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X-ray Photoelectron Spectroscopic Studies of Interactions between Poly(4-vinylpyridine) and Poly(styrenesulfonate) Salts

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ABSTRACT: Poly(4-vinylpyridine) (P4VPy) was blended with the lithium or zinc salt of poly(styrenesulfonate) (PSSLi and PSSZn, respectively). P4VPy formed complexes with PSSZn but not with PSSLi in water/ethanol (2:1) solutions, indicating the presence of a strong interaction between PSSZn and P4VPy. P4VPy is immiscible with PSSLi, as shown by the appearance of two glass transitions in each P4VPy/PSSLi blend. Fourier transform infrared spectroscopic measurements showed the development of a new pyridine ring mode in P4VPy/PSSZn complexes. X-ray photoelectron spectroscopic (XPS) studies showed the development of high-binding-energy (BE) N 1s peaks in all the P4VPy/PSSZn complexes but not in the P4VPy/PSSLi blends. Interaction between P4VPy and Zn^{2+} is also evidenced by the development of a low-BE S 2p doublet in each complex. Therefore, XPS reveals the existence of coordination between Zn^{2+} and P4VPy but not between Li^+ and P4VPy.

Introduction

The importance of specific interactions to achieve miscibility in polymer blends is well recognized. Interaction between an ionomer and a polar polymer can induce miscibility or improve compatibility. While polystyrene (PS) is immiscible with poly(ethylene oxide) or poly(propylene oxide), polystyrene ionomers containing 5−10 mol % lithium methacrylate show considerable miscibility with the two polar polymers.[1] A recent study showed that the zinc salts of lightly sulfonated polystyrene were effective compatibilizers for liquid-crystalline polymer (LCP)/polycarbonate and LCP/polyamide-66 blends.[2]

Poly(4-vinylpyridine) (P4VPy), a proton-accepting polymer, is miscible with a large number of proton-donating polymers such as poly(*p*-vinylphenol),[3,4] poly(acrylic acid) (PAA),[5] poly(methacrylic acid),[5,6] poly(monoalkyl itaconate)s,[7−11] and poly[2-(acrylamido)-2-methylpropanesulfonic acid].[12,13] Depending on the nature of the solvent, P4VPy can form interpolymer complexes with these proton-donating polymers by coprecipitating from their common solvent in which both polymers are initially soluble. The formation of complexes is a manifestation that interpolymer interaction is much stronger than polymer−solvent interaction.

Blends of P4VPy or pyridine-containing polymers and ionomers have also been studied.[14−19] Ionomer blends of poly(ethyl acrylate-*co*-4-vinylpyridine) with various metal salts of sulfonated poly(ethylene terephthalate) were examined in detail by MacKnight and coworkers.[14−17] The existence of specific interactions between the pyridine groups and transition-metal ions was shown by Fourier transform infrared spectroscopy (FTIR) and the blends were miscible. On the other hand, the absence of interactions between pyridine groups and alkali- or alkaline-earth metal ions led to immiscibility.

We have recently used X-ray photoelectron spectroscopy (XPS) to study specific interactions in polymer blends.[20−25] When the chemical environment of an atom in a polymer blend is perturbed due to specific interaction, the development of a new peak can be observed in the XPS spectrum. For example, the N 1s spectra of blends of poly(vinylpyridine) show the appearance of a high-binding-energy (BE) peak. So far, our studies have been focused on blends involving hydrogen bonding or ionic interaction. It is of interest to study whether XPS is useful to monitor specific interactions in ionomer or polyelectrolyte blends.

This paper reports an XPS study on two P4VPy/polyelectrolyte systems. The two polyelectrolytes are the zinc and lithium salts of poly(styrenesulfonate) (PSSZn and PSSLi, respectively). It will be shown that XPS reveals the existence of interaction between Zn^{2+} and P4VPy but not between Li^+ and P4VPy.

Experimental Section

Materials. Poly(styrenesulfonic acid) (PSSA) in a form of 30% aqueous solution was purchased from Polysciences, Inc. The number-average molecular weight of PSSA was found to be 22.5 kg mol^{-1} based on intrinsic viscosity measurements using the appropriate Mark−Houwink−Sakurada equation.[26] Zinc acetate and lithium acetate were obtained from Ajax Chemicals Ltd. and Aldrich Chemical Co., Inc., respectively. PSSZn and PSSLi were prepared by neutralizing an aqueous PSSA solution with a 25% excess of acetate in aqueous solution. The product was dried by rotary evaporation, followed by further drying in vacuo at 80 °C for 2 days, and then ground to a fine powder. The powder was washed with toluene/methanol (90:10, v/v) five times to remove the excess acetate and finally dried *in vacuo* at 80 °C for 1 week. The molar ratio of zinc to sulfur for PSSZn and that of lithium to sulfur for PSSLi are 0.53 and 1.08, respectively. The ratios are close to the expected values of 0.50 and 1.0, respectively. The infrared spectra of PSSZn and PSSLi do not show the presence of hydroxyl and carboxylate bands, indicating that PSSA has been completely converted to its salts and the excess acetate has been removed by washing.

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Table 1. Characteristics of the PSSZn/P4VPy Complexes

complex	0.34SSZn0.66VP	0.37SSZn0.63VP	0.47SSZn0.53VP
mole fraction of PSSZn in the feed	0.30	0.50	0.70
mole fraction of PSSZn in the bulk	0.34	0.37	0.47
mole fraction of PSSZn in the surface region of the complex	0.40	0.48	0.55
yield of the complex (%)	25	52	41
N 1s peaks of the complex (eV)	399.0, 400.3	399.0, 400.3	399.0, 400.4
Fraction of the high-BE N 1s peak	0.40	0.49	0.53

Table 2. Characteristics of the PSSLi/P4VPy Blends

blend	0.30SSLi0.70VP	0.50SSLi0.50VP	0.70SSLi0.30VP
mole fraction of PSSLi in the bulk of the blend	0.30	0.50	0.70
mole fraction of PSSLi in the surface of the blend	0.36	0.59	0.76
T_g (°C)	145, 160	147, 161	145, 160
N 1s peaks (eV)	399.0	399.0	399.0

P4VPy with a weight-average molecular weight of 200 kg mol^{-1} was purchased from Scientific Polymer Products, Inc.

Preparation of Complexes. P4VPy and PSSZn were separately dissolved in water/ethanol (2:1) at a concentration of 10 g L^{-1}. Appropriate amounts of the two solutions were then mixed. Precipitates formed immediately upon mixing of the two solutions. The mixture was stirred continuously for 1 h. The precipitates were then separated by centrifugation, washed with the solvent, and dried *in vacuo* at 90 °C for 2 weeks. The dried complexes were ground to a fine powder and then stored in a desiccator. The bulk compositions of the complexes were determined by nitrogen and sulfur analysis using a Perkin-Elmer 2400 elemental analyzer. In the following discussion, the complex is denoted as *x*SSZn*y*VP where *x* and *y* are the mole fractions of PSSZn and P4VPy, respectively, in the bulk of the complex. The surface compositions of the complexes were determined by the nitrogen/zinc peak area ratios from XPS measurements after correction with appropriate sensitivity factors.

Preparation of Blends. The mixing of water/ethanol (2:1) solutions of PSSLi and P4VPy did not produce precipitation. The PSSLi/P4VPy blends of various compositions were obtained by solution casting from their water/ethanol (2:1) solutions. Initial removal of solvent was done on a hot plate at 90 °C. The blends were then dried in vacuo at 90 °C for 2 weeks. The dried blends were also ground to a fine powder and stored in a desiccator. The blend is denoted as *x*SSLi*y*VP where *x* and *y* are the mole fractions of PSSLi and P4VPy, respectively, in the blend.

T_g Measurements. The glass transition temperatures (T_gs) of various samples were measured with a TA Instruments 2920 differential scanning calorimeter (DSC). 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.

FTIR Measurements. Infrared spectra were recorded on a Bio-Rad 165 FTIR spectrophotometer; 32 scans were signal-averaged with a resolution of 2 cm^{-1}. Samples were prepared by dispersing the complexes/blends in KBr and compressing the mixture to form disks. Spectra were acquired at 150 °C to exclude moisture, using a SPECAC high-temperature cell.

XPS Measurements. XPS measurements were carried out on a VG Scientific ESCALAB MkII spectrometer using a Mg Kα X-ray source (1235.6-eV photons). The complex was 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 to the C 1s neutral carbon peak at a binding energy (BE) of 284.6 eV. All spectra were obtained at a takeoff angle of 75° and were curve-fitted with VGX-900i software. In spectral deconvolution, the widths (fwhm) of Gaussian peaks were maintained constant for all components in a particular spectrum.

Results and Discussion

Interpolymer Complexation between P4VPy and PSSZn. Complexation between P4VPy and PSSZn indicates a strong interaction between the two polymers. Some characteristics of the complexes are shown in Table 1. Mixing stoichiometric amounts of PSSZn and P4VPy led to the highest yield of the complex. All the complexes showed a surface enrichment in PSSZn.

A distinct glass transition for PSSZn could not be detected by DSC up to 280 °C where the polymer started to show signs of degradation. The T_g value of zinc-neutralized sulfonated polystyrene increases with increasing degree of sulfonation, ranging from 114 °C for 2.48 mol % sulfonation to 122 °C for 7.74 mol % sulfonation.[27] The PSSZn used in the present study is 100% sulfonated. It is conceivable that the T_g value of PSSZn is so high that it could not be detected prior to the onset of degradation. The glass transitions for the P4VPy/PSSZn complexes could not be detected as well. The T_g values of complexes involving P4VPy are usually higher than those predicted by a linear additivity rule, and in some cases the complexes degrade before the glass transitions could be observed.[9,21,28]

Miscibility of PSSLi/P4VPy Blends. DSC measurements were carried out to determine the miscibility of the blends. The T_gs of PSSLi and P4VPy are 161 and 140 °C, respectively. As shown in Table 2, all the PSSLi/P4VPy blends exhibit two glass transitions at 145 and 161 °C, indicating that the blends are immiscible. The formation of P4VPy/PSSZn complexes and the immiscibility of P4VPy/PSSLi blends suggest that P4VPy interacts more strongly with PSSZn than with PSSLi.

FTIR Characterization. In the present work, FTIR characterization focused on the ring-stretching modes of pyridine in the complexes. As shown in Figure 1, P4VPy exhibits a pyridine ring-stretching band at 1597 cm^{-1}. However, complexation with PSSZn leads to the appearance of a new band at 1618 cm^{-1}, which remains at the same wavenumber irrespective of the complex composition. This pyridine ring mode is obviously different from the pyridinium ring mode, which is located at 1635 cm^{-1} as observed in PAA/P4VPy, poly(vinylphosphonic acid)/P4VPy, and PSSA/P4VPy complexes.[21,22,24] The characteristic band at 1618 cm^{-1} is attributed to the ring-stretching mode of the pyridines whose nitrogen atoms coordinate with the zinc cations of PSSZn in the complexes. The 1618-cm^{-1} band becomes more intense with increasing content of PSSZn in the complexes, indicating that the extent of coordination of the pyridine nitrogen atoms increases with the PSSZn content in the complex. Peiffer et al. examined a blend formed between poly(ethyl acrylate-*co*-4-vinylpyridine) (P(EA-*co*-VP)) and zinc-neutralized sul-

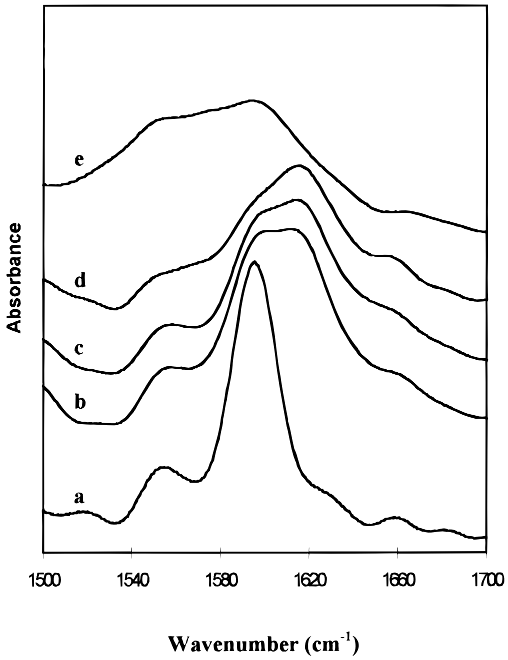

Figure 1. FTIR spectra of PSSZn/P4VPy complexes: (a) P4VPy; (b) 0.34SSZn0.66VP complex; (c) 0.37SSZn0.63VP complex; (d) 0.47SSZn0.53VP complex; (e) PSSZn.

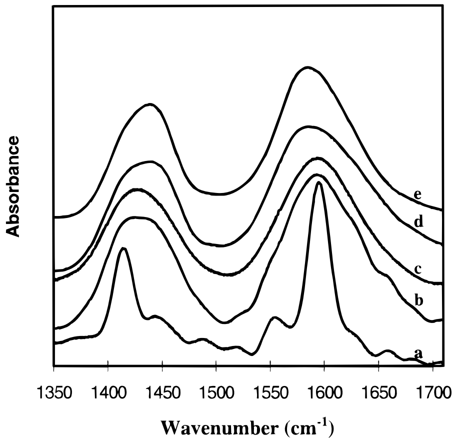

Figure 2. FTIR spectra of PSSLi/P4VPy blends: (a) P4VPy; (b) 0.30SSLi0.70VP blend; (c) 0.50SSLi0.50VP blend; (d) 0.70SSLi0.30VP blend; (e) PSSLi.

fonated EPDM.[18] They reported a new band at 1618 cm^{-1}, which was ascribed to the pyridine ring stretching as a result of the formation of zinc–pyridine complexes. MacKnight and co-workers[14–17] studied several ionomer blends of P(EA-*co*-VP). They also found the appearance of a new pyridine mode at 1620 cm^{-1}.

For the PSSLi/P4VPy blends, the two major pyridine ring-stretching bands at 1597 and 1415 cm^{-1} completely overlap with the bands of PSSLi (Figure 2), making the characterization of interpolymer interaction very difficult. The subtraction method is also difficult to perform because nearly all the bands of these two polymers show some degree of overlapping and no appropriate reference band can be used for successful subtraction.

XPS Characterization

N 1s Spectra. The N 1s spectra of P4VPy and the P4VPy/PSSZn complexes are shown in Figure 3. The N 1s spectrum of P4VPy features a symmetric peak at 399.0 eV. However, the N 1s peaks of the complexes are broader and asymmetric, and each peak can be deconvoluted into two component peaks, with one still remaining at 399.0 eV and the other appearing at 400.3 eV. The appearance of the high-BE peak indicates that a fraction of the pyridine nitrogens participate in interaction with the zinc cations of PSSZn. We have earlier observed that when the pyridine nitrogen atom is protonated by PSSA, a high-BE peak at 401.4 eV appears.[24] Thus, the nitrogen atoms in the P4VPy/PSSZn complexes are not protonated. The conclusion is in accordance with that revealed by FTIR studies as mentioned earlier. The high-BE N 1s peaks at 400.3 eV in P4VPy/PSSZn complexes are an indication of coordination between Zn^{2+} and the pyridine nitrogen atoms. The coordination caused the formation of the PSSZn/P4VPy complexes from the common solvent. The BE value of the high-BE N 1s peak of the PSSZn/P4VPy complex is slightly larger than that of the hydrogen-bonded PVPh/P4VPy complex (400.0 eV)[23] but smaller than that of the PSSA/P4VPy complex.[24] This suggests that the strength of the coordination interaction in the PSSZn/P4VPy complexes is between those of hydrogen bonding and ionic interaction.

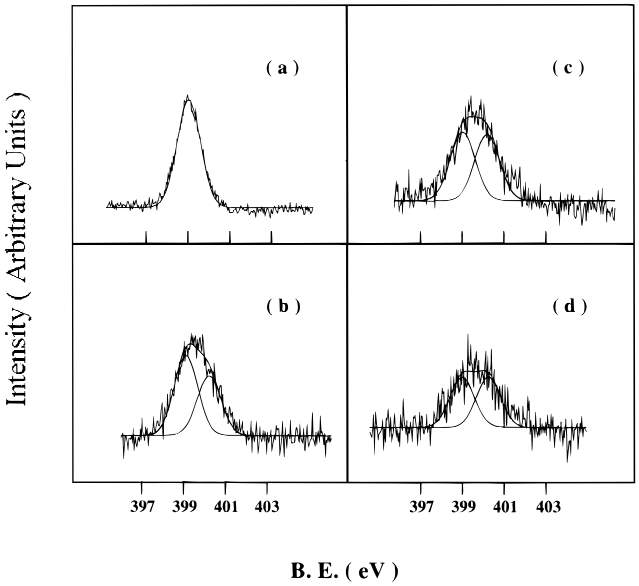

Figure 3. N 1s spectra of PSSZn/P4VPy complexes: (a) P4VPy; (b) 0.34SSZn0.66VP complex; (c) 0.37SSZn0.63VP complex; (d) 0.47SSZn0.53VP complex.

The extent of the coordination of the pyridine nitrogen atoms in a PSSZn/P4VPy complex can be estimated from the area percentage of the high-BE N 1s component peak of the complex. As shown in Table 1, only a moderate fraction of the pyridine nitrogen atoms in the complex coordinate with Zn^{2+}, and the fraction of coordinated pyridine nitrogens increases with increasing PSSZn content in the complex.

As shown in Figure 4, all the P4VPy/PSSLi blends show a single N 1s peak at 399.0 eV. The result indicates that there is no change in the electronic environment of pyridine nitrogen atoms accompanying the blending of P4VPy with PSSLi. Thus, the pyridine nitrogen atoms of P4VPy are not involved in interaction with Li^{+}.

S 2p Spectra. The S 2p spectra of PSSZn and the 0.37SSZn0.63VP complex are shown in Figure 5. The S 2p peak of PSSZn consists of a spin–orbit split doublet S2p$_{1/2}$ and S2p$_{3/2}$ located at 170.1 and 168.9 eV, respec-

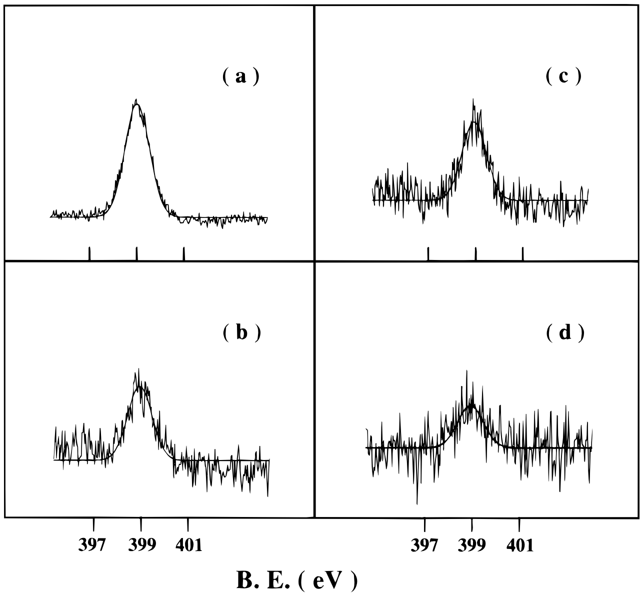

Figure 4. N 1s spectra of PSSLi/P4VPy blends: (a) P4VPy; (b) 0.30SSLi0.70VP blend; (c) 0.50SSLi0.50VP blend; (d) 0.70SSLi0.30VP blend.

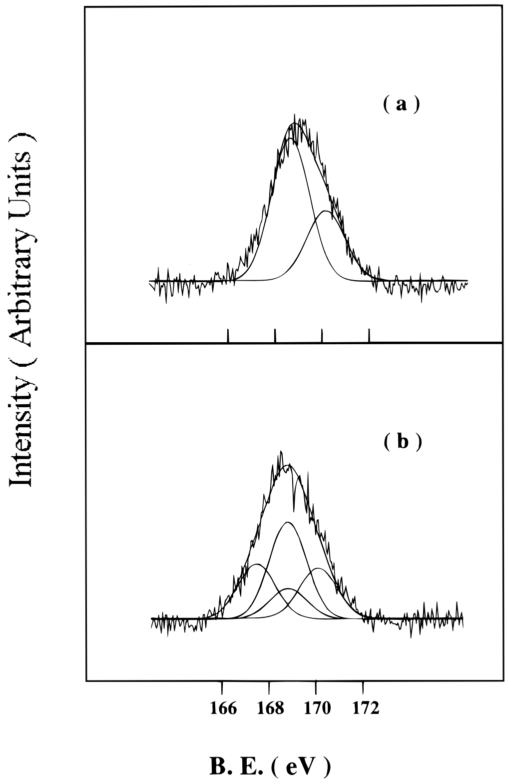

Figure 5. S 2p spectra of (a) PSSZn and (b) 0.37SSZn0.63VP complex.

tively. However, the complexation of PSSZn with P4VPy brings about a new doublet at 168.9 and 167.7 eV. The appearance of low-BE S 2p peaks indicates that a fraction of the sulfonate anions in PSSZn become more electron-rich. Thus, the coordination between Zn^{2+} and P4VPy partially removes the metal ion from the sulfonate anion, making the sulfur atom in the sulfonate anion more electron-rich.

As shown in Figure 6, no changes in the S 2p spectra are observed after the blending of PSSLi with P4VPy. This result shows that no coordination interaction is formed in the PSSLi/P4VPy blends.

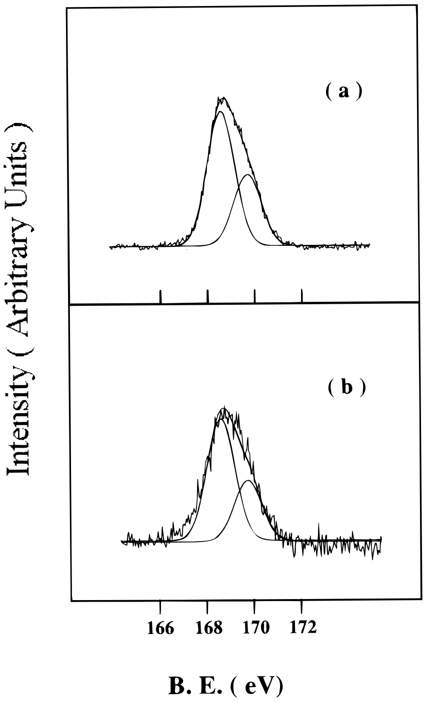

Figure 6. S 2p spectra of (a) PSSLi and (b) 0.50SSLi0.50VP blend.

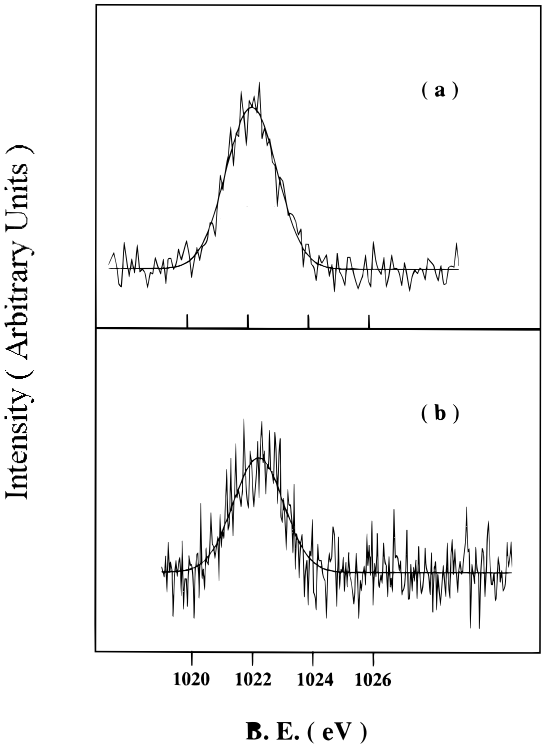

Figure 7. Zn $2p_{3/2}$ spectra of (a) PSSZn and (b) 0.37-SSZn0.63VP complex.

Zn $2p_{3/2}$ and Li 1s Spectra. As shown in Figure 7, the Zn $2p_{3/2}$ peak of PSSZn is located at 1022.3 eV. However, the 0.37SSZn0.63VP complex also shows a single Zn $2p_{3/2}$ peak at 1022.3 eV, indicating that the electronic environment of the zinc cation is not appreciably affected by the coordination. The observation may appear to indicate that the effects due to the dissociation of Zn^{2+} and the sulfonate anion and the coordination between Zn^{2+} and P4VPy nearly balance out each other or may be due to the fact that the Zn

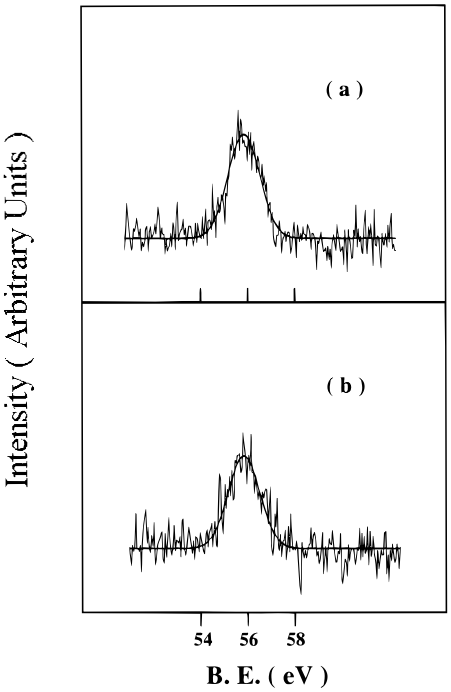

Figure 8. Li 1s spectra of (a) PSSLi and (b) 0.50SSLi0.50VP blend.

$2p_{3/2}$ peak is not sensitive to any change of the 3d orbitals of zinc upon coordination. For instance, the BE value of the Zn $2p_{3/2}$ peak for PSSZn is 1022.3 eV, which is only slightly larger than that of 1021.8 eV for metallic zinc.[29−31]

As shown in Figure 8, the Li 1s spectra remain unchanged after blending PSSLi with P4VPy. From the combined analysis of the Li 1s, S 2p, and N 1s spectra of the PSSLi/P4VPy blends, it can be concluded that no appreciable interaction exists between PSSLi and P4VPy. The conclusion is consistent with the immiscibility of the PSSLi/P4VPy blends.

Conclusions

The present study leads to the following conclusions:

(1) P4VPy forms complexes with PSSZn but not with PSSLi in water/ethanol (2:1) solutions. P4VPy is immiscible with PSSLi as each blend shows the existence of two glass transitions.

(2) The appearance of a new high-binding-energy peak in the N 1s spectra of P4VPy/PSSZn complexes suggests the coordination between Zn^{2+} and the pyridine nitrogen atom.

(3) The S 2p spectra of P4VPy/PSSZn complexes show the development of a new spin−orbit split doublet at a low-binding-energy region, indicating that the interaction between Zn^{2+} and the pyridine nitrogen atom loosens the original ionic interaction between Zn^{2+} and the sulfonate anion.

(4) The N 1s and S 2p spectra of P4VPy/PSSLi blends remain unchanged, indicating that no appreciable interaction exists between P4VPy and PSSLi.

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