Two-Dimensional NMR of Synthetic Polymers: Polymer Blend Miscibility at the Molecular Level

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ABSTRACT: Two-dimensional NMR is used to probe polymer blend interactions. The nuclear Overhauser effect (NOE) results in correlation peaks when polymer chains approach within 5 Å of each other. Polymers studied include poly(*N*,*N*-dimethylacrylamide) (PDMA) blended with poly(styrene-*co*-styrenesulfonic acid) [P(S–SA(12))], polystyrene (PS), poly(4-vinylphenol) (PVPh), and poly(styrene-*co*-vinylphenol) [P(S–VPh-(22))]. Interactions between polymers and between polymer and solvent (dimethyl sulfoxide (DMSO-d_6) or pyridine (PYD-d_5)) are discussed. When strong interactions (ion–ion or hydrogen bonding) between polymers are present, the two polymers mix well and show strong correlations by 2D-NOESY. When the solvent can effectively compete with PDMA, by abstracting a hydrogen or acting as a hydrogen bond acceptor, phase separation can occur. Subtleties of the experiment and polymer blend structures are discussed.

Introduction

Two-dimensional nuclear Overhauser effect spectroscopy (2D-NOESY) has been used extensively over the last 10 years for structural characterization of biological macromolecules.[1,2] Only a few 2D-NOESY studies on synthetic polymers have appeared. A number of inherent differences exist between synthetic polymers and biological polymers. Biomolecules offer advantages amenable for NOESY experiments not available with synthetic polymers (see discussion below). This report discusses the application of 2D-NOESY to polymer blends.

2D-NOESY is an NMR correlation experiment. Diagonal resonances in the 2D contour plots represent the normal 1D spectrum. Cross peaks are correlations between spins at different chemical shifts. Chemical shifts fall on the two axes (see, for example, Figure 3). Two types of interaction are observable: (1) through-space (dipole–dipole interactions) and (2) chemical exchange. For this work, phase-sensitive 2D-NOESY is used to probe interactions between different polymer chains in polymer blends.

Several restrictions limit the measurement of dipole–dipole interactions. These fall into two broad categories: distance restrictions and motional restrictions. The nuclear Overhauser effect falls off as the inverse sixth power (r^{-6}) of the distance separating interacting nuclei. Therefore, only nuclei in close proximity (2–5 Å) show NOE cross peaks. The distance between protons is determined from the initial buildup rate (see below) and the relative intensity of the cross peaks. Typically, strong cross peak intensities signify the interacting nuclei are 1.8–2.7 Å apart, medium cross peaks that nuclei are 1.8–3.3 Å apart, and weak cross peaks that nuclei are 1.8–5.0 Å apart.[2]

Motional restrictions also play a large role in determining the intensity of NOE cross peaks.[2-7] Cross peak intensity depends upon the effective correlation time[5] (τ_c) or the time that it takes interacting protons to realign themselves. At a correlation time of 0.3 ns, the cross relaxation rate is zero (internal bond rotations weaken the interactions) and no cross peaks are observed (at 500 MHz for ^{1}H).[5] When cross relaxation rates are faster or slower than determined by the above correlation time, NOEs are classified as in the fast-motion limit or slow-motion limit.[6] Cross peaks appear out of phase or in phase (with the diagonals) in the fast-motion and slow-motion limits, respectively. If $\omega\tau_c > 1.12$ (where ω is the spectrometer frequency) the NOE effect will be negative. If $\omega\tau_c < 1.12$ the NOE will be positive. When $\omega\tau_c$ is approximately 1, the NOESY spectra may not show cross peaks for protons within 5 Å of each other. In this case, the rotating frame Overhauser effect spectroscopy (ROESY) experiment is preferable. In the ROESY experiment, the cross peaks always appear as positive intensities. Although the overall intensities are usually lower (compared to NOESY), ROESY is necessary for synthetic polymers of intermediate size (molecular weight approximately 2–15K) and has other advantages discussed below. In the ROESY experiment, a field gradient pulse or a series of equally spaced 180° pulses are applied during the mixing time. This locks the magnetization in the X–Y plane and delays relaxation along the Z axis or gives a dependence based on $T_{1\rho}$ rather than T_1.

The distance nuclei are from each other determines the strength of their dipolar interaction. However, at longer mixing times polymer chains have more time to interact and longer distances can be measured for a given τ_c. All diagonal and cross peaks decrease and eventually disappear, however, if the mixing time is much longer than the spin–lattice relaxation times (the time during which NOE interactions take place).

Any condition that mighty hold the polymer chains in close proximity for a longer period of time (chemical interactions are considered below) increases the probability of 2D-NOESY revealing intermolecular interactions. Local motions attenuate NOEs by moving the interacting protons away from each other and by enhancing other, nondipole–dipole interaction, relaxation mechanisms. For biopolymers, interactive forces restrict local motions relative to similar motions in synthetic polymers. Therefore, polymer entanglements are necessary for NOEs to be seen in synthetic polymers. For effective entanglements to occur, polymer molecular weights in excess of 20 000 are desirable. Also, high weight percent solutions are necessary.[5,6]

Spin diffusion often leads to uncertainties in measuring NOEs by increasing cross peak intensities through relayed interactions. This is especially problematic when long mixing times, as used in our work, are employed. Many solutions to this problem have been proposed.[8-12] One solution is to use ROESY. As stated above, ROESY cross peaks are positive if direct distances are measured. If

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spin diffusion from a third nucleus is present, the cross peaks will be negative. From our work, since we are observing interactions between different polymers with distinct chemical shifts, even if the cross peaks are mediated by cross relaxation the polymer chains still must be close (within 5 Å), or no cross peaks would appear. Also, the buildup rate for cross peaks mediated by spin diffusion show a modified dependence. If spin diffusion is a contributing factor to cross peak intensities, a lag period appears at short mixing times.

Biopolymers have unique sequences of monomer units and well-defined three-dimensional structures. Proton resonances can frequently be assigned to specific sites. Synthetic polymers, on the other hand, are more likely to have a random coil configuration and contain a statistical distribution of stereocenters or defects. Since segmental motion averages dipolar interactions, correlation times for high molecular weight synthetic polymers will approximate those of small, rigid biopolymers. Even though the magnitude of dipolar interactions is similar to that of small proteins, in terms of inhomogeneous line broadening, synthetic polymers behave like the extremely large molecules that they are.

Synthetic polymers fail to show the chemical shift specificity of biopolymers, but they do show other unique specificity aspects such as tacticity and sequencing sensitivity. Two-dimensional experiments, since they present cross peaks only between specific protons, often given connectivities between specific protons within broad overlapping resonances in the one-dimensional spectrum. By cross-referencing these specific interactions with specific protons, more complete spectral assignments and a better understanding of polymer packing and polymer/polymer interactions in blends is obtained.

In a previous report,[13] the miscibilities of an amide polymer, poly(*N*,*N*-dimethylacrylamide) (PDMA), with acidic polymers such as poly(4-vinylphenol) (PVPh) and poly(styrene-*co*-styrene-4-sulfonic acid) (P(S–SA)) were investigated. It was found that phase separation between the polymers did occur when cast from certain solvents, even when the two polymers were themselves thermodynamically miscible. It was also found that in some solvents, the polymers complex and form a gel or precipitate. A fair amount of work has been reported on polymers that form mutual precipitates or complexes when they are combined from certain solvents. Many of these involve polymers where one contains an acidic functionality. Morawetz et al.[14] studied the phase separation of poly(methyl methacrylate) (PMMA) and polystyrene (PS) when methacrylic acid is copolymerized with methyl methacrylate and vinylpyridine with styrene. Solvent effects on polymer complexation have been studied for blends of poly(acrylic acid) (PAA) or poly(methacrylic acid) with poly(ethylene oxide) or poly(*N*-vinyl-2-pyrrolidone). Several groups[15–21] have studied mixtures of PDMA or its isomeric form poly(ethyloxazoline) with PAA, phenol–formaldehyde resins, or PVPh in terms of the glass transition temperatures (T_g) of blends formed when the polymers undergo complex formation in solution as compared to simple blends.

Polymer blends are often prepared via some type of solution-casting technique. In such circumstances, equilibrium miscibility may be shadowed by solvent-induced phase separation, or the $\Delta\chi$ effect,[22,23] where phase separation of polymers in solution is enhanced when polymer–solvent interactions are different, although the two polymers may be miscible in the bulk. Therefore, whenever polymers are blended in, and cast from, solution, one must regard the system as a ternary system of two polymers and a solvent, each pair having its own interaction parameter. Knowledge of the phase diagrams and interaction equilibria in solution are therefore of extreme importance.

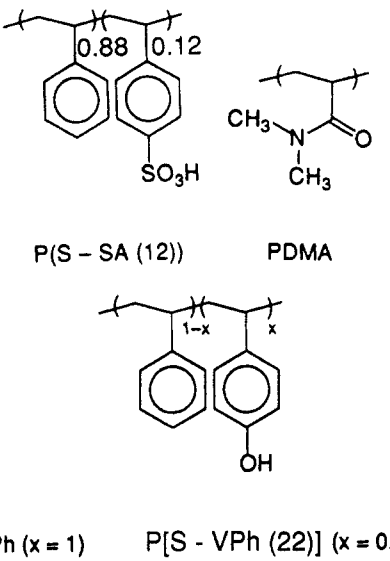


Figure 1. Structures for poly(styrene-*co*-styrenesulfonic acid) (PS–SA(12)), poly(*N*,*N*-dimethylacrylamide) (PDMA), poly(4-vinylphenol) (PVPh), and poly(styrene-*co*-vinyphenol) [P(S–VPh(22))], the polymers used for this study.

The present work utilizes primarily 2D NMR to elucidate the nature and proximity of specific interactions between polymers and to explain some of the observed phase behavior.

Experimental Section

Polymers. Poly(*N*,*N*-dimethylacrylamide) was purchased from Polysciences. The polymer was further purified by dissolving it in water and filtering the solution through Celite to remove insoluble gel. The solution was then freeze-dried, followed by drying at 90 °C for 24 h under vacuum. The molecular weight was determined by size exclusion chromatography (SEC) using PW gel columns in a 5% poly(ethylene glycol) in water solution. The molecular weight $\bar{M}_w$ was 490K in polysaccharide equivalents and the molecular weight distribution was broad. The following polymers were synthesized in this laboratory and the details are reported elsewhere.[13] Poly(4-vinylphenol) has an absolute molecular weight (as determined by SEC with viscosity detection and universal calibration curve) $\bar{M}_w$ = 35.0K, with $\bar{M}_w/\bar{M}_n$ = 1.7. Poly(styrene-*co*-4-vinylphenyl) [P(S–VPh(22))] is a random copolymer of styrene and 22 mol % vinylphenol and has a polystyrene equivalent molecular weight (determined on the protected polymer) of $\bar{M}_w$ = 95.6K with $\bar{M}_w/\bar{M}_n$ = 2.0. Poly(styrene-*co*-styrene-4-sulfonic acid) [P(S–SA(12))] is a random copolymer containing 12 mol % sulfonic acid monomer and has a $\bar{M}_w$ = 241.0K and $\bar{M}_w/\bar{M}_n$ = 3.0. The structures of these polymers are shown in Figure 1.

Deuterated solvents were obtained from MSD Isotopes as sealed ampules, which were used immediately upon opening. *N*,*N*-Dimethylpropionamide was obtained from Aldrich and used as received.

Preparation of Blends. Generally, the polymer blends and complexes were prepared by dissolving each component in a common, good solvent at a level of 1 or 5 wt %. The solutions were then combined in the desired amounts. If the solution was stable, it was then cast into a shallow dish and the solvent was removed slowly in order to obtain equilibrium conditions. For the blends that formed precipitates or gels, one component solution was added dropwise, under continuous mixing, to the other solution. The precipitate or gel was removed by filtration and dried. For these blends, the compositions studied were in general formulated so that there was an equimolar amount of

Table I. Blend Compositions

poly-1	poly-2	feed wt ratio poly-1/ poly-2	solvent	concn (wt %)	result
PDMA	P(S–SA(12))	1:8.3	MEK	1	clear gel
PDMA	P(S–SA(12))	1:10	MEK	1	clear gel
PDMA	P(S–SA(12))	1:10	pyridine	5	opaque film
PDMA	PVPh	1:1.2	MEK	1	white ppt
PDMA	PVPh	1:1.2	MEK, acetone	5	clear gel
PDMA	PVPh	1:10	pyridine	5	clear film
			DMF		clear film
PDMA	P(S–VPh(22))	1:4.2	MEK	1	clear gel
PDMA	P(S–VPh(22))	1:10	MEK	1	clear gel
PDMA	PS	1:10	pyridine	5	opaque film

donor and acceptor groups. The observed phase behavior for these blends is summarized in Table I.

Blend samples for NMR experiments were prepared as follows. Blends of PDMA and P(S–SA(12)) were prepared by dissolving each component in MEK at a concentration of 1 wt %. The PDMA solution was added dropwise to the P(S–SA(12)) solution with continuous stirring. A white gel immediately appeared. Although complexation occurs instantaneously, the final solutions were allowed to mix for several hours. Then the precipitate or gel was removed via filtration and dried under vacuum from ambient temperature to a temperature that is close to the glass transition temperature of the blend. The resulting blend was optically clear. This blend was then redissolved in the NMR solvent of choice (either DMSO-d_6 or PYD-d_5 at a concentration of 20 wt %) and the NMR spectra were collected. An alternative method of sample preparation, which consisted of mixing the desired dry amounts of each blend component directly in the NMR tube and then adding DMSO-d_6 or PYD-d_5 to dissolve the polymers, was also evaluated. This method gave the same NMR results as the first method and therefore was adopted for all subsequent blend preparations. The final solutions were at least 20 wt % solids unless otherwise specified.

Experimental Techniques. Transmission electron microscopy (TEM) was performed on thin (750 Å), microtomed sections using a JEOL JEM 100CX-II (JEOL Ltd., Tokyo, Japan) transmission electron microscope. The samples were not stained, the inherent contrast between the polymers being sufficient.

NMR spectra were obtained at 500 MHz on a Bruker AM 500 spectrometer using the $(\pi/2\text{-}t_1\text{-}\pi/2\text{-}t_m\text{-}\pi/2\text{-acquire})_n$ pulse sequence with a mixing time (t_m) varying from 0.05 to 0.80 s (0.10–0.40 s gave the best spectra). Standard NOESYPH (phase-sensitive NOESY) phase cycling[1] was used. The free induction decays (fid's) were processed with shifted sine bell multiplication. Pulse repetition rates in excess of 3 s were used. The solvent is designated in the text and figure captions (either DMSO-d_6, or PYD-d_5). The 2D-NOESY spectra consist of 128 or 256 incremented spectra. Spectra were obtained at a temperature of 25 °C.

Results and Discussion

Homogeneous blends between PDMA and PVPh or P(S–SA(12)) can form if specific interactions between the two polymers take place. This interaction may be either hydrogen bonding or proton transfer, the latter giving rise to the formation of ion pairs. Either of these interactions should bring the two polymer chains in close enough proximity for dipole–dipole relaxation between protons on the two chains to take place and thus give rise to NOE cross peaks. Correlations between the PDMA methyl resonance and aromatic resonances on the proton donor polymers should be ideal for NOESY cross peaks since these resonances are well-separated in the 1D proton spectrum. Other studies on similar blends with P(S–SA)[24–28] and with PDMA/PVPh[29] have been reported.

PDMA/P(S–SA(12)) Blends. Figure 2 contains 1D spectra for the PDMA/P(S–SA(12)) blends prepared in MEK, dried, and redissolved at 20 wt % in DMSO-d_6 (A) and PYD-d_5 (B). Resonance assignments are shown in the figure. In addition to the slight solvent-induced shifts, the main difference in the two spectra is the significant downfield shift of the aromatic protons ortho to the sulfonic acid group (H_f) in PYD-d_5. The 1D spectrum (not shown) of P(S–SA(12)) in *N,N*-dimethylpropionamide ($C_2H_5CON(CH_3)_2$ (DMP), a model compound for PDMA) shows a small shift in the aromatic protons ortho to the sulfonic acid group. Table II shows the chemical shift difference between the PS meta and para protons and the protons ortho to the sulfonic acid group. The shift in DMSO-d_6 is the slightest so this is taken as zero. These shifts indicate a significant change, such as deprotonation of the sulfonic acid group, both when PYD-d_5 and when DMP are the solvent as reported by others.[24]

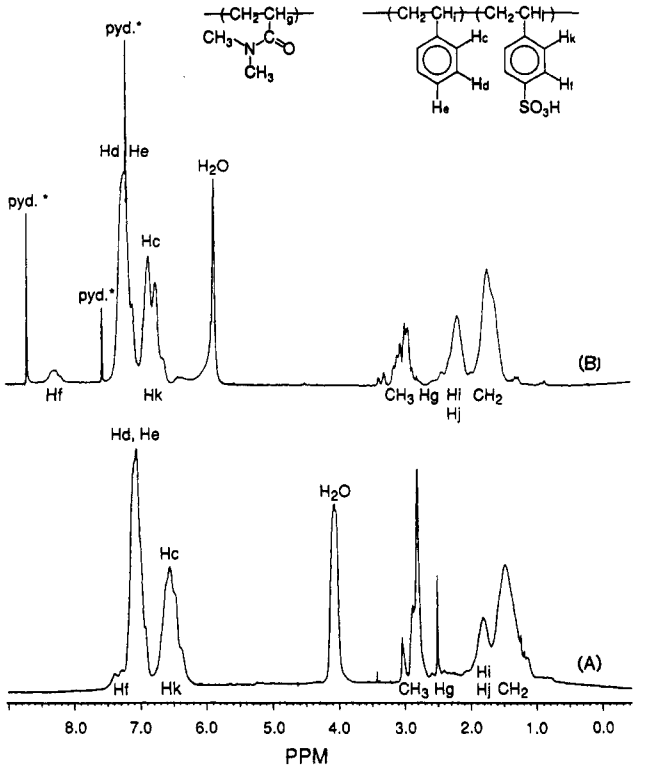


Figure 2. One-dimensional proton NMR spectra of PDMA/P(S–SA(12)) (1/8.3) blends dissolved in (A) DMSO-d_6 (20 wt %) and (B) PYD-d_5 (25 wt %). The blend composition was such that an equal molar number of interacting groups were present (i.e., number of sulfonic acid groups = number of PDMA monomeric units).

Table II. Solvent-Induced Shifts

sample	solvent	shift[a] (ppm)
PDMA/P(S–SA(12))	DMSO-d_6	0.00
PDMA/P(S–SA(12))	PYD-d_5	0.75
P(S–SA(12))	DMP	0.25

[a] The chemical shift is for the protons ortho to the sulfonic acid group in P(S–SA(12)). All shifts are referenced to the shift of this proton in a DMSO-d_6 solution of the PDMA/P(S–SA(12)) blend. When pyridine is the solvent, the resonance shifts 0.75 ppm downfield, and when *N,N*-dimethylpropionamide (DMP) is the solvent, the resonance (in P(S–SA(12)) alone) is shifted 0.25 ppm.

The 2D-NOESY spectrum (contour plot) for this blend in DMSO-d_6 is shown in Figure 3. Resonance A is a cross peak between PS aromatic protons ortho to the polymer backbone and the PS methine proton. Resonance B is a correlation between the same PS aromatic protons and the methylene protons. Resonances C and D are cross peaks between the meta and para aromatic PS protons and the methine and methylene protons. Cross peaks A

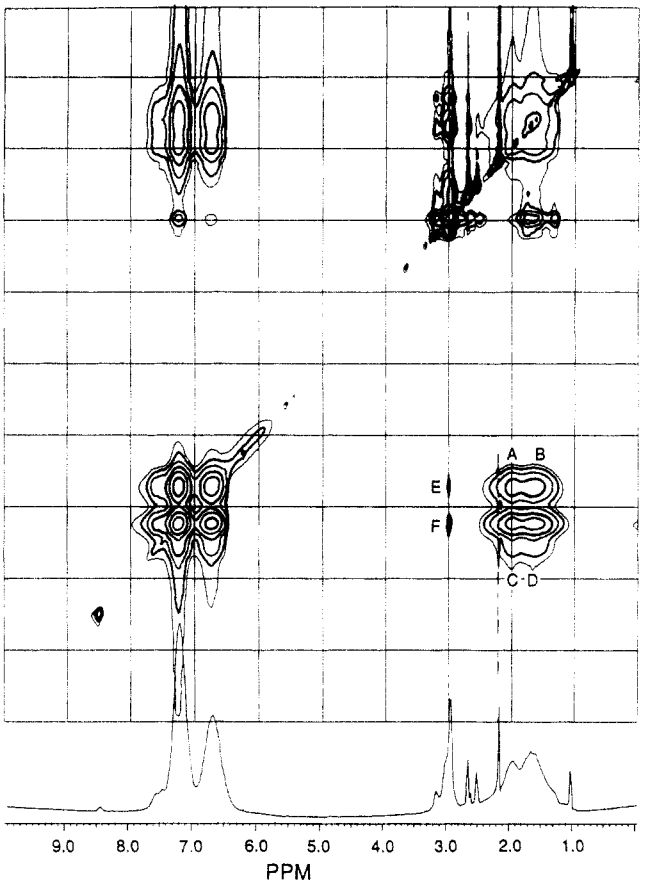


Figure 3. 2D-NOESY spectrum of the blend show in Figure 2A (25 wt %), mixing time 0.40 s.

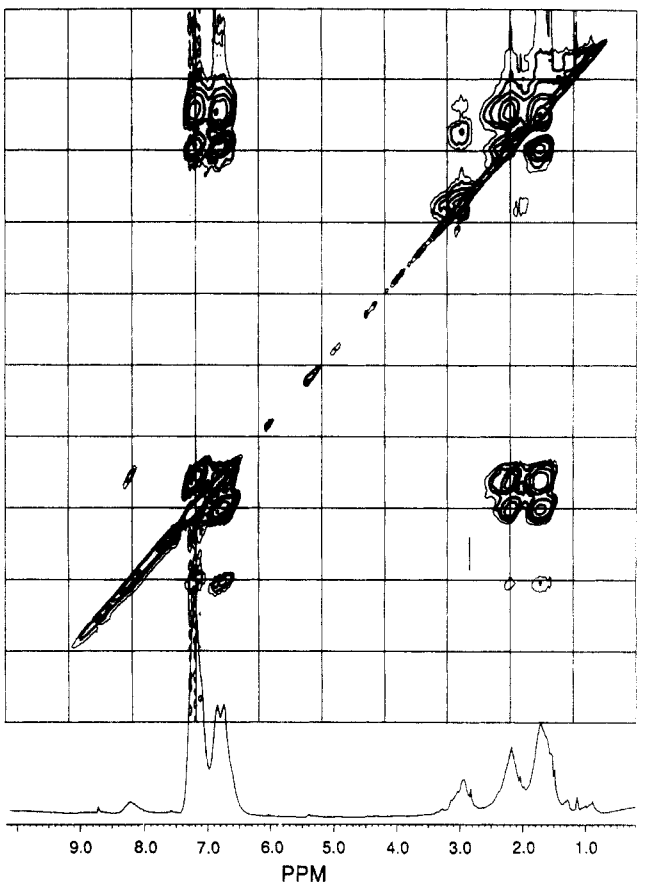
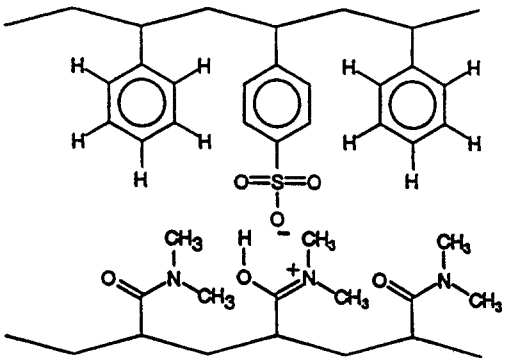


Figure 4. 2D-NOESY spectrum of the blend shown in Figure 2B, mixing time 0.40 s.

and B probably represent intramolecular interactions between neighboring protons. Resonances C and D, since they are more intense than A and B and represent correlations between aromatic protons further from the backbone protons, probably represent intermolecular interactions with another P(S–SA(12)) chain or a chain that has folded back on itself. Although these results are not quantitative, the concentrations used and the growth of cross peaks as a function of mixing time (see below) suggest these interactions are intermolecular. Resonances E and F (Figure 3) are intermolecular cross peaks between the ortho (to the backbone) aromatic protons (E) or meta and para aromatic protons (F) of PS and the methyl protons of PDMA. The cross peak between the meta and para PS protons and the *N,N*-dimethyl protons is significantly larger that that between the ortho (to the backbone) PS protons and the *N,N*-dimethyl protons. This is reasonable, since the meta and para protons would be expected to be closer if the PDMA approaches the copolymer from the pendant sulfonic acid group (Scheme I—assumes noninteracting solvent, DMSO). No cross peaks were obtained between protons on the sulfonic acid group where these resonances were separate from PS protons (i.e., those ortho to the sulfonic acid group and the acidic proton). The 2D-NOESY spectrum of this blend in PYD-d_5 (Figure 4) shows no intermolecular cross peaks between the two blend components.

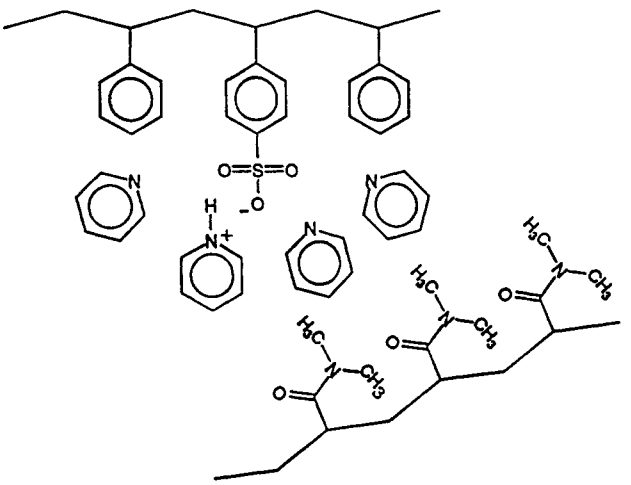
Blends of PDMA and P(S–SA(12)) prepared in pyridine are stable in solution, but when the solvent is evaporated, the resulting material is an opaque, inhomogeneous blend. Those prepared in MEK or acetone gel precipitate immediately and separate from the solvent. However, the resulting blends are homogeneous. Transmission electron microscopy (TEM) performed on a 50/50 (by weight) blend prepared from pyridine revealed the presence of a micron-

Scheme I



size-dispersed phase in contrast to results on the blend prepared from MEK, where no phase separation was observed by TEM. The pyridine nitrogen is more basic than the amide carbonyl oxygen of PDMA and thus would preferentially abstract the sulfonic acid proton. The 1D spectrum in pyridine shows that the sulfonic acid group exists as the anion. Coulombic interaction has been shown to occur in blends of poly(vinylpyridine) and poly(styrene-*co*-styrenesulfonic acid) between the pyridinium and sulfonate ions formed by transfer of a proton from sulfonic acid to the pyridine moiety.[28] In the present case, ion–ion interactions between protonated solvent and sulfonate groups tend to exclude the PDMA (Scheme II), resulting in the two polymer phases separating upon drying. The 1D spectrum in DMSO-d_6 gives less evidence for proton abstraction, owing perhaps to the decreased concentration and strength of the hydrogen-abstracting group and the decreased strength of the ion–ion interaction. The shift for the ortho protons on the aromatic sulfonic acid ring will be a weighted average of protonated and deprotonated species and also reflect the abstracting strength. Since

Scheme II



the molar ratio of sulfonic acid groups in the copolymer to amide groups in PDMA homopolymer is 1:1, conformational restrictions of the polymer chains allow only a small portion of the sulfonic acid groups to interact at any one time. The ratio of pyridine to sulfonic acid is, of course, high, so deprotonated sulfonic acid will predominate in the pyridine spectrum. If the concentration of amide groups were increased as was the case when DMP was used as solvent, then deprotonation would be expected. The 1D spectrum shows this (Table II) and shows a shift in the proton ortho to the sulfonic acid. This indicates that the concentration of interacting groups affects the shift observed in the 1D spectrum. The magnitude of the shift reflects the strength of the interaction. This interaction is much stronger with PYD-d_5 than with DMP. All the spectroscopic evidence suggests that the interaction observed is one of proton abstraction followed by an ion–ion interaction.

NOE cross peaks seen in the DMSO-d_6 2D-NOESY spectrum establish an interaction between the two polymers [PDMA and P(S–SA(12))] when the blend is formed out of MEK and redissolved in DMSO-d_6. The cross peaks are weak, suggesting that the two polymers approach within 1.8 and 5.0 Å of each other. In solutions (DMSO-d_6) containing less than 10 wt % PDMA/P(S–SA(12)) no intermolecular cross peaks were observed. This suggests that the concentration of polymer chains must be large enough to force the PS close to the PDMA chains, where it is already held by an ion–ion interaction between SA(−) and PDMA(+).

The groups that are in close proximity are the PDMA methyls and the protons on the PS ring, not those ortho to the sulfonate on the SA ring (see Scheme I). This is probably due to the geometry at the polymer interaction site (see discussion below). The aromatic protons on the ring with the attached sulfonic acid may be held too far from the PMDA methyl protons. The presence of these cross peaks is interesting in that these groups normally prefer not to come into close contact, but in these blends are held within 5 Å of each other. The blend of PDMA/PS (normally immiscible) is insoluble in DMSO-d_6. In PYD-d_5, the PDMA/PS 25 wt % solution shows no intermolecular cross peaks.

PDMA Homopolymer. Figure 5 is the 2D-NOESY spectrum of PDMA homopolymer dissolved in DMSO-d_6. Resonances marked A are the backbone methylene protons. Those marked B are the methine proton resonances, and those marked C are the *N,N*-dimethyl resonances. The cross peaks in the box marked D represent correlations between the methyl protons and the methine proton. There

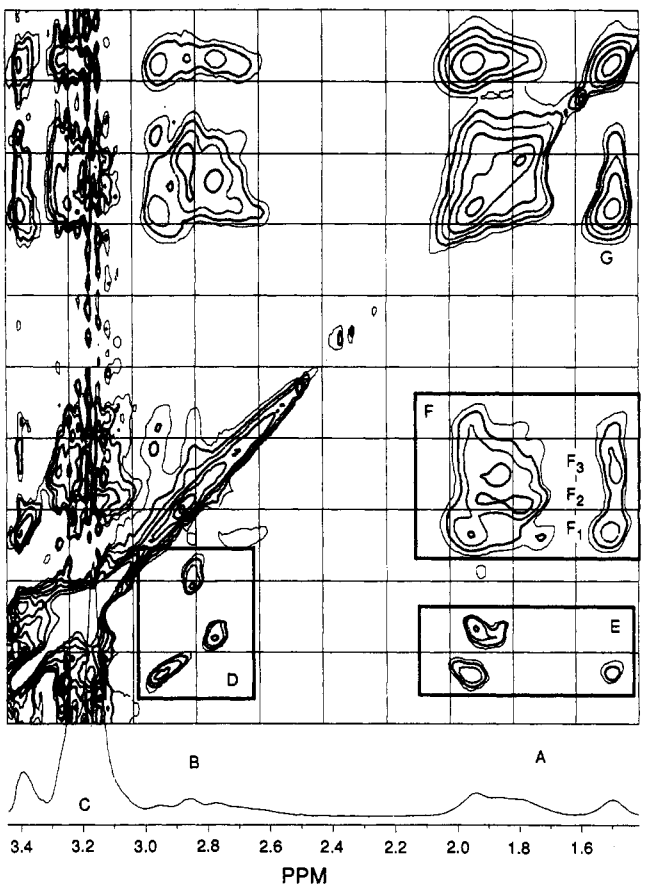


Figure 5. 2D-NOESY spectrum of a 20 wt % solution of PDMA in DMSO-d_6, mixing time 0.30 s. The assignments are discussed in the text.

are several correlations (correlations between resonances at three different chemical shifts) because the PDMA is atactic. Since there are three resonances, it is conceivable that they represent correlations between isotactic, heterotactic, and syndiotactic triads.

Cross peaks in the E box are due to correlation between methyl protons and methylene protons. Cross peaks in the F box are due to correlations between the methine proton and methylene protons. The cross peak labeled G is a correlation between nonequivalent methylene protons and must be due to an isotactic pair. By tracing which methyl protons and which methine protons correlate to these isotactic methylene protons, we can assign the isotactic and part of the heterotactic triads. The resonance at approximately 1.8 ppm, which is due to a syndiotactic methylene pair, has no cross peak to the *N,N*-dimethyl groups. This suggests that for the most part the correlations are between intermolecular pairs (or distant intramolecular groups folded back upon the chain), since intramolecular pairs should have similar distances between the backbone protons and the methyl protons regardless of tacticity. On the other hand, accessibility of the backbone protons on one chain to the methyls from another chain would be greater if the pendant groups were all on one side (isotactic). This spectrum shows the detail that can be obtained using 2D-NOESY on synthetic polymers.

PDMA/PVPh Blends. Close inspection of Figures 5 and 6 shows that the cross peaks between the methine protons and methylene protons of PDMA (Figures 5 and 6) and PVPh (Figure 6 only) would be at different locations in the spectrum. This can be seen by drawing horizontal lines from the aromatic cross peaks (cross peaks above B and to the right of C) into the backbone protons. These lines do not go through the cross peaks between the PDMA

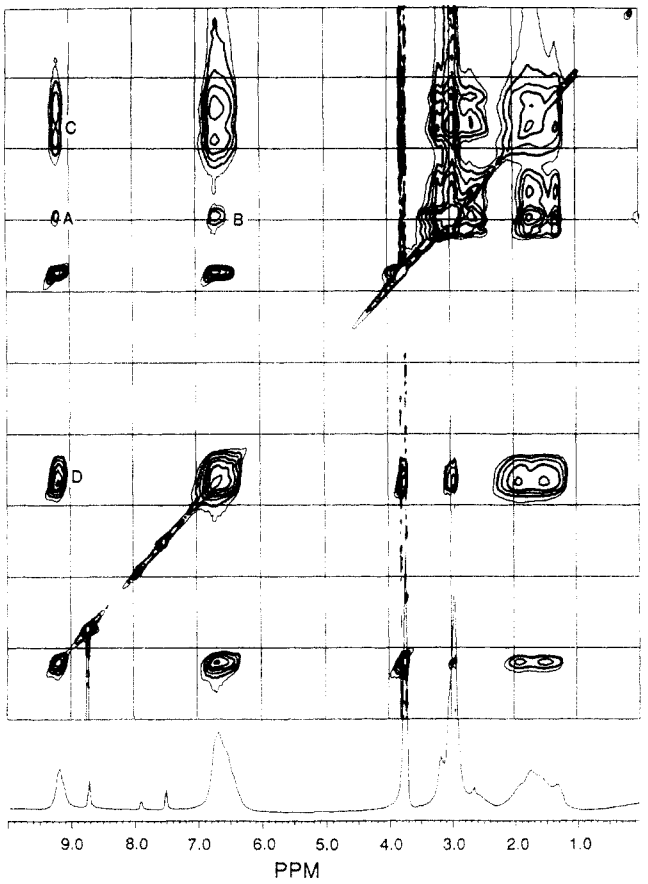


Figure 6. 2D-NOESY spectrum of a 25 wt % solution PVPh/PDMA (1.2/1) blend in DMSO-d_6, mixing time 0.30 s.

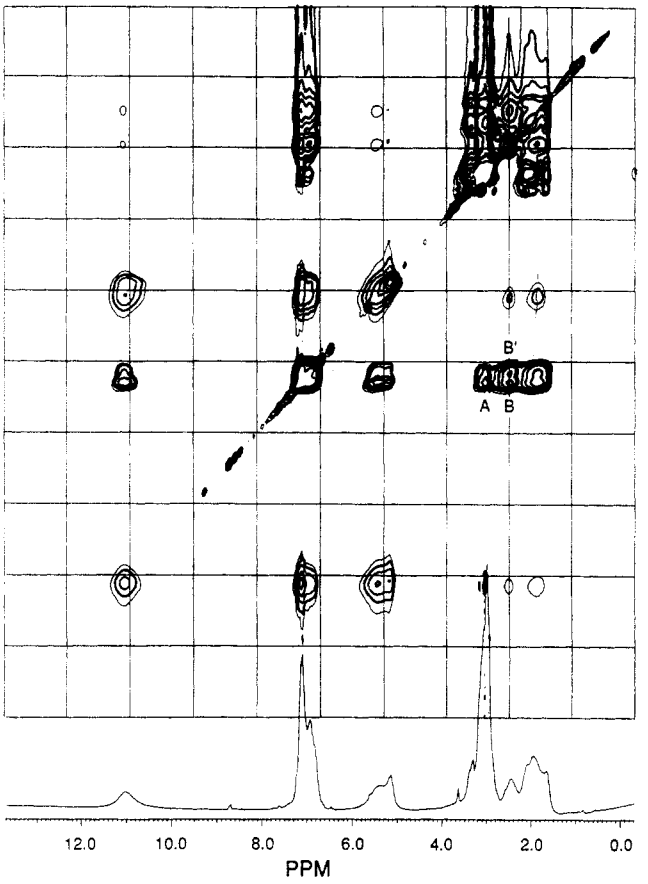


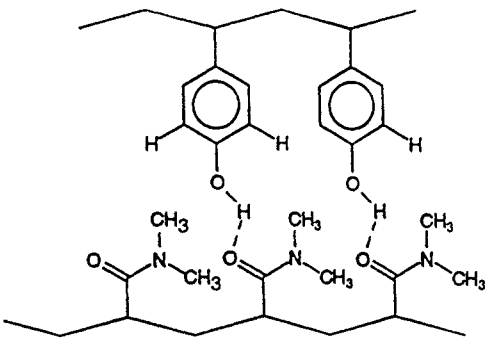
Figure 7. 2D-NOESY spectrum of a 25 wt % solution PVPh/PDMA (1.2/1) blend in PYD-d_5, mixing time 0.30 s.

methine and methylene protons (shown in Figures 5 and 6). This selectivity allows us to assign the backbone resonances in both polymers of the blend. We are thus able to determine if the protons of one polymer approach within 5 Å of the backbone protons of the other polymer or if the two polymers approach only at pendant groups.

Figure 6 is the 2D-NOESY spectrum of the PDMA/PVPh blend in DMSO-d_6. Cross peaks between PDMA and PVPh chains are labeled A and B. A is a correlation peak between the hydroxyl proton of PVPh and the methyl protons of PDMA. B is a correlation between the aromatic protons (ortho and meta protons overlap and therefore specific assignments are not possible) of PVPh and the methyl protons of PDMA. Cross peaks designated as C are correlations between the hydroxyl proton of PVPh and the backbone methine and methylene protons of PVPh. The buildup rate for these cross peaks indicates that they are between different polymer chains or chains that have folded back upon each other and not due to spin diffusion. The large cross peak designated D is an intramolecular correlation between the hydroxyl proton and the aromatic protons of PVPh. This indicates that the hydroxyl proton is attached to the oxygen on the aromatic ring and no hydrogen abstraction has taken place. Of course, this proton is labile, and cross peaks between it and water at 3.8 ppm are due to exchange. The magnitude and number of cross peaks indicate these two polymers are homogeneously mixed and within 1.8–2.7 Å of each other in DMSO-d_6 solution (Scheme III).

Figure 7 is the 2D-NOESY spectrum of the PDMA/PVPh blend in PYD-d_5. The hydroxyl proton is shifted almost 2 ppm downfield, indicating stronger hydrogen bonding than when DMSO-d_6 is the solvent. In PYD-d_5, the hydroxyl proton shows no correlation to the PDMA methyls and much weaker cross peaks to the PVPh backbone protons. There is still a strong cross peak between the PVPh aromatic protons and the PMDA methyl protons (A). The two cross peaks between the aromatic protons and the PVPh backbone methine proton show specificity between the proton ortho to the backbone (B′) and ortho to the hydroxyl group (B). From this we see that the aromatic protons closest to the PDMA methyls are those ortho to the hydroxyl group.

Scheme III



When the proton is phenolic (a weaker acid than sulfonic acid), the interaction between PDMA and PVPh appears to be hydrogen bonding (Scheme III). However, as in the PDMA/P(S–SA(12)) blend, when the solvent is PYD-d_5, interaction with solvent becomes more favorable. In these systems, the hydrogen-donating group determines the type of interaction, and the hydrogen-accepting group determines where the interaction takes place. The strong cross peak between the hydroxyl proton and the aromatic protons indicates the hydroxyl proton is still attached to the oxygen. The downfield shift indicates stronger hydrogen bonding to the pyridine than to PDMA. In this case, hydrogen bonding is to the pyridine nitrogen. The

polymers (PDMA and PVPh) are still within 1.8–3.3 Å of each other, but now only the aromatic protons are close to the PDMA methyls. The hydroxyl proton is shielded from the PDMA methyls by the pyridine solvent molecules. Since the PDMA and PVPh are still held close together, there must be some favorable interaction between the two. Most likely there is still some hydrogen bonding to the PDMA, but now the concentration of these interacting groups, at any given time, must be less than approximately 10% or cross peaks between the hydroxyl proton and the PDMA methyls would be visible.

Previously, PDMA/PVPh blends were also solution-cast into solid pieces. The results are summarized in Table I. When prepared in pyridine, the solution was clear and stable. When the solvent was evaporated, a clear, homogeneous film was formed. When prepared in MEK, a homogeneous gel or precipitate was immediately formed. This confirms a stronger interaction between polymers in solution when the solvent interacts weakly with one of the polymers (PVPh would interact stronger with PYD than with MEK).

The question as to why cross peaks between the PDMA methyl groups and the protons located on the substituted ring were not observed in the PDMA/P(S–SA(12)) blends in DMSO-d_6, whereas these were observed in the PDMA/PVPh blends, was somewhat puzzling, since one would expect these protons to be the closest to the interaction site. Two possibilities come to mind. The first would be that the sulfonic acid group is large and bulky, thus keeping the adjacent protons far enough away from the methyl groups so that no signal is observed (discussed above). The second possibility would be that the concentration of these protons, with only 12% of the rings being functionalized, is too low to be detected. Similar results were observed by Natansohn et al.[24] for blends of poly(methyl methacrylate-*co*-vinylpyridine) with P(S–SA) of low substitution. Therefore, a copolymer of styrene and vinylphenol [P(S–VPh(22))], where the amount of the functionalized monomer (22 mol %) was similar to that found in P(S–SA(12)), was studied.

PDMA/P(S–VPh(22)) Copolymer Blends. Figure 8 is the 2D-NOESY spectrum of PDMA/P(S–VPh(22)) blend in DMSO-d_6. All resonances that showed cross peaks in the PDMA/PVPh blend in DMSO-d_6 show cross peaks in this solution. The correlations between the hydroxyl proton and (A) the PDMA methyls or (B) the PVPh (or PS) backbone protons are much weaker, but observable. This is probably because only 22% of the copolymer contains hydroxyl protons. Because of the separate resonance for the aromatic protons meta and para from the PS backbone protons, specific correlations between the hydroxyl proton and the styrene aromatic rings and phenol rings are seen (C). Also, there are strong cross peaks between the PS aromatic protons and the PDMA methyls (D). This means that both components of the copolymer are held close to the PDMA. However, this 25 wt % solution appears hazy, which indicates there are regions of heterogeneity within the solution. Perhaps in regions of the copolymer where there are significant blocks of PS, the copolymer tends to separate from PDMA. Other regions in the copolymer, where there are more PVPh rings, mix well with the PDMA and give correlations resulting in the cross peaks observed. Therefore, the protons adjacent to the position of the hydroxy group are in close proximity to the PDMA methyl groups. The fact that the signal is observed even though the styrene copolymer contains only 22% of the functionalized monomer suggests that the lack of observed cross peaks between the protons

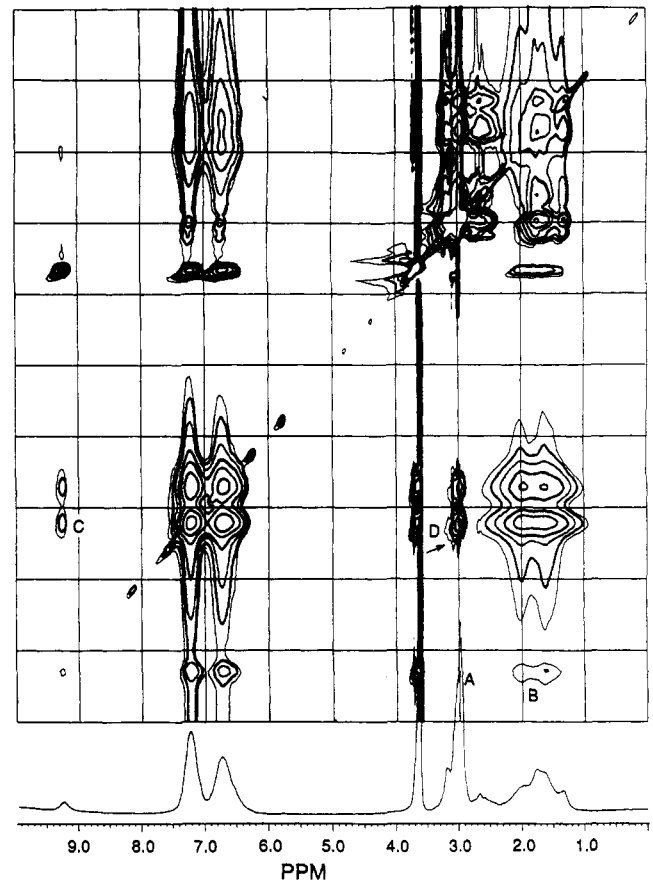


Figure 8. 2D-NOESY spectrum of a 25 wt % solution PDMA/P(S–VPh(22)) (1/4.2) blend in DMSO-d_6, mixing time 0.40 s.

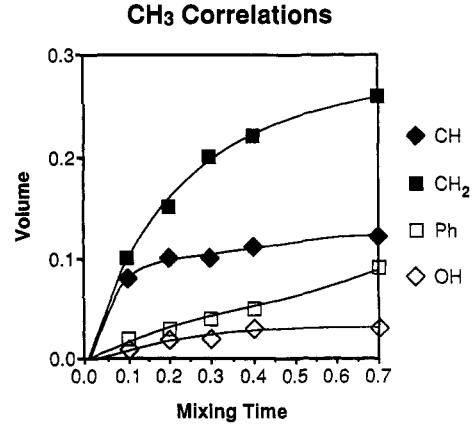


Figure 9. Plot of the correlations between the PDMA methyls and the PDMA backbone methine and methylene protons and the PVPh phenyl and hydroxyl protons. Intensities are plotted as a function of mixing time. The data are from the PVPh/PDMA (1.2/1) 25 wt % solution in DMSO-d_6.

on the styrenesulfonic acid ring and the PDMA is not a question of detection limit due to the low concentration of sulfonated moiety but rather than the sulfonic acid group is large enough to keep the protons in question from approaching each other to within 5 Å.

Another observation, not yet mentioned, from these 2D-NOESY spectra of PDMA blends is that in no cases were there cross peaks of PDMA protons with PS or PVPh backbone protons. Also, there were no cross peaks of PVPh, PS, or P(S–SA(12)) with the PDMA backbone protons. This means that in all blends the two polymers approach each other through interactions between pendant groups.

Figures 9 and 10 show plots of the cross peak buildup intensities vs mixing time. In all cases, the intramolecular

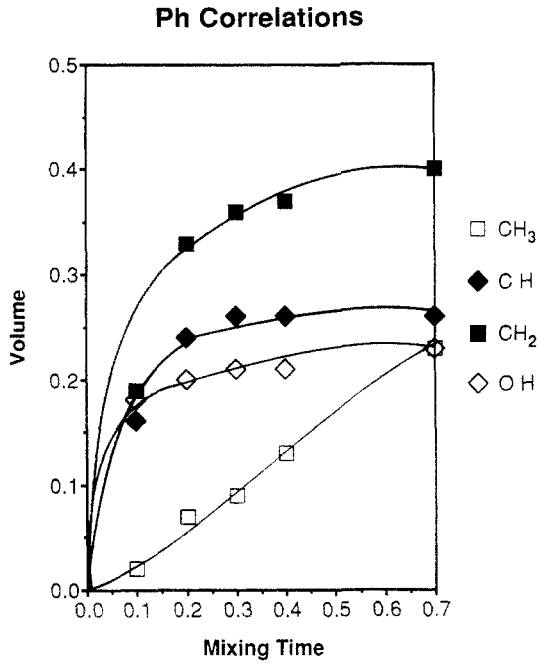


Figure 10. Plot from the same data set as in Figure 9, but showing correlations between the PVPh phenyl protons and the PVPh backbone protons and hydroxyl proton and PDMA methyl.

connections show steeper curves for intensity buildup and thus are closer than intermolecular distances.

These blends were originally pictured as containing strong interactive groups and thus as having similarities to the biological molecular model. The two interacting polymers form a complex that has similarities to the folded structure of biological macromolecules. If this were the case, the need for high weight percent solutions and high molecular weight polymers should be relaxed.

Dilute solutions (10 wt %) were analyzed for all the blends reported above. In no case were any intermolecular cross peaks seen. These observations might be interpreted to indicate that the interactions in synthetic polymers are weaker than hydrogen-bonding interactions in biological macromolecules. Another interpretation is that the weak interactions arise from two other basic differences between synthetic and biological macromolecules: (1) biological macromolecules have unique backbone groups that contribute to the molecule twisting and folding in upon itself, whereas synthetic polymer backbone units are not as conformationally restrained, and (2) many interactions in biological molecules are intramolecular and can be observed even though the distances between backbone units might be large.

We conclude that in a relatively weak interacting solvent, strong interactions are established in polymer blend solutions. These hold the polymers close to each other when the polymers are of sufficient molecular weight and high enough concentration for polymer entanglements to take place.

Conclusions

Two-dimensional NOESY was used to measure through-space intra- and intermolecular distances in polymer blends. In the PDMA/P(S–SA(12)) blend in DMSO-d_6, ionic interactions bring the PDMA methyl protons within 1.8–5.0 Å of the PS aromatic protons. In PYD-d_5 the sulfonic acid proton transfers to the pyridine nitrogen and an ion pair is set up between PS(S–SA(12)) and the solvent. Therefore, blends of PDMA/P(S–SA(12)) cast from pyridine are heterogeneous. The spectra for the two polymers in PYD-d_5 show no intermolecular distances within 5 Å.

Spectra of the PDMA/PVPh blend contain intermolecular cross peaks in both DMSO-d_6 and PYD-d_5. However, the cross peaks in DMSO-d_6 are stronger and appear between the PDMA methyl protons and both PVPh hydroxyl proton and aromatic protons. In contrast, in PYD-d_5, cross peaks are only between PVPh aromatic protons and PDMA methyl protons. In all cases, the hydroxyl proton is hydrogen-bonded, but in PYD-d_5 the hydrogen bond is stronger with the solvent. In the PDMA/P(S–VPh(22)) blend (in DMSO-d_6), there is some phase separation in the solution, but intermolecular cross peaks are present. This is attributed to sequencing effects in the copolymer (close polymer–polymer distances where the copolymer chain is rich in PVPh and phase-separated where PS exists as a block) or solubility problems in the solvent (DMSO-d_6).

Within each polymer of the blend, close distances (1.8–5.0 Å) are seen between pendant group protons and backbone protons from the same polymer folded back upon itself or another similar polymer chain. However, no close distances are seen between pendant group protons of one polymer chain and the backbone protons from the other polymer chain. All interactions and all close contact between different polymers in these blends are from interacting pendant groups.

When blending polymers, knowledge of the phase diagram is of ultimate importance. This is particularly true when the blending process is performed with the aid of a solvent that can compete with one of the polymers for interaction sites on the other polymer. In such a situation, phase separation of the two polymers can occur in solution, and if the kinetics are such as to prevent rapid diffusion back to a single phase as the solvent is removed (as is most often the case), the resulting solid-state morphology will be nonequilibrium. Although ternary phase diagrams have been generated using the Flory–Huggins theory and are successful in predicting this phenomenon for polymers with weak interactions,[22,29] they are not satisfactory for systems where strong negative interaction parameters are involved. Furthermore, these theories would not predict the chemistry that can occur in some of the systems considered here, that is, deprotonation of the sulfonic acid by the pyridine solvent, resulting in rendering it immiscible with PDMA. Therein still lies the necessity to bring theory and experiment together.

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