

Preparation and Characterization of Soluble Polyaniline

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ABSTRACT: Polyaniline, which is soluble in common organic solvents, has been synthesized through the oxidative chemical polymerization of aniline in the presence of benzene diazonium chloride salt in an aqueous HCl acid medium. The blue-black polyaniline thus prepared exists in a lower oxidation state than emeraldine. An X-ray photoelectron spectroscopy study has shown that the intrinsic oxidation state of the polymer is 0.38. An elemental analysis has shown

that the fractional doping level or degree of oxidation of the blue-black polyaniline is 0.26. The product is believed to consist of a lower number of imine nitrogens in comparison with the polyemeraldine base. This fact is also corroborated by the lower electrical conductivity of the polymer. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2675–2682, 2007

Key words: azo polymers; FTIR; UV-vis spectroscopy

INTRODUCTION

Polyaniline (PANI) is one of the important classes of conjugated polymers that possess excellent electronic, optical, and redox properties and environmental stability. It also exhibits solution processability and has potential applications in electrochromic displays,¹ organic storage batteries,² and microelectronic devices.³

This polymer is basically poly(paraphenylene amine imine), the oxidation state of which can vary from fully reduced poly(paraphenylene amine) to fully oxidized poly(paraphenylene imine).⁴

It consists of reduced base units and oxidized base units,⁵ as shown in Figure 1; the oxidation state of the polymer increases with a decreasing value of y ($0 \leq y \leq 1$).

The values of y are 1, 0.5, and 0 for the three oxidation states of PANI, that is, leucoemeraldine, emeraldine, and pernigraniline, respectively. There are two intermediate oxidation states, that is, protoemeraldine and nigraniline, with y values of 0.75 and 0.25, respectively. The repeating units for PANI can be represented as octamers containing different numbers of quinone imine moieties depending on the oxidation state of the polymer. Thus, leucoemeraldine has no quinone imine moieties, protoemeraldine has one quinone imine moiety, emeraldine has two quinone imine moieties, nigraniline has three quinone imine moieties, and pernigraniline has four quinone imine moieties.⁶

PANI in the base form (emeraldine or emeraldine base) dissolves partially in *N*-methylpyrrolidinone (NMP)⁷ or concentrated H₂SO₄.⁸ However, PANI salts are not soluble in organic solvents. The solubilization of PANI is an important criterion for studying its physicochemical properties and for its commercial applications. The physical properties of PANI, including the solubility and electrical conductivity, are strongly dependent on the method of preparation of the polymer.^{9,10}

Extensive studies have led to the development of a synthetic route toward soluble PANI through the synthesis of PANI protonated with organic protonic acids of a large molecular size^{11,12} or through the synthesis of graft or block copolymers.^{13–16} The polymerization has also been studied under conditions including organic solvents,⁹ micelles, reverse micelles,¹⁷ and emulsions¹² to improve the processability of the polymer. However, the possibility of improving the solubility through changes in the oxidation state of the polymer has not been explored so far. Most earlier reports describe the use of different oxidizing and reducing agents for the preparation of PANI with different degrees of oxidation.^{18–20}

This study was undertaken to alter the existing properties of PANI and to improve the solubility behavior of the polymer. To fulfill these objectives, the polymerization of aniline was carried out in the presence of benzene diazonium chloride. The reaction pathway was monitored through an ultraviolet-visible (UV-vis) spectroscopy study of the reaction

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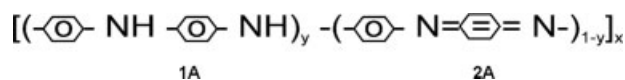


Figure 1 Repeating unit of PANI. 1A is the completely reduced PANI base repeat unit; 2A is the completely oxidized PANI base repeat unit.

mixture at different time intervals before there was any precipitation. The structure of the derived polymer was elucidated with different spectroscopic techniques, particularly X-ray photoelectron spectroscopy (XPS), which was applied to determine the oxidation state of the polymer.

EXPERIMENTAL

Materials

Reagent-grade $\text{C}_6\text{H}_5\text{NH}_2$, HCl (39%), H_2SO_4 (98%), an aqueous NH_4OH solution (25%), $(\text{NH}_4)_2\text{S}_2\text{O}_8$, NaNO_2 , NMP, tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF) were purchased from E. Merck (Mumbai, India). $\text{C}_6\text{H}_5\text{NH}_2$ was vacuum-distilled before use, and all other reagents were used as received.

Preparation

Aniline was chemically polymerized in dilute HCl at 2–5°C in the presence of benzene diazonium chloride with ammonium peroxydisulfate as an oxidant. The reaction was carried out through the partial diazotization of aniline at ~ 5°C with sodium nitrite. The molar ratio of NaNO_2 to aniline was maintained at 0.93, and the resulting diazotized solution containing unreacted aniline was polymerized. The molar ratio of the oxidant to aniline was maintained at 1 : 1 to obtain the maximum yield of the product. No polymerization occurred for the fully diazotized solution of aniline. However, the polymerization was also carried out with 84, 74, 65, and 56% diazotized solutions of aniline. In all cases, the product was a blue-black solid with similar properties, as discussed in a later section.

In a typical procedure, 8 mL of aniline (0.086 mol) was dissolved in 25 mL of 2M HCl, and the mixture was cooled below 5°C in an ice bath. A solution of 5.6 g (0.080 mol) of NaNO_2 in 20 mL of water, pre-cooled to 5°C, was added dropwise to the dilute HCl solution of aniline and maintained at 2–5°C over a period of 10 min with stirring. To the cold diazotized solution containing unreacted aniline (<5°C), a cold solution of 1.37 g (0.006 mol) of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 25 mL of 2M HCl was added dropwise with constant stirring. The temperature of the reaction was always maintained below 5°C. The reaction was continued for 2 h. The blue-black pre-

cipitate thus obtained was washed with 2M HCl until the filtrate was colorless. The polymer thus obtained was purified through washing with methanol and then with THF. The solid was dried under a dynamic vacuum at 50°C.

The base form of the polymer was obtained by the stirring of 1 g of the acid-doped polymer in 160 mL of a 3% aqueous NH_4OH solution for 4 h at room temperature. The solid was then filtered, washed with distilled water until it was free from NH_4OH , and dried at 50°C under a dynamic vacuum.

The acid form of the polymer was prepared by a treatment with dilute HCl (2M). The base form of the polymer powder was equilibrated with constant stirring in dilute HCl for 24 h and dried at 50°C under a dynamic vacuum.

Characterization of the polymers

The acid and base forms of blue-black polyaniline (PANI-1) were characterized with elemental analysis, Fourier transform infrared (FTIR) spectroscopy, UV-vis spectroscopy, thermogravimetric analysis (TGA), and XPS. The viscosity and electrical conductivity measurements were also carried out.

Elemental analysis

Elemental analyses of both doped and undoped forms of PANI-1 were performed on a PerkinElmer CHN model 2400 elemental analyzer (Shelton, CT).

Viscosity measurements

The intrinsic viscosity (dL/g) was obtained through the measurement of the solution viscosity of PANI-1 at 35°C with an Ubbelohde capillary viscometer (S.B. Scientific Co., Kolkata, India). Concentrated H_2SO_4 (98%) was used as the solvent.

UV-vis spectroscopy

The UV-vis spectra of the base form of PANI-1 were recorded on a Hitachi model U 3200 UV-vis double-beam, monochromatic spectrometer (Japan) in the wavelength range of 250–800 nm with NMP as the solvent.

FTIR spectroscopy

The FTIR spectrum of PANI-1 was recorded in KBr pellets on a PerkinElmer FTIR model 1600 spectrometer (Shelton, CT) with 16 scans at a resolution of 4 cm^{-1} .

TGA

The TGA thermogram of PANI-1 was recorded on a PerkinElmer series 7 thermal analyzer (Shelton, CT)

system fitted with a data station. A 2–3-mg sample was placed in an Al pan, and the sample was heated from 50 to 650°C at a heating rate of 10°C/min under a nitrogen atmosphere.

Electrical conductivity measurements

The electrical conductivity of the doped PANI-1 was measured at room temperature by a collinear four-probe technique. A DFP-2 digital four-probe setup (S.B. Scientific Co., Kolkata, India) was used for this measurement.

XPS

XPS measurements were made on a VG Escalab MK II spectrometer with a Mg K α X-ray source (1253.6 eV of photons) (VG Scientific, England). The samples were mounted on standard sample studs with double-sided adhesive tape. A takeoff angle of 75° was used in all XPS runs. The X-ray source was run at 12 kV and 20 mA. The pressure in the analysis chamber was maintained at 10⁻⁸ mbar or lower during the measurements. All binding energies were referenced to the C 1s neutral carbon peak at 284.6 eV.

RESULTS AND DISCUSSION

UV–vis spectroscopy study of the reaction mixture

The oxidative polymerization of aniline in the presence of benzene diazonium chloride in aqueous HCl proceeds through the formation of different reaction intermediates according to UV–vis spectroscopy at different intervals before any precipitation. The UV–vis spectrum (Fig. 2) of the reaction mixture, which has ini-

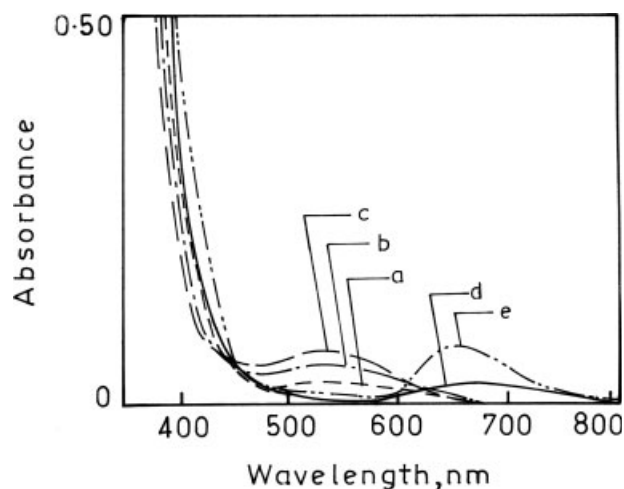


Figure 2 UV–vis spectra of a reaction mixture in 2M HCl containing an approximately 93% diazotized solution of aniline and (NH₄)₂S₂O₈ at different times from the initial addition of the oxidant: (a) 5, (b) 10, (c) 15, (d) 18, and (e) 24 min.

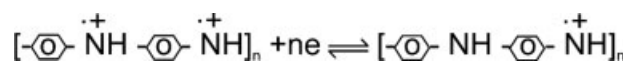


Figure 3 Protonated pernigraniline form of PANI.

tially a pink color upon the addition of (NH₄)₂S₂O₈, shows an absorption maxima at 510 nm. The intensity of this peak increases with time, and the absorption maximum is gradually shifted to 650 nm as the color of the reaction mixture changes from pink to blue.

The appearance of the pink color is due to the formation of an anilinium radical cation ($\overset{\cdot+}{\text{C}_6\text{H}_5}\text{-NH}_2$) in the reaction mixture.²¹ The blue precipitate that appears in the course of the reaction is believed to be protonated pernigraniline, the repeating unit of which is a dication diradical.²²

In the case of aniline polymerization in HCl (~1M) in the presence of (NH₄)₂S₂O₈, the blue solid, that is, protonated pernigraniline (Fig. 3), acts as an oxidant and is reduced by excess aniline present in the reaction medium into green polyemeraldine salt.²¹

However, in this case, it is quite possible that protonated pernigraniline is reduced by free HNO₂ present in the reaction medium to form PANI having an oxidation state somewhat lower than the emeraldine oxidation state. The exact role of benzene diazonium chloride in the chemical synthesis and solubilization of the polymer is not clear. Benzene diazonium chloride does not take part in the polymerization reaction as there is no polymerization with a fully diazotized solution of aniline. The presence of benzene diazonium chloride salt in the reaction medium retards the process of polymerization by coupling with an aniline or anilinium radical cation and thus inhibits the formation of high-molecular-weight, long-chain PANI.

Intrinsic viscosity of the polymer

The product, obtained as a blue-black solid, has a low molecular weight, as evidenced by its intrinsic viscosity of 0.30 dL/g versus 0.81 dL/g for the polyemeraldine base (PEB).²³

Solubility behavior of the polymer

The polymer is completely soluble in NMP, DMSO, and DMF, forming bluish-violet solutions, and is completely soluble in concentrated H₂SO₄, forming a blue solution, and 85% HCOOH, forming a green solution. Upon a treatment with dilute HCl, the blue-black solid changes to dark green, and its solubility in organic solvents such as NMP, DMSO, and DMF decrease slightly, whereas the solubility in concentrated H₂SO₄ and 85% HCOOH does not change appreciably. The basification of the blue solid with

TABLE I
Elemental Composition of PANI-1

Sample	C	H	N	Cl	S
Base form	6.30	5.25	1.00	—	0.049
Acid form	6.50	5.80	1.00	0.16	0.049

3% NH_4OH changes the color of the polymer to bluish-violet, and it remains soluble in all the aforementioned solvents.

Characterization

Elemental analysis

The chemical composition of PANI-1 in its base form and acid form (doped with 1M HCl) is shown in Table I.

Because the atomic ratios are normalized with respect to nitrogen, the degree of oxidation is indicated by the sum of the relative fractions of the chloride and sulfate anions.²¹ Sulfate anions appear from the reduction of the oxidant $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The degree of oxidation in terms of the fractional doping level is calculated as follows: degree of oxidation = $(0.16 + 0.049 \times 2) = 0.26$. A factor of 2 is used for the doubly charged sulfate anion. The fractional doping level of doped PANI-1 is 0.26 versus 0.46 for the polyemeraldine salt.²¹ During protonation with HCl, PANI is protonated at quinoid imine sites ($\text{N}=\text{C}_6\text{H}_4=\text{N}$), with dopant anions Cl^- and SO_4^{2-} being localized in their close vicinity, and the lower value of the fractional doping level for PANI-1 clearly indicates the presence of a lower number of quinoid imine moieties in the polymer chain that can undergo protonation as well as a lower degree of oxidation compared with that of PANI in the emeraldine oxidation state.

FTIR spectroscopy

The oxidation level of PANI is qualitatively estimated by the intensity ratio of the IR absorption peaks for quinoid ring stretching at $\sim 1600 \text{ cm}^{-1}$ and for benzenoid ring stretching at $\sim 1500 \text{ cm}^{-1}$.²⁴ The FTIR spectrum of the base form of PANI-1 (Fig. 4) shows that the relative intensity of benzenoid ring stretching at 1493 cm^{-1} is higher than that of the quinoid ring stretching vibration at 1584 cm^{-1} . The value of the imine-to-amine ratio, calculated from the FTIR data, is between 0.4 and 0.5, whereas the ratio is between 0.9 and 1.0 for PEB. This indicates that PANI-1 exists in an oxidation state lower than PEB.

HCl-doped PANI-1 shows a shift in the frequency for benzenoid and quinoid ring stretching vibrations

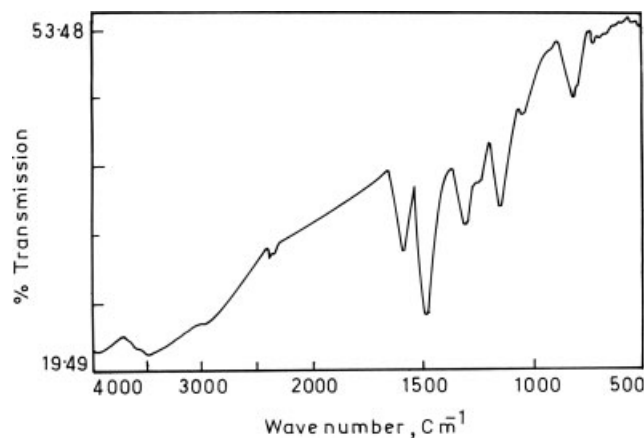


Figure 4 FTIR spectrum of the base form of PANI-1.

toward a lower wave-number region, and they appear at 1488 and 1575 cm^{-1} , respectively (Fig. 5). The appearance of an absorption peak at 1302 cm^{-1} for the base form and at 1296 cm^{-1} for the acid form of the polymer has been assigned to C—N stretching of the aromatic amine. The intensity of this peak increases with HCl doping and decreases with dedoping with NH_4OH . The appearance of a peak at 1145 cm^{-1} in the case of the undoped polymer may be assigned to a mode of $\text{N}=\text{Q}=\text{N}$ (where Q is the quinoid ring) vibrational stretching.^{25,26} The intensity of this peak increases to a large extent on HCl doping. Its frequency is shifted toward a lower wave-number region and appears at 1134 cm^{-1} , indicating the presence of the $\text{Q}=\overset{+}{\text{N}}\text{H}-\text{B}$ or $\text{B}-\overset{+}{\text{N}}\text{H}-\text{B}$ structure (where B is the benzenoid ring) in the polymer.²⁶ The presence of 1,4-disubstituted benzene in the acid and base forms of the polymer is indicated by the appearance of absorption peaks at 800 and 825 cm^{-1} , respectively, which are ascribed to C—H out-of-plane bending modes.

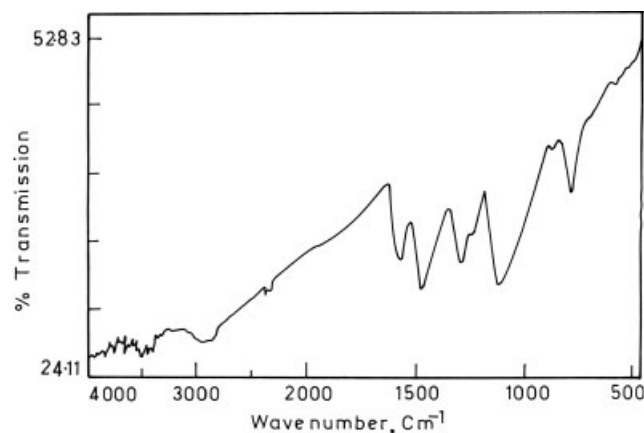


Figure 5 FTIR spectrum of the HCl-doped form of PANI-1.

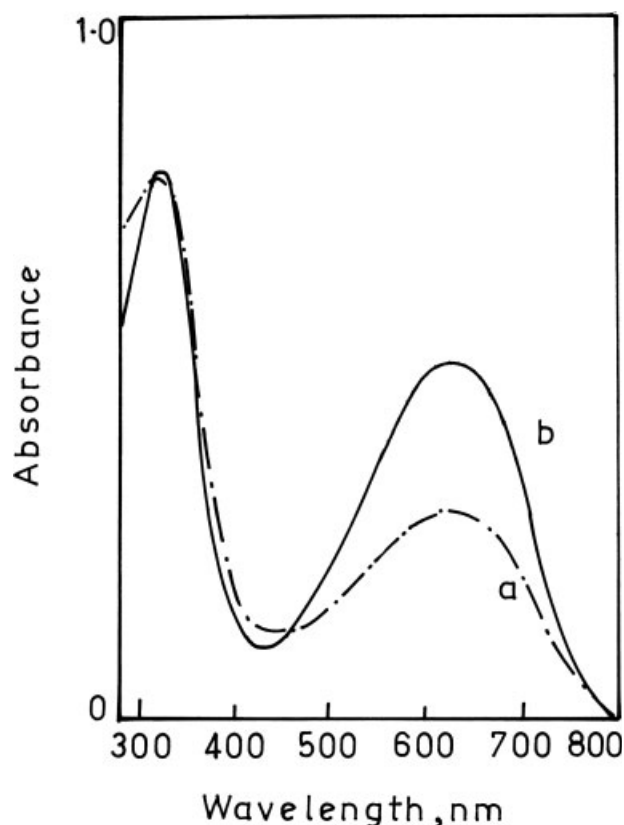


Figure 6 UV-vis spectra of (a) the base form of PANI-1 and (b) PEB.

UV-vis spectroscopy

The UV-vis spectrum of PANI-1 in NMP shows two absorption bands: the π - π^* transition band at 320 nm and the exciton transition from a higher energy occupied benzenoid moiety to a lower energy unoccupied quinoid moiety at 620 nm (Fig. 6).

The UV-vis spectrum (Fig. 6) of PEB in NMP shows a peak for the π - π^* transition at 325 nm and a peak for the exciton transition at 625 nm.^{27,28} The UV-vis spectrum of PANI-1 shows blueshifts in both the π - π^* transition and exciton transition, suggesting a shorter chain length for the polymer compared with that of PEB.²⁹ The intensity of the exciton band with respect to that of the π - π^* transition band of PANI-1 is lower than that of PEB, and this is probably due to the lower quinoid imine content and the lower oxidation state of the polymer.²⁹ These findings are also corroborated by the FTIR spectroscopy results.

TGA

Figure 7 shows the TGA thermogram of PANI-1. The thermal stability of PANI-1 is lower than that of PEB. PANI in the emeraldine oxidation state is

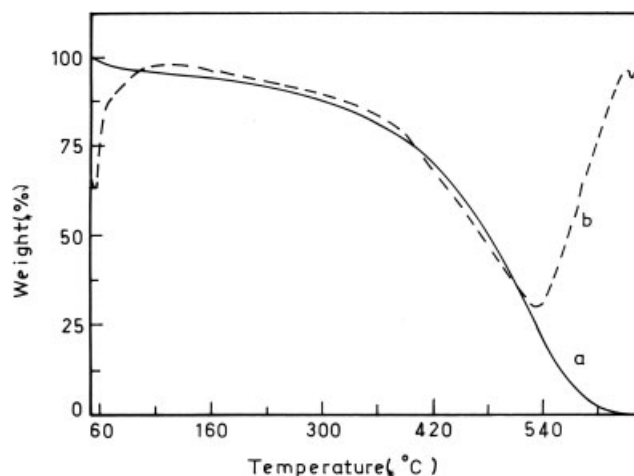


Figure 7 (a) TGA thermogram and (b) differential thermal analysis curve of the base form of PANI-1.

stable up to 380°C, whereas an approximately 18% weight loss occurs in the case of PANI-1; it undergoes complete degradation at 600°C, whereas PEB leaves an approximately 30% residue at this temperature. The thermal degradation of the acid form (HCl-doped) of PANI-1 occurs through a number of steps (Fig. 8). The initial weight loss of about 10–12% in the temperature range of 50–100°C is due to a loss of moisture and free acid present in the polymer sample. The second step involves a 4–5% weight loss in the temperature range of 220–270°C and can be attributed to the loss of dopant anions.³⁰ A third weight-loss step in the temperature range of 280–340°C indicates the loss of the dopant, probably in two steps, the first being the loss of chloride anions followed by a rearrangement with the loss of low-molecular-weight material. The thermal deg-

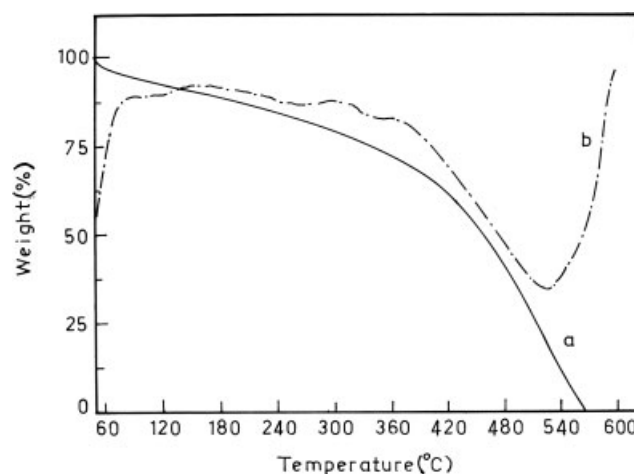


Figure 8 (a) TGA thermogram and (b) differential thermal analysis curve of the acid form of PANI-1.

radiation of the polymer backbone occurs around 350°C, and it undergoes complete degradation around 520°C.

Electrical conductivity

The electrical conductivity of PANI depends on two variables: the oxidation state and the extent of protonation of the polymer.³¹ On protonation with an aqueous, nonoxidizing protonic acid, the imine nitrogens present in the polymer are protonated, forming radical cations (polarons) that result in an increase in the conductivity (ca. 10 orders of magnitude in the case of PANI in the emeraldine oxidation state). The oxidation state of the polymer plays an important role in this process. PANI in other oxidation states lower than the emeraldine state does not exhibit the same conductivity/doping relationship.³¹ The conductivity of the leucoemeraldine base shows no measurable increase in the conductivity on protonation. In this case, doping results in an increase in the conductivity of approximately 6 orders of magnitude (from 3.1×10^{-9} to 9.4×10^{-3} S/cm). The higher conductivity of undoped PANI-1 compared with that of PEB is due to the presence of protonated species, as indicated by the XPS results. The lower conductivity of doped PANI-1 compared with that of the polyemeraldine-HCl salt may be explained by the generation of a lower number of polarons on HCl doping as PANI-1 contains a lower number of imine nitrogens (=N—).

XPS

XPS allows the tracking of structural changes during PANI oxidation or reduction and has been used for

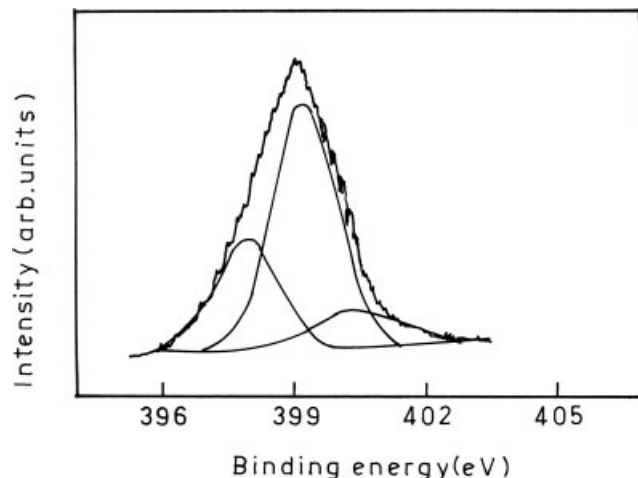


Figure 9 N 1s XPS core level spectra of PANI-1 (base form).

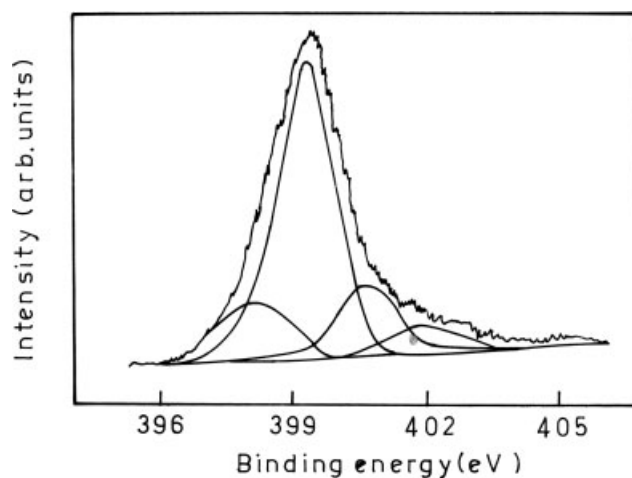
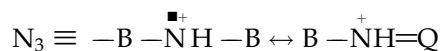
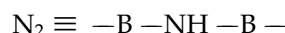
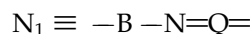


Figure 10 N 1s XPS core level spectra of PANI-1 (acid form).

the quantitative determination of the proportion of benzenoid amine, quinoid imine, and protonated units in chemically synthesized PANI.^{32,33} The intrinsic oxidation state and protonation characteristics of PANI can be readily elucidated with XPS.³⁴⁻³⁶

The N 1s core level spectrum for the base form and acid form of the polymer are shown in Figures 9 and 10, respectively. Both spectra are deconvoluted into two major components along with a high-binding-energy component. The peaks for the two major components are centered at 398.1 ± 0.1 and 399.5 ± 0.1 eV, and the high-binding-energy component is centered at 401 eV. The two major peaks are assigned to the quinoid imine structure (N_1) and benzenoid amine structure (N_2), respectively. The high-binding-energy lines may be assigned to the positively charged nitrogen (N_3):³⁴



where B is the benzenoid ring and Q is the quinoid ring.

TABLE II
XPS Experimental Results and Surface Stoichiometries for the Base Form and Acid Form of the Polymer

Sample	N 1s core level spectrum			Surface stoichiometry		
	=N—/N (N_1)	—NH/N (N_2)	—N ⁺ /N (N_3)	C	N	Cl
Base form	0.28	0.62	0.10	86.8	13.2	—
Acid form	0.14	0.64	0.22	89.8	8.8	1.4

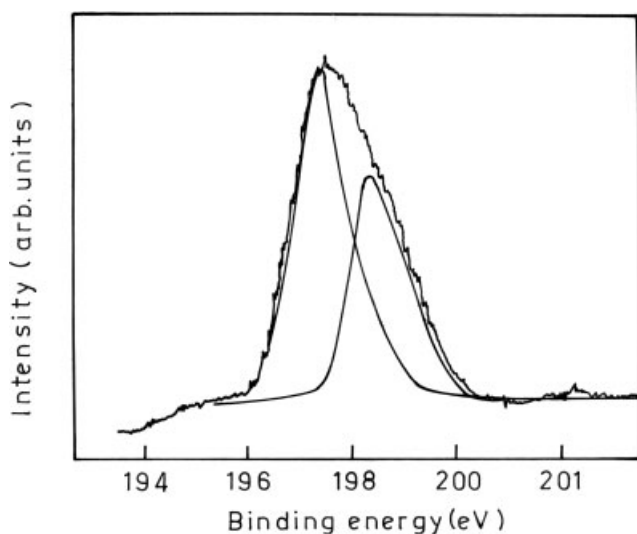


Figure 11 Cl 2p XPS core level spectra of PANI-1.

The proportions of the different nitrogen species and surface stoichiometries of the polymer in the base form and acid form are shown in Table II.

The proportion of the quinoid imine structure is much lower than that of the benzenoid amine structure present in the polymer, as determined from the integrated area under binding energy peaks. Positively charged nitrogen species observed in the doped polymer indicate the presence of neutral imine species in addition to the amine and protonated nitrogen (—N^+) species. The low electrical conductivity of the polymer ($\sigma = 10^{-2}$ S/cm) can be explained by the presence of a substantial number of unprotonated imine species.

The intrinsic oxidation state or oxidation level of the polymer can be calculated from the relative intensities of the deconvoluted N 1s spectra of the polymer in the undoped form.³⁴ Thus, the oxidation level or intrinsic oxidation state is equal to $N_1 + N_3/N_{\text{total}} = 0.28 + 0.10/1.00 = 0.38$.

The deconvoluted profile of the Cl 2p core level spectra of the doped polymer (Fig. 11) shows only two components centered at 197.1 eV for Cl 2p_{1/2} and at 198.6 eV for Cl 2p_{3/2}. These peaks are attributable to the chloride anion. No covalent chlorine atom is present, as indicated by the absence of a high-binding-energy peak at 200.1 eV. A comparison of the N 1s and Cl 2p spectral areas of the doped polymer indicate a Cl/N concentration ratio of 0.159.

CONCLUSIONS

The chemical oxidative polymerization of a partially diazotized aniline solution results in the formation

of PANI-1, which is highly soluble in common organic solvents. The degree of oxidation in terms of the fractional doping level and the intrinsic oxidation state of the polymer is lower than 0.5, as indicated by an elemental analysis and XPS study. The lower oxidation state of the polymer compared with that of PEB is due to a lower number of quinoid imine moieties compared with the benzenoid amine moieties in the polymer backbone. This fact is also corroborated by FTIR and UV-vis spectroscopy studies of the polymer and its low room-temperature electrical conductivity. TGA indicates the lower thermal stability of the polymer compared with that of PEB.

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