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X-ray photoelectron spectroscopic studies of ionic interactions between sulfonated polystyrene and poly(styrene-*co*-4-vinylpyridine)

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X-ray photoelectron spectroscopic measurements were made on complexes obtained from sulfonated polystyrene (SPS) and poly(styrene-*co*-4-vinylpyridine) (PSVP). The N1s spectrum of PSVP shows the existence of a single nitrogen environment. Two different nitrogen environments are discernible in the N1s spectra of the complexes, indicating that some of the pyridine units have been protonated. The S2p peak of SPS in the complex is shifted to a lower binding energy upon complexation with PSVP, indicating the existence of sulfonate ion. About 60% of the sulfonic acid groups in the complexes is ionized. Copyright © 1996 Elsevier Science Ltd.

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Introduction

The importance of ionic interactions to achieve miscibility between dissimilar polymers is well documented[1–5]. For example, while polystyrene (PS) is immiscible with poly(ethyl acrylate), sulfonated polystyrene (SPS) is miscible with poly(ethyl acrylate-*co*-4-vinylpyridine) when each polymer contains about 5 mol% of acidic or basic groups[2]. Miscibility arises from ionic interactions following proton transfer from the acidic to the basic groups. Strong ionic interactions are also shown by the formation of interpolymer complexes in the form of gel-like precipitates upon mixing the tetrahydrofuran (THF) solutions of the two polymers.

The existence of ionic interactions between SPS and pyridine-containing polymers is evidenced from Fourier-transform infrared spectroscopy as shown by the changes in the i.r. bands associated with S – O and O = S = O stretching, and pyridine ring vibration[6,7]. Nuclear magnetic resonance spectroscopy has also been used to study blends involving ionic interactions[8,9]. For blends of SPS with poly(methyl methacrylate-*co*-4-vinylpyridine) the aromatic carbon signals of the pyridine units shift downfield, indicating a change from pyridine to pyridinium ion[8].

X-ray photoelectron spectroscopy (X.p.s.) has been used widely to study the surface characteristics of multicomponent polymer systems such as block and graft copolymers, and polymer blends[10–14]. Since the binding energy (BE) of a core-level electron depends on its chemical environment within the molecule, the X.p.s. spectrum provides information on the type and number of different species of a given atom in the molecule. The BE of the N1s electron of pyridinium ion is larger than that of pyridine by 2.5 eV[15]. In this respect, X.p.s. would be useful to study the ionic interactions in blends involving pyridine-containing polymers and acid polymers . This communication reports on the X.p.s. study of interactions between SPS and poly(styrene-*co*-4-vinylpyridine) (PSVP).

Experimental

Materials. Two SPS samples were prepared by sulfonation of PS with acetyl sulfate following the procedures reported in the literature[16,17], with some modifications. Acetyl sulfate was generated by mixing concentrated sulfuric acid with acetic anhydride in a molar ratio of 1/1.6 in an ice-bath. The mixture was allowed to react at room temperature for 10 min and was then diluted with 1,2-dichloroethane (DCE) to a concentration of acetyl sulfate of 1.0 M. PS (10 g) was dissolved in DCE (50 ml) and the solution was heated to 50°C. An appropriate amount of acetyl sulfate solution was added to the PS solution and sulfonation was allowed to proceed at 50°C for 5 h. The resulting SPS was obtained by precipitating the solution in water. The gel-like precipitate was separated and washed repeatedly with water and then dried *in vacuo* at 60°C for one week. The degrees of sulfonation of the two SPS samples, as determined by elemental analysis for sulfur, are 17 and 27 mol%.

Two PSVP samples were prepared by solution polymerization in toluene at 80°C, initiated by 0.5 wt% of azobisisobutyronitrile. An appropriate feed composition was selected based on the monomer reactivity ratios[18] to produce PSVP with a vinylpyridine content similar to the sulfonic acid content of SPS. The vinylpyridine contents of the two samples, as determined by elemental analysis for nitrogen, are 17 and 30 mol%. In the following discussion, the number after SPS or PSVP denotes the acid or base content of the sample.

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Table 1 Yields and T_g of SPS/PSVP complexes

Complex	Yield (%)	T_g (°C)
SPS17/PSVP17 (from THF)	93	167
SPS17/PSVP17 (from DMF)	88	147
SPS27/PSVP30 (from THF)	95	165
SPS27/PSVP30 (from DMF)	94	151

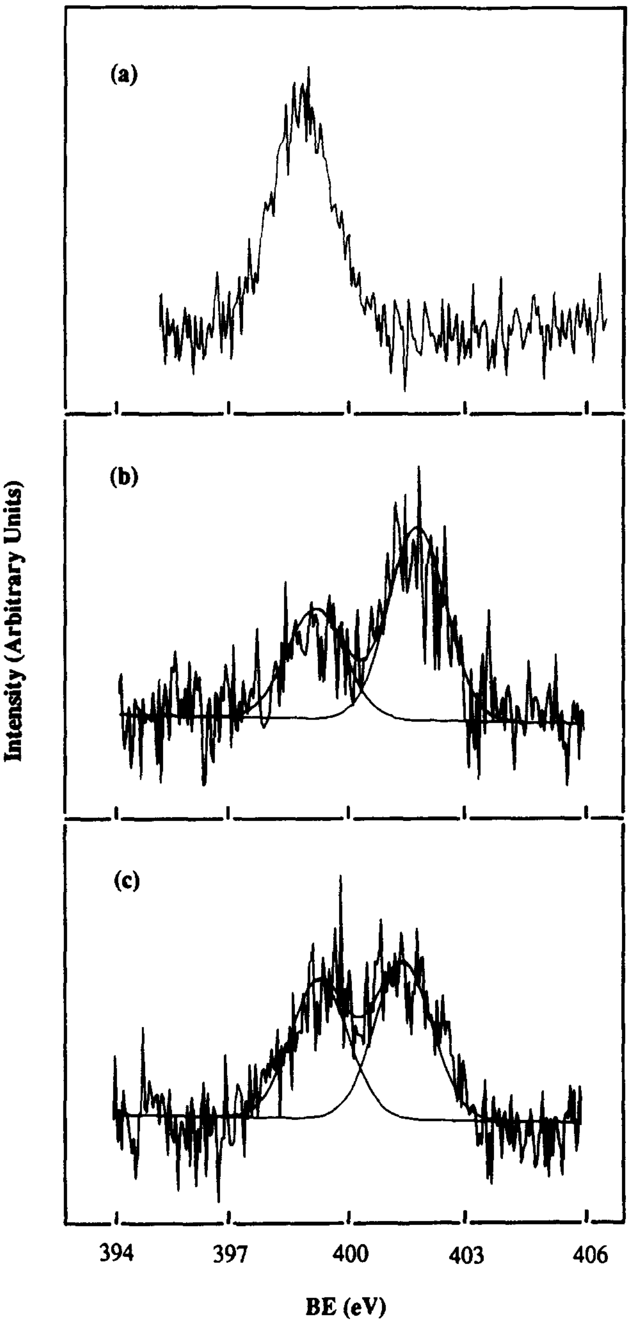

Figure 1 N1s spectra of (a) PSVP30; (b) SPS27/PSVP30 complex from THF; (c) SPS27/PSVP30 complex from DMF

Preparation of samples. SPS and PSVP were separately dissolved in THF or *N*,*N*-dimethylformamide (DMF) (1% w/v). Appropriate amounts of the solutions were mixed as to contain stoichiometric amounts of sulfonic acid and pyridine groups. Two systems, SPS17/PSVP17 and SPS27/PSVP30, were studied, each of which contains polymers having similar functional group contents. In all four cases, mixing of the two polymer solutions led to the formation of gel-like precipitates. The precipitates, thereafter denoted as complexes, were separated from the solution by centrifugation, washed with the solvent, and dried *in vacuo* at 90°C. The ratio of the amount of the dried complex to the total amount of the two polymers in the initial solution gives the yield of the complex.

T_g *measurements.* The glass transition temperature (T_g) of various samples were measured with a Perkin-Elmer DSC-4 differential scanning calorimeter, using a heating rate of $20°C\,min^{-1}$. The T_g value was taken as the initial onset of the change of slope in the d.s.c. curve. The reported values are the average values of several runs. The T_g values of SPS17, SPS27, PSVP17 and PSVP30 are 138, 153, 104 and 113°C respectively.

X.p.s. measurements. X.p.s. measurements were made on a VG scientific Escalab MKII spectrometer with an MgKα X-ray source (1253.6 eV photons). The polymer samples 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; all spectra were obtained with a take-off angle of 75°.

Results and discussion

The occurrence of interpolymer complexation depends on the nature of the solvent[19–24]. Complexation does not occur if the solvent interacts strongly with the component polymers. Moreover, the yields and compositions of the complexes obtained from a given system are also dependent on the choice of solvent[19–23]. DMF, which is able to interact strongly with acidic polymers, usually prevents interpolymer complexation[19–21]. The formation of SPS/PSVP complexes in both THF and DMF indicates that the interactions between the two polymers are particularly strong. *Table 1* shows the yields and the T_g values of the complexes. The yields are high. The T_g values of the complexes are higher than those calculated from the linear additivity rule, another indication of strong interpolymer interactions[22–24].

Figure 1 shows the N1s core-level spectra of PSVP30 and SPS27/PSVP30 complexes obtained from THF and from DMF. The N1s spectrum of PSVP30 shows a single nitrogen environment at a BE of 399.0 eV. However, two different nitrogen environments can be discerned in the spectra of the two complexes. The low BE component is characteristic of neutral nitrogen of pyridine; the high BE component is associated with pyridinium nitrogen. The results show that some of the pyridine units in PSVP30 have been protonated and there are ionic interactions between SPS27 and PSVP30. The extents of protonation of the pyridine units, as estimated from the deconvoluted pyridinium nitrogen peaks, are 64% and 53% for complexes obtained from THF and DMF respectively. Thus the extent of ionic interaction is also dependent on the nature of the solvent. The surface compositions of the two complexes are slightly different. The ratios of SPS27 to PSVP30 in the surface regions are 0.57:1 and 0.50:1 for complexes obtained from THF and DMF respectively, showing that the surface is enriched with PSVP30. Since the surface regions of polymer blends are enriched with the component polymer with a lower surface energy[25–27], the present results indicate that PSVP30 has a lower surface energy than SPS27.

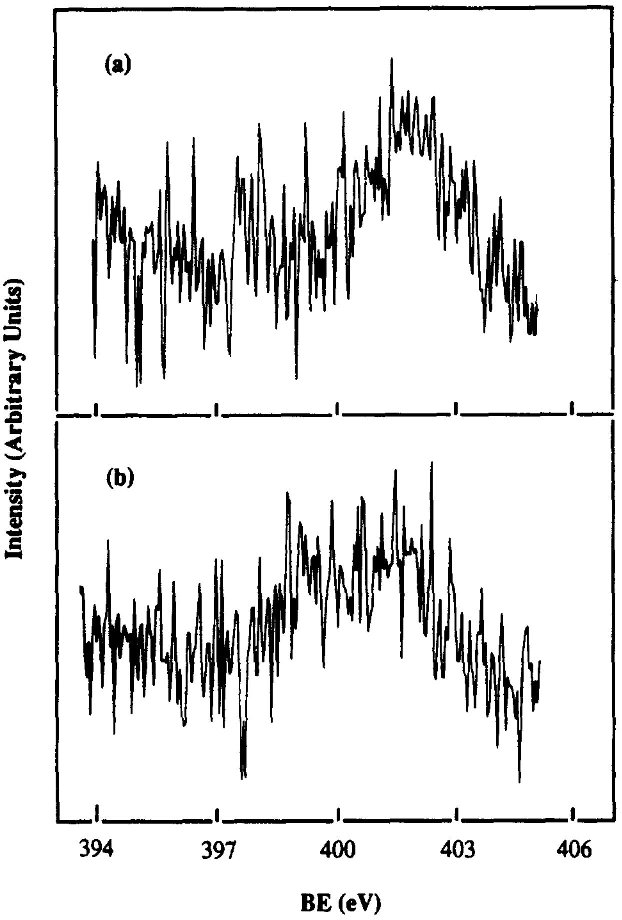

Figure 2 N1s spectra of (a) SPS17/PSVP17 complex from THF; (b) SPS17/PSVP17 complex from DMF

Figures 2a and *2b* show the N1s spectra of SPS17/PSVP17 complexes obtained from THF and DMF respectively. The signals are weak and noisy because of the lower nitrogen content of PSVP17. Nevertheless, the presence of two different nitrogen environments is still discernible.

Figure 3 shows the S2p core-level spectra of SPS27 and the two SPS27/PSVP30 complexes. The S2p peak of SPS27 consists of a main spin-orbit split doublet S2p$_{3/2}$ and S2p$_{1/2}$ with BE of 168.4 and 169.6 eV, respectively, arising from free sulfonic acid groups. There is a minor spin-orbit doublet with BE of 170.2 and 171.4 eV attributed to hydrogen-bonded sulfonic acid groups (self-association). About 30% of the sulfonic acid groups is self-associated as estimated from the deconvoluted peaks. For the two SPS27/PSVP30 complexes, the S2p peaks are located at lower BE values, indicating the existence of sulfonate ion. This is consistent with an earlier study that the S2p electron of bisulfate ion has a lower BE than that of molecular H_2SO_4[28]. The S2p peak of each of the two complexes, as shown in *Figures 3b* and *3c*, is deconvoluted into two environments, one arising from the sulfonic acid with BE of 168.4 and 169.6 eV (dashed curve) and one from the sulfonate ion with BE of 167.3 and 168.5 eV (full curve). The absence of spin-orbit doublets with BE of 170.2 and 171.4 eV indicates the absence of self-associated sulfonic acid groups in the complexes. The extent of ionization of sulfonic acid groups for the complex obtained in THF is estimated to be 63%, which is in good agreement with the extent of protonation of pyridine units, as mentioned earlier. However, the extent of ionization of sulfonic acid groups for the complex obtained in DMF is estimated to be 64%, which is quite different from the extent of protonation estimated from the N1s spectrum. The deconvolution results based on the N1s spectra are taken to be more reliable because the neutral nitrogen and the pyridinium nitrogen peaks are well separated.

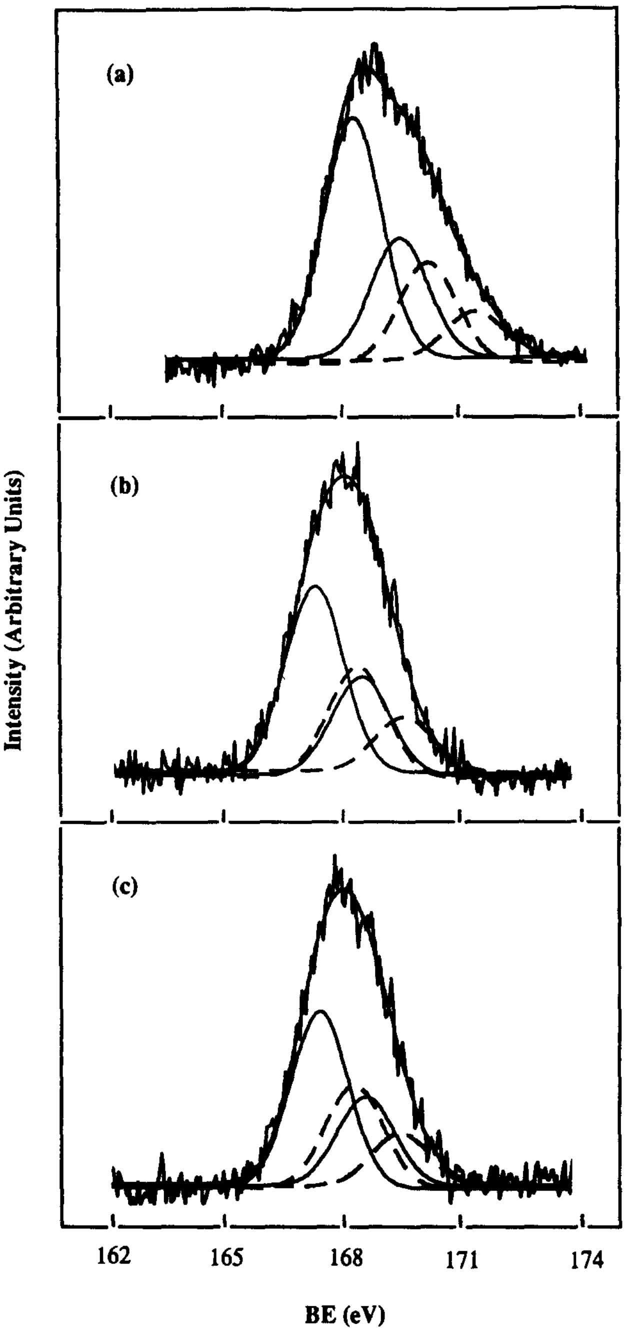

Figure 3 S2p spectra of (a) SPS27; (b) SPS27/PSVP30 complex from THF; (c) SPS27/PSVP30 complex from DMF

In summary, the existence of ionic interactions between SPS and PSVP is evidenced from X.p.s. studies. The extent of ionization and the surface composition of the complex are dependent on the nature of the solvent.

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