N.m.r. study of hydrogen bonded polymer blends: influence of the tacticity of poly(methyl methacrylate) on its miscibility with poly(styrene-co-vinylphenol)

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The miscibility of poly(styrene-co-vinylphenol) containing 5% vinylphenol monomer units (MPS-5) with syndiotactic poly(methyl methacrylate) (PMMA-s) and with isotactic poly(methyl methacrylate) (PMMA-i) was studied with ^{13}C solid state n.m.r. complemented with cloud point and differential scanning calorimetry measurements. Above room temperature, the results indicate that the PMMA-s blends have a wider composition range over which the system exists in a single phase. In the time scale of spin-lattice proton relaxation, or a dimensional scale of about 25 nm, PMMA-s is miscible with MPS-5 in all compositions studied, namely 30, 50, and 70 wt% of MPS-5; PMMA-i is miscible only at one composition, namely 70% styrene copolymer. Both PMMA-s and PMMA-i blends indicate the existence of heterogeneities in the time scale of rotating frame spin-lattice relaxation $(T_{1\rho}^H)$, or a dimensional scale of about 2 nm, for all compositions studied except for 70/30 MPS-5/PMMA-i, which shows a single $T_{1\rho}^H$. The glass transition temperature data of these blends are consistent with the n.m.r. observation. The cloud point diagram is also in agreement with n.m.r. results.

INTRODUCTION

It has been known for many years that the stereoregularity of a polymer chain influences polymer–polymer miscibility. Some of the past studies include poly(vinylidene fluoride) (PVDF)–poly(methyl methacrylate) (PMMA)[1,2], PVDF–poly(ethyl methacrylate)[3], poly(ethylene oxide) (PEO)–PMMA[4–8], poly(vinyl chloride) (PVC)–PMMA[9–15], polystyrene–poly(vinyl methyl ether)[16]. Due to its availability in both syndiotactic and isotactic forms, PMMA has been used frequently in the investigation of the effect of tacticity on miscibility. According to Vorenkamp et al.[10], the poor miscibility of isotactic PMMA (PMMA-i), with PVC, in comparison with atactic or syndiotactic PMMA (PMMA-s), is largely due to the differences in the equation of state parameters[10] or the 'free volume' term. Other factors may also contribute to the disparate miscibility behaviours. For example, conformational difference may cause a difference in the accessible specific surface area and hence the number of interacting contacts between the polymer pairs. However, the number of interacting contacts is usually difficult to assess experimentally and the free volume contribution in the case of PVC–PMMA blends appears to account for the salient features of the phase diagrams.

In the examples cited above, the strengths of interactions between polymer pairs are relatively weak. The effect of tacticity on the miscibility of strongly interacting pairs, on the other hand, has not been studied extensively. The role of hydrogen bonding in promoting polymer–polymer miscibility has been documented extensively[17–25] in recent investigations. In many systems, the contribution of hydrogen bonding interaction to the free energy of mixing dominates over other factors such as dispersion forces and free volume effects. We have deliberately chosen, as the first part of our study, a counterpolymer which contains only a small number of hydrogen bond donating groups. The polymer so chosen is poly(styrene-co-vinylphenol) containing 5 mol% of vinylphenol comonomer units, henceforth designated as MPS-5. Chen and Morawetz[26] and Coleman and co-workers[27,28] have shown that similar copolymers are miscible with atactic PMMA. Since the copolymer contains only 5% vinyl phenol units, the hydrogen bonding interaction is not overwhelming. One would expect the system to be finely balanced between the contribution of physical forces, hydrogen bonding and equation-of-state effects[28]. Accordingly, even small perturbation of these contributions caused by tacticity differences may disturb the delicate balance among them and change the sign (positive or negative) of the net free energy of mixing. The rationale of our study rests on this premise. We have employed nuclear magnetic resonance (n.m.r.) as the principal tool of our investigation. Glass transition temperature (T_g) and cloud point measurements were also made to complement n.m.r. results.

EXPERIMENTAL

Poly(styrene-co-vinylphenol) chosen for this study contained 5% vinylphenol monomer units and was synthesized by the copolymerization of styrene and p-acetoxystyrene with azobis(isobutyronitrile) as the initiator. Acetoxy functional groups were subsequently reduced to hydroxyl groups using hydrazine hydrate. Copolymer composition was determined by n.m.r. from the methyl group content of the precursor polymer and compared with the known composition used in the synthesis. The error incurred in this determination is estimated to be ±20%. Syndiotactic and isotactic PMMA samples were obtained from Polymer Laboratory, Inc. They were dissolved in tetrahydrofuran and filtered through a 0.7 μm glass fibre filter to remove insoluble impurity. The molecular weight and polydispersity of polymers were measured by g.p.c. (Waters Chromatography) using polystyrene as standards. The tacticity was determined from solution n.m.r. spectra, which were obtained at 110°C with a GE 300 MHz n.m.r. spectrometer, using o-dichlorobenzene as the solvent[29]. The characteristics of polymers used in the blends are listed in *Table 1*. Blends of 30/70, 50/50, and 70/30 MPS-5/ PMMA by weight were prepared by mixing the two components in toluene. Films were cast by evaporating toluene under vacuum at 100°C for 3 days. T_g measurements were carried out using a Du Pont 9900 thermal analyser equipped with a d.s.c. cell (model 910). The scanning range was from 30 to 170°C and a heating rate of 15°C min^{-1} was used in all experiments.

Cloud points were measured with temperature-scanning light scattering. A 4 mW He–Ne laser equipped with a photo-cell and temperature controller was set up for these measurements; the heating rate was 0.1°C min^{-1} and the scattering angle was 15°. The cloud points for two of the samples were also determined by visual observation after the samples were annealed, under vacuum, at different temperatures for 3 days each.

A GE 300 MHz n.m.r. spectrometer with solid accessory was used in this study with ^{13}C observed at 75.5 MHz and 4.8 μs 90° pulses for both ^{1}H and ^{13}C. About 100–200 mg of sample in Zirconia rotors with Vespel or Kel F end caps was spun at 4.0–4.9 kHz in a Chemagnetics solids n.m.r. probe with ~20 psi air drive. Spin–lattice proton relaxation time, T_1^H, at 20°C was obtained from 180°–τ–90° pulse sequence[30] followed by simultaneous 2.5 ms ^{13}C and ^{1}H spin lock and then acquisition of the ^{13}C magnetization with ^{1}H decoupling. Rotating frame spin–lattice relaxation time, $T_{1\rho}^H$, was measured by 90°–90° phase shift spin locking sequence[30].

RESULTS AND DISCUSSION

The characteristics of the component polymers used in the preparation of blends are summarized in *Table 1*. The PMMA-i is found to contain 95% isotactic triads. However, the as-received sample contains an extraneous high molecular weight (M_w) fraction (*Figure 1*). In order to minimize the effect of molecular weight distribution on miscibility, we have removed the high M_w portion from the sample by fractionation (*Figure 1*). The polydispersity index, M_w/M_n, of the fractionated PMMA-i is comparable to that of PMMA-s or the styrene copolymer (*Table 1*). The fractionated sample has the same triad contents. Its number average molecular weight decreases from 6.5×10^4 to 5.9×10^4 and its polydispersity of 1.7

Table 1 Characteristics of poly(styrene-co-vinylphenol) and poly-(methyl methacrylate)

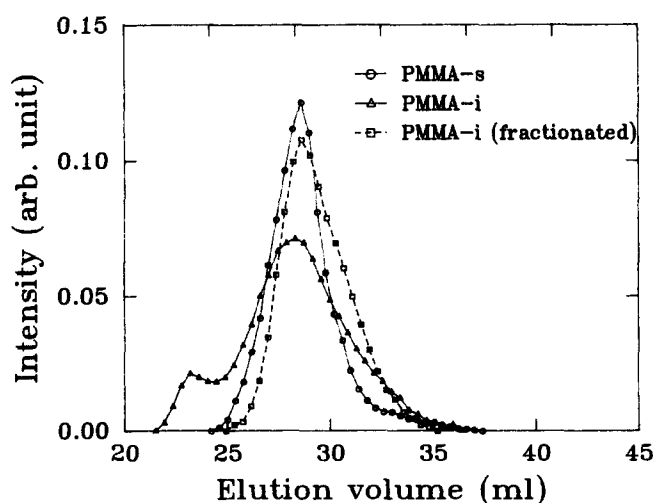| Polymer	M_n	M_w/M_n	Triads I	H	S
Poly(styrene-co-vinylphenol) (5%)	84 900	1.70	atactic		
Syndiotactic poly(methyl methacrylate)	73 500	2.00	2	22	76
Isotactic poly(methyl methacrylate)	65 300	4.00	95	4	1
Isotactic poly(methyl methacrylate)^a	59 400	1.74	95	4	1

^{a} Fractionated sample

Figure 1 Molecular weight distributions of PMMA-s, PMMA-i and fractionated PMMA-i

is more in line with that of MPS-5 or PMMA-s. N.m.r. experiments were conducted on the blends of both original and fractionated PMMA-i. The PMMA-s was found to be comprised of 76% syndiotactic, 22% heterotactic and about 2% isotactic triads. Concerning the possibility of crystallization, previous study[31] indicates that crystallization can be induced in PMMA-i and PMMA-s by stretching them to about 5–10 times the original lengths. However, without any orientation, the crystallization of our homopolymer and miscible blends was not detected by d.s.c. and light scattering; the crystallization of immiscible blends was also not detected by d.s.c. Therefore, all blends presented here are considered amorphous blends. The density of the component polymers and their blends are measured with a density gradient column; the results are shown graphically in *Figure 2*. The PMMA-i sample has a higher density than its syndiotactic counterpart and this is consistent with the greater chain flexibility and closer chain packing in the PMMA-i[32]. The density results also show that the excess volumes of mixing are negative for the blends of PMMA-i, while the blends of PMMA-s have positive excess volumes. As shall be seen later, the excess volume of mixing does not seem to have a one-to-one relationship with miscibility behaviour in our blends.

Glass transition temperatures

The results of T_g measurements by d.s.c. are displayed in *Figure 3*. Each of the PMMA-s blends shows a single T_g. The T_g values of the PMMA-s blends are lower than the predictions of the Fox equation or the weight average
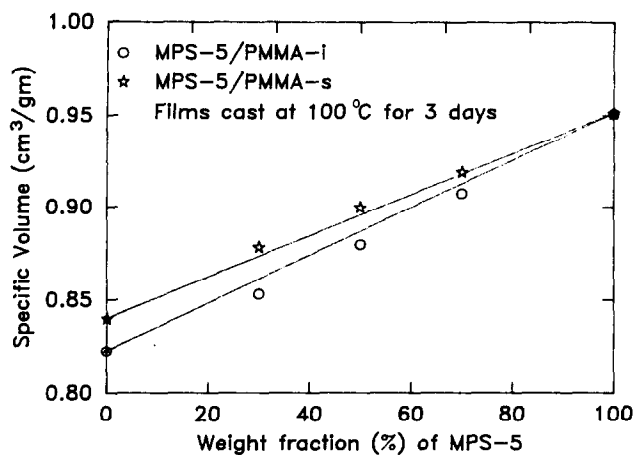
Figure 2 Specific volumes of homopolymers and blends at various compositions
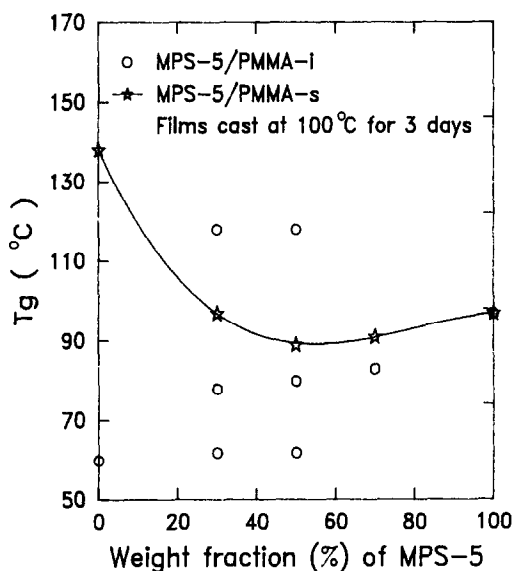

Figure 3 Glass transition temperatures of homopolymers and blends at various compositions

values. This is to be contrasted with the results found for the blends of MPS-5 with atactic PMMA. In the latter blends, the T_g values are higher by 1–4°C, than the weight average predictions[33]. The PMMA-i blends behave differently from their syndiotactic and atactic counterparts. The d.s.c. scan of the 70% PMMA-i shows three transitions, at 62, 78 and 118°C, which are indicative of multiple phases present in the blend. The coincidence of the 62°C transition with the T_g of 60°C for PMMA-i indicates that the phase is composed of nearly 100% PMMA-i. The transition temperature of 78°C lies in between the T_g values of the component polymers and presumably represents the segmental motion in a phase which is intermediate in composition. Unexpectedly, the third transition at 118°C is higher than the T_gs of both component polymers. We do not have an explanation for this observation except to mention that unusually high T_g values of a similar nature have been reported[17] for blends of a phenol-formaldehyde resin with isotactic but not with syndiotactic PMMA. The 50% blend also shows three T_gs, at 62, 80 and 118°C. Again, the lower T_g corresponds to the PMMA-i value and the 80°C transition represents the motion in a phase

of intermediate composition. The 30% PMMA-i blend shows a single T_g at 83°C, which, perhaps coincidentally, is equal to the weighted average of the component T_g values.

If we adopt the argument of Vorenkamp that the free volume effect is a major cause for the difference in the phase behaviours of PVC blends with syndiotactic and isotactic PMMA, then the heterogeneous nature of the 70 and 50% PMMA-i blends can be attributed, at least in part, to the same effect. Although we do not know the characteristic pressure and temperature of MPS-5 in the equation of state theory, the thermal expansion coefficient, characteristic temperature and characteristic pressure of polystyrene[34] are closer to the values for atactic than for isotactic PMMA[31,35,36]. Therefore, the free volume term is very likely to be larger in the two blends of PMMA-i. However, the extent of hydrogen bonding is possibly also different in the two systems.

Phase diagram

Since the PMMA-s blends prepared by casting films at 100°C are single-phased materials, we have determined the temperatures of thermally induced phase separation by observing the cloud points in temperature-scan light scattering experiments. A slow heating rate of 0.1°C min^{-1} was used in hope of approximating equilibrium conditions. The results are shown in *Figure 4* as starred points. In a second set of experiments, a 50/50 film was heated in a vacuum oven by raising the temperature at 10°C intervals and maintaining the oven temperature at each step for 3 days. The temperature of appearance of cloudiness, indicated by a star with an error bar in *Figure 4*, was ~125°C instead of the value of 174°C determined by temperature scan experiments. The large difference of ~50°C between the cloud points determined by temperature scan and oven annealing experiments indicates that even a slow heating rate of 0.1°C min^{-1} is too fast for the kinetics of the phase separation process to take full effect. The determination of the equilibrium phase diagram is obviously a laborious task for our blends. We
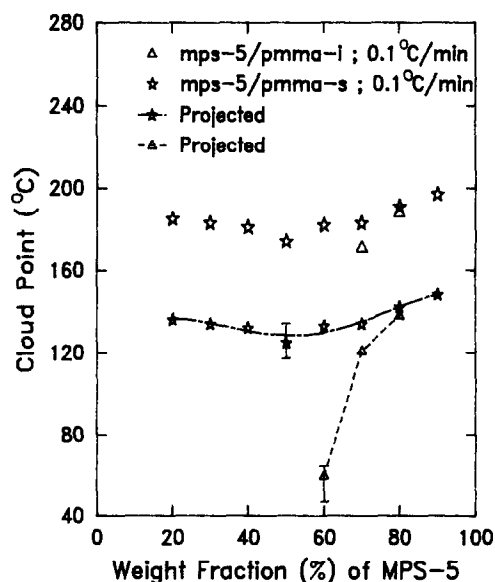

Figure 4 Cloud point temperatures of blends at various compositions. Data points located at higher temperatures are obtained from light scattering; data points with an error bar are obtained from longer time of annealing in vacuum oven; data points connected by a dashed line are the projected values (see text)

Table 2 The relaxation times of component polymers[a]

Resonance lines (ppm)	T_1^H (s)[b]	$T_{1\rho}^H$ (ms)[b]
Poly(styrene-*co*-vinylphenol) (5%)		
39.9	1.63	6.4
127.4	1.70	6.1
145.5	–	–
Syndiotactic poly(methyl methacrylate)		
15.8	0.53	18.1
44.4	0.54	18.0
51.4	0.53	18.1
177.3	0.54	17.7
Isotactic poly(methyl methacrylate)[c]		
15.8	0.68	13.9
44.4	0.67	13.6
51.4	0.67	13.6
177.3	0.67	14.3

[a] $T = 293$ K
[b] $H_1 = 12.4$ Gauss, 90° pulse $= 4.8\ \mu$s
[c] $M_n = 59\,400$, $M_w/M_n = 1.74$

know, however, that the phase boundary ought to lie above 100°C because the three blend films prepared at that temperature are all single-phased. Since the phase boundary is located between 100 and ~170°C, the dashed line in *Figure 4*, obtained by shifting downward by 50°C all the data points from temperature scan light scattering measurements, is an expedient approximation of the lower limit of the boundary location.

Among the PMMA-i blends, the 20 and 30% PMMA-i blends are single-phased and their cloud points determined by temperature scan experiments are 188 and 171°C, respectively. They are indicated by open triangles in *Figure 4*. For the same reason as stated earlier, the equilibrium phase separation temperatures of the two blends must lie between 100°C and the triangles. Again, the two open triangles are shifted downward by 50°C to form part of a dotted line. The 40% blend film was opaque when prepared at 100°C; therefore, its cloud point must lie below 100°C. In order to obtain a better idea of the location of the phase boundary, we have prepared a film of that composition by removing the solvent at a much lower temperature, namely, 38°C. The as-prepared film is transparent although the complete removal of the solvent from the film is not achieved even after evacuation for several days in a vacuum oven. The amount of residue toluene determined from the weight loss of the film after drying at 100°C for 1 day is ~6%. The film was subsequently annealed at 50, 68, 83 and 101°C for 3 days at each temperature. Visually, the blend turned slightly cloudy at 68°C. The cloud point of the film is therefore taken to be about 65°C. Again, this may not be the equilibrium phase separation temperature because the T_g values of MPS-5 and PMMA-i are 100 and 60°C, respectively, and segmental mobilities of both polymers are limited at 65°C. We regard 65°C as the upper limit of the true cloud point of the 40% PMMA-i blend. The dotted line then represents our estimate of the position of the phase boundary in the composition range of 20–40% PMMA-i. We did not determine the phase boundary for blends rich in isotactic PMMA because the equilibrium phase separation temperature of

the 50 and 70% blend were below the T_g of both polymers (<60°C), and therefore could not be detected in a reasonable period of time.

Solid state n.m.r. experiments

Complementary to T_g and phase diagram determination are n.m.r. relaxation time measurements. The spin-lattice and the rotating frame relaxation times, T_1^H and $T_{1\rho}^H$, of the component polymers are given in *Table 2*; an example of the n.m.r. spectra of MPS-5, PMMA-i and their 50/50 blend is given in *Figure 5*. In the measurements of $T_{1\rho}^H$, the magnetization intensities show a single exponential decay with delay times for both the component polymers and the blends. Examples of the magnetization decay with spin-lock delay time for the component polymers are shown in *Figure 6*. All the protons in each component have the same relaxation rate within experimental error; this is due to the averaging of the relaxation processes of all protons by spin diffusion. The results of solid state n.m.r. are given in *Figures 7–9*. Within the experimental error of 5% determined from duplicate experiments, each of the three PMMA-s blends has a single T_1^H (*Figure 7*). Therefore, the blends are homogeneous when probed by T_1 experiments with a time scale of about 1 s. Theoretically, the relaxation rates of a homogeneous blend can be calculated from the linear model[37,38]:

$$k = k_A^0(N_A/N_T) + k_B^0(N_B/N_T) \tag{1}$$

where k_A^0 and k_B^0 denote the intrinsic relaxation rate of protons in component polymers A and B, respectively, and k is the observed spin-lattice (T_1^{-1}) or rotating frame ($T_{1\rho}^{-1}$) relaxation rate of the blend. N_A and N_B are the
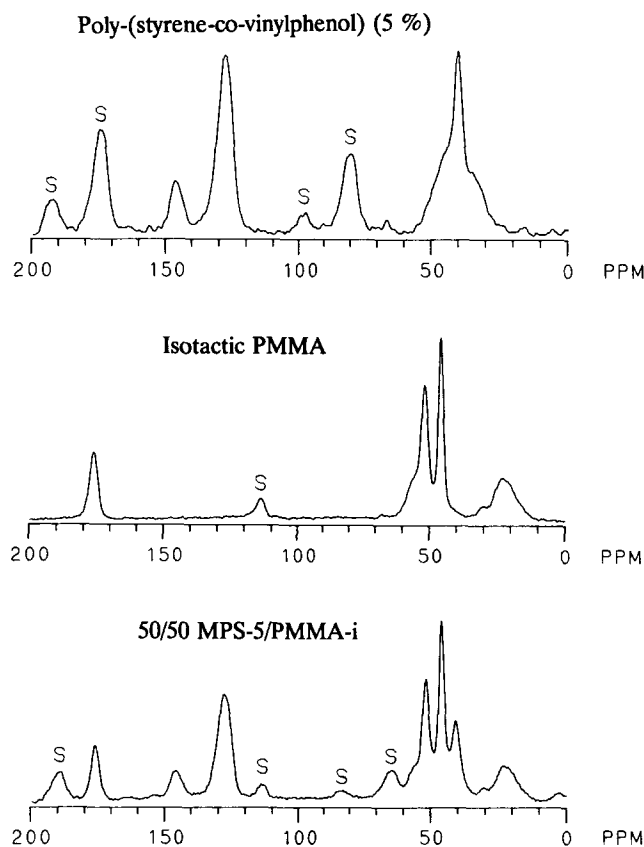

Figure 5 N.m.r. spectra of MPS-5, PMMA-i and their 50/50 blend. 'S' indicates the locations of spinning side bands
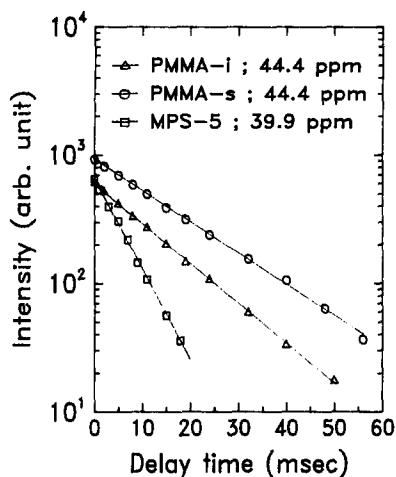
Figure 6 Decay of magnetization with spin-lock delay time for PMMA-s, PMMA-i and MPS-5; values indicated in ppm represent the chemical shift of resonance line shown in *Figure 5*

total number of protons in components A and B, respectively. The experimental T_1^H values are in approximate agreement with the calculated ones, but the discrepancies of about 0.1 s or 10–14% are somewhat outside the experimental error of 5%.

The effective diffusion path length, L, can be estimated for miscible blends by the formula[38,39]:

$$L \sim (6D/k)^{1/2} \qquad (2)$$

where D is the spin diffusion coefficient and k is the intrinsic relaxation rate in equation (2). Typically, for T_1^H of ~ 1 s found for PMMA-s blends and a diffusion coefficient of $10^{-12}\,cm^2\,s^{-1}$, L is approximately 25 nm. Therefore if aggregates of component polymers are present in the blends, their linear dimensions are less than 25 nm on the basis of T_1^H data.

When probed by $T_{1\rho}$ experiments with a time scale of ~ 10 ms, a different picture emerges. The three PMMA-s blends, which are considered to be miscible according to the criteria of T_g and T_1^H, now show two $T_{1\rho}^H$ values for each composition (*Figure 7*). The two sets of $T_{1\rho}^H$ values become closer to each other as the amount of MPS-5 increases in the blend. Although we have not determined the number of interpolymer hydrogen bonds, previous FTi.r. experiments[40] leave no doubt that more hydrogen bonds would be formed when MPS-5 content increases. The gradual converging of the $T_{1\rho}^H$ values with increasing MPS-5 composition can then be interpreted as a decrease in heterogeneities with increasing amounts of hydrogen bonds. We have also noticed that the $T_{1\rho}^H$ values of both the PMMA-s and the MPS-5 protons vary linearly with MPS-5 content of the blends. The two straight lines can be extrapolated to intersect at a point corresponding to a composition of 80% MPS-5 and a $T_{1\rho}^H$ value of 7.3 ms, which is in excellent agreement with the value of 7.2 ms predicted by equation (1). The experimental $T_{1\rho}^H$ for this blend was not measured because longer acquisition time is required to obtain good resolution for the resonance line of the minor component, PMMA-s. The diffusion path length estimated from the extrapolated value is ~ 2 nm for the 20/80 PMMA-s/MPS-5 blend.

The poor miscibility of PMMA-i with MPS-5 is also reflected in n.m.r. results. Two T_1^H values were found for the 70 and 50% blends (*Figure 8*). Although these blends show three transitions in d.s.c. scans and one would

expect multiple relaxation times, the decay of magnetization intensities in T_1^H experiments does not justify data fitting with more than one exponential (*Figures 9* and *10*); hence only one relaxation time is reported here for the protons of each polymer in the blends. The very slight curvature in the short delay time (< 5 ms) represents only an insignificant fraction of the relaxation time in a two-exponential fit and, within the experimental error, its value is very close to that of main decay.

In order to ascertain that the high M_w fraction of the PMMA-i sample is not responsible for the immiscibility of the 70 and 50% blends and hence two T_1^H values, we have carried out the same experiments with the fractionated sample. The results are shown in *Figure 11*. Although there are some differences in the measured relaxation times when compared to the values in *Figure 8*, the discrepancies do not alter the conclusions with regard to miscibility.

The blend of 30% PMMA-i, having a single T_g, shows a single T_1^H and a single $T_{1\rho}^H$ (*Figure 8*). The experimental T_1^H of 1.2 s is in close agreement with the predicted value of 1.1 s; the rotating frame relaxation time of 7.7 ms also compares favourably with the calculated values of 7.5 ms.

The blend containing 30% fractionated PMMA-i shows two $T_{1\rho}^H$ values (*Figure 11*); the two values, 6.9 and 7.7 ms respectively, are close to each other and to the value determined for the blend composed of 30% unfractionated PMMA-i. Thus, although the $T_{1\rho}^H$ values in *Figures 8* and *11* differ for the other compositions, the
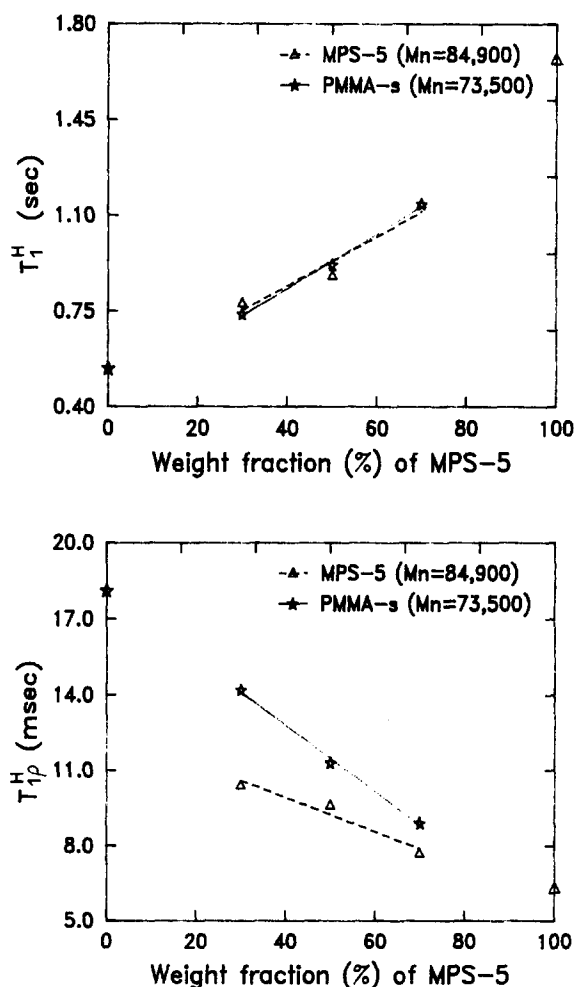

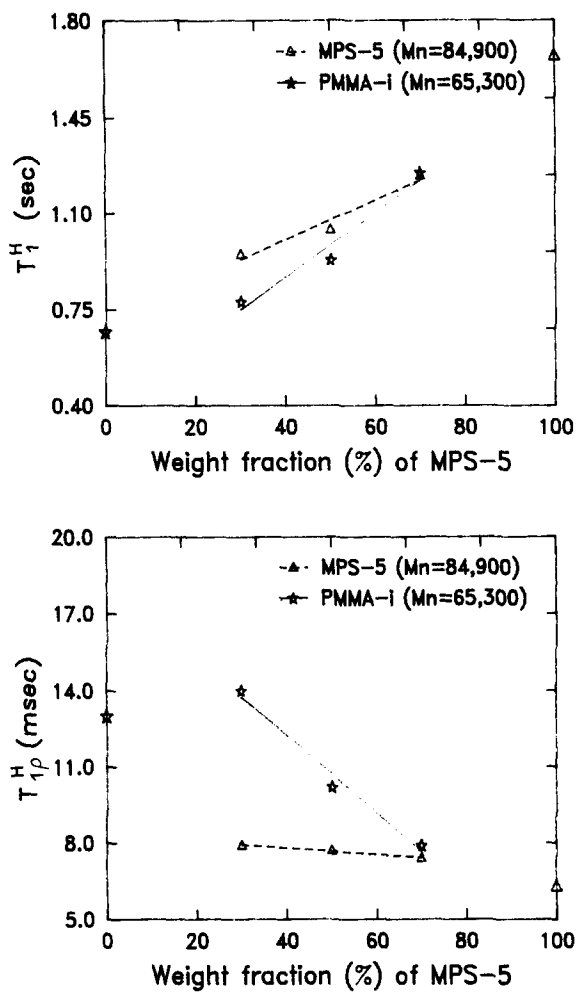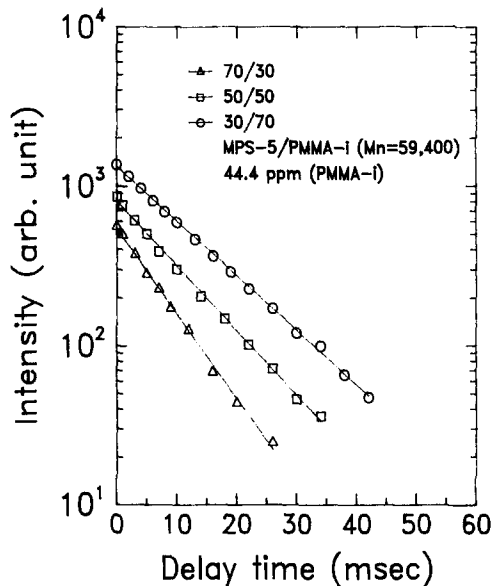**Figure 7** T_1^H and $T_{1\rho}^H$ of blends of PMMA-s at 22°C

Figure 8 T_1^H and $T_{1\rho}^H$ of blends of PMMA-i at 22°C

intimate state of mixing in this blend compared to other PMMA-i compositions is attributed to the increase in the number of hydrogen bonds in the blend. It has been known that in blends[41] of modified polystyrene and atactic PMMA, miscibility can be attained at a fixed

Figure 10 Decay of magnetization with spin-lock delay time for MPS-5/PMMA-i blends; value indicated in ppm represents the chemical shift of resonance line of PMMA-i shown in *Figure 5*
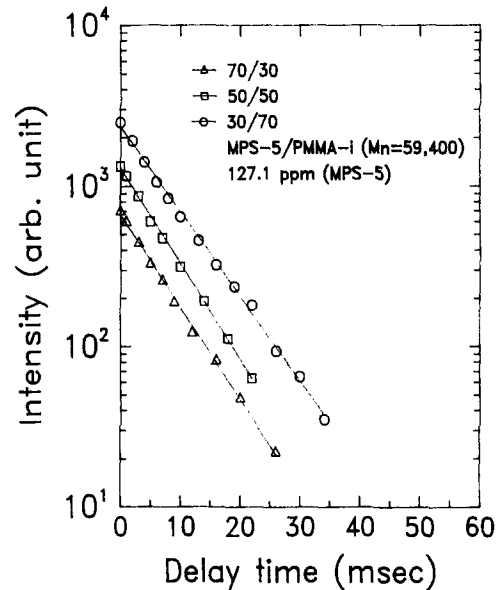

Figure 9 Decay of magnetization with spin-lock delay time for MPS-5/PMMA-i blends; value indicated in ppm represents the chemical shift of resonance line of MPS-5 shown in *Figure 5*
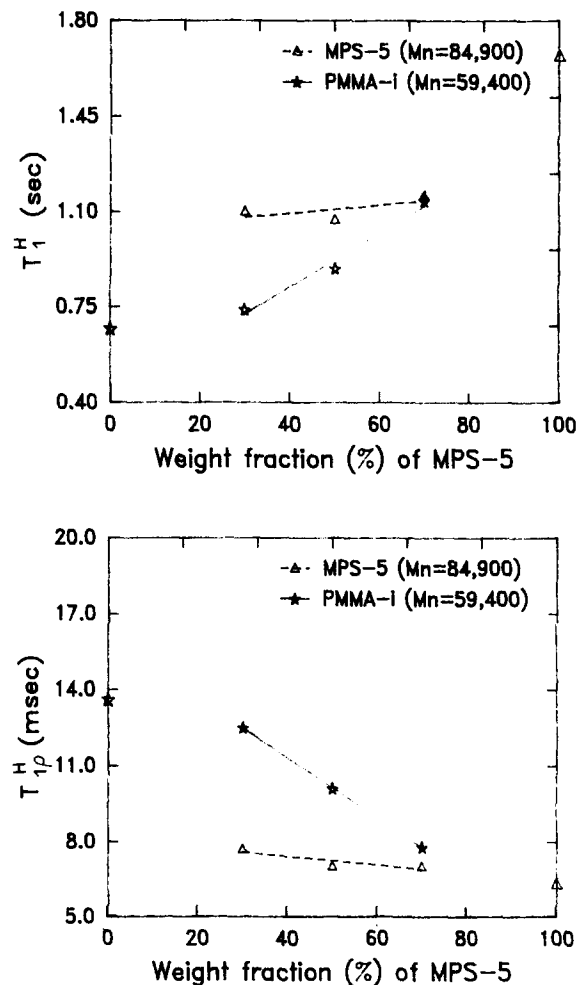
values for the 70% MPS-5 blends show no significant difference. By comparing the $T_{1\rho}^H$ values in *Figure 7* and *Figure 11*, we arrive at the conclusion that, at a blend composition of 70% MPS-5, PMMA-i is as intimately mixed with the styrene copolymer as PMMA-s. The more

Figure 11 T_1^H and $T_{1\rho}^H$ of the blends of fractionated PMMA-i at 22°C
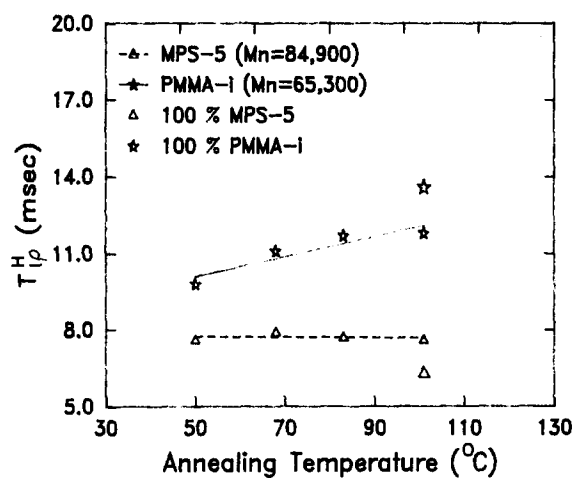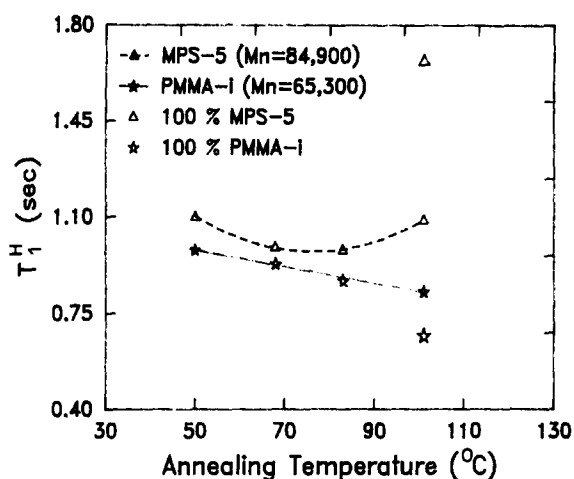
Figure 12 T_1^H and $T_{1\rho}^H$ at 22°C of a 60/40 blend of MPS-5/PMMA-i as a function of annealing temperature

blend composition by increasing the number of hydroxyl groups in the modified polystyrene[24]. In the present case, as the weight fraction of MPS-5 increases from 30% to 70%, the system undergoes two major changes, namely the dilution by MPS-5 and an increase in the number of hydrogen bonds. Both effects can cause changes in miscibility. However, that the PMMA-i is as intimately mixed with the styrene copolymer at this blend composition as the PMMA-s is unexpected and intriguing. Aside from hydrogen bonding, conformation change of PMMA-i is also a possible contributing factor, but we have no experimental evidence to pass judgment on this possibility. The issue is further complicated by the observation that the PMMA-i blend undergoes thermally induced phase separation at a lower temperature than the corresponding PMMA-s blend, that is, the PMMA-i blend is thermodynamically less stable at high temperatures. If we assume that the observed difference is not totally kinetic in origin, the result highlights the interplay of many contributing factors and no simple explanation can be totally satisfactory.

Additional n.m.r. experiments were performed on the 40% PMMA-i blend. As described earlier, the film was cast at 38°C and subsequently annealed at 50, 68, 83 and 101°C for 3 days at each temperature. The relaxation times of the annealed specimens are shown in *Figure 12*. Since the film was initially transparent, one would expect the relaxation times to diverge as the film was annealed

at successively higher temperatures, i.e. as phase separation progressed. The general trend of the experimental T_1^H and $T_{1\rho}^H$ relaxation times indeed meets the expectation. The only exception is the T_1^H result at 50°C. The somewhat larger difference between the two T_1^H values at 50°C than at 68°C is inconsistent with the appearance of cloudiness at 68°C. The discrepancy, however, is not large. Since we did not determine the temperature dependence of the T_1^H values of the component polymers and since the presence of a trace amount of solvent could cause some uncertainties in data interpretation, we did not pursue this issue.

CONCLUSIONS

1. Each of the three PMMA-s/MPS-5 blends shows a single T_g and a single T_1^H. However, when probed by rotating frame experiments, the blends show two relaxation times. Therefore, heterogeneities with a dimension between 25 and 2 nm are present in these blends.

2. Both the 70 and 50% PMMA-i blends exhibit more than one T_g, two T_1^H, and two $T_{1\rho}^H$. When compared to PMMA-s, the poor miscibility of the isotactic polymer in the two blends is caused either by a larger free volume term or a smaller number of hydrogen bonds, or both. If a smaller number of hydrogen bonds is a contributing factor, the conformational effect is suggestive of less accessibility of the carbonyl groups of PMMA-i, in its helical form[32], to the phenol groups of MPS-5, whereas PMMA-s has a planar structure[42] and its carbonyl groups are presumably more accessible.

3. The blend of 30% fractionated PMMA-i shows a single T_g and a single T_1^H. The isotactic polymer exhibits similar miscibility to the syndiotactic material at this particular composition, but it is thermodynamically less stable at temperatures greater than 120°C. The results suggest a different dependence of the interaction parameter on blend composition for these two systems. The change of miscibility of PMMA-i blends from the phase segregated state to the miscible state as the percentage of MPS-5 increases is attributed to the increase in the number of hydrogen bonds in the blends. This is expected to cause the net free energy of mixing to become negative. The possibility of conformation change of PMMA-i during blend formation requires further study.

4. Lastly, we return to the subject of volume of mixing. The negative excess volume of mixing of the 30% PMMA-i blend, when compared to the positive excess volume of the PMMA-s counterpart, would suggest that chain packing is more efficient in the former blend. However, since the two immiscible PMMA-i blends also have negative excess volumes of mixing, excess volume seems to be only one of the factors governing miscibility. Although a majority of the miscible blends have zero or negative excess volumes, positive excess volumes of mixing have been reported for a number of miscible pairs: PVDF–PMMA at temperatures above the melting point of PVDF[43], PEO–PMMA above the melting temperature of PEO[44], and several hydrogen bonded blends[45] similar to the ones studied here.

ACKNOWLEDGEMENTS

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