows a cross section through the poly(vinyl methyl ether) methoxyl protons. The strongest correlation in this case is also intramolecular, i.e., between the poly(vinyl methyl ether) methine and methoxyl protons. Weaker interactions are observed to both the polystyrene phenyl protons and the overlapping upfield protons.

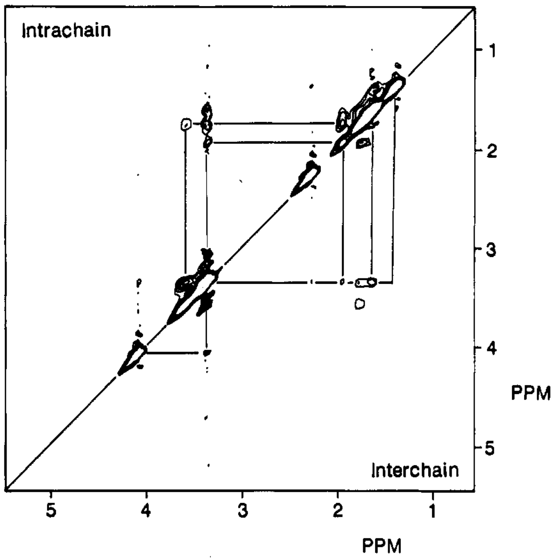

Figure 5. 500-MHz 2D NOE spectrum of a 50% w/v equal weight mixture of polycaprolactone/poly(vinyl methyl ether) at 65 °C with a 0.35-s mixing time. Intrachain connectivities are traced in the upper portion of the spectra and interchain ones in the lower part.

The intra- and intermolecular effects can be separated by observation of the differences in line width between the polystyrene and poly(vinyl methyl ether) chains. The cross sections in Figure 4 show that the poly(vinyl methyl ether) methine and methoxy line widths are narrower than for the polystyrene phenyl protons and that the poly(vinyl methyl ether) cross peaks to the 1–2 ppm region are sharper than those for polystyrene. This evidence shows that the segmental dynamics of the poly(vinyl methyl ether) chains are rapid enough to sharpen the lines, and that these sharp lines are characteristic of the poly(vinyl methyl ether) chains. Cross sections through the 2D NOE spectrum show the interaction of the polystyrene phenyl protons with the broad resonances in the 1–2 ppm region and the poly(vinyl methyl ether) protons with sharper ones. These features are expected if the methylene cross peaks are due predominantly to intramolecular effects.

The spectrum of the 50% solution of equal concentrations of polycaprolactone and poly(vinyl methyl ether) shows slightly higher resolution than for polystyrene/poly(vinyl methyl ether) mixtures (compare Figures 1C and 2C), presumably due to more rapid segmental motion in the polycaprolactone chains. Figure 5 shows the 2D NOE spectrum for the polycaprolactone/poly(vinyl methyl ether) mixture obtained with a 0.35-s mixing time. The longer mixing time is required because the dipolar interactions are weaker than for the polystyrene/poly(vinyl methyl ether) mixture. As in the case of the polystyrene/poly(vinyl methyl ether) mixtures, both intra- and intermolecular cross peaks are observed. Connectivities for the intrachain interactions are shown in the top portion of Figure 5. One remarkable feature is that intrachain peaks are only observed for the poly(vinyl methyl ether) protons. No cross peaks are observed connecting the neighboring polycaprolactone protons presumably because the correlation time for this interaction is near the motional regime wherein the cross relaxation rate is zero (0.3 ns) or the averaging of the dipolar interactions by internal motions (bond rotations) weakens the interactions to such

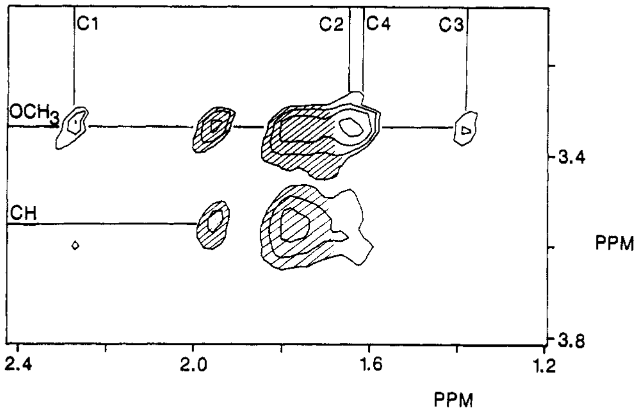

Figure 6. Expansion of the 2D NOE spectrum of the 50% w/v mixture of polycaprolactone/poly(vinyl methyl ether) showing the poly(vinyl methyl ether) intrachain and the polycaprolactone/poly(vinyl methyl ether) intermolecular interactions.

an extent that the cross peaks are not visible at this mixing time. The lower portion of the 2D spectra traces out the connectivities due to interchain interactions. These peaks have the same phase as the poly(vinyl methyl ether) intrachain ones and show that the interchain interactions are slow on the NMR time scale.[4] Note that cross peaks are observed to all of the polycaprolactone protons.

To estimate the strength of the interactions between chains, we compare the intensity of the methoxy proton cross peaks with protons C1 through C5 on the polycaprolactone chain. An expanded plot of the 2D spectrum showing the methine and methoxy proton interactions with the poly(vinyl methyl ether) and polycaprolactone methylene protons C1–C4 is shown in Figure 6. The intrachain peaks for the poly(vinyl methyl ether) methine and methoxy with their own methylenes are shown by cross hatches. The resolved polycaprolactone C1 and C3 cross peaks are slightly weaker than the C5 interaction (Figure 5) and the interaction with the overlapping C2/C4 cross peaks. Thus, the interchain interaction is mediated by the poly(vinyl methyl ether) methoxy group, but there is no strong preference for the poly(vinyl methyl ether) methoxy protons to interact with specific hydrogens on the polycaprolactone chain.

The proton NMR spectrum of polycaprolactone and polycaprolactone/poly(vinyl methyl ether) mixtures is sufficiently well resolved that it may be studied in the bulk state above the melting temperature. Figure 7 shows the 2D NOE spectrum obtained with a 0.35-s mixing time for the 90:10 polycaprolactone/poly(vinyl methyl ether) mixture. As shown in Figure 2, this mixture contains only three resolved cross peaks, the poly(vinyl methyl ether) methoxy protons (3.4 ppm) and the C1 and C5 protons of polycaprolactone (4.0 and 2.1 ppm). The poly(vinyl methyl ether) methylene protons and the remaining polycaprolactone protons resonate in the broad band at 1.8 ppm.

The 2D NOE spectrum shows cross peaks connecting all of the resonances in polycaprolactone. This is direct experimental evidence for close association of the polycaprolactone and poly(vinyl methyl ether) chains in the bulk. However, it is difficult to determine if the interactions are specific when all of the possible cross peaks are present and are of the same magnitude. It may be possible to measure specific interactions with additional experiments at shorter mixing times. The presence of intramolecular polycaprolactone cross peaks shows that chain motions are restricted in the bulk state.

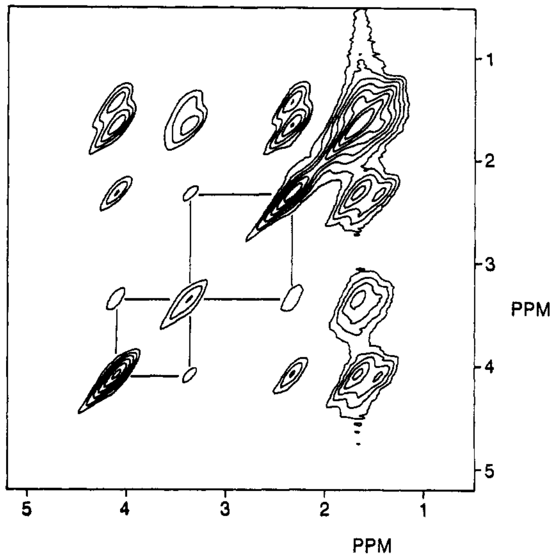

Figure 7. 2D NOE spectrum of a 90:10 bulk mixture of polycaprolactone/poly(vinyl methyl ether) at 65 °C, obtained with a 0.35-s mixing time.

Discussion

The ability of polymers to form compatible blends is due to the interaction between unlike polymer chains being at least as favorable as the self-interaction. Polymer blends have important mechanical and other properties and for this reason have been extensively investigated. However, there are relatively few techniques capable of probing the interactions between polymer chains on the molecular level. Among these techniques are FTIR[1–3] and the measurement of deuterium substitution on the properties of the blends.[8,9] Here we use the proton–proton dipolar interactions as a measure of the strength and specificity of the interaction between the polymer chains. These dipolar interactions are particularly useful as they provide information on a very local scale, less than 4 Å.[4,14,15] We have studied these interactions in concentrated solutions in order to determine the specific interactions that accompany the formation of a compatible blend. The dipolar interactions are much stronger in the solid state where the spin systems are more strongly coupled together. This makes it easier to measure the interactions between chains but harder to determine if there are any specific interactions. In concentrated solutions we expect to measure those specific interactions that nucleate the formation of compatible blends.

In the present study we chose to examine two polymers that form compatible blends, polystyrene/poly(vinyl methyl ether) and polycaprolactone/poly(vinyl methyl ether).[16,17] The former is a mixture of amorphous polymers and the latter is mixture of a crystalline and an amorphous polymer. The data from these solution studies can be correlated with other results (including those in the solid), as the polystyrene/poly(vinyl methyl ether) mixture has been extensively studied.[1–3,8,9,16–18] The polycaprolactone/poly(vinyl methyl ether) mixture is unique because the melting temperature of polycaprolactone is low (65 °C) as is the glass transition temperature for poly(vinyl methyl ether). The polycaprolactone/poly(vinyl methyl ether) mixture has a lower critical solution temperature phase diagram above 200 °C.[18]

The observation of cross peaks in a 2D NOE spectrum depends on the inverse sixth power of the distance separating protons, the motional properties of the polymer, and the time allowed for the dipolar interactions to evolve. The spectra of the polymer mixtures show only minor variations in the line widths at concentrations below 30% (w/v). 2D NOE spectra measured under identical conditions at 10%, 18%, and 25% (not shown) contained no cross peaks due to intermolecular interactions. Therefore, the strength of the dipolar interactions parallels the changes in line width (Figure 1) as a function of concentration. Only when the lines begin to broaden did we detect the interchain interactions that result from the chain entanglements.

The main requirement for the observation of cross peaks in the 2D NOE spectrum is that the time-averaged distance between the two protons be within 2–4 Å. Because of the constraints of chemical bonding, intrachain interactions are expected give rise to NOE cross peaks. In the polystyrene/poly(vinyl methyl ether) solution, we can estimate the average distance between the phenyl protons and the poly(vinyl methyl ether) methoxyl group by comparison to the cross peaks arising from protons at fixed distances within the polymer; e.g., the fixed distance is between the polystyrene ortho and meta protons (2.48 Å). When the interactions are properly scaled to account for the number of protons involved,[20] the time-averaged distance is approximately 3.5 Å. The smaller polycaprolactone C5 to poly(vinyl methyl ether) methoxyl cross peak is indicative of an average distance of 4 Å.

These solution studies may be directly compared with other studies of polymer blends. The polystyrene/poly(vinyl methyl ether) system has been extensively studied both by FTIR[1-3] and specific deuterium labeling effects on the lower critical solution temperature.[8,9] The lower critical solution temperature for polystyrene/poly(vinyl methyl ether) blends made with fully deuteriated polystyrene is 40 °C higher than that found for the corresponding blend with hydrogenated polystyrene. If only the phenyl protons are deuteriated, the lower critical solution temperature is the same as for the fully deuteriated polystyrene. However, if only the main-chain hydrogens are exchanged, the lower critical solution temperature is the same as for hydrogenated polystyrene. Thus, the deuterium substitution experiment clearly shows that the solid-state interactions between the polymers are primarily mediated by the polystyrene phenyl protons. A similar conclusion is reached on the basis of FTIR studies on polystyrene/poly(vinyl methyl ether) blends.[1-3] In addition, the FTIR studies showed that the $CHOCH_3$ vibrations are altered in the blend relative to poly(vinyl methyl ether). Taken together, these data suggest that the interaction between the polystyrene phenyl and poly(vinyl methyl ether) methoxy protons plays a critical role in blend compatibility. The close correspondence between these results and the solution results reported here demonstrates that 2D NMR methods can measure the interactions between chemical groups that lead to the formation of compatible polymer blends.

In summary, we have used 2D NMR to measure the dipolar interactions between protons on different polymer chains in concentrated solutions and in the bulk. Specific interactions can be observed and the identity of the interacting groups can be determined from their NMR spectra. For polystyrene/poly(vinyl methyl ether) and polycaprolactone/poly(vinyl methyl ether) the results parallel those reported in the solid and suggest that 2D NMR has the potential to determine at a molecular level those interactions that lead to the formation of compatible polymer blends.

Registry No. PS, 9003-53-6; PVME, 9003-09-2; polycaprolactone (homopolymer), 24980-41-4; polycaprolactone (SRU), 25248-42-4.

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