

Interactions in miscible blends and complexes of poly(*N*-acryloylmorpholine) with poly(*p*-vinylphenol)

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Abstract

Poly(*p*-vinylphenol) (PVPh) and poly(*N*-acryloylmorpholine) (PACM) form interpolymer complexes in ethanol/water (1:1) solution. However, only ordinary blends are obtained from dimethylformamide solution. Each of the complexes and ordinary blends shows one composition-dependent glass transition temperature, indicating its single-phase nature. Fourier transform infrared spectroscopy and ¹³C solid-state nuclear magnetic resonance spectroscopy reveal the existence of hydrogen-bonding interactions between the hydroxyl groups of PVPh and the carbonyl groups as well as the ether oxygen of PACM in the blends and complexes. In addition, X-ray photoelectron spectroscopy shows that the nitrogen atoms in PACM are also involved in hydrogen-bonding interactions. Measurements of proton spin–lattice relaxation time in the rotating frame, $T_{1\rho}(H)$, reveal that each of the complexes and ordinary miscible blends has one composition-dependent $T_{1\rho}(H)$, indicating an intimate mixing on a scale of about 1.5 nm. The blends show a higher degree of surface enrichment of PVPh than the complexes. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Miscible blends; Complexes; Poly(*N*-acryloylmorpholine)

1. Introduction

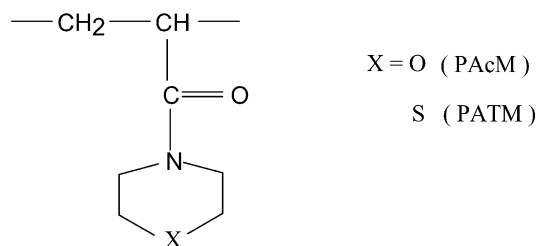
Polymers are generally immiscible with each other in the absence of specific interactions. However, two dissimilar polymers possessing complementary functional groups are likely to be miscible with each other arising from interactions involving the functional groups. For polymer blends prepared by solution blending, when polymer–polymer interaction outweighs polymer–solvent interaction, the two polymers co-precipitate from the solution as a highly associated material called complex [1]. For an immiscible polymer blend, it is then possible to induce miscibility or even complexation when one or both polymers are functionalized to contain interacting groups [2–8].

Poly(*p*-vinylphenol) (PVPh), a proton-donating polymer, is miscible with a large number of proton-accepting polymers such as poly(alkyl methacrylate)s [9–15], poly(4-vinylpyridine) [16–18], poly(1-vinylimidazole) [19],

tertiary amide polymers [20–22] and polyamide-6 [23]. The presence of hydrogen-bonding interactions in these blends is shown by Fourier transform infrared spectroscopy (FTIR), solid-state ¹³C nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS). PVPh forms complexes with some of these polymers [16,17,19,20].

Our recent studies focus on blends of PVPh with polymers possessing multiple types of interacting groups [24–30]. In some cases, all the different types of interacting groups of proton-accepting polymers, for example, poly(*N*-acryloyl-*N'*-phenylpiperazine) and poly(*N*-acryloylthiomorpholine) (PATM), interact with the hydroxyl groups of PVPh [28,30]. On the other hand, PVPh interacts with the thioether sulfur atoms but not the carbonyl groups of poly(methylthiomethyl methacrylate) [24]. The present work deals with the miscibility and interactions in blends and complexes of PVPh with poly(*N*-acryloylmorpholine) (PACM). PACM possesses three types of proton-accepting sites: carbonyl oxygen, ether oxygen and amide nitrogen. It will be shown that PVPh interacts with all the three types of interacting sites.

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2. Experimental section

2.1. Materials

Acryloyl chloride and morpholine were supplied by Aldrich Chemical Co. Inc., and triethylamine was from Fluka Company. PVPh ($M_w = 22\,000$) was supplied by Polysciences, Inc.

2.2. Synthesis of PAcM

Morpholine (0.125 mol, 11 ml) and triethylamine (0.175 mol, 20 ml) were dissolved in 150 ml of dry tetrahydrofuran (THF) in a 250 ml two-necked round-bottom flask fitted with a nitrogen inlet. The flask was cooled in an ice-water bath (4 °C) and maintained under flowing nitrogen. THF solution (30 ml) containing acryloyl chloride (0.13 mol, 10.5 ml) was added dropwise over a period of 60 min with constant stirring. The reaction mixture was then allowed to equilibrate to room temperature and continuously stirred overnight. Triethylamine hydrochloride was removed by filtration and washed repeatedly with warm THF solution. The filtrate was concentrated using a rotary evaporator. *N*-acryloylmorpholine in a form of brown liquid was obtained by distillation at 98–100 °C under a reduced pressure of 5 mmHg. Hydroquinone (0.5 wt%) was added prior to distillation to inhibit any spurious polymerization of the monomer. ^1H NMR: 2.33–2.59 (m, 2H + 2H, (CH₂O–), 3.34–3.51 (br, 2H + 2H, OCN(CH₂)₂), 5.45–5.57 (m, 1H, CH=C–CON<, *trans*), 6.01–6.10 (m, 1H, CH=C–CON<, *cis*), 6.15–6.44 (m, 1H, =CHCON<). Elemental analysis: calculated for C₇H₁₁O₂N, C (59.6%), H (7.8%), N (9.9%); found C (60.0%), H (8.0%), N (9.8%).

PAcM was prepared by solution polymerization using azobisisobutyronitrile (AIBN) as initiator. *N*-acryloylmorpholine (3 g) and AIBN (0.5 wt%) were dissolved in 90 ml freshly distilled dioxane in a 150 ml round-bottom flask fitted with a vacuum tap. The flask was heated in an oil bath at 70 °C for 24 h with constant stirring. The viscous content of the flask was poured into a large volume of hexane to precipitate the polymer. The polymer was purified by two dissolution/precipitation cycles using dioxane as solvent and hexane as nonsolvent. The molecular weights ($M_w = 8000$, $M_n = 5000$) of the polymer were determined by gel permeation chromatography.

2.3. Preparation of blends and complexes

PVPh and PAcM were separately dissolved in ethanol/water (1:1) or DMF to form 1% (w/v) solutions. Appropriate amounts of PAcM and PVPh solutions were mixed under continuous stirring for 3 h. In the case where precipitation occurred, the complex in the form of precipitate was isolated by centrifugation, followed by washing with the solvent three times. The complex was dried in vacuo at 60 °C for 2 weeks. The ratio of the amount of dried complex to the total weight of two polymers in the initial solution gives the yield of the complex. The nitrogen contents of various complexes were determined by elemental analysis using a Perkin–Elmer 2400 elemental analyzer. In the case where precipitation did not occur, the solution was allowed to evaporate to dryness to give an ordinary blend. The blend was also dried in vacuo at 60 °C for 2 weeks.

2.4. 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 refractive index detector. A 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 that agrees well with that provided by the manufacturer.

2.5. DSC measurements

The glass transition temperature (T_g) values of various complexes and 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 .

2.6. FTIR characterization

FTIR spectra were acquired using a Bio-Rad 165 FTIR spectrophotometer. Both the blend and complex samples were prepared by grinding the dry powders with KBr and compressing the mixture to form disks. The disks were stored in a desiccator to avoid moisture absorption. All spectra were recorded at 140 °C to ensure the exclusion of absorbed moisture. Sixteen scans were signal-averaged at a resolution of 4 cm⁻¹.

2.7. NMR measurements

High-resolution solid-state ¹³C NMR experiments were

Table 1
Characteristics of PAcM/PVPh complexes

Complex	1	2	3	4	5
Feed composition ^a	0.80	0.60	0.50	0.40	0.20
Feed composition ^b	0.77	0.56	0.46	0.32	0.18
Bulk composition ^b	0.57	0.52	0.43	0.30	0.12
Surface composition ^b	0.45	0.42	0.35	0.23	0.10
α	1.62	1.49	1.40	1.44	1.23
Yield (%)	40	54	76	70	26
T_g (°C)	183	185	184	181	180
T_g (°C) after annealing	190	193	192	190	190
N1s peaks (eV)	399.7, 400.6	399.7, 400.7	399.7, 400.8	399.7, 400.7	399.7, 400.7
Fraction of high-BE N1s peak	0.58	0.75	0.84	0.80	0.54

^a Weight fraction of PAcM.

^b Mole fraction of PAcM.

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

2.8. XPS measurements

X-ray photoelectron spectroscopic (XPS) measurements were made on a VG ESCALAB MkII spectrometer equipped with an Mg K α X-ray source (1253.6 eV photons) and a hemispherical energy analyzer. Various blends and complexes 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 C1s peak at 285.0 eV.

3. Results and discussion

3.1. General characteristics of complexes and blends

PAcM and PVPh formed complexes in ethanol/water (1:1) but not in DMF or THF. We have earlier reported that ordinary PATM/PVPh blends cast from THF are miscible [30]. Since PATM is insoluble in ethanol/water (1:1), we were unable to study whether PATM could form complexes with PVPh in ethanol/water (1:1). Nevertheless, the present results show that the interaction between PAcM and PVPh is stronger than those between polymers and ethanol/water.

Many polymer complexes have T_g values higher than those calculated from the weight average values of the T_g values of the component polymers [18,21,26]. The high T_g has been ascribed to interactions between the component polymers which act as physical crosslinks, thus reducing segment mobility. As shown in Table 1, the T_g values of the complexes are in the range of 180–185 °C which are even higher than that of PVPh, the high- T_g component. All the DMF-cast PAcM/PVPh blends were transparent and each showed a single T_g , indicating miscibility. As shown in Fig. 1, the T_g -composition curve for PAcM/PVPh blends is S-shaped and can be fitted by Kwei equation [31,32]:

$$T_g(\text{blend}) = [(w_1 T_{g1} + k w_2 T_{g2}) / (w_1 + k w_2)] + q w_1 w_2$$

where k and q are fitting constants. The curve in Fig. 1 was drawn using $k = 0.15$ and $q = 55$. The formation and dissociation of hydrogen bonds are reversible with temperature for small molecules as well as for polymers in the solid state. The number of hydrogen bonds might be increased if a specimen was annealed for a period of time in its rubbery state, at which the increased chain mobility might permit additional interaction groups to approach each other [20]. Therefore, the various samples were subjected to

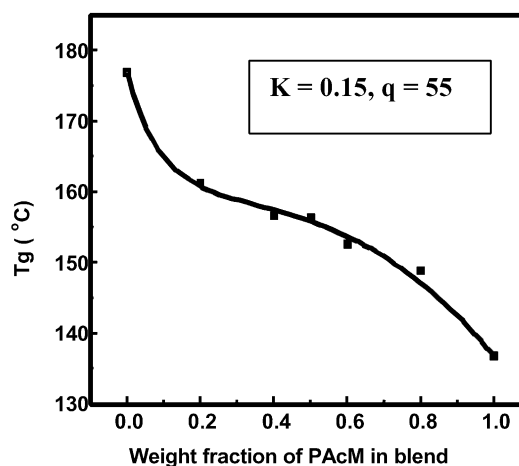


Fig. 1. T_g -composition curve of PAcM/PVPh blends.

Table 2
Characteristics of PAcM/PVPh blends

Complex	1	2	3	4	5
Feed composition ^a	0.80	0.60	0.50	0.40	0.20
Feed composition ^b	0.77	0.56	0.46	0.32	0.18
Bulk composition ^b	0.60	0.53	0.43	0.29	0.16
Surface composition ^b	0.39	0.37	0.31	0.19	0.10
α	2.35	1.92	1.68	1.74	1.72
T_g (°C)	149	152	156	157	161
T_g (°C) after annealing	181	183	187	189	190
N1s peaks (eV)	399.7, 400.6	399.7, 400.7	399.7, 400.7	399.7, 400.7	399.7, 400.7
Fraction of high-BE N1s peak	0.43	0.71	0.73	0.71	0.48

^a Weight fraction of PAcM.

^b Mole fraction of PAcM.

annealing at 190 °C for 24 h. Indeed the annealing process resulted in increased T_g values for the ordinary blends as well as the complexes (Tables 1 and 2). Furthermore, the T_g values of the ordinary miscible blends approach those of the complexes after annealing. While two different types of polymer molecules mix randomly in an ordinary miscible blend, they are considered to be paired in a complex [2,33]. Thus annealing at an elevated temperature promotes pairwise interaction and an ordinary miscible blend can be transformed to a complex. Similar increases in T_g values for hydrogen-bonded blends and complexes upon annealing have also been reported [20,27].

As shown in Table 1, the yields and the compositions of PAcM/PVPh complexes depend on the feed composition as commonly observed in other systems [18–21]. Furthermore, all the PAcM/PVPh complexes and blends show a surface enrichment of PVPh (Tables 1 and 2). The surface enrichment can be compared by relative enrichment factor (α) which is expressed by

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

where S_i and B_i are the surface composition and bulk composition of polymer i in a blend or complex [34]. The α values of various complexes and blends are around 1.4 and 1.8, respectively, showing that the blends show a higher degree of surface enrichment of PVPh than the complexes. This result is in agreement with the report of Liu et al. that the surface enrichment of the lower surface energy component can be reduced or even eliminated via interpolymer complexation [6]. Recently, Duan et al. [35] also reported that hydrogen-bonding interaction reduces surface enrichment.

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 [36]. Since hydrogen bonding is of a highly directionally dependent nature, it is of interest to study the LCST behavior. Various complexes and ordinary miscible 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 280 °C. This result indicates a strong interaction between the two polymers.

3.2. FTIR characterization

Fig. 2 shows the IR spectra in the 3000–3800 cm^{-1} region (OH stretching) of PVPh, PAcM and their complexes obtained from ethanol/water (1:1) solution. The hydroxyl band of pure PVPh consists of two components: a broad band centered at 3384 cm^{-1} , attributed to hydrogen-bonded hydroxyl groups (self-association), and a relative narrow band at 3525 cm^{-1} , assigned to free (non-associated) hydroxyl groups. The center of the broad hydrogen-bonded hydroxyl band of the complex shifts from 3384 to 3355 cm^{-1} , indicating that the intermolecular hydrogen-bonding interaction is stronger than the self-association of PVPh. As the PAcM content in the complex increases, the intensity of the free hydroxyl band at 3525 cm^{-1} decreases, indicating that more free hydroxyl groups are involved in intermolecular association with PAcM. In comparison, the hydroxyl band of PVPh in ordinary PVPh/PATM blends shift from 3384 to 3369 cm^{-1} (we erroneously stated in Ref. [30] that the hydroxyl band shift from 3369 to 3384 cm^{-1}). Thus the larger frequency shift observed in the present system suggests that the overall interaction between PVPh and PAcM is slightly stronger than that

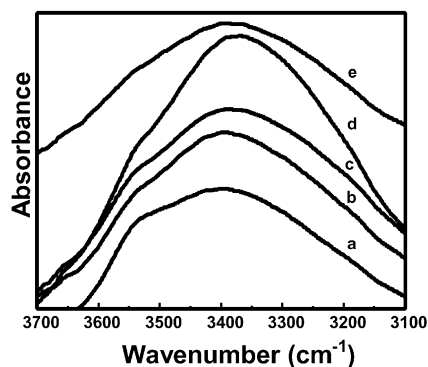


Fig. 2. FTIR spectra, recorded at 140 °C, of the hydroxyl-stretching region of PVPh/PAcM complexes: (a) 100; (b) 88; (c) 70; (d) 48; (e) 43 mol% PVPh.

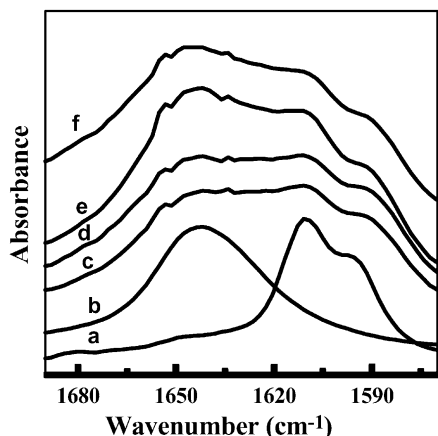


Fig. 3. FTIR spectra, recorded at 140 °C, of the carbonyl-stretching region of PVPh/PACM complexes: (a) 100; (b) 0; (c) 88; (d) 70; (e) 48; (f) 43 mol% PVPh.

between PVPh and PATM. Since oxygen is more electro-negative than sulfur, the ether oxygen atoms in PACM interact more strongly with the hydroxyl groups as compared to the thioether sulfur atoms in PATM.

Fig. 3 shows the carbonyl-stretching region of PACM/PVPh complexes. The amide group of PACM may be described as a hybrid of two resonance structures with two possible hydrogen-bond interacting sites, the amide nitrogen and the carbonyl oxygen, at which interactions can occur with proton-donating polymers [37,38]. The absorption band of this amide group, the so-called amide I, is a combination of the C=O and C–N stretching mode [38]. If the interaction is through the oxygen, the stretching energy of the C=O bond should decrease and the infrared absorption for the carbonyl group will shift to a lower frequency. However, if the interaction is through the lone-pair electrons on the nitrogen atom, the frequency of the carbonyl band should increase [37]. Fig. 3 shows the carbonyl-stretching region of the FTIR spectra for PACM/PVPh complexes. PACM has a strong carbonyl-stretching absorption at 1643 cm⁻¹. It is of interest to note the presence of a new band at 1653 cm⁻¹ in the complexes, which indicates that the hydroxyl group of PVPh interacts with the lone-pair electrons on the nitrogen atom of the amide group through hydrogen bonding. On the other hand, there is another band located at 1633 cm⁻¹, showing the presence of hydrogen-bonding interaction between the hydroxyl groups of PVPh and carbonyl oxygen of PACM. The results suggest that the hydroxyl groups of PVPh interact with both hydrogen-bond interacting sites in the amide groups of PACM.

Fig. 4 shows the infrared spectra of the PVPh/PACM complexes in the ether oxygen region at 140 °C. PACM has a C–O–C band centered at 1115 cm⁻¹. Upon mixing with PVPh, a slight decrease (1–3 cm⁻¹) in the stretching frequency is noted. Although the change is rather small, the involvement of ether oxygen atoms in hydrogen-bonding interactions is further confirmed by NMR as

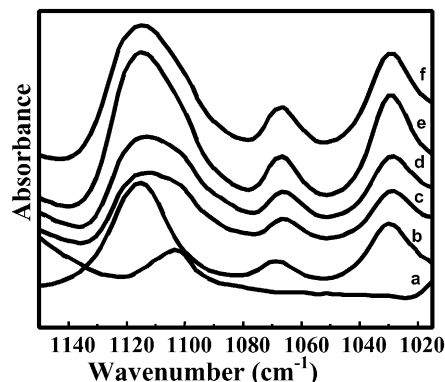


Fig. 4. FTIR spectra, recorded at 140 °C, of the ether-stretching region of PVPh/PACM complexes: (a) 100; (b) 0; (c) 88; (d) 70; (e) 48; (f) 43 mol% PVPh.

discussed in Section 3.3. The FTIR spectra of the ordinary blends also show similar features as those of the complexes and their spectra are not shown.

3.3. NMR characterization

Evidence on interpolymer interactions in polymer blends and complexes can also be obtained from high-resolution solid-state ¹³C NMR as demonstrated by changes in chemical shift and/or line shape. The ¹³C CP/MAS spectra of PACM, PVPh and their complexes are shown in Fig. 5. In various complexes both the carbonyl carbon peak at 176 ppm and the phenolic carbon resonance peak at 153 ppm show a clear downfield shift of about 1–3.5 ppm upon blending, while the ether carbon (–OCH₂) peak at 69 ppm also shifts downfield by about 1 ppm. Furthermore, a broader lineshape of carbonyl carbon and ether carbon is noted in the complexes. The NMR spectra of the ordinary blends show essentially the same features as those of the complexes and their spectra are not shown for brevity. Thus, the NMR results confirm that the carbonyl groups and ether oxygen atoms in PACM interact with the hydroxyl groups in PVPh.

The scales of mixing in various ordinary blends and complexes were determined through measurements of proton spin–lattice relaxation time in the rotating frame, $T_{1\rho}(H)$. The $T_{1\rho}(H)$ values of the complexes and ordinary blends were measured through delayed-contact ¹³C CP/MAS experiments. The $T_{1\rho}(H)$ values were calculated from

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

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.

Fig. 6 shows the plots of $\ln(M_\tau/M_0)$ vs. τ , for the ether carbon of PACM and PVPh/PACM complexes and for the phenolic carbon at 157 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.

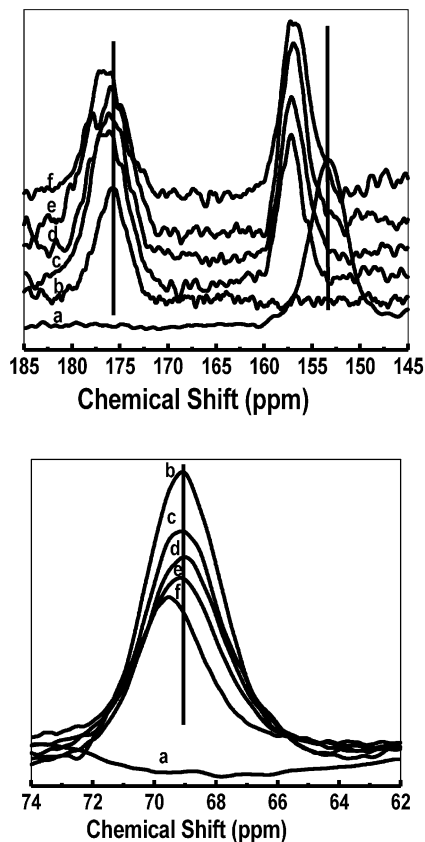


Fig. 5. ^{13}C CP/MAS spectra of PAcM, PVPh and their complexes: (a) PVPh; (b) PAcM; (c) complex 1; (d) complex 2; (e) complex 4; (f) complex 5.

Tables 3 and 4 list the $T_{1\rho}(\text{H})$ values for the PAcM/PVPh complexes and ordinary blends. A single composition-dependent $T_{1\rho}(\text{H})$ was found for each of the complexes and the ordinary blends. Furthermore, the $T_{1\rho}(\text{H})$ values of the complexes and the ordinary blends are intermediate between those of the two pure polymers, suggesting that the complexes and the blends are homogeneous to a scale where the spin-diffusion occurs within the time $T_{1\rho}(\text{H})$. The upper limit of the spin-diffusion path length L can be estimated using the following equation [39]:

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

where D is the effective spin-diffusion coefficient depending on the average proton to proton distance as well as the

Table 3
 $T_{1\rho}(\text{H})$ values of PAcM, PVPh and PAcM/PVPh complexes

Resonance line (ppm)	$T_{1\rho}(\text{H})$ (ms)						PVPh
	PAcM	80/20 ^a	60/40 ^a	50/50 ^a	40/60 ^a	20/80 ^a	
176	3.80	6.01	6.56	7.01	7.27	7.80	
157		6.04	6.60	7.21	7.31	7.60	11.30
117		6.03	6.58	7.11	7.30	7.70	11.10
69	3.84	6.02	6.58	7.14	7.29	7.70	

^a Weight fraction of PAcM.

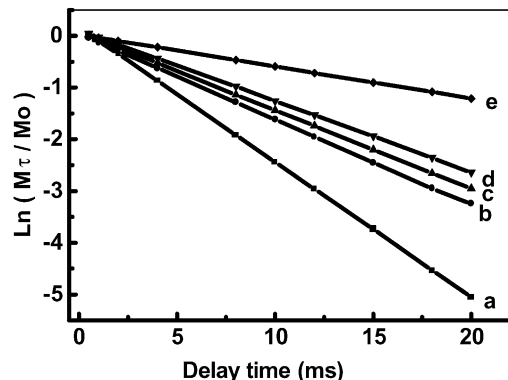


Fig. 6. Logarithmic plots of resonance of relative ^{13}C resonance intensity vs. delay time: (a) PAcM; (b) complex 1; (c) complex 3; (d) complex 5; (e) PVPh.

dipolar interaction. The typical value of D is $10^{-16} \text{ m}^2 \text{ s}^{-1}$. Therefore, the upper limit of the domain size for the PAcM/PVPh complexes and blends is estimated to be around 1.5 nm, and there is no significant difference between the domain sizes of ordinary blends and complexes. We [40] as well as the research groups of Maunu [41] and Jiang [33] have previously found that NMR relaxation study is unable to distinguish a complex from an ordinary miscible blend. However, Lau and Mi [42] recently reported that the homogeneity scale for poly(acrylic acid)/poly(vinyl pyrrolidone) complexes is 1.5 nm and that for the ordinary miscible blends is 2.0 nm based on $T_{1\rho}(\text{H})$ measurements.

3.4. XPS characterization

Fig. 7 shows the N1s spectra of PAcM and PAcM/PVPh complexes. For PAcM, the N1s peak at 399.7 eV is attributed to the amide nitrogen. The N1s peaks of the complexes are broader and asymmetric, and the peak maxima shift to a higher binding energy region. Each peak can be fitted by two component peaks, with one remaining at 399.7 eV. The presence of one new high-BE N1s peaks at 400.7 eV is evidenced in the spectra of all the complexes. Our recent studies on complexes of poly(vinylpyridine) have shown that a shift of about 1.0 eV for N1s is observed for complexes involving hydrogen-bonding interactions [43,44]. Therefore, the XPS results also confirm the existence of hydrogen-bonding interaction between PAcM and PVPh.

Table 4
Average $T_{1\rho}(H)$ values and domain sizes for the PAcM/PVPh system

Weight fraction of PAcM	1	0.8	0.6	0.5	0.4	0.2	0
$T_{1\rho}(H)$ of complex (ms)	3.82	6.02	6.58	7.10	7.30	7.70	11.20
$T_{1\rho}(H)$ of blend (ms)		5.82	6.12	6.45	6.95	7.20	
Domain size of complex (nm)	1.07	1.34	1.40	1.46	1.48	1.52	1.83
Domain size of blend (nm)	1.07	1.32	1.35	1.39	1.44	1.47	1.83

The fractions of the amide nitrogen of PAcM involved in hydrogen-bonding interactions can be estimated from the area of the high-BE N1s peaks. As shown in Tables 1 and 2, more nitrogen atoms of PAcM in the complexes undergo hydrogen-bonding interactions with PVPh than in the ordinary blends.

The O1s spectra of various ordinary blends and complexes are very broad and asymmetric. Since FTIR and NMR studies have shown that the hydroxyl groups of PVPh interact with the ether oxygens and carbonyl oxygens of PAcM, there will be changes in the environments of all the three types of oxygen. In principle, each O1s peak of the ordinary blends and complexes will then consist of six component peaks. Therefore, the curve fitting of O1s peak is not as straightforward as that of N1s peak, and the results may not be meaningful.

4. Conclusions

PAcM forms complexes with PVPh in ethanol/water (1:1) solution, and DMF-cast blends are miscible. FTIR and NMR studies show the existence of hydrogen-bonding interactions between all the three types of interaction sites in PAcM and hydroxyl groups in PVPh. XPS studies also

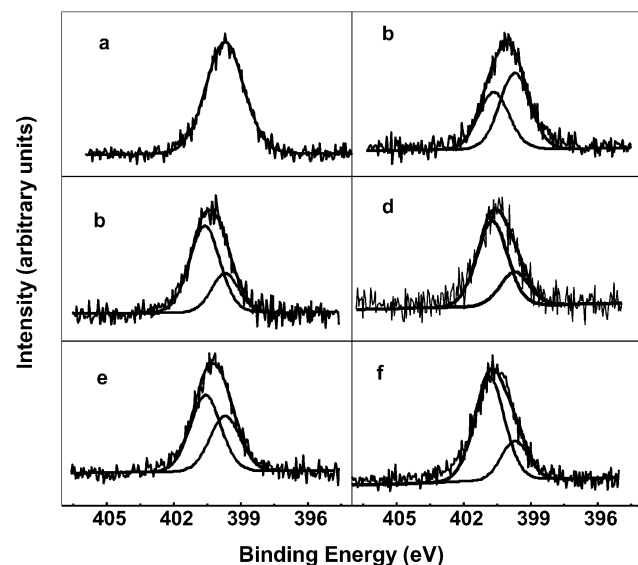


Fig. 7. XPS N1s core-level spectra of PAcM (a); PAcM/PVPh blends containing (b) 20 (c) 40 and (d) 50 wt% PVPh; PAcM/PVPh complexes containing (e) 20 and (f) 40 wt% PVPh.

demonstrate the involvement of the nitrogen atoms and ether oxygen atoms in PAcM in hydrogen-bonding interactions with the hydroxyl groups in PVPh. Spin–lattice relaxation measurements in the rotating frame have shown that both the complexes and the ordinary blends are homogeneous to a scale of 1.5 nm. The ordinary blends show a higher degree of surface enrichment of PVPh than the complexes.

Acknowledgments

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