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Miscibility and Interactions in Poly(methylthiomethyl methacrylate)/Poly(*p*-vinylphenol) Blends

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ABSTRACT: Poly(methylthiomethyl methacrylate) (PMTMA) is miscible with poly(*p*-vinylphenol) (PVPh) as shown by the existence of a single glass transition temperature in each blend. Fourier transform infrared spectroscopy, solid-state ^{13}C nuclear magnetic resonance spectroscopy, and X-ray photoelectron spectroscopy show that miscibility arises mainly from interactions between the hydroxyl groups of PVPh and the thioether sulfur atoms of PMTMA. Measurements of proton spin−lattice relaxation time in the rotating frame, $T_{1\rho}$(H), reveal that each of the blends has one composition-dependent $T_{1\rho}$(H), indicating that the blends are homogeneous on a scale of about 3 nm.

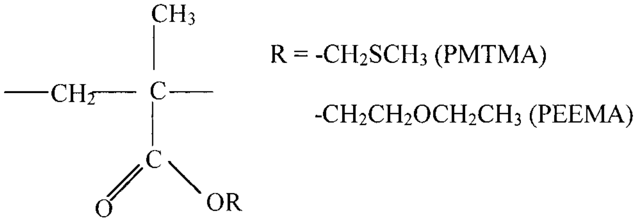
Introduction

Poly(*p*-vinylphenol) (PVPh) is capable of interacting with proton-accepting polymers through hydrogen-bonding interactions involving its hydroxyl groups.[1] As a result of such interactions, PVPh is miscible with a large variety of polymers including polyacrylates,[2] polymethacrylates,[3−10] polyethers,[11,12] polyesters,[13,14] poly(vinylpyridine)s,[15−17] and a number of polymers possessing multiple types of interacting sites.[18−22]

PVPh is miscible with poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate), poly(*n*-propyl methacrylate), and poly(isopropyl methacrylate) but not with poly(*n*-butyl methacrylate).[3,5] For miscible PVPh/PMMA blends, miscibility arises from hydrogen-bonding interactions between the carbonyl groups of PMMA and the hydroxyl groups of PVPh as evidenced by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopic studies.[5,8−10] As the size of the pendant group of polymethacrylate increases, the carbonyl group becomes less accessible and eventually immiscibility sets in.

Hill et al.[7] reported that PVPh is miscible with poly(ethoxyethyl methacrylate) (PEEMA). FTIR and NMR studies also show the existence of hydrogen-bonding interactions between carbonyl groups and hydroxyl groups. They pointed out that the ether oxygen atoms in PEEMA are also available for interactions. However, they did not provide spectroscopic evidence to show the involvement of ether oxygen atoms in hydrogen-bonding interaction. Since PVPh is not miscible with poly(*n*-butyl methacrylate), the miscibility of PVPh with PEEMA suggests that the ether oxygen atoms might actually be involved in hydrogen-bonding interactions with PVPh.

We have recently reported that PVPh is miscible with poly(*N*-acryloylthiomorpholine) (PATM).[22] Using FTIR and X-ray photoelectron spectroscopy (XPS), the hydroxyl groups of PVPh were found to interact with all the three types of interacting sites of PATM, namely, the carbonyl group, the amide nitrogen atom, and the thioether sulfur atom. In this paper, we report the miscibility and interactions in blends of PVPh with poly(methylthiomethyl methacrylate) (PMTMA). It will be shown that PVPh is miscible with PMTMA, and miscibility mainly arises from interactions between the hydroxyl groups of PVPh and the thiother sulfur atoms of PMTMA.



Experimental Section

Materials and Sample Preparation. Chloromethyl methyl sulfide and methacrylic acid were supplied by Aldrich Chemical Co., Inc. Triethylamine was from Fluka Co. PVPh with a reported weight-average molecular weight of 22 000 was supplied by Polysciences, Inc.

The monomer, methylthiomethyl methacrylate, was prepared by reacting chloromethyl methyl sulfide with methacrylic acid in the presence of triethylamine.[23] ^{1}H NMR: 1.92 (s, 3H, CH_3C), 2.2 (s, 3H CH_3S), 5.1 (s, 2H, CH_2S), 5.55−5.58 (m, 1H, $CH_2{=}C-$, trans), 6.09−6.12 (m, 1H, $CH_2{=}C$, cis). Elemental analysis: calculated for $C_6H_{10}SO_2$: C, 49.3%; H, 6.89%; S, 21.9%. Found: C, 49.2%; H, 6.6%, S, 21.3%.

PMTMA was prepared by solution polymerization in tetrahydrofuran (THF) at 70 °C using azobis(isobutyronitrile) as initiator. The molecular weights ($M_w = 12\,000$, $M_n = 6000$) of PMTMA were determined by gel permeation chromatography.

PVPh and PMTMA were separately dissolved in THF to form 1% solutions. Appropriate amounts of PMTMA and PVPh solutions were mixed, and stirring was continued for 3 h. The solution was allowed to evaporate to dryness at room temperature. The blend was then dried in vacuo at 60 °C for 2 weeks.

GPC Measurements. The molecular weights of polymers were determined by a Waters 486 gel permeation chromatograph (GPC) with a Gordi Gel 300 mm × 4.6 mm column. The THF solutions of the polymers were first filtered through a Teflon membrane before injecting into the GPC for a 40 min run at a flow rate of 0.35 mL/min. The elution was monitored using a Waters 410 differential refraction index detector. A

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calibration curve was constructed using several monodisperse polystyrene standards of known molecular weights. The M_w value of the PVPh sample was found to be 20 000, which agrees well with that provided by the manufacturer.

Differential Scanning Calorimetry. The glass transition temperature (T_g) values of various blends were measured with a TA Instruments 2920 differential scanning calorimeter using a heating rate of 20 °C/min. Each sample was subjected to several heating/cooling cycles to obtain reproducible T_g values. The initial onset of the change of slope in the DSC curve is taken to be the T_g.

FTIR Characterization. FTIR spectra were acquired using a Bio-Rad 165 FTIR spectrophotometer. All the samples were prepared by grinding the dry polymers or blends with KBr and compressing the mixtures to form disks. The disks were stored in a desiccator to avoid moisture absorption. Thirty-two scans were signal-averaged at a resolution of 4 cm^{-1}.

NMR Measurements. High-resolution solid-state ^{13}C NMR experiments were carried out on a Bruker DRX-400 MHz NMR spectrometer operating at resonance frequencies of 400 and 100 MHz for ^1H and ^{13}C, respectively. The high-resolution solid-state ^{13}C NMR spectra were obtained by using the cross-polarization (CP)[24]/magic angle spinning (MAS)[25]/high-power dipolar decoupling (DD)[26] technique. A 90° pulse width of 2.75 μs and a contact time of 3 ms were used in ^{13}C CP/MAS experiments. The MAS rate was 8 kHz for measurements of both ^{13}C spectra and relaxation time. The ^{13}C chemical shift of the methine carbon of solid adamantane (29.5 ppm relative to TMS) was used as an external reference standard.

XPS Measurements. XPS measurements were made on a VG ESCALAB MkII spectrometer equipped with a Mg Kα X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Various blends were ground to fine powders and were then mounted on standard sample studs by means of a double-sided adhesive tape. The X-ray source was run at 12 kV and 10 mA, and a pass energy of 20 eV was used in the analyzer. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during measurements. All core-level spectra were referenced to the saturated hydrocarbon C 1s peak at 285.0 eV.

Results and Discussion

General Characteristics of Blends. All the PMTMA/PVPh blends were transparent, and each showed a single T_g, indicating miscibility. As shown in Figure 1, the T_g values of the blends are slightly higher than those expected from the linear additivity rule, and the T_g–composition curve of the PMTMA/PVPh blends can be fitted by the Kwei equation:[27,28]

$$T_g(\text{blend}) = [(w_1T_{g1} + kw_2T_{g2})/(w_1 + kw_2)] + qw_1w_2$$

where k and q are fitting constants. The curve in Figure 1 was drawn using k and q values of 1 and 86, respectively.

Lower critical solution temperature (LCST) behavior in polymer blends is shown to be the result of compressible nature of the system, the directional-specific character of the intermolecular interaction, or a combination of the both.[29] Since hydrogen bonding is of a highly directionally dependent nature, it is of interest to study whether the blends show LCST behavior. The blends were heated in a Fisher-Johns melting point apparatus using a heating rate of about 10 °C/min. However, all the samples remained clear until they began to show signs of decomposition around 280 °C. This result indicates that there exists a strong interaction between the two polymers.

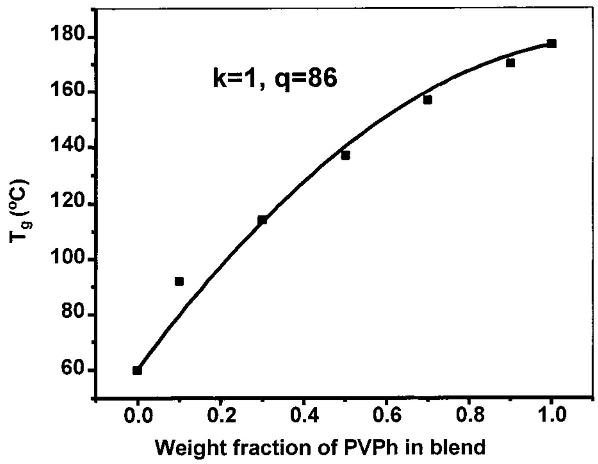

Figure 1. T_g–composition curve of PMTMA/PVPh blends.

Table 1. Characteristics of PMTMA/PVPh Blends

blend	1	2	3
feed comp[a]	0.70	0.50	0.30
feed comp[b]	0.66	0.45	0.26
bulk comp[b]	0.64	0.43	0.24
surf. comp[b]	0.90	0.80	0.64
α	5.06	5.31	5.62
S 2p peak (eV)	163.48, 164.68 164.16, 165.36	163.48, 164.68 164.16, 165.36	163.48, 164.68 164.16, 165.36
fraction of high-BE S 2p peak	0.54	0.63	0.68

[a] Weight fraction of PMTMA. [b] Mole fraction of PMTMA.

Table 1 lists the characteristics of PMTMA/PVPh blends. All the blends show a surface enrichment of PMTMA. Pan and Prest[30] suggested the use of relative enrichment factor (α) to compare surface enrichment. In the present case, α is expressed by

$$\alpha = (S_{\text{PMTMA}}/B_{\text{PMTMA}})/(S_{\text{PVPh}}/B_{\text{PVPh}})$$

where S_i and B_i are the surface composition and bulk composition of polymer i in the blend. The α values of various blends are around 5.3.

FTIR Characterization. PVPh has an excellent potential for hydrogen bonding as a proton donor because of its phenolic hydroxyl groups. Figure 2 shows the IR spectra recorded at room temperature in the 3000–3800 cm^{-1} region (O–H stretching) of PVPh and various PMTMA/PVPh blends. The hydroxyl band of pure PVPh consists of two components: a broad band centered at 3363 cm^{-1}, attributed to hydrogen-bonded hydroxyl groups (self-association), and a relative narrower band at 3530 cm^{-1}, assigned to free (nonassociated) hydroxyl groups. The center of the broad hydrogen-bonded hydroxyl band of the blend shifts slightly to a lower frequency, showing that the intermolecular hydrogen-bonding interactions between PVPh and PMTMA are stronger than the self-association of PVPh. In addition, the intensity of the free hydroxyl band at 3530 cm^{-1} of the blends is reduced significantly, indicating that an increasing number of hydroxyl groups are involved in intermolecular association upon the addition of PMTMA.

Figure 3 shows the carbonyl stretching region of PMTMA/PVPh blends. PMTMA has a strong carbonyl stretching absorption band at 1731 cm^{-1}. There is no peak shift or the development of new peak in the blends, indicating that the involvement of carbonyl groups in interaction with PVPh is not significant. It is then likely that the thioether sulfur atoms are involved instead. In

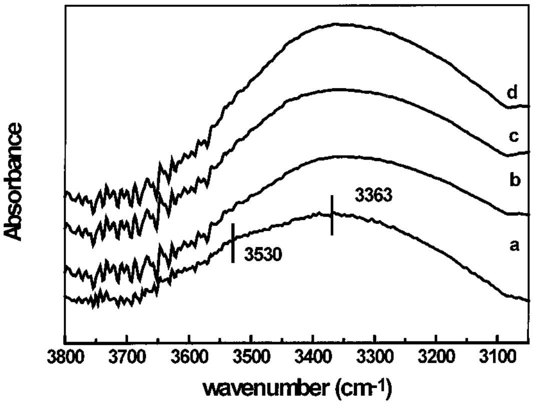

Figure 2. FTIR spectra, recorded at room temperature, of the hydroxyl stretching region of PVPh/PMTMA blends containing (a) 100 (b) 70, (c) 50, and (d) 30 wt % PVPh.

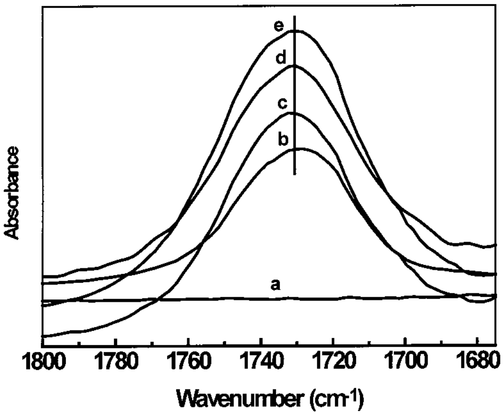

Figure 3. FTIR spectra, recorded at room temperature, of the carbonyl stretching region of PVPh/PMTMA blends containing (a) 0, (b) 100, (c) 70, (d) 50, and (e) 30 wt % PMTMA.

view of the hygroscopic nature of PVPh, FTIR spectra were also recorded at 140 °C, and the spectra show the same features as those recorded at room temperature. Therefore, interaction between PVPh and PMTMA still exists at 140 °C. As mentioned earlier, phase separation was not detected visually up to 280 °C.

NMR Characterization. Evidence on interpolymer interactions in polymer blends and complexes can also be obtained from high-resolution solid-state ^{13}C NMR as demonstrated by changes in chemical shift and/or line shape. For miscible blends of PVPh with PEEMA,[7] poly(methyl acrylate) (PMA),[8] and poly(vinyl methyl ketone),[31] the phenolic carbon resonance peak gradually shifts downfield by 2–2.5 ppm. As shown in Figure 4, the phenolic carbon resonance peak of PVPh at 153 ppm shows a downfield shift upon blending with PMTMA. The shift is about 1.5 ppm for a blend containing 50 wt % PMTMA. On the other hand, the carbonyl carbon resonance peak of PMTMA at 177.3 ppm does not show a significant change in shape and position. In contrast, the carbonyl carbon resonance peak of PMA shows a downfield shift of 0.4–2.4 ppm upon blending with PVPh.[8] For PVPh/PEEMA blends, the development of a new carbonyl carbon resonance peak at 2.5 ppm downfield is observed.[7] Therefore, both FTIR and NMR studies show that interactions between the hydroxyl groups of PVPh and the carbonyl groups of PMTMA, if any, are very weak. However, the resonance peak around 69 ppm arising from $-OCH_2S$ carbon shifts downfield by about 1.5 ppm upon blending. The NMR results therefore also show that the thioether sulfur atoms in PMTMA interact with the hydroxyl groups in PVPh.

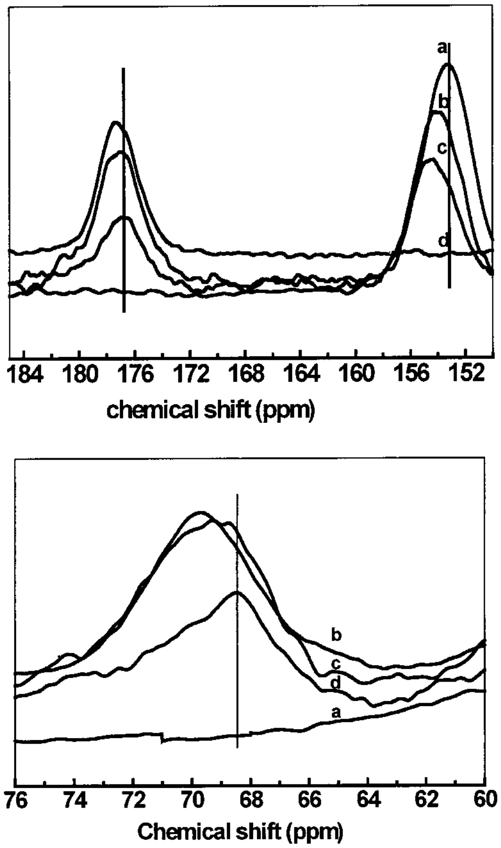

Figure 4. ^{13}C CP/MAS spectra of PMTMA, PVPh, and their blends: (a) PVPh, (b) PMTMA, (c) blend 2, and (d) blend 3.

Table 2. $T_{1\rho}$(H) Values of PMTMA, PVPh, and PMTMA/PVPh Blends

resonance line (ppm)	$T_{1\rho}$(H) (ms)				
	PMTMA	70/30[a]	50/50[a]	30/70[a]	PVPh
177.3	16.1	14.7	13.5	12.3	
153		14.9	13.7	12.5	11.3
128		14.8	13.8	12.6	11.2
69	16.5	15.1	13.9	12.7	
16.5	16.3	15.0	13.9	12.7	11.5

[a] Weight ratio of PMTMA to PVPh in the blend.

Although the existence of a single T_g shows that the two polymers mix to a scale of about 10–30 nm,[32,33] it is worthy to find out if PMTMA and PVPh mix to an even smaller scale through measurements of $T_{1\rho}$(H). The $T_{1\rho}$(H) values of the blends were measured through delayed-contact ^{13}C–CP/MAS experiments. The $T_{1\rho}$(H) values were calculated from eq 1:

$$\ln(M_\tau/M_0) = -\tau/T_{1\rho}(\mathrm{H}) \qquad (1)$$

where τ is the spin-lock time used in the experiment, and M_0 and M_τ are the intensity of peak at zero time and at τ, respectively.

Figure 5 shows the plots of $\ln(M_\tau/M_0)$ vs τ for the carbonyl carbon of PMTMA and PVPh/PMTMA blends and for the phenolic carbon at 153 ppm for PVPh. It is noted that the experimental data are in good agreement with eq 1. From the slope of the fitted line, the $T_{1\rho}$(H) value was determined. Table 2 lists the results of the $T_{1\rho}$(H) values for the PMTMA/PVPh blends. A single composition-dependent $T_{1\rho}$(H) was found for each of the

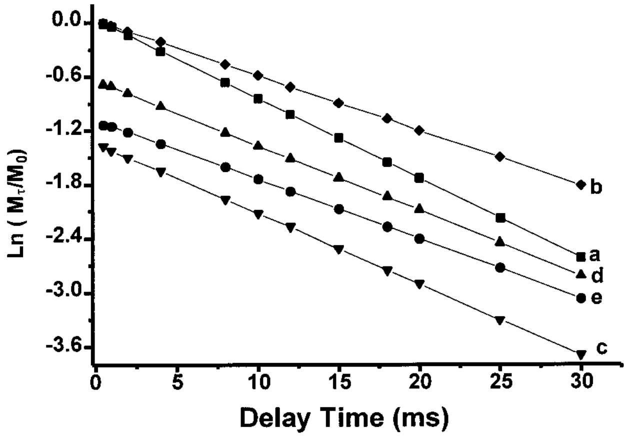

Figure 5. Logarithmic plot of resonance of relative ^{13}C resonance intensity vs delay time: (a) PMTMA, (b) PVPh, (c) blend 1, (d) blend 2, and (e) blend 3. Lines c–e have been shifted down vertically for clearer presentation.

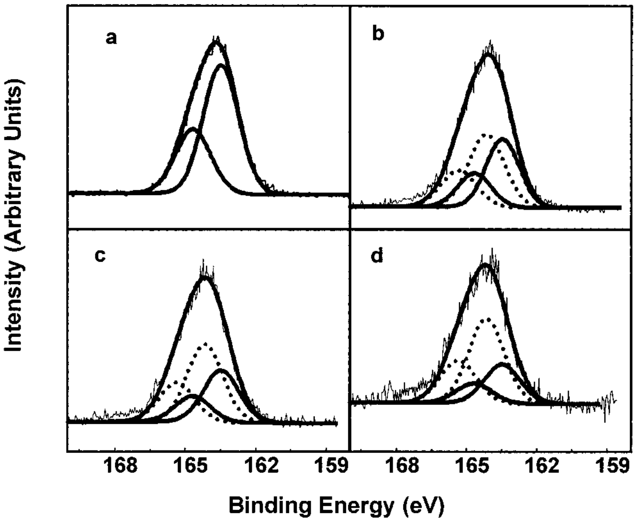

Figure 6. XPS S 2p core-level spectra of PMTMA (a) and PMTMA/PVPh blends containing (b) 30, (c) 50, and (d) 70 wt % PVPh.

blends. Furthermore, the $T_{1\rho}(\mathrm{H})$ values of the blends are intermediate between those of the two pure polymers, suggesting that the blends are homogeneous to a scale where the spin-diffusion occurs within the time $T_{1\rho}(\mathrm{H})$. The upper limit of the spin-diffusion path length L can be estimated using the following equation:[34]

$$L = (6DT_{1\rho}(\mathrm{H}))^{1/2} \tag{2}$$

where D is the effective spin-diffusion coefficient depending on the average proton-to-proton distance as well as the dipolar interaction. The typical value of D is 10^{-16} m^2 s^{-1}. Therefore, the upper limit of the domain size for the PMTMA/PVPh system is estimated to be around 3 nm.

XPS Characterization. The involvement of thioether sulfur atoms in specific interactions with PVPh is also confirmed by XPS. Figure 6 shows the S 2p spectra of PMTMA and three PMTMA/PVPh blends. For PMTMA, the S 2p spin–orbit split doublet is located at 163.48 and 164.68 eV, with an intensity ratio of 2 to 1, attributed to S 2p$_{3/2}$ and S 2p$_{1/2}$, respectively. The S 2p peaks of the blends are broader, and their maxima shift to a higher binding energy region by about 0.6 eV, indicating a change in the environment of sulfur upon blending. Each peak can be curve-fitted by two doublets, with the original doublet remaining at 163.48 and 164.68 eV (full curves). The curve fitting is based on the principle that the new doublet also maintains an intensity ratio of 2:1 for S 2p$_{3/2}$ and S 2p$_{1/2,}$ and the difference in the binding energy values of S 2p$_{3/2}$ and S 2p$_{1/2}$ is also kept at 1.2 eV. In all the cases, the sum of the intensities of the two doublets agrees well with the experimental signals. The presence of a new high-BE S 2p doublet (dashed curves) is evidenced in the spectra of all the blends, showing the interactions between the sulfur atoms in PMTMA and PVPh.

Conclusions

FTIR, NMR, and XPS have been used to investigate specific interactions in miscible PMTMA/PVPh blends. The most interesting and important finding of the present study is that the miscibility of the PMTMA/PVPh blend system mainly arises from interactions between the hydroxyl groups of PVPh and the thioether sulfur atoms of PMTMA. The involvement of the carbonyl groups of PMTMA is not significant. The big sulfur atom might have reduced the accessibility of the carbonyl group. In comparison, the ether oxygen atom in PEEMA is smaller and is one methylene group further away from the carbonyl group. Therefore, the carbonyl groups in PEEMA are still accessible for interaction. Spin–lattice relaxation measurement in rotating frame has shown that the blends are homogeneous down to a scale of 3 nm.

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