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Interpolymer complexation between poly(vinylphosphonic acid) and poly(vinylpyridine)s

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Poly(vinylphosphonic acid) (PVPA) forms interpolymer complexes with poly(4-vinylpyridine) and with poly(2-vinylpyridine) in ethanol/water (1/1) solution. Both the yield and the composition of the complex depend on the feed composition. All the complexes do not show distinct glass transition temperatures (T_gs) up to the onset of degradation. It is conceivable that the strong interactions between PVPA and poly(vinylpyridine)s might raise the T_gs above the degradation temperatures. An X-ray photoelectron spectroscopic study shows that some of the pyridine groups in various complexes are protonated as shown by the existence of two nitrogen environments in the N1s spectra. The extent of protonation of pyridine increases with increasing PVPA content in the complex. The P2p spectra show the existence of two phosphorus environments, one arising from phosphonic acid and the other from phosphonate. Therefore, ionic interactions between pyridinium and phosphonate ions are responsible for the complexation. © 1997 Elsevier Science Ltd.

(Keywords: interpolymer complexes; poly(vinylphosphonic acid); poly(vinylpyridine)s)

INTRODUCTION

Polymers are generally immiscible with each other in the absence of specific interactions. Interactions such as hydrogen-bonding, dipole–dipole, charge transfer and acid–base complexation are necessary to achieve miscibility. In cases where the interactions are particularly strong, polymers form interpolymer complexes (or simply complexes) as manifested by the formation of insoluble precipitates upon mixing of two polymer solutions in a common solvent. It is not surprising that suitable acidic polymers can form interpolymer complexes with basic polymers. Polycarboxylic acids such as poly(acrylic acid) and poly(methacrylic acid) form complexes with poly(4-vinylpyridine)[1,2] (P4VPy), poly(2-vinylpyridine)[1,2] (P2VPy) and with tertiary amide polymers such as poly(*N*-vinyl-2-pyrrolidone)[3] (PVP) and poly(2-ethyl-2-oxazoline)[4,5]. Similarly, polymers containing sulfonic acid groups are also capable of forming complexes with pyridine-containing polymers[6–10]. In recent years, interpolymer complexation involving poly(monoalkyl itaconate)s has received increasing attention[11–16].

Interpolymer complexation involving other types of acidic groups is not that well studied. Zhuang *et al.*[17] studied the miscibility of blends of poly(styrene-*co*-4-vinylbenzenephosphonic acid). They found that copolymers containing 4.3–13.3 mol% of phosphonic acid groups are immiscible with poly(n-butyl methacrylate) and with poly(vinyl methyl ether). They concluded that phosphonic acid was not a good hydrogen-bonding donor for miscibility enhancement of polymer blends due to its strong self-association. On the other hand, poly(styrene-*co*-4-vinylbenzenephosphonic acid diethyl ester) containing 13.3 mol% of phosphorus moieties forms complexes with poly(*p*-vinylphenol)[18]. The miscibility enhancement effect of acidic silanol groups has recently been studied by the research group of Pearce and Kwei[19–21]. A polymer containing a sufficiently large amount of silanol groups is able to form complexes with PVP. We now report the interpolymer complexation between poly(vinylphosphonic acid) (PVPA) and poly(vinylpyridine)s. Our recent study has shown that X-ray photoelectron spectroscopy (X.p.s.) provides information on interpolymer interactions in complexes involving pyridine-containing polymers[10]. In this study, we used X.p.s. to characterize PVPA/P4VPy and PVPA/P2VPy complexes.

EXPERIMENTAL

Materials

P2VPy, P4VPy and PVPA were obtained from Polysciences. The weight-average molecular weights of P2VPy and P4VPy are 200 and 60 kg mol^{-1}, respectively; information on the molecular weight of PVPA is not available.

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Preparation of interpolymer complexes

Polymers were separately dissolved in water/ethanol (1/1) solution at a concentration of $10\,g\,l^{-1}$. Appropriate amounts of the two polymer solutions were then mixed. After 1 h of continuous stirring, an interpolymer complex in the form of a precipitate was separated by centrifugation, washed repeatedly with water/ethanol (1/1) solution and then dried *in vacuo* at 90°C for 2 weeks. The dried complex was then ground to fine powder and stored in a desiccator. 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 various complexes were determined based on the nitrogen and phosphorus contents as determined using a Perkin-Elmer 2400 elemental analyser. The surface compositions of the complexes were determined from X.p.s. measurements based on the nitrogen/phosphorus peak-area ratios after correction with appropriate sensitivity factors.

Glass transition temperature measurements

The glass transition temperatures (T_gs) of various samples were measured with a TA Instruments 2920 differential scanning calorimeter using a heating rate of $20°C\,min^{-1}$. The initial onset of the change of slope in the differential scanning calorimetry curve was taken as the T_g. Each sample was scanned several times to check the repeatability of the T_g values.

X.p.s. measurements

The X.p.s. measurements were performed on a VG Scientific ESCALAB MKII spectrometer with a Mg K_α X-ray source (1253.6 eV photons). Samples in the form of fine powder were mounted on a standard sample stud 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 by the C1s neutral carbon peak at the binding energy (BE) of 284.6 eV. All spectra were obtained with a take-off angle of 75°. In spectral deconvolution, the widths (FWHM) of Gaussian peaks were maintained constant for all components in a particular spectrum.

*Fourier transform infra-red (*FT *i.r.) measurements*

The *FT* i.r. measurements were performed on a Perkin-Elmer 1725X *FT* i.r. spectrophotometer; 32 scans were signal-averaged at a resolution of $2\,cm^{-1}$. Samples were prepared by dispersing the polymer powder in KBr to form discs. In view of the hygroscopic nature of the polymers, spectra were acquired at 150°C to exclude moisture.

RESULTS AND DISCUSSION

Complex formation

In all cases, mixing of polymer solutions led to the formation of insoluble interpolymer complexes. The characteristics of various PVPA/P4VPy and PVPA/P2VPy complexes are shown in *Tables 1* and *2*, respectively. The yield as well as the composition of the complex depends on feed composition as commonly observed in other interpolymer complexes[11–14]. The complex becomes richer in PVPA with increasing PVPA content in the feed. The results also show that the PVPA content is higher in the PVPA/P2VPy complex than in the PVPA/P4VPy complex when prepared from the same feed composition. Such a behaviour could arise from the different molecular weight of P2VPy and P4VPy as the chain length of polymer is also an important factor in polymer complexation[22]. For some of the complexes, the bulk composition is similar to the surface composition. With increasing amounts of PVPA in the complex, the surface region becomes richer in PVPA.

It is commonly observed that the T_g value of an interpolymer complex is larger than that calculated from

Table 1 Characteristics of PVPA/P4VPy complexes

	Complex sample number				
	1	2	3	4	5
Feed composition (mole fraction of PVPA)	0.11	0.25	0.33	0.43	0.66
Yield of complex (%)	10	21	52	50	51
Bulk composition of complex (mole fraction of PVPA)	0.42	0.44	0.45	0.49	0.55
Surface composition of complex (mole fraction of PVPA)	0.42	0.44	0.46	0.50	0.60
Fraction of protonated pyridine groups	0.13	0.17	0.21	0.24	0.51

Table 2 Characteristics of PVPA/P2VPy complexes

	Complex sample number			
	6	7	8	9
Feed composition (mole fraction of PVPA)	0.25	0.33	0.43	0.66
Yield of complex (%)	11	26	27	37
Bulk composition of complex (mole fraction of PVPA)	0.47	0.48	0.52	0.62
Surface composition of complex (mole fraction of PVPA)	0.47	0.54	0.62	0.71
Fraction of protonated pyridine groups	0.23	0.34	0.37	0.49

a linear additivity rule. Such a positive deviation in T_g values of complexes is taken to indicate the presence of strong intermolecular interactions which restrict chain motion. The T_g values of P2VPy, P4VPy and PVPA are 80, 135 and 165°C, respectively. The glass transition of PVPA is quite difficult to detect because of the small change in heat capacity. However, distinct glass transitions for all the complexes could not be observed up to the degradation temperature near 250°C. The small change in heat capacity upon glass transition of PVPA renders the detection of the glass transitions of complexes difficult. The T_g values of some complexes involving poly(vinylpyridine)s are nearly 80°C higher than those expected from the linear additivity rule[23]. It is conceivable that the intermolecular interactions in the complexes are so strong that the T_g values are raised to near the degradation temperatures. It is of interest to note that Huglin *et al.*[24] recently reported that the glass transitions of complexes formed between poly(4-vinylpyridinium chloride) and poly[sodium (2-acrylamido-2-methylpropanesulfonate)] could not be detected, presumably due to the very high ionic crosslinking density. A similar problem in detecting T_gs has also been encountered in complexes formed between poly(monomethyl itaconate) with P4VPy or P2VPy[16].

X.p.s. characterization

Figures 1 and *2* show the N1s core-level spectra of PVPA/P4VPy and PVPA/P2VPy complexes, respectively. A single nitrogen environment with a BE value of 399.0 eV in P4VPy and P2VPy is evidenced by the spectra. However, there are two different nitrogen environments in the spectra of all the complexes. The low-BE component at 399.0 eV is associated with the neutral nitrogen of pyridine; the high-BE component at 401.1 eV is associated with pyridinium nitrogen. The results show that some of

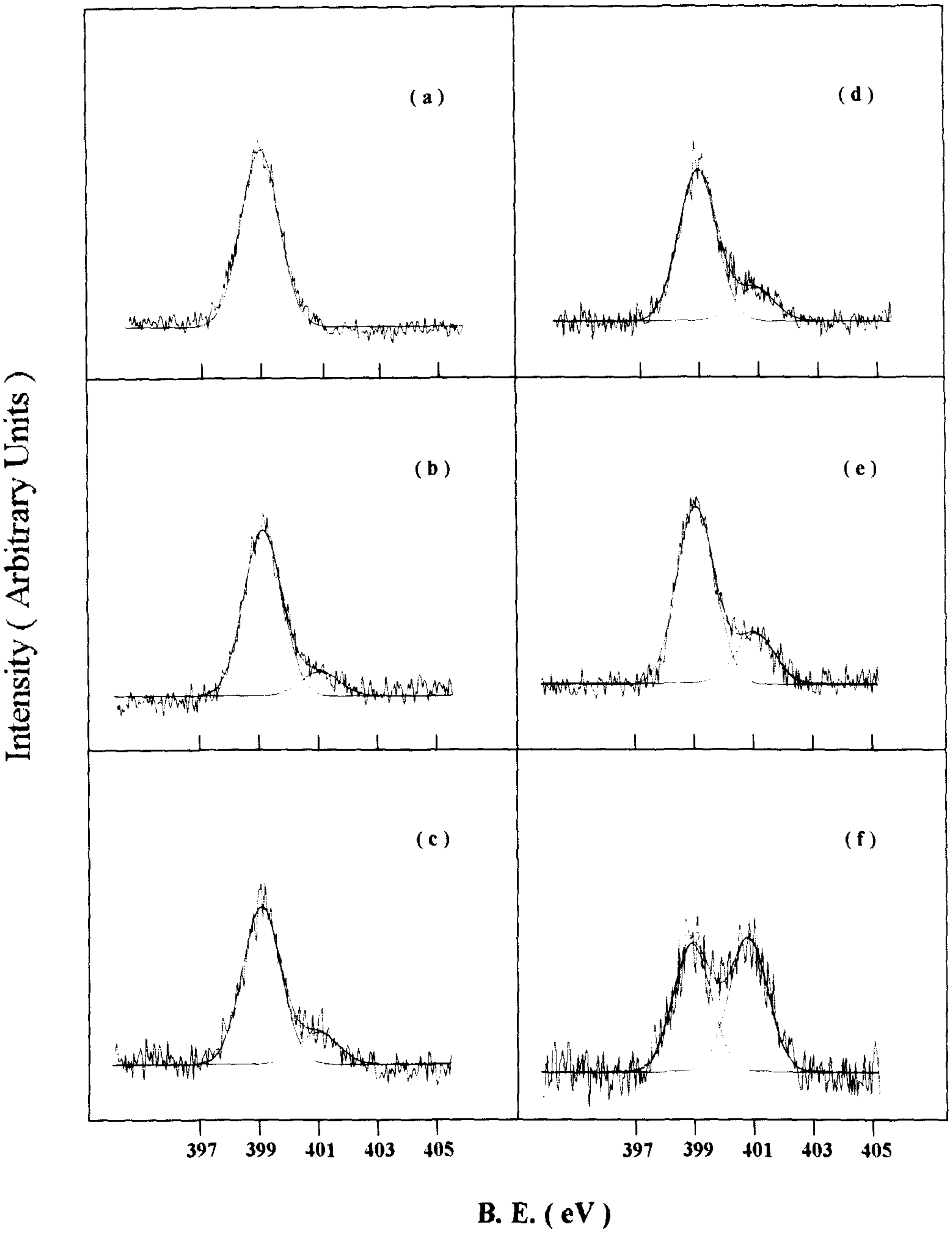

Figure 1 N1s spectra of PVPA/P4VPy complexes: (a) P4VPy; (b) complex 1; (c) complex 2; (d) complex 3; (e) complex 4; (f) complex 5

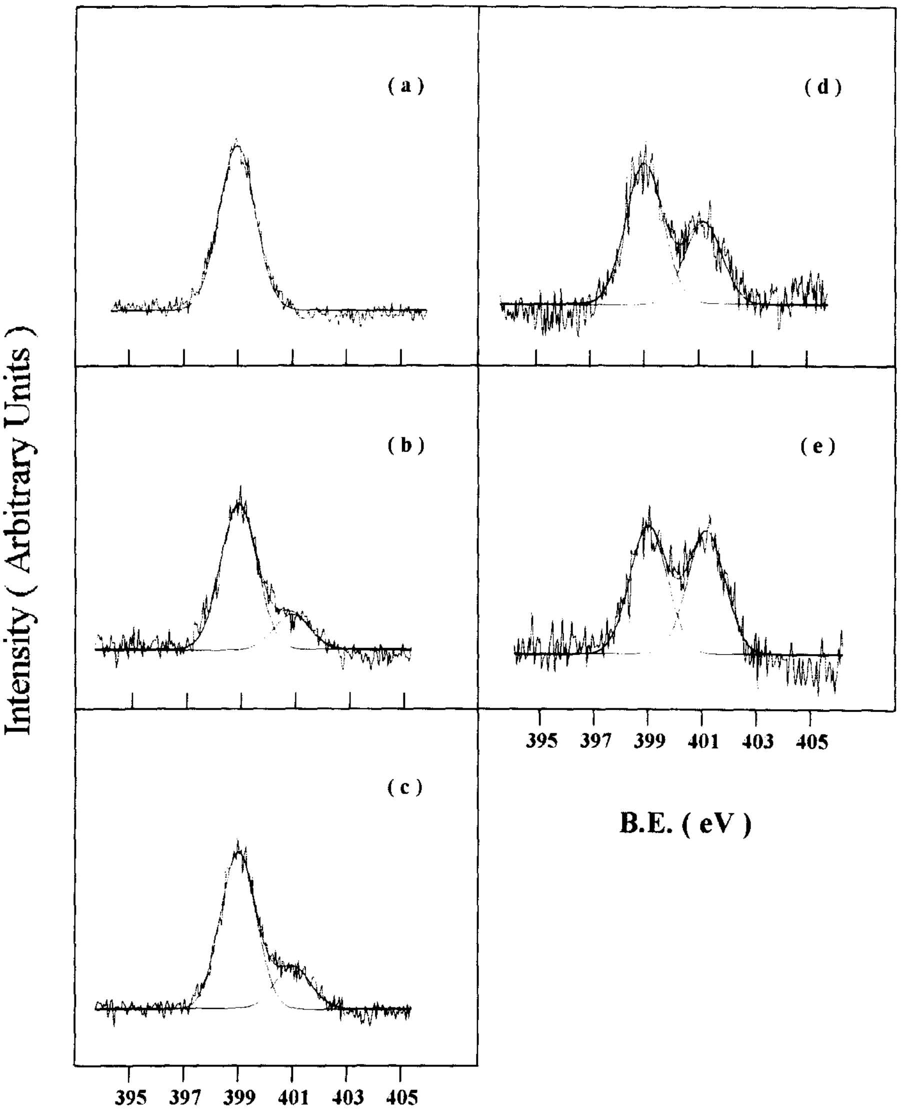

Figure 2 N1s spectra of PVPA/P2VPy complexes: (a) P2VPy; (b) complex 6; (c) complex 7; (d) complex 8; (e) complex 9

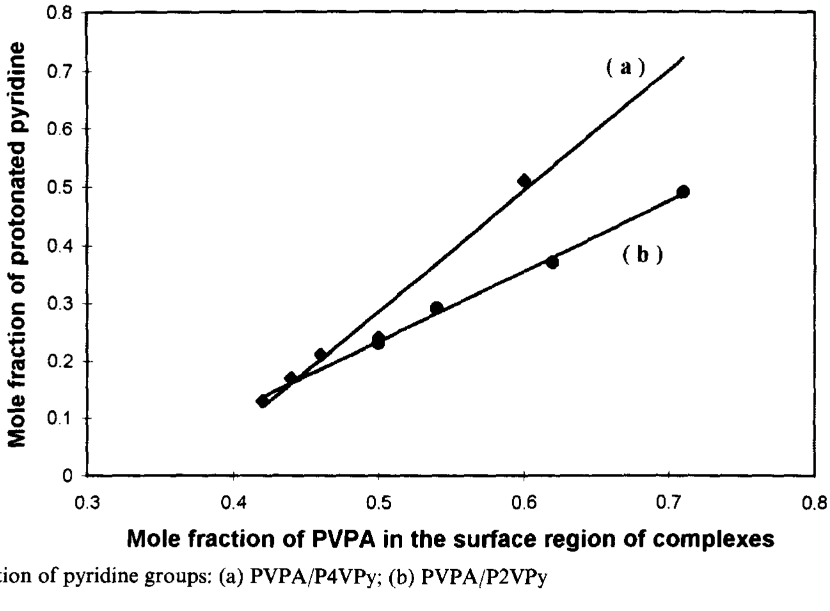

Figure 3 Extent of protonation of pyridine groups: (a) PVPA/P4VPy; (b) PVPA/P2VPy

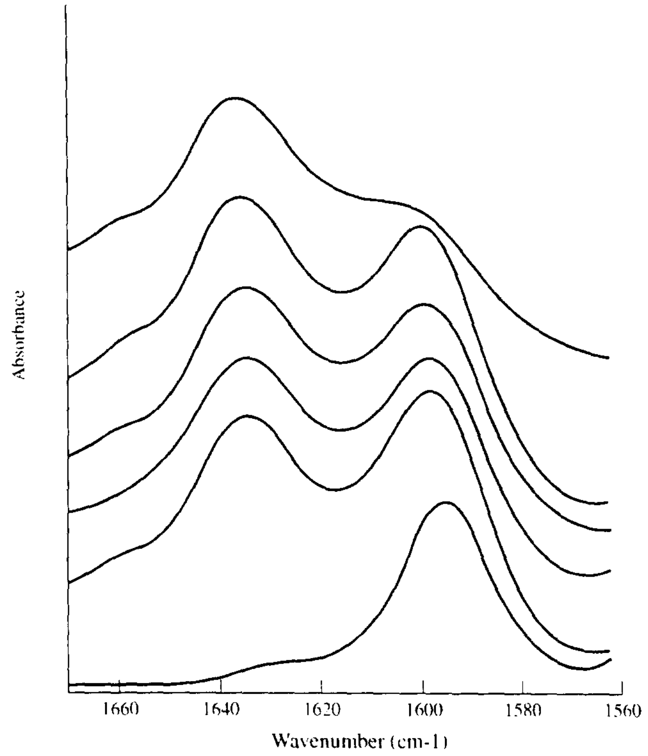

Figure 4 *FT* i.r. spectra of PVPA/P4VPy complexes: (a) P4VPy; (b) complex 1; (c) complex 2; (d) complex 3; (e) complex 4; (f) complex 5

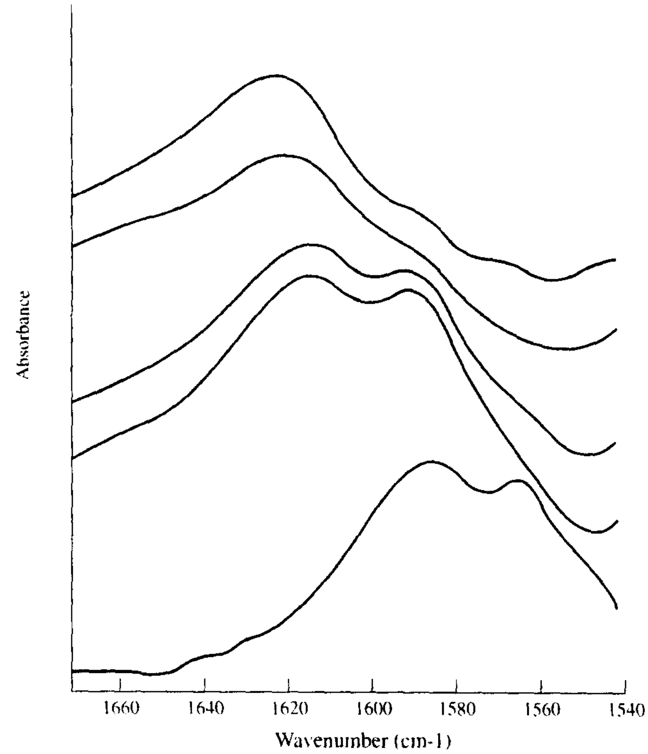

Figure 5 *FT* i.r. spectra of PVPA/P2VPy complexes: (a) P2VPy; (b) complex 6; (c) complex 7; (d) complex 8; (e) complex 9

the pyridine groups in P4VPy and P2VPy in the complexes have been protonated. The extent of protonation of the pyridine groups can be estimated from the deconvoluted peaks, and the results are summarized in *Tables 1* and *2*. The fraction of protonated pyridine groups increases linearly with increasing PVPA content in the complex, as shown in *Figure 3*. The fraction of protonated pyridine groups is higher in the PVPA/P4VPy complex than in the PVPA/P2VPy complex. A similar trend has also been observed in poly(monoalkyl itaconate)/poly(vinyl pyridine) complexes[15]. Such a behaviour conforms with the general view that the nitrogen in P4VPy is more accessible than that in P2VPy due to steric effects.

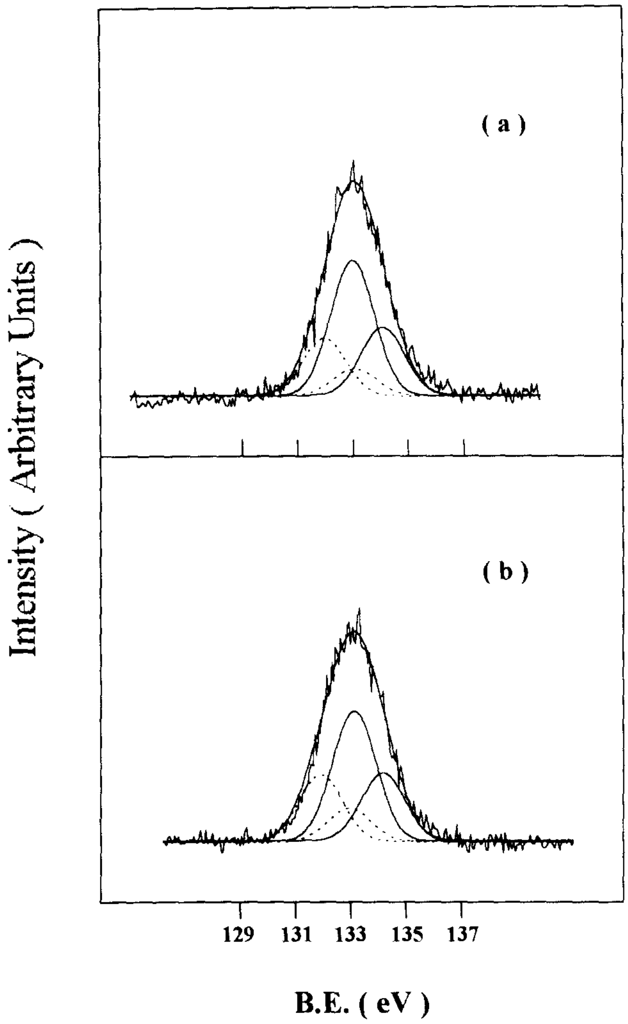

Figure 6 P2p spectra of complexes: (a) PVPA/P4VPy complex 3; (b) PVPA/P2VPy complex 7

The existence of protonated pyridine groups is also evidenced by *FT* i.r. spectroscopic studies. *Figure 4* shows the *FT* i.r. spectra of the 1595 cm^{-1} pyridine ring mode of P4VPy and various PVPA/P4VPy complexes. A shift of the 1595 cm^{-1} band to higher frequencies with increasing PVPA content is clearly seen. Such a shift of the pyridine ring mode to higher frequencies has been observed in other complexes involving P4VPy[11]. The shift is due to an increase in the rigidity of the pyridine ring arising from intermolecular interactions[11]. The existence of protonated pyridine groups is shown by the presence of a band at 1634 cm^{-1}, a tell-tale sign of pyridinium ion[9], in each of the complexes. For PVPA/P2VPy complexes, the pyridine ring modes of P2VPy at 1565 cm^{-1} diminish with increasing PVPA content, as shown in *Figure 5*. A similar observation has been reported by Huglin and Rego[6] on complexes of P2VPy with poly(2-acrylamido-2-methylpropanesulfonic acid). The other pyridine ring mode at 1588 cm^{-1} gradually shifts to higher frequencies, and the existence of protonated pyridine groups in PVPA/P2VPy complexes is evidenced by the development of a new band at 1620 cm^{-1}.

We were unable to obtain an X.p.s. spectrum for PVPA due to its extremely hygroscopic nature. Nevertheless, the P2p spectra of the complexes also provide evidence of ionic interactions. For poly(phenoxyphosphazine), the P2p peak consists of two spin-orbit split doublet $P2p_{3/2}$ (BE = 133.85 eV) and $P2p_{1/2}$ (BE = 134.72 eV) peaks with an intensity ratio of 1.94[25]. The P2p spectra of the two complexes are shown in *Figure 6* as examples. The P2p peak can be deconvoluted into two environments, one arising from the neutral phosphonic acid with BE of 133.2 eV for $P2p_{3/2}$ and 134.1 eV for $P2p_{1/2}$ (full curve) and one from the phosphonate with BE of 132.4 eV for $P2p_{3/2}$ and 133.3 eV for $P2p_{1/2}$ (dashed curve).

CONCLUSIONS

PVPA forms interpolymer complexes with P4VPy and P2VPy in ethanol/water (1/1) solutions arising from ionic interactions between PVPA and the two poly(vinylpyridine)s. The presence of a pyridinium ion is shown by the development of a high-BE component peak in the N1s spectra of the complexes, and the fraction of protonated pyridine groups increases linearly with PVPA content of the complex. The *FT* i.r. spectra also show the development of a pyrdinium ring band at 1634 cm^{-1} for PVPA/P4VPy and at 1620 cm^{-1} for PVPA/P2VPy complexes.

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