Miscibility Studies in Blends of Poly(methyl methacrylate) with Poly(styrene-*co*-methacrylonitrile) Using Solid-State NMR and Fluorescence Spectroscopy

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Received February 15, 1994; Revised Manuscript Received June 16, 1994®

ABSTRACT: The miscibility in blends of poly(methyl methacrylate) (PMMA) with poly(styrene-*co*-methacrylonitrile) (SMAN) was examined by solid-state NMR and fluorescence spectroscopy. The value of the excimer/monomer fluorescence intensity (I_E/I_M) in the blends provides a sensitive measure of phase separation. A miscibility window in the blends of PMMA and SMAN containing about 30-65 mol % methacrylonitrile (MAN) monomer has been observed by fluorescence experiments. Measurements of $T_{1\rho}{}^H$ by solid-state NMR have shown that blends containing 50:50 wt % PMMA blended with each of polystyrene, poly(methacrylonitrile), SMAN (MAN: 18.9 mol %), and SMAN (MAN: 87.6 mol %) are phase-separated. There is an intermolecular penetration between PMMA and copolymers in the blends of PMMA with SMAN (MAN: 43.8 mol %) and SMAN (MAN: 70.9 mol %) at a level of less than about 6 nm. However, the fluorescence data would indicate that intimate mixing does occur below this level. An analysis of the $T_{1\rho}{}^H$ values for SMAN has indicated that the sequence distribution has an important effect on the interactions in the copolymer system.

Introduction

It has been known for more than a decade that poly(methyl methacrylate) (PMMA) forms miscible blends with copolymers of styrene and acrylonitrile over a limited window of comonomer compositions, while PMMA is not miscible with homopolymers of styrene or acrylonitrile.[1-4] It is generally recognized that strong intrachain repulsions between styrene and acrylonitrile comonomer units may make an important contribution to the heat of mixing and can be the cause of the exothermic mixing.[5-7] Similar behavior has been noted for other copolymer-homopolymer systems.[8-11] In this paper, the blends of PMMA with poly(styrene-*co*-methacrylonitrile) (SMAN) are investigated and compared with the blends of PMMA with poly(styrene-*co*-acrylonitrile).

The miscibility of polymers in blends may be studied by measuring the behavior of the glass transition temperatures (T_g) on blending. A miscible blend will have a single T_g at a temperature which is intermediate between the T_g's of the individual polymers. However, the closeness of the T_g of PMMA (105 °C), polystyrene (PS) (100 °C), and poly(methacrylonitrile) (PMAN) (115-123 °C)[12,13] makes such an approach for assessing mixing in the PMMA/SMAN blend system difficult and prone to errors.

It has been recognized for some time that solid-state NMR relaxation time measurements of polymer blends can detect molecular mixing on the nanometer scale.[14] The spin-lattice relaxation times of the ^{1}H nuclei in the laboratory or rotating frames are partially averaged by spin diffusion through the matrix of ^{1}H nuclei. Spin diffusion proceeds until relaxation occurs at a relaxation sink, which usually is associated with a particular structural unit, such as a methyl group. In this way the individual relaxation times for the component polymers tend to be averaged to a single value. The extent to which the averaging of relaxation times occurs depends on the degree of mixing and the relaxation times of the individual components. To separate the contributions to the ^{1}H relaxation behavior, it is possible to transfer the residual ^{1}H magnetization to the ^{13}C spins by cross-polarization, thereby allowing one to relate a particular ^{1}H relaxation decay with a ^{13}C NMR signal, which in turn can be assigned to a component of the blend.

At the same time, it has also been suggested that fluorescence techniques may be a sensitive probe of molecular mixing in polymer blends.[15-18] Frank and coworkers found that the excimer fluorescence from blends of poly(2-vinylnaphthalene) with a variety of host polymers was a sensitive probe of polymer miscibility.[19-21] Excimer formation occurs when an electronically excited chromophore interacts with a ground-state chromophore to form an excited-state dimer. In a polymer blend, the changes in the excimer/monomer fluorescence intensity for one blend component containing a fluorescent chromophore will reflect changes in the extent of formation of nonadjacent intramolecular and intermolecular excimers, which in turn depends on the degree of polymer coiling and interchain entanglements, respectively.[22] Since the formation of excimers requires the two interacting chromophores to approach each other to within 0.3-0.4 nm, there should be a decrease in excimer fluorescence in miscible systems where extensive interpenetration of the two polymer chains causes a decrease in the contribution from both the nonadjacent intramolecular and intermolecular excimer sites. The ratio of excimer to monomer fluorescence (I_E/I_M) should thus provide a direct measure of blend miscibility at a molecular level.

In the present paper, solid-state NMR and fluorescence spectroscopy are used to provide information on the miscibility of PMMA/SMAN blends. The dependence on copolymer composition and blend phase structure are discussed.

Experimental Section

Materials. SMAN samples of varying compositions were prepared by free radical polymerization in the bulk at 60 °C

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® Abstract published in *Advance ACS Abstracts,* August 15, 1994.

0024-9297/94/2227-5912$04.50/0

Table 1. Characterization of the Homopolymers and Copolymers

polymer	mol % MAN in copolymer	$10^{-4}M_N$	M_W/M_N
PS	0.0	7.2	2.4
SMAN-1	0.0	7.2	2.4
SMAN-2	18.9	8.5	2.2
SMAN-3	32.7	7.8	2.1
SMAN-4	35.8	9.5	2.1
SMAN-5	43.8	9.4	2.0
SMAN-6	48.0	10.6	1.8
SMAN-7	53.0	7.4	1.9
SMAN-8	65.1	5.1	1.9
SMAN-9	70.9	5.6	1.9
SMAN-10	79.9	4.7	1.9
SMAN-11	87.6	2.6	1.9
PMAN	100.0	2.5	2.2
PMMA		6.1	1.9

initiated by benzoyl peroxide. The conversion was limited to less than 5% in general. The methacrylonitrile (MAN) contents of the copolymers were determined from the NMR spectra recorded on a Bruker AC200 NMR spectrometer. The copolymer compositions and methacrylonitrile triad fractions obtained from the NMR analysis have been analyzed, and the copolymerization was shown to follow a penultimate model.[26] The reactivity ratios for this model have been reported previously.[26] The molecular weights of the polymers were estimated by gel permeation chromatography in DMF solvent at 80 °C using polystyrene standards. The characteristics of the samples are listed in Table 1.

Fluorescence Spectroscopy. Films of SMAN and their blends with PMMA were prepared by solution casting onto glass slides from stock solutions containing 5% by weight of the polymer in pyridine. The films were dried at 80 °C in a nitrogen atmosphere for up to 48 h and then in vacuum at 80 °C for 48 h to remove residual solvent. Steady-state fluorescence spectra with excitation at 260 nm were measured using an Hitachi F-4014 fluorescence spectrophotometer. The miscibility of the blends was characterized by the relative emission intensity of the phenyl chromophore excimer at 330 nm (I_E) and the monomer at 285 nm (I_M).

Solid-State NMR. Samples of SMAN and their blends with PMMA for solid-state NMR measurements were prepared by precipitation from a 0.2% wt pyridine solution into a 10-fold excess of methanol. The samples were dried in vacuum at 80 °C for 48 h. Solid-state NMR measurements were made on a Bruker MSL 300 NMR spectrometer operating at 75.482 MHz for ^{13}C. The $\pi/2$ pulse times were 3.5 μs for ^{1}H and ^{13}C. Samples were spun at 3 kHz in zirconium oxide rotors at the magic angle in Bruker 7 mm MAS probes. The proton spin–lattice relaxation time in the rotating frame, $T_{1\rho}{}^H$, was measured by spin-locking the ^{1}H magnetization prior to cross-polarization (1 ms contact time) to the ^{13}C nuclei. A spin-locking field of 71 kHz was applied for up to 30 ms. Measurements were made at 25 and 60 °C.

Results and Discussion

Fluorescence Spectroscopy. The fluorescence emission spectra of films of 50:50 wt % SMAN/PMMA blends, as a function of copolymer compositions, are shown in Figure 1. It is apparent that at the highest MAN content in the copolymer (MAN: 87.6 mol %) the major contribution to the fluorescence emission is from single phenyl moieties (λ_{max} = 285 nm), while in the pure PS the majority of the emission arises from the excimer band (λ_{max} = 330 nm). The ratio of excimer/monomer fluorescence intensities (I_E/I_M) was used to provide a direct measure of blend miscibility in the following manner. To account for the difference in the intrinsic I_E/I_M values with varying amounts of styrene in the SMAN copolymers, the I_E/I_M value for each copolymer blend was divided by the value of I_E/I_M obtained for the pure copolymer film. For a completely phase separated blend, the normalized I_E/I_M ratio should be close to unity. Any ratio less than this indicates a decrease in I_E/I_M of the blend due, most probably, to a decrease in the intermolecular contribution to the total excimer emission. Such a decrease can only occur if the SMAN chains are diluted by intimate mixing with PMMA.

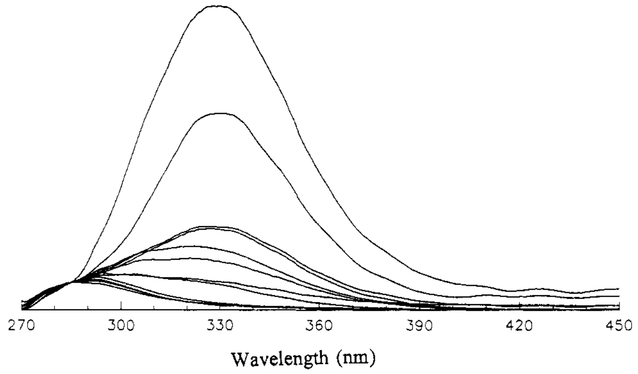

Figure 1. Fluorescence spectra of PMMA/SMAN blends. The intensity at 330 nm decreases with increasing MAN content in SMAN (mol %): 0, 15.2, 18.9, 32.7, 35.8, 43.8, 48.0, 53.0, 65.1, 70.9, 79.9, and 87.6.

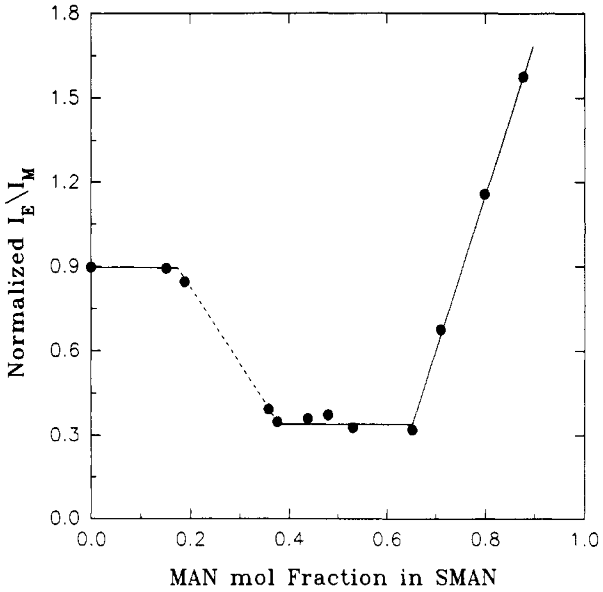

Figure 2. Normalized I_E/I_M for 50:50 wt % blends of PMMA with SMAN as a function of MAN content of the copolymers.

Figure 2 is a plot of the normalized I_E/I_M for each SMAN/PMMA blend against the mole percentage of MAN in the SMAN component. The results show that there is a range of SMAN compositions for which the normalized I_E/I_M value is reduced to between about 0.3 and 0.4. It is suggested that in this region the greatest level of mixing between SMAN and PMMA molecules is achieved, and thus the contributions to the fluorescence emission from the inter- and intramolecular excimers in the SMAN are decreased markedly. Therefore, the SMAN/PMMA blends are miscible over a limited window of SMAN comonomer compositions from about 30 to 65 mol % MAN. Previous studies of the poly(styrene-*co*-acrylonitrile)/PMMA blend system have also revealed a similar situation.[23] However, the miscibility window for the SMAN/PMMA blends has been shifted to higher MAN contents in the SMAN copolymers compared with the poly(acrylonitrile-*co*-styrene)/PMMA blend system. Meanwhile, the miscibility range is obviously widened, which is in agreement with estimates made using the non-hydrogen-bonded solubility parameter approach.[24]

A final observation concerning the SMAN/PMMA blend system is that the values of the normalized I_E/I_M for SMAN (MAN: 79.9 mol %) and SMAN (MAN: 87.6 mol %) are 1.16 and 1.57, respectively. Values greater than unity suggest that the SMAN polymer chains are more aggregated in the blends than they are in films of these copolymers. Assuming that energy migration does occur in SMAN copolymers, the enhanced excimer fluorescence in the blends may result from an increase in the probability of energy migration across coiled loops. Such a phenomenon has been proposed by Guillet and co-workers,[25] who observed an increase in excimer fluorescence from solutions of vinyl aromatic polymers when the thermodynamic quality of the solvent was reduced. They proposed that as each polymer chain becomes more tightly coiled, and the probability of energy migration across loops increases, the region of space that may be traversed is also increased, thus leading to more efficient sampling of excimer sites. An analogous situation may be envisaged for blends such as SMAN (MAN: 79.9 mol %)/PMMA and SMAN (MAN: 87.6 mol %)/PMMA, where tight coiling of the SMAN chain may occur so as to minimize contacts with the PMMA molecules.

Solid-State NMR for SMAN, PMMA, and SMAN/PMMA Blends. A series of samples of SMAN, PMMA, and blends of SMAN with PMMA, respectively, has been studied by solid-state NMR at 25 °C. Typical ^{13}C cross-polarization magic angle spinning (CPMAS) NMR spectra of SMAN with 70.9 mol % MAN content, PMMA, and a blend of these two polymers are shown in Figure 3. The assignments for the peaks have been indicated on the figure, which are in accord with previous assignments in solution.[26] The spectra are composed of relatively broad lines typical for glassy polymers well below their glass transition temperature. ^{1}H $T_{1\rho}$ relaxation time measurements were made prior to cross-polarization to the ^{13}C nuclei, so that individual relaxation times for each carbon type were obtained.

$T_{1\rho}^{H}$ for SMAN Copolymers. Figure 4 shows the rotating-frame proton spin–lattice relaxation behavior for a SMAN sample (MAN: 70.9 mol %) at 25 °C. All four peaks detected for the different carbons exhibit a single exponential decay described by nearly identical $T_{1\rho}^{H}$, the proton spin–lattice relaxation time in the rotating frame. This is due to averaging of the relaxation times of all protons by spin diffusion in this homogeneous system. Four other SMAN copolymers containing 0, 43.8, 87.6, and 100 mol % MAN were also investigated by measurements of their rotating-frame proton relaxation behavior at 25 °C. In the measurements of $T_{1\rho}^{H}$, all protons in each polymer have the same relaxation rate within experimental error. The deviation in $T_{1\rho}^{H}$ values measured for the different carbon peaks in each polymer was less than 0.5 ms. Curve a in Figure 5 shows the $T_{1\rho}^{H}$ values as a function of the MAN mol % content in the SMAN copolymers.

In the analysis of such data, it is assumed that the rate of relaxation ($1/T_{1\rho}^{H}$) of homogeneous mixtures (such as copolymers) should appear as the proton weight average of the rate of relaxation for the individual homopolymers if the styrene and MAN units behave independently of each other.[27-29] Curve b in Figure 5 shows the calculated $T_{1\rho}^{H}$ for the copolymers based on this assumption. It is evident that the measured values (curve a) for $T_{1\rho}^{H}$ are greater than the predictions (curve b). We attribute the increase in $T_{1\rho}^{H}$, $\Delta T_{1\rho}^{H}$, to a reduction in the extent of molecular reorientation in the copolymers. This conclusion follows from the observation that when the temperature is increased, and presumably the rate and amplitude of molecular motion increase, $T_{1\rho}^{H}$ decreases for all of the polymers in this study. We suggest that the interactions between the styrene and MAN groups force the polymer to adopt conformations which result in a reduction in the spectral density of molecular reorientation in the mid-kilohertz frequency range. The motions affected by this interaction appear to be associated principally with the side chains, since the glass transition temperature, which is sensitive to co-operative motions of the backbone, varies only from 100 to 115 °C across the composition range. Additional measurements of NMR relaxation parameters on these copolymers are currently in progress and will be reported in a subsequent paper.

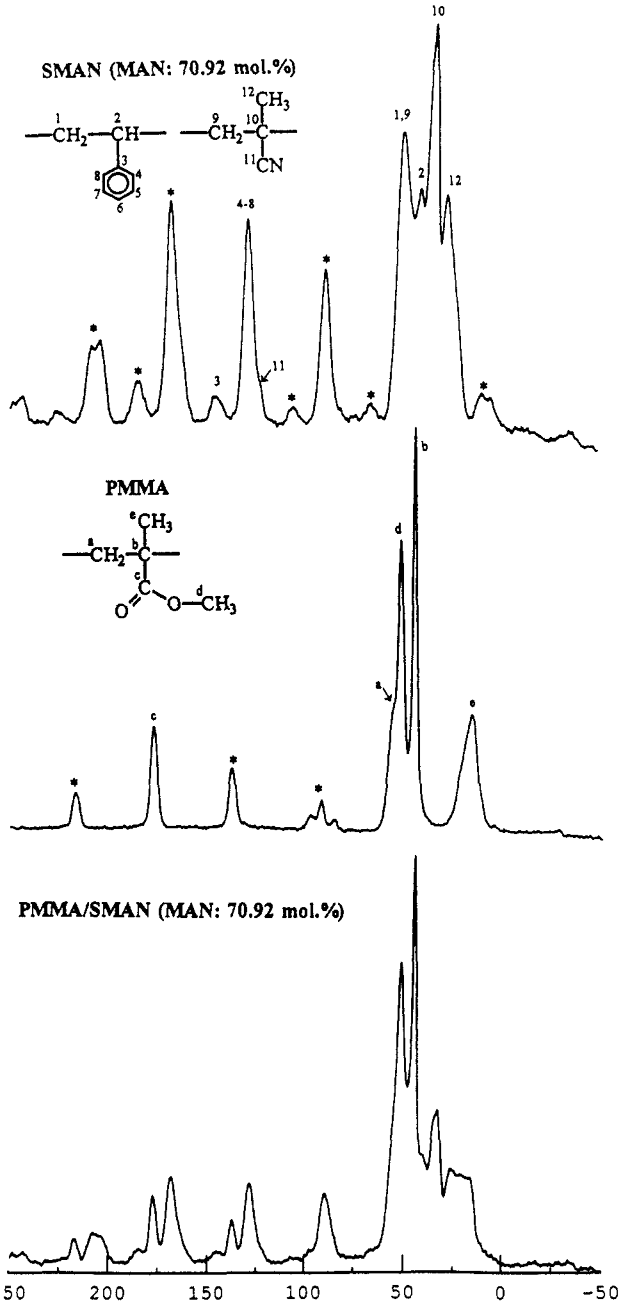

Figure 3. ^{13}C NMR CPMAS spectra of (a) SMAN (MAN: 70.9 mol %), (b) PMMA, and (c) the PMMA/SMAN (MAN: 70.9 mol %) blend. * indicates the location of spinning sidebands.

Comparison with the Binary Interaction Model. Previous work on the poly(styrene-*co*-acrylonitrile)/PMMA blend system has indicated that there is a strong "repulsion" between styrene and acrylonitrile comonomer

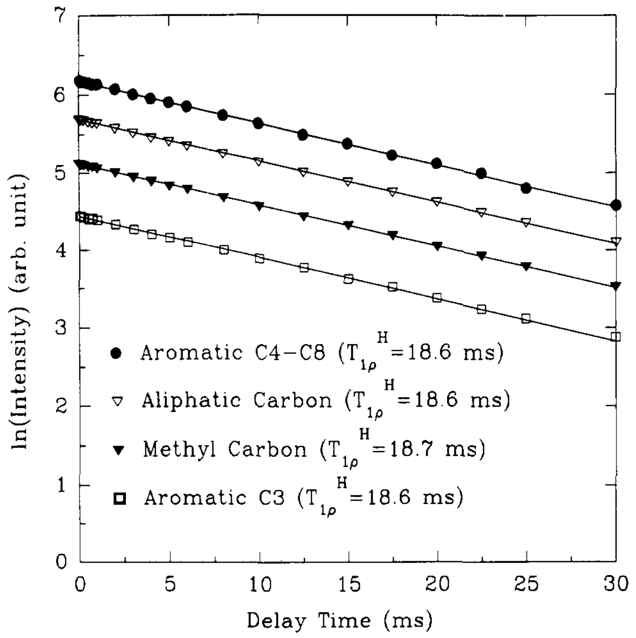

Figure 4. Decay of magnetization with spin-lock delay time for SMAN (MAN: 70.9 mol %). The four lines represent different carbon resonances.

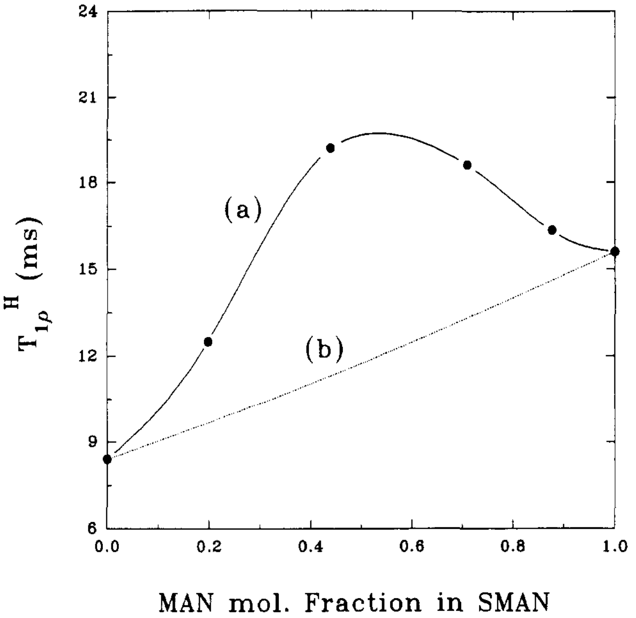

Figure 5. $T_{1\rho}^{H}$ of SMAN as a function of mol % MAN in the copolymer: (a) experimental values; (b) predicted values.

units.[30] This conclusion has been reached from a theoretical treatment for the binary interaction model developed by Paul and co-workers.[31]

The Flory–Huggins theory states that the change in the Gibbs free energy per unit volume, ΔG_{mix}, is expressed as a sum of the combinational entropy and noncombinational terms as follows:

$$\Delta G_{\text{mix}} = RT\left(\frac{\Phi_A \ln \Phi_A}{\overline{V}_A} + \frac{\Phi_B \ln \Phi_B}{\overline{V}_B}\right) + B\Phi_A\Phi_B \qquad (1)$$

where R is the universal gas constant, T is the absolute temperature, and Φ_i and $\overline{V}_i$ are the volume fraction and molar volume of component i, respectively. The noncombinational term in this theory employs the van Lear form, where B is the Flory–Huggins interaction energy density. The binary interaction model provides a simple expression for B for the mixing of a random copolymer composed of 1 and 2 units with a homopolymer of unit 3 in terms of the monomer unit pair interaction energy densities, B_{ij}:

$$B = B_{13}\Phi_1' + B_{23}\Phi_2' - B_{12}\Phi_1'\Phi_2' \qquad (2)$$

where Φ_i' indicates the volume fraction of component i in the copolymer. According to this treatment, the interaction in the copolymer chain will not be affected by the comonomer sequences. When the copolymer contains a 50:50 volume fraction of units 1 and 2, the interaction between the comonomer units in the copolymer will be the greatest.

This model has been tested using low molecular weight liquids, methyl cyanide, toluene, and methyl isobutyrate, which approximately model the monomer residues in the blend system PMMA/poly(styrene-*co*-acrylonitrile).[31] Paul et al. found a good agreement for this model system between the experimental and calculated enthalpies of mixing, obtained according to eq 2. In this system, the binary interaction energy density characteristic of mixing methyl cyanide with toluene has a large position value (B_{12} = 8.35), which has been attributed to a strong repulsion between these two molecules. Therefore, by analogy, it might be inferred that there is a strong intramolecular repulsion between adjacent nitrile and phenyl groups in poly(styrene-*co*-acrylonitrile).

The binary interaction model is oversimplified because it does not take into account the effects of comonomer sequence distribution or conformation in assessing the thermodynamic parameters of mixing. Specifically, the binary interaction model treats, for example, block copolymers and strictly alternating copolymers as being identical. Additionally, the binary interaction model has been found to not account adequately for the properties of ternary blends of homopolymers.

Paul et al.[31] have stated that the binary interaction model predicts that both inter- and intramolecular repulsion between the comonomer units in a copolymer would induce formation of a miscible blend of the copolymer with another appropriate homopolymer over a limited window of comonomer compositions. The model predicts that the enthalpy of mixing will depend on the volume fraction of the two comonomers in the copolymer. If we assume that the volumes of comonomer units in the copolymers are the same as in the respective homopolymers, we can plot $\Delta T_{1\rho}^{H}$ as a function of the MAN volume fraction in the SMAN copolymers (Figure 6). It is evident that the curve is not symmetrical about the 50:50 volume fraction of MAN and styrene units, as predicted by the binary interaction model (eq 2).

The electrostatic forces effective in polyacrylonitrile (or PMAN) and corresponding small molecules, e.g. acetonitrile, arise predominantly from interactions of the strongly polar CN groups.[32] In liquid acetonitrile, it has been estimated that some 70–90% of molecules are in an associated state in which the CN groups of interacting pairs of molecules adopt an antiparallel alignment.[33] Studies of the IR spectra of these systems have shown that the stretching frequency of the CN bond in acetonitrile in the vapor phase (where supposedly the monomeric form predominates) (2267 cm^{-1}) decreases when acetonitrile is in the liquid state (2252 cm^{-1}), where the dimer is formed. Therefore, we suggest that the results obtained for a binary system with a sufficiently large positive binary interaction energy density, which would be characteristic of mixtures of methyl cyanide with toluene,[31] may be attributed to the dissociation of the dimer when the two liquids are mixed.

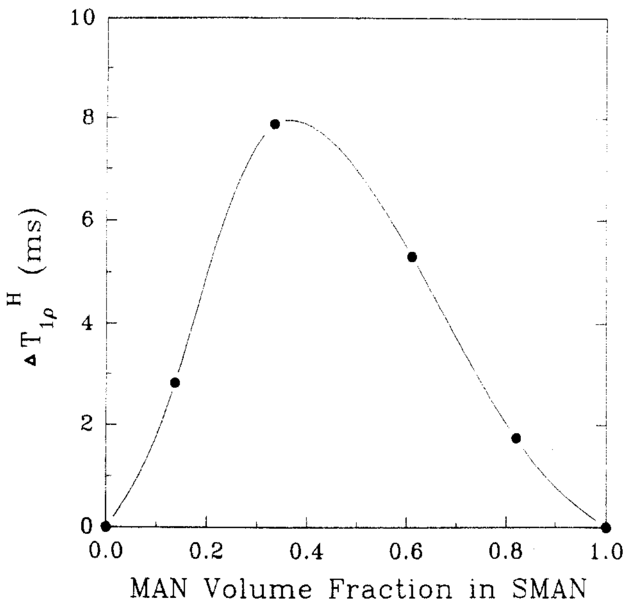

Figure 6. $\Delta T_{1\rho}^{H}$ values of SMAN as a function of MAN volume fraction in the copolymers.

However, in macromolecules, adjacent nitrile groups in the same macromolecule will repel each other, since the adjacent CN groups cannot adopt the fully antiparallel alignment.[34] This intramolecular repulsion compels the individual macromolecules to adopt a somewhat irregular helical conformation.[35] The twisted, kinked molecule may be thought of as being a more or less rigid structure, fitting within a cylinder of about 0.6 nm (for polyacrylonitrile) in diameter. Some of the CN groups will extend beyond the confines of the cylinder. These groups are potentially available for intermolecular dipole–dipole interaction. However, when styrene is copolymerized with MAN, the phenyl rings of the styrene monomers will disrupt the cylindrical conformation of the PMAN, and therefore the intramolecular interactions between the phenyl and CN groups may assume greater importance than the intermolecular interactions. Previous work has shown that introduction of styrene units into polyacrylonitrile (or PMAN) chains decreases the stretching frequency of the CN bond.[36] On the other hand, introducing the monomers containing CN groups into a PS chain to form a copolymer will reduce the aggregation between styrene units. Therefore, the magnitude of the above effects in the copolymer bulk system should be related to the fraction of adjacent units or 10+01 diads in the copolymers, F_{10+01}, where 0 and 1 represent the two different monomeric units in the copolymers. The values of F_{10+01} may be calculated from the reactivity ratios for the penultimate model of copolymerization.[39] In the styrene–MAN copolymer system, the maximum value of F_{10+01} of 0.69 occurs for a copolymer with a mole fraction of 0.51.[26] Figure 7 shows the relationship between $\Delta T_{1\rho}^{H}$ and F_{10+01} for SMAN. The maximum in $\Delta T_{1\rho}^{H}$ occurs for the largest value of F_{10+01} (0.69), and the curve is symmetrical about F_{10+01} = 0.69, as shown in the figure. This suggests that the comonomer sequence (intramolecular contacts between adjacent styrene and MAN units) and molecular conformations in the copolymers have a very important effect on the interactions in this copolymer system.

Thus, using the van Lear form to model the mixing enthalpy for this copolymer/homopolymer blend system is an oversimplification. In some homopolymer/copolymer blends it is clearly necessary to include the contributions due to the sequence distributions and the conformation of the copolymer. This is likely to be particularly necessary for copolymers in which neighboring groups are characterized by strong interaction effects, as found in copolymers of styrene and acrylonitrile (or MAN).

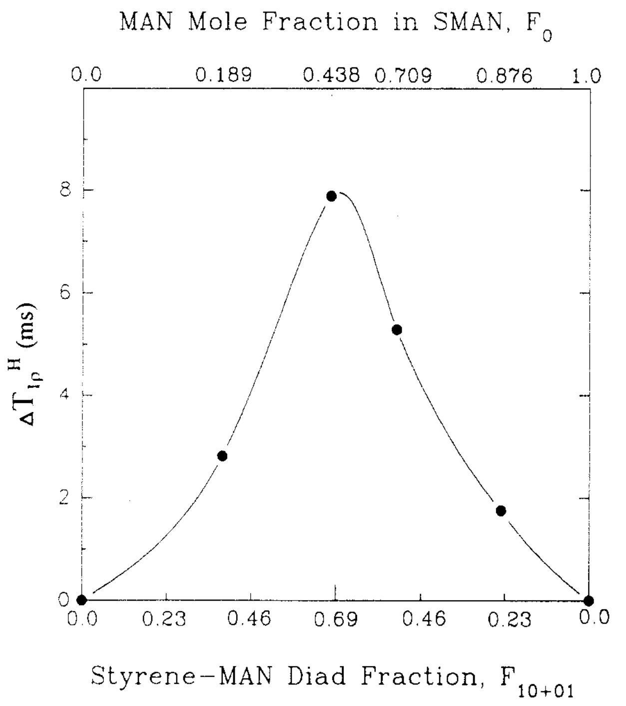

Figure 7. $\Delta T_{1\rho}^{H}$ values of SMAN as a function of the styrene (1) and MAN (0) diad fraction F_{10+01} in the copolymers.

$T_{1\rho}^{H}$ for Blends of SMAN with PMMA. The miscibility of blends of SMAN with PMMA have been examined by measurements of $T_{1\rho}^{H}$. As seen in Figure 3, the aliphatic peak region of the ^{13}C NMR spectra contains overlapping peaks from both SMAN and PMMA components. Therefore, it was not possible to separate the individual SMAN and PMMA components and to investigate their individual relaxation behaviors separately using this region. However, the aromatic resonances for SMAN (or nitrile resonance for PMAN) and the carbonyl resonance for PMMA are well-separated from other resonances and, therefore, may be used as probes of the relaxation behaviors of the individual SMAN and PMMA components in the blends.

Assuming a spin-diffusion relaxation mechanism, the mean-square diffusion path length $\langle L^2 \rangle$ may be estimated from the approximate formula[37]

$$\langle L^2 \rangle = \left(\frac{t}{T_2}\right)\langle l_0^{\,2} \rangle \qquad (3)$$

where t is the time over which spin diffusion takes place (which is of the order of $T_{1\rho}^{H}$), $\langle l_0^2 \rangle$ is the mean-square jump length (which is taken to be the distance between neighboring protons, typically 0.1 nm), and T_2 is the proton spin–spin relaxation time (which is normally around 10^{-5} s for polymers below their glass transition temperature).[14] From eq 3, the maximum diffusion path lengths for spin–lattice relaxation in the rotating frame (t = 15 ms) may be calculated to be approximately 6 nm. Therefore, when two polymers are blended, if phase separation occurs and the phase dimensions are larger than 6 nm, individual $T_{1\rho}^{H}$ values for the two phases should be detected. If the phase dimensions are less than 6 nm, only a single $T_{1\rho}^{H}$ should be obtained. Thus, for phase-separated blends where the domain sizes are large, the relaxation times of the individual components should be similar to those for the corresponding pure polymers. Otherwise, for systems

Table 2. $T_{1\rho}^{H}$ (ms) Values[a] for Blends of 50:50 wt % SMAN with PMMA Measured at 25 °C

MAN content in SMAN (mol %)	before blend		after blend	
	SMAN	PMMA	SMAN	PMMA
0.0	8.4	19.1	8.8	18.9
18.9	12.5	19.1	12.2	17.8
43.8	19.2	19.1	20.1	19.6
70.9	18.6	19.1	20.5	20.7
87.6	16.3	19.1	16.5	19.1
100.0	15.6	19.1	17.4	19.4

[a] Experimental error ±0.3 ms.

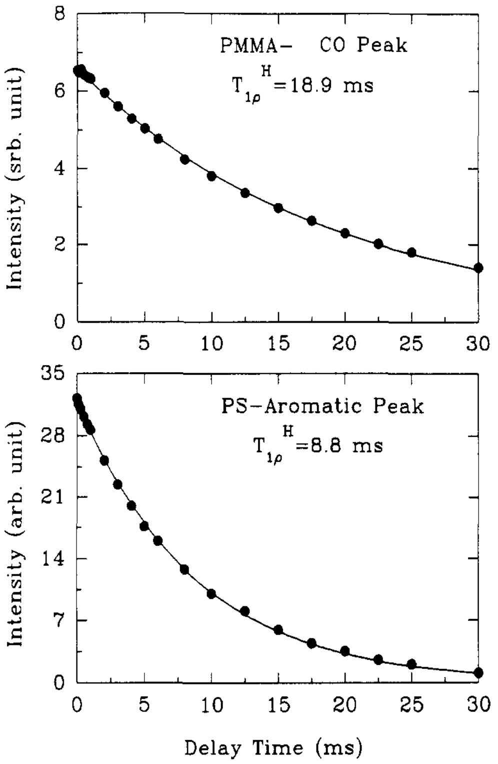

Figure 8. Variation in the magnetization intensity with spin-lock delay time for the PMMA and PS components in the PMMA/PS blend.

in which the phase dimensions are less than 6 nm, spin diffusion proceeds across the phase boundaries and this leads to partial averaging of the relaxation times.

$T_{1\rho}^{H}$ values have been measured at 25 °C for blends containing a 50:50 wt % PMMA/copolymer blend with each of four SMAN copolymers of different compositions, as well as with PS and PMAN homopolymers. The relaxation times are given in Table 2. Figure 8 shows the rotating-frame proton relaxation behavior for the PS/PMMA blend system. The PS and PMMA components in the blend each exhibit a single exponential decay; however, the $T_{1\rho}^{H}$ values for the two components are quite different, being nearly identical to those of the homopolymers, within experimental error. By assuming a simple one-dimensional model for the polymer morphology, and using the approach of Packer and co-workers[40] to solve the diffusion problem, we are able to show that partial averaging of the $T_{1\rho}^{H}$ relaxation times is measurable up to domain sizes of 50 nm for the PS/PMMA blend system. For larger domain sizes the calculated relaxation times are within experimental error of those for the individual polymers. Therefore, we can say that the blend of PS and PMMA is phase-separated on a scale larger than 50 nm. The PS and PMMA phases in the blend may be expected to exhibit the bulk properties of their respective homopolymers.

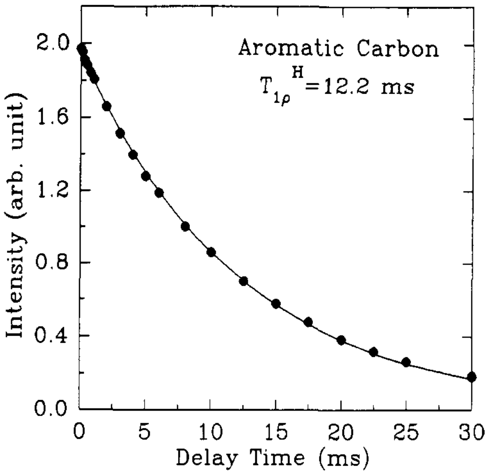

Figure 9. Variation in the magnetization intensity with spin-lock delay time for the SMAN component in the PMMA/SMAN (MAN: 18.9 mol %) blend.

For the blend of SMAN containing 18.9 mol % MAN with PMMA, the $T_{1\rho}^{H}$ value is the same as the value for the corresponding SMAN copolymer. However, the $T_{1\rho}^{H}$ for the PMMA component in the blend is lower than the value of the corresponding PMMA homopolymer. Thus it appears that the PMMA phase contains a small fraction of the SMAN copolymer. This suggests that the SMAN component in the blend should have two rotating-frame proton spin–lattice relaxation times. However, Figure 9 shows that the rotating-frame proton spin–lattice relaxation behavior for the SMAN component in the SMAN (MAN: 18.9 mol %)/PMMA blend system exhibits a single exponential curve. It is likely that the SMAN content in the PMMA phase is relatively small, and therefore the decay curve for SMAN appears identical to that of the pure copolymer.

Previous studies of blends of SMAN/PMMA using cloud point and DSC measurements indicated that PMMA is miscible with SMAN having MAN contents between 11.9 and 72.6 mol % (8 and 63 wt %).[38] However, the thermal history of the samples studied by Goh et al. was different from those studied in this work. Our work using both solid-state NMR and fluorescence spectroscopy clearly shows that blends of SMAN/PMMA containing MAN of less than 18.9 mol % are phase-separated.

At the other end of the composition scale, blends of PMMA with both PMAN and SMAN (MAN: 87.6 mol %) also have two single exponential decay $T_{1\rho}^{H}$ values for each component of the blend. For the PMMA/SMAN (MAN: 87.6 mol %) blend, the $T_{1\rho}^{H}$ values for the PMMA and SMAN components are identical to those of the corresponding pure homopolymer and copolymer. This means that phase separation at a level greater than 6 nm occurs in this blend. However, in the PMMA/PMAN blend a slight increase in $T_{1\rho}^{H}$ for the PMAN component has been observed. This may arise from a tightening of the coil of the PMAN chains to minimize contacts with PMMA, so that molecular motion of PMAN at frequencies of about 71 kHz may be restricted.

When SMAN (MAN: 43.8 mol %) and SMAN (MAN: 70.9 mol %) were blended with PMMA, we find that the SMAN and PMMA components in each blend have the same $T_{1\rho}^{H}$ values at 25 °C, within experimental error. Unfortunately, in these two systems, the $T_{1\rho}^{H}$ values for the PMMA homopolymer and the SMAN copolymers before mixing are also very close, and therefore we cannot confirm that the identical $T_{1\rho}^{H}$ values for the two components in the blends indicate interpenetration of the

SMAN and PMMA molecules. Further measurements of $T_{1\rho}^{H}$ for these blends were therefore made at 60 °C, where the $T_{1\rho}^{H}$ values for PMMA ($T_{1\rho}^{H}$ = 17.3 ms) and the copolymers (SMAN (MAN: 43.8 mol %) ($T_{1\rho}^{H}$ = 13.0 ms) and SMAN (MAN: 70.9 mol %) ($T_{1\rho}^{H}$ = 15.0 ms)) are sufficiently different to allow discrimination. The $T_{1\rho}^{H}$ values of both components in the blend of PMMA with SMAN (MAN: 43.8 mol %) are nearly identical within experimental error, and both values lie between the $T_{1\rho}^{H}$ values of pure PMMA and SMAN (MAN: 43.8 mol %) (PMMA component, $T_{1\rho}^{H}$ = 15.8 ms; SMAN (MAN: 43.8 mol %) component, $T_{1\rho}^{H}$ = 15.1 ms). Thus, we can conclude that SMAN (MAN: 43.8 mol %), which lies in the miscibility window determined by fluorescence spectroscopy, forms a miscible blend with PMMA at a level of less than about 6 nm. Meanwhile, measurements in the blend of PMMA with SMAN (MAN: 70.9 mol %) at 60 °C have shown that the $T_{1\rho}^{H}$ values of both components also lie between the $T_{1\rho}^{H}$ values of pure PMMA and SMAN (MAN: 70.9 mol %) (PMMA component, $T_{1\rho}^{H}$ = 16.7 ms; SMAN (MAN: 70.9 mol %) component, $T_{1\rho}^{H}$ = 15.8 ms). Therefore, we can suggest that there is an intermolecular penetration of the PMMA and SMAN (MAN: 70.9 mol %) components in the blend of PMMA with SMAN (MAN: 70.9 mol %) at a level of less than about 6 nm.

Conclusions

The present work has shown that the excimer/monomer fluorescence intensity (I_E/I_M) in PMMA/SMAN blends provides a sensitive probe of polymer interactions at a molecular level (0.3–0.4 nm scale). A miscibility window for blends of PMMA/SMAN has been observed by this method, in which the MAN content is about 30–65 mol % in the copolymers. On a scale of about 6 nm, the values of $T_{1\rho}^{H}$ measured by solid-state NMR indicate that there is phase separation for blends containing 50:50 wt % PMMA with each of PS, PMAN, SMAN (MAN: 18.9 mol %), and SMAN (MAN: 87.6 mol %). However, $T_{1\rho}^{H}$ measurements at 60 °C demonstrate that there is intermolecular penetration between PMMA and SMAN for blends of PMMA with SMAN, in which the MAN content is 43.8 or 70.9 mol % in the copolymers. An analysis of the $T_{1\rho}^{H}$ values for SMAN copolymers indicates that sequence distribution has a profound effect on the interactions in this copolymer system.

Acknowledgment. The authors wish to thank the Australian Research Council and the Australian Institute for Nuclear Science and Engineering for supporting this research.

References and Notes

(1) Naito, K.; Johnson, G. E.; Allara, D. L.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1260.
(2) Suess, M.; Kressler, J.; Kammer, H. W. *Polymer* **1987**, *28*, 957.
(3) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.
(4) Nishimoto, M.; Keskkula, H.; Paul, D. R. *Macromolecules* **1990**, *23*, 3633.
(5) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(6) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(7) ten Brinke, G.; Karasz, F. E.; Macknight, W. J. *Macromolecules* **1983**, *16*, 1827.
(8) Callaghan, T. A.; Takakuwa, K.; Paul, D. R. *Polymer* **1993**, *34*, 3797.
(9) Kim, J. H.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 2221.
(10) Chiu, S. C.; Smith, T. G. *J. Appl. Polym. Sci.* **1984**, *29*, 1797.
(11) Lath, D.; Lathova, E. *Makromol. Chem.* **1993**, *194*, 3087.
(12) Peyser, P. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; p VI-209.
(13) Kroschwitz, J. I., Ed. *Encyclopedia of Polymer Science and Engineering*; John Wiley and Sons: New York, 1987; Vol. 9, p 669.
(14) McBrierty, V. J.; Douglas, D. C. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 295.
(15) Amrani, F.; Hung, J. M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649.
(16) Mikes, F.; Morawetz, H.; Dennis, K. S. *Macromolecules* **1984**, *17*, 60.
(17) Zhao, Y.; Levesque, J.; Roberge, P. C.; Prud'Homme, R. E. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 1955.
(18) Frank, C. W.; Gashgari, M. A. *Macromolecules* **1979**, *12*, 163.
(19) Semerak, S. N.; Frank, C. W. *Macromolecules* **1981**, *14*, 443.
(20) Gashgari, M. A.; Frank, C. W. *Macromolecules* **1981**, *14*, 1558.
(21) Semerak, S. N.; Frank, C. W. *Macromolecules* **1984**, *17*, 1148.
(22) Semerak, S. N.; Frank, C. W. *Adv. Chem. Ser.* **1983**, *204*, 757.
(23) Haines, D. J.; Wilson, G. J.; Ghiggino, K. P.; Hill, D. J. T. *Polym. Int.* **1991**, *26*, 267.
(24) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic Publishing: Lancaster, PA, 1991.
(25) Aspler, J. S.; Hoyle, C. E.; Guillet, J. E. *Macromolecules* **1978**, *11*, 925.
(26) Hill, D. J. T.; Dong, L.; O'Donnell, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 2951.
(27) McBrierty, V. J.; Douglass, D. C.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1265.
(28) Gao, Z.; Molnar, A.; Morin, F. G.; Eisenberg, A. *Macromolecules* **1992**, *25*, 6460.
(29) Li, S.; Dickinson, L. C.; Chien, J. C. W. *J. Appl. Polym. Sci.* **1991**, *43*, 1111.
(30) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(31) Pfennig, J. L. G.; Keskkula, H.; Barlow, J. W.; Paul, D. R. *Macromolecules* **1985**, *18*, 1937.
(32) Freedman, T. B.; Nixon, E. R. *Spectrochim. Acta* **1972**, *28A*, 1375.
(33) Henrici-Olive, G.; Olive, S. *Adv. Polym. Sci.* **1979**, *32*, 123.
(34) Bohn, C. R.; Schaefgen, J. R.; Statton, W. O. *J. Polym. Sci.* **1961**, *55*, 531.
(35) Rosenbaum, S. *J. Appl. Polym. Sci.* **1965**, *9*, 2071.
(36) Sargent, M.; Koenig, J. L.; Maecker, N. L. *Appl. Spectrosc.* **1991**, *45*, 1726.
(37) Smith, P.; Hara, M.; Eisenberg, A. In *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Hanser Publishers: New York, 1987; Vol. 2, p 255.
(38) Goh, S. H.; Lee, S. Y.; Siow, K. S.; Chen, J. *Polymer* **1993**, *34*, 2898.
(39) Hill, D. J. T.; O'Donnell, J. H. *Makromol. Chem. Macromol. Symp.* **1987**, *10/11*, 375.
(40) Packer, K. J.; Pope, J. M.; Yeung, R. R.; Cudby, M. E. A. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 589.