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Miscibility and specific interactions in two polyelectrolyte/poly(2-ethyl-2-oxazoline) blend systems

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Abstract

Poly(2-ethyl-2-oxazoline) (PEOx) was blended with the lithium or zinc salt of poly(styrenesulfonic acid) (PSSLi and PSSZn, respectively). Each PEOx/PSSLi blend showed the existence of two glass transition temperatures (T_gs). The lower T_g value is close to that of PEOx. The upper T_g value is substantially lower than that of PSSLi, indicating that the two polymers do interact to a certain extent. The T_gs of PSSZn and some PEOx/PSSZn blends could not be detected. A single T_g was observed for PEOx/PSSZn blends containing 0.20 and 0.40 mole fraction of PSSZn, and the value is substantially higher than that of PEOx. PEOx/PSSZn blends are considered to be miscible. Fourier transform infrared spectroscopic measurements showed that both PSSLi and PSSZn interact with amide carbonyl oxygen atoms of PEOx. X-ray photoelectron spectroscopic studies showed the development of high-binding energy (BE) N1s peaks in all the PEOx/PSSZn blends but not in the PEOx/PSSLi blends. The interaction between Zn^{2+} and the carbonyl oxygen atom is so strong that there is an electron migration from the nitrogen atom to Zn^{2+} via the carbonyl group. Interaction between PEOx and PSSLi or PSSZn is also evidenced by the development of a low-BE S2p doublet in the blends. However, the Li1s and Zn2p peaks did not show significant changes upon blending the polyelectrolytes with PEOx. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Miscibility; Specific interactions; Polyelectrolyte blends

1. Introduction

The importance of specific interactions in achieving miscibility in polymer blends is well recognized. Interaction between an ionomer and a polar polymer can induce miscibility or improve compatibility [1,2]. Ionomer/polyamide blends have received considerable attention in recent years [3–12]. It has been established that the choice of metal ion affects significantly the miscibility of the blends. Transition metal ions such as Zn^{2+} and Mn^{2+} produce stronger miscibility effects than alkali metal ions such as Na^+ and Li^+. Spectroscopic techniques such as Fourier transform infrared (FT-i.r.) spectroscopy and ^{13}C-nuclear magnetic resonance (n.m.r.) spectroscopy have been used to probe the nature of specific interactions in various ionomer/polyamide blends. For blends of Li-containing ionomer, interaction has been attributed to be between Li^+ and the carbonyl oxygen atoms of the polyamide. For Zn-containing ionomer blends, ^{13}C-n.m.r. showed down-field shifts of the two carbon atoms adjacent to the amide nitrogen atom, suggesting the existence of an interaction between Zn^{2+} and the amide nitrogen atom [5].

However, it was recognized that the amide hydrogen atoms of the polyamide might be involved in hydrogen-bonding with the sulfonate groups of the ionomer, complicating the assignment of the observed spectral changes. To avoid such a complication of competing hydrogen bonding interaction, Feng et al. [8] studied blends of metal salts of lightly sulfonated polystyrene (MSPS, with M denoting the metal ion) and an N-methylated polyamide, poly(*N*,*N*′-dimethylethylene sebacate) (mPA). Their FT-i.r. studies showed that the addition of MSPS to mPA does lead to the development of a low-frequency peak in the carbonyl band, indicating the presence of interaction between the metal ion and the carbonyl oxygen atom. In addition, ^{15}N-n.m.r. studies showed the development of a new down-field peak, indicating the involvement of the amide nitrogen atom in specific interaction with MSPS.

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However, the amide nitrogen atom was considered to participate in the specific interaction through electron migration from the nitrogen atom to the metal ion via the carbonyl group.

We have recently used X-ray photoelectron spectroscopy (XPS) to study specific interactions in polymer blends [13–19]. Li et al. [20] have recently used XPS to study the effects of specific interactions on the surface structure and composition of miscible poly(vinyl alcohol)/poly(*N*-vinyl-2-pyrrolidone) blends. 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 polyelectrolyte blends of poly(4-vinylpyridine) (P4VPy) with the lithium and zinc salts of poly(styrenesulfonic acid) (PSSLi and PSSZn, respectively), XPS revealed the presence of an interaction between Zn^{2+} and P4VPy but not between Li^{+} and P4VPy [19].

The present work deals with the miscibility and specific interactions in blends of poly(2-ethyl-2-oxazoline) (PEOx) with PSSLi or PSSZn. PEOx has been found to be miscible with a large number of polymers [21–30]. PEOx is a tertiary amide polymer and hence the problem of the involvement of an amide hydrogen atom in any specific interaction does not arise. FT-i.r. studies [23–29] have shown that PEOx interacts with some proton-donating polymers through the carbonyl oxygen atoms. However, there has been no experimental evidence to show the involvement of the amide nitrogen atoms of PEOx in a specific interaction. It will be shown that the nitrogen atoms of PEOx do interact indirectly with Zn^{2+} but not with Li^{+}.

2. Experimental

2.1. Materials

Poly(styrenesulfonic acid) (PSSA) in the form of a 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 [31]. PSSLi and PSSZn were prepared by neutralizing the aqueous PSSA solution with lithium acetate and zinc acetate, respectively [19]. PEOx with a weight-average molecular weight of 70 kg mol^{-1} was purchased from the Aldrich Chemical Company, Inc.

2.2. Preparation of blends

The two polymers were separately dissolved in an ethanol/water (1:2) solution at a concentration of 10 g l^{-1}. Appropriate amounts of the two polymer solutions were then mixed and stirred continuously for 1 h. The solvent was initially removed using a hot plate at 90°C, and the blend was then dried in vacuo at 100°C for 2 weeks and finally stored in a desiccator to prevent moisture absorption. All the blends were transparent and brittle. For XPS measurements, the dried blends were ground to fine powders.

2.3. T_g measurements

The glass transition temperatures (T_gs) of the blends were measured using a TA Instruments 2920 differential scanning calorimeter (d.s.c.). The scanning rate was 20°C min^{-1}. The initial onset of the change of slope in the d.s.c. curve was taken as the T_g.

2.4. FT-i.r. 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 blends in KBr and compressing the mixture to form discs. Spectra were acquired at 150°C to exclude moisture, using a SPECAC high-temperature cell.

2.5. XPS measurements

XPS measurements were carried out on a VG Scientific ESCALAB MkII spectrometer using a Mg K_α X-ray source (1235.6 eV photons). The samples were mounted on a standard sample stud by means of a 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 the binding energy (BE) of 284.6 eV. All spectra were obtained at a take-off angle of 75° and were curve fitted using VGX-900i software. In spectral deconvolution, the widths (FWHM) of the Gaussian peaks were maintained constant for all components in a particular spectrum.

3. Results and discussion

3.1. Miscibility of blends

The d.s.c. curves of various PEOx/PSSLi blends are shown in Fig. 1. Each of the PEOx/PSSLi blends showed two glass transitions, indicating that the two polymers are not completely miscible with each other. The lower T_g value of the blends was close to that of PEOx, showing that one of the phases is essentially pure PEOx. The upper T_g value was lower than that of PSSLi, especially for blends containing 0.20 and 0.40 mole fraction of PSSLi. Thus, PEOx and PSSLi interact with each other to a certain extent, leading to the formation of a mixed phase. Nevertheless, all the blends were transparent and the transparency could be due to a matching of refractive indices of the two polymers or the presence of a submicron dispersed phase. Transparent two-phase ionomer blends have also been reported for

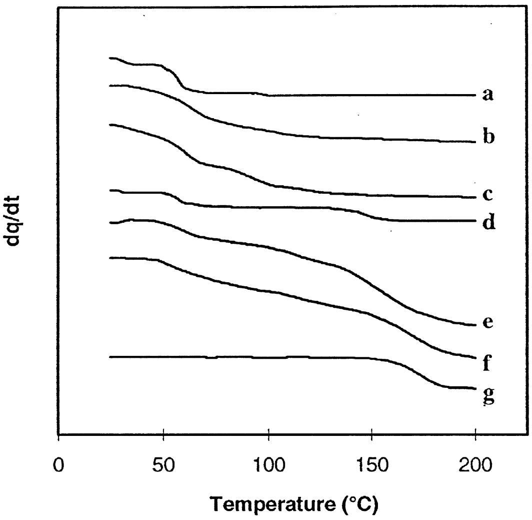

Fig. 1. DSC curves of PSSLi/PEOx blends: (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6; (f) 0.8 and (g) 1.0 mole fraction of PSSLi.

NaSPS/poly(2,6-dimethyl-1,4-phenylene oxide) [32] and ZnSPS/poly(styrene-*co*-4-vinylpyridine) [33] blends. Distinct glass transition for PSSZn could not be detected by d.s.c. up to 280°C where the polymer started to show signs of degradation. The T_g value of ZnSPS has been reported to depend on the degree of sulfonation, ranging from 114°C for 2.48 mol% of sulfonation to 122°C for 7.74 mol% of sulfonation [34]. The PSSZn used in the present study is 100 mol% sulfonated. It is therefore likely that the T_g value of PSSZn is so high that it could not be detected prior to the onset of degradation. All the PEOx/PSSZn blends were also transparent. A single glass transition was found for blends containing 0.20 and 0.40 mole fraction of PSSZn but the glass transitions could not be found for blends containing 0.50, 0.60 and 0.80 mole fractions of PSSZn. Although glass transitions could not be detected for some of the blends, we consider that the two polymers are miscible with each other. The T_g values for the blends containing 0.20 and 0.40 mole fractions of PSSZn are 67 and 105°C, respectively, which are substantially higher than that of PEOx (53°C). If the two polymers are not completely miscible with each other, it is likely that a T_g value close to that of PEOx will be observed for all the blends as in the case of PEOx/PSSLi blends. Furthermore, spectroscopic studies also show that PEOx interacts more intensively with PSSZn than with PSSLi, and this will be discussed in the following sections.

3.2. FT-i.r. characterization

Fig. 2 shows the FT-i.r. spectra of PEOx and PEOx/PSSLi blends in the amide carbonyl stretching region. The amide carbonyl band of PEOx absorbs at 1652 cm^{-1}. When PSSLi is added to PEOx, a band at 1640 cm^{-1} begins to appear, showing that the carbonyl group interacts with PSSLi. At a higher PSSLi content, the 1640 cm^{-1} band overlaps considerably with the other bands of PSSLi. Similarly, the addition of PSSZn to PEOx also leads to the appearance of a new band at 1630 cm^{-1} (Fig. 3). The larger shift of the carbonyl band in the PEOx/PSSZn blends than in the PEOx/PSSLi blends indicates a stronger interaction in the former blend system. This is consistent with the earlier findings that Zn^{2+} interacts more strongly with polymers under study than Li^{+} in several ionomer blend systems [6–8]. The appearance of a low-frequency carbonyl band

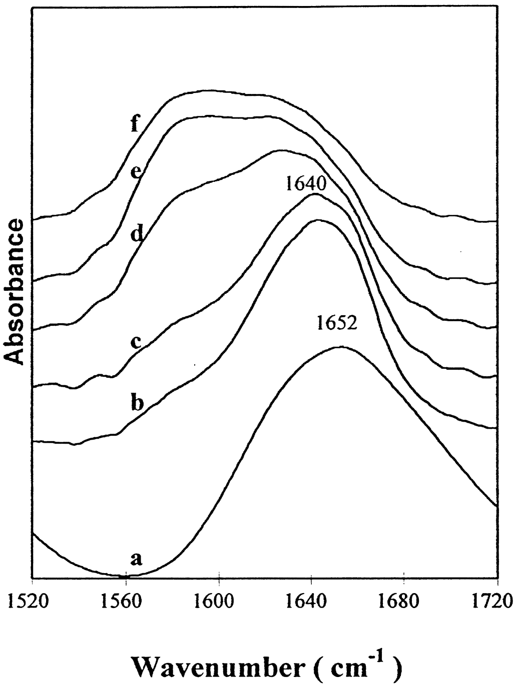

Fig. 2. FT-i.r. spectra of PSSLi/PEOx blends: (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6 and (f) 0.8 mole fraction of PSSLi.

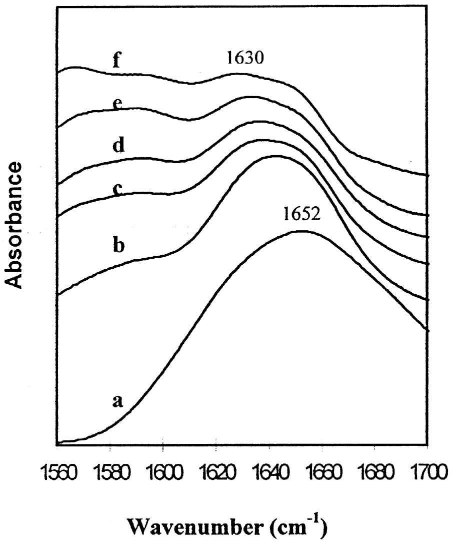

Fig. 3. FT-i.r. spectra of PSSZn/PEOx blends: (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6 and (f) 0.8 mole fraction of PSSZn.

shows that the metal ion interacts with the carbonyl oxygen atom of PEOx. If the metal ion were to interact with the lone pair of electrons of nitrogen, a high-frequency band would have developed [8,35,36].

3.3. XPS characterization

The N1s spectra of various PEOx/PSSLi and PEOx/PSSZn blends are shown in Figs 4 and 5, respectively. The N1s peak of PEOx is symmetrical and has a binding energy (BE) value of 399.4 eV. All the PEOx/PSSLi blends also show a single N1s peak at 399.4 eV, indicating that the amide nitrogen atoms are not involved in any specific interaction with PSSLi. In contrast, the N1s peaks of all the PEOx/PSSZn blends are asymmetrical and each can be deconvoluted into two component peaks, with one remaining at 399.4 eV and the other one at about 400.8 eV. The development of the high-BE N1s peak indicates that some of the amide nitrogen atoms have become electron-deficient as a result of the interaction between PEOx and Zn^{2+}. Since Zn^{2+} interacts with the carbonyl oxygen atom of PEOx as shown by FT-i.r., the development of a high-BE N1s peak supports the electron migration model suggested by Feng et al. [8]. They suggested that the strength of an ion–amide complex depended on the ionic potential and the ratio of the ionic charge to the ionic radius of the metal ion [8]. The ionic potentials of Li^+ and Zn^{2+} are 14.08 and 27.78, respectively, and hence polyamide would interact more strongly with Zn^{2+} than with Li^+. The absence of high-BE N1s peaks in PEOx/PSSLi blends also shows that the interaction between Li^+ and PEOx is not strong enough to perturb the electronic environment of the nitrogen atom.

Fig. 6 shows the S2p spectra of PSSLi and PEOx/PSSLi (1:1) blend. The S2p peak of PSSLi consists of one spin-orbit split doublet $S2p_{3/2}$ (168.7 eV) and $S2p_{1/2}$ (169.9 eV). The single S2p environment shows that all the sulfonate groups are in the ionized form. However, the S2p spectrum of the PEOx/PSSLi (1:1) blend shows the presence of two environments. In addition to the original doublet at 168.7 and 169.9 eV, there is a new doublet set at 167.6 and

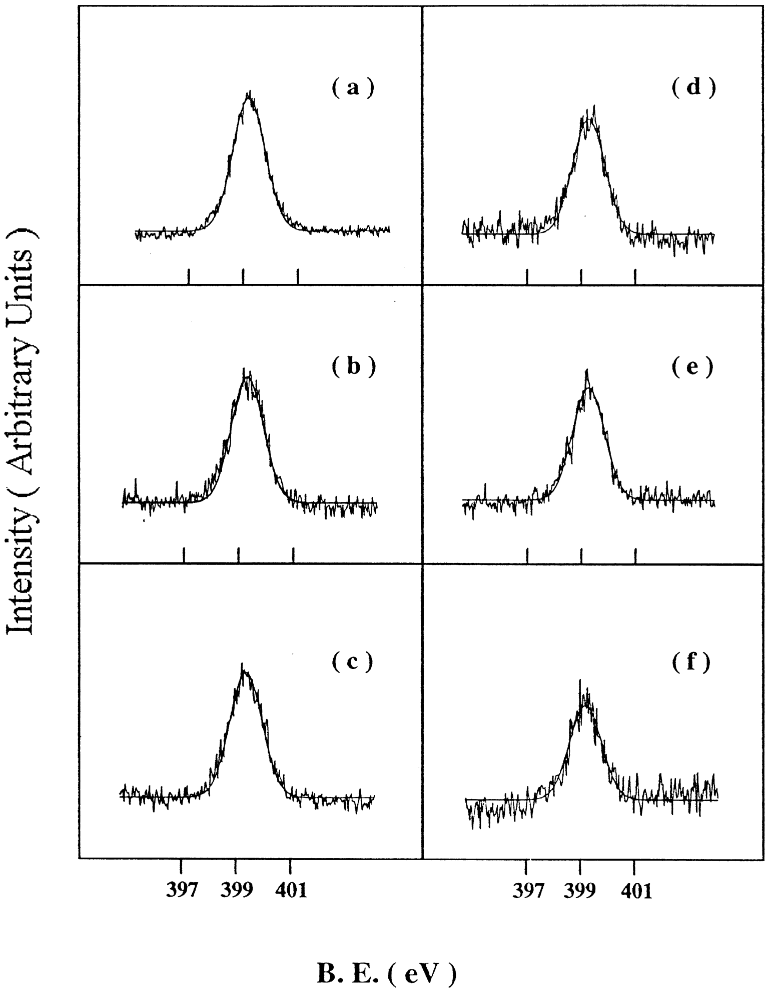

Fig. 4. N1s spectra of PSSLi/PEOx blends: (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6 and (f) 0.8 mole fraction of PSSLi.

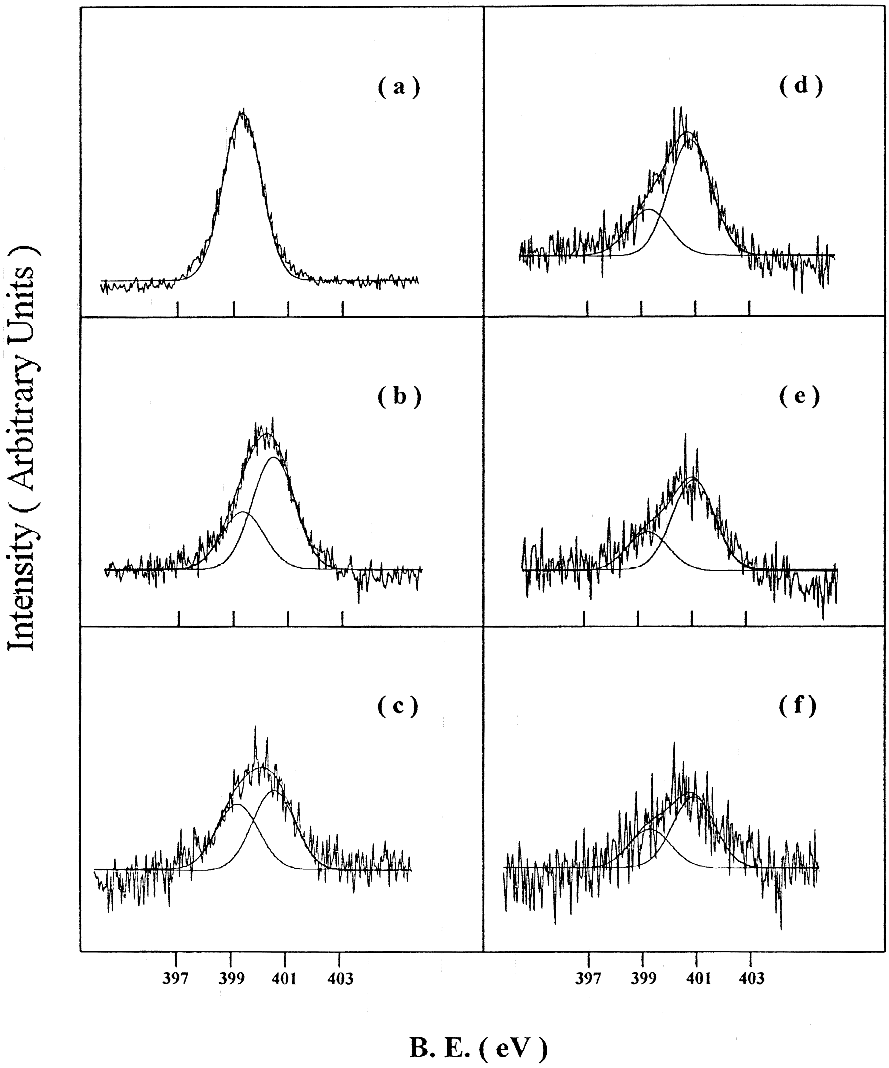

Fig. 5. N1s spectra of PSSZn/PEOx blends: (a) 0; (b) 0.2; (c) 0.4; (d) 0.5; (e) 0.6 and (f) 0.8 mole fraction of PSSZn.

168.8 eV. The existence of the low-BE doublet shows that the interaction between Li^+ and PEOx does remove the metal ion from the sulfonate anion, making the sulfur atom in the sulfonate ion more electron-rich.

Similarly, the S2p spectrum of PSSZn consists of a single spin-orbit split doublet $S2p_{3/2}$ (168.9 eV) and $S2p_{1/2}$ (170.1 eV) (Fig. 7). The S2p spectrum of the PEOx/PSSZn (1:1) blend also shows the appearance of a new doublet at 167.6 and 168.8 eV, once again indicating the interaction between Zn^{2+} and PEOx. The difference in the BE values of the two pairs of doublets is 1.3 eV which is more than that of the PEOx/PSSLi system (1.1 eV). This can also be taken to further indicate a stronger interaction between Zn^{2+} and PEOx than that between Li^+ and PEOx.

Fig. 8 shows the Li1s peaks of PSSLi and the PEOx/PSSLi (1:1) blend. No significant difference can be observed. Similarly, the $Zn2p_{3/2}$ peaks of PSSZn and the PEOx/PSSZn (1:1) blend do not show any significant difference as shown in Fig. 9. This observation appears to indicate that any effect due to the dissociation of the metal ion from the sulfonate anion and the effect due to the association between the metal ion and PEOx nearly balance each other out, producing no significant net changes in the electronic environments of Zn^{2+} and Li^+.

The differences in the miscibility and interactions in PSSLi/PEOx and PSSLi/P4VPy blends are noteworthy. PSSLi is immiscible with P4VPy since each blend shows two T_g values close to those of the component polymers [19]. The absence of interaction between PSSLi and P4VPy is evidenced by XPS measurements [19]. The N1s and S2p peaks of PSSLi do not develop new peaks upon blending with P4VPy. However, in the present study, we have demonstrated that PSSLi is able to interact with PEOx through the amide carbonyl groups even though the interaction is not strong enough to produce complete miscibility.

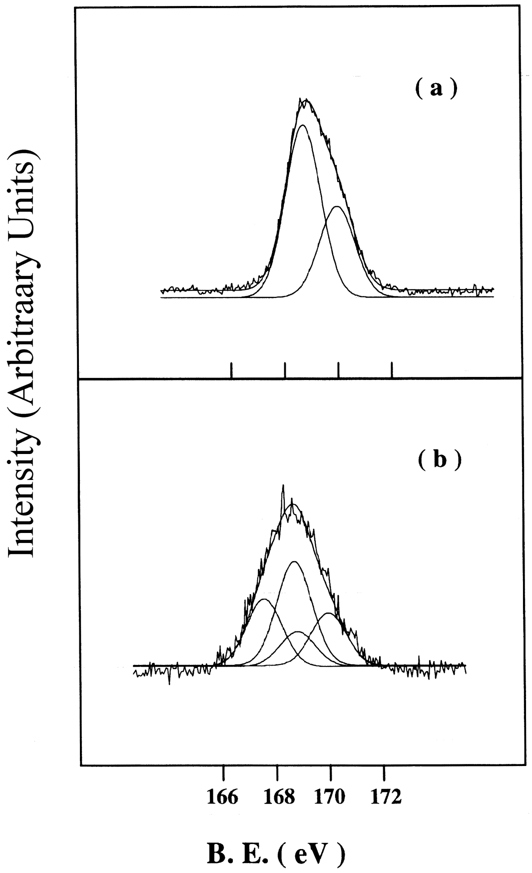

Fig. 6. S2p spectra of (a) PSSLi and (b) PSSLi/PEOx blend with 0.5 mole fraction of PSSLi.

4. Conclusions

The present study leads to the following conclusions:

1. PEOx is not completely miscible with PSSLi as evidenced by the appearance of two glass transitions for each blend. The lower T_g value is close to that of PEOx and the upper T_g value is substantially lower than that of PSSLi, indicating that mixing between the two polymers occurs to a certain extent.
2. Although the glass transitions of some of the PEOx/PSSZn blends could not be detected, the blends are considered to be miscible.
3. FT-i.r. studies show that both PSSZn and PSSLi interact with the amide carbonyl oxygen atoms.
4. The appearence of a new high-BE peak in the N1s spectra of PEOx/PSSZn blends suggests that the strong coordination between Zn^{2+} and the carbonyl oxygen atom induces electron migration from the amide nitrogen atom. However, the PEOx/PSSLi blends did not show any high-BE N1s peaks, indicating that Li^+ interacts exclusively or predominantly with the amide carbonyl oxygen atoms.
5. The S2p spectra of both PEOx/PSSZn and PEOx/PSSLi blends show the development of a new low-BE spin-orbit split doublet, indicating that the interaction

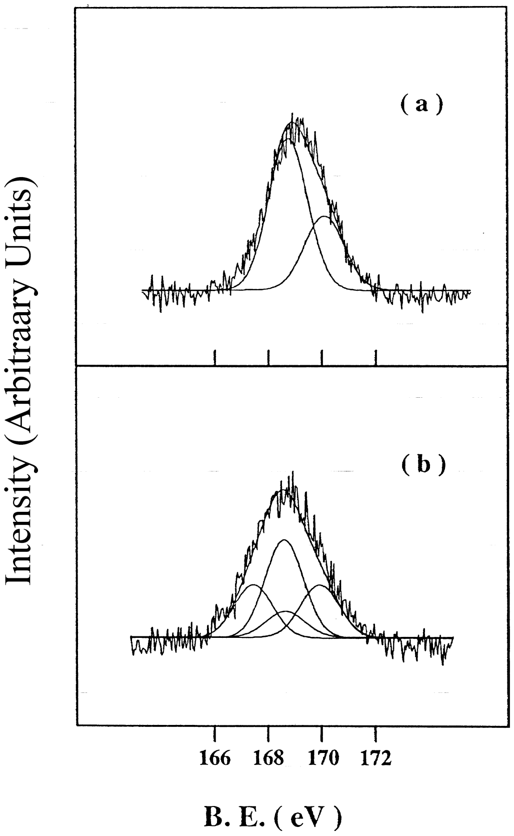

Fig. 7. S2p spectra of (a) PSSZn and (b) PSSZn/PEOx blend with 0.5 mole fraction of PSSZn.

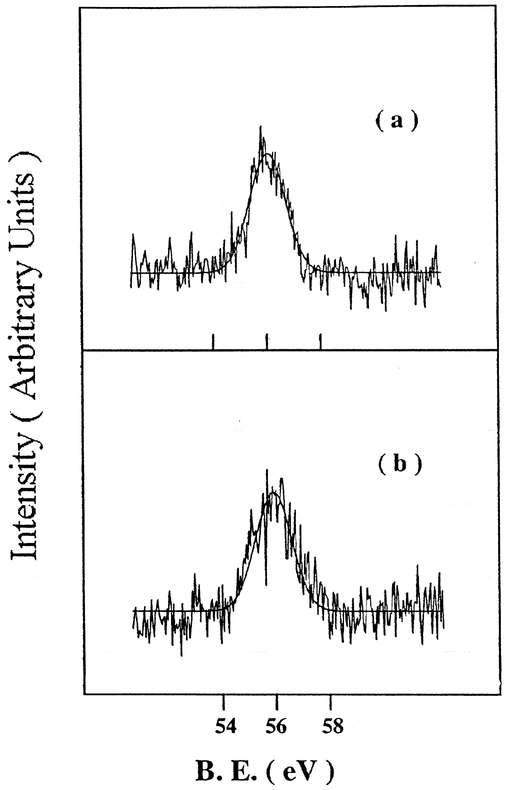

Fig. 8. Li1s spectra of (a) PSSLi and (b) PSSLi/PEOx blend with 0.5 mole fraction of PSSLi.

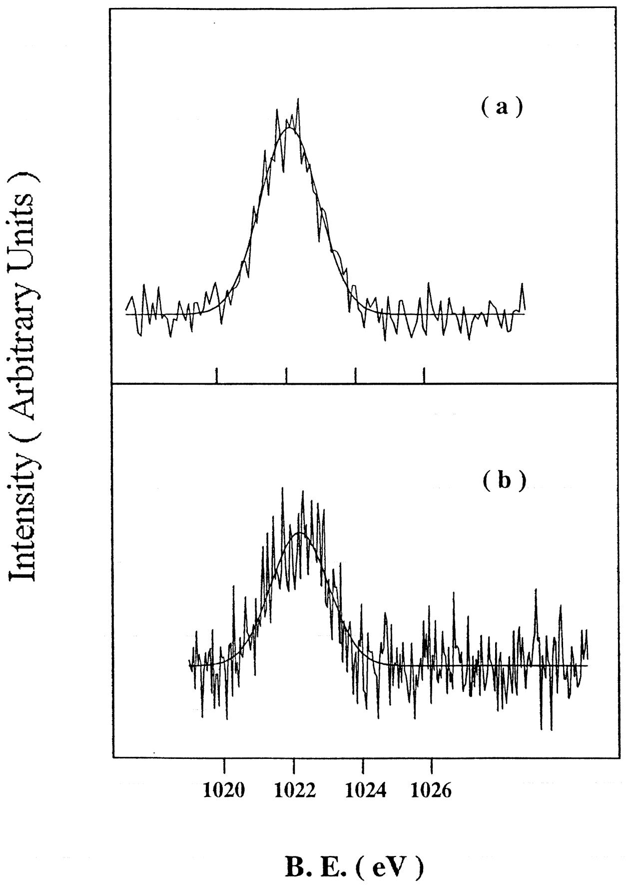

Fig. 9. Zn2p$_{3/2}$ spectra of (a) PSSZn and (b) PSSZn/PEOx blend with 0.5 mole fraction of PSSZn.

between the metal ion and the PEOx loosens the original ionic interaction between the metal ion and the sulfonate anion.

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