

# Synthesis and Characterization of Electrically Conducting Polyaniline Doped with Glacial Acetic Acid (CH<sub>3</sub>COOH) at Room Temperature

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**Abstract:** Polyaniline (PANI) has been prepared by chemical oxidation method at room temperature and the effect of concentration of dopant Glacial Acetic Acid (CH<sub>3</sub>COOH) on the structure of the polymer was investigated. Polymers prepared in absence and in the presence of varying concentrations of CH<sub>3</sub>COOH were characterized using UV-visible, FTIR spectroscopy and conductivity measurements. In UV-visible spectra of PANIs recorded in DMSO revealed that absorption bands increases with increasing concentration of CH<sub>3</sub>COOH. The FTIR spectra shows the absorption bands related to quinoid and benzenoid rings for the undoped and doped PANI in CH<sub>3</sub>COOH indicating that the polymer is composed of amine and imine units. Highest conductivity value was obtained in presence of 1.0 M CH<sub>3</sub>COOH indicating that the more preferable doping of PANI will be at this concentration of CH<sub>3</sub>COOH. The effect of the temperature upon the conductivity of PANI synthesized with different concentrations of CH<sub>3</sub>COOH has been studied.

**Keywords:** Doped PANI, CH<sub>3</sub>COOH, FTIR, UV-visible, Conductivity.

## 1. INTRODUCTION

During the last decade polyaniline (PANI) and its derivatives has become the polymer of great scientific and industrial importance because of their electronic properties for use in electronic devices, electro chromic devices, sensors, batteries and optical switching devices [1-7]. Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family has been prepared through chemical polymerization in acidic media using an oxidizing agent such as potassium dichromate, ammonium persulphate, hydrogen peroxide, cerium nitrate, etc. [7-14]. The advantage of chemical synthesis is that, it offers mass production of conducting polymer at low cost. Although the synthetic methods to produce polyaniline (PANI) are quite simple, its mechanism of polymerization and the exact nature of its oxidation chemistry are quite complex. In addition, the electrical and optical properties of PANI conducting polymers are highly dependent on the presence of substituent, the nature of the dopant, other synthetic conditions (temperature, time, etc.) [15]. The properties of conducting PANI are affected by the type of dopant ion employed. The dopants increase the solubility as well as the conductivity of PANI [16-19]. Polyaniline doped or protonated with acids like HCl, H<sub>2</sub>SO<sub>4</sub> or some organic sulphonic acid exhibited good electrical conductivity value. Also, the dopants having carboxyl group were reported to increase the solubility of PANI [16]. In our previous work [20], the effect of different dopants such as Hydrochloric acid (HCl), Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and

Formic acid (HCOOH) on the structure of PANI was achieved and reported. In this work the effect of different concentrations of Glacial acetic acid (CH<sub>3</sub>COOH) as a doping agent on the structure of polyaniline (PANI) prepared at room temperature are discussed using UV-visible, FTIR spectroscopy and conductivity measurements.

## 2. EXPERIMENTAL

### 2.1. Materials

Aniline (ANI) (ADWIC, Egypt), potassium dichromate (Merk, Germany), Glacial acetic acid (CH<sub>3</sub>COOH 99.5 % by mass) (Merk, Germany), Ethanol and dimethyl sulfoxide (DMSO) are used for filtration and UV-visible measurements respectively. All chemicals, acid and solvents were used as received without further purifications.

### 2.2. Measurements

For measuring the UV-visible absorption spectra, spectrophotometer (UV-1601 SHIMADZU) was used. The FTIR spectra were recorded using FTIR 8201PC (SHIMADZU) instrument by KBr Pellets techniques. Conductivity measurements were made at room temperature by dissolving 0.03 g of the polymer sample in 15 ml of DMF solvent using conductivity meter (CM-30V).

### 2.3. Synthesis of Polyaniline (PANI) at Different Concentrations of Glacial Acetic Acid (CH<sub>3</sub>COOH) Using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as Oxidizing Agent in the Following Procedure

Poly aniline (PANI) was prepared at 1M CH<sub>3</sub>COOH using K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> as follow: (0.974 ml) (0.0107 mol) of

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previously distilled aniline was dissolved in 25 ml  $\text{CH}_3\text{COOH}$  1M (99.5 % wt) at room temperature. The obtained solution was cooled to about  $2^\circ\text{C}$  in an ice bath. A solution of 3.147 g  $\text{K}_2\text{Cr}_2\text{O}_7$  dissolved in 25ml  $\text{CH}_3\text{COOH}$  was added drop wise into the cold aniline acid solution under constant stirring over a period of 30 min. The mixture was stirred over additional 2 hrs and its temperature was kept in  $2^\circ\text{C}$  during this period, at the end of this period of time, a dark green solid was formed in the reaction medium. This solid was filtered, thoroughly rinsed with distilled water and ethanol. A desired product of PANI produced. The above procedure repeated using 0M and 2.5M of  $\text{CH}_3\text{COOH}$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. UV-Visible Spectroscopy

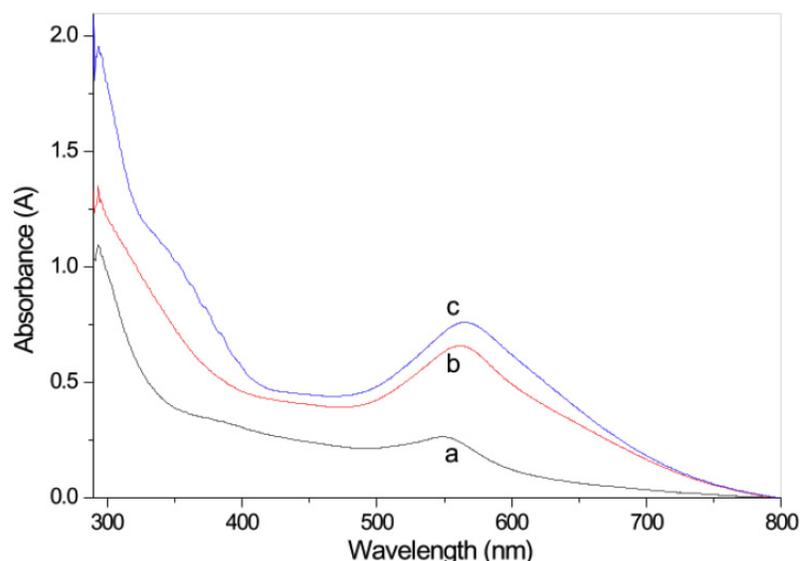
A key property of a conductive polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localized "sigma"  $\sigma$  bond which forms a strong chemical bond. In addition, every double bond also contains a less strongly localized "pi"  $\pi$  bond which is weaker. However, conjugation is not enough to make the polymer material conductive. In addition - and this is what the doping does [21] - charge carriers in the form of extra electrons or holes have to be injected into the material. A hole is a position charge where an electron is missing. When such a hole is filled by an electron jumping in from a neighboring position, a new hole is

created and so on, allowing charge to migrate a long distance [21]. The ability of the anion and proton of an acid to interact with PANI is related to the relative strength of the acid and to the amine ( $-\text{NH}_2^+$ ) and imine ( $-\text{NH}^+=$ ) groups within the polymer. A strong acid such as (HCl,  $\text{H}_2\text{SO}_4$ , etc.) will protonate both groups, while a weak acid as  $\text{CH}_3\text{COOH}$  is sufficiently strong to protonate the imine group only [21]. In our previous work [22], and other works [23, 24] UV-visible spectra of PANI synthesized at  $25^\circ\text{C}$  in the presence of strong acid (HCl) shows the absorption bands 325 and 605 nm corresponding to the benzenoid  $\pi$ - $\pi^*$  transition of phenyl ring and quinoid excitation transition  $n$ - $\pi^*$  respectively. Figure 1 shows UV-visible spectra of PANI doped in different concentrations of  $\text{CH}_3\text{COOH}$ .

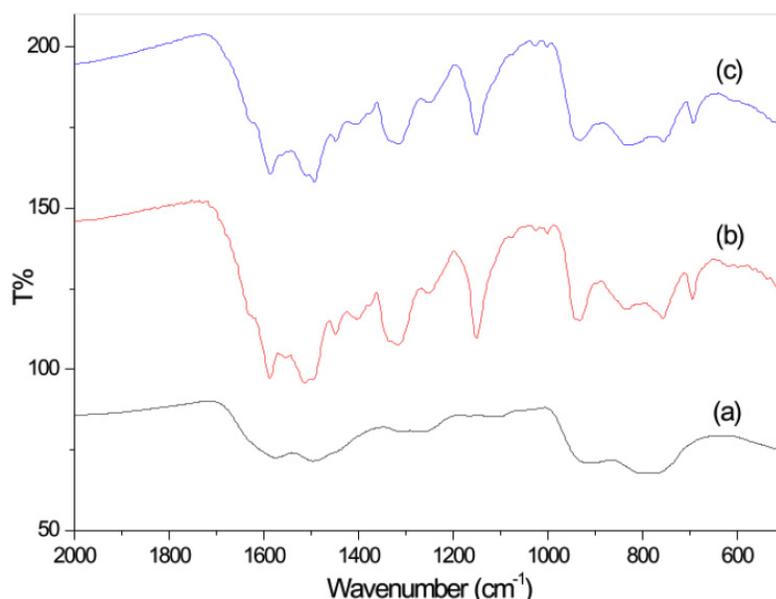
An increase in the absorption bands will be observed when doping in different concentrations of  $\text{CH}_3\text{COOH}$ . This increase may indicate the formation of more emeraldine base form with increasing  $\text{CH}_3\text{COOH}$  concentration. Also it may be attributed that the acetic acid is sufficiently strong to protonate the imine group of PANI only, also the steric effect of  $-\text{COOH}$  group of the acetic acid which cause lower the degree of conjugation as well as hindering charge transfer between chains.

#### 3.2. Fourier Transform Infrared (FTIR)

FTIR is one of the most important methods of spectroscopy. In our work, the importance of FTIR is concentrated in the comparison of band position for determining functional groups present in both pure and



**Figure 1:** UV-visible spectra of polyaniline doped with (a) 0M acetic acid (b) 1M acetic acid (c) 2.5M acetic acid and recorded using DMSO as the solvent.



**Figure 2:** FTIR spectra of polyaniline doped with (a) 0M acetic acid (b) 1M acetic acid (c) 2.5M acetic acid.

doped PANI. The FTIR can be distinguish between the two important rings Benzenoid(B) and Quinoid(Q) in the ( $1400-1600\text{ Cm}^{-1}$ ) region in the spectrum in both cases of pure and doped polymers [25, 26]. The intensity of peaks depends on factors such as polymer coil size, the nature of polymer-solvent polymer doping. Figure 2 shows FTIR spectra of PANI doped with different concentrations of  $\text{CH}_3\text{COOH}$ .

An intense peak observed at  $1371\text{ Cm}^{-1}$  shown in Figure 2b and c is related to stretching of C-N bonds of secondary aromatic amines dopes in  $\text{CH}_3\text{COOH}$  and displacement of  $\pi$  electrons, while this band is absent in Figure 2a. The intense bands at  $1143\text{ Cm}^{-1}$  and  $1150\text{ Cm}^{-1}$  in Figure 2b and c are related to the vibration of  $-\text{NH}^+$  formed in the acid doping process of PANI. An increase in the quinoid and benzenoid rings absorption bands of ( $1496\text{ Cm}^{-1}$ ,  $1513\text{ Cm}^{-1}$  and  $1498\text{ Cm}^{-1}$ ) and ( $1577\text{ Cm}^{-1}$ ,  $1587\text{ Cm}^{-1}$ ,  $1586\text{ Cm}^{-1}$ ) respectively for undoped and doped PANI in different concentrations of  $\text{CH}_3\text{COOH}$  is observed. The presence of these bands clearly shown that the polymer is composed of amine and imine units. The bands between  $700-900\text{ Cm}^{-1}$  to aromatic ring deformation and C-H bond vibrations out of ring plane [19].

### 3.3. Electrical Conductivity

The electrical conductivity values of the PANI of undoped and doped  $\text{CH}_3\text{COOH}$  at  $30^\circ\text{C}$  are presented in Table 1.

The highest value of electrical conductivity when PANI doped with 1M  $\text{CH}_3\text{COOH}$  compared to the value

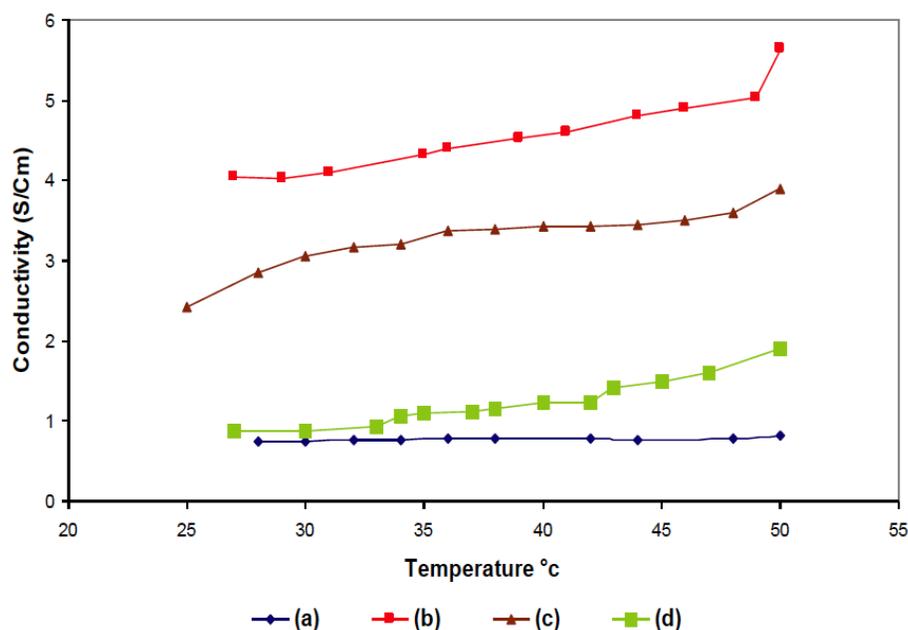
of 0 M  $\text{CH}_3\text{COOH}$  indicating a successful doping of PANI in  $\text{CH}_3\text{COOH}$  are more preferable if the concentration of  $\text{CH}_3\text{COOH}$  is 1M. The decrease in the conductivity values of PANI doped with concentrations higher than 1 M  $\text{CH}_3\text{COOH}$  as shown in Table 1, may be attributed to the decrease of efficiency of charge transfer between the polymer chains. Figure 3 shows the effect of the temperature upon the conductivity of PANI synthesized at different concentrations of  $\text{CH}_3\text{COOH}$ . It can be observed that the conductivity increased with the increase in temperature in all concentrations, which is characteristic of thermal activated behavior and is in good agreement with the literature [25]. The increase in conductivity is attributed to the increase in the temperature [26]. In addition, it should be expected that the molecular motion becomes non negligible in the high temperature ranges, which leads to the recombination and /or relocation of the dopant ion [27].

**Table 1: Electrical Conductivity of PANI Doped in Different Concentrations of  $\text{CH}_3\text{COOH}$**

Conc. $\text{CH}_3\text{COOH}$ (M)	Conductivity ( $\text{S Cm}^{-1}$ )
0 M	0.748
1M	4.27
1.5 M	2.49
2.5 M	0.872

## 4. CONCLUSION

The effect of different concentrations of Glacial acetic acid ( $\text{CH}_3\text{COOH}$ ) as a doping agent on the



**Figure 3:** The temperature dependent conductivity plot of polyaniline doped in Different concentrations of acetic acid a) 0M, b) 1M, c) 1.5M, d) 2.5M.

structure of polyaniline (PANI) prepared by oxidative polymerization at room temperature are discussed using UV-visible and FTIR spectroscopy and conductivity measurements. In the UV-visible, the absorption bands increases on doping with different concentrations of  $\text{CH}_3\text{COOH}$  solution, may be attributed that  $\text{CH}_3\text{COOH}$  is sufficiently strong to protonate the imine group of PANI. In the FTIR spectra results, an increase in the absorption bands related to quinoid and benzenoid rings for the undoped and doped in different concentrations of  $\text{CH}_3\text{COOH}$  is clearly shown that the polymer is composed of amine and imine units indicating a successful doping of PANI with 1M  $\text{CH}_3\text{COOH}$ , this result is in accordance with the conductivity measurement results indicating that the doping PANI in  $\text{CH}_3\text{COOH}$  is more preferable if the concentration of  $\text{CH}_3\text{COOH}$  is 1M. The conductivity increased with the increase in temperature in all concentrations of  $\text{CH}_3\text{COOH}$  studied, because of the thermal curing affects the chain alignment of the polymer, which lead to the increase of the conjugation length and brings about the increase of the conductivity.

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