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# Specific interactions in complexes of poly(*N*-methyl-4-piperidyl methacrylate) and poly(styrenesulfonate) salt

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**Abstract**

Poly(*N*-methyl-4-piperidyl methacrylate) (PMPMA) was blended with the lithium or zinc salt of poly(styrenesulfonate) (PSSLi and PSSZn, respectively). PMPMA formed complexes with PSSZn but not with PSSLi in water/ethanol (2:1) solutions, indicating the presence of a strong interaction between PSSZn and PMPMA. PMPMA is immiscible with PSSLi as shown by the appearence of two glass transitions in each blend. Fourier transform infrared spectroscopic measurements showed a shift of the Bohlmann band in all the PMPMA/PSSZn complexes but not in the PMPMA/PSSLi blends. X-ray photoelectron spectroscopic (XPS) studies showed the development of high-binding-energy (BE) N 1s peaks in all the PMPMA/PSSZn complexes but not in the PMPMA/PSSLi blends. Interaction between PMPMA and $Zn^{2+}$ is also evidenced by the development of a low-BE S 2p doublet and a low-BE Zn $2p_{3/2}$ peak in each complex. Therefore, XPS reveals the existence of coordination between $Zn^{2+}$ and PMPMA but not between $Li^+$ and PMPMA. The coordination number of $Zn^{2+}$ is estimated to be 2 from the XPS results. The coordination interaction between $Zn^{2+}$ and PMPMA is stronger than that between $Zn^{2+}$ and poly(4-vinylpyridine). © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords*: Poly(*N*-methyl-4-piperidyl methacrylate); Poly(styrenesulfonate) salt; X-ray photoelectron spectroscopy

## 1. Introduction

The use of ionomers for achieving specific interactions with another polar polymer is a particularly effective approach to develop miscible polymer blends [1–5]. Recently, a number of studies have examined blends of polyamides and lightly sulfonated polystyrene ionomers [6–9]. The enhancement of miscibility for blends of sulfonated polystyrene ionomers with polyamides is due to interactions between the metal sulfonate and amide groups. The choice of the metal counterion significantly affects the interactions in the blends [7,10]. The strongest interactions between the two polymers occur when a transition metal cation such as $Mn^{2+}$ or $Zn^{2+}$ is used. Among the alkali-metal cations, lithium provides substantial improvement on miscibility, while sodium does not [7,10,11]. Moreover, the sulfonation levels and sulfonate concentration also influence the miscibility.

Blends of poly(4-vinylpyridine) (P4VPy) or pyridine-containing polymers and ionomers have been studied [12–15]. However, blends of ionomers and piperidine-containing polymers have not been studied. In view of the basicity of piperidine, we have recently studied the blends of poly(*N*-methyl-4-piperidyl methacrylate) (PMPMA) with poly(*p*-vinylphenol) (PVPh), poly(methacrylic acid) (PMAA), poly(acrylic acid) (PAA), poly(styrenesulfonic acid) (PSSA), and poly(vinylphosphonic acid) (PVPA) [16]. The interactions between PMPMA and the acidic polymers are so strong that they form complexes by coprecipitating from their common solvent in which the polymers are initially soluble. The existence of specific interactions between the piperidine groups and the acidic polymers was shown by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS).

In this article, we examine the interactions between PMPMA and two polyelectrolytes, the zinc and lithium salts of poly(styrenesulfonate) (PSSZn and PSSLi, respectively) using FTIR and XPS. The results will be compared to the corresponding P4VPy systems [17].

## 2. Experimental

### 2.1. Materials

Poly(styrenesulfonic acid) (PSSA) in a form of 30%

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Table 1
Characteristics of PMPMA/PSSZn complexes

| Complex | 0.60SSZn0.40MP | 0.45SSZn0.55MP | 0.38SSZn0.62MP |
|---|---|---|---|
| Mole fraction of PSSZn in feed | 0.70 | 0.50 | 0.30 |
| Yield of complex (%) | 69 | 83 | 56 |
| $T_g$(°C) | nil | nil | 132 |
| Mole fraction of PSSZn in the bulk | 0.60 | 0.45 | 0.38 |
| Mole fraction of PSSZn in the surface region of the complex | 0.69 | 0.62 | 0.58 |
| Fraction of coordinated piperidine groups | 0.71 | 0.59 | 0.56 |
| Coordination number of $Zn^{2+}$ | 2.0 | 1.8 | 1.7 |

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 [18]. PSSZn and PSSLi were prepared by neutralizing PSSA with zinc acetate and lithium acetate, respectively [17]. The synthesis of PMPMA was reported previously [19].

### 2.2. Preparation of complexes

PMPMA 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 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 two weeks. The dried complexes were ground to 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$y$MP where $x$ and $y$ are the mole fractions of PSSZn and PMPMA, respectively, in the bulk of the complex. The surface compositions of the complexes were determined by the nitrogen:sulfur peak-area ratios from XPS measurements after correction with appropriate sensitivity factors.

### 2.3. Preparation of blends

The mixing of water/ethanol (2:1) solutions of PSSLi and PMPMA did not produce precipitation. PSSLi/PMPMA blends of various compositions were obtained by solution casting from their water/ethanol (2:1) solutions. PMPMA/LiCl and PMPMA/$ZnCl_2$ blends were prepared by mixing stoichiometric amounts of water/ethanol (2:1) solutions (1%w/v) of PMPMA and LiCl or $ZnCl_2$. Initial removal of solvent was done on a hot-plate at 90°C. The blends were then dried in *vacuo* at 90° for two weeks. The dried blends were also ground to fine powder and stored in a desiccator. The PMPMA/PSSLi blend is denoted as $x$SSLi$y$MP where $x$ and $y$ are the mole fractions of PSSLi and PMPMA, respectively, in the blend. The PMPMA/LiCl and PMPMA/$ZnCl_2$ blends are denoted as 0.50LiCl0.50MP and 0.50$ZnCl_2$0.50MP, respectively.

### 2.4. Differential scanning calorimetric measurements (DSC)

The glass transition temperatures ($T_g$) of various samples were measured with a TA Instruments 2920 differential scanning calorimeter. The scanning rate was 20°C min$^{-1}$. The initial onset of the change of slope in the DSC curve was taken as the $T_g$.

### 2.5. 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 discs. Spectra were acquired at 150°C to exclude moisture, using a SPECAC high-temperature cell.

### 2.6. XPS measurements

XPS measurements were carried out on a VG Scientific ESCALAB MkII spectrometer equipped with a Mg $K_\alpha$ X-ray source (1235.6 eV photons) and a hemispherical energy analyzer. The complex was mounted on a standard sample stud by means of a double-sided adhesive tape. The analyzer pass energy was set at 20 eV and several scans of the C 1s, N 1s, Li 1s, S 2p and Zn 2p spectra were obtained. 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 an emission angle of 75° to the sample surface and were curve-fitted using the VGX-900i software. In spectral peak fits, the widths (FWHM) of Gaussian peaks were maintained constant for all components in a particular spectrum.

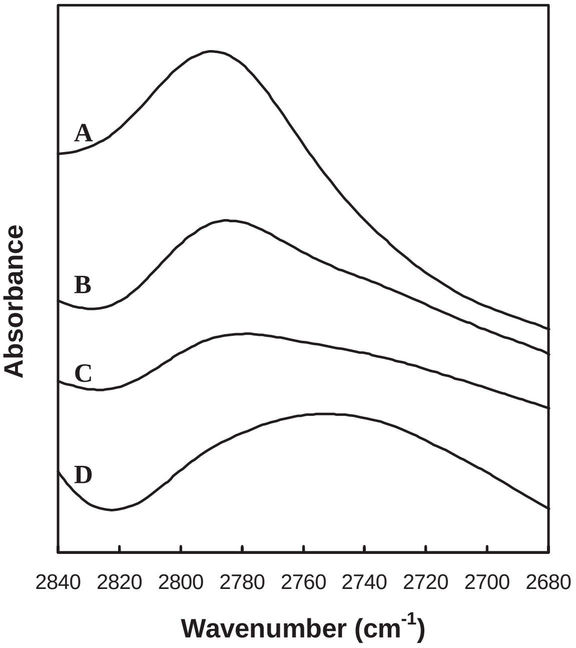

Fig. 1. FTIR spectra in the Bohlmann band region: (A) PMPMA; (B) 0.38SSZn0.62MP complex; (C) 0.45SSZn0.55MP complex; (D) 0.60SSZn0.40MP complex.

## 3. Results and discussion

### 3.1. General characteristics of complexes and blends

Similar to P4VPy [17], PMPMA formed complexes with PSSZn but not with PSSLi. These results suggest that intermolecular interactions in the complexes of PMPMA/PSSZn are stronger than those in the PMPMA/PSSLi blends. The characteristics of the PMPMA/PSSZn complexes are shown in Table 1. The yields of the complexes are in the range of 56–83% which are higher than those of the P4VPy/PSSZn complexes (40–55%) [17]. This may be taken as an indication of a stronger interaction between PSSZn with PMPMA than with P4VPy. Mixing stoichiometric amounts of PMPMA and PSSZn led to the highest yield of complex. All the complexes showed a surface enrichment in PSSZn.

Only the 0.38SSZn0.62MP complex exhibits a single $T_g$ at 132°C, which is higher than that of PMPMA at 96°C, while all the PMPMA/PSSLi blends show two $T_g$ which are close to those of the two component polymers. The $T_g$ of PSSZn could not be detected, presumably due to the very high ionic cross-linking density which restrict chain motion. As the content of PSSZn in the complexes increases, the glass transition temperatures for the 0.45SSZn0.55MP and 0.60SSZn0.40MP complexes could not be observed up to the degradation temperature near 280°C. Based on the single $T_g$ criterion, PMPMA is judged to be miscible with PSSZn but immiscible with PSSLi over the entire composition range.

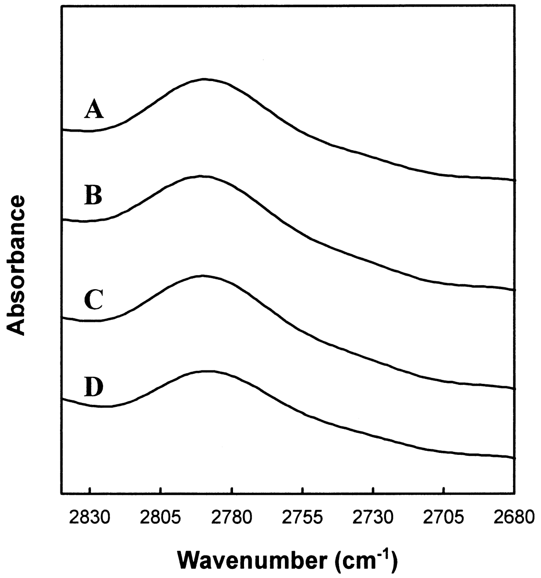

Fig. 2. FTIR spectra in the Bohlmann band region: (A) PMPMA; (B) 0.70SSLi0.30MP blend; (C) 0.50SSLi0.50MP blend; (D) 0.30SSLi0.70MP blend.

### 3.2. FTIR characterization

The FTIR spectra of PMPMA/PSSZn complexes and PMPMA/PSSLi blends in the 2680–2840 $cm^{-1}$ region are shown in Figs. 1 and 2, respectively. In the spectrum of PMPMA (Fig. 1, curve A), a peak at 2786 $cm^{-1}$, the so-called "Bohlmann" band, is related to the interaction between the free axial electron lone pairs of the nitrogen atom and the axial C–H bonds in the $\alpha$-position in relation to the nitrogen atom of the heterocycle [20,21]. When the piperidine nitrogen atom is protonated, a new band at a lower frequency appears [20]. For the three PMPMA/PSSZn complexes, the Bohlmann bands shift to lower frequencies, suggesting that the coordination between $Zn^{2+}$ and the piperidine nitrogen has changed the steric environment of the C–H band. In contrast, Fig. 2 clearly reveals that there is no interaction between $Li^{+}$ and PMPMA as the Bohlmann bands are not shifted in all the PMPMA/PSSLi blends. Similarly, a low-frequency shift of the Bohlmann band is observed in the 0.50ZnCl$_2$0.50MP blend but not in the 0.50LiCl0.50MP blend (Fig. 3).

There are three possible electron-donating sites in PMPMA where a metal ion may coordinate: nitrogen, C=O oxygen or C–O oxygen. If the metal ion coordinates to the oxygen, the C=O and C–O bands should shift to low frequencies in FTIR spectra. However, there are no shifts of C=O bands in the PMPMA/PSSZn complexes (Fig. 4) and the PMPMA/PSSLi blends (Fig. 5). These results show that coordination does not occur between the C= O of PMPMA and $Zn^{2+}$ or $Li^{+}$. The overlapping of the spectra of PSSZn, PSSLi and PMPMA in the C–O band region makes it impossible to detect the coordination of metal ion and the oxygen of C–O.

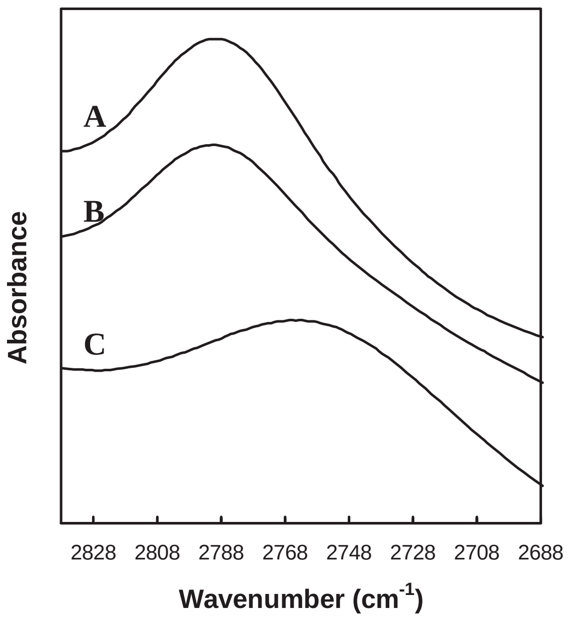

Fig. 3. FTIR spectra in the Bohlmann band region: (A) PMPMA; (B) 0.50LiCl0.50MP blend; (c) 0.50ZnCl$_2$0.50MP blend.

### 3.3. XPS characterization

*N 1s spectra:* PMPMA form complexes with poly(acrylic acid) (PAA), poly(methacrylic acid) (PMAA), poly(styrenesulfonic acid) (PSSA), and poly(vinylphosphonic acid) (PVPA) [16]. There are two different nitrogen environments in the XPS spectra of the four complexes. The low-BE component at 399.0 eV is associated with the neutral nitrogen of piperidine; the high-BE component around 401.0 eV is associated with the piperidinium nitrogen. Similarly, two different nitrogen environments can also be discerned in the spectra of the PMPMA/PSSZn complexes (Fig. 6). The results show that some of the piperidine groups of PMPMA in the complexes were coordinated with Zn$^{2+}$. As the PSSZn content increases, the fraction of the coordinated piperidine nitrogens increases. The BE value of the high-BE N 1s peak of the PSSZn/PMPMA complex is nearly the same as those of the ionic-bonded PMPMA/

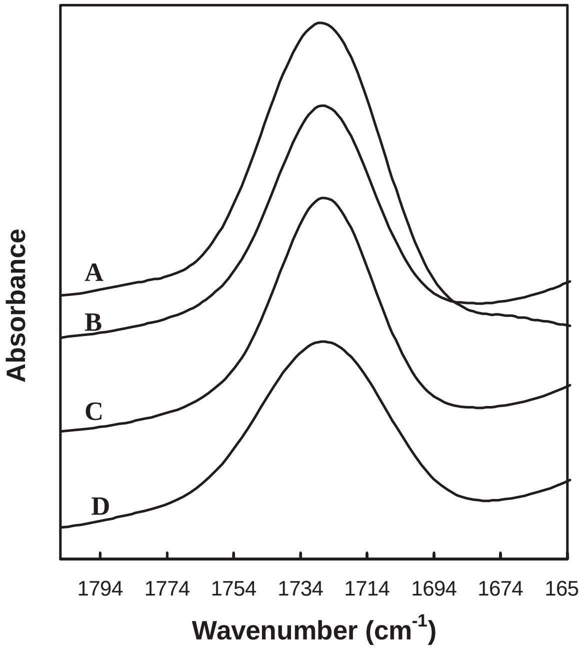

Fig. 4. FTIR spectra of PMPMA/PSSZn complexes in the carbonyl band region: (A) PMPMA; (B) 0.60SSZn0.40MP complex; (C) 0.45SSZn0.55MP complex; (D) 0.38SSZn0.62MP complex.

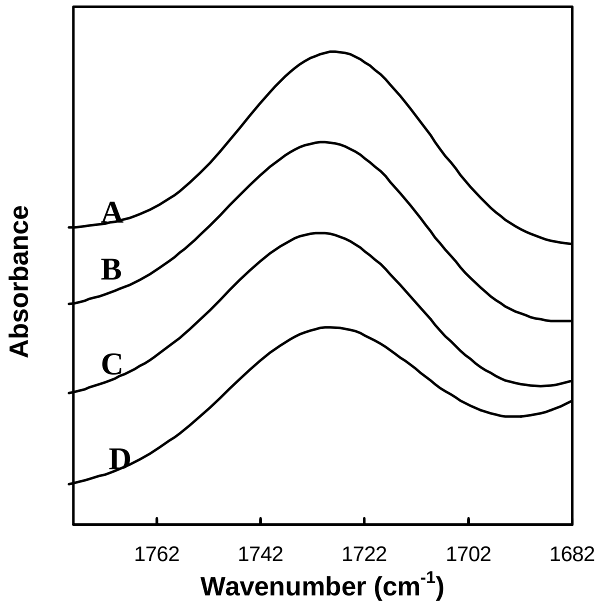

Fig. 5. FTIR spectra of PMPMA/PSSLi blends in the carbonyl band region: (A) PMPMA; (B) 0.70SSLi0.30MP blend; (C) 0.50SSLi0.50MP blend; (D) 0.30SSLi0.70MP blend.

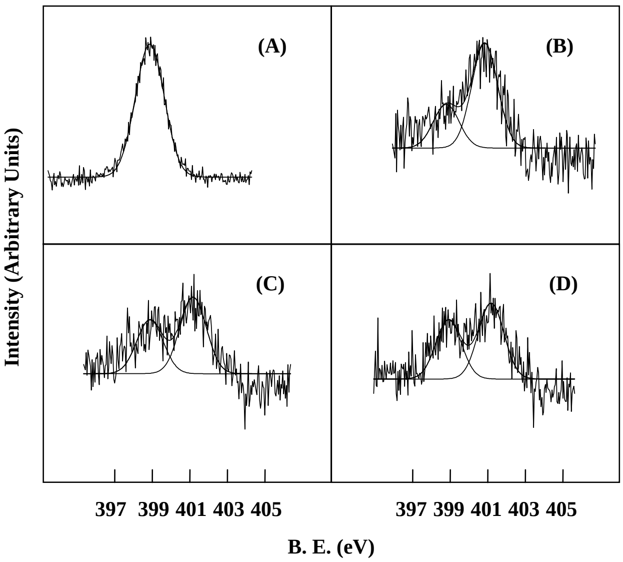

Fig. 6. N ls spectra of PMPMA/PSSZn complexes: (A) PMPMA; (B) 0.60SSZn0.40MP complex; (C) 0.45SSZn0.55MP complex; (D) 0.38SSZn0.62MP complex.

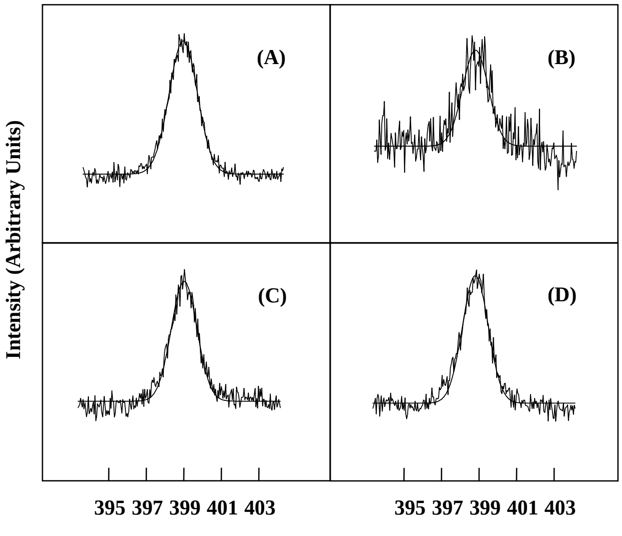

Fig. 7. N ls spectra of PMPMA/PSSLi blends: (A) PMPMA; (B) 0.70SSLi0.30MP blend; (C) 0.50SSLi0.50MP blend; (D) 0.30SSLi0.70MP blend.

PAA, PMPMA/PMAA, PMPMA/PVPA, and PMPMA/PSSA complexes [16]. This suggests that the strength of the coordination interaction in the PSSZn/PMPMA complexes is similar in magnitude as those in the four ionic-bonded complexes. It is of interest to note that the BE-shift value of the pyridine nitrogen in the PSSZn/P4VPy complex is around 1.4 eV [17], while that of the piperidine nitrogen in the PSSZn/PMPMA complex is around 2.4 eV. Therefore, the coordination between $Zn^{2+}$ and PMPMA is stronger than that between $Zn^{2+}$ and P4VPy. This is not surprising as PMPMA is more basic than P4VPy, and thereby the electrons of nitrogen coordinate to zinc more strongly.

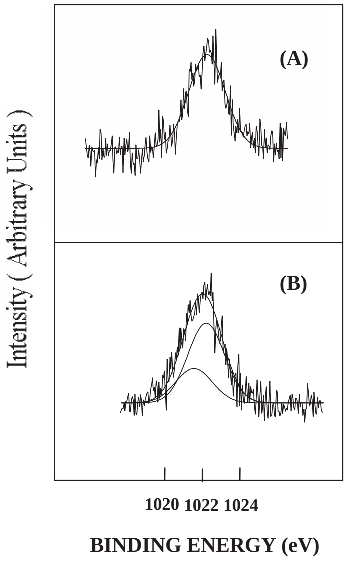

Fig. 8. Zn $2p_{3/2}$ spectra of (A) PSSZn and (B) 0.60SSZn0.40MP complex.

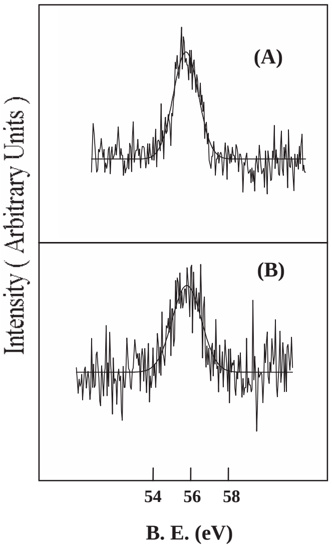

Fig. 9. Li ls spectra of (A) PSSLi and (B) 0.70SSLi0.30MP blend.

Fig. 7 shows the N 1s core-level spectra of the PMPMA/PSSLi blends. The N 1s spectra of the PMPMA/PSSLi blends can not be deconvoluted into different nitrogen environments. This result shows that the nitrogen in the piperidine ring is not involved in coordination. This conclusion is in agreement with the FTIR results.

*Zn $2p_{3/2}$ and Li 1s spectra:* As shown in Fig. 8, the Zn $2p_{3/2}$ peak of PSSZn is located at 1022.3 eV. However, the 0.60SSZn0.40MP complex shows a new peak located at 1021.6 eV, indicating that the electronic environment of the zinc cation is significantly affected by the coordination. In contrast, PSSZn/P4VPy complex shows a single Zn $2p_{3/2}$ peak even though $Zn^{2+}$ is coordinated to P4VPy [17]. The observation also suggests that the interaction in the PMPMA/PSSZn complex is stronger than that in the P4VPy/PSSZn complex. As shown in Fig. 9, no change in the Li 1s spectrum is observed after the blending of PSSLi with PMPMA.

*S 2p spectra:* The S 2p spectra of the complexs also provide evidence of coordination interactions in the PMPMA/PSSZn complexes. For PSSZn, the S 2p peak consists of a spin–orbit split doublet S $2p_{3/2}$ (BE = 168.9 eV) and S $2p_{1/2}$ (BE = 170.1 eV). The S 2p spectrum of the 0.60SSZn0.40MP complex is shown in Fig. 10(B). The S 2p peak of the complex can be deconvoluted into two environments, one arising from the S 2p in the uncoordinated PSSZn with BE values of 168.9 eV for S $2p_{3/2}$ and 170.1 eV for S $2p_{1/2}$ (full curve), and one from the the S 2p in coordinated PSSZn with BE values around 167.6 eV for S $2p_{3/2}$ and 168.8 eV for S $2p_{1/2}$ (dashed curve). The coordination between $Zn^{2+}$ and the piperidine nitrogen has loosened the metal ion from the sulfonate anion. The sulfur atoms in the complexes become more electronegative, leading to the development of a low-BE doublet. However, no changes in the S 2p spectra are observed in the PMPMA/PSSLi blends (Fig. 11).

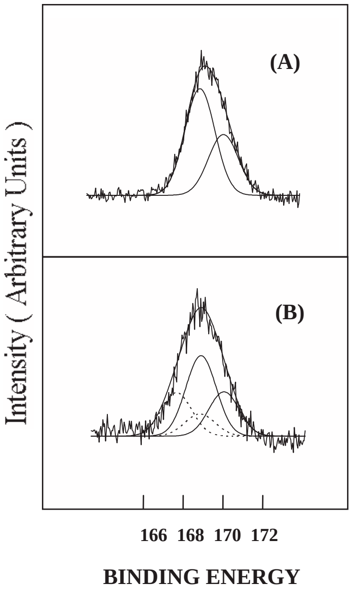

Fig. 10. S 2p spectra of (A) PSSZn; (B) 0.60SSZn0.40MP complex.

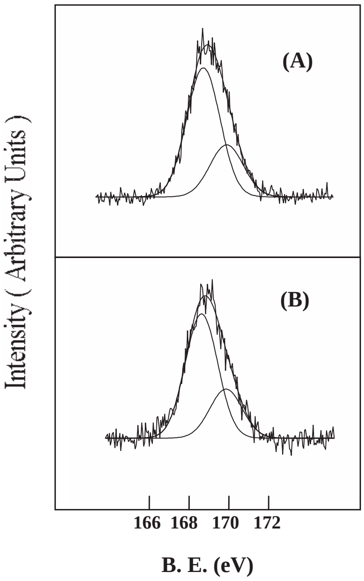

Fig. 11. S 2p spectra of (A) PSSLi and (B) 070SSLi0.30MP blend.

*$Zn^{2+}$ coordination number:* It appears anomalous that the fraction of high-BE N 1s component does not agree with those of low-BE Zn $2p_{3/2}$ component and low-BE S 2p component for a given complex. When the surface stoichiometry of the complex is taken into consideration, the coordination number of $Zn^{2+}$ in each complex can be estimated. For the 0.60SSZn0.40MP complex, the fraction of coordinated piperidine units is 0.71 from the deconvolution result. When this value is multiplied by 0.31, the fraction of PMPMA in the surface region, a value of 0.22 is obtained. Similarly, when the fraction of coordinated units of $Zn^{2+}$, 0.30, is multiplied by 0.69, the fraction of PSSZn in the surface, then divided by 2 (as one $Zn^{2+}$ is associated with two sulfonate groups), a value of 0.11 is obtained. Thus, two piperidine units coordinate with one $Zn^{2+}$ ion. The same result is obtained from the S 2p data. When the fraction of low-BE sulfur atoms, 0.33, is multiplied by 0.69, the fraction of PSSZn in the surface, then divided by 2, a value of 0.11 is obtained. Similarly, the coordination numbers of $Zn^{2+}$ in the 0.45SSZn0.55MP and 0.38SSZn0.62MP complexes are calculated to be 1.8 and 1.7, respectively. It is of interest to note that for Zn-ionomer/polyamide blends, the coordination number of $Zn^{2+}$ was estimated to be 2 based on the analysis of FTIR and $^{15}$N NMR results [22].

## 4. Conclusions

The present study leads to the following conclusions:

(1) PMPMA forms complexes with PSSZn but not with PSSLi in water/ethanol (2:1) solutions. PMPMA is immiscible with PSSLi as each blend shows the existence of two glass transitions.
(2) FTIR studies show that $Zn^{2+}$ coordinates to the piperidine nitrogens, but not to the oxygens in C=O, or C–O groups, while there is no coordination between $Li^+$ and PMPMA.
(3) The appearance of a new high-BE peak in the N 1s spectra and a new low-BE peak in the Zn $2p_{3/2}$ spectra of PMPMA/PSSZn complexes shows the existence of coordination between $Zn^{2+}$ and the piperidine nitrogen atom. The coordination interactions in the PMPMA/PSSZn complexes are stronger than those in the P4VPy/PSSZn complexes.
(4) The S 2p spectra of PMPMA/PSSZn complexes show the development of a new spin–orbit split doublet at a low-BE region, indicating that the interaction between $Zn^{2+}$ and the piperidine nitrogen atom has loosened the original ionic interaction between $Zn^{2+}$and the sulfonate anion.
(5) The coordination number of $Zn^{2+}$ is estimated to be 2 from XPS results.
(6) The Li 1s, N 1s, and S 2p spectra of PMPMA/PSSLi blends remain unchanged, indicating that no appreciable interaction exists between PMPMA and PSSLi.

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