

X-Ray Photoelectron Spectroscopy of Conducting Polyaniline and Polyaniline–Polystyrene Blends

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ABSTRACT: Conductive polyaniline solutions were chemically prepared using bis(2-ethylhexyl)hydrogen phosphate (DiOHP) as the dopant chemical species. The codissolution method leads to conductive polyaniline–polystyrene (PANI–PSt) composites with good mechanical properties. The electronic structure of both conducting PANI films and PANI–PSt blends was investigated by X-ray photoelectron spectroscopy, which allowed one to quantify the proportion of benzenoid amine, quinoid imine, and protonated units. Blending polyaniline with PSt does not involve important modifications in the polymer electronic structure. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1209–1214, 1998

Key words: conducting polymers; polyaniline; XPS

INTRODUCTION

Blends of polyaniline with classical polymers which can cumulate high electrical conductivity and good mechanical properties deserve great attention for applications in electronic industrial technology (antistatic packaging,¹ applications in batteries,² etc.). Recent progress has shown that functionalized sulfonic acids, such as camphor sulfonic acid (CSA), can be used to simultaneously protonate polyaniline (PANI) and induce solubility of PANI in its conducting form.³ Pron et al. showed that phosphoric acid diesters with alkyl substituents constitute a new group of protonating agents which improve the processability of PANI in its conducting state.⁴

In this article, we report on the synthesis of PANI films and polyaniline–polystyrene (PANI–

PSt) blends by using bis(2-ethyl hexyl)hydrogen phosphate (DiOHP) as a counterion. Conducting blends are obtained by codissolution of both polymer solutions. A detailed X-ray photoelectron spectroscopy (XPS) study of the structure of PANI films and PANI blends is described.

EXPERIMENTAL

Polyemeraldine was synthesized by the oxidative polymerization of aniline with ammonium persulfate $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in a hydrochloric acid solution according to conventional methods.⁵ Polyemeraldine base was obtained by deprotonation of PANI hydrochloride in 0.1M ammonium solution.⁶ Bis(2-ethyl hexyl)hydrogen phosphate (DiOHP), purchased from Aldrich (purity 97%), was used without further purification to protonate PANI. Due to the presence of the acid center and two hydrophobic groups, DiOHP can solubilize and plasticize PANI while protonating it.⁷ A half

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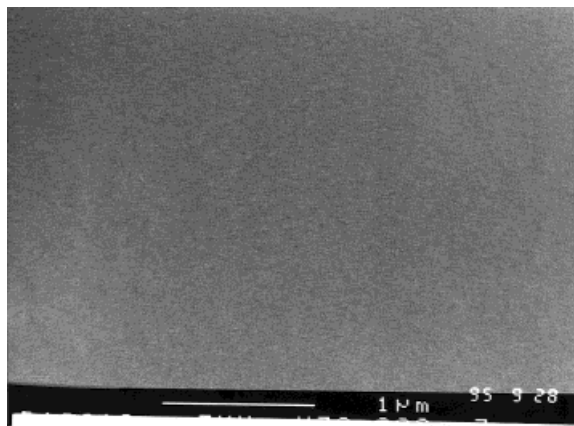
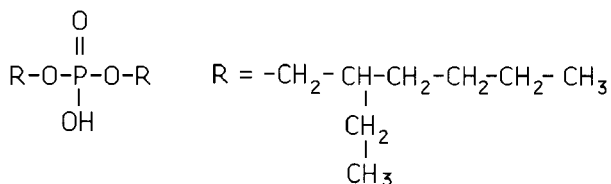


Figure 1 Scanning electron micrograph of PANI(DiOHP)-PSt blends.

molecule was used per repeat polymer unit involving one ring and one nitrogen. The DiOHP formula is



Plasticized PANI-DiOHP can be dissolved in several common solvents such as *m*-cresol, toluene, and chloroform. To obtain PANI-PSt blends, a PSt solution was prepared by dissolving PSt in *m*-cresol. This solution was then mixed in an appropriate ratio with the PANI (DiOHP) solution in *m*-cresol. The blend solution was cast onto a glass substrate and then dried at 60°C in a neutral atmosphere for 24 h. Free-standing films of about 100 μm with high electrical conductivity and good mechanical properties were obtained.

The morphology of the films was visualized by scanning electron microscopy (SEM). The PANI (DiOHP)-PSt blends exhibit a smooth surface as

shown in Figure 1. Optical measurements were performed at room temperature using a CARG 2000 spectrometer and XPS analysis was carried out with a Leybold LHS.12 apparatus (University of Nantes-C.N.R.S.) using a magnesium source radiation (1253.6 eV) operating at 10 kV and 10 mA. The energy resolution was better than 1 eV at a pass energy of 50 eV and the vacuum in the analysis chamber was about 10⁻⁶ Pa.

This study was performed on a polyemeraldine base powder, PANI (DiOHP) films, and PANI (DiOHP)-PSt blends. High-resolution scans with a good signal ratio were obtained in the C1s, N1s, O1s, and P2p regions of the spectrum.

RESULTS AND DISCUSSION

The quantitative analysis was based on the determination by XPS of the C1s, N1s, O1s, and P2p peak areas with 0.2, 0.36, 0.61, and 0.3 as sensitivity factors, respectively (Table I). The XPS data were analyzed with a least-square fitting routine which decomposed each spectrum into individual Gaussian peaks and assumed a linear background over the energy range of the fit. Decomposition was performed with the constraint of having a nearly equal full-width at half-maximum (fwhm) value for a particular line among different spectra. This, together with the peak position and height, was optimized for modeling the experimental spectra.

In the polyemeraldine base, the decomposition of the N1s core-level spectrum is presented in Figure 2(a). The first peak at 398.5 eV can be assigned to quinoid imine (=N-). The second component at about 399.6 eV can be assigned to benzenoid amine (-NH). Two other peaks with binding energies at 401.3 and 402.8 eV can be attributed to positively charged nitrogens (Table II). These results are in good agreement with the polyemeraldine base decomposition of Kang et al.⁸

Table I Relative Surface Composition of C, N, O, and P (as atm % of All the Elements Present) in Polyaniline Films

	Sample Composition (%)					
	C1s	N1s	O1s	P	P/N	P/O
Polyemeraldine base	84	9	7	—	—	—
PANI(DiOHP)	75	4	19	2	0.5	0.1
PANI(DiOHP)-PSt	86	2	11	1	0.5	0.1

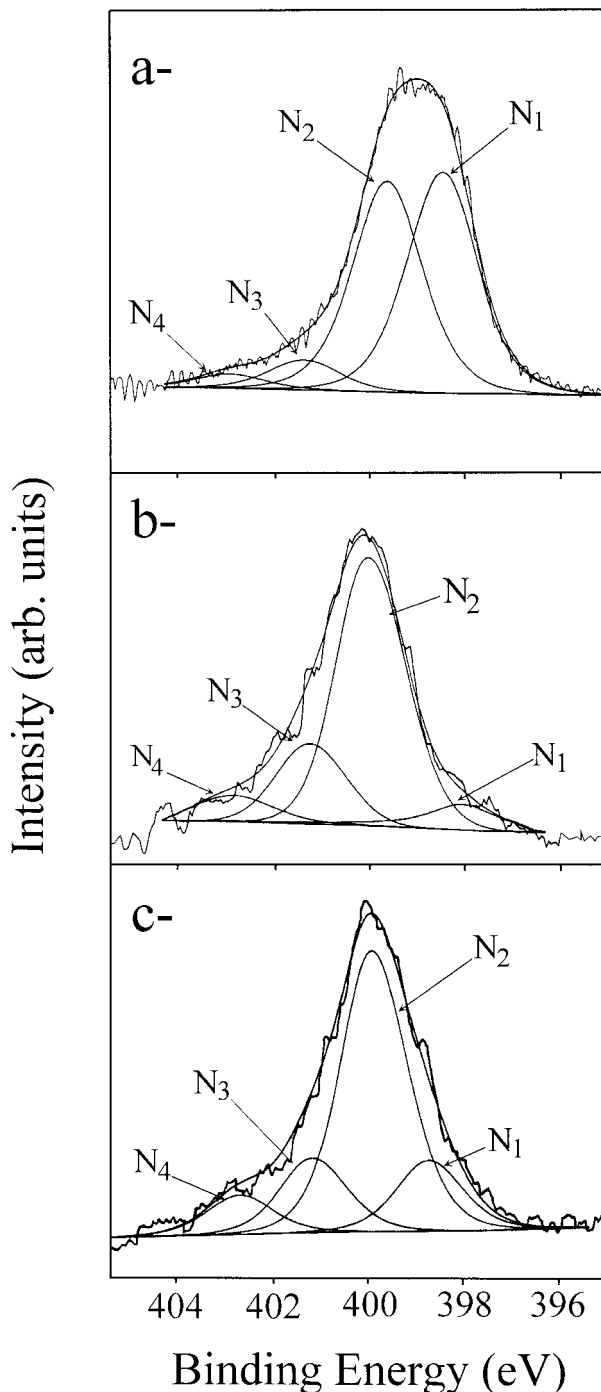


Figure 2 XPS spectra: N1S peak curve fit of (a) polyemeraldine base, (b) PANI(DiOHP) films, (c) PANI(DiOHP)-PSt blends.

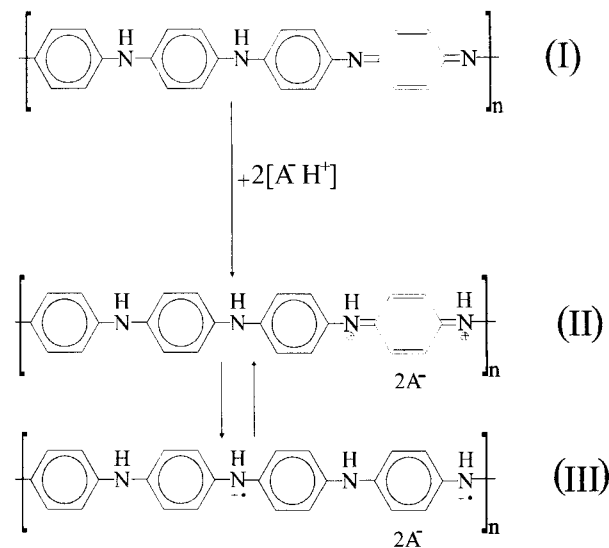
The presence of about equal amounts of imine and amine nitrogens (Table III) is consistent with the intrinsic oxidation state of the polymer [ratio ($-\text{NH}-/\text{=N}-$) ~ 1].⁹ The residual high binding energy (BE) tail above 400 eV in the spectra

is associated with surface oxidation products or weakly charge-transfer-complexed oxygen species by Kang et al.¹⁰ A small protonation by water molecules was even recognized in XPS studies by Dziembaj and Piwowarska.¹¹

In the conducting PANI-DiOHP and PANI-DiOHP-PSt films, the P/N ratio is nearly 0.5 according to the proportion used in the synthesis (0.5 DiOHP molecule per repeat polymer unit). Oxygen was also found in excess and the phosphore-to-oxygen ratio is 0.1 for all conducting films, whereas the theoretical ratio P/O as derived from the counterion chemical formula ($\text{C}_{16}\text{H}_{35}\text{O}_4\text{P}$) is 0.25. The experimental lower ratio confirms the oxygen surface contamination. Next, the protonation of PANI and the distribution of the positive charges in the polymer chain were examined.

The UV-vis absorption spectrum of a PANI (DiOHP) solution mixed in *m*-cresol for 72 h shows a long absorption tail extending into the IR region (Fig. 3). The 635 nm exciton band, present in the polyemeraldine base, disappears and the $\pi-\pi^*$ transition band is no longer well defined. This spectra is representative of highly protonated PANI.¹²

It must be recalled that the protonation of PANI produces electronic defects in the polymer chain. Polarons or bipolarons can be formed by the addition of protons to the neutral polymer chain. The formation of different protonated structures for polyemeraldine can be represented by the following simplified scheme (A^-H^+ symbolize DiOHP):

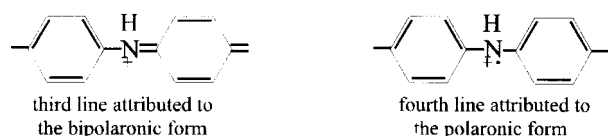


Protonation of polyemeraldine (I) occurs with

Table II Ratio of $-\text{N}=\text{N}$, $-\text{NH}/\text{N}$, N^+/N , and $-\text{NH}/-\text{N}=\text{N}$ in Polyaniline Films

	$-\text{N}=\text{N}$	$-\text{NH}/\text{N}$	N^+/N	$-\text{NH}/-\text{N}=\text{N}$
Polyemeraldine base	0.46	0.44	0.10	0.96
PANI(DiOHP)	0.09	0.65	0.26	7.2
PANI(DiOHP)-PSt	0.15	0.61	0.25	4.1

the formation of a bipolaron-type defect structure (II). This phenomenon affects preferentially the imine nitrogen site.¹³ Furthermore, any delocalization of charge on the nitrogen atom in a bipolaronic structure to the adjacent quinoid ring leads to a polaron lattice (III).¹⁴ More recently, Louarn et al.¹⁵ showed that bipolaronic and polaronic structures coexist in conducting PANI. These defect states were related to the two charged nitrogen species by Kumar et al.¹⁶:



However, for Rodrigue et al., this distinction between polarons and bipolarons is impossible since each N^+ peak can be interpreted in term of charge localization on nitrogen and charge delocalization on the aromatic cycle of the polymer chains.¹⁷

Concerning PANI (DiOHP) films, doping by the phosphoric acid diester broadens the $\text{N}1s$ XPS envelope [Fig. 2(b)] and increases the fraction of the higher BE states. The $\text{N}1s$ core-level spectrum is deconvoluted into four components as in the

polyemeraldine base. The imine ($-\text{N}=\text{N}$) and amine ($-\text{NH}-$) peaks are at 398.1 and 399.9 eV, respectively. The N^+ species are assigned to two peaks separated by 1.3 and 2.9 eV of the imine component (Table II).

The higher proportion of the N^+ species confirms the effective protonation of PANI by doping with DiOHP. The $-\text{N}=\text{N}$ ratio decrease to 9% (Table III). This result shows that the quinoid imine units ($=\text{N}-$ structure) are preferentially protonated. However, the protonation rate of PANI-DiOHP, as indicated by the N^+/N ratio, reaches only 0.3 to be compared to the expected protonation rate (0.5). This result is in agreement with the Raman studies of Laska et al.¹⁸ who showed that the fraction of the dopant which effectively protonates the polymer is limited. The $\text{N}1s$ spectrum decomposition of PANI-PSt blends is similar [Fig. 2(c)]. All binding energies are tabulated in Table II.

Figure 4(a)–(c) shows the carbon $\text{C}1s$ XPS core-level spectrum. In the polyemeraldine base, a first component at 284.6 eV can be attributed to the neutral $\text{C}-\text{C}$ or $\text{C}-\text{H}$ bonds. The second contribution at 285.6 eV can be assigned to the carbon bonded with neutral nitrogen atoms ($\text{C}-\text{N}$ and $\text{C}=\text{N}$). According to the $\text{N}1s$ line as-

Table III XPS Analysis of Polyaniline Films

	$\text{N}1s$				$\text{C}1s$			
	N_1	N_2	N_3	N_4	C_1	C_2	C_3	C_4
Polyemeraldine base								
BE (eV)	398.5	399.6	401.3	402.8	284.6	285.6	287.2	288.6
Intensity (%)	46	44	6	62	31	5	2	
PANI(DiOHP)								
BE	398.1	399.9	401.2	402.8	284.7	285.4	286.3	288
Intensity (%)	9	65	19	7	55	21	15	9
PANI(DiOHP)-PSt								
BE (eV)	398.6	399.8	401.1	402.7	284.9	—	286.3	287.2
Intensity (%)	15	60.5	16	8.5	90	—	7	3

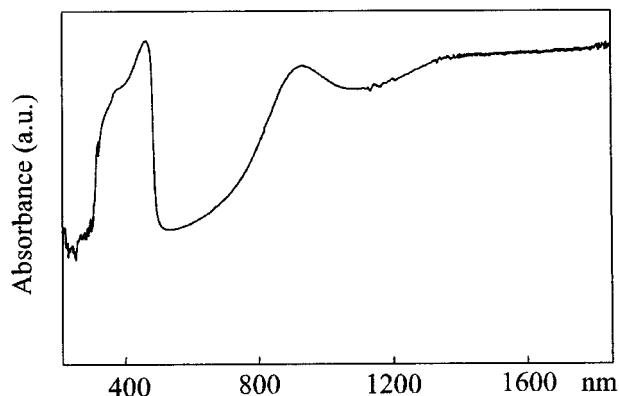


Figure 3 UV-vis absorption spectrum of PANI-(DiOHP).

segment, the third line at 287.2 eV can be attributed to the carbon atoms bonded to the polaronic-type nitrogen atoms and the last peak at 288.6 eV can be assigned to the carbon atoms bonded to the bipolaronic-type nitrogen atoms (Table II). However, the percentage of oxygen detected is probably associated with the presence of residual $(C-O)_x$ bonds. The ratio of total carbon to nitrogen is higher than the theoretical C/N ratio derived from the molecular formula $(C_6H_5N)_n$. Furthermore, a relatively important amount of oxygen was detected. Additional carbon reveals an impurity contamination during atmosphere exposure while the presence of oxygen is due to the superficial oxidation.

In PANI-DiOHP films, the C1s core-level spectrum shows four contributions as in the polyemeraldine base. However, an additional C—O counterion contribution participates to the third line at 286.3 eV and a contamination due to C=O bonds cannot be excluded at 288 eV.

Three main contributions are obtained in the C1s peak of the PANI-PSt blends. The first one at 284.9 eV C1s corresponds essentially to C—C or C—H bonds. The second line is principally assigned to C—O bonds due to the counterion and to an oxygen contamination. Because of the small $(CN^+)_x$ relative percentage, the last peak reflects mainly the carbonyl C=O bonds caused by a surface oxidation. The small relative percentage of $(CN)_x$ bonds does not allow one to detect the line at 285.4 eV as in PANI-DiOHP.

CONCLUSION

New PANI-DiOHP-PSt composites were chemically prepared by codissolution of conducting

PANI-DiOHP with a solution of PSt in *m*-cresol. This method leads to free-standing films with good mechanical properties and a high electrical conductivity.

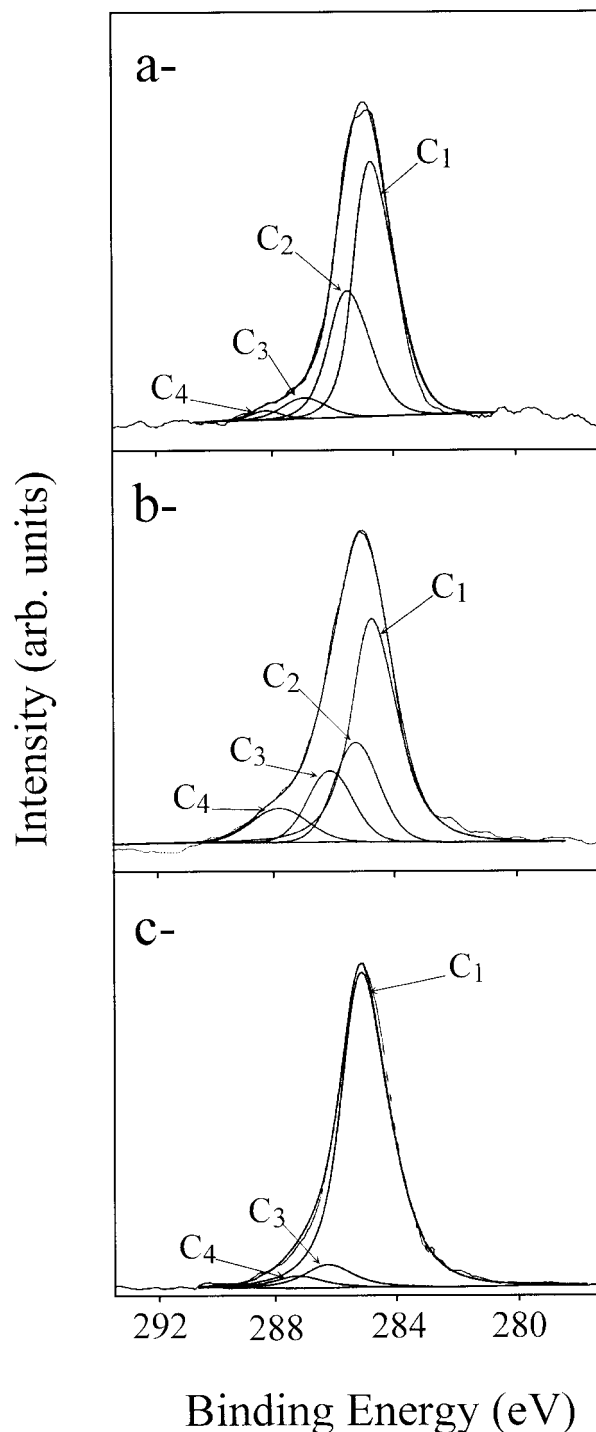


Figure 4 XPS spectra: C1s peak curve fit of (a) polyemeraldine base, (b) PANI(DiOHP) films, and (c) PANI(DiOHP)-PSt blends.

XPS analysis has allowed us to distinguish four different nitrogen species for all samples (imine, amine, and two protonated nitrogen species) and to determine the proportion of these species in the total amount of nitrogen atoms. DiOHP appears to be effective in converting the imine nitrogen atoms to positively charged nitrogen atoms (N^+). This study confirms the effective protonation of PANI by doping with DiOHP and the presence of polaronic and bipolaronic defect charges.

No particular changes between the peak positions of the PANI–DiOHP and PANI–DiOHP blends were observed. It appears that the blending of PANI with a host matrix like PSt does not involve important modifications in the polymer electronic structure.

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