Figure 11 shows a 125-MHz ^{13}C NMR spectrum of the olefinic region for a hydrogenated NBR (N-45(90)). A number of peaks observed are assigned as shown in Table V on the basis of the previous assignments for NBR[10] and the chemical shift parameters.[11,12] There are good agreements between the observed and the calculated chemical shifts of main peaks. The intensities of these peaks before and after hydrogenation are given in Table VI. The fact that ABBB sequences are hydrogenated to AEBB 2 or more times more easily than to ABEB suggests that 1,4-BD units adjacent to AN units are preferentially hydrogenated.

Conclusion

The microstructural change of NBRs during the hydrogenation reaction was studied by means of PyGC, IR, and ^{1}H and ^{13}C NMR. Specific absorption bands in the IR spectra, resonance peaks in the ^{1}H NMR spectra, and characteristic peaks on the pyrograms by PyGC proved to be good measures for tracing the degree of hydrogenation reaction. Among these, the peak intensity of C$_7$-MN(A) by PyGC provided a practical calibration curve applicable even to highly hydrogenated NBRs. On the other hand, the IR spectra of various hydrogenated NBRs suggested a preferential hydrogenation reaction of 1,2-BD units over 1,4-units. PyGC and ^{13}C NMR also supplied good complementary information about longer sequences along the chains and the mechanisms of the hydrogenation reaction. The ^{13}C NMR spectra suggested that the BD units next to the AN units in the polymer chain were more likely to be hydrogenated than those next to the same units (BD).

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A NMR Study of Miscible Blends in Concentrated Solution. 1. Poly(vinyl methyl ether)/Polystyrene

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ABSTRACT: High-resolution proton spectra of the miscible polymer blend polystyrene/poly(vinyl methyl ether) (PS/PVME) in concentrated solution have been used to examine intermolecular interactions. The spectral resolution achieved in solution allows the polymer components and the chemically different types of protons within each component to be well resolved. A one-dimensional cross-relaxation experiment shows that the polymers are intimately mixed in toluene solution but not in chloroform. The minimum concentration where magnetization exchange between the polymer pair (in toluene) can be observed lies between 30 and 40 wt % total polymer, of which 50 wt % is polystyrene. The chemical shift difference between the methine and methoxy resonances of PVME is found to vary with the mole ratio of PVME to the total aromatic functionality, from either PS or toluene. Line width vs temperature measurements seem to indicate hindrance of motion for the blend in toluene at elevated temperatures, as the gross phase separation is approached, that is not observed for the pure homopolymer. A two-dimensional exchange experiment was performed at a series of mixing times to measure the intra- and intermolecular spin-diffusion rates. Specific intermolecular rates could not be differentiated in the presence of the very fast intramolecular distribution of the magnetization via spin diffusion.

Introduction

Physical blending of polymers offers a new route to interesting properties and products.[1] Although the possible number of combinations is endless, only very few polymer pairs form miscible blends. The thermodynamic reason for incompatibility is an endothermic free energy of mixing associated with a diminishing contribution, with increasing molecular weight, of the entropy term.[2] Therefore, mixing of polymers is enthalpy-driven and thus favorable intermolecular interactions must exist for a polymer pair to be "compatible". The ongoing quest for the specific interactions responsible for miscibility on the microscopic level, which ultimately affect macroscopic behavior, can be greatly assisted by high-resolution nuclear magnetic resonance (NMR) spectroscopy.

NMR is particularly useful for examining miscibility at the molecular level. Magnetization transfer between nuclei by dipolar interactions has a distance dependence of $1/r^6$.[3] Thus, microhomogeneity in a blend can be demonstrated by the exchange of magnetization from one polymer to the other. This has been observed in the solid state by both one- and two-dimensional techniques via proton–proton,[4–7] proton–carbon,[8–10] proton–fluorine,[11] carbon–fluorine,[12] and carbon–carbon[13–15] dipolar interactions.

The purpose of the present study is to examine polymer–polymer interactions for blends in concentrated solution for which there are limited experimental data. A strong motive establishing the study of polymer blends in solution is the broad availability and experimental simplicity of solution NMR compared to solid state. Although

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the solid morphology is lost in solution, the interactions responsible for mixing may persist while a significant gain in spectral resolution is simultaneously achieved. The latter may enable observation of specific intermolecular interactions. NMR parameters such as the proton spin-diffusion rate, chemical shift, and line width have been used to probe compatibility for the polystyrene/poly(vinyl methyl ether) (PS/PVME) blend. In solvent cast films of this blend, the solvent significantly affects the miscibility.[16] The blend cast from chloroform yields a heterogeneous film, but toluene yields a homogeneous film. Hence, the ternary system is of special interest.

Experimental Section

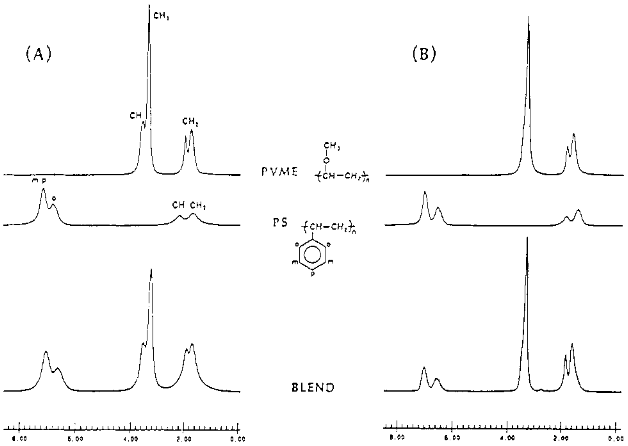
Materials. Two monodisperse polystyrene (PS) samples were obtained from Waters Associates (Milford, MA) having nominal molecular weights of 470 000 (PS-I) and 110 000 (PS-II). The poly(vinyl methyl ether) (PVME) was a secondary standard material, with $M_w = 99\,000$ and $M_w/M_n = 2.12$, obtained from Scientific Polymer Products, Inc. (Ontario, NY). Gel permeation chromatography was performed to confirm the weight distributions and to ensure absence of low molecular weight fractions. The PVME, purchased as a 50% solution in H_2O, was dried in a vacuum oven at 40 °C for at least 48 h. High-purity deuteriated toluene (99.96% D) and chloroform (99.8% D) were obtained from Cambridge Isotopes Laboratories (Woburn, MA) and ICN Biomedicals, Inc. (Cambridge, MA), respectively.

Several samples of pure and blended polymer(s) in toluene-d_8 and chloroform-d_1 were prepared. All samples were weighed and placed into 5-mm NMR tubes, and then deuteriated solvent was added to obtain the desired concentration. Samples were mixed mechanically in the NMR tube, gently degassed on an aspirator for a few hours to remove dissolved oxygen, and sealed. Solutions containing only a single polymer, PVME (ca. 50 and 70 wt %), PS-I (ca. 50 wt %), and PS-II (ca. 50 wt %) were prepared in both toluene-d_8 and chloroform-d_1. Other samples contained both polymers in a 1:1 weight ratio. One such blended sample containing PS-I and PVME in toluene-d_8 was determined to be 60 wt % polymers as determined by subsequent sampling and removal of the solvent in a vacuum oven for 48 h. The proton spectrum showed that this blend was 0.33 mol fraction PS. The same sample composition was prepared in chloroform-d_1. Five additional solutions containing PS-II and PVME in a 1:1 weight ratio in toluene-d_8 were also prepared at 30, 40, 50, 60, and 70 wt % polymer. These last samples were used in the concentration study and were not degassed since some solvent was lost and dissolved oxygen was found to have a negligible contribution to the relaxation.

Since solution concentration was very high, mixing was found to be an important step in the sample preparation. Mechanical mixing was conducted by inserting a long needle, zigzagged at the bottom, into the NMR tube containing the sample. The needle, fixed to a motor, rotated gently for 12 h. Samples that were not mechanically mixed in this fashion showed no intermolecular nuclear Overhauser effect (NOE) by one-dimensional techniques except following at least 1 month of aging. The dependence of blend miscibility on the solvent was visually apparent in such concentrated solutions. Toluene solutions were clear, and chloroform solutions were opaque.

NMR Spectroscopy. All experiments were performed on a General Electric GN-500 spectrometer at 500 MHz. For the one-dimensional transient NOE experiments,[16,17] the pulse sequence 180° (selective)–t_m–90° was used. The selective pulse, 2.2 ms (230 Hz), inverted the meta/para proton resonance of PS. The observation pulse is preceeded by a mixing time, t_m, during which cross-relaxation occurs. Acquisition was interleaved between experiments with $t_m = 0.2$ s and $t_m = 12$ s (eight scans each) for a total of 24 scans. The difference spectrum was obtained by subtracting the transient NOE spectrum, with $t_m = 0.2$ s, from the equilibrium spectrum, with $t_m = 12$ s.

Phase sensitive two-dimensional NOESY (nuclear Overhauser enhancement spectroscopy) experiments[18,19] were performed with the pulse sequence 90°–t_1–90°–t_m–90°–t_2 and the method of States et al.[21] Five experiments were run consecutively with mixing times equal to 20, 50, 100, 150, and 200 ms. For each experiment, 256 1K complex spectra were aquired with 128 scans each and a +2250-Hz sweep width. The evolution time was incremented to give the same sweep width in the second dimension. The total time required, for the five experiments, was less than 35 h.



$$\text{PVME}\quad -\!\!\left(\text{CH}(\text{OCH}_3)-\text{CH}_2\right)_n\!\!-$$

Figure 1. Proton solution spectra at 500 MHz of PS-I, PVME, and their blend in concentrated solution: (A) in toluene solution; (B) in chloroform solution. The molar ratio of PS-I to PVME in the blend sample is 1:2.

The spectra were processed identically. The free induction decays were digitally filtered by a phase-shifted sine-bell function before a double transform. After being transposed, the first point in the time-domain data was multiplied by 0.5 to reduce ridges along F1 in the final spectrum.[22] The time domain signals were then multiplied by a squared phase-shifted sine-bell function, zero-filled once to 512 data points, and Fourier transformed giving the two-dimensional spectrum. To reduce ridges along the F2 dimension, a projection was obtained by using the first 35 files, smoothed by a seven-point smoothing function, and then subtracted from each file in the corresponding two-dimensional spectrum.[23] Finally, peak integrals were obtained by saving a summed projection (parallel to F1) and curve-fitting the one-dimensional spectrum.

Results and Discussion

Figure 1 shows the proton solution spectra at 500 MHz of the pure homopolymers (PS-I and PVME) and their blend in toluene-d_8 (Figure 1A) and chloroform-d_1 (Figure 1B). The aliphatic region (1–2 ppm) in the spectra of the pure homopolymers overlap in the spectra of the blend, but the other resonances are well resolved. The methoxy resonance in the toluene solution of pure PVME is shielded (ca. 40 Hz) relative to the other resonances as compared to the chloroform solution. The separation of the methine and methoxy resonances of PVME was observed to vary with the mole fraction of aromatic functionality present, from either PS or toluene. For example, with decreasing concentration of PVME in toluene, an increase in the chemical shift separation was observed. But, no change in chemical shift was observed for these resonances when PS in a blended sample was substituted with an equivalent mole fraction of toluene.

1D NOE Measurements and Concentration Dependence. A one-dimensional transient NOE experiment was performed to determine whether intermolecular cross-relaxation does indeed exist and is observable in concentrated solution. This measurement was also expected to confirm the solvent-dependent compatibility of the two polymers. Figure 2 shows the NOE difference spectra obtained for the blend in toluene (Figure 2A) and in chloroform (Figure 2B). In both cases, the aromatic meta/para resonance of PS was inverted by the initial selective pulse. Negative NOE is observed at the methine and methoxy resonances of PVME (ca. 3–4 ppm) for the blend in toluene. Consequently, interpolymer cross-re-

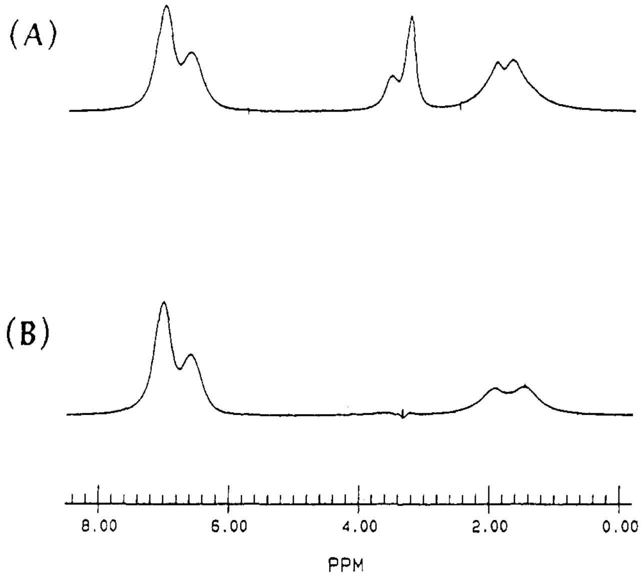


Figure 2. NOE difference spectra for PS-I/PVME blend in toluene (A) and in chloroform (B). Negative NOE is observed at the methine and methoxy resonances of PVME in the toluene solution. No NOE is observed in this region (ca. 3–4 ppm) for the blend in chloroform.

Table I
Concentration Dependence of NOE for Poly(vinyl methyl ether)/Polystyrene (1:1 by Weight) in Toluene at 25 °C

soln concn (wt %)[a]	% NOE[c]	soln concn (wt %)[a]	% NOE[c]
30	0.7	70	72.9
40	6.2	50[b]	0.3
50	24.0	70[b]	2.6
60	57.4		

[a] Total amount of polymer in toluene. [b] PVME only in toluene. [c] Intensity change observed at the methoxy resonance of PVME when the meta/para resonance of PS is irradiated.

laxation is observable in solution and the polymers are intimately mixed. As expected, no NOE is observed in this region for the opaque (phase-separated) mixture in chloroform.

Several concentrations of the blend in toluene (containing PS-II) were prepared to determine the minimum concentration at which interpolymer cross-relaxation can be detected. The meta/para aromatic resonance of PS was selectively saturated for a relatively long period ($>5T_1$) so that a steady-state is reached. Acquisition was alternated, every eight scans, with the saturating field placed off resonance (control spectrum), for a total of 40 scans. The area of the methoxy resonance of PVME was measured with irradiation on and off the PS resonance. Table I reports the relative difference in percent as a function of total polymer concentration. The same saturation experiment was performed on samples of pure PVME (50 and 70 wt %) with irradiation at the frequency of the PS resonance. In both cases, no direct saturation (<3%) of the PVME resonances was observed. The % NOE observed for the 30 wt % blend solution may be considered within experimental error. Hence, the minimum concentration that magnetization exchange can be observed lies between 30 and 40 wt %. All values were reproducible in separate measurements conducted about 3 months later. Figure 3 shows the % NOE plotted vs total polymer concentration. Although the functional dependence between concentration and NOE may be other than linear, a line is drawn since curvature was not found to be statistically significant especially when the first point (30 wt %) is ignored. In any case, extrapolation to 100% NOE, corresponding to complete absence of the PVME resonance, occurs well before 100 wt % total polymer. In addition, since the mole fraction of PS is only half that of PVME, indirect saturation by spin diffusion is expected to contribute significantly. While only a fraction of the PVME may be in close proximity with the PS for direct magnetization exchange, total saturation can occur if relaxation to the lattice is slow enough and if isolated portions of pure polymer do not exceed the size in which complete saturation via spin diffusion can occur.

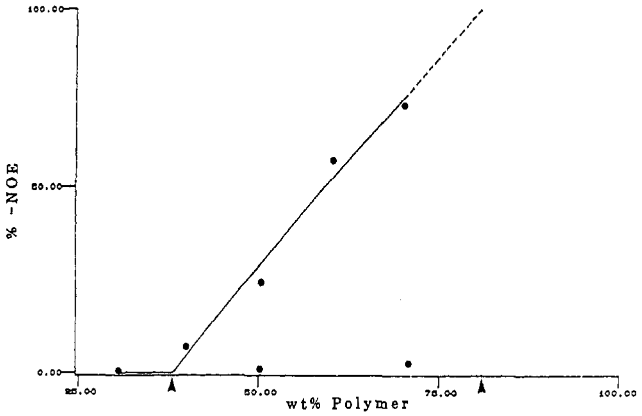


Figure 3. Plot of total polymer concentration (wt %) vs % NOE for blend solutions in toluene. The asterisk indicates samples with PVME only in toluene.

Line-Width Experiments. The temperature dependence of the line width for the pure homopolymers and the blend in toluene was also examined. The line width is inversely related to the spin–spin relaxation time (T_2). A quantitative discussion of the motional effects on T_2 is not pertinent here, except to say that as molecular motion and T_2 increase, the line width decreases. Field inhomogeneities, spin–spin splitting, and tacticity, however, may also contribute to the line width.

Figure 4 shows the aromatic region in spectra of the pure homopolymer (PS-I) and the blend (PS-I/PVME) in a 60 wt % solution from 30 to 107 °C. The meta/para resonance of PS was fitted to a Lorentzian line shape. Figure 5 shows a plot of the line width vs temperature for the pure and blended polymer. At elevated temperature (>55° C), there is a significant decrease in the mobility of the polymer in the blend solution. This represents, perhaps, the start of a phase separation. Between 100 and 110 °C a gross phase-separation (opaque solution) occurs. The curves, however, were not clearly reproducible with a solution of PS-II and a 50 wt % blend solution. A problem associated with this type of experiment is solvent evaporation and condensation in the tube leading to concentration gradients.

2D NOESY Experiment. The two-dimensional NOESY (nuclear Overhauser enhancement spectroscopy) experiment is completely analogous to the one-dimensional transient experiment.[24,25] However, the 180° pulse in the one-dimensional experiment cannot be fully selective. Instead, the 2D NOESY experiment was chosen which permitted the simultaneous observation of the spin-diffusion pathways. The two-dimensional phase-sensitive spectrum with t_m = 200 ms is shown in Figure 6. The diagonal and cross peaks are both phased positively, indicating that the correlation time for molecular tumbling is in the slow-motion limit. Cross peaks representing both intra- and intermolecular exchange of magnetization during the mixing time are observed. Intermolecular cross peaks between the aromatic resonances of PS and the methine and methoxy resonances of PVME are circled.

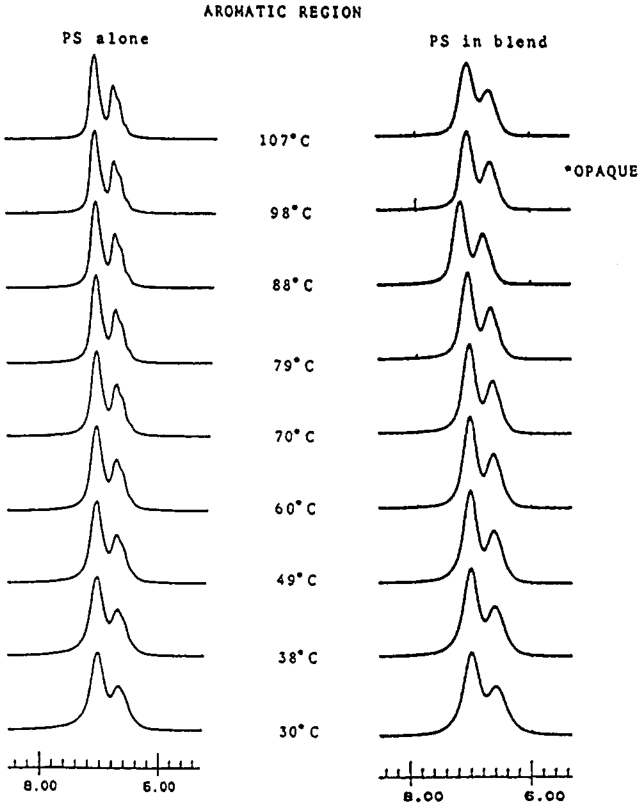


Figure 4. Aromatic region in spectra of the pure homopolymer (PS-I) and the blend in toluene at ca. 10 °C increments. A visible-phase separation of the blend solution occurred between 100 and 110 °C.

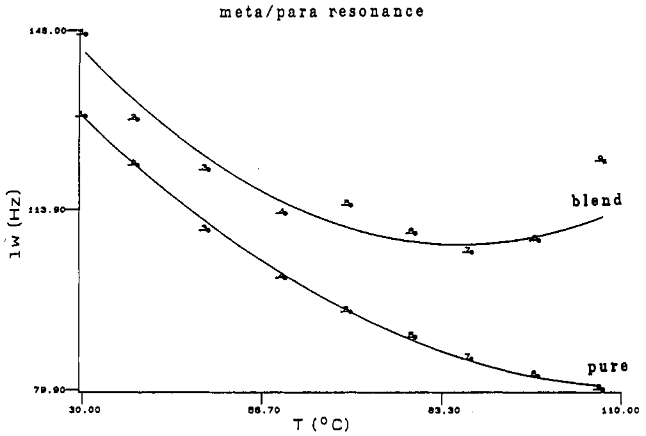


Figure 5. Plots of the meta/para line width from spectra in Figure 4 vs temperature. The top curve is for the blended sample (PS-I:PVME, 1:2 mole ratio), and the lower curve is for the pure polymer (PS-I). The data point at 107 °C, in the top curve, is after the gross phase separation.

Possible intermolecular cross peaks involving the aliphatic protons are obscured since the aliphatic regions for the two polymers overlap.

A series of mixing times was employed to measure intra- and intermolecular spin-diffusion rates. The initial time development of a cross-peak volume is equivalent to the cross-relaxation rate between two protons. Relative interproton distances (r_{ij} and r_{kl}) can be obtained from the cross-relaxation rates (σ_{ij} and σ_{kl}) since

$$(r_{ij}/r_{kl}) = (\sigma_{kl}/\sigma_{ij})^{1/6}$$

assuming a single correlation time.[26-29] Figure 7 shows stacked plots of peaks in the circled region of Figure 6 at the various mixing times and their assignments (F2 ← F1).

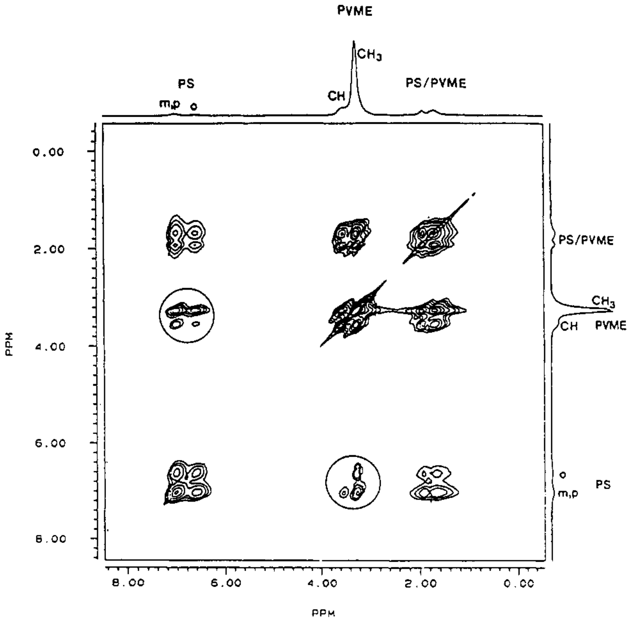


Figure 6. Two-dimensional phase sensitive NOESY spectrum of the PS-I/PVME blend (60 wt %) in toluene. The mixing time is 200 ms. Inter-polymer cross peaks between the aromatic protons on PS and the methine and methoxy protons on PVME are circled.

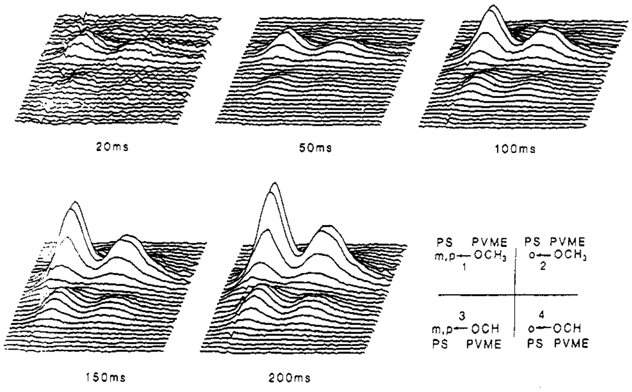


Figure 7. Three-dimensional plots showing the time development of peaks in the circled region in Figure 6.

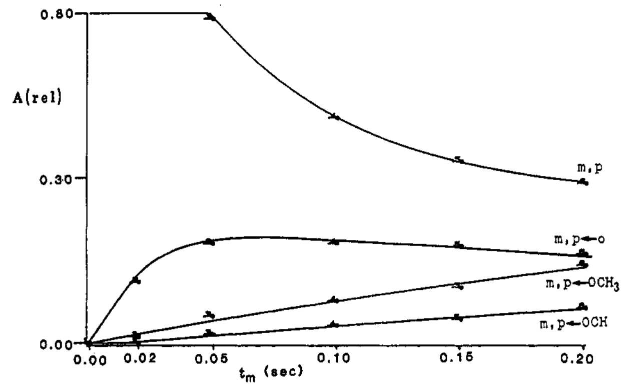


Figure 8. Relative cross peak areas vs mixing time for peaks 1 and 3 in Figure 7, the intramolecular cross peak between the meta/para and ortho protons of PS and the diagonal meta/para resonance.

Figure 8 shows the cross-peak integrals as a function of mixing time for peaks 1 (m, p ← OCH_3) and 3 (m, p ← OCH) in Figure 7 representing intermolecular exchange along with the intramolecular cross peak between the meta/para and ortho protons of PS and the diagonal decay of the meta/para resonance. Peak integrals are normalized relative to the area of the diagonal peak (at F2) at zero mixing time ($A_{ii}(0)$) which was obtained by extrapolation using the relationship

$$A_{ii}(t_m) = A_{ii}(0) \exp(-D/t_m)$$

where $A_{ii}(t_m)$ is the peak area at mixing time t_m and D is the decay constant.

Several inferences can be made from inspection of the curves in Figure 8. It is immediately apparent that the intramolecular cross relaxation (m,p ← o) reaches equilibrium well before the intermolecular (m,p ← OCH or m,p ← OCH_3). Evaluation of the initial slopes after a least-squares fit to an exponential indicated that the intramolecular cross-relaxation rate is at least 1 order of magnitude larger than the intermolecular rate. The intermolecular rates are very nearly equivalent after accounting for differences in spin population. Hence, very fast intramolecular redistribution of the magnetization renders the intermolecular spin-diffusion rates indistinguishable. A relaxation matrix approach to deconvolute the direct and indirect exchange was not attempted. Since the aliphatic regions overlap and such a dataset should contain most of all the proton neighbors, too many matrix elements would be missing. An induction period, which indicates indirect or two-step exchange of magnetization, however, may be evident in the bottom curve. While indirect paths are no doubt present, it is difficult to detect the very short induction periods that would be expected with longer correlation times.[30]

Conclusion

The examples shown in this work suggest that "polymer–polymer" interactions of miscible polymer blends are preserved in concentrated solution and with a significant increase in spectral resolution. Miscibility and interactions can subsequently be examined through various means. The observation of magnetization exchange between polymers indicates that the polymers are intimately mixed because of the distance dependence of cross relaxation. The minimum concentration for detection of intermolecular cross relaxation for polystyrene/poly(vinyl methyl ether) in a 1:1 weight ratio in toluene is between 30 and 40 wt % total polymer. Intimate mixing may also be reflected in chemical shift behavior of the methoxy resonance of PVME that indicates a change in the electronic environment upon changing the ratio of PVME to the total aromatic functionality.

Line width vs temperature plots indicate that the onset of the phase separation may be observed by NMR well before the gross phase separation is visible. The resolution advantage in solution experiments could be utilized to determine the role of individual functionalities in the mixing. In the 2D NOESY experiment, the large competition from intramolecular spin diffusion may prohibit the separation of specific interactions. Indirect paths of magnetization exchange, as evidenced by an induction period in the time development of the NOE, are difficult to recognize conclusively since long correlation times make this period very short. Specific cross-relaxation rates between single resonances of each polymer may be obtainable by deuteriation of all other resonances or saturation of those resonances in the recycle delay and mixing time during the 2D NOESY experiment.[30]

Since the solid morphology is lost, solution experiments cannot replace those done in solid state but may supply complementary information or be useful where there is insufficient resolution in the solid-state spectrum. ^1H–^1H magnetization exchange experiments avoid selective deuteriation or isotopic enrichment required in experiments for the observation of ^1H–^{13}C or ^{13}C–^{13}C exchange, respectively. Finally, the solution experiments may be attractive because of the broad availability and comparable experimental simplicity to the solid-state analogues.

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Registry No. PS, 9003-53-6; PVME, 9003-09-2; toluene, 108-88-3.

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