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Miscibility of poly(methacrylic acid)/poly(4-vinylpyridine) blends and complexes investigated by high-resolution solid-state ^{13}C NMR

J.Z. Yi, S.H. Goh*

Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore, Singapore 117543

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Abstract

Polymer blends and complexes prepared from poly(methacrylic acid) (PMAA) and poly(4-vinylpyridine) (P4VPy) were investigated by differential scanning calorimetry (DSC) and high-resolution solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Complexes were obtained from ethanol/water (1:1) solutions, whereas blends were cast from dimethylformamide (DMF) solutions. Each of the complexes and blends showed one composition-dependent glass transition temperature (T_g), indicating that both the complexes and the blends are homogeneous on a scale of 10–30 nm. Furthermore, the T_g value of a complex is much higher than that of a blend with the same composition. Measurements of the proton spin–lattice relaxation time in the rotating frame, $T_{1\rho}$(H), reveal that each of the complexes and blends has one composition-dependent $T_{1\rho}$(H), indicating that both the complexes and the blends are homogeneous on a scale of 1–3 nm. However, the calculated domain sizes of the complexes and blends are almost the same.

Keywords: Miscibility; Poly(methacrylic acid); Poly(4-vinylpyridine)

1. Introduction

Two dissimilar polymers are likely to form a miscible blend if they are capable of undergoing specific interactions such as hydrogen-bonding or dipole–dipole interaction. The miscibility of polymer blends is commonly ascertained through the measurements of glass transition temperatures (T_gs) by differential scanning calorimetry (DSC). The existence of a single composition-dependent T_g indicates miscibility on a scale of about 10–30 nm [1,2]. Recently, high-resolution solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy has been used to study the scale of miscibility in polymer blends [2,3]. Mirau and White [4,5] used solid-state 2D HETCOR NMR to study intermolecular interactions in several polymer blend systems. For example, the spectrum of a 1:1 poly(methyl acrylate) (PMA)/poly(*p*-vinylphenol) (PVPh) blend shows the presence of intermolecular carbon–proton dipolar interaction arising from hydrogen-bonding interaction between the carbonyl carbon of PMA and the hydroxyl hydrogen of PVPh. Ruhnau and Veeman [6] used ^{1}H/^{13}C/^{14}N triple resonance solid-state NMR to study the miscibility of poly(methacrylic acid) (PMAA)/poly(*N*-vinylimidazole) blends. The loss of ^{13}C spin-echo intensity upon the irradiation of ^{14}N shows that most of the PMAA carbons are within 0.3 nm from the imidazole ring, and thus, the two polymers mix intimately. The domain size in a polymer blend can be estimated from measurements of T_2-, $T_{1\rho}$-selective Goldman–Shen experiment [7,8] and from measurements of spin–lattice relaxation times in the laboratory frame, T_1(H), and in the rotating frame, $T_{1\rho}$(H) [9–18]. The measurements are frequently performed through the carbon spins. If the two polymer chains in a blend mix intimately, spin-diffusion occurs quickly among the chemically different components, which equilibrates the magnetization, and so single values of the T_1(H) and $T_{1\rho}$(H) are obtained. If not, different T_1(H) and $T_{1\rho}$(H) values are obtained for the carbons corresponding to the different polymers. A single T_1(H) value indicates mixing to a scale of about 20–30 nm, whereas a single $T_{1\rho}$(H) value indicates mixing to a scale of about 1–3 nm.

As mentioned earlier, the formation of a miscible polymer blend requires the presence of specific interactions between the two polymers. When the polymer–polymer interaction outweighs the polymer–solvent interaction, the two polymers form precipitates upon mixing the two polymer solutions, and the precipitates are commonly called a complex [19]. Complex formation depends on the nature of solvent used. If the solvent interacts strongly with the polymers and thus prevents precipitation, the resulting material obtained upon evaporation of the solvent is called a blend. It is commonly observed that the T_g value of a complex is

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* Corresponding author. Tel.: +65-874-2844; fax: +65-779-1691.
E-mail address: chmgohsh@nus.edu.sg (S.H. Goh).

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higher than that of a miscible blend of the same system with similar compositions [20–23]. While two polymers mix randomly in a miscible blend, they are considered to pair in a complex [24,25]. PMAA forms complexes with poly(4-vinylpyridine) (P4VPy) [26,27]. Both Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) have shown that PMAA interacts with P4VPy through hydrogen-bonding interactions [26,27]. In this paper, we report a high-resolution solid-state NMR study on the scale of mixing in the PMAA/P4VPy system. Blends and complexes of PMAA/P4VPy are compared in terms of the scale of mixing.

2. Experimental

2.1. Materials and sample preparation

PMAA and P4VPy with weight-average molecular weights (M_w) of 400 and 200 kg mol^{-1}, respectively, were obtained from Polysciences, Inc.

Various PMAA/P4VPy complexes were prepared as follows. PMAA and P4VPy were separately dissolved in ethanol/water (1:1) to form 3% (w/v) solutions. Appropriate amounts of PMAA and P4VPy solutions were mixed and precipitation occurred, and stirring was continued for 3 h. The complex in the form of precipitate was then isolated by centrifugation, followed by washing with the solvent three times. The complex was dried in vacuo at 60°C for two weeks. The dried complex was ground to fine powder, and then, stored in a desiccator. The ratio of the amount of the complex to the total amount of the two polymers in the initial solutions gives the yield of complex. The bulk compositions of the complexes were determined by nitrogen analysis using a Perkin–Elmer 2400 elemental analyzer. PMAA/P4VPy blends with the same compositions as those of the complexes were then prepared by solution casting from DMF solutions. PMAA and P4VPy were separately dissolved in DMF to form 3% (w/v) solutions. Appropriate amounts of the DMF solutions of PMAA and P4VPy solutions were mixed, and stirring was continued for 3 h. The solvent was then allowed to evaporate slowly at room temperature for several days. The resulting blends were finally dried in vacuo at 60°C for two weeks.

2.2. Differential scanning calorimetry

The T_gs of various samples were measured with a TA Instruments 2920 differential scanning calorimeter. The scanning rate was 20°C min^{-1}. The initial onset of the change of slope in the DSC curve was taken as the T_g.

2.3. NMR experiments

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 ^{1}H and ^{13}C, respectively. The high-resolution solid-state ^{13}C NMR spectra were obtained by using the cross-polarization (CP) [28]/magic angle spinning (MAS) [29]/high-power dipolar decoupling (DD) [30] 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. The proton spin–lattice relaxation times in the rotating frame, $T_{1\rho}(\mathrm{H})$, were determined by spin-locking method [31].

3. Results and discussion

3.1. Differential scanning calorimetry

The mixing of the ethanol/water (1:1) solutions of PMAA and P4VPy led to immediate precipitation. Therefore, the PMAA–P4VPy interaction is stronger than the PMAA–solvent and the P4VPy–solvent interactions, leading to the formation of insoluble polymer complexes. The main characteristics of various complexes are given in Table 1. The yield of complex depends on the feed composition, and reaches a maximum when nearly stoichiometric amounts of PMAA and P4VPy were mixed. The composition of the complex also depends on the feed composition, as commonly observed in other complex systems [22,23,27]. The T_g values of the complexes are even higher that those of PMAA and P4VPy.

The mixing of the DMF solutions of PMAA and P4VPy did not lead to precipitation. The amide carbonyl groups of DMF are able to compete with P4VPy for the interactions with the carboxylic acid groups of PMAA, thus preventing complex formation. Each of the DMF-cast blends also exhibits a single T_g. However, the T_g values of the blends are substantially lower than those of the complexes with the same compositions. It is generally believed that the pairwise association between two different polymer chains in a complex reduces segmental mobility, thus increasing its T_g. Nevertheless, the existence of a single T_g in each complex or blend shows that the two polymers mix to a scale of about 10–30 nm. The T_g-composition curve for PMAA/P4VPy blends as shown in Fig. 1 can be fitted by

Table 1
Characteristics of PMAA/P4VPy complexes

Complex number	1	2	3	4
Feed composition[a]	0.80	0.65	0.47	0.20
Bulk composition[a]	0.82	0.69	0.40	0.17
Bulk composition[b]	0.85	0.73	0.45	0.20
Yield of complex (%)	33	55	75	53
T_g of complex (°C)	182	199	180	181

[a] Weight fraction of PMAA.

[b] Mole fraction of PMAA.

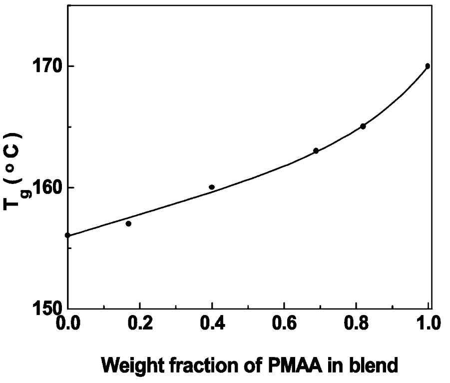

Fig. 1. T_g-composition curve of PMAA/P4VPy blends.

Kwei equation [32,33]

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

where k and q are fitting constants. The curve in Fig. 1 was drawn using $k = 3$ and $q = 5$.

3.2. CP/MAS ^{13}C spectra

In addition to FTIR and XPS, 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. Hydrogen-bonding interactions between PMAA and poly(vinyl alcohol) (PVA) in PMAA/PVA complexes cause an high-field shift of about 3 ppm for the carboxyl carbon of PMAA [9]. The line shapes of the resonance peaks of pyridine ring carbons of P4VPy show changes in miscible P4VPy/cellulose and P4VPy/methylolcellulose blends, and the development of a slight but perceptible shoulder could be observed in the resonance peaks in some blends [10].

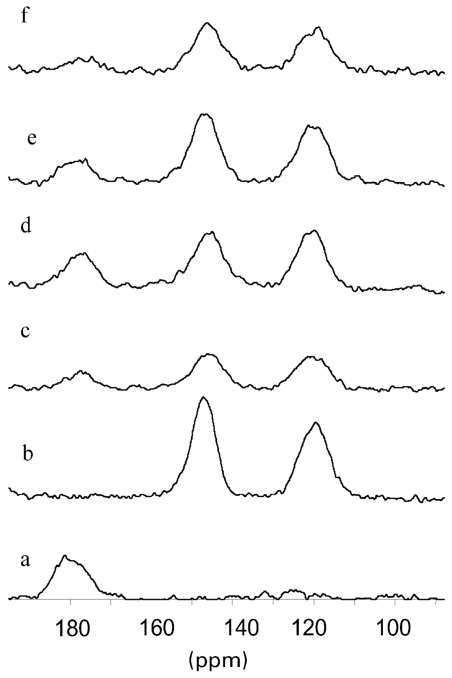

Fig. 2. Part of ^{13}C CP/MAS spectra of PMAA, P4VPy and their complexes: (a) PMAA; (b) P4VPy; (c) complex 1; (d) complex 2; (e) complex 3; (f) complex 4.

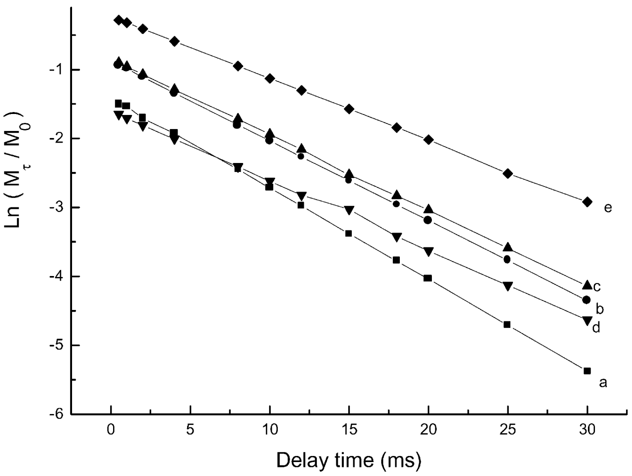

Fig. 3. Logarithmic plot of resonance of C=O in PMAA vs delay time to measure $T_{1\rho}$(H). (a) PMAA; (b) complex 1; (c) complex 2; (d) complex 4; (e) P4VPy. Lines (a)– (d) have been shifted down vertically for clearer presentation.

The ^{13}C CP/MAS spectra in the low-field region of PMAA, P4VPy and their complexes are shown in Fig. 2. The carboxyl carbon peak of PMAA at 181.2 ppm shows a high-field shift in various complexes. The resonance peak around 150 ppm originates from the two carbons adjacent to nitrogen and also the pyridine ring carbon linked to the polymer main chain, whereas the resonance peak around 120 ppm arises from the other two pyridine ring carbons. A change in the line shape of these two resonance peaks in the complexes is noted although the development of a shoulder cannot be clearly observed. The NMR spectra of the four blends show essentially the same features as those of the complexes and their spectra are not shown for brevity. Nevertheless, the NMR spectra provide evidence of the existence of interpolymer interactions between PMAA and P4VPy.

3.3. Relaxation time $T_{1\rho}(H)$

Although the existence of a single T_g shows that the two polymers mix to a scale of about 10–30 nm, it is worthwhile to find out if PMAA and P4VPy mix to an even smaller scale through measurements of $T_{1\rho}$(H). The $T_{1\rho}$(H) values of the blends and the complexes were measured through the delayed-contact ^{13}C CP/MAS experiments. The $T_{1\rho}$(H) values were calculated from the following equation:

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

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.

Table 2
$T_{1\rho}$(H) values of PMAA, P4VPy and PMAA/P4VPy complexes

Resonance line (ppm)	$T_{1\rho}$(H) (ms)					
	PMAA	85/15[a]	73/27[a]	45/55[a]	20/80[a]	P4VPy
179.2	7.56	8.64	9.12	9.21	9.89	
147.6		8.65	9.11	9.22	9.90	11.21
118.6		8.63	9.10	9.20	9.88	11.20

[a] Molar ratio of PMAA to P4VPy in the complex.

Table 3
Average $T_{1\rho}$(H) values and domain sizes for the PMAA/P4VPy system

Mole fraction of PMAA	1	0.85	0.73	0.45	0.2	0
$T_{1\rho}$(H) of complex (ms)	7.56	8.64	9.12	9.21	9.89	11.21
$T_{1\rho}$(H) of blend (ms)		7.82	8.56	9.03	9.57	
Domain size of complex (nm)	1.51	1.61	1.65	1.66	1.72	1.84
Domain size of blend (nm)	1.51	1.53	1.60	1.65	1.69	1.84

Fig. 3 shows the plots of $\ln(M_\tau/M_0)$ vs τ, for the carboxyl carbon of PMAA and P4VPy/PMAA complexes and for the pyridine carbon at 147.6 ppm for P4VPy. It is noted that the experimental data were in good agreement with Eq. (1). From the slope of the fitted line, the $T_{1\rho}$(H) value was determined. Tables 2 and 3 list the results of the $T_{1\rho}$(H) values for the PMAA/P4VPy complexes and blends.

A single composition-dependent $T_{1\rho}$(H) was obtained for each of the complexes and blends. Furthermore, the $T_{1\rho}$(H) values of the complexes and the blends are intermediate between those of the two pure polymers, suggesting that the blends and the complexes are homogeneous to a scale where the spin-diffusion occurs within the time $T_{1\rho}$(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 $10^{-16}\ \mathrm{m}^2\ \mathrm{s}^{-1}$. Therefore, the upper limit of the domain size for the PMAA/P4VPy system is estimated to be around 2 nm (Table 3). The domain sizes of a blend and its corresponding blend are nearly the same. Thus, there is no significant difference between a blend and a complex in terms of the scale of mixing based on NMR studies.

4. Conclusion

PMAA and P4VPy form complexes in ethanol/water (1:1) solutions. The two polymers form miscible blends when cast from DMF solutions. Each of the complexes and blends shows a single T_g. The T_g of a complex is significantly higher than that of a blend with the same composition. Changes in chemical shift and line shape of the carbon resonance peaks show the existence of interpolymer interactions.

Each of the complexes and blends also possesses a single composition-dependent $T_{1\rho}$(H), indicating that they are homogenous to a scale of 1–3 nm. The domain sizes of a blend and a complex of the same composition are almost the same.

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