Two-Dimensional NMR Studies of Intermolecular Interactions in Poly(vinyl chloride)/Poly(methyl methacrylate) Mixtures

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ABSTRACT: Two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY) is used to study intermolecular interactions in concentrated mixtures of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC), a polymer mixture capable of forming compatible blends. Cross peaks in the 2D NOESY spectra that result from internuclear separations of less than 5 Å are observed between PMMA and PVC for polymer concentrations greater than 25 wt %. The intermolecular cross peaks do not depend on PMMA or PVC tacticity, but decrease with increasing temperature, and the intermolecular complex is disrupted by trace amounts of water. The distances measured from a quantitative analysis of the NOESY spectra as a function of temperature show that the PMMA has a preferred conformation, and that the intermolecular complex has a defined geometry. Determination of the interaction mechanism and geometry from structural studies is the first step toward the molecular design of new compatible blends.

Introduction

Polymer blends are an important class of materials that may exhibit a variety of mechanical, thermal, optical, or electrical properties that depend on the blend composition and the properties of the homopolymers.[1] Intermixing at the molecular level is thermodynamically unfavorable and is not observed for most polymer systems. However, specific intermolecular interactions occasionally provide sufficient free energy to drive the molecular level mixing. Understanding the specific interactions at a molecular level in terms of the interacting groups and the strength and specificity of the interactions remains an important goal in materials science.

Several carbonyl-containing polymers, such as poly(methyl methacrylates) and polyethers, are reported to form miscible blends with chlorinated polymers.[2–4] Among the most important and intensively studied in this group are the blends of poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC). PMMA has been reported to form compatible blends with chlorinated polyethylene with chlorine contents greater than 49%.[5,6] While some studies report incompatibility[7] or miscibility over a small concentration range,[8] others report evidence for interchain mixing at the molecular level.[9–21] In some reports, the miscibility depends strongly on the PMMA tacticity.[9] Isotactic PMMA (i-PMMA) is reported immiscible,[9] while atactic and syndiotactic (a-PMMA, s-PMMA) are reported miscible for concentrations below 60 wt % PMMA[9] (the 1:1 molar mixture). At higher PMMA concentrations, phase separation between a 40:60 PVC/s-PMMA phase and an s-PMMA-rich phase occurs.[9] Other authors have not observed this phase separation,[10] and compatible blends of PMMA and PVC or other chlorinated polymers have been obtained with PMMA of all tacticities for mixtures annealed between the glass transition temperature and the lower critical solution temperature (LCST).[11,12] A dependence of the LCST on PMMA tacticity has also been reported.[12,13] The observation of an LCST may reflect the competition between specific intermolecular interactions and entropic or free-volume effects that cause incompatibility at higher temperatures. It has also been suggested that the tacticity effects on the miscibility of PVC/PMMA blends are related to differences in the chain mobility of i-PMMA and a-PMMA.[12,22,23]

The existence of specific intermolecular PVC/PMMA interactions has been the subject of several studies. The negative heats of mixing that are frequently cited as evidence for specific interactions are observed for PVC/PMMA mixtures.[5] Frequency shifts in the IR spectra of the carbonyl peak of PMMA in $CHCl_3$ compared to CCl_4,[15] and shifts of the bands in α-deuterated PVC/polyester blends,[16] are interpreted in terms of specific hydrogen-bond-type interactions between the carbonyl oxygen of PMMA and the electron-deficient α-protons of PVC. The miscibility of PMMA with Saran, a poly(vinylidine chloride)/poly(vinyl chloride) copolymer, suggests that this is not the only factor affecting miscibility.[13] Such hydrogen-bonding or dipole–dipole interactions between the PMMA and PVC are expected to be relatively weak and strongly affected by the solvent polarity and hydrogen-bonding capacity. This may account for the strong effect of solvents on blend compatibility. Films cast from methyl ethyl ketone, for example, are more homogeneous than those cast from tetrahydrofuran.[21] In addition, residual moisture may influence the compatibility.[21] Weak intermolecular interactions combined with a sensitivity to the solvent may partially account for the conflicting reports of miscibility in the PVC/PMMA blends.

In this study, the PVC/PMMA intermolecular interactions are investigated using two-dimensional nuclear Overhauser effect spectroscopy (2D NOESY) in concentrated solutions, and the effects of polymer concentration, tacticity, solvent, and temperature on intermolecular complex formation are reported. The NMR relaxation and NOEs depend on the inverse sixth power of the internuclear distances and provide information about interactions over the length scale of 2–5 Å.[24,25] These results provide an insight into the mechanism and specificity of the intermolecular interactions.

Methods and Materials

Atactic poly(methyl methacrylate) (M_w = 31 000) and poly(vinyl chloride) (M_w = 112 000) were obtained from Aldrich, while the isotactic (M_w = 10 000) and syndiotactic poly(methyl methacrylates) (M_w = 27 000) were obtained from Polysciences. The sample referred to as syndiotactic PMMA is 30% atactic, 65% syndiotactic, and 5% isotactic. The polymer mixtures were dissolved in deuterated tetrahydrofuran under a nitrogen atmosphere and stirred for 24 h to ensure complete mixing. Sample

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concentrations were adjusted by evaporating the solvent until the desired weight was achieved. The samples were then sealed in NMR tubes for the 2D NMR studies.

Two-dimensional NOESY data were acquired at 500 MHz on a JEOL GX-500 NMR spectrometer using the 90°-t_1-90°-τ_m-90°-t_2 pulse sequence.[25,26] A total of 256 complex 1K t_1 data points were acquired with a sweep width of 4 kHz in each dimension. Phase-sensitive 2D NOESY spectra were obtained with the procedure of States et al.[27] The diagonal and cross peak volumes were obtained by a manual fit of the peaks using in-house Fortran programs, in which the peak volume, the line width, and the ratio of Gaussian-to-Lorentzian line shape are adjustable parameters. Nonselective relaxation rates were obtained by inversion recovery, and selective relaxation rates were obtained either from the relaxation rate matrix analysis or by magnetization recovery following selective inversion using a DANTE pulse train of 15 12° pulses.[28,29] The selective relaxation rates were used to normalize the NOESY peak volumes relative to zero mixing time.

Results

High-resolution 2D NMR in concentrated solutions is used to study the formation of the intermolecular polymer complexes of poly(vinyl chloride) and isotactic, syndiotactic, and atactic poly(methyl methacrylate) (i-PMMA, s-PMMA, a-PMMA). Complex formation is measured by two-dimensional nuclear Overhauser effect spectroscopy since intermolecular cross peaks are only observed for protons separated by less than 5 Å. The NOESY spectra can be quantitatively interpreted to obtain distances between the pairs of protons to probe the structure and the mechanism of intermolecular complex formation.[24,25]

The 500-MHz ^{1}H NMR spectra of 5 wt % PVC and PMMA homopolymers of different tacticities in deuterated THF at 60 °C are shown in Figure 1a–c, and the spectrum of the 38 wt % 2:3 PVC/s-PMMA mixture is shown in Figure 1d. Due to the high molecular weights, the high concentrations, and the complex stereochemistry of both PVC and PMMA, the spectrum of the mixture is heavily overlapped. As an approximation, the spectrum of the mixture is represented as nine major signals that are assigned by comparison to the homopolymers. The signals 1–3 (4.6–4.3 ppm) are assigned to the rr, mr, and mm diads of the PVC methine protons,[30] and peak 4 (3.6 ppm) is assigned to the PMMA methoxyl protons that do not show any resolvable stereosequence splittings. Peaks 5–7 (2.4–1.9 ppm) are assigned to the PVC and PMMA methylene protons.[31] Other studies have shown that the broad methylene peaks result from a superposition of the signals from different stereosequences that are not resolved, even at 500 MHz. The PVC methylene protons are approximated as peaks 5 and 6, which do not overlap with the PMMA methylene protons (peak 7). The sharp, intense signals 8 and 9 (1.03–0.9 ppm) are attributed to the atactic and syndiotactic PMMA methyl protons.[31]

As in previous studies of intermolecular polymer interactions, high concentrations are required to observe intermolecular NOEs.[32,33] Parts a–d of Figures 2 compare the NOESY spectra (0.8-s mixing time) for 2:3 PVC/s-PMMA mixtures as a function of concentration in THF at 22 °C. At concentrations less than 22 wt %, the NOESY spectra are a composite of those expected from the homopolymers. In addition to the intense diagonal peaks, intramolecular cross peaks are observed between the neighboring protons, such as between the PVC methine (peaks 1–3) and methylene (peaks 5 and 6) resonances, and between the PMMA methoxyl (peak 4), methylene (peak 7), and methyl (peaks 9 and 10) proton signals. For concentrations greater than 25 wt %, intermolecular cross peaks are visible between the PVC methine (peaks 1–3) and methylene peaks (peaks 5 and 6) and the s-PMMA methoxy (peak 4), methylene (peak 7) and methyl signals (peaks 8 and 9). Since intermolecular cross peaks may only arise from through-space magnetization transfer, the average distances between the proton pairs must be less than 5 Å. The cross peaks are weak in the 25 wt % spectrum, but increase with the concentration until they are only slightly weaker than the intermolecular cross peaks. The high concentrations required to observe the intermolecular cross peaks show that these interactions are relatively weak.

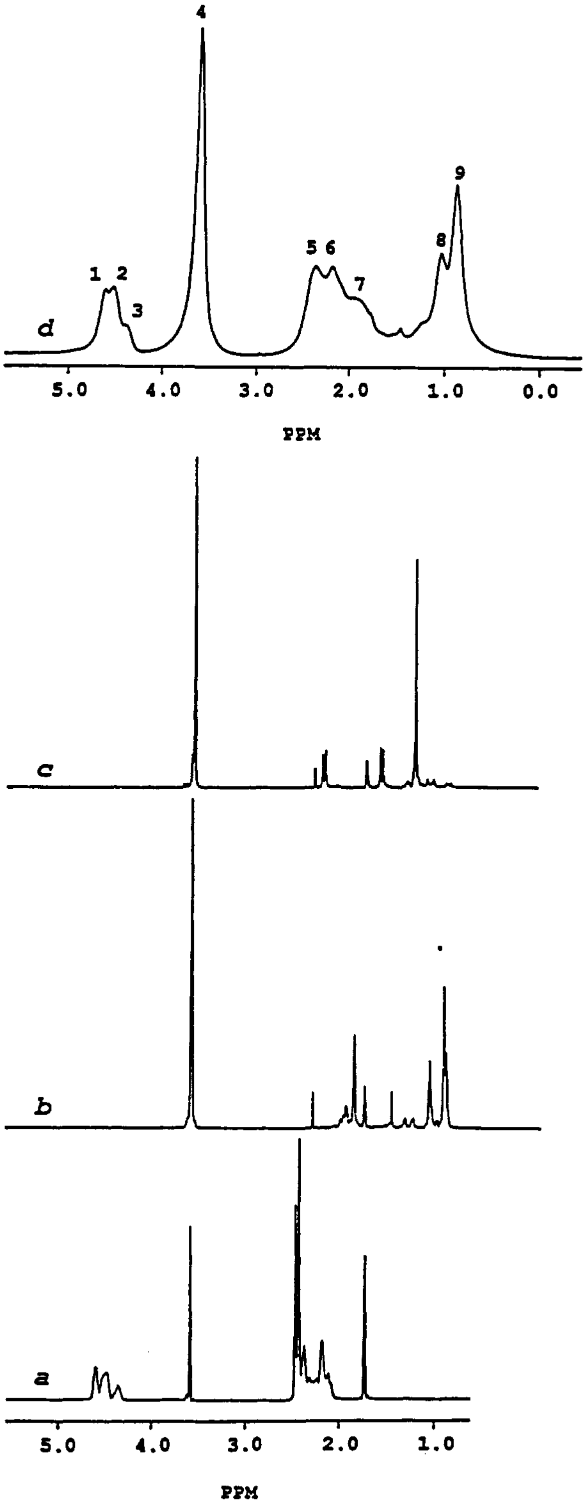

Figure 1. The 500-MHz ^{1}H NMR spectra of (a) PVC, (b) s-PMMA, (c) i-PMMA, and (d) the 2:3 PVC/s-PMMA mixture in deuterated THF at 60 °C. The concentrations are 5 wt % for the homopolymers and 38 wt % for the mixture.

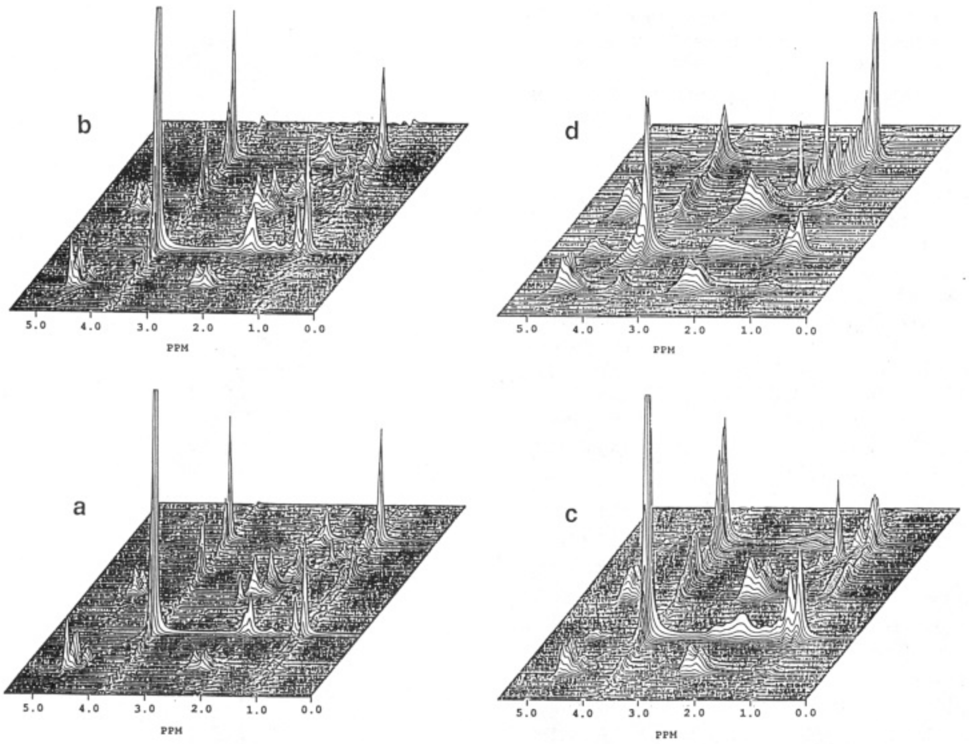

Figure 2. 2D NOESY spectra of 2:3 PVC/s-PMMA mixtures in deuterated THF at 22 °C for (a) 22, (b) 25, (c) 28, and (d) 38 wt % concentrations.

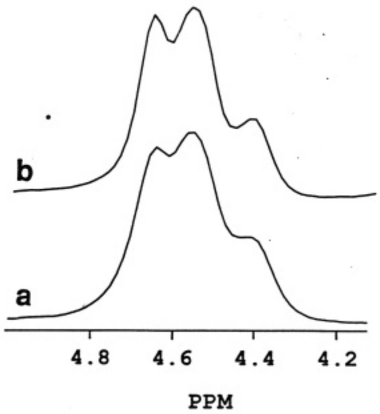

Figure 3. Comparison of (a) the 1D spectrum of the methine protons with (b) a slice through the 2D spectrum at the methine–methoxyl cross peak for a 38 wt % PVC/s-PMMA mixture.

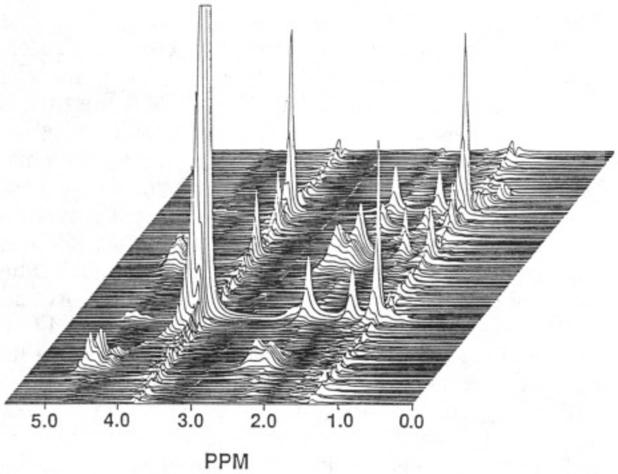

Figure 4. 2D NOESY spectrum of a 35 wt % PVC/i-PMMA mixture in deuterated THF at 22 °C recorded with a 0.8-s mixing time.

The NOESY experiments provide information about the stereoselectivity of the intermolecular complex. If peaks from different stereosequences are resolved, as for the PVC methine and PMMA methyl protons, comparison of the 1D spectrum with cross sections through the NOESY spectrum reveals the degree to which the different stereosequences are preferentially involved in complex formation. If, for example, the PVC mm diads preferentially interact with PMMA, then the mm PMMA cross peaks will be enhanced relative to other stereosequence cross peaks. Figure 3 compares PVC NOESY methine–methoxy cross peaks with the 1D spectrum. The identical intensity pattern observed in the 1D spectrum and the 2D cross sections demonstrates that there is no stereosequence preference for PVC in intermolecular complex formation.

The influence of PMMA tacticity is investigated by the same method, and by comparison of the NOESY spectra for the PVC/s-PMMA and PVC/i-PMMA mixtures. Figure 4 shows the 2D NOESY spectrum for the 35 wt % PVC/i-PMMA mixture, which may be compared with the PVC/s-PMMA mixtures shown in Figure 2. Intermolecular cross peaks are observed for PVC complexes with both s-PMMA and i-PMMA, demonstrating that complex formation does not depend strongly on the PMMA tacticity. While it is difficult to quantitatively compare the two complexes because they differ in concentration and molecular weight, we note that the cross peaks in the i-PMMA complex are reduced compared to the s-PMMA complex. This may be attributed to either weaker complex formation with i-PMMA or an effect of the differences in the molecular dynamics of the polymers that reduces the cross peaks for i-PMMA.[22,23]

It has been proposed that the PVC/PMMA complex is stabilized by hydrogen bonds between the PMMA carbonyl oxygen and the PVC α-hydrogen, or by intermolecular dipole–dipole interactions. Both mechanisms are expected to depend strongly on the solvent polarity and hydrogen-bonding capacity. To evaluate this hypothesis, we compare the NOESY spectrum of a 38 wt % PVC/s-

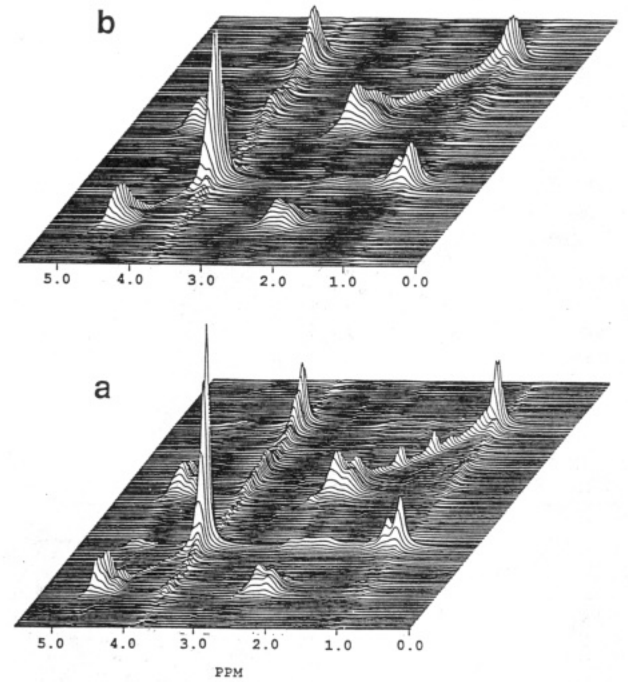

Figure 5. 2D NOESY spectra of 2:3 PVC/s-PMMA mixtures at 35 wt % in (a) deuterated THF and (b) deuterated THF with a trace of D_2O.

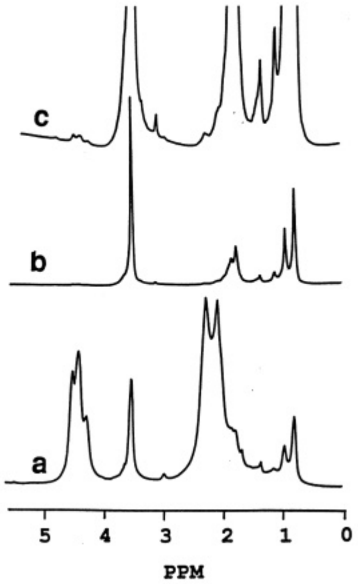

Figure 6. The 500-MHz ^{1}H NMR spectra of the (a) lower and (b, c) upper phases of a phase-separated PVC/s-PMMA mixture with D_2O. The spectra of the upper phase are shown for two vertical expansions.

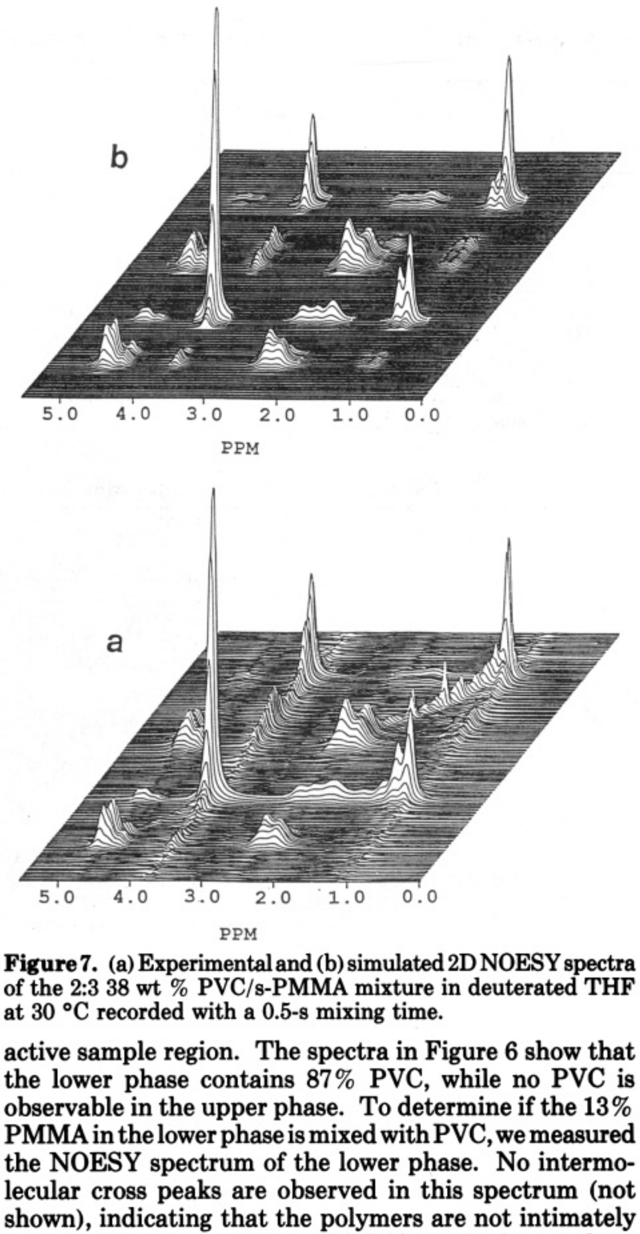

Figure 7. (a) Experimental and (b) simulated 2D NOESY spectra of the 2:3 38 wt % PVC/s-PMMA mixture in deuterated THF at 30 °C recorded with a 0.5-s mixing time.

PMMA complex in THF with an identical sample that contains a trace of D_2O. Upon standing for several days, the D_2O-containing sample phase separates in the NMR tube. However, since the phase separation is slow compared to the time required to obtain a 2D spectrum, the 2D NOESY spectrum can be obtained for physically homogeneous mixtures containing D_2O before macroscopic phase separation occurs. These results are shown in Figure 5a,b. The absence of cross peaks in the wet sample demonstrates that the intermolecular complex formation is extremely sensitive to the hydrogen-bonding capacity of the solvent.

The compositions of the phases after phase separation are investigated by placing the tube in the NMR spectrometer such that the upper or lower portion is in the active sample region. The spectra in Figure 6 show that the lower phase contains 87% PVC, while no PVC is observable in the upper phase. To determine if the 13% PMMA in the lower phase is mixed with PVC, we measured the NOESY spectrum of the lower phase. No intermolecular cross peaks are observed in this spectrum (not shown), indicating that the polymers are not intimately mixed. The observation of PMMA in the lower phase may be due to the difficulties in precisely locating the sample in the active area of the spectrometer, or to the long time required to reach equilibrium in these viscous samples.

The cross relaxation rates that result in observable cross peaks depend on the molecular dynamics and on the internuclear distances.[24,25] If the correlation times can be measured, information regarding the structure of the complex can be determined. The time evolution of the NOESY diagonal and cross peaks can be written in matrix form as[34]

$$\mathbf{A}(\tau_m) = \mathbf{A}(0)e^{-R\tau_m} \tag{1}$$

where **A** is the matrix of diagonal and cross peaks at mixing times τ_m and zero, and **R** is the relaxation rate matrix

$$\mathbf{R} = \begin{bmatrix} \rho_{11} & \sigma_{12} & \sigma_{13} & \cdots \\ \sigma_{21} & \rho_{22} & \sigma_{23} & \cdots \\ \sigma_{31} & \sigma_{32} & \rho_{33} & \cdots \\ & \vdots & & \end{bmatrix} \tag{2}$$

Structural information is obtained from the cross relax-

Table I

Normalized Peak Volumes Used for the Simulation of the 2D NOESY Spectrum of the 2:3 PVC/s-PMMA 38 wt % Mixture in Deuterated THF at 30 °C[a]

	PVC					PMMA			
	CClH			CH_2		CH_2	CH_3		OCH_3
CClH	0.3256	0.006	0.0038	0.021	0.025	0.002	0.0015	0.003	0.005
	0.006	0.327	0.006	0.045	0.028	0.002	0.0016	0.003	0.0067
	0.0038	0.006	0.2361	0.0235	0.012	0.001	0.0006	0.0016	0.0026
CH_2	0.021	0.045	0.0235	0.3625	0.041	0.0045	0.0035	0.0081	0.018
	0.025	0.028	0.012	0.041	0.213	0.0042	0.0033	0.006	0.015
CH_2	0.002	0.002	0.001	0.0045	0.0042	0.057	0.009	0.0155	0.030
CH_3	0.0015	0.0016	0.0006	0.0035	0.0033	0.009	0.085	0.020	0.044
	0.003	0.003	0.0016	0.0081	0.006	0.0155	0.020	0.291	0.077
OCH_3	0.005	0.0067	0.0026	0.018	0.015	0.030	0.044	0.077	0.324

[a] The mixing time is 0.5 s.

Table II

Diagonal (ρ_{ii}) and Cross Relaxation Rates (σ_{ij}) Obtained from the Peak Volumes in Table I

	PVC					PMMA			
	CClH			CH_2		CH_2	CH_3		OCH_3
CClH	3.328	−0.077	−0.041	−0.151	−0.241	−0.019	−0.005	−0.011	−0.044
	−0.077	3.387	−0.042	−0.332	−0.220	−0.025	−0.008	−0.014	−0.047
	−0.041	−0.042	4.042	−0.155	−0.089	−0.014	−0.005	−0.008	−0.026
CH_2	−0.151	−0.332	−0.155	3.044	−0.324	−0.040	−0.027	−0.032	−0.118
	−0.241	−0.220	−0.089	−0.324	3.878	−0.058	−0.033	−0.031	−0.115
CH_2	−0.019	−0.025	−0.014	−0.040	−0.058	6.149	−0.177	−0.128	−0.401
CH_3	−0.005	−0.008	−0.005	−0.027	−0.033	−0.177	5.991	−0.075	−0.594
	−0.011	−0.014	−0.008	−0.032	−0.031	−0.128	−0.075	2.706	−0.515
OCH_3	−0.044	−0.047	−0.026	−0.118	−0.115	−0.401	−0.594	−0.515	3.025

Table III

Intra- and Interchain Separations (Å) for the PVC/s-PMMA Mixtures Obtained from the Relaxation Rates Listed in Table II

	PVC					PMMA			
	CClH			CH_2		CH_2	CH_3		OCH_3
CClH		3.4	3.7	3.0	2.8	4.3	>5.0	4.7	3.7
	3.4		3.7	2.6	2.8	4.0	4.9	4.5	3.6
	3.7	3.7		3.0	3.3	4.5	>5.0	4.9	4.0
CH_2	3.0	2.6	3.0		2.6	3.7	4.0	3.9	3.1
	2.8	2.8	3.3	2.6		3.5	3.9	3.9	3.1
CH_2	4.3	4.0	4.5	3.7	3.5		2.9	3.1	2.5
CH_3	>5.0	4.9	>5.0	4.0	3.9	2.9		3.4	2.4
	4.7	4.5	4.9	3.9	3.9	3.1	3.4		2.4
OCH_3	3.7	3.6	4.0	3.1	3.1	2.5	2.4	2.4	

ation rates σ_{ij}, which depend on the internuclear distances and on the correlation time[24]

$$\sigma_{ij} = ({}^1/_{20})\gamma^4 h^2 r^{-6}[6J_2(2\omega) - J_0(0)] \tag{3}$$

where γ is the gyromagnetic ratio r_{ij} is the internuclear distance, and the spectral density terms $J_2(2\omega)$ and $J_0(0)$ depend on the effective correlation time τ_c and the spectrometer frequency ω. If the peak volumes of the diagonal and cross peaks can be determined, eq 1 can be rearranged to[34]

$$\mathbf{R} = -(1\ \ln/\tau_m)\ \ln\,(\mathbf{A}(\tau_m)/\mathbf{A}(0)) \tag{4}$$

and solved as[34]

$$\mathbf{R} = -(1/\tau_m)(\mathbf{T}\ \ln\,[\mathbf{D}]\ \mathbf{T}^{-1}) \tag{5}$$

where **D** is the diagonal matrix of eigenvalues and **T** and $\mathbf{T}^{-1}$ are its eigenvector matrix and its inverse. The strategy for determining the relaxation rate matrix from the experimental data in these studies is to simulate the NOESY spectra as a function of mixing time and temperature to obtain the normalized peak volume matrix $\mathbf{A}(\tau_m)/\mathbf{A}(0)$. The effective correlation time τ_c is determined from the ratio of the nonselective relaxation rate, measured by inversion recovery, to the selective rate, determined from the diagonal elements of the rate matrix, and the internuclear distances are calculated according to eq 3.[35]

This procedure is illustrated in parts a and b of Figure 7, which compare the experimental spectrum of the 2:3 PVC/s-PMMA complex with the spectrum simulated from the normalized peak volumes listed in Table I. Since the simulated spectrum approximates the experimental spectrum as nine major signals, there is some deviation from the experimental spectrum in the region between 2.0 and 1.4 ppm. In general, however, the close correspondence between the simulated and experimental spectra shows that the peak volumes are accurately estimated by this procedure. The two signals at 1.4 and 1.7 ppm arise from impurities and are not included in the simulation.

The relaxation rate matrix is calculated from the simulated peak volumes using eq 5, and the diagonal and cross relaxation rates are listed in Table II. The average correlation time calculated from the ratio of the selective to nonselective relaxation rates for the complex at 30 °C is 2 ± 0.5 ns. The correlation time is calculated by assuming isotropic motion, an assumption that is known to be inaccurate for systems as anisotropic as synthetic polymers.[36] However, errors introduced by this assumption

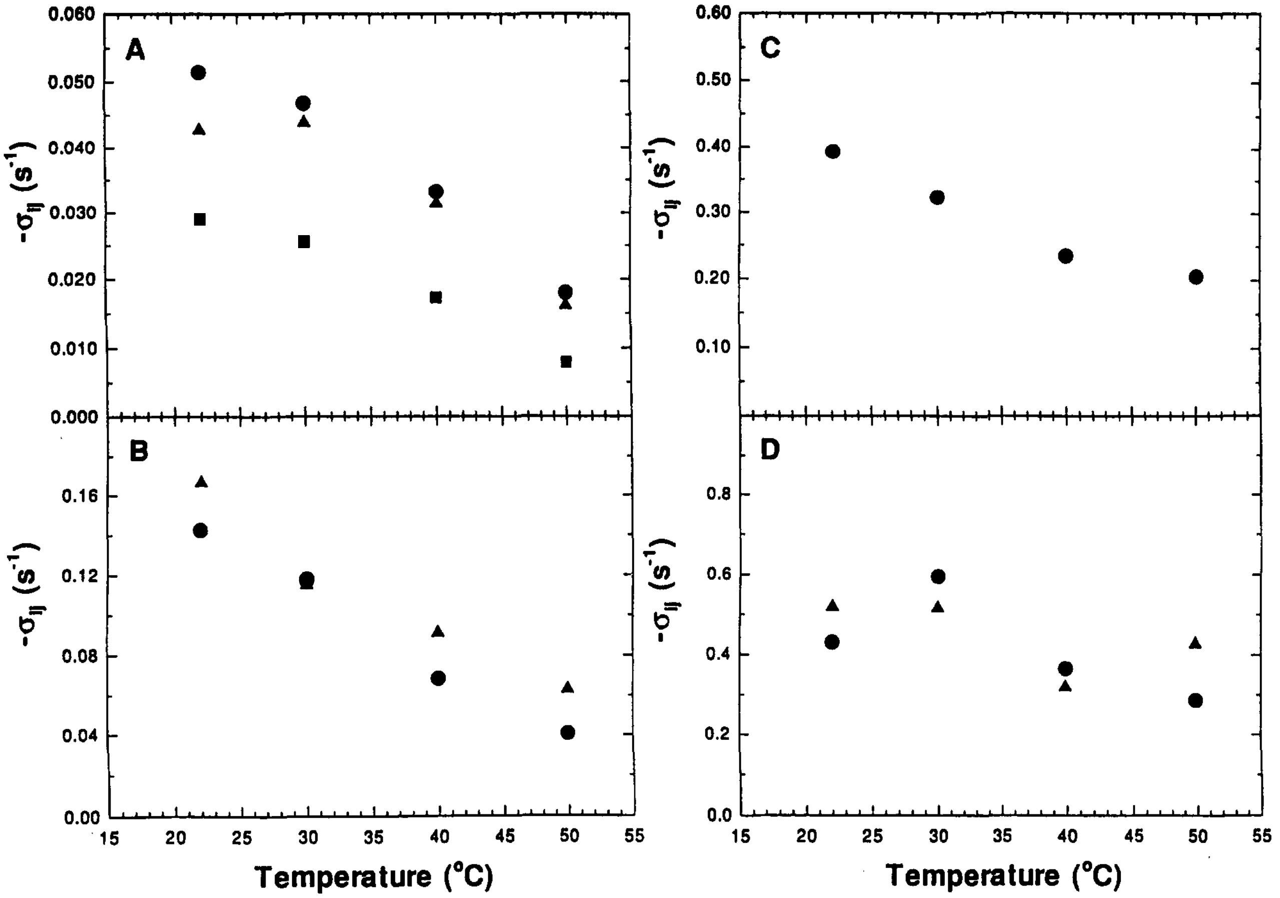

Figure 8. Temperature dependence of the cross relaxation rates for the 2:3 PVC/s-PMMA mixture at 38 wt % in deuterated THF. The cross relaxation rates are shown for (A) the PVC methine–PMMA methoxyl cross peak (mm, ■; rm, ▲; rr, ●), (B) the PMMA methoxyl–PVC methylene cross peaks (peak 5, ●; peak 6, ▲), (C) the intramolecular PVC methine cross peaks, and (D) the intramolecular PMMA methyl–methoxyl cross peaks (s-PMMA, ▲; a-PMMA, ●).

are minimized by the fact that the distances are derived from the inverse sixth power of the distance, so a 30% error in τ_c results in only a 5% error in the internuclear distance. By use of this effective correlation time and the cross relaxation rates listed in Table II, the internuclear distances are calculated from eq 3, and the results are listed in Table III.

Since both polymers are flexible in solution from gauche–trans isomerization and segmental motion,[36] the distances are determined by the time-averaged structure. This quantitative analysis of the 2D spectra yields reasonable distances for the PVC and PMMA intrachain separations and justifies the assumptions used for calculating the effective correlation time. The PVC methine–methylene and methylene–methylene distances (2.6–3.3 Å and 2.6 Å) are close to the values expected from the chemical structure of PVC. The intrachain distances in PMMA depend not only on the main-chain conformation, but also on the torsion angles between the main chain and carbonyl carbon, and between the carbonyl carbon and the ether oxygen. The short distances observed between the methoxyl protons and the methylene and methyl protons shows that the methoxyl group is not extended away from the main chain, but rotated over the hydrophobic surface of PMMA.

In addition to the intrachain interactions, several intermolecular interactions are observed. The closest contacts are between the PMMA methoxyl protons and the PVC methylenes (3.1 Å). The PMMA methylene–PVC methine distances are in the range of 3.5–4 Å, and the PMMA methyl protons are separated from the PVC by 4–5 Å. This range of observed distances shows that the intermolecular complex is relatively well defined. If the complex has no preferred geometry, then the distances between all pair of protons would be approximately equal. The measured internuclear distances show that the PVC surface defined by the methylene protons is oriented toward the PMMA surface covered by the methoxyl protons, and the PMMA methyl protons are oriented away from the surface of molecular contact. Current efforts are directed toward more precisely defining the structure of the complex using restrained molecular dynamics and distance geometry calculations.

Temperature effects on the structure of the complex are investigated by quantitative analysis of the NOESY spectra between 20 and 50 °C. The effect of temperature on the cross relaxation rates for several intra- and intermolecular cross peaks is shown in Figure 8. All cross peaks are observed to decrease with increasing temperature. The major part of the decrease can be attributed to a decrease in the effective correlation time, which decreases from 2 ± 0.5 ns at 30 °C to 1 ± 0.5 ns at 50 °C. This shows that the structure of the complex does not change significantly over this temperature range.

Discussion

The compatibility of PVC/PMMA blends is a topic of intense interest and controversy. By use of a variety of chemical and spectroscopic methods on polymers that differ in molecular weight and tacticity, the miscibility, partial miscibility, and compatibility of PVC and PMMA have been reported. We are investigating the molecular basis for compatibility in the PVC/PMMA system using 2D NMR in concentrated solutions. These experiments are simpler than analyzing cast films, where the rate of solvent evaporation and other experimental variables may affect the miscibility. In a study of polystyrene (PS) and poly(vinyl methyl ether) (PVME) mixtures,[32] we found that the results from the studies using concentrated mixtures could be correlated with other spectroscopic and chemical evidence used to identify the specific intermolecular interactions in this system. We believe that concentrated solutions are a suitable model system to investigate the fundamental molecular interactions that lead to the formation of compatible blends.

Intermolecular NOESY cross peaks are observed only in mixtures with concentrations greater than 25 wt %. The concentration dependence of the NOEs for PVC/PMMA mixtures is similar to that observed for PS/PVME mixtures, which suggests that the strengths of the intermolecular interactions are of similar magnitude in both systems. On the basis of chemical, IR, and LCST evidence, it has been suggested that the compatibility of PVC and PMMA arises from specific hydrogen-bond types of interactions between the PVC methine and the carbonyl oxygen of PMMA. Such O–H–C hydrogen bonds are expected to be much weaker that the typical N–H–N, O–H–N, or O–H–O hydrogen bonds, and we note that the concentrations required for the observation of intermolecular cross peaks are much higher than for the 1 wt % required in the poly(ethylene oxide)/poly(acrylic acid) mixtures under conditions promoting the formation of O–H–O hydrogen bonds. Weak hydrogen bonds would also explain the extreme sensitivity of the blends to environmental factors, such as trace amounts of water.

The quantitative analysis of the NOESY spectra shows that the intermolecular complex has a defined structure that does not depend strongly on polymer tacticity or temperature. These conclusions are obtained from a rate matrix analysis of the NOESY spectra as a function of mixing time. This relatively new method for NOESY analysis has been previously applied to peptides[37] and nucleic acids,[38] but has not been previously applied to the study of the structure of synthetic macromolecules. This method leads to more precise measures of the internuclear distances, but the interpretation of the distance information is more difficult because of the statistical nature of vinyl polymers compared to the uniquely defined monomer sequence and stereochemistry of biological polymers. While the structures of biopolymers are usually interpreted in terms of a single solution structure, the structures of synthetic polymer complexes are probably more statistical in nature. Instead of a single structure, the distances measured in the NOESY experiments are probably due to a family of structures with similar intermolecular interactions. Solving the structure of intermolecular complexes will require generating the families of structures that on average satisfy the NMR distance constraints.

Another factor complicating interpretation of NMR distance information is the effect of structural averaging. This averaging could be both from monomers interacting with different geometries and from some monomers not participating at all. The distances listed in Table III are calculated by assuming all monomers participate in the intermolecular complex. Two pieces of experimental evidence support this assumption. First, a different rate matrix solution would be required to fit the data over a range of mixing times if the complex had a large fraction of noninteracting monomers. Second, if the distances were an average of 50% strongly interacting and 50% noninteracting, for example, then the closest distances would have to be on the order of 2 Å, which is shorter than physically reasonable.

In summary, we have used quantitative solution 2D NMR spectroscopy to study intermolecular interaction in solution for a polymer pair capable of forming compatible blends. The intermolecular complex appears to have a well-defined structure that is attributable to hydrogen-bonding interactions. As judged from the concentration dependence of the NOEs, these interactions are relatively weak. Our future efforts are directed toward using the distance information to determine the family of structures compatible to the experimental data.

References and Notes

(1) Walsh, D. J.; Rostani, S. *Adv. Polym. Sci.* **1985**, *70*, 119.

(2) Prud'homme, R. E. *Polym. Eng. Sci.* **1982**, *22*, 1138.

(3) Tremblay, C.; Prud'homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1857.

(4) Ziska, J. J.; Barlow, J. W.; Paul, D. R.; *Polymer* **1981**, *22*, 918.

(5) Walsh, D. J.; Higgins, J. S.; Zhikuan, C. *Polym. Commun.* **1982**, *23*, 336.

(6) Zhikuan, C.; Ruona, S.; Walsh, D. J.; Higgins, J. S. *Polymer* **1983**, *24*, 263.

(7) Razinskaya, I. N.; Stharkman, B. P.; Batuyeva, L. I.; Tyves, B. S.; Shlyrova, M. N. *Vyskomol. Soedin.* **1979**, *A21*, 1860.

(8) Vanderschueren, J.; Janssens, A.; Ladang, M.; Niezette, J. *Polymer* **1982**, *23*, 395.

(9) Schurer, J. W.; de Boer, A.; Challa, G. *Polymer* **1975**, *16*, 201.

(10) Walsh, D. J.; McKoewn, J. G. *Polymer* **1980**, *21*, 1330.

(11) Jager, H.; Vorencamp, E. J.; Challa, G. *Polym. Commun.* **1983**, *24*, 290.

(12) Vorenkamp, E. J.; ten Brinke, G.; Meijer, J. G.; Jager, H.; Challa, C. *Polymer* **1985**, *26*, 1725.

(13) Lemieux, E.; Prud'homme, R. E.; Forte, R.; Jerome, R.; Teyssie, P.; *Macromolecules* **1988**, *21*, 2148.

(14) Zhao, Y.; Prud'homme, R. E. *Macromolecules* **1990**, *23*, 713.

(15) Parmer, J. F.; Dickinson, L. C.; Porter, R. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Sci.)* **1986**, *27*(1), 205.

(16) Varnell, D. F.; Moskala, E. J.; Painter, P. C.; Coleman, M. M. *Polym. Eng. Sci.* **1983**, *23*, 658.

(17) Tremblay, C.; Prud'homme, R. E. *J. Polym. Sci., Polym. Ed.* **1984**, *22*, 1857.

(18) Parmer, J. F.; Dickinson, C.; Chien, J. C. W.; Porter, R. S. *Macromolecules* **1987**, *20*, 2308.

(19) Parmer, J. F.; Dickinson, L. C.; Chien, J. C. W.; Porter, R. S. *Macromolecules* **1989**, *22*, 1078.

(20) Albert, B.; Jerome, R.; Teyssie, P.; Smyth, G.; Boyle, N. G.; McBrierty, V. J. *Macromolecules* **1985**, *18*, 388.

(21) Schmidt, J. J.; Gardella, J. A., Jr., Salvati, L., Jr. *Macromolecules* **1989**, *22*, 4489.

(22) Leyerla, J. R., Jr.; Horikawa, T. T.; Johnson, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2463.

(23) Bywater, S.; Toporowski, P. M. *Polymer* **1972**, *13*, 94.

(24) Abragam, A. *The Principles of Nuclear Magnetic Resonance*; Oxford University Press; Oxford, UK, 1961.

(25) Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

(26) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95.

(27) States, D. J.; Heberkorn, R. A.; Ruben, D. I. *J. Magn. Reson.* **1982**, *48*, 286.

(28) Wu, X.-L.; Xu, P.; Friedrich, J.; Freeman, R. *J. Magn. Reson.* **1989**, *81*, 206.

(29) Green, H.; Wu, X.-L.; Xu, P.; Friedrich, J.; Freeman, R. *J. Magn. Reson.* **1989**, *81*, 646.

(30) Mirau, P. A.; Bovey, F. A. *Macromolecules* **1986**, *19*, 210.

(31) Schilling, F. C.; Bovey, F. A.; Bruch, M. D.; Kozlowski, S. A. *Macromolecules* **1985**, *18*, 1418.

(32) Mirau, P. A.; Tanaka, H.; Bovey, F. A. *Macromolecules* **1988**, *21*, 2929.

(33) Crowther, M. W.; Cabasso, I.; Levy, G. C. *Macromolecules* **1988**, *21*, 2924.

(34) Perrin, C. L.; Gipe, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 4036.

(35) Mirau, P. A.; Bovey, F. A. *J. Am. Chem. Soc.* **1986**, *108*, 5130.

(36) Heatley, F. *Prog. Nucl. Magn. Reson. Spectrosc.* **1978**, *13*, 47.

(37) Olejniczak, E. T.; Gampe, R. T.; Fesik, S. W. *J. Magn. Reson.* **1989**, *81*. 178.

(38) Mirau, P. A. *J. Magn. Reson.*, in press.

Registry No. PVC (homopolymer), 9002-86-2; s-PMMA (homopolymer), 25188-97-0; i-PMMA (homopolymer), 25188-98-1; a-PMMA (homopolymer), 9011-14-7.