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A process for the preparation of polyaniline salt doped with acid and surfactant groups using benzoyl peroxide

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This paper relates to a process for preparation of polyaniline salts such as polyaniline-sulfate, polyaniline-nitrate and polyaniline-hydrochloride by emulsion polymerization pathway. Aniline was oxidized to polyaniline salt using benzoyl peroxide as an oxidizing agent in the presence of sulfuric, nitric, or hydrochloric acid by emulsion polymerization pathway. Polyaniline salts and their corresponding bases were characterized by infrared, electronic absorption, X-ray diffraction spectral techniques, scanning electron microscope, X-ray photoelectron, elemental analysis and conductivity measurement. The results of this study indicate that both acid and surfactant group are present in the polyaniline salt as dopants. The values of yield were found to be 59.6, 55.0 and 53.9% for polyaniline-sulfate, polyaniline-nitrate and polyaniline-hydrochloride salt respectively. Conductivity of the polyaniline-sulfate (0.08 S/cm) was found to be same as that of polyaniline-nitrate salt (0.08 S/cm) and however, one order of magnitude lower conductivity was obtained for polyaniline-hydrochloride salt (0.004 S/cm). The semiconducting range (10^{-1} to 10^{-4} S/cm) can be used for EMI shielding and antistatic applications.

1. Introduction

Polyaniline, the air stable-conducting polymer, can be synthesized both by electro chemical and chemical oxidative polymerization methods [1]. The chemical oxidative polymerization process is of particular importance since this synthesis is the most feasible route for the production of polyaniline on a large scale.

In the chemical oxidative polymerization process aniline is being oxidized mostly using ammonium persulfate. Armes *et al.* [2] have studied the use of ammonium persulfate as an oxidant in the polymerization of aniline and concluded that the conductivity, yield, elemental composition and degree of oxidation of the resulting polyaniline were essentially independent of the oxidant/monomer initial mole ratio below 1.15. Pron *et al.* [3] have compared the use of four different oxidizing agents $(NH_4)_2S_2O_8$, $K_2Cr_2O_7$, H_2O_2 and KIO_3 in the polymerization of aniline. They found that KIO_3 was the most convenient oxidant in the sense that it produced good quality product over a wide range of reaction conditions, whereas, H_2O_2 was not a good oxidizing agent for preparing polyaniline. In order to obtain high quality polyaniline the activity of H_2O_2 must be improved.

Cao *et al.* [4] have studied the effects of the different types of oxidizing agents, protonic acids, aniline/oxidizing agent mole ratio, pH, polymerization temperature, and time on the polyaniline properties. The reaction yield was not strongly sensitive to most synthesis variables, while the viscosity, molecular weight and the electrical conductivity of the as-polymerized or post-treated polyaniline salt was found to be markedly affected. The use of ammonium persulfate and potassium dichromate as oxidizing agents resulted in high yield, conductivity and viscosity of the polyaniline. KIO_3, $FeCl_3$ have also shown similar conductivity but the viscosity of the polyaniline was much lower. The use of $KMnO_4$ resulted in much lower conductivity of the polymer whereas with $KClO_3$ and $KBrO_3$ the reaction rate and yield were low. Armes *et al.* [5] have extensively investigated the bulk polymerization of aniline by KIO_3 in aqueous acidic media and concluded that substantial quantities of iodine are incorporated into the polymer matrix and leaches out when washed with organic solvents. The high iodine content in polyaniline could prevent the material finding use in several application areas.

Yasuda and Shimadzu [6] synthesized polyaniline using $FeCl_3$ as oxidant, but the yield and conductivity of the polymer produced were very low. Moon *et al.* [7] have used H_2O_2 as the oxidant and $FeSO_4$ as the catalyst

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for the preparation of polyaniline at 30–35°C. However, the yield and conductivity were not satisfactory. Sun *et al.* [8] have prepared polyaniline with H_2O_2-Fe^{2+} system at 0–5°C. The polymer was obtained in 60% yield with a conductivity of 10 S/cm.

Toshima *et al.* have used a novel synthesis method to prepare polyaniline using iron (III) catalyst and ozone [9]. Molecular weight and electrical conductivity of the polyaniline film prepared by iron (III) catalyst and ozone oxidant were compared with those prepared by ammonium persulfate oxidant. Electrical conductivity of the film prepared by both methods was comparable and however, lower molecular weight (2×10^4) was obtained with iron (III) and ozone system.

Akita *et al.* [10] have recently used oxidants such as ammonium persulfate, iron (III) chloride, manganese dioxide and hydrogen peroxide to prepare solid polymer electrolyte membrane.

The oxidizing agents generally used in the chemical oxidative polymerization process are soluble in aqueous medium. Among the different oxidizing agents in the above processes, ammonium persulfate is the most widely used oxidizing agent. However, ammonium persulfate loses its stability on standing (poor shelf life), resulting in lower yield and conductivity.

In the present work, bulk polymerization of aniline in aqueous-organic media was carried out using benzoyl peroxide (soluble in most of the organic solvents) as oxidizing agent. Advantages of using benzoyl peroxide (BP) oxidizing agent are: (i) good stability of benzoyl peroxide, (ii) reaction can be controlled in presence of surfactant and thereby, acid as well as surfactant group can be incorporated in polyaniline salt as dopants, (iii) reaction can be carried out at 25–40°C and (iv) processable polyaniline salt can be prepared due to the solubility of benzoyl peroxide in most of the organic solvents.

An attempt was made to correlate the yield, chemical composition and solid state conductivity of the polyaniline product with the solution acidity, reaction time, reactant concentrations, and dopants. The effect of the surfactant sodium lauryl sulfate on the yield and conductivity of the polymer was also investigated. The polyaniline obtained was well characterized by infrared, electronic absorption, X-ray diffraction spectral techniques, scanning electron microscope, X-ray photoelectron, elemental analysis and conductivity measurement.

2. Experimental

2.1. Material

Aniline (reagent grade) from E. Merck was distilled prior to use. Reagent grade sodium laurylsulfate, acids, solvents (BDH, India) were used without further purification. Reagent grade benzoyl peroxide (BDH, India) was recrystallized from chloroform/methanol system.

2.2. Sample preparation

2.2.1. Polyaniline salt

In a typical experiment, 4.85 g of benzoyl peroxide was dissolved in 1.5×10^{-4} m^3 dioxane taken in a 5×10^{-4} m^3 round bottom flask. To this solution, 2×10^{-5} m^3 aqueous solution of sodium lauryl sulfate (1.44 g) was added under stirring. To the above mixture, 3×10^{-5} m^3 aqueous solution containing 2.4×10^{-6} m^3 aniline and mineral acid (9×10^{-6} m^3 H_2SO_4/1.75×10^{-5} m^3 HCl/1.26×10^{-5} m^3 HNO_3) was added and stirred constantly at 35°C for 24 h. At the end, the reaction mixture was filtered under vacuum, the powder was washed with 2×10^{-3} m^3 of water followed by 5×10^{-4} m^3 methanol and 5×10^{-4} m^3 of acetone to remove oligomers and other impurities. The polyaniline powder was dried at 100°C until it reached a constant weight (see table for reaction conditions).

2.2.2. Polyaniline base

Polyaniline powder (300 mg) synthesized above was stirred in 1×10^{-4} m^3 aqueous sodium hydroxide solution (1.0 M) for 8 h at ambient temperature. Polyaniline powder in solution was filtered under vacuum, washed with excess water and finally with acetone and dried at 100°C till a constant weight.

2.3. Resistance measurement

Polyaniline samples were pressed into disks of 8 mm-diameter and ca 2-mm thickness under a pressure of 400 MPa. Resistance measurement of the pellets was carried out by the two probe method using a Keithley constant current source (MODEL–230) and digital voltmeter (MODEL–195A). Resistance was calculated based on the average of at least three pairs of consistent readings at different points on the pressed pellet. Since, the mean value was used in the calculation of resistance, the total error involved is $<1\%$.

2.4. Infrared spectra

The polyaniline sample was mixed with KBr powder and compressed into pellet, wherein, the polyaniline powder was evenly dispersed. Fourier transform infrared spectra were recorded using GC-FTIR spectrometer (MODEL740 Nicolet, USA).

2.5. Electronic absorption spectra

Electronic absorption spectrum of the polyaniline sample was recorded at ambient temperature using GBC cintra 10e UV/V spectrophotometer. The solution for the absorption spectrum of polyaniline base was prepared by dissolving the sample in dimethyl sulfoxide (DMSO) and filtered through whatman 41 filter paper. Absorption spectrum of the dilute solution was recorded in the range 950–200 nm using a pair of matched 3×10^{-6} m^3 stoppered silica cells of 10 mm path length.

2.6. X-ray diffraction spectra

Wide angle X-ray diffraction spectra for the polyaniline powder samples were obtained using a Siemens/D-5000 X-ray diffractometer using Cu K_α radiation of wave length 1.54×10^{-10} m and continuous scan speed of 0.045°/min.

2.7. Scanning electron microscope

Morphology studies of the polyaniline samples were carried out using Hitachi S520 scanning electron microscope instrument operating at 10 kV. The samples were mounted on a double-sided adhesive carbon disc and sputter-coated with a thin layer of gold to prevent sample charging problems.

2.8. X-ray photo electron spectra

The core level spectra of the polyaniline samples were recorded using KRATOS AXIS 165 (Shimadzu) with a Mg K_α X-ray source 253.6 eV. The X-ray power supply was operated at 75 W and 5 mA. The pressure in the analysis chamber during scans was kept below 1.33 MPa. The peak area ratios for various elements were corrected by experimentally determined instrumental factors. N1s and Cl2p spectra, after background subtractions were decomposed into suitable components consisting of a Gaussian line shape with a Lorentzian broadening function. All fitting parameters including the number of components, widths and intensities were freely adjustable and determined for each spectrum with an iterative, least square fitting routine.

2.9. Elemental analysis

The content of elements in the polyaniline samples was determined using Elementor Vario EC Germany elemental analyzer.

3. Results and discussion

Polyaniline salts such as polyaniline-hydrochloride (PANI-HCl), polyaniline-sulfate (PANI-H_2SO_4) and polyaniline-nitrate (PANI-HNO_3) were prepared by chemical oxidative polymerization of aniline using benzoyl peroxide as an oxidizing agent. Polyaniline-sulfate salt was prepared by varying the reaction time, amount of benzoyl peroxide, acid concentration and the amount of sodium lauryl sulfate (SLS) surfactant and the results are presented here.

3.1. Effect of variation of reaction time

The polymerization reaction for the preparation of polyaniline-sulfate salt was carried out for various periods of time to find out the effect of the variation of time on polymer yield and conductivity. The reaction condition, yield and conductivity of the polyaniline salt are reported in Table I. The yield of PANI-H_2SO_4 salt (calculated based on the amount of aniline used) was found to be 14 and 51% for 4 and 8 h respectively. The yield attained almost constant value (58–60%) after 12 h. There is no marked change in the conductivity (0.06–0.08 S/cm) of polyaniline sulfate salt after 8 h of reaction. This result indicates that the reaction could be completed in 12 h.

TABLE I Yield and conductivity of polyaniline salt prepared under different reaction conditions in H_2SO_4

Method	Reaction conditions	Variable	Yield (%)	Conductivity (S/cm)
1	Aniline–2.4×10^{-6} m^3	Time (h)		
	BP–4.85	4	14.3	0.02
	SLS–1.44 g	8	51.4	0.08
	Solvent-Dioxane	12	59.5	0.06
	Acid-9×10^{-6} m^3	16	58.4	0.06
		20	58.5	0.06
		24	59.6	0.08
		28	58.1	0.08
		32	59.1	0.07
2	Aniline–2.4×10^{-6} m^3	BP (g)		
	SLS–1.44 g	1.5	Nil	Nil
	Solvent-Dioxane	3.0	22.5	0.05
	Acid-9×10^{-6} m^3	4.8	59.6	0.08
	Time–24 h	6.5	59.0	0.06
		8.5	56.8	0.04
3	Aniline–2.4×10^{-6} m^3	Acid		
	SLS–1.44 g	($\times 10^{-6}$m^3)		
	Solvent-Dioxane	3	31.0	0.006
	Time–24 h	6	55.9	0.04
		9	59.6	0.08
		12	26.9	0.009
		15	Nil	Nil
4	Aniline–2.4×10^{-6} m^3	SLS (g)		
	BP–4.85 g	1.0	58.7	0.08
	Solvent-Dioxane	2.0	55.0	0.08
	Acid-9×10^{-6} m^3	3.0	58.0	0.06
	Time–24 h	4.0	55.1	0.08
		5.0	55.9	0.07

3.2. Effect of oxidant concentration

The polymerization reaction of aniline was conducted with different amount of BP and the results are tabulated in Table I. For low concentration of BP (1.5 g), the polymerization reaction did not undergo and hence no yield was observed. When the concentration of BP was raised to 3 g, 22.5% of PANI-H_2SO_4 was obtained. For oxidant concentrations at and above 4.8 g, the yield (58–60%) and conductivity (0.04–0.08 S/cm) of the PANI-H_2SO_4 are found to be independent of the amount of BP used.

3.3. Effect of acid concentration

The bulk polymerization reaction was carried out with varying acid concentration and the effect of concentration of acid on yield and conductivity of the PANI-H_2SO_4 was examined. The reaction condition, yield and the conductivity of the PANI-H_2SO_4 samples were shown in Table I. The yield (31%) and conductivity (0.006 S/cm) of the PANI-H_2SO_4 salt are found to be low with the use of 3×10^{-6} m^3 of sulfuric acid. Reasonably good yield and conductivity were observed when polyaniline was prepared with 6×10^{-6} and 9×10^{-6} m^3 of sulfuric acid (Table I).

At higher acid concentrations (above 1.2×10^{-5} m^3 of H_2SO_4), the polyemeraldine chain undergo hydrolysis and as a consequence, the yield of polyaniline salt decreases.

3.4. Effect of sodium lauryl sulfate

The bulk polymerization of aniline was conducted with different amount of SLS (1 to 5 g in steps of 1 g) to study the effect of SLS on the polyaniline yield and conductivity. The yield (55–59%) and conductivity (0.07 to 0.08 S/cm) were found to be independent on the amount of SLS surfactant used.

The above results indicate that PANI-H_2SO_4 salt with reasonable yield and conductivity could be prepared with BP (5 g), SLS (1.0 g), H_2SO_4 (9×10^{-6} m^3) and reaction time (12 h).

The polymerization reaction was carried in presence and absence of SLS surfactant using three different acids, H_2SO_4, HCl and HNO_3. Electrical, physical and spectral results of the polyaniline salts are presented here.

3.5. Effect of different acids on the polymer yield and conductivity

Generally, higher yield and conductivity are observed for the polyaniline-sulfate, polyaniline-nitrate and polyaniline-hydrochloride salt with the use of SLS surfactant (Table II). As a representative case, the yield of polyaniline-hydrochloride salt is found to be 53.9% with the use of SLS when compared with that of the salt prepared without using SLS (46.8%). Similarly, higher conductivity (0.004 S/cm) is observed with the use of SLS than without using SLS (0.0003 S/cm).

The bulk polymerization of aniline was carried out with three different mineral acids HCl, H_2SO_4 and HNO_3 and the results are shown in Scheme 1. The values of yield (around 60%) and conductivity (around 0.08 S/cm) are found to be nearly the same for the polyaniline- sulfate and polyaniline-nitrate salts. However, conductivity of polyaniline-hydrochloride salt (0.004 S/cm) shows one order of magnitude lower than that of polyaniline-sulfate salt (0.08 S/cm).

The amount of dopant per aniline unit in polyaniline salt was calculated based on the weight of polyaniline base obtained from polyaniline salt using aqueous sodium hydroxide solution. The amount of acid group present in the polyaniline salt was found to be 29, 20 and 16 wt% for polyaniline-sulfate, polyaniline-nitrate and polyaniline-hydrochloride salt respectively. The conductivity of the polyaniline bases was found to be in the insulator range (10^{-10} S/cm) and this result indicates that all the acid part has come out from the polyaniline salt.

TABLE II Yield and conductivity of polyaniline prepared with and without SLS

	Yield (%)		Conductivity (S/cm)	
Polyaniline salt	With SLS	Without SLS	With SLS	Without SLS
PANI-H_2SO_4	59.6	52.4	0.08	0.01
PANI-HNO_3	55.0	51.7	0.08	0.02
PANI-HCl	53.9	46.8	0.004	0.0003

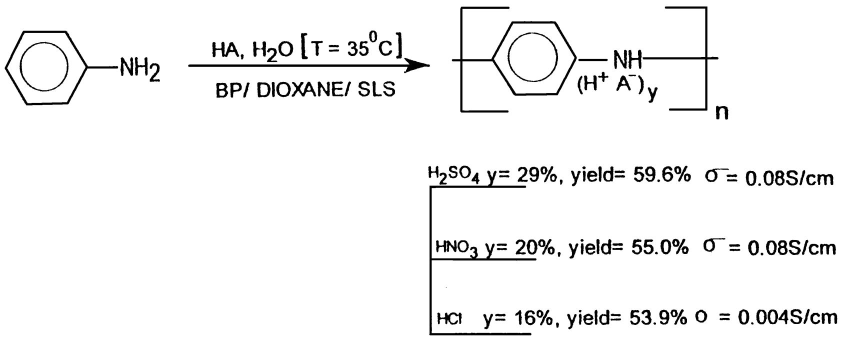
3.6. Effect of solvents

Chemical oxidative polymerization of aniline using cheaper mineral acids (H_2SO_4, HCl or HNO_3) by benzoyl peroxide in aqueous-organic medium (water miscible organic solvent-dioxane) yield polyaniline-sulfate salt in powder form. Whereas with benzene (water immiscible organic solvent), polyaniline-sulfate salt is solublized in organic carrier solvent (benzene). Organic solvent (benzene) soluble insulating polymers can be processed to electrically conducting polyaniline blends by solution processing method using this cheaper process.

The polyaniline salts were characterized by spectral measurements and the results are presented here.

3.7. Infrared spectra

Generally, similar infrared spectral behavior was observed for the polyaniline bases prepared from their corresponding salts. As a representative example, the infrared spectrum of polyaniline base PANI-BASE (HCl) is shown in Fig. 1a. The vibrational bands observed for the polyaniline base are reasonably explained on the basis of the normal modes of aniline and benzene; a broad band at 3415–3460 cm^{-1} is assigned to the N—H stretching vibration. The bands at 2920 and 2850 cm^{-1} are assigned to vibrations associated with the N—H part in $C_6H_4NHC_6H_4$ group or sum frequency.



Scheme 1

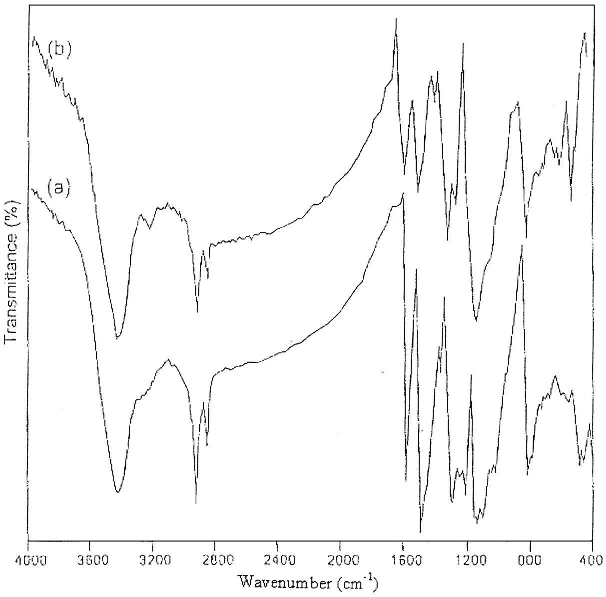


Figure 1 Infrared spectra of: (a) PANI-BASE (HCl) and (b) PANI-HCl salt.

1565 and 1490 cm^{-1} bands are due to quinonoid ring (Q) and benzenoid ring (B). The bands at 1370 and 1300 cm^{-1} are assigned to C—N stretching vibration in QBQ, QBB and BBQ, a 1240 cm^{-1} band to the C—N stretch vibration of aromatic amine. In the region of 1020–1170 cm^{-1}, aromatic C—H in-plane-bending modes are usually observed. For polyaniline, a strong band characteristically appears at 1140 cm^{-1}, which has been explained as an electronic band or a vibrational band of nitrogen quinone. A band at 705 cm^{-1} is assigned to ring C$\overset{\cdots}{-}$C bending vibration and the band at 580 cm^{-1} to ring in plane deformation. The C—H out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. For the polyaniline base, this mode was observed as a single band at 825 cm^{-1}, which falls in the range 800–860 cm^{-1} and is reported for 1,4-disubstituted benzene. The infrared spectra of polyaniline bases prepared are very close to the infrared spectra of the polyaniline base systems reported in the literature [11–14].

The infrared spectrum of polyaniline salt (PANI-HCl) is shown in Fig. 1b. The infrared spectrum of PANI-HCl is similar to that of PANI-BASE except a band around 3230 cm^{-1} that is assigned to the NH_2^+ group and indicates the protonated polyaniline salt. The doublet band at 1140 and 1110 cm^{-1} in the polyaniline base which is assigned to mode of Q=N^+H-B or Q-NH-B becomes a singlet in the salt spectrum.

3.8. Electronic absorption spectra

The electronic absorption spectra of polyaniline bases and polyaniline salts have been reported in the literature [15–17]. Absorption spectrum of polyaniline base shows two distinct absorption bands located between 320–340 and 600–650 nm depending on the method of preparation and/or processing of polyaniline. The band around 320–340 nm and the band around 600–650 nm are assigned to the excitation of the amine and imine segments of the polymer chain.

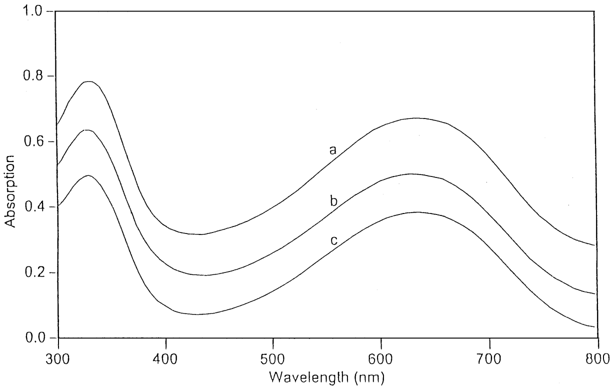


Figure 2 Electronic absorption spectra of: (a) PANI-BASE (HCl), (b) PANI-BASE (H_2SO_4) and (c) PANI-BASE (HNO_3) recorded in DMSO.

Polyaniline salt in the powder form is not soluble in most of the organic solvents. However, polyaniline base is sparingly soluble in 1-methyl-2-pyrrolidone (NMP), Dimethyl sulfoxide (DMSO) and Dimethyl formamide (DMF). The electronic absorption spectra of the DMSO soluble fractions of the polyaniline bases prepared from their corresponding salts are very nearly the same (Fig. 2). The electronic absorption spectra of polyaniline bases showed a band around 320–330 nm and another broad band around 620–650 nm. These two peaks are assigned to the excitation of the amine and imine segments of the polymer chain respectively and are consistent with literature reports on polyaniline base. The absence of the peak above 725 nm, which is due to the polaron, shows that dedoping of the salt is complete.

3.9. X-ray diffraction studies

The X-ray diffraction patterns of PANI-HCl, PANI-H_2SO_4 and PANI-HNO_3 are shown in Fig. 3a to c. The X-ray diffraction pattern of the PANI-HCl

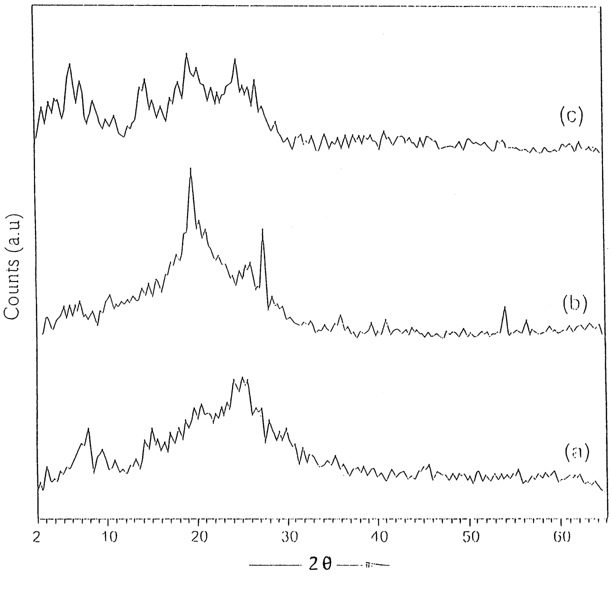


Figure 3 X-Ray diffraction pattern of: (a) PANI-HCl, (b) PANI-H_2SO_4 and (c) PANI-HNO_3.

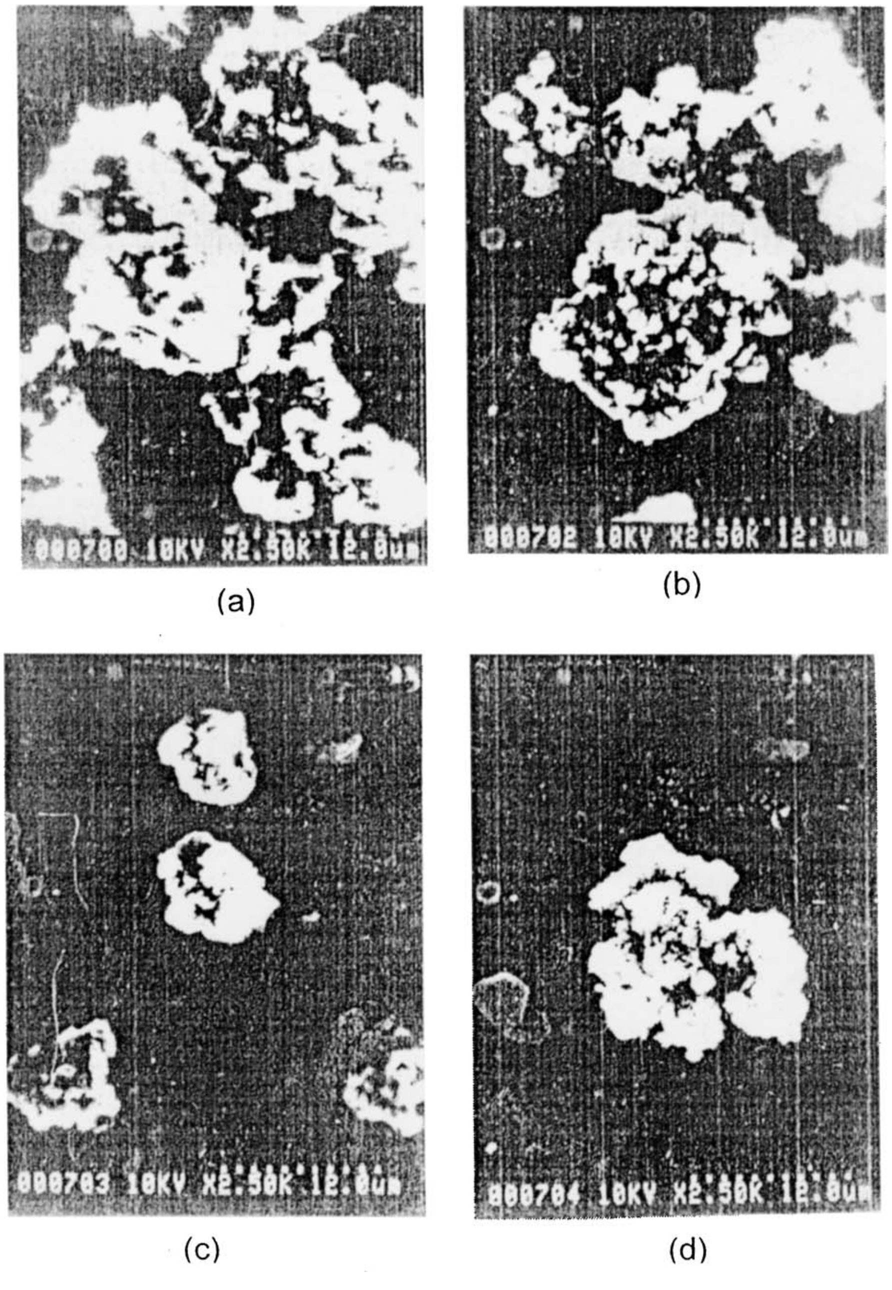
shows sharp peaks 2θ at 9°, 20°, 25°, 30° and 35°. These positions are in accordance with the earlier report [18]. A similar X-ray diffraction pattern was observed for PANI-H_2SO_4 and PANI-HNO_3 salt. The positions of the peaks vary with the dopant indicating different inter chain packing. In all cases, the peak at 2θ–10° is observed which arises from scattering with momentum transfer approximately parallel to the polyaniline chains [19]. PANI-H_2SO_4 show more crystalline (more sharper) than that of PANI-HCl and PANI-HNO_3.

3.10. Scanning electron microscopy

The morphology of PANI-H_2SO_4, PANI-HCl and PANI-HNO_3salts, and PANI-BASE of H_2SO_4 salt is shown in Fig. 4a to d. Generally, polyaniline salts and bases prepared in the present work show aggregated granular form, with moderate degree of crystallinity and lack macroscopic molecular orientation. The shape of the chemically polymerized polyaniline particles is generally difficult to control in bulk polymerization process.

3.11. X-Ray photoelectron spectra

The X-ray photoelectron spectrum (XPS) for the polyaniline base [PANI BASE (H_2SO_4)] shows two peaks, the N1s peak centered at 399 eV due to nitrogen and 284 eV due to carbon-C1s (Fig. 5a). The N1s peak can be deconvoluted into two peaks with one at 398.0 eV and other at 399.1 eV. The peak at 398.0 corresponds to the imine nitrogen atoms and one at 399.1 eV to the amine nitrogen atoms. The ratio of the integrated area of these two peaks is 1:1.1. The absence of the peaks at 401.3 and 402.6 eV supports the observed insulating nature of the sample due to complete dedoping. The peak positions are in good agreement with those



(a) (b)

(c) (d)

Figure 4 Scanning electron micrograph of: (a) PANI-H_2SO_4, (b) PANI-HCl, (c) PANI-HNO_3 and (d) PANI-BASE (H_2SO_4).

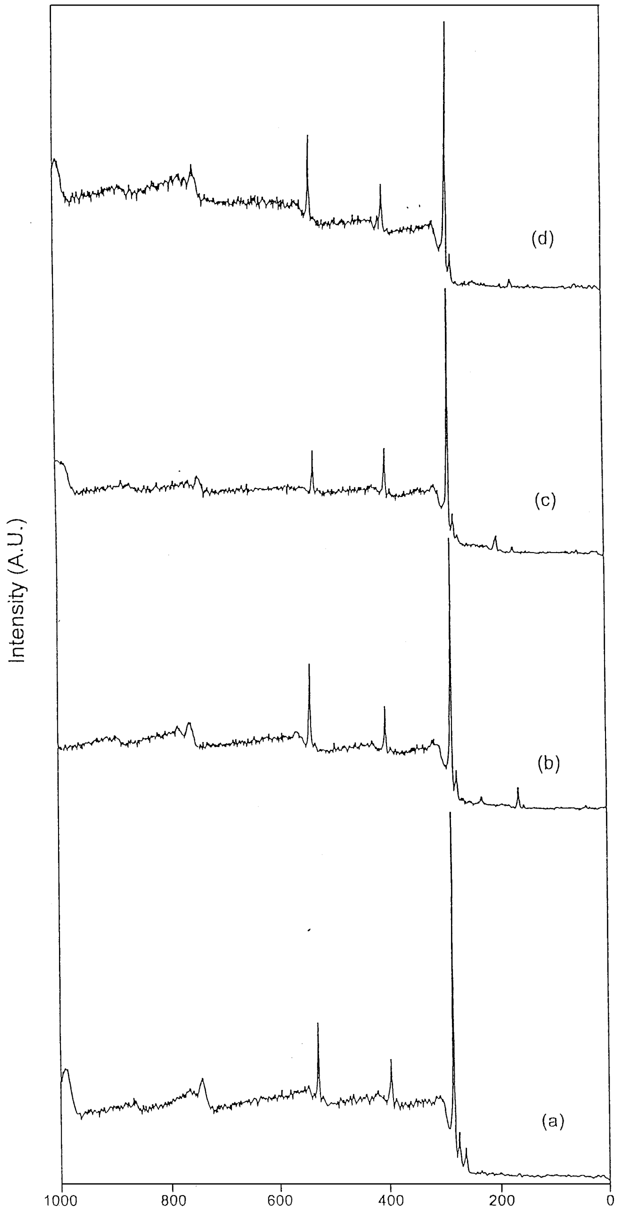


Figure 5 XPS spectra of: (a) PANI-BASE (H_2SO_4), (b) PANI-H_2SO_4, (c) PANI-HCl and (d) PANI-HNO_3.

found in literature on XPS spectral analysis of emeraldine base and its salt [20] and also in the study on the interconversion of unit structures in polyaniline [21].

The XPS spectrum of the polyaniline sulfate salt shows peaks at 534.0, 402.0, 287.0 and 171.0 eV (Fig. 5b) corresponding to the elements oxygen, nitrogen, carbon and sulfur respectively. The elements carbon and nitrogen are due to polyaniline system and oxygen is due to sulfuric acid dopant. In order to find out the presence of SLS dopant in addition to the presence of sulfuric acid dopant, the peak due to sulfur (171 eV) was deconvoluted. The sulfur peak can be split in to four components located at 169.9, 171.2, 170.6 and 171.8 eV (Fig. 6a). The peaks at 169.9 and 170.6 eV are due to the S $2p_{1/2}$ and S $2p_{3/2}$ originating from the $-SO_3^-$ group of the sodium lauryl sulfate which was used as a surfactant. The peaks at 171.2 and 171.8 eV correspond to the S $2p_{1/2}$ and S $2p_{3/2}$ of the $-SO_4$ group of the dopant.

The XPS spectrum of PANI-HCl salt (Fig. 5c) show peaks at 287 eV due to C1s, 401 eV due to N1s, 199.1 & 202.3 eV due to Cl $2p_{3/2}$ & Cl $2p_{1/2}$ and 171 eV due to S 2p. The S 2p peak at 171 eV can be split into two components one located at 170.1 and 171.0 eV due to S $2p_{1/2}$ and S $2p_{3/2}$ originating from the $-SO_3^-$ group of the sodium lauryl sulfate (Fig. 6b). The elements carbon and nitrogen correspond to polyaniline system and the presence of chlorine and sulfur elements in the polyaniline salt is due to hydrochloric acid and sodium lauryl sulfate respectively.

The XPS spectrum of PANI-HNO_3 salt shows peaks at 534.0, 402.0, 287.0 and 170.0 eV which are attributed to the presence of oxygen, nitrogen, carbon, sulfur elements present in the polyaniline nitrate salt (Fig. 5d). The sulfur peak at 170.0 eV arises due to the doping of the surfactant sodium lauryl sulfate on to the polyaniline backbone. The sulfur peak can be deconvoluted into two components one located at 170.1 eV and the other at 171.29 eV (Fig. 6c).

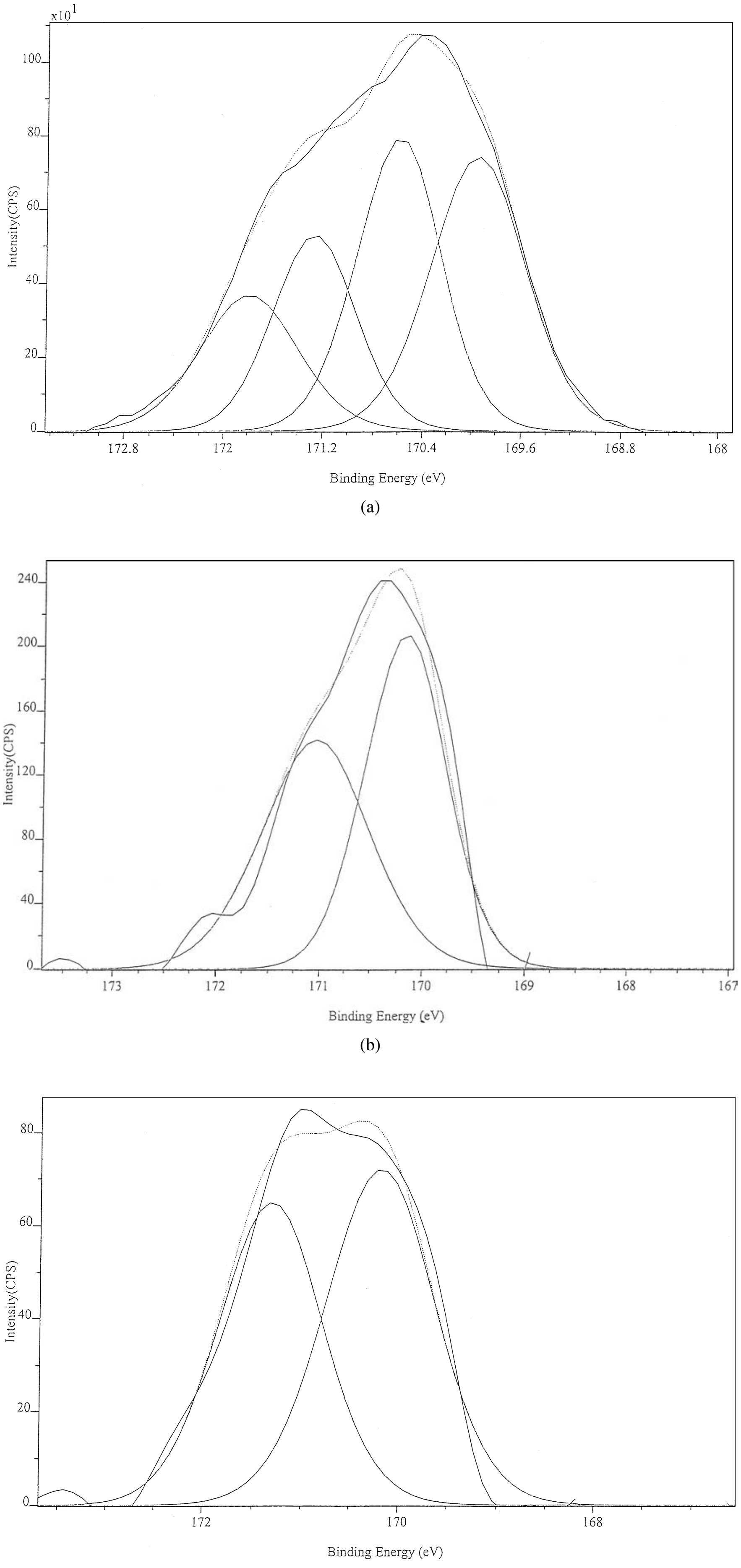
The presence of the S 2p peak in all the samples shows that the surfactant sodium lauryl sulfate used in the synthesis of polyaniline salts gets converted to the corresponding sulfonic acid under acidic conditions and doped onto the polyaniline back bone along with the mineral acid.

3.12. Elemental analysis

The elemental analyses of polyaniline bases, polyaniline salts and the polyaniline salt prepared without using SLS are given in Table III. The percentage of carbon, hydrogen and nitrogen of polyaniline bases are found to be nearly the same as that of the theoretically calculated value. This result shows the formation of polyaniline bases and all the acid part has been removed from the corresponding salts by dedoping. The sulfur content of the polyaniline-sulfate salt (due to the presence of H_2SO_4 dopant.) prepared without using SLS was found to be 3.2%. The value of sulfur content increased from 3.2 to 7.4% in the case of polyaniline sulfate salt prepared using SLS and this result indicates that both SLS and H_2SO_4 dopants are present in the polyaniline sulfate salt. Also, the presence of sulfur element was observed in the case of polyaniline-nitrate (2.3%) and polyaniline-hydrochloride salt (2.1%). The elemental analysis results indicate the presence of both lauryl sulfate and acid group as dopants in the polyaniline salt. From the present study, it is difficult to calculate

TABLE III Elemental analysis result of polyaniline base, polyaniline salt prepared with and without SLS

Polyaniline	C%	H%	N%	S%
PANI-HCl-base	78.3	5.2	14.7	
PANI-H_2SO_4-base	78.8	5.1	14.3	
PANI-HNO_3-base	78.2	5.4	15.1	
Polyaniline-base (theoretical)	79.1	5.5	15.5	
PANI-H_2SO_4 (without using SLS)	58.9	4.3	11.5	3.2
With SLS				
PANI-HCl	62.3	4.5	11.2	2.1
PANI-H_2SO_4	52.9	3.2	10.4	7.4
PANI-HNO_3	58.5	4.2	14.0	2.3



(a)

(b)

(c)

Figure 6 S2p XPS spectrum of: (a) PANI-H_2SO_4, (b) PANI-HCl and (c) PANI-HNO_3.

the amount of SLS or H_2SO_4 dopant present in the polyaniline salt.

4. Conclusions

The results in this paper show that it is possible to prepare polyaniline salts such as polyaniline-sulfate, polyaniline-nitrate or polyaniline-hydrochloride with reasonable yield and conductivity by emulsion polymerization pathway using benzoyl peroxide as an oxidizing agent. Infrared, electronic absorption, X-ray diffraction spectral techniques, scanning electron microscope, X-ray photoelectron, elemental analysis and conductivity measurement results support the formation of polyaniline salts which are prepared using benzoyl peroxide. Both acid and surfactant group are present in the polyaniline salts as dopant. The optimum reaction conditions for the polymerization of aniline by benzoyl peroxide are: aniline –2.4×10^{-6} m^3, BP –4.85 g, SLS–1.45 g, reaction temperature –35°C, reaction time –12 h, protic acids (a) sulfuric acid (9×10^{-6} m^3), (b) hydrochloric acid (1.75×10^{-5} m^3), and (c) nitric acid (1.26×10^{-5} m^3).

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