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Limits to Compatibility in Poly(*x*-methylstyrene)/Poly(2,6-dimethylphenylene oxide) Blends by NMR

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ABSTRACT: Spin–lattice relaxation of protons in the rotating frame, $T^{H}_{1\rho}$, for homopolymers and several blends of poly(4-methylstyrene), P4MS, and poly(2,6-dimethylphenylene oxide), PDMPO, has been measured. The relaxation times for resolved resonances of the two polymers in the blend change significantly with thermal history, indicating inhomogeneity on a 3-nm scale. The 25 P4MS/75 PDMPO blend shows evidence of heterogeneous domains. Both components of a 50 P2MS/50 PDMO system were shown to separate into heterogeneous phases with nonexponential decays of proton magnetization even though the material exhibits only a single broad T_g by DSC. Miscibility of PS with PDMPO is markedly reduced by methyl substituents; the effect is greater for the ortho methyl than the para methyl derivative.

Introduction

Many techniques have been used to characterize polymer blends including macroscopic and thermal properties, scattering of various types of radiation, and infrared and nuclear magnetic resonance (NMR) spectroscopies. In early NMR studies, it was only possible to determine the average relaxation time for all the protons in solid polymers, as in "wide-line NMR". More recently, magic angle spinning cross polarization (MASCP) and high-power decoupling enable the resolution of ^{13}C resonances in solid polymers.[1] Thus, it is possible to study motions of individual carbon atoms of the macromolecule and of those discrete components in a composite system. With proper choices of samples and pulse sequences and two-dimensional techniques, solids NMR can reveal details of molecular motion in the blend phases and interfaces.

The PS/PDMPO pair has been established to form a miscible blend.[2-4] Blends of P4MS with PDMPO have also been shown by microscopic and thermal measurements to be compatible[5] (i.e., they show a single T_g transition by DSC over a range of compositions). The impact strength of the blend increases with increasing PDMPO content. Stejskal et al.[6] have found in the PS/PDMPO blends by MASCP-NMR a very small fraction of apparently free PS content blends.

Since methyl substituents are known to influence blend miscibility,[7] we have used MASCP-NMR to investigate the limits to homogeneity in the blends of PDMPO with P4MS and P2MS.

Materials and Methods

P4MS, MW 108 000, $M_w/M_n = 1.1$, was obtained from Polysciences; PDMPO, MW 47 400, $M_w/M_n = 2.03$, was obtained from Mobil Coporation. PS, MW 110 000, $M_w/M_n = 1.1$, was obtained from Pressure Chemicals. P2MS, MW = 170 000, $M_w/M_n = 2.78$, was prepared by Vanzo.[8]

Blends were prepared by freeze drying benzene solutions of the constituent polymers. The procedure was identical with that used in other structural investigations of Stein and co-workers.[7,8] This preparation technique leads to compatible blends as seen by DSC. The fluffy product was pressed into either a sheet at room temperature for DSC measurements or hand compacted into a solids NMR rotor. Heat treatments were carried out in vacuo as detailed in Table I.

NMR spectra were obtained on an IBM AF200 spectrometer with dedicated solids accessory. $T^{H}_{1\rho}$ was measured as the slope of the intensity of the ^{13}C NMR spectrum vs. time of proton spin lock. The pulse sequence employed was $H^1\,(90°_x)(90°_{y},\tau)$ followed by simultaneous 2-ms ^{13}C and ^1H spin lock and then acquisition of the ^{13}C magnetization with ^1H decoupling. The length of τ ranged from 1 to 40 ms. Twelve τ values were usually taken to determine each slope. Depending upon blend composition, 256–1000 scans were necessary per τ value for a satisfactory signal-to-noise ratio. About 200 mg of blend in sapphire cylinders with Vespel or KelF end caps was spun at 3500–4500 rps in a Doty Scientific Co. (Columbia, SC) solids NMR probe with ~30 psi air drive. All spectra were obtained at ambient probe temperatures of 22 ± 2 °C with 5 μs 90° pulses for both ^1H and ^{13}C nuclei (50-kHz rotating frame).

Table I
Relaxation Parameters for Blends of Poly(4-methylstyrene) and Poly(2,6-dimethylphenylene oxide)

weight fraction PDMPO		$T^{H}_{1\rho}$ (ms)[a] at	
		40 ppm[b]	154 ppm[b]
0(0.0)		8.0 ± 0.5	
0.25	freeze dried	9.2	8.9
	12 h, 70 °C	7.4	8.2[d]
	12 h, 130 °C	9.8	9.8[d]
	12 h, 240 °C	10.3	10.4
0.50	freeze dried	18 (4, 50%)[c]	24 (7.2, 50%)[c]
	12 h, 70 °C	(4, 50%)	20
	12 h, 130 °C	17 (4.1, 50%)	17
	12 h, 240 °C	13	14
0.75	freeze dried	(6.1, 20%)[c]	18
	12 h, 70 °C	21 (6.2, 17%)[c,d]	19
	12 h, 130 °C	25 (5.8, 40%)[c,d]	22
	12 h, 240 °C	19 (2.0, 42%)[c]	20
1.00			31.4

[a] Nominal error, ≤±10%. [b] ^{13}C resonance position at which $T^{H}_{1\rho}$ is observed. [c] Numbers in parentheses represent respectively faster process $T^{H}_{1\rho}$ (method in text) and apparent % of total for that process. [d] Nominal error, ±20%.

Results

The NMR spectra of P4MS, PDMPO, and a 50/50 blend are shown in Figure 1. The low field aromatic unprotonated carbon resonance of PDMPO at 154 ppm (a in Figure 1) and the backbone carbon peak of P4MS at 39 ppm (b in Figure 1) were monitored in the $T^{H}_{1\rho}$ determinations. The chemical shift anisotropy of the former generates spinning side bands which can easily cause interference at 40 ppm. Spinning speeds were optimized to overcome this complication.

The results were treated according to first-order kinetics. Figure 2 shows an example of semilog plot of the intensity of these resonance lines (I_n) vs. proton spin-lock time, τ,

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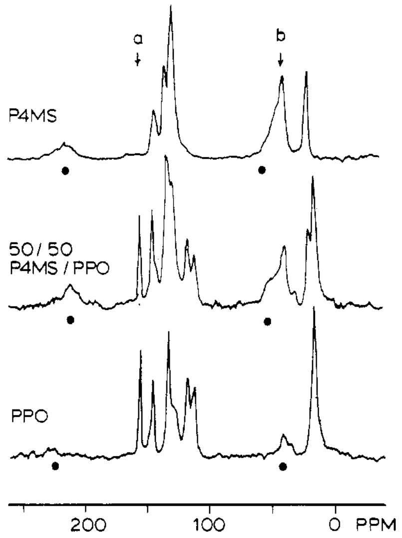

Figure 1. ^{13}C NMR (50.13 MHz) spectra of poly(4-methylstyrene) (upper spectrum), poly(2,6-dimethylphenylene oxide) (lower spectrum), and a 50/50 blend of these two polymers (middle spectrum): (a) the backbone PDMPO resonance at 154 ppm followed in $T^{\rm H}_{1\rho}$ determination; (b) the 39 ppm P4MS resonance. The filled dots designate side-band positions from the major aromatic peaks at 4500 rps spinning rate.

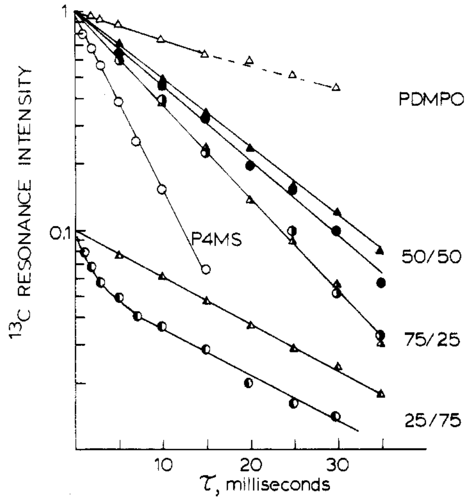

Figure 2. Logarithmic intensity vs. τ, proton spin-lock time for homopolymers PDMPO (△), P4MS (○), and blends of the two homopolymers: 75 P4MS/25 PDMPO (right-filled symbol), 50 4P4MS/50 PDMPO (filled symbols), 25 P4MS/75 PDMPO (left-filled symbols). The triangles refer to PDMPO relaxation at 154 ppm, the circles to P4MS relaxation in the blends. The ordinate for the 75/25 blend has been lowered one decade for clarity.

before cross polarization. The slopes of these plots have good accuracy except for long τ's. Duplicate experiments have reproducibility of better than ±10%.

In most cases the log I_n–τ plot is linear out to 40 ms, giving single $T^{\rm H}_{1\rho}$ times. A few systems showed decay of magnetization which was not simply exponential; the data were analyzed as biphasic parallel first-order processes. These two processes are adequate to describe all data. However, the apparent fraction of each decay component is without quantitative significance because of the complicated effect of spin diffusion on intensity of each component. $T^{\rm H}_{1\rho}$ values so determined are listed in Table I.

The method of sample preparation has a marked effect on the relaxation parameters (Table I). The blends, which had been heated at 240 °C, have monotonic change of $T^{\rm H}_{1\rho}$ with composition. Their decay of magnetization plots are single exponential with the exception of the 40 ppm resonance in the 25 P4MS/75 PDMPO blend.

Table II
Relaxation Times, $T^{\rm H}_{1\rho}$, for Homopolymers PxMS, P2MS, PS, and Their 50/50 Blends with PDMPO

sample	obsd peak, ppm	$T^{\rm H}_{1\rho}$[a] (ms)
P2MS[c]	33.8	68
50/50 P2MS/PDMPO	33.8	39 (2.7, 11%)[b]
50/50 P2MS/PDMPO	154	25 (1.7, 21%)[b]
PS[c]	39.9	6.1
50/50 PS/PDMPO	39.9	10
50/50 PS/PDMPO	154	11

[a] ±10%. [b] Figures in parentheses describe rate constant and apparent fraction of decay for faster process. [c] All homopolymer ^{13}C peaks give same $T^{\rm H}_{1\rho}$.

Judging by MASCP-NMR, the 75 P4MS/25 PDMPO has good miscibility. The components have the same $T^{\rm H}_{1\rho}$ values. There is, however, a slight indication of lengthening of $T^{\rm H}_{1\rho}$ with heat treatment.

For the 50 P4MS/50 PDMPO blend prepared by simply freeze drying, the decay of magnetization for both components is heterogeneous. The $T^{\rm H}_{1\rho}$ values for the slow components are longer than expected. Heat treatments can eliminate the heterogeniety in $T^{\rm H}_{1\rho}$ and also increase the relaxation rates. The $T^{\rm H}_{1\rho}$ heterogeneity is absent for the PDMPO resonance with heat treatment at any temperature. In contrast a single $T^{\rm H}_{1\rho}$ for the P4MS resonance is obtained only by heat treatment at 240 °C. This suggests that the homogeneity of the PDMPO component is greater than that of the P4MS component. Blends heat treated at 240 °C have nearly the same $T^{\rm H}_{1\rho}$ for the two resonance under observation, indicating strong coupling by spin diffusion.

For the 25 P4MS/75 PDMPO blend, the 154 ppm resonance of PDMPO has a single-valued $T^{\rm H}_{1\rho}$ independent of heat treatment. On the other hand, the 40 ppm resonance of P4MS has biphasic decay for samples heat treated at any temperature. Therefore, the heterogeneity of P4MS in blends of this composition is not eliminated by heating at 240 °C.

Data for homopolymer, P2MS, and for a 50/50 blend of P2MS and PDMPO are given in Table II. All the resonance lines of pure P2MS have the same single $T^{\rm H}_{1\rho}$ within ±10%. In the P2MS/PDMPO blend, the resonances of *both* components show biphasic decay. The deviation appears as rapid relaxation processes in the first 5–7 ms for the PDMPO and P2MS resonance lines with a time constant of 1.7 and 2.7 m s^{-1}, respectively. The slow relaxing component of P2MS in the blend has a $T^{\rm H}_{1\rho}$ value of 39 ms which is intermediate between the respective $T^{\rm H}_{1\rho}$ values of P2MS and PDMPO homopolymer of 68 and 31 ms. But the longer relaxation time of PDMPO in the 50/50 blend is only 25 ms, which is shorter than the relaxation times of the homopolymers. Both the fast and slow components of P2MS and PDMPO have different relaxation times.

To ascertain the relaxation behavior of a well-known compatible blend, a 50/50 mixture of PS and PDMPO in benzene was freeze dried. The resonances of both components have the same single-exponential decay $T^{\rm H}_{1\rho}$ values of 10.5 ± 0.5 ms.

Discussion of Results

With the introduction of each new or improved technique, the criteria for compatibility in polymer blends is refined. The current criteria are usually the existence of a single T_g in a DSC scan or the absence of small-angle scattering contributions from domains. The former is a macroscopic thermodynamic second-order transition, the latter measures compatibility on the dimensional scale of several hundred angstroms. The interfacial region is treated qualitatively as domain-boundary mixing or mixing in domains.[9]

Solid-state NMR offers the possibility of examining blends at the molecular level by virtue of the effect of segmental and side-chain motion on relaxation rates of the coherent magnetization. This finer scale of observability complicates the terminology based on macroscopic criteria for compatibility. Miscibility has been a term based on thermodynamics and phase diagram related criteria. We are beginning to be able to "see" blends on a molecular scale where criteria for homogeneity within the possibilities of random or nonrandom molecular scale mixing are not yet clear. Although "miscibility" has been a thermodynamic term, we have used it rather interchangeably with "homogeneity" and compatibility for this molecular scale discussion.

In the present study the relaxation of proton spins in the rotating frame is observed by its effect on the NMR of the carbon nucleus to which proton is bonded. When the different protons are not in contact, each would have its own characteristic relaxation times. In the other extreme, if the protons are closely coupled by rapid spin–spin exchange through dipole–dipole interactions, i.e., spin diffusion, then these protons share the same $T^{\mathrm{H}}{}_{1\rho}$. The latter is usually the case for all protons on a given homopolymer.

The protons of the two components of a compatibile blend have the same $T^{\mathrm{H}}{}_{1\rho}$ values if the molecules are in contact on an intimate molecular distance, L, over which protons can effectively diffuse in a given time, t, related by[1]

$$\langle L^2 \rangle \sim (t/T_2)\langle l_0{}^2 \rangle \qquad (1)$$

where l_0 is the distance between protons and $T_2{}^{-1}$ is the proton spin–spin relaxation or hopping rate. The available time for spin diffusion, t, is equal to spin–lattice relaxation time, T_1 or $T_{1\rho}$. For $t = 10$ ms, $T_2 = 10$ μs, and $l_0 = 0.1$ nm, the observation diameter for spin diffusion is about 3 nm. In other words, when the blend components have the same $T^{\mathrm{H}}{}_{1\rho}$, then the blend is homogeneous at the 3-nm scale. This is the case for 50 PS/50 PDMPO, 75 P4MS/25 PDMPO, and 50 P4MS/50 PDMPO blends.

When there is more than one relaxation process, the observed $T^{\mathrm{H}}{}_{1\rho}$ is that for the fastest process at the temperature of observation. In the present systems, the aromatic groups probably dominant the proton relaxation with contributions from the methyl group and segmental motions. The importance of the methyl group is shown by the fact that the various methyl-substituted styrene molecules have $T^{\mathrm{H}}{}_{1\rho}$ values differing by as much as an order of magnitude. PS (6 ms) < P4MS (8 ms) < P2MS (68 ms). While methyl group rotation is coupled to other motions through dipolar interaction, at room temperature methyl relaxation itself should be too rapid to contribute to $T_{1\rho}$. It appears that the hindered methyl of P2MS greatly diminishes the relaxation rate, probably through inhibition of aromatic group motion. The densities of the P*x*MS homopolymers vary by only 3%, so the relaxation time range of the homopolymers has little to do with differences in packing of molecules.

In an intimately compatible binary blend, the protons of the two components would be interconnected via dipolar interactions, resulting in a common relaxation rate for all protons in the blend. There have been models proposed for the cross-relaxation kinetics of blend components as they approach a final, identical relaxation rate[6] as well as simple linear models for change in final relaxation rate of the blend with composition.[10] The kinetic model has been used to describe an initial curvature such as we observed in the 25 P4MS/75 PDMPO blend, but the quantitative predictions were unsatisfactory. The linear model has been applied to PMMA/PSAN blends at temperatures corresponding to $T^{\mathrm{H}}{}_{1\rho}$ and $T^{\mathrm{H}}{}_1$ minima[11] with due considerations of contributions to relaxation rate by methyl and phenyl groups. If one is willing to sacrifice the specific assignment of contributions of given groups to the relaxation, a general simple linear model can be developed on the observed uniform relaxation rate of a given component containing a known number of protons:

$$(T^{\mathrm{H}}{}_{1\rho})^{-1}_{\mathrm{AB}} = N_{\mathrm{A}}M_{\mathrm{A}}(N_{\mathrm{TOT}}T^{\mathrm{H}}{}_{1\rho,\mathrm{A}})^{-1} + N_{\mathrm{B}}M_{\mathrm{B}}(N_{\mathrm{TOT}}T^{\mathrm{H}}{}_{1\rho,\mathrm{B}})^{-1} \qquad (2)$$

where A and B are components of blend A/B, M_i is the mole fraction of component i, N_i is the number of protons of component i, and $N_{\mathrm{TOT}} = M_{\mathrm{A}}N_{\mathrm{A}} + M_{\mathrm{B}}N_{\mathrm{B}}$. This reduces for the P4MS/PDMPO (A/B) case to

$$(10 - 2M_{\mathrm{B}})(T^{\mathrm{H}}{}_{1\rho})^{-1}_{\mathrm{OBS}} = 10(T^{\mathrm{H}}{}_{1\rho})^{-1}_{\mathrm{A}} + [8(T^{\mathrm{H}}{}_{1\rho})^{-1}_{\mathrm{B}} - 10(T^{\mathrm{H}}{}_{1\rho})^{-1}_{\mathrm{A}}]M_{\mathrm{B}} \qquad (3)$$

So a plot of the left-hand side of eq 3 vs. M_{B} should be linear for a molecularly compatible blend. There is no significant excess volume correction for this case, as density changes with composition are very nearly linear.[2] A plot of the $T^{\mathrm{H}}{}_{1\rho}$ values observed for PDMPO and for P4MS in Figure 3 show eq 3 to describe rather well the relaxation properties of samples heat treated at 240 °C. On the other

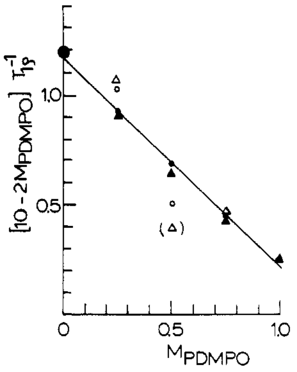

Figure 3. Composition dependence of relaxivity of P4MS/PDMPO blends. Triangles (▵) are for PDMPO relaxation, circles (○) for P4MS. Filled symbols are for 250 °C treated samples, open symbols for samples which were freeze dried at room temperature. The straight line is from eq 2.

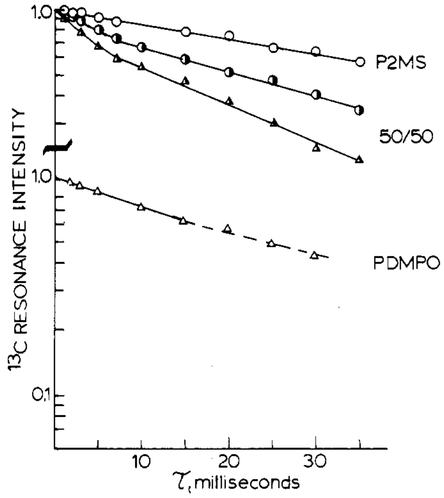

Figure 4. Logarithmic intensity vs. τ, proton spin-lock time for P2MS (○), 50 P2MS (◑)/50 PDMPO (▲), and (▵) PDMPO.

hand, the results of samples prepared by freeze drying only or heat treated at lower temperatures deviate markedly from eq 3. This demonstrates the ability of MASCP-NMR to distinguish adequacy of blending.

The inadequately blended P4MS/PDMPO materials exhibit two other characteristics: each component has a different $T^{\mathrm{H}}_{1\rho}$ or each or both constituents have biphasic decay of magnetization. The former is attributable to dissimilar proton spin temperatures due to phase separation of component macromolecules at scales in excess of 3 nm. The latter suggests heterogeneity in the separated domains. Phase separation and domain heterogeneity are thus distinguishable by MASCP-NMR. The present results showed the P4MS/PDMPO system to have limited homogeneity. In particular the 25/75 blend is incompatible at 3-nm scale even after 12 h of heating at 240 °C. In this instance, it is the minor P4MS component which is separated into heterogeneous domains.

The preliminary results on the P2MS/PDMPO system showed it to be incompatbile for the 50/50 blend. Furthermore both constituent phases separate into heterogeneous domains. Blend samples similarly prepared display a single broad T_g by DSC.[7] Therefore, this blend would be considered compatible according to the T_g criteria but not by MASCP-NMR of relaxation of the protons in P2MS (or PDMPO). That the proton relaxation is faster in the blend for P2MS shows a peculiar interaction with PDMPO or marked changes in the internal dipolar relaxations within the P2MS molecules themselves due to packing in the blend.

A close examination of Figure 2 shows that for 75 P4MS/25 PDMPO, both components relax at exactly the same rate. The data points taken at 154 or 40 ppm compose a single straight line. However, for the 50 P4MS/50 PDMPO blend, the P4MS decays distinguishably faster than that PDMPO. This indicates that at the 50/50 composition, we are on the edge of detecting incompatibility on the ~3-nm scale: the 75/25 blend appears to be more homogeneous than the 50/50 blend.

The P4MS and P2MS blends also show anomalies (Table II). P2MS/PDMPO is more interesting. The relaxation time of PDMPO in the blend is 25 ms, which is faster than for either homopolymer. In the linear additivity model (eq 2), the relaxivity of the blend should lie within the bounds of the relaxation rates of the two components. Nonadditivity of relaxation rates could arise from a marked change in the protons of a given chain due to imposed configurational changes from interaction with the other component. For example, influence of the methyl and aromatic rotations and segmental motion on the proton relaxation rate may be changed due to changes in the compatible blend.

Nonexponential decay such as we see for 25 P4MS/75 PDMPO in Figure 2 was also observed by Stejskal et al.[6] for 25 PS/75 PDMPO blend. Their kinetic cross-relaxation model interpretation involves, qualitatively, the protons of each polymer relaxing initially at a rate closely related to that of the respective homopolymer, followed by decay rates drawn toward equality by a cross-relaxation process. This curvature is only observable on the decay of the fastest component, and although the slow component decay data fit a concave line, the evidence for such curvature of the slow component is poor. Our observation in P2MS/PDMPO that both components show a curvature of the same sign suggests that the kinetic model of these authors is inadequate to explain the cases at hand. The relaxation of proton spins in phase separated heterogeneous domains is anomalous. In cases when the decay of magnetization is biphasic, the initial stage relaxes much faster than the $T^{\mathrm{H}}_{1\rho}$ for the corresponding homopolymer. For the P2MS/PDMPO blend, even the slow decay component for PDMPO has relaxation times shorter than those expected from eq 2. This suggests a distribution of correlation times upon phase separation.

An important conclusion of this work is that methyl substitution of PS can markedly influence miscibility with PDMPO.

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Registry No. P4MS, 24936-41-2; PDMPO (SRU), 24938-67-8; PDMPO (homopolymer), 25134-01-4; P2MS, 25087-21-2; PS, 9003-53-6.

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