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Full Length Article

## Synthesis and optical characterization of benzene sulfonic acid doped polyaniline

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## ARTICLE INFO

## Article history:

Received 3 July 2018

Revised 5 September 2018

Accepted 24 September 2018

Available online 5 October 2018

## Keywords:

Acid doped polyaniline

Benzene sulfonic acid

Conducting polymer

Optical band gap

## ABSTRACT

In this study, Polyaniline emeraldine base (PANI-EB) and benzene sulphonic acid (BSA) doped polyaniline (PANI-BSA), HCl doped Polyaniline (PANI-HCl), and BSA and HCl doped Polyaniline (PANI-HCl-BSA) polymers were synthesized. Synthesizing was accomplished by chemical oxidative polymerization of aniline in acidic environment at room temperature (20 °C). Aniline to ammonium peroxydisulfate (APS) ratio is 1:1.25, and aniline to acid ratio is 1:1 for PANI-HCl and 1:0.5:0.5 for PANI-HCl-BSA. PANI-EB was obtained by de-doping PANI-HCl with NH<sub>3</sub>. In order to determine the type and degree of doping, electrical conductivity, band gap values, physical and structural properties were investigated. Structural properties of the doped and undoped PANI samples were determined using Fourier transform infrared spectroscopy (FT-IR), Ultraviolet visible spectroscopy (UV-vis) and (SEM), and electrical was determined using four-point probe method. PANI-BSA, PANI-HCl-BSA and PANI-HCl doped polymers conductivity were measured as 1.39, 0.77 and 0.54 S.cm<sup>-1</sup> respectively. Band gap values calculated by Kubelka-Munk equation are 2.35, 2.38, 2.40 eV respectively. The conductivity of the insulating PANI-EB polymer was measured as 2.9.10<sup>-4</sup> S.cm<sup>-1</sup> and its energy band gap was found as 3.06 eV. PANI-BSA, showed higher solubility in dimethylsulphoxide (DMSO) compared to PANI-HCl which is more commonly known. With its high conductivity, high resolution and low band gap, PANI-BSA has proven to be a suitable interface for electronic devices.

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## 1. Introduction

Polymeric systems offer new opportunities to synthesize promising new materials with better electrical, optical and magnetic properties. Conductive polymers have many areas of application such as light-emitting diodes [1], field-effect transistors [2], photovoltaic cells [3], solar cells [4] and Schottky diodes [5]. Conductive polymers have many advantages such as improved interface properties, suitability for lightweight device production, lower cost, and increased productivity [6–8]. On the other hand, polymerization process should involve a simple organic synthesis method for repeatable control of macromolecular architecture. As a conductive polymer, polyaniline (PANI), does not require any special equipment or precaution during the synthesis stage [9]. In addition, PANI is one of the most popular research topics in the field of conducting polymers due to its good electrical proper-

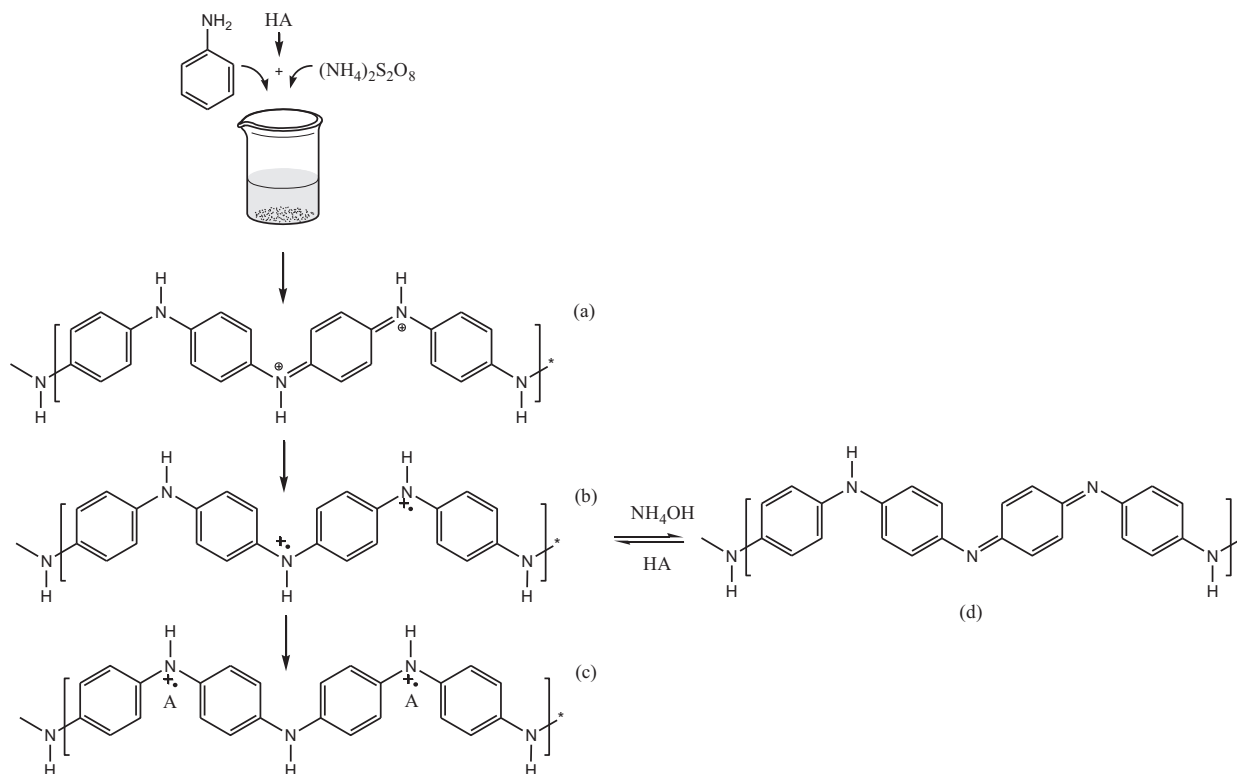
ties, controllable conductivity via reversible acid / base conversion, and excellent environmental stability [10]. When PANI contains 50% reduction and 50% oxidation conditions, such structure is called emeraldine base (PANI-EB) (Fig. 1d). That is, after two aromatic amine atoms, two aromatic imine atoms must be arranged in order. From the oxidation of aniline in the presence of acid, the emeraldine salt (PANI-ES) is formed. PANI-ES is the protonated form of PANI-EB. Properties of conductive polymers depend on dopant and solvent type, protonation level, dopant ion size, and preparation conditions (temperature, monomer/oxidant ratio, etc.) [11]. Due to these modifications, considerable changes in electrical, optical and structural properties have been achieved [11]. Generally, PANI is produced in a dark green solid phase with oxidative polymerization in an acidic aqueous medium [12,13]. Different acids have been used as dopant in the preparation of PANI, including organic and inorganic acids [14–17].

Many researchers have used functionalized dopants such as organic acids (sulfonic or carboxylic) to produce a more stable, more soluble (easier processed) and more conductive polyaniline [18]. As shown in Fig. 1, when PANI is synthesized in the presence of acid, initially a bipolar structure is formed which is followed by

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Peer review under responsibility of Karabük University.



**Fig. 1.** PANI chemical oxidative polymerization (a) protonated PANI (b) polaron formation (c) polaron regulation (d) PANI-EB formation.

formation of a polar structure [19]. Polaron structure formation produces PANI-ES with protonation. When a conductive polymer is electrified, the dopant begins to move along the polymer, which impairs the steady state as polarons are able to move along polymer chains, thus allowing electrical conductivity [20]. Doping effect is the removal of electrons from the molecular orbital of the valence band or their transfer to the lowest empty molecular orbital of the transmission band. This leads to formation of load carriers such as polaron and bipolaron in the polymer [21]. Thus, polaron charge carriers, that form energy levels in the forbidden energy band through doping, allow electrons to pass from the valence band to the conduction band.

In this study doped PANI samples were synthesized by the help of HCl and BSA acids for the first time to determine the effects of these acids on the structural, electrical and optical properties of the conductive PANI-ES and insulating PANI-EB samples which were synthesized by doping and de-doping. Studies have shown that PANI increases its solubility when doped with sulfonic acid. This is important for coating the polymer as a thin film. Due to its high conductivity and good solubility, PANI-BSA has a good interface potential for the production of many optoelectronic devices such as diodes and transistors.

## 2. Experimental procedures

In this study, Aniline (99.5%) (Aldrich chemicals) was used as freshly distilled. Aniline hydrochloride (>99%) (Aldrich) was used as an alternative monomer to aniline monomer which is toxic and difficult to transport. Ammonium peroxydisulfate ( $\geq 98\%$ ) (Aldrich), Benzenesulfonic acid (98%) (Aldrich), Hydrochloric acid (37%) (Merck), Acetone (>99.8%) (Merck), DMSO (>99.9%) (Merck) were also used in the study. Doped PANI samples were synthesized using a standard method which was reported to result in high conductivity [22].

Polymerization was achieved by dropwise addition of an aqueous solution of aniline and acid ammonium peroxydisulfate at room temperature. The resulting solid PANI-ES was separated by filtration and drying. Using this method, it is possible to prepare the PANI with a predefined conductivity although not the highest possible level. PANI was produced by the oxidation of 0.2 M aniline monomers in aqueous medium with 0.25 M ammonium peroxydisulfate. 50 ml of an aqueous solution of aniline hydrochloride (2.59 g, 20 mmol) was prepared, and 50 ml of APS (5.71 g, 0.25 mmol) was added dropwise into this solution. Conductive PANI precipitated with a dark green color in 30 min. Stirring period was 1 h. After the polymerization was maintained at room temperature for 24 h, the reaction was completed. After the filtration in vacuum, it was initially washed three times by 0.1 M 100 ml HCl solution, and three times by 100 ml Acetone, which was followed by drying at 60 °C temperature. HCl doped PANI (PANI-HCl) was produced with 87% yield. PANI-BSA on the other hand was synthesized with 80% yield with the same method by taking Aniline/BSA ratio as 1:1 equivalent mol. PANI-HCl-BSA was synthesized with 83% yield by taking Aniline/BSA/HCl ratio as 1:0.5:0.5 mol. After the HCl-PANI washing step, it was mixed with 1 M 100 ml Ammonia (NH<sub>4</sub>OH) solution for 1 h at room temperature for de-doping again. PANI-EB was obtained by filtration of the reaction mixture which turned into a dark blue color after drying at 60 °C.

To measure conductivity, the powder polymer samples were pelleted (7 mm diameter) with KBr using an IR pelletizer and I-V measurements were done with 4-point using KEITHLEY 2400 SourceMeter and 2100/220 KEITHLEY Multimeter. FT-IR spectra of the pelleted polymers were recorded using FT-IR spectrometer (BRUKER ALPHA with a resolution of 4 cm<sup>-1</sup>; instrument has a DTGS detector and 10 scans were conducted for each spectrum). 2D surface morphologies were investigated with high resolution SEM (Carl Zeiss ULTRA PLUS GEMINI FESEM). UV-vis spectra of PANI samples dissolved in DMSO were recorded as the absorbance and

reflectance measurements at room temperature in 300–1000 nm wavelength range using a Perkin Elmer Lambda 35 Spectrophotometer.

### 3. Results and discussion

#### 3.1. Structural and surface properties

In Fig. 2, the FT-IR spectrum was recorded at 400–2000  $\text{cm}^{-1}$ . Fig. 2 shows that doping with acid effectively changed the PANI-EB environment. Doped PANI and PANI-EB forms are quite different from each other. The peaks in PANI-EB form are sharper and higher as compared to the doped forms. By protonation, the imine nitrogen atom of the structure of PANI-EB transforms into the amine nitrogen atom. The degree of oxidation can be predicted depending on the relative intensities of FTIR absorption peaks of benzenoid and quinoid stretching vibrations [23]. These peaks, which are at 2:3 ratio in PANI-EB, have a ratio of about 1:1 in the doped PANI samples. This shows that the rate of protonation in the conductive samples is 50%. The peaks observed in the PANI-EB, PANI-HCl, PANI-BSA and PANI-HCl-BSA polymers are

given in Table 1 and appear to be very consistent with the literature [24].

The peaks at 1589 and 1497  $\text{cm}^{-1}$  in PANI-EB were shifted to 1578 and 1483  $\text{cm}^{-1}$ , in the doped samples. This can be explained by the benzenoid-quinoid ring transitions depending on the degree of protonation. Also, a doped  $\text{C-N}^+$  2° aromatic amine peak which indicates conductive structure was observed at  $\sim 1250 \text{ cm}^{-1}$ .

Fig. 3 shows the SEM images of 2D surface morphologies of the PANI salts, which indicate that PANI salts have an isometric shape and particle clusters are formed. Fig. 3(a) at 20.00 K magnification shows that the granules of PANI-HCl are spherical and those of PANI-BSA and PANI-HCl-BSA are tubular at the same magnification. This fibrillar structure of the polymer chains ensures that the polymer chain is arranged or closely packed in a sequential manner which allows easy transfer of the load carriers on the polymer chains and provides a better conductivity [25].

#### 3.2. Optical properties

Fig. 4 shows the UV-vis spectra of PANI structures dissolved in DMSO. Spectroscopic scanning was performed at a wavelength

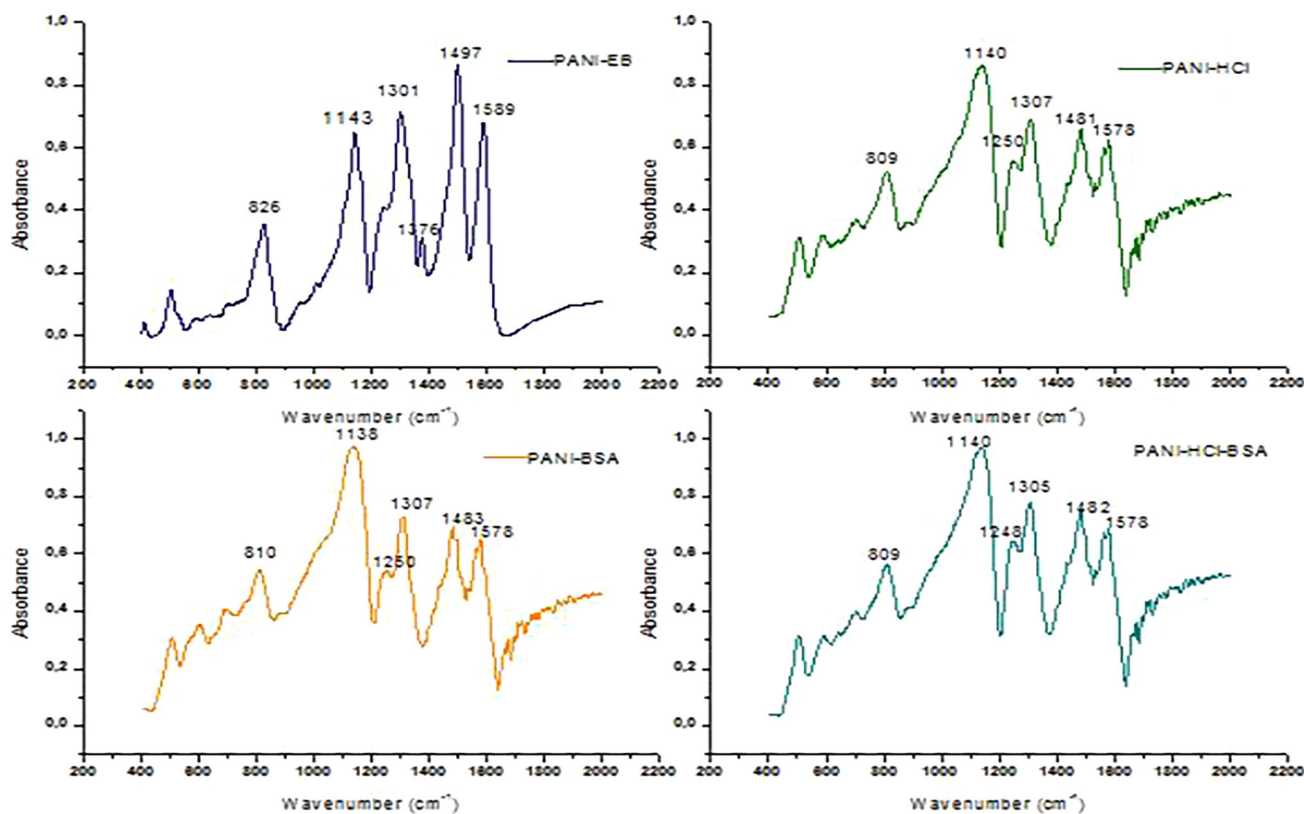


Fig. 2. FT-IR spectra of PANI-EB and PANI-ES.

Table 1

Peaks for the functional groups observed in FT-IR spectrum.

Assignments		PANI-Baz	PANI-HCl	PANI-BSA	PANI-HCl-BSA
Quinoid (Q) ring stretching	$\text{N}=\text{Q}=\text{N}$	1589	1578	1578	1578
Benzenoid (B) ring stretching	$\text{N}-\text{B}-\text{N}$	1497	1481	1483	1482
C-N of secondary aromatic amine [22]	C-N	1301	1307	1307	1305
C-N stretching in QBQ units [22]	C-N	1376	-	-	-
C-N <sup>+</sup> in the polaron lattice of PANI	C-N <sup>+</sup>	-	1250	1250	1248
Q=NH <sup>+</sup> -B or B-NH <sup>+</sup> -B	C-H	1143	1140	1138	1140
(1,4-disubstituted ring)/Q ring deformation	C-H	826	810	809	810



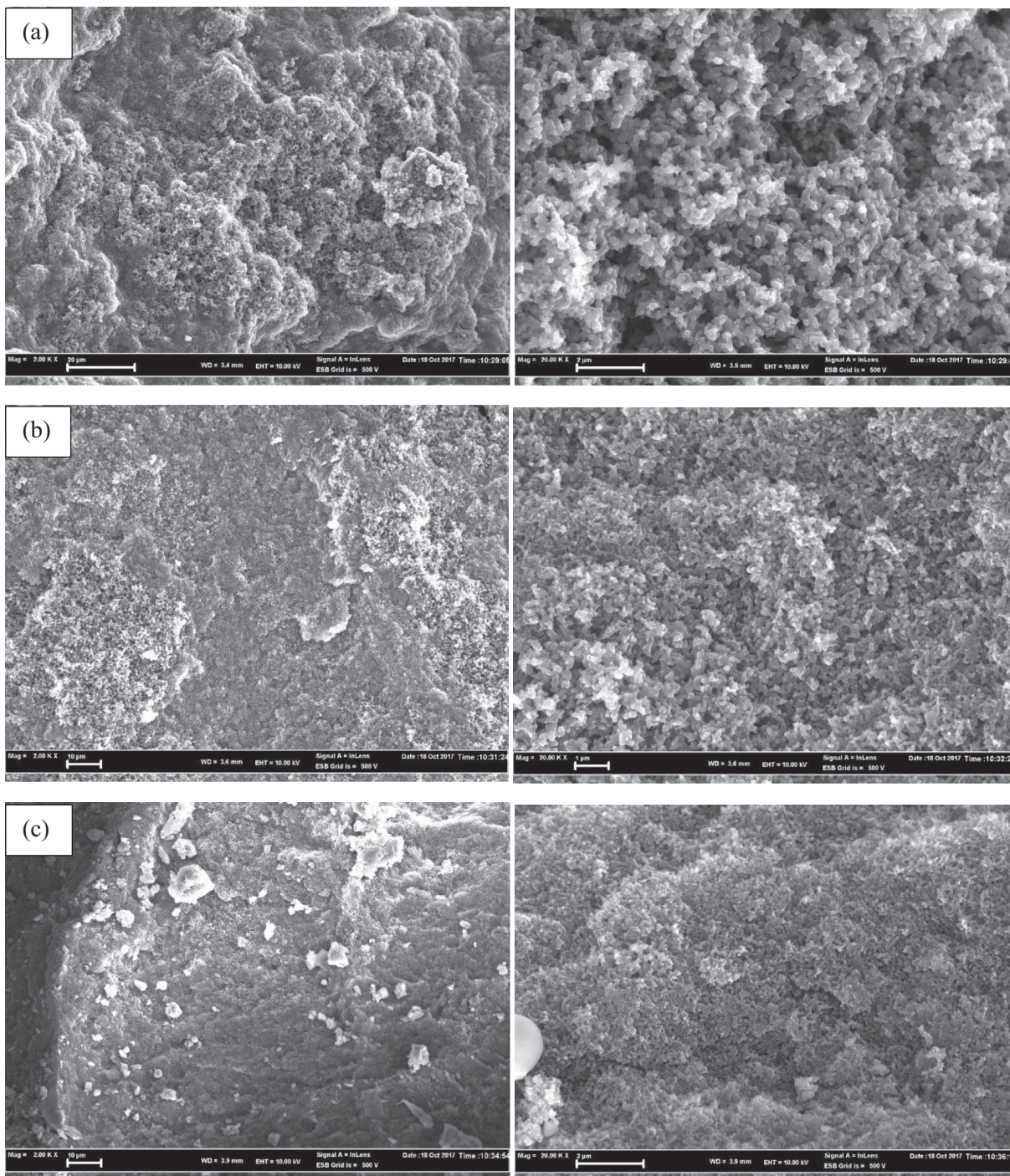


Fig. 3. SEM micrographs of PANI salts (a) PANI-HCl (b) PANI-HCl-BSA and (c) PANI-BSA.

range from 300 to 1000 nm. The UV-vis spectrum is useful for measuring the amount of conjugation, and for this reason, conductive polyaniline samples exhibit a broad absorbance, referred to as a free carrier tail, at wave lengths greater than about 800 nm. As the conjugation length gets longer, the peak shifts to broader wavelengths and becomes extremely large [18]. Fig. 4 shows two characteristic absorption bands of 320 nm and 630 nm of the PANI-Base showing the  $\pi$ - $\pi^*$  transition of benzenoid rings and quinoid rings, respectively [26].

Conjugate-structured molecules are quite colorful since the  $\pi$ - $\pi^*$  energy range is in the visible range. PANI is; purple in the fully oxidized form which is pernigraniline, dark blue in protonated

pernigraniline, dark green in emeraldine and dark blue in protonated emeraldine. The decrease in the absorption band at about 630 nm in the case of doped PANI indicates that the imine nitrogen atoms of the quinoid rings are converted to benzenoid rings by protonation by HCl and BSA dopants. The decrease in the peak of the doped samples at 630 nm can be attributed to the steric effect of dopant anions. Typically, the emeraldine base shows  $\pi$ - $\pi^*$  transition absorption at approximately 320 nm and quinoid exciton absorption at approximately 630 nm (Table 2). Upon doping, the quinoid transition disappears and two new absorbances occur (Table 3). These new absorbances point to polaron and bipolar transitions at 920 and 440 nm respectively.

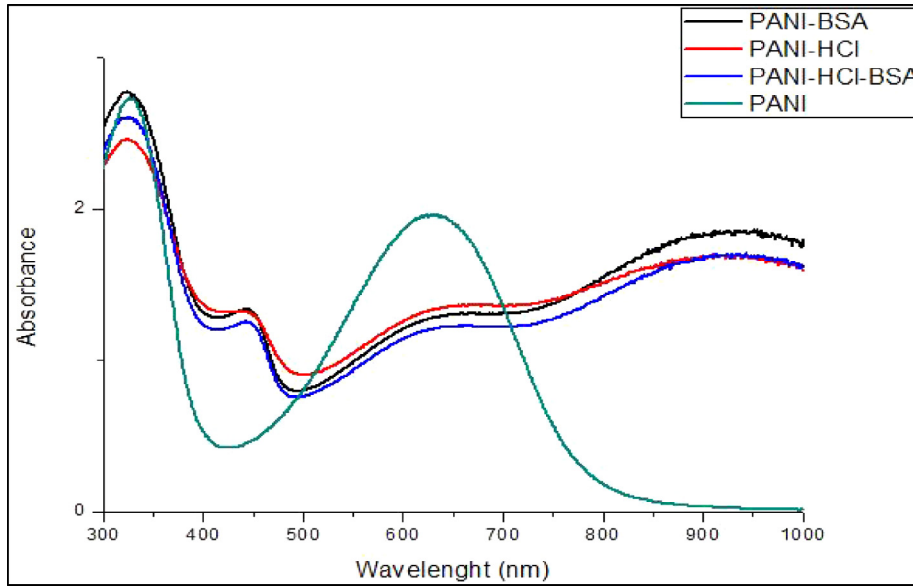


Fig. 4. UV-visible spectra measurements of PANI-EB and PANI-ES.

**Table 2**  
Absorption values observed in the UV-vis spectrum of PANI-EB.

Absorption Wavelength (nm)	Assignment
320	Benzenoid $\pi-\pi^*$ transition
630	Exciton absorption of the quinoid ring

**Table 3**  
Absorption values observed in the UV-vis spectrum of PANI-ES.

Absorption Wavelength (nm)	Assignment
328	Benzenoid $\pi-\pi^*$ transition
440	Bipolaron
920	Polaron

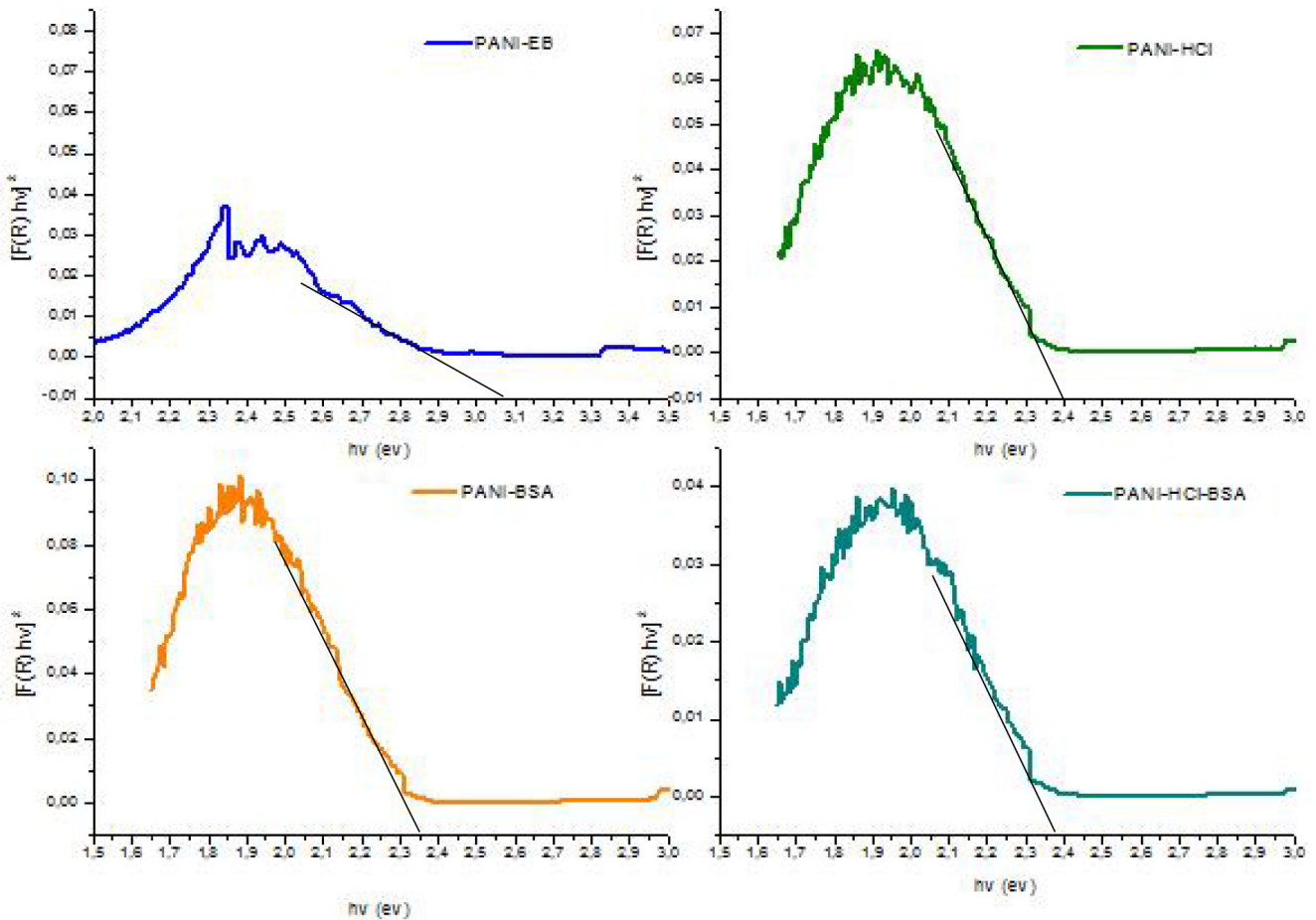



Fig. 5. Optic band gap graph for PANI and doped polymers.



**Table 4**  
Conductivity and solubility values of PANI polymers.

	$\sigma$ (S.cm <sup>-1</sup> )	E <sub>g</sub> (eV)	Solubility (g/L)
PANI-EB	0.00029	3.06	3
PANI-BSA	1.39	2.35	1.4
PANI-HCL-BSA	0.77	2.38	0.8
PANI-HCL	0.54	2.40	0.6



(PANI-EB)

(PANI-ES)

In order to obtain the optical properties and energy range of the PANI samples, diffuse-reflection measurements were performed on the samples on the UV–vis region at room temperature. The band gap energies of acid-doped PANI samples were calculated from diffuse-reflection spectrum by applying Kubelka-Munk function [27] in Eq. (1):

$$F(R) = \frac{(1 - R)}{2R} \quad (1)$$

where, R is the observed reflection in UV/vis spectrum. The intersection point in the  $[F(R) h\nu]^2 - h\nu$  graph (Fig. 5) shows the optical band gap, where h is the Plank constant and  $\nu$  is the photon frequency. Using this method, the optical band gaps of the un-doped PANI-EB, PANI-BSA, PANI-HCl-BSA and PANI-HCl polymers were found to be 3.06, 2.35, 2.38 and 2.40 eV, respectively. Experimental results show that the band gap of PANI varies considerably with doping. As the interactions between the PANI matrix and the HCl and BSA dopant anions increase, conductivity of the particles and the number of load carriers increase and the band gap value decreases.

The E<sub>g</sub> value of the doped PANI samples is in agreement with the conductivity results (Table 4). The highest conductivity and the lowest E<sub>g</sub> value were obtained with PANI-BSA. PANI-HCl was observed to be less environmentally stable and less soluble, probably due to the high mobility of the chloride ion. BSA doping was found to contribute to the improvement of solubility by decreasing the interchain interaction (Table 4).

#### 4. Conclusion

- a) Pure PANI, PANI-BSA, PANI-HCl and PANI HCl-BSA polymers were successfully synthesized by chemical oxidation.
- b) FT-IR and UV studies confirm that doping causes structural changes in the polymer chains.
- c) Conductivity increased considerably due to the load carrier levels (polaron, bipolaron) formed by the doping. Similarly, the optical band gaps of the pure PANI, PANI-HCl, PANI-BSA and PANI-HCl-BSA polymers were found to be 3.06, 2.40, 2.35 and 2.38 eV, respectively.
- d) BSA doping provided both high conductivity and better solubility. Organic acids (sulfonic) were found to be suitable for use as dopant to produce more stable, more soluble (improved processability) and more conductive polyaniline. As a result conductive PANI-BSA and PANI-HCl polymers

with advanced optical properties seem to have a good interface potential for the production of many optoelectronic devices such as diodes and transistors.

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