Polymer Vol. 39 No. 16, pp. 3631–3640, 1998
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0032-3861/98/$19.00+0.00

PII: S0032-3861(97)10271-3

XPS and *FT*i.r. studies of interactions in poly(carboxylic acid)/poly(vinylpyridine) complexes

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(Received 15 September 1997; revised 7 November 1997)

Both poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) form complexes with poly(4-vinylpyridine) (P4VPy) and poly(2-vinylpyridine) (P2VPy) in ethanol/water (1:1) solution. All the complexes show a positive deviation in their glass transition temperature values. The nature of interpolymer interactions in various complexes was studied by Fourier transform infrared (*FT*i.r.) spectroscopy and X-ray photoelectron spectroscopy (XPS). PMAA interacts with P4VPy and P2VPy via hydrogen-bonding interactions. However, both *FT*i.r. and XPS provide evidence of ionic interactions in the PAA complexes. The different complexation behaviour between PMAA and PAA is attributed to the higher acidity of PAA than that of PMAA. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: intermolecular interactions; poly(carboxylic acid); poly(vinylpyridine))

INTRODUCTION

Interpolymer complexes (or simply complexes) have been the subject of many recent studies[1–15]. There are four types of complexes, namely, polyelectrolyte complexes, hydrogen-bonding complexes, stereocomplexes and charge-transfer complexes, of which the first two types receive the most attention. Polyelectrolyte complexes are formed by ionic interactions between two oppositely charged polyelectrolytes in solutions. Hydrogen-bonding complexes arise from hydrogen-bonding interactions between proton-donating polymers and proton-accepting polymers.

Poly(carboxylic acid)s, such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA), are able to form complexes with poly(2-vinylpyridine) (P2VPy) and with poly(4-vinylpyridine) (P4VPy)[16–18]. However, there are still controversies on the nature of the interaction in the complexes. Abe *et al.*[16] suggested that ionic and hydrogen-bonding interactions appeared to co-exist in both PMAA/P2VPy and PMAA/P4VPy complexes. Fujimori *et al.*[17] suggested that hydrogen-bonding complexes were formed between PAA or PMAA with P4VPy. Oyama and Nakajima[18] reported evidence of ionized carboxylic groups in PAA/P4VPy complexes by infrared spectroscopy, but they were unable to find evidence for pyridinium ions by X-ray photoelectron spectroscopy (XPS). On the other hand, Inai *et al.*[11] reported the presence of a hydrogen-bonding interaction in PAA/P4VPy complexes. Lee *et al.*[19] reported the existence of hydrogen-bonding interactions in blends and complexes of poly(ethylene-co-methacrylic acid) (EMAA) with P2VPy.

Our recent studies[13,14,20,21] have shown that XPS is useful to study ionic and also hydrogen-bonding interactions in complexes involving P4VPy or P2VPy. We now report our XPS studies on PMAA/P2VPy, PMAA/P4VPy, PAA/P2VPy and PAA/P4VPy complexes. All the complexes were prepared using the same ethanol/water (1:1) solvent system. In addition, Fourier transform infrared (*FT*i.r.) spectroscopy was also used to complement the XPS results.

EXPERIMENTAL

Materials

PAA with a reported viscosity-average molecular weight of 450 kg mol^{-1} was obtained from Aldrich Chemical Company, Inc. PMAA and P2VPy with weight-average molecular weights ($\bar{M}_w$) of 400 and 200 kg mol^{-1}, respectively, were both purchased from Polysciences. P4VPy with $\bar{M}_w$ of 200 kg mol^{-1} was purchased from Scientific Polymer Products, Inc. The glass transition temperatures (T_g) of PAA, PMAA, P4VPy and P2VPy are 127, 156, 140 and 80°C, respectively.

Preparation of interpolymer complexes

Polymers were individually dissolved in ethanol/water (1:1) solution at a concentration of 10 g l^{-1}. Appropriate amounts of the two polymer solutions were mixed and stirred for 1 h. The complex in a form of precipitate was separated by centrifugation, washed with the original solvent three times, and then dried in vacuo at 60°C for 2 weeks. Finally the complex was ground to fine powder and stored in a desiccator to prevent absorption of moisture. The ratio of the amount of the dried complex to the total amount of the two polymers in the initial solutions gives the yield of complex. The compositions of the complexes were determined based on the nitrogen contents as determined by elemental analysis using a Perkin-Elmer

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Table 1 Characteristics of PAA/P4VPy complexes

	Complex no.				
	1	2	3	4	5
Mole fraction of PAA in the feed	0.2	0.4	0.5	0.6	0.8
Mole fraction of PAA in the bulk of complex	0.54	0.59	0.63	0.66	0.73
Mole fraction of PAA in the surface of complex	0.49	0.51	0.63	0.65	0.71
Yield of complex (%)	13	48	61	59	58
T_g of complex (°C)	199	202	208	215	219
N1s peaks (eV)	399.0, 400.4	399.0, 400.4	399.0, 400.7	399.0, 400.8	399.0, 401.1
Area fraction of the high-BE peak	0.12	0.18	0.21	0.29	0.42

Table 2 Characteristics of PAA/P2VPy complexes

	Complex no.				
	6	7	8	9	10
Mole fraction of PAA in the feed	0.2	0.4	0.5	0.6	0.8
Mole fraction of PAA in the bulk of complex	0.63	0.64	0.65	0.74	0.76
Mole fraction of PAA in the surface of complex	0.64	0.67	0.68	0.77	0.81
Yield of complex (%)	4	22	23	20	21
T_g of complex (°C)	174	177	175	178	177
N1s peaks (eV)	399.0, 400.7	399.0, 401.0	399.0, 400.9	399.0, 401.1	399.0, 401.1
Area fraction of the high-BE peak	0.19	0.21	0.22	0.30	0.36

Table 3 Characteristics of PMAA/P4VPy complexes

	Complex no.				
	11	12	13	14	15
Mole fraction of PMAA in the feed	0.2	0.4	0.5	0.6	0.8
Mole fraction of PMAA in the bulk of complex	0.41	0.49	0.61	0.66	0.75
Mole fraction of PMAA in the surface of complex	0.53	0.60	0.73	0.81	0.90
Yield of complex (%)	22	57	75	60	33
T_g of complex (°C)	170	183	180	174	181
N1s peaks (eV)	399.0, 400.1	399.0, 400.3	399.0, 400.3	399.0, 400.2	399.0, 400.2
Area fraction of the high-BE peak	0.65	0.63	0.63	0.67	0.67

Table 4 Characteristics of PMAA/P2VPy complexes

	Complex no.				
	16	17	18	19	20
Mole fraction of PMAA in the feed	0.2	0.4	0.5	0.6	0.8
Mole fraction of PMAA in the bulk of complex	0.44	0.47	0.48	0.66	0.71
Mole fraction of PMAA in the surface of complex	0.52	0.58	0.62	0.74	0.88
Yield of complex (%)	28	63	70	67	34
T_g of complex (°C)	133	150	151	151	158
N1s peaks (eV)	399.0, 399.9	399.0, 399.9	399.0, 400.0	399.0, 400.1	399.0, 400.2
Area fraction of the high-BE peak	0.52	0.52	0.70	0.67	0.69

2400 elemental analyzer. The surface compositions of the complexes were determined from XPS measurements based on the nitrogen/oxygen peak-area ratios after correction with appropriate sensitivity factors.

T_g measurements

The T_g values of the complexes were measured using a TA Instruments DSC2920 differential scanning calorimeter. The scanning rate was 20°C min^{-1}. T_g was taken as the initial onset of the change of slope in the d.s.c. curve. All the reported T_g values are the averages of three runs.

***FT*i.r. spectroscopic measurements**

Infrared spectra were recorded on a Perkin-Elmer 1725X FTIR spectrophotometer at 130°C using a SPECAC high-temperature cell equipped with an automatic temperature controller. Samples were prepared by mixing the polymer powder with KBr and compressing the mixture to form discs.

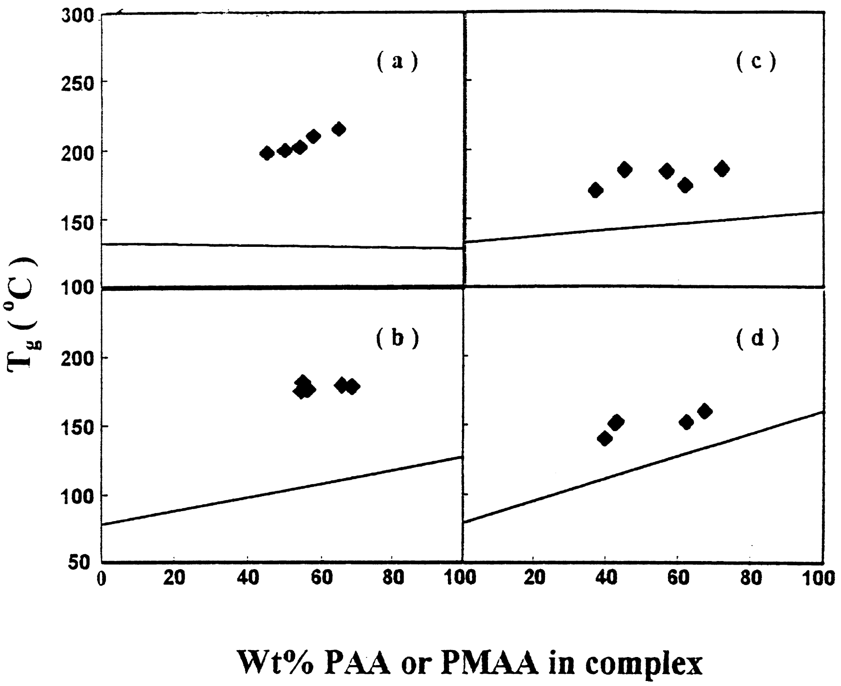

Figure 1 T_g–composition relation of complexes: (a) PAA/P4VPy; (b) PAA/P2VPy; (c) PMAA/P4VPy; (d) PMAA/P2VPy. Straight line shows T_g values calculated by linear additivity rule

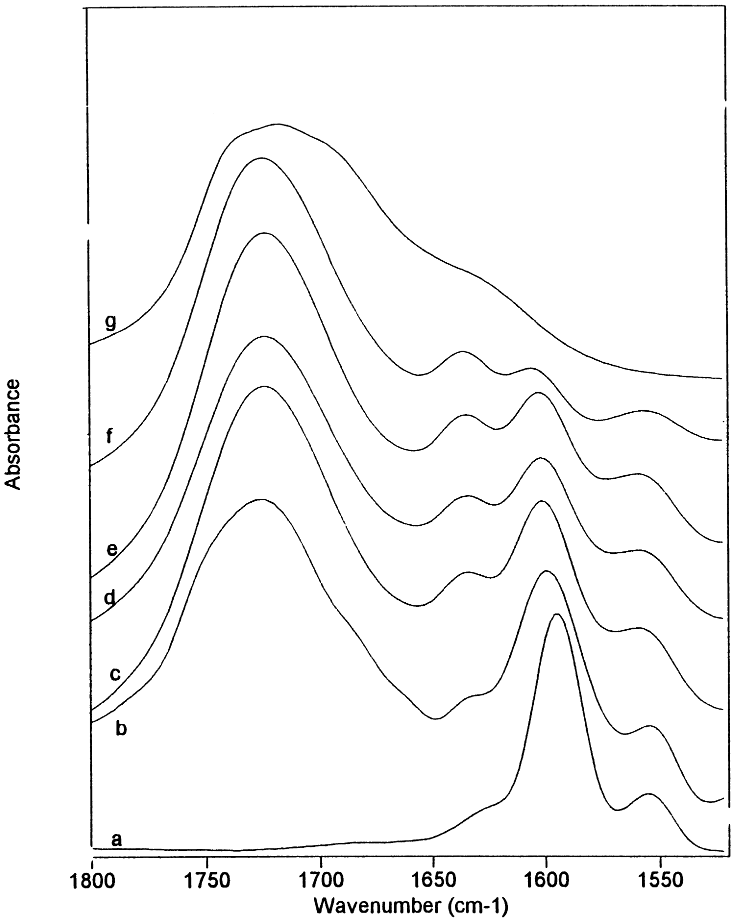

Figure 2 *FT*i.r. spectra of PAA/P4VPy complexes: (a) P4VPy; (b) complex 1; (c) complex 2; (d) complex 3; (e) complex 4; (f) complex 5; (g) PAA

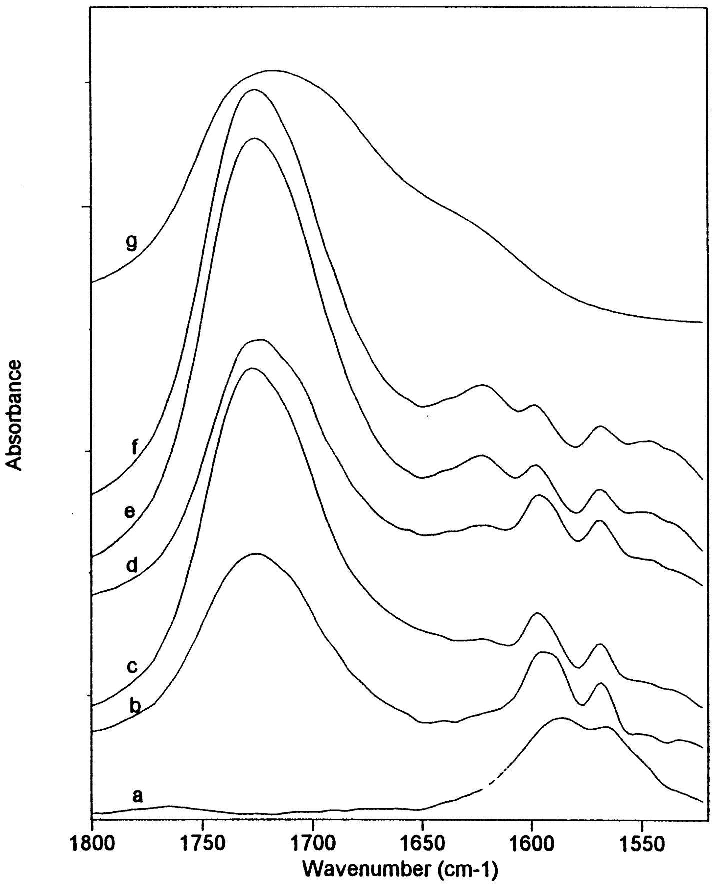

Figure 3 *FT*i.r. spectra of PAA/P2VPy complexes: (a) P2VPy; (b) complex 6; (c) complex 7; (d) complex 9; (e) complex 10; (f) PMAA

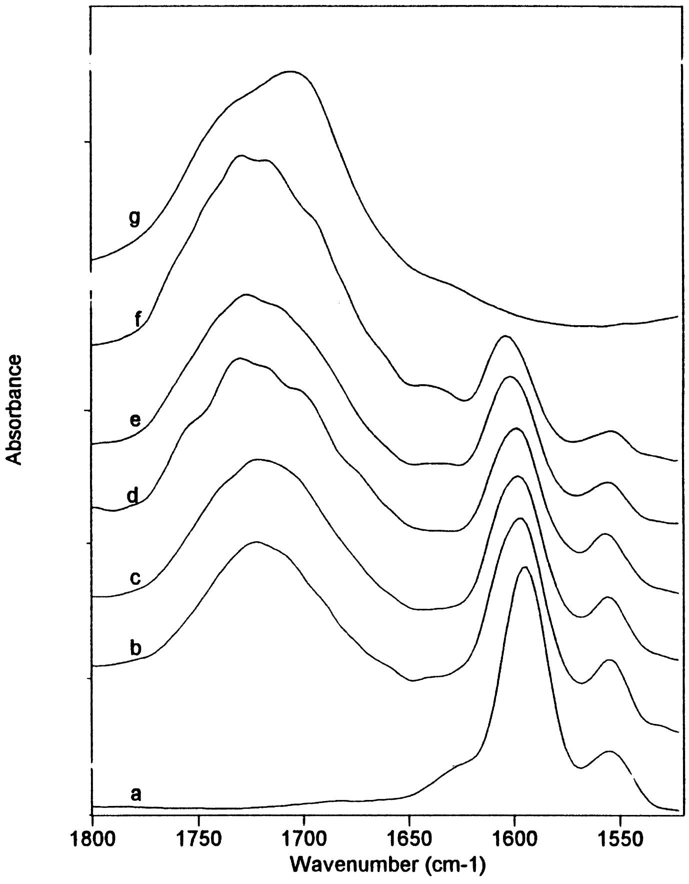

Figure 4 *FT*i.r. spectra of PMAA/P4VPy complexes: (a) P4VPy; (b) complex 11; (c) complex 12; (d) complex 13; (e) complex 14; (f) complex 15; (g) PAA

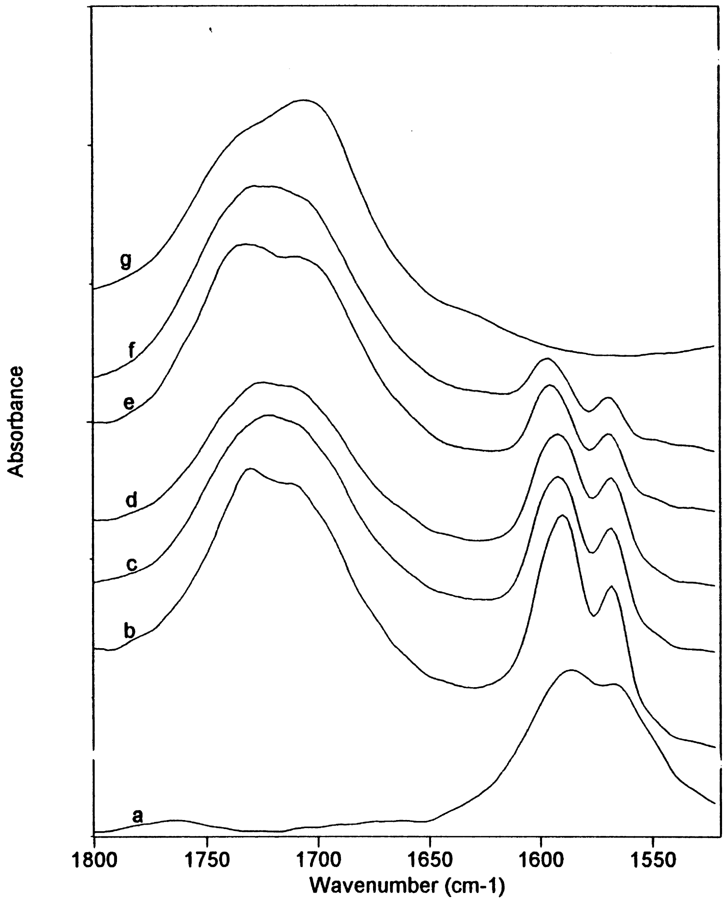

Figure 5 *FT*i.r. spectra of PMAA/P2VPy complexes: (a) P2VPy; (b) complex 16; (c) complex 17; (d) complex 18; (e) complex 19; (f) complex 20; (g) PMAA

XPS measurements

The XPS measurements were performed on a VG Scientific ESCALAB MkII spectrometer using a Mg Kα X-ray source (1253.6 eV photoelectrons). The complex powders were mounted on standard sample studs by means of double-sided adhesive tape. The X-ray source was run at 12 kV and 10 mA. All core-level spectra were referenced to the C1s neutral carbon peak at 284.6 eV and obtained with a take-off angle of 75°. Each spectrum was curve fitted using the VGX-900i software. In the curve fitting, the widths (FWHM) of Gaussian peaks were maintained constant for all components in a particular spectrum.

RESULTS AND DISCUSSION

Interpolymer complexation

Both PAA and PMAA formed interpolymer complexes with P4VPy and P2VPy throughout the entire feed composition range in ethanol/water (1:1) solution. The complexation between P4VPy and PAA or PMAA resulted in white precipitates. Transparent gels were formed when P2VPy was mixed with PAA or PMAA. After repeated washing with ethanol/water (1:1) solution, the gels became white solid.

Tables 1–4 show the characteristics of various complexes. The yield of complex depends on feed complexation and reaches a maximum when stoichiometric amounts of acid and base groups are mixed. The composition of the complex is also a function of feed composition. In all cases, the complex becomes richer in PAA or PMAA with increasing acid content in the feed. The bulk composition and surface composition of the PAA complex are nearly the same, while the PMAA complex shows some degree of surface enrichment of the acidic polymer.

Only one glass transition temperature was observed for each complex. As shown in *Figure 1*, the T_g values of the complexes are higher than those calculated from the linear additivity rule. The PAA complexes show a larger positive deviation in their T_g values than those of the PMAA complexes. This result may be taken to indicate that PAA interacts more strongly with P4VPy and P2VPy than PMAA does.

FTi.r. characterization of interpolymer complexes

All four complex systems were studied by *FT*i.r. with emphasis on the carbonyl stretching bands of PAA and PMAA and the pyridine ring stretching bands of P4VPy and P2VPy in the complexes. The spectra of the component polymers and all the complexes in these two regions are shown in *Figures 2–5*.

P4VPy exhibits a pyridine ring band at 1595 cm^{-1}. However, this band shifts slightly to a higher wavenumber with increasing PAA content in the PAA/P4VPy complexes. The shift is due to an increase in the rigidity of the pyridine ring arising from interpolymer interactions[8]. Moreover, the complexation with PAA brings about a new band at 1632 cm^{-1}, which is ascribed to the ring stretching of pyridinium ions in the complexes[22]. This pyridinium ion band becomes more intense with increasing PAA content in the complex, showing that the extent of protonation of

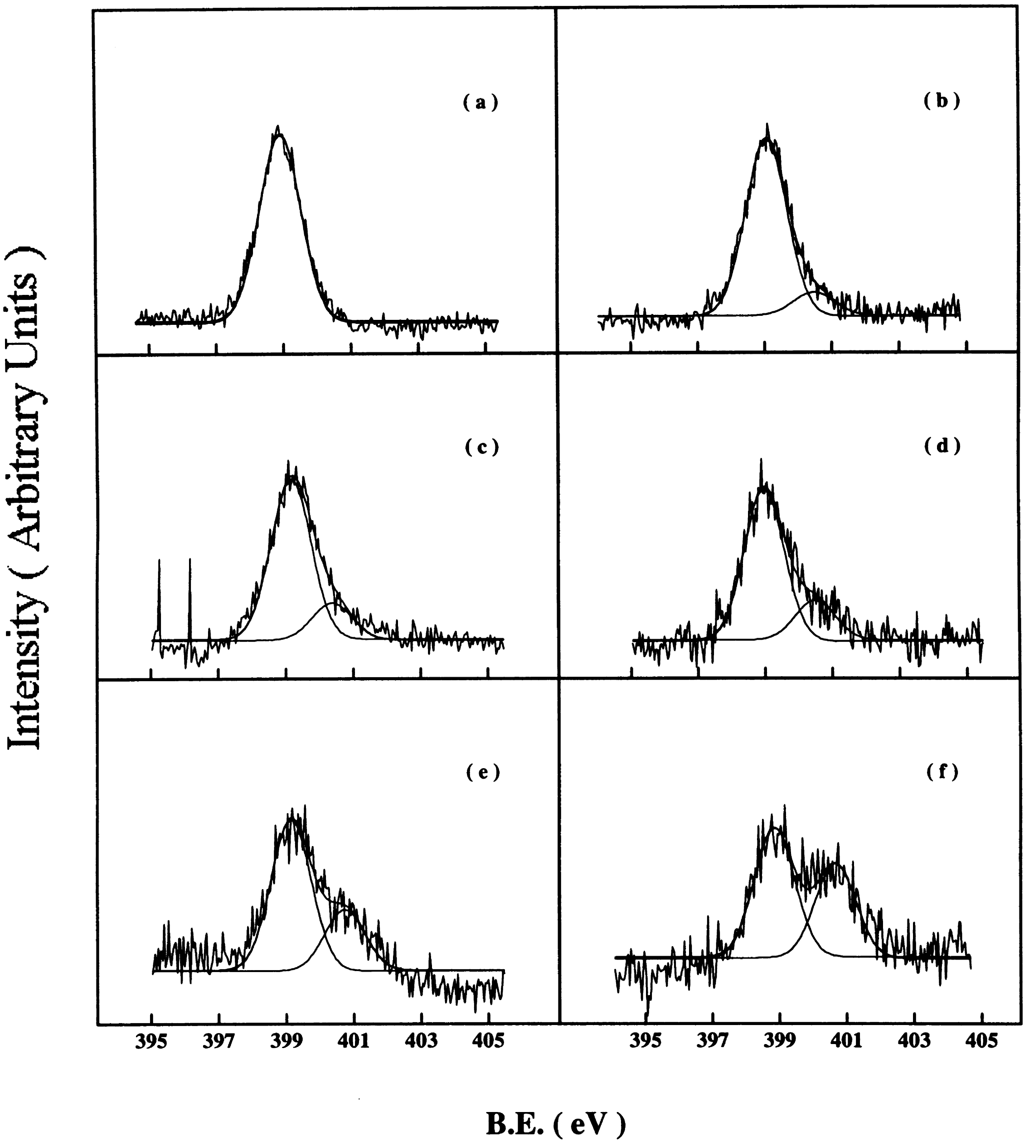

Figure 6 N1s spectra of PAA/P4VPy complexes: (a) P4VPy; (b) complex 1; (c) complex 2; (d) complex 3; (e) complex 4; (f) complex 5

pyridine in the complex increases with the PAA content. Similar phenomena have also been observed for the PAA/P2VPy complexes. As shown in *Figure 3*, the pyridine ring stretching band of P2VPy at 1585 cm^{-1} shifts to a higher wavenumber with increasing PAA content in the PAA/P2VPy complexes, and a new ring stretching band of pyridinium ion in the complex is observed at 1620 cm^{-1}. Thus it is evident that ionic interactions are present in the PAA/P4VPy and PAA/P2VPy complexes.

For the PMAA/P4VPy and PMAA/P2VPy complexes, although the ring stretching band of pyridine of poly(vinylpyridine) also shifts to a higher wavenumber with the increasing PMAA content, there is no evidence for the existence of pyridinium ion in the complexes (*Figures 4 and 5*). Thus ionic interactions do not exist in these complexes. The shift of the pyridine ring band shows the presence of the hydrogen bonding between PMAA and P4VPy or P2VPy.

As shown in *Figures 2 and 3*, PAA exhibits a rather broad carbonyl stretching band around 1710 cm^{-1} comprising two overlapping carbonyl stretching modes of the free and self-associated carboxylic acid groups in PAA. The latter is at a lower wavenumber than the former. However, for both the PAA/P4VPy and PAA/P2VPy complexes, the carbonyl stretching band narrows sharply with the band center moving to 1730 cm^{-1}. Such a change can be attributed to the ionization of carboxylic acid groups. When ionization occurs, resonance is possible between the two C–O bonds in the COO$^-$ group and, consequently, the characteristic carbonyl stretching absorption vanishes[23]. The characteristic anti-symmetric vibration band of COO$^-$ usually appears in the 1550–1600 cm^{-1} region. In the present case, this band overlaps the pyridine ring band.

As shown in *Figures 4 and 5*, PMAA also shows two overlapping carbonyl stretching modes. The carbonyl mode of the self-associated carboxylic acid groups is more extensive than that of the free ones. In contrast to the PAA/PVPy system, no significant narrowing of the carbonyl absorption is observed for both the PMAA/P4VPy and PMAA/P2VPy complexes. Instead the carbonyl bands are reshaped due to the breaking of the self-association of PAA and the occurrence of the new hydrogen bonding between acid groups and pyridine nitrogens in the complexes. Therefore, the *FT*i.r. studies show the existence of ionic interactions in the PAA/PVPy complexes but not in the PMAA/PVPy complexes.

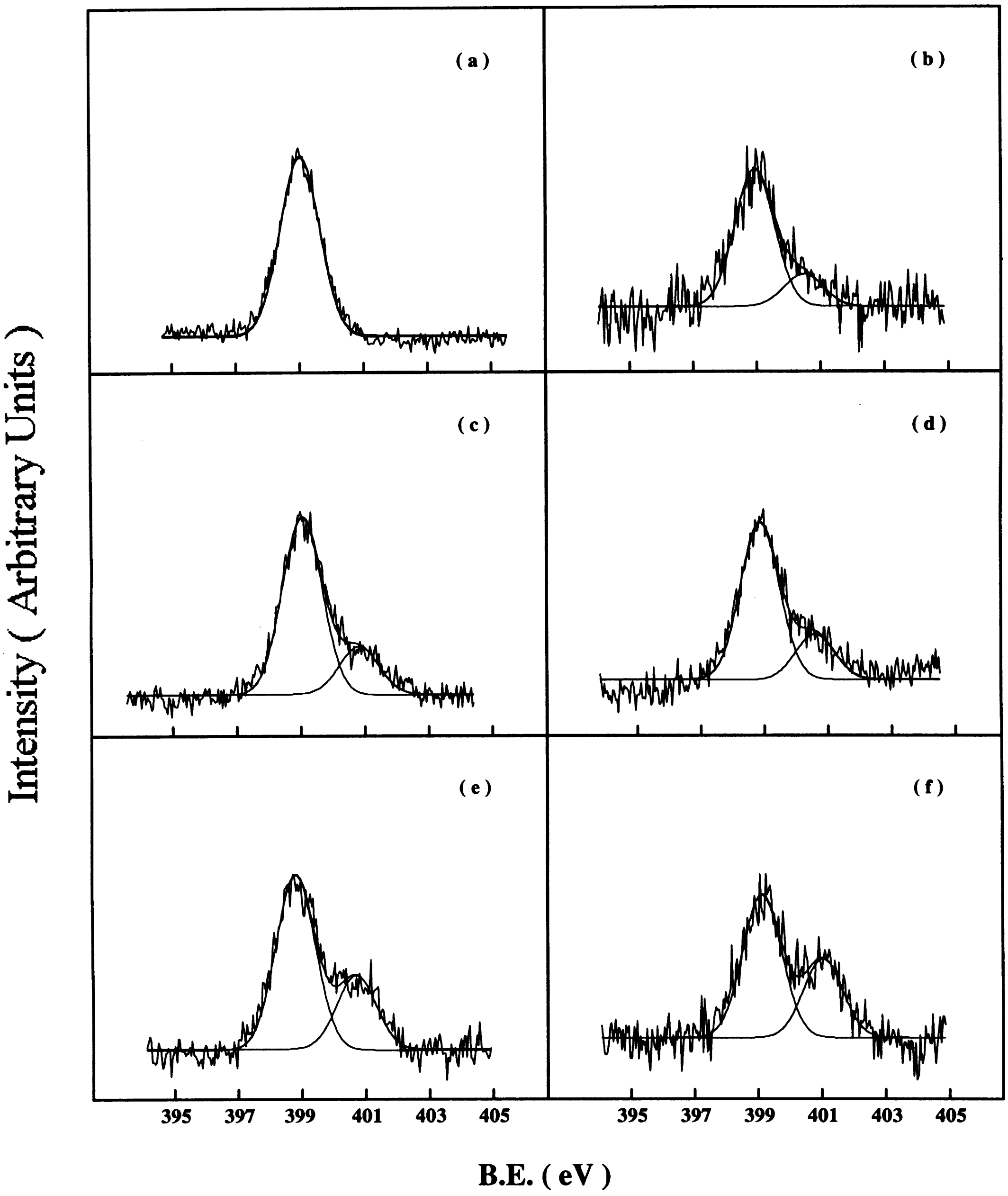

Figure 7 N1s spectra of PAA/P2VPy complexes: (a) P2VPy; (b) complex 6; (c) complex 7; (d) complex 8; (e) complex 9; (f) complex 10

XPS characterization of interpolymer interactions

Our previous studies have shown that when P4VPy or P2VPy interacts with poly(*p*-vinylphenol) (PVPh) via a hydrogen-bonding interaction[20], the N1s spectra show the development of a high-binding energy (BE) peak at 400 eV. On the other hand, when P4VPy or P2VPy interacts with poly(vinylphosphonic acid) (PVPA) or poly(styrenesulfonic acid) (PSSA) via ionic interactions, the high-BE peak is located around 401.0–401.5 eV [14,21].

Figures 6–9 show the N1s spectra of various complexes. The N1s spectra of P4VPy and P2VPy show a symmetrical N1s peak at 399.0 eV. However, the presence of a high-BE N1s peak is evidenced in the spectra of all the complexes, indicating that pyridine nitrogen atoms interact with PMAA and PAA. The BE values of the high-BE N1s peaks of the PMAA complexes are around 400 eV which are similar in magnitude to those of the P4VPy/PVPh and P2VPy/PVPh complexes. The results suggest that PMAA interacts with P4VPy or P2VPy via a hydrogen-bonding interaction. In comparison, the BE values of the high-BE peaks of the PAA complexes are in the range of 400.4–401.1 eV, and are larger than those of the PMAA complexes. The results indicate that the nature of interpolymer interactions in the two systems is quite different. The higher BE values of the high-BE peaks of the PAA complexes suggest the presence of an ionic interaction. For the complex with a lower PAA content, both hydrogen-bonding and ionic interactions are present. As the PAA content in the complex increases, the ionic interaction becomes predominant. Therefore, XPS studies support the *FT*i.r. studies that PMAA interacts with poly(vinylpyridine)s via hydrogen-bonding interactions while PAA can interact with poly(vinylpyridine)s via an ionic interaction. As mentioned earlier, Oyama and Nakajima[18] were unable to detect the existence of pyridinium ions in PAA/P2VPy complexes by XPS. They suggested that the ionic interactions between PAA and P2VPy were located in the interior of the complexes and XPS was unable to detect them. However,

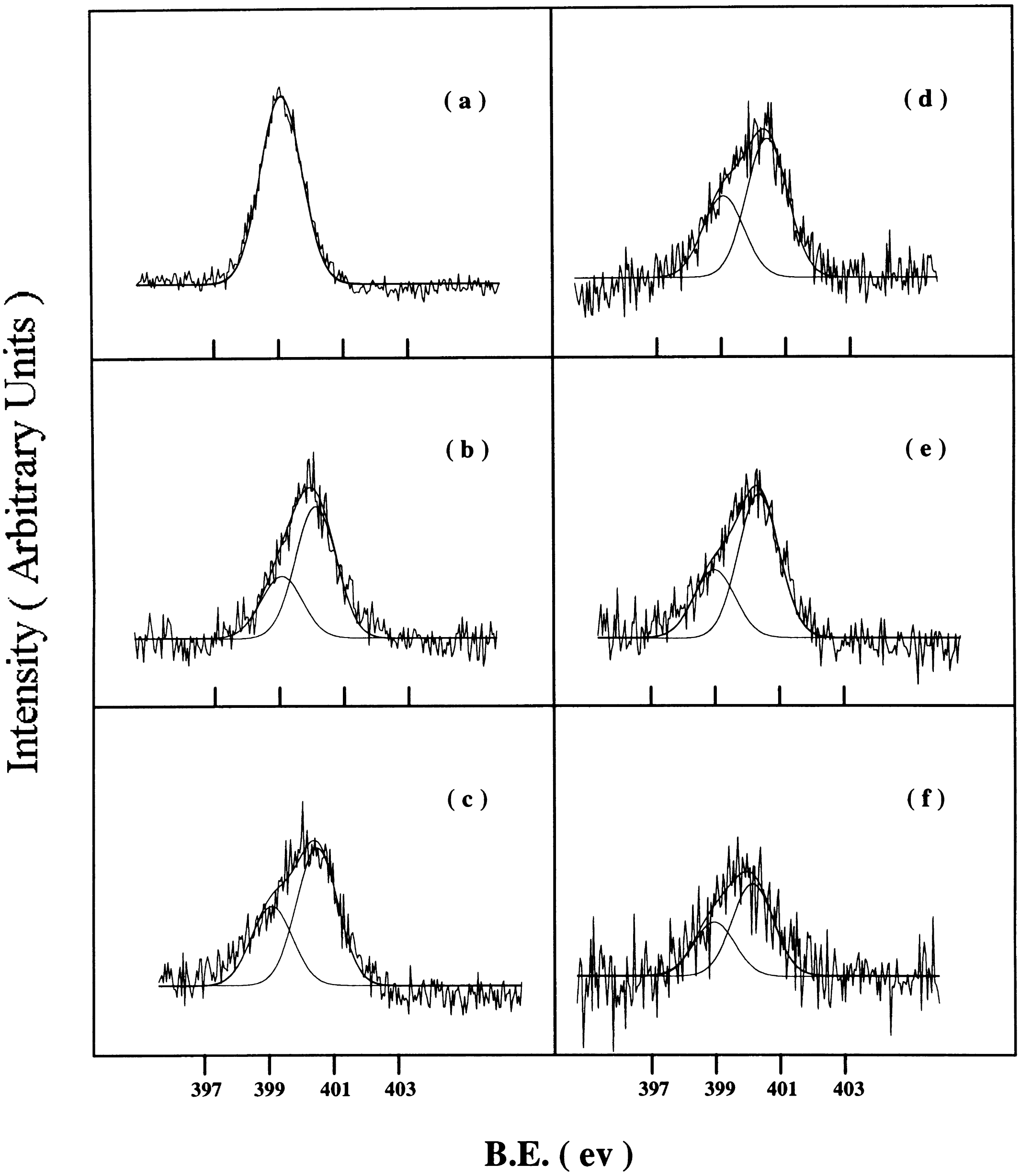

Figure 8 N1s spectra of PMAA/P4VPy complexes: (a) P4VPy; (b) complex 11; (c) complex 12; (d) complex 13; (e) complex 14; (f) complex 15

the present study clearly shows the existence of ionic interactions in the PAA complexes. The reason why PMAA and PAA behave differently is likely due to their different acidities. The pH values of 0.10 M ethanol/water (1:1) solutions of PMAA and PAA are 3.57 and 3.04, respectively. The stronger acidity of PAA enables proton transfer to the pyridine nitrogen, leading to an ionic interaction. Our previous studies also revealed a similar trend. PVPA and PSSA interact with poly(vinylpyridine)s via an ionic interaction, and the pH values of 0.10 M ethanol/water solutions are 2.33 and 1.36, respectively. The weaker acid PVPh, with a pH value of 6.68 for a 0.10 M ethanol/water (1:1) solution, interacts with poly(vinylpyridine)s via a hydrogen-bonding interaction. The stronger ionic interaction in PAA complexes also accounts for the larger positive deviation in their T_g values as mentioned earlier.

The fractions of pyridine groups undergoing interpolymer interactions in various complexes can be quantified from the areas of the deconvoluted N1s peaks, and the results are shown in *Tables 1–4* and in *Figure 10*. For PAA complexes, the extent of protonation of pyridine groups is a linear function of the PAA content. The extents of protonation in the PAA/P4VPy complexes are higher than those in the PAA/P2VPy complexes. Although similar trends have also been observed in other polyacid/poly(vinylpyridine) complexes[8,9,14], we have recently observed that the extents of protonation of pyridine groups in the PSSA/poly(vinylpyridine) complexes are not significantly affected by the relative position of nitrogen in the pyridine ring [21]. We have postulated that when the polyacid is sufficiently acidic, the relative position of nitrogen in the pyridine ring is no longer an important factor in protonation. It is also noted that the extents of protonation in the PAA complexes (12–42%) are smaller than those in the PVPA complexes (13–51%)[14] and in the PSSA complexes (34–86%) [21]. Once again, this can be attributed to the higher acidity of PSSA and PVPA as compared with PAA.

The fractions of pyridine groups involved in the hydrogen-bonding interactions remain fairly constant in the PMAA/P4VPy complexes, while those in the PMAA/P2VPy

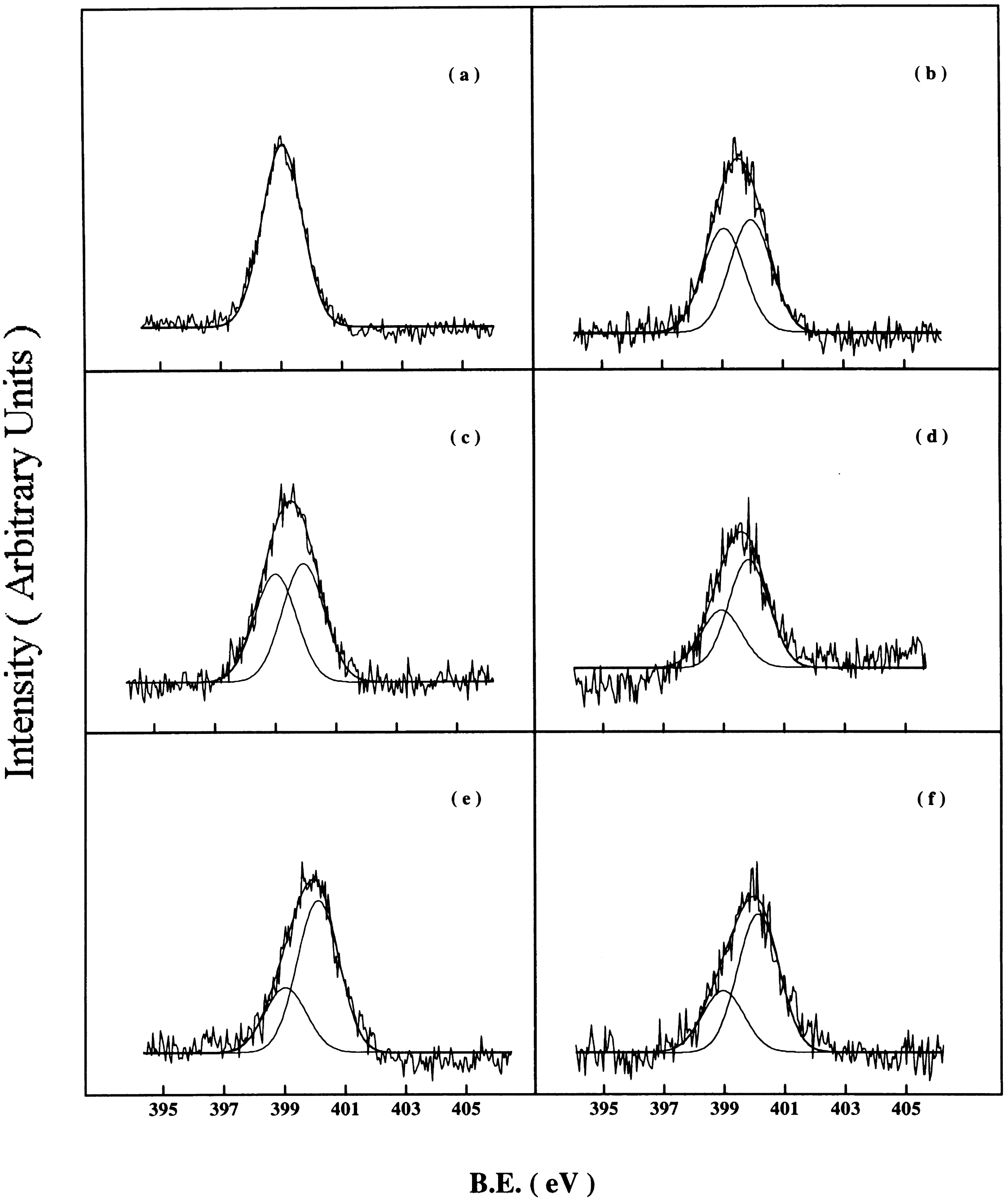

Figure 9 N1s spectra of PMAA/P2VPy complexes: (a) P2VPy; (b) complex 16; (c) complex 17; (d) complex 18; (e) complex 19; (f) complex 20

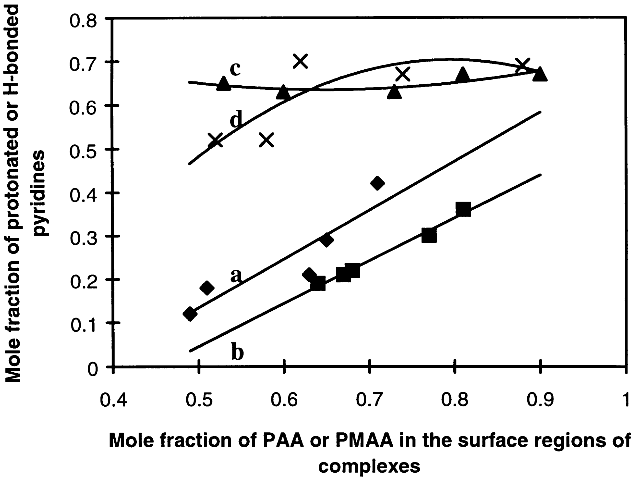

Figure 10 Extents of protonation of pyridine groups: (a) PAA/P4VPy; (b) PAA/P2VPy; (c) PMAA/P4VPy; (d) PMAA/P2VPy

complexes increase with increasing PMAA content in the complexes. In fact, the fractions of pyridine groups involved in the hydrogen-bonding interaction in the PMAA/P2VPy complexes are in good agreement with those in the miscible blends of EMAA containing 32 wt.% of MAA (EMAA32) and poly(styrene-co-2-vinylpyridine) containing 70 wt.% of 2VPy (SV2Py70) obtained from infrared studies. Lee *et al.*[19] reported that 49–73% of the pyridine groups in SV2Py70 are involved in the hydrogen-bonding interaction with EMAA32 when the blends contain a 0.46–0.69 mole fraction of EMMA32. In comparison, 52–67% of the pyridine groups of P2VPy interact with PMAA when the complexes contain a 0.52–0.74 mole fraction of PMAA (*Table 4*).

Conclusion

The present study has shown the existence of ionic interactions in the PAA complexes but not in the PMAA complexes. The higher acidity of PAA enables proton transfer to the pyridine nitrogen atom, leading to ionic interaction.

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