Asian Journal of Chemistry Vol. 21, No. 1 (2009), 128-138

Cost-Effective Synthesis and Spectroscopic Characterization of Polyphenyl Amines

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Polyanilines were chemically synthesized by one step polymerization of aniline using 3 different oxidants-ammonium persulphate, potassium iodate and hydrogen peroxide. Standard redox potentials and redox couples were studied. The samples were characterized by UV, FTIR, FT Raman spectroscopy, X-ray ^{13}C NMR and conductivity of polyanilines.

Key Words: Polyanilines, Conducting polymers, FTIR spectroscopy, PANI ED and PANI ES, X-ray absorption near edge structure (XANES at k edge).

INTRODUCTION

The usual doping process of conducting polymers consists of a redox reaction where the neutral polymer is oxidized or reduced. Thus, the insulating neutral polymer is converted into an ionic macromolecule and a counter-ion neutralizes its charges[1]. During the doping process, the number of electrons associated with the polymer decreases or increases. Polyaniline (PANI) was the first example of a conjugate polymer doped by a process where no change in the number of the electrons is observed[2,3]. Emeraldine base (EB-PANI) can be doped by protonic acids leading to emeraldine salt (ES-PANI), the conducting form of PANI. This doping effect is accompanied by an increase in its electrical conductivity of *ca.* 10 order of magnitude[3]. EB-PANI possesses equal amount of imine nitrogen and amine nitrogen as shown in Fig. 1. In the doping process using protonic acids, protonation preferentially occurs at imine nitrogen atoms followed by an internal redox reaction that results in the formation of semiquinone segments (radical cation)[2,4]. UV-VIS-NIR and FT-IR spectroscopic studies have been used to characterize EB-PANI & ES-PANI metal salts. UV-Vis-NIR spectra of PANI doped with metal cations shown bands at *ca.* 360, 440 nm and an absorption tail

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in the NIR[5-7]. The absorption band at 360 nm is assigned to π-π^* transition, the band at 440 nm is due to localized polar ions and the tail in the NIR is ascribed to free charge carriers. FT-IR spectra of these samples present some characteristic features of conducting form of ES-PANI[7,8]. The metal cations are also probed using Mossbauer spectroscopic[5,9] and the data demonstrate that Fe(III) and Sn(IV) are coordinated to amine and imine nitrogen sites.

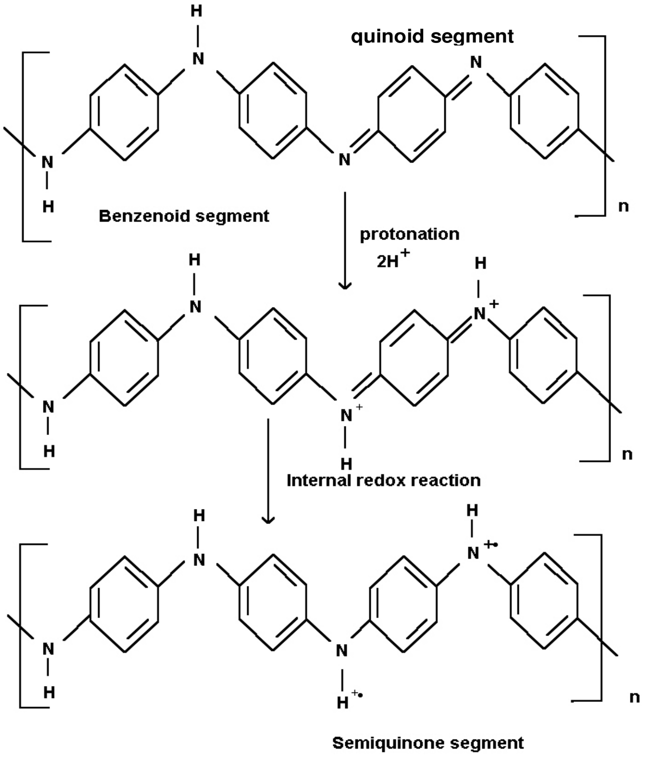

Fig. 1. EB-PANI structure and schematic representation of protonic doping process

In present study, authors used the resonance Raman spectroscopy for the characterization of conducting polymers. It is shown that this technique is excellent for discerning secondarily doped ES-PANI from primarily doped PANI[10,11]. One of the remarkable properties of this technique is the possibility of selecting each chromophoric segment present in the polymeric chain by changing the exciting radiation[12].

In the present work, the reaction, between EB-PANI and ES-PANI is studied and characterized through resonance Raman, X-ray absorption near edge structure (XANES at k edge).

EXPERIMENTAL

All the reagents were of analytical grade purchased of international quality. Only aniline (Merck) was distilled under reduced pressure prior to use.

Ammonium persulphate: AnalaR grade ammonium persulphate (99 %) was obtained from Ranbaxy, India and estimated by titration with standard sodium thiosulphate, using starch and indicator[1].

Potassium iodate: AnalaR grade potassium iodate (99.5 %) was obtained from Ranbaxy (India) and was used as such.

Hydrogen peroxide: 48.52 % of hydrogen peroxide was purchased from E. Merck India, Ltd. and was standardized, using a titrimetric method.

Acetonitrile: AnalaR grade acetonitrile, Ranbaxy (India) was distilled at atmospheric pressure. The middle fraction was collected and used for extraction of soluble species of PANI, in Soxhlets.

Chemical synthesis of polyphenyl amines: Polymerization of aniline in aqueous perchloric acid solution using ammonium per sulphate was carried out as described in the literature. PANI was obtained in the salt form ES-PANI and the base form EB-PANI was obtained by treating ES-PANI with aqueous solution of ammonium hydroxide 1 mol L^{-1}.

The availability of selective oxidants for organic compounds and simple sources of radicals to be used for selective synthesis of desired polymers, are of obvious importance for both research and applications.

Three oxidants, namely, ammonium persulphate, potassium iodate and hydrogen peroxide have satisfied most of the aforesaid requirements. Their redox couples and their standard redox potentials are listed in Table-1. Such a high potential that in many instances, the reduced species of the oxidizing agents is oxidized back to its original state

TABLE-1
OXIDIZING AGENTS, REDOX COUPLES AND THEIR STANDARD REDOX POTENTIALS

Oxidizing agents	Redox couple	Standard redox potential (V) *vs.* NHE	Natural of species
Ammonium persulphate	$S_2O_8^{2-}/SO_4^{2-}$	2.010	Non-metalic
Potassium iodate	IO_3^-/I_2	1.195	Non-metalic
Hydrogen peroxide	H_2O_2/H_2O	1.775	Non-metalic

Ammonium persulphate: The persulphate ion $S_2O_8^{2-}$ is one of the strongest oxidizing agents. Its standard redox potential has been estimated to be 2.01 V *vs.* NHE. In aqueous solutions, under mild conditions, thermal, photochemical or radiolytic decomposition of this bivalent ion ($S_2O_8^{2-}$) yields the radicals anion SO_4^{2-} which appears to be a very effective electron transfer oxidizing agent[13].

Its oxidative action on amines, for example, is represented as shown below:

$$\text{R-NH}_2 + \text{SO}_4^- \rightarrow \text{R-NH}_2 + \text{SO}_4^{2-} \quad E^o = 1.96 \text{ V}$$

$$\text{S}_2\text{O}_8^{2-} + 2e^- + 2\text{H}^+ \rightarrow 2\text{HSO}_4^- \quad E^o = 2.08 \text{ V}$$

Potassium iodate: Iodate is reduced to hypoidous acid, iodine or iodide depending on the pH of the solution. The dissociation constant of HIO_3 is K = IO_3 is K = 0.169[14]. The Gibbs energy of IO_3^- from emf measurement[15] is 134.938 KJ mol^{-1}. The standard potentials for the half reactions are

$$2\text{HIO}_3 \text{ (aq)} + 1\text{OH}^+ \text{ IOe}^- \rightarrow \text{I}_2 \text{ (aq)} + 6\text{H}_2^o \quad E^o = 1.195 \text{ V}$$

$$2\text{IO}_3^- + 12\text{H}^+ + \text{IOe}^- \rightarrow \text{I}_2 \text{ (aq)} + 6\text{H}_2^o \quad E^o = 1.195 \text{ V}$$

For the iodate-iodine couple, the value E° = 1.1942 V has been obtained from emf measurements[16]. In acid media, iodate is a strong and rapid oxidizing agent. It oxidizes iodide to iodine quantitatively and this reaction is important in preparation of standard iodine solutions as well as in the analytical determination of iodide.

Hydrogen peroxide: Hydrogen peroxide is a weak acid with pK of 11.7 and the second ionization constant is very small ($16 < pK < 18$). In acid solutions, hydrogen peroxide decomposes to give water as the product. The standard reduction potential for the following reaction is

$$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \quad E^o = 1.763\text{V}$$

Such a high positive potential places peroxide in the group of most powerful oxidizing agents known. Peroxide is unstable not only with respect to the oxidation of water, but also with respect to its own oxidation and reduction in acid media.

The strong oxidizing agents can oxidize peroxide to oxygen, but the H_2O_2/H_2O couple has such a high potential that in many instances, the reduced species of the oxidizing agent is oxidized back to its original state. The result of this behaviour is the decomposition of peroxide to oxygen and water.

Synthesis of polyaniline perchlorate (conductor): PANI was prepared by oxidative action of ammonium persulphate on aniline. Purified aniline (0.4 mol) was dissolved in 1000 mL of a perchloric acid solution containing 0.5 M sodium perchlorate (pH = 1) and the required amount of ammonium persulphate was added while stirring. The reaction was allowed to continue for 1 h. The insoluble precipitate formed after each synthesis was filtered through a sintered glass crucible (porosity 2) and washed with perchloric acid solution (pH = 1), until the filtrate is colourless. The black precipitate was air-dried, transferred to a Soxhlet and washed with acetonitrile (to remove soluble species) until the extract was colourless. The resultant material was dried in a vaccum desiccator for about 24 h. The black amorphous powder was polyaniline perchlorate. The synthesis were carried out at different persulphate/aniline molar ratios. Z = 0.5, 1.0, 1.5, 2.0, 3.0 4.0 and 5.0. For each Z value, the synthesis reactions were also carried out for different periods of time *viz.*, 0.25, 0.50, 1.00, 2.00, 4.00, 6.00 and 8.00 h (Table-2).

TABLE-2
EFFECT OF PERSULPHATE/ANILINE INITIAL MOLE RATIO (z) AND DURATION OF REACTION ON THE YIELD OF POLY ANILINE, IN PERCHLORIC ACID MEDIUM AT ROOM TEMPERATURE

Duration of reaction (h)	% Yield of insoluble polymer at different persulphate/ aniline initial mole ratio (z)							
	0.25	0.50	1.00	1.50	2.00	3.00	4.00	5.00
0.25	22.5	48.5	93.6	86.6	74.8	64.1	54.2	47.2
0.50	22.6	45.3	94.8	90.3	74.6	56.6	53.6	46.6
1.00	19.8	44.8	96.6	89.4	78.6	60.8	51.4	45.6
2.00	20.6	46.8	89.7	89.7	87.6	55.7	54.8	46.6
4.00	21.3	44.4	89.7	89.9	73.5	60.6	58.7	45.8
6.00	21.4	45.9	90.3	91.4	80.6	61.4	55.7	45.8
8.00	23.4	46.6	90.4	92.3	76.3	64.5	55.5	45.3

The syntheses were also carried out at low temperature, *i.e.*, *ca.* 4 ºC. The conditions were similar as those for room temperature, except that the aniline solution was precooled to *ca.* 4 ºC before the addition of ammonium persulphate and the temperature of the reaction mixture was kept below 4 ºC by keeping reaction vessel in a freezing mixture or ice-bath. The syntheses were carried out at different persulphate/aniline molar ratios: Z = 0.25, 0.50, 1.00, 1.50, 2.00, 3.00, 4.00 and 5.00. For each Z value the syntheses were also carried out for different reaction times, *viz.*, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 8.0 h. The results are given in Table-3.

TABLE-3
EFFECT OF PERSULPHATE/ANILINE INITIAL MOLE RATIO (z) AND DURATION OF REACTION ON THE YIELD OF ANILINE, IN PERCHLORIC ACID MEDIUM AT 4 ºC

Duration of reaction (h)	% Yield of insoluble polymer at different persulphate/ aniline initial mole ratio (z)							
	0.25	0.50	1.00	1.50	2.00	3.00	4.00	5.00
1	20.8	44.9	90.2	85.6	46.4	35.8	36.7	33.2
2	20.4	44.9	90.4	85.6	51.6	38.2	35.5	35.1
3	21.4	46.3	89.1	92.5	47.4	34.6	28.8	31.5
4	20.9	45.4	90.5	84.3	43.6	28.5	33.3	31.6
5	20.7	46.6	95.0	89.9	48.3	34.1	31.1	32.1
6	21.6	45.0	92.0	90.9	47.2	31.8	34.1	32.1
8	20.5	45.6	91.3	89.2	46.2	31.1	30.1	28.6

In the case of potassium iodate and hydrogen peroxide the synthesis was carried out for several, different iodate/aniline and peroxide/aniline molar ratios, *viz.*, Z = 0.5, 1.0, 2.0 and 4.0. For each Z-value the syntheses reaction were allowed to go on for different periods of time, *viz.*, 1.00, 3.00, 5.00, 7.00, 10.00 and 15.00 h (Tables 4-6).

TABLE-4
EFFECT OF IODATE/ANILINE INITIAL MOLE RATIO (z) AND DURATION OF REACTION ON THE YIELD OF POLY ANILINE, IN PERCHLORIC ACID MEDIUM AT ROOM TEMPERATURE

Duration of reaction (h)	% Yield of insoluble polymer at different persulphate/ aniline initial mole ratio (z)			
	0.25	1.00	2.00	4.00
1	10.3	16.5	27.8	30.5
3	24.5	46.7	63.5	69.8
5	26.8	51.3	65.8	73.4
7	31.5	68.5	76.3	81.6
10	41.1	82.5	87.5	89.5
15	47.3	98.6	91.5	86.4

TABLE-5
EFFECT OF PEROXIDE/ANILINE INITIAL MOLE RATIO (z) AND DURATION OF REACTION ON THE YIELD OF POLY ANILINE, IN PERCHLORIC ACID MEDIUM AT ROOM TEMPERATURE

Duration of reaction (h)	% Yield of insoluble polymer at different persulphate/ aniline initial mole ratio (z)			
	0.50	1.00	2.00	4.00
1	6.5	8.3	14.6	21.4
3	11.6	24.8	30.6	37.8
5	18.7	31.2	33.8	34.6
7	24.1	43.6	47.8	49.3
10	26.3	47.6	51.2	53.5
15	31.1	41.6	64.8	73.8

TABLE-6
USE OF OXIDIZING AGENTS-EFFECT OF STANDARD REDOX POTENTIAL OF THE OXIDANT (1:1 OXIDANT SUBSTRATE RATIO)

Oxidizing agent	Standard redox potential (V) *vs.* NHE	Time of reaction insoluble (h)	Yield of polyaniline
Ammonium persulphate	2.010	1.0	96.6
Potassium iodate	1.195	15.0	98.6
H_2O_2	1.775	15.0	61.6

Preparation of polyaniline chloride: 1 g of polyaniline perchlorate (synthesized using ammonium persulphate oxidant) was transferred to a 250 mL beaker containing 100 mL of 1 M HCl and the mixture was stirred for about 12 h (equilibration) at room temperature. The mixture was then filtered through a sintered glass crucible (porosity 4). The powder retained on the sintered glass crucible was rinsed with acetonitrile and dried under vacuum. The resultant powder was weighed as polyaniline chloride.

Preparation of polyaniline sulphate: 1 g of polyaniline perchlorate (synthesized using ammonium persulphate oxidant) was transferred to a 250 mL beaker containing 100 mL of 1 M sulphuric acid and the mixture was stirred for about 12 h and then possibility of dedoping through diffusion from the skin of the base cause heterogeneities in the base structure. Doping of polyaniline in solution however results in more homogenous doping and a more uniform material after casting.

Preparation of polyaniline chloride in hydrochloric acid medium: For comparison, production of polyaniline chloride was achieved by direct synthesis - as in the case of polyaniline perchlorate - in a hydrochloric acid solution containing 0.5 M sodium chloride (pH = 1).

Preparation of polyaniline sulphate in sulphuric acid medium: For comparison, production of polyaniline sulphate was achieved, as in the case of polyaniline perchlorate, by direct synthesis in sulphuric acid solution containing 0.5 M sodium sulphate. (pH = 1)

Preparation of polyaniline base (insulator): 1 g of polyaniline perchlorate, polyaniline chloride or polyaniline sulphate was transferred to a 250 mL beaker containing 100 mL of 1:1 aqueous (v/v) ammonia solution and the mixture was stirred for about 12 h. It was filtered and the material retained was dried, as mentioned above. The resultant powder was polyaniline base (EB-PANI).

RESULTS AND DISCUSSION

Complexation occurs preferentially at imine nitrogen of EB-PANI[1]. Fig. 2 shows the resonance Raman spectra of ES-PANI and EB-PANI for the indicated exciting radiation. A drastic change is observed in the EB-PANI spectral profile on the other hand, a quite similarity could be notice between ES-PANI and EB-PANI.

At the 632.8 nm exciting radiation, resonance Raman spectrum of EB-PANI shows bands at 1160 cm^{-1} (βC-H of quinoid ring). 1217 cm^{-1} ν(C=C) characteristic of the quinone segments[17]. In ES-PANI spectrum, the ν(C=C) mode can be attributed to the band at 1579 cm^{-1}. The intense band at 1470 cm^{-1} of the EB-PANI spectrum decrease in its relative intensity and a doublet at 1315/1336 cm^{-1}, assigned to $\nu(C\text{-}N)^{+}$. of semiquinone segments, appears[18]. For 514.5 nm exciting radiation, the ES-PANI spectrum presents, besides

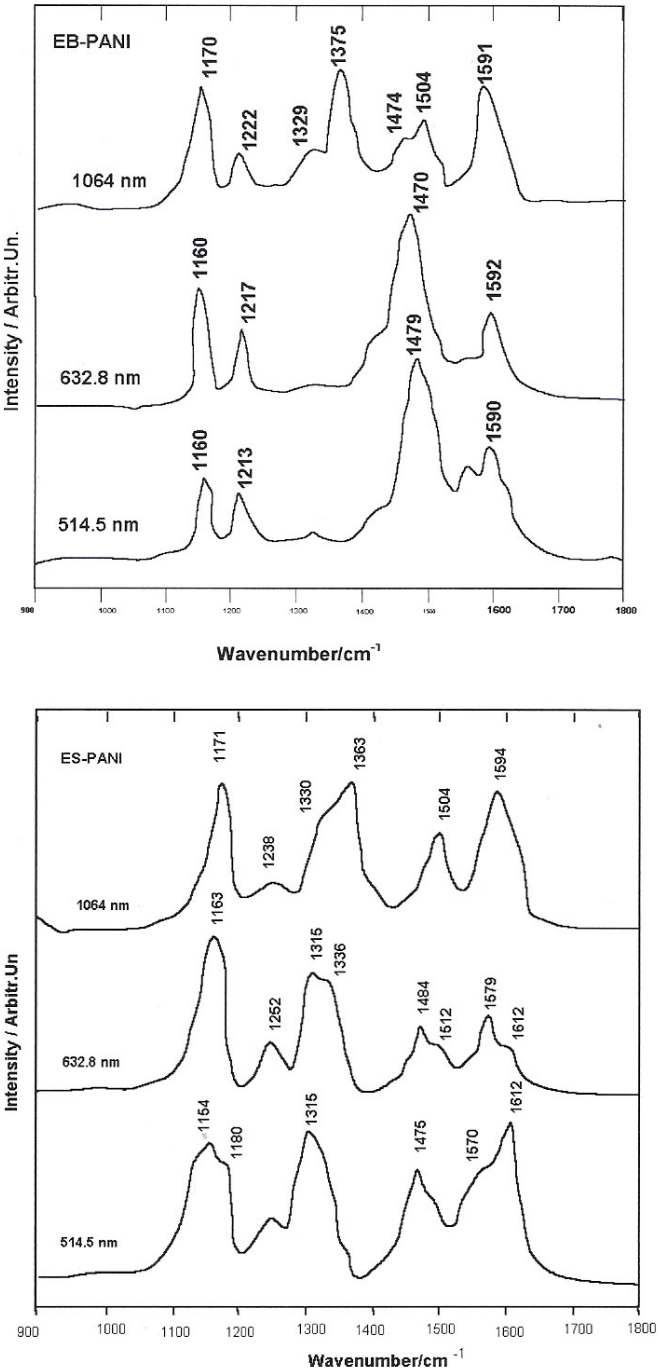

Fig. 2. Resonance Raman spectra of ES-PANI and EB-PANI

the characteristic bands of semiquinone segments, the bands at 1154 (βC-H), 1252 ν(C-N) and 1612 cm^{-1} ν(C=C) related to the reduced aminobenzene ring. For 1064 nm exciting radiation, the ES-PANI spectra presents only the bands due to semiqunione segments (radical cation) since at this wavelength occurs the resonance Raman condition of these segments. Because of this enhancement effect in the EB-PANI spectrum, the bands at 1329, 1375, 1504 and 1591 cm^{-1} were observed, which are characteristic of semiquinone segments that are present in a very small amount in the EB-PANI polymeric chains. X-ray absorption near edge structure (XANES) of nitrogen at K edge is a useful technique to characterize the nature of nitrogen atom and was successfully used for the investigation of the oxidation states of nitrogen in PANI[19], XANES spectra of EB-PANI and ES-PANI are shown in Fig. 4. The N K absorption spectrum of PANI is dominated by N1s → 2pπ* resonances which are influenced by changes of partial charges and bonding at the nitrogen atom[19]. The XANES spectrum of ES-PANI presents the peaks at 399.1 ($-NH^{\bullet}+-$) and 402.7 eV (-NH=) while EB-PANI spectrum shows peaks at 397.7 (=N-) and 402.7 eV (-NH=).

Fig. 3 shows the UV-vis-NIR spectra of EB-PANI and ES-PANI. It can be seen that EB-PANI presents bands at 335 and 640 nm.The former corresponds to the π-π* transition, whereas the absorption at 640 nm is associated with the presence of quininoid segments[20]. ES-PANI presents the band at 350 nm assigned to π-π* transition, the band at 440 nm is due to polaron transition and the tail in the NIR is attributed to free charge carriers[20,21].

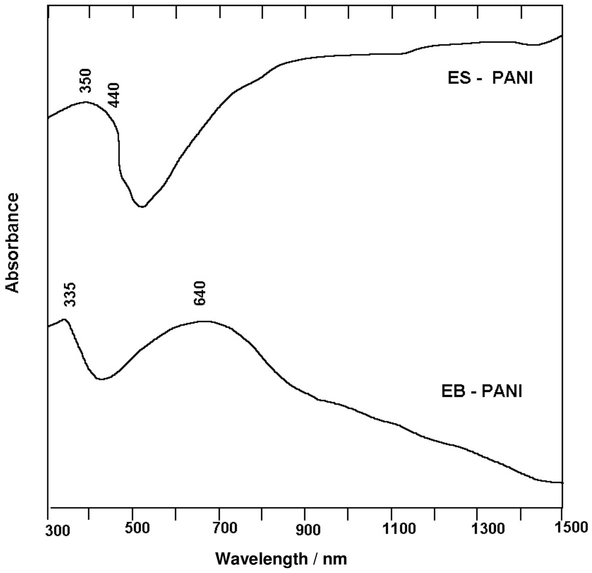

Fig. 3. UV-Vis-NIR spectra of ES-PANI and EB-PANI

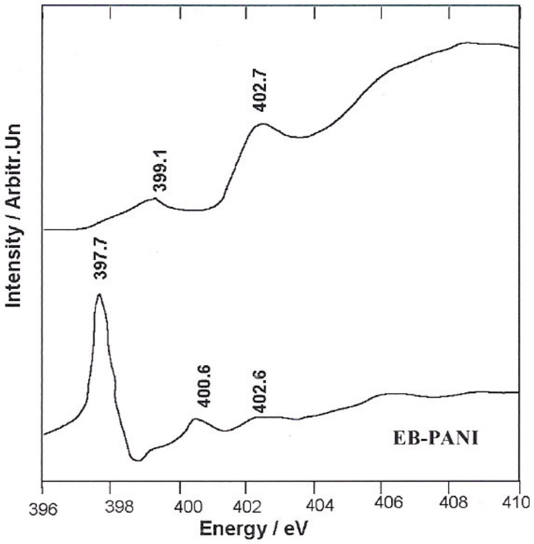

Fig. 4. Nitrogen K edge XANES spectra of EB-PANI and ES-PANI

Resonance Raman spectrum obtained for EB-PANI and ES-PANI are shown in Fig. 5. The ν(C=N) strectching is observed at 1470 cm^{-1} for EB-PANI. In the spectrum recorded at 5 min, the bands at 1336 and 1315 cm^{-1} are observed, which indicates that radical cations are formed.

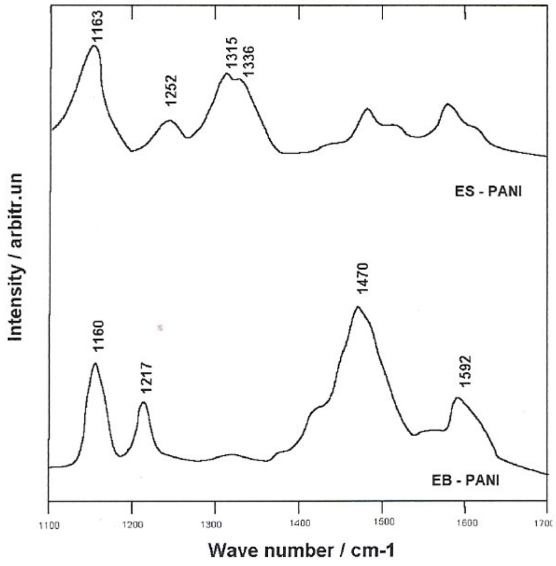

Fig. 5. Resonance Raman spectra of ES-PANI and EB-PANI

Conclusion

Resonance Raman, XANES and EPR results obtained in the work are in agreement with the UV-vis and FT-IR characterization reported in the literature shows semi-quinone segments on EB-PANI. From the results together with resonance Raman as a function of doping reaction time it is possible to conclude that doping process of EB is a psuedo-protonation mechanism.

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(*Received*: 5 November 2007; *Accepted*: 11 August 2008) AJC-6749