X-ray Photoelectron Spectroscopic Studies of Interactions between Styrenic Polymers and Poly(2,6-dimethyl-1,4-phenylene oxide)

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Introduction

When two dissimilar polymers are able to interact through specific intermolecular interactions, the two types of polymer molecules mix intimately to form a miscible blend. It is therefore important to study the nature of intermolecular interactions in polymer blends. Fourier transform infrared (FTIR) spectroscopy has been widely used to study intermolecular interactions in polymer blends, especially those involving hydrogen-bonding interactions.[1−3] The existence of intermolecular interactions is evidenced from changes in the absorption frequency and bandwidth of bands associated with certain functional groups. Nuclear magnetic resonance (NMR) spectroscopy is also useful to study the miscibility of polymer blends.[4] Proton relaxation times and proton spin diffusion experiments provide information on domain sizes down to tens of nanometers. Intermolecular interactions can also be detected through changes in chemical shifts. We have recently used X-ray photoelectron spectroscopy (XPS) to study interactions in polymer blends.[5−10] The binding energy (BE) of a core-level electron depends on its chemical environment within the molecule. As a result, the XPS spectrum provides information on the type and number of different species of a given atom in the molecule. For blends involving poly(vinylpyridine), the N 1s peak consists of two components—one for the neutral nitrogen and the other for nitrogen involved in ionic or hydrogen-bonding interaction.

Polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends are a well-known example of miscible polymer blends. The nature of intermolecular interactions in PS/PPO blends has been extensively studied. Wellinghoff et al.[11] carried out an IR−UV study on PS/PPO blends and found that blending of PS with PPO had induced a conformation change in PPO, arising from van der Waals interaction between the phenyl rings of PS and the phenylene rings of PPO. On the basis of a solution NMR study on low molecular weight model compounds, Djordjevic and Porter[12] concluded that the main interaction was between the electrodeficient methyl groups of PPO and the π-orbitals of PS. In another study, carbon−carbon nuclear spin diffusion experiments on PS/PPO blends showed the existence of intimate mixing at a distance of 0.4−0.6 nm and a preferential interaction between the methyl groups of PPO and the phenyl rings of PS.[13] A recent study using proton spin diffusion experiments also showed that PPO and PS were mixed on a molecular level, but the experiments could not test the validity of the hypothesis that the major interaction was between the PPO methyl protons and the π-orbitals of PS.[14] However, the miscibility of PS with PPO is markedly reduced by methyl substitution. Poly(*p*-methylstyrene) (P*p*MS)/PPO blends show inhomogeneity on a 3 nm scale based on an NMR study on the relaxation of proton spins in the rotating frame.[15]

Our previous studies[5−10] have shown the usefulness of XPS in studying intermolecular interactions in blends involving nitrogen-containing polymers. It is of interest to see whether XPS can be used to probe intermolecular interactions in other types of polymer blends. In this paper, we report our XPS studies on PS/PPO, P*p*MS/PPO, and poly(styrene-*co*-*p*-methylstyrene) (PSMS)/PPO blends.

Experimental Section

Materials. PPO with a weight-average molecular weight (M_w) of 40.7 kg mol^{-1} was supplied by General Electrical Co. (Singapore). P*p*MS ($M_w = 240$ kg mol^{-1}) was purchased from Polysciences, Inc. PS ($M_w = 150$ kg mol^{-1}) was obtained from BDH Chemicals, Inc. Three PSMS samples were prepared by solution polymerization in 2-butanone at 80 °C using azobis(isobutyronitrile) as initiator. The copolymers contain 15, 54, and 80 mol % styrene, and their M_w's are 36, 31, and 38 kg mol^{-1}, respectively. The three copolymers are denoted as PSMS15, PSMS54, and PSMS80.

Preparation of Blends. The PS/PPO, P*p*MS/PPO, and PSMS/PPO blends were prepared by solution casting from benzene. Initial removal of benzene was done on a hot plate at 60 °C. (Benzene is hazardous; evaporation is to be done in a well-ventilated fume hood.) The blends were then dried in vacuo at 80 °C for 2 weeks.

T_g Measurements. The glass transition temperatures (T_g's) of the blends were measured using a TA Instruments DSC2920 differential scanning calorimeter. The scanning rate was 20 °C min^{-1}. T_g was taken as the initial onset of the change of slope in the DSC curve. All the reported T_g values are the averages of three runs.

XPS Measurements. The XPS measurements were performed on a VG Scientific ESCALAB MKII spectrometer using a Mg Kα X-ray source (1253.6 eV photons). The blends were mounted on standard sample studs by means of double-sided adhesive tapes. The X-ray source was run at 12 kV and 10 mA. All core-level spectra were referenced to the C 1s carbon peak of PS at 284.6 eV and obtained with a takeoff angle of 75°. Each spectrum was curve fitted using a VGX-900i software. In the curve fitting, the widths (fwhm) of Gaussian peaks were maintained constant for all components in a particular spectrum.

Results and Discussion

PS/PPO Blends. Figure 1a shows the O 1s spectrum for pure PPO. The O 1s peak is symmetrical and has a binding energy (BE) of 533.2 eV. The PPO sample was prepared by solution casting from benzene and dried under the same conditions as those of the blends. In addition, a benzene-cast PS sample did not show the presence of O 1s peak. Therefore, surface oxidation did not occur during the casting and drying process, and any changes in the O 1s spectra of the blends do not arise from surface oxidation.

Figure 1b−e shows the O 1s spectra of four PS/PPO blends. The O 1s peaks of all the blends become broader and asymmetric. Each peak can be deconvoluted into

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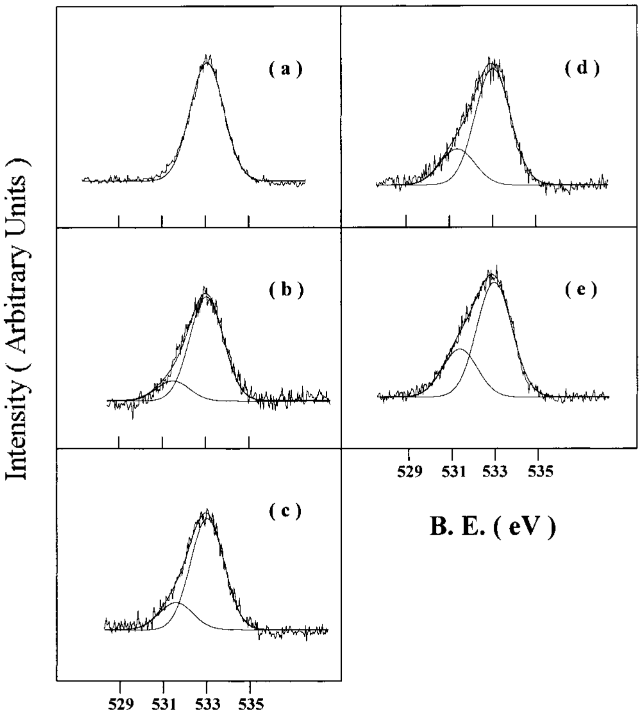

Figure 1. O 1s spectra of PS/PPO blends: (a) PPO; (b) 20, (c) 40, (d) 60, and (e) 80 mol % PPO in the blend.

two components, with one remaining at 533.2 eV and the other around 531.6 eV. The fraction of the low-BE component increases with increasing PPO content in the blend. The appearance of a low-BE peak in the O 1s spectrum shows that some of the ether oxygen atoms of PPO become more electron-rich after blending. The results rule out a direct involvement of ether oxygen atoms of PPO in intermolecular interactions with PS. If such interactions were present, the oxygen atoms would become more electron-poor and a high-BE peak would develop. Djordjevic and Porter[12] have also ruled out the formation of hydrogen bonds between the oxygen atoms of PPO and the ring hydrogen atoms of PS.

The appearance of the low-BE O 1s peak can be attributed to the formation of π complexes between PPO and PS. The nucleophilic aromatic ring can form π complexes with electrophilic reagents. For PPO, the ether oxygen atom has a strong electron-withdrawing effect on the phenylene ring and thus renders it electrophilic. On the other hand, the phenyl ring of PS will act as a typical nucleophilic agent. Thus, the so-formed π complex results in an increase in the electron density of the PPO phenylene ring and causes the attached oxygen atom to be electron-rich.

The surface composition of the blends can be estimated from the peak areas of O 1s and C 1s after correction by the appropriate sensitivity factors. The results show that the surface regions of the blends are slightly enriched with PS. Each blend also shows a single T_g, a characteristic of miscible blends.

P*p*MS/PPO Blends. The P*p*MS/PPO blends were also cast from benzene solutions in the same manner as the PS/PPO blends. The T_g values of P*p*MS and PPO are 106 and 210 °C, respectively. DSC measurements show the existence of two glass transitions for each blend. The lower T_g values are close to that of P*p*MS, and the higher T_g values (120−150 °C) are substantially lower than that of PPO. The results indicate that the blends are partially miscible over the whole composition range. One of the two phases is essentially P*p*MS, and the other is a mixed phase of P*p*MS and PPO. The partial miscibility of P*p*MS/PPO blends suggests that the interaction is weaker than that between PS and PPO, and/or the number of such interactions formed is reduced.

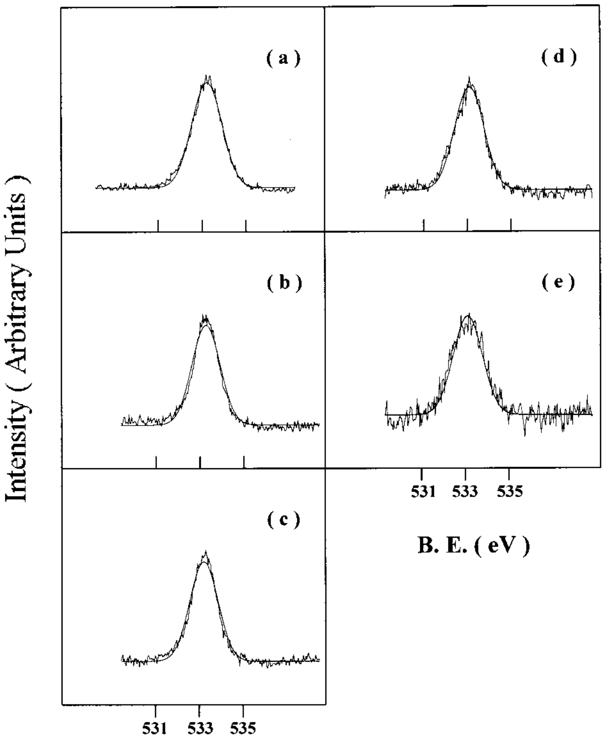

Figure 2. O 1s spectra of P*p*MS/PPO blends: (a) PPO; (b) 20, (c) 40, (d) 60, and (e) 80 mol % PPO in the blend.

Fried et al. reported the miscibility of P*p*MS/PPO blends prepared by coprecipitation from chloroform solutions into methanol.[16] Each P*p*MS/PPO blend showed a broad glass transition whose width increased with increasing PPO content in the blend. The broadening of glass transition has been attributed to composition fluctuation in the blend, and the magnitude of fluctuation increases as the affinity between the components in the blend decreases.[17] P*p*MS/PPO blends prepared by freeze-drying benzene solutions of the two polymers were also found to show a single T_g.[15] It appears that the miscibility behavior of P*p*MS/PPO blends is affected by the blending method, and this may be taken to suggest a weak interaction in the P*p*MS/PPO system.

The O 1s spectra of PPO and the P*p*MS/PPO blends are shown in Figure 2. Each blend shows a single O 1s peak at the same BE value as that of PPO. Therefore, there is no appreciable change in the electron environment of the oxygen atoms of PPO after blending with P*p*MS as shown by XPS. Apparently, the interaction between P*p*MS and PPO is weaker than that between PS and PPO.

In a magic-angle spinning/cross-polarization ^{13}C NMR study of the miscibility of PS/PPO and P*p*MS/PPO blends prepared by freeze-drying from benzene solutions, Dickinson et al.[15] measured the spin−lattice relaxations of protons in the rotating frame ($T^{H}{}_{1\rho}$) for polymers and blends. For the PS/PPO (1:1) blend, the resonances of both components had the same single-exponential decay $T^{H}{}_{1\rho}$ values, indicating that the blend

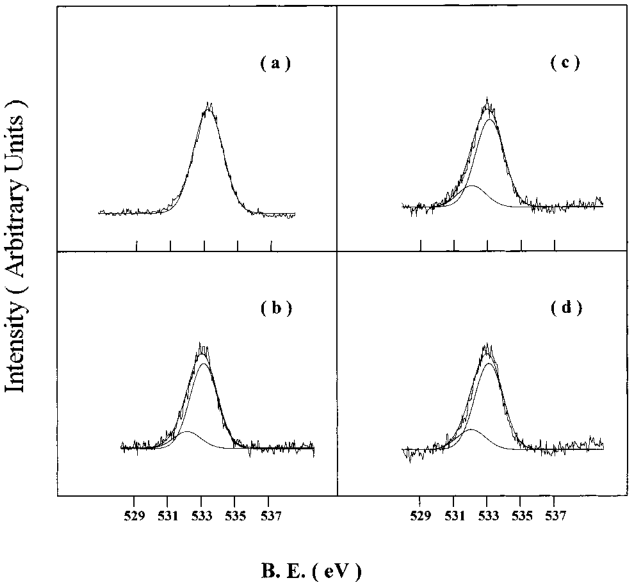

Figure 3. O 1s spectra of (a) PPO, (b) PSMS15/PPO blend, (c) PSMS54/PPO blend, and (d) PSMS80/PPO blend.

is homogeneous at the 3 nm scale. However, for the P*p*MS/PPO (1:1) blend, each component had a different $T^{\mathrm{H}}_{1\rho}$, revealing phase separation at scales in excess of 3 nm. Moreover, both constituents of the P*p*MS/PPO blend showed a biphasic decay of magnetization, suggesting heterogeneity in the separated domains. In addition, a small-angle neutron scattering (SANS) study also showed that interactions are less favorable for the P*p*MS/PPO blends than for the PS/PPO blends.[18] Thus, NMR, SANS, and XPS studies all show that the miscibility of PS with PPO is markedly reduced by methyl substitution.

PSMS/PPO Blends. Blends of PPO with PSMS containing 15, 54, and 80 mol % styrene were cast from benzene solutions at a 1:1 mole ratio. DSC measurements show a single T_g for each of the three blends, indicating that the blends are miscible. The results imply that the interactions in the PSMS/PPO blends are stronger than those in the P*p*MS/PPO blends. The incorporation of 15 mol % styrene onto the P*p*MS chains can bring about complete miscibility between the copolymer and PPO.

Figure 3 shows the O 1s spectra of PPO and the three PSMS/PPO (1:1) blends. The O 1s peak of each blend can be deconvoluted into two component peaks with one at 533.2 eV and the other one at 532.2 eV. The occurrence of the low-BE O 1s peak indicates that π complexes also exist in the PSMS/PPO blends. However, the area fraction of the low-BE O 1s peak of each blend is less than 0.2, and the BE value of the low-BE O 1s peak is larger than that of the PS/PPO blend system (531.6 eV), indicating that the interactions in the PSMS/PPO blends are weaker than those in the PS/PPO blends.

In conclusion, the present XPS study shows the existence of π complexation between PS and PPO, and methyl substitution of PS markedly reduces intermolecular interactions.

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