Miscibility Study of Poly(styrene-*co*-vinylphenol) with Poly(*n*-butyl methacrylate) by NMR

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ABSTRACT: The miscibility of poly(styrene-*co*-vinylphenol) (MPS) containing 1%, 2%, and 4.4% vinylphenol monomer units with poly(*n*-butyl methacrylate) (PnBMA) was studied with ^{13}C solid-state NMR complemented with DSC, FTIR, and cloud point measurements. Results indicate that the number of vinylphenol monomer units determines the domain size of these blends. The 4.4% MPS/PnBMA blend exhibits a single T_g. The limit of miscibility of this blend calculated from the NMR experiment indicates a scale of homogeneity corresponding to a $T_{1\rho}^H$ value of ~8 ms.

Introduction

The enhancement of polymer–polymer miscibility through chemical modification to introduce functional groups capable of engaging in specific interactions has been the subject of many investigations.[1-8] It has been demonstrated in several cases that small amounts of interacting groups suffice to produce miscible blends. For example, polystyrene (PS) is immiscible with poly(*n*-butyl methacrylate) (PnBMA); but when it is modified to contain ca. 2% of *p*-hydroxystyrene or *p*-(hexafluoro-2-hydroxyisopropyl)styrene as comonomers, hydrogen-bonding interation between the hydroxyl and carbonyl groups renders the modified PS to become miscible with PnBMA.[9]

However, there is a lingering question about the scale of homogeneity of mixing of the long sequences of inherently immiscible styrene and methyl methacrylate units between the sparsely distributed hydrogen bonds. In this paper we report the results of a preliminary study of nuclear magnetic relaxation times which provide an estimate of homogeneity of mixing in these blends.

Experimental Section

Poly(styrene-*co*-vinylphenol) copolymers chosen for this study contain 1%, 2%, and 4.4% vinylphenol monomer units, respectively, and were synthesized by the copolymerization of styrene and *p*-acetoxystyrene with AIBN as initiator.[9] Acetoxy functional groups were subsequently reduced to hydroxyl groups with hydrazine hydrate. Copolymer composition was determined by NMR using the methyl groups in the precursor polymer and compared with the known composition used in the synthesis. The error incurred in this determination is estimated to be ±20%. Poly(*n*-butyl methacrylate) was obtained from Aldrich Chemical Co. Molecular weight and polydispersity of the polymers were measured by GPC (Waters chromatograph) using polystyrene as standards. The characteristics of the polymers used in the blends are listed in Table I. Blends, 50/50 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.

An IBM 200 AF spectrometer (at the University of Massachusetts, Amherst) with a solid accessory was used in this study with ^{13}C observed at 50.3 MHz and 5-μs 90° pulses for both ^1H and ^{13}C. About 100–200 mg of sample in sapphire cylinders with Vespel or KelF end caps was spun at 3.5–4.5 kHz in a Doty Scientific Co. (Columbia, SC) solids NMR probe with ≈40 psi air drive. Spin–lattice relaxation times for protons, T_1^H, at 20 °C were obtained from a 180°–τ–90° pulse sequence[10] followed by simultaneous 2-ms ^{13}C and ^1H spin lock and then acquisition of the ^{13}C magnetization with ^1H decoupling. Rotating-frame spin–lattice relaxation times, $T_{1\rho}^H$, were measured by a 90°–90° phase shift spin-locking sequence.[11]

T_g of the polymer blends was measured with a Du Pont 9900 analyzer equipped with a 910 DSC cell. The scanning range is from −40 to +140 °C with a heating rate of 20 °C/min. The cloud point of the polymer blend was determined with 2-mW He–Ne laser light scattering at a scattering angle of 30° and a heating rate of 0.1 °C/min. Conversion of the free hydroxyl group in poly(styrene-*co*-vinylphenol) to the hydrogen-bonded hydroxyl group in the polymer blend was observed at room temperature with an FTS-60 FTIR spectrometer (Bio-Rad Laboratory, Inc., Cambridge, MA). Average spectra were obtained with 64 scans at a resolution of 2 cm^{-1}.

Table I
Characteristics of Poly(styrene-*co*-vinylphenol) and Poly(*n*-butyl methacrylate)

	mol % of vinylphenol unit	M_n	M_w/M_n
poly(styrene-*co*-vinylphenol)	1	100 900	1.57
	2	101 000	1.63
	4.4	67 400	1.79
poly(*n*-butyl methacrylate)		94 800	2.15

Table II
Glass Transition of Homopolymer and 50/50 Blend of Poly(styrene-*co*-vinylphenol) and Poly(*n*-butyl methacrylate)

	T_{g1}	T_{g2}
poly(styrene-*co*-vinylphenol)	108	
poly(*n*-butyl methacrylate)		34
MPS(1%)/PnBMA	105	*a*
MPS(2%)/PnBMA	109	*a*
MPS(4.4%)/PnBMA	69[b]	

[a] Not observed clearly. [b] A single T_g.

Results and Discussion

The 1% MPS/PnBMA blend was opaque at room temperature; except for the glass transition temperature and NMR relaxation times, other properties were not measured. The glass transition temperatures measured for the 50/50 blend with varying percentages of hydroxyl groups in the modified polystyrene (MPS) are summarized in Table II. A single T_g was observed for the 50/50 blend of MPS (4.4%) and PnBMA. This blend shows a LCST

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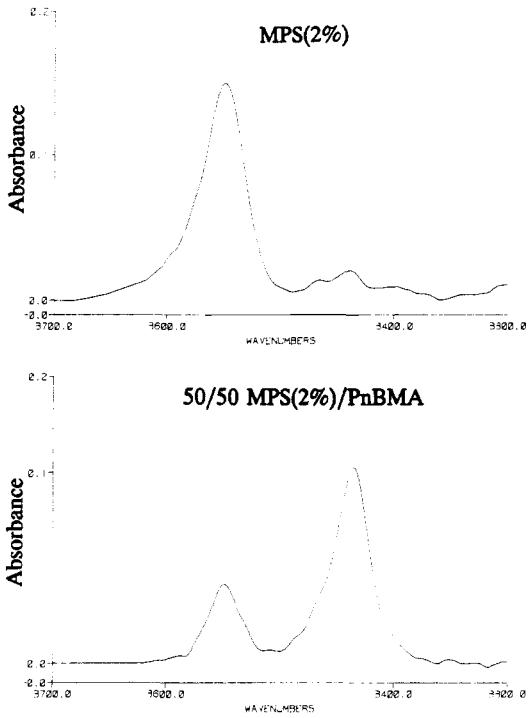

Figure 1. IR absorption spectra of free OH and hydrogen-bonded OH for MPS(2%) and 50/50 MPS(2%)/PnBMA.

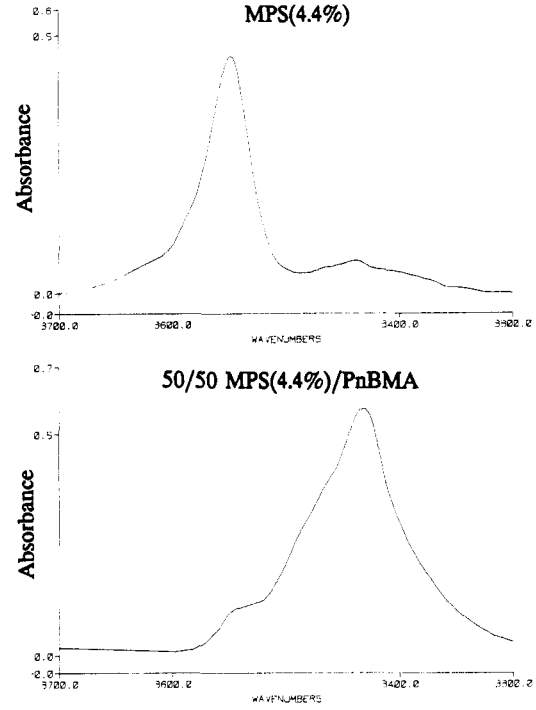

Figure 2. IR absorption spectra of free OH and hydrogen-bonded OH for MPS(4.4%) and 50/50 MPS(4.4%)/PnBMA.

at 138 °C as measured by laser light scattering. The extent of cloudiness in this series of polymer blends decreases as the percentage of hydroxyl groups in MPS increases. For example, the 2% MPS/PnBMA blend shows a scattering maximum at $\theta = 20°$, indicating distinct phases at 25 °C. The domain size in this blend began to increase at 154 °C and reached a constant size at 177 °C. This was observed from the shifting of the scattering maximum toward smaller angles. In the case of the 4.4% MPS/PnBMA blend, no scattering maximum was observed below the LCST, indicating a homogeneous mixture. FTIR measurements of the free hydroxyl groups and hydrogen-bonded hydroxyl groups for the 2% and 4.4% MPS/PnBMA blends are also given in Figures 1 and 2, respectively. For MPS, the absorption of free OH is observed at 3548 cm^{-1}, while a small peak is observed at 3430 cm^{-1}, indicating self-association of hydroxyl groups. In the blend the conversion of free OH into hydrogen-bonded OH increases with the number of OH groups present in MPS. This is due to the larger domain size of MPS in the 2% MPS/PnBMA blend than in the 4.4% MPS/PnBMA blend as observed from light scattering measurements. Consequently, the number of hydrogen bonds between MPS and PnBMA in the 2% MPS/PnBMA blend is less than that in the 4.4% MPS/PnBMA blend. The combination of DSC, light scattering, and FTIR results indicates that the number of vinylphenol units determines the domain size in this series of blends. However, the limits of miscibility in the 4.4% MPS/PnBMA blend cannot be seen from the aforementioned techniques.

One of the powerful means to explore such limits is solid-state CPMAS ^{13}C NMR. Through the understanding of the spin diffusion mechanism and the determination of proton spin–lattice relaxation times, the inhomogeneity of a blend on the nanometer scale can be estimated.[12,13] In a compatible binary polymer blend with a common relaxation rate for all protons in the blend, the relationship between the final relaxation rate of the blend and that of the individual pure compnoents can be described by a linear model. For example, by considering α-methyl motion of PMMA and phenyl group motion of PSAN as relaxation sites in the blend of PMMA/PSAN,[12] one can express the proton relaxation rate of blend as follows:[12]

$$k_1^0(N_m/N_T) + k_2^0(N_\varphi/N_T) = k \quad (1)$$

where k_1^0 and k_2^0 respectively denote the intrinsic relaxation rate of a methyl proton and a phenyl proton, k is the observed spin–lattice (T_1^{-1}) or rotating-frame ($T_{1\rho}^{-1}$) relaxation rate, N_m and N_φ are the number of α-methyl protons and the number of phenyl protons in the blend, respectively, and N_T is the total number of protons in the blend. Without specifying the proton relaxation sites, one can also describe the relaxation rate of a blend by the following equation:[13]

$$k_1^0(N_A/N_T) + k_2^0(N_B/N_T) = k \quad (2)$$

where N_A and N_B respectively are the total number of protons in component A and component B. The effective diffusive path length L can be estimated for a compatible blend of the same proton relaxation rate by the formula[14-16] $L = (6D/k)^{1/2}$. However, since the formula is only approximate, the numerical value of L will not be given here. It suffices to say, in the context of this study, that L and proton relaxation rate go hand in hand with each other.

For this series of MPS/PnBMA blends, the proton relaxation rates of homopolymers are listed in Table III. An example of the NMR spectra of MPS(4.4%), PnBMA, and their 50/50 blend is given in Figure 3. Spinning sidebands in Figure 3 are indicated by arrows. In the measurements of $T_{1\rho}^H$, magnetization intensities show a single exponential decay with delay times for both homopolymers and blends. All the protons in each component have the same relaxation rate within experimental error. The variations of T_1^H and $T_{1\rho}^H$ for MPS and PnBMA in the 50/50 blends with the number of OH groups in MPS are summarized in Figures 4 and 5. The proton relaxation times shown in Figures 4 and 5 are the average values of the relaxation rates measured from different resonance lines corresponding to the relaxation of different protons in the same polymer. Figure 4 shows

Table III
Proton Relaxation Times for Poly(styrene-*co*-vinylphenol) and Poly(*n*-butyl methacrylate)

Poly(styrene-*co*-vinylphenol)

resonance line, ppm	MPS(1%)		MPS(2%)		MPS(4.4%)	
	T_1^H, s	$T_{1\rho}^H$, ms	T_1^H, s	$T_{1\rho}^H$, ms	T_1^H, s	$T_{1\rho}^H$, ms
39.9	1.45	5.4	1.66	5.5	1.69	5.8
127.4	1.46	5.3	1.68	5.8	1.68	6.1
145.5	1.45	5.2	1.71	5.6	1.68	5.7

Poly(*n*-butyl methacrylate)

resonance line, ppm	T_1^H, s	$T_{1\rho}^H$, ms
13.5	0.40	9.7
19.2	0.39	9.6
30.2	0.39	10.1
44.6	0.39	9.6
54.9		
63.6	0.40	8.9
174.6	0.39	9.3

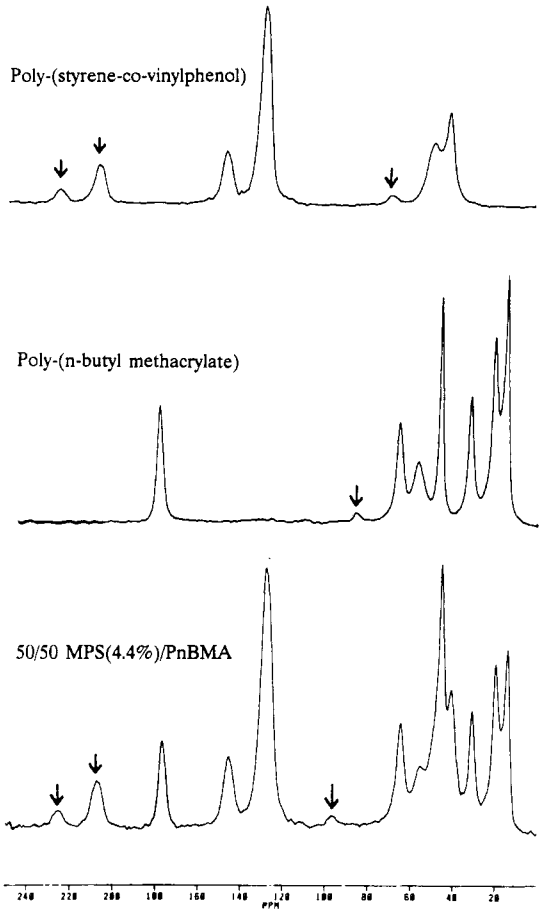

Figure 3. ^{13}C NMR spectra of MPS(4.4%), PnBMA, and 50/50 MPS(4.4%)/PnBMA at 20 °C.

that the T_1^H of each component approaches the same value of 0.61 s as the number of OH in MPS reaches 4.4%. The value 0.61 s compares well with the theoretical value of 0.58 s from eq 2.

To measure the heterogeneity of the blend on a scale less than that indicated by T_1^H, $T_{1\rho}^H$, which measures the molecular motion in the range of kilohertz, was used. Figure 5 shows that the $T_{1\rho}^H$'s of MPS and PBMA for the 1% and 2% MPS/PnBMA blends are almost identical with the $T_{1\rho}^H$'s homopolymers. This means that the diffusive path length in these blends is much smaller than the phase domain. In the 4.4% MPS/PBMA blend, the $T_{1\rho}^H$'s of MPS and PnBMA become very close to each other. $T_{1\rho}^H$'s are 8.2 and 7.7 ms for PBMA and MPS, respectively.

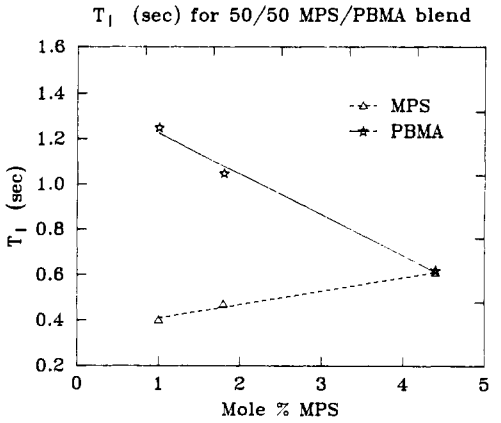

Figure 4. Variations of average relaxation time of different protons in the same polymer, T_1^H, with mole percent of vinylphenol unit in MPS for 50/50 blends of 1% MPS/PnBMA, 2% MPS/PnBMA, and 4.4% MPS/PnBMA at 20 °C.

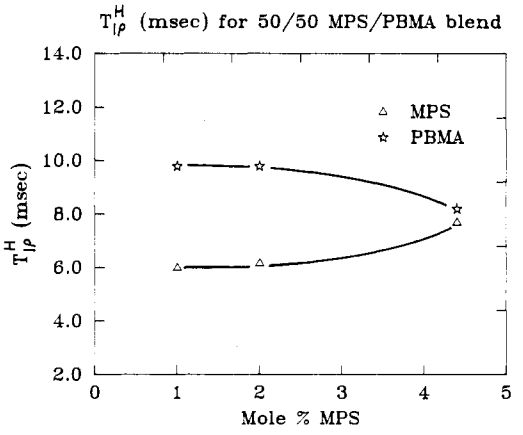

Figure 5. Variations of average relaxation time of different protons in the same polymer, $T_{1\rho}^H$, with mole percent of vinylphenol unit in MPS for 50/50 blends of 1% MPS/PnBMA, 2% MPS/PnBMA, and 4.4% MPS/PnBMA at 20 °C.

Considering an experimental error of ±5% in $T_{1\rho}^H$, one can take 8 ms as the common $T_{1\rho}^H$ in the blend. The predicted value from eq 2 is 7.7 ms. A recent theoretical model predicts the minimum amount of vinylphenol monomer units in a miscible poly(styrene-*co*-vinylphenol) blend with with PnBMA[18] to be ~2%. Our results indicate that a slightly higher vinylphenol content of ~4% is necessary for MPS/PnBMA to become miscible on a scale corresponding to ~8 ms in $T_{1\rho}^H$.

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