

Polyaniline Doped with Sulphosalicylic, Salicylic and Citric Acid in Solution and Solid-state

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ABSTRACT

Considerable progress has been made in characterizing and understanding the properties of polyaniline doped with some protonic acids. In this work polyaniline was synthesized by chemical method in the presence of HCl, then undoped polyaniline was obtained with NH_3 solution. The undoped polyaniline was doped with the protonic acid such as sulphosalicylic acid, salicylic acid and citric acid. The protonic acids can be used to dope poly-aniline (PANI) by mixing a protonic acid in common solvents such as *N*-methyl pyrrolidone and dimethylformamide. The structure and properties of protonic acid doped-PANI are investigated by UV-vis, IR and conductivity measurement. It is found that the PANI, therein, is doped by protonation of imine nitrogen. In the case of protonation-doped PANI, polarons/bipolarons are generated as reflected in the presence of UV-vis absorption peaks at 420 and 850 nm. The minimum amount of appropriate acid to obtain optimum level of doping was estimated by UV spectroscopy. Also polyaniline base was doped with these acids by blending in the solid-state. The electrical conductivity in the solid state increased several times after heating the mixture and increasing the heating time. The dependence of the electrical conductivity on the composition of blends differs for the partly protonated polyaniline and mixtures of protonated polyaniline with an excess acid.

Key Words: polyaniline, conducting polymer, thermally doping, solid-state, characterization

INTRODUCTION

Polyaniline (PANI) is an important conducting polymer because of its good environmental stability, high conductivity and low cost [1-4]. It is the conjugated conducting polymer that can be doped either by

protonation with a protonic acid or charge-transfer with an oxidation agent. Its electronic and optical properties can be controlled reversibly by varying the doping level [5]. PANI can be used as an electrode material for organic batteries, in microelectronics as electrochromic material for displays and as antistatic

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coating [5–6]. Unfortunately, PANI, especially in its conductive form, is difficult to process. This fact severely impedes its large-scale technological applications [7]. In the past few years, considerable progress has been made in the processing of PANI by, for example, synthesis of alkyl or alkoxy ring-substituted or *N*-substituted polyanilines [5,8], but most of the produced polyanilines are lower in conductivity.

Conventional PANI doped with HCl is susceptible to dedoping due to the small size of the dopant, which can evaporate from the polymer. The evolution of corrosive HCl can cause damage to equipment and pose a health hazard. Also, polyaniline doped with HCl, is insoluble in common organic solvent [9]. Recently functionalized protonic acids (FPAs) have been used as dopants in place of inorganic acids. The incorporation of FPAs onto the polyaniline backbone via a doping process results to improve of PANI-FPA solubility in organic solvents [10,11]. Cao et al. [11] showed that use of surfactant type protonating agents such as dodecylbenzenesulphonic acid facilitates the dissolution of protonated PANI in weakly polar solvents. Recently, thermal doping of polyaniline with FPAs without auxiliary solvent has been used.

Leaven et al. [12] have reported that doping of polyaniline is obtained by introducing the dodecylbenzenesulphonic acid into the undoped polymer, without the use of auxiliary solvent. Complex formation in the solid phase occurs at elevated temperatures and results in the formation of a soluble and processable conducting complex. Cao et al. [11] have observed conductivity as high as 20 Scm^{-1} for equimolar blends of polyaniline base with various sulphonic acids prepared in the solid state and then treated for 1 min at 165°C . In 1998 Stejskal et al. [13] have observed that, beside sulphonic acids, picric acid also protonates polyaniline base and yields electrically conducting polymer.

In this paper, the emeraldine base of polyaniline was doped with sulphosalicylic, salicylic and citric acid in dimethylformamide (DMF) and NMP as solvent and doping process was investigated by UV-vis spectrophotometer. The influence of the concentration of each acid on the protonation level was observed. Polyaniline base was thermally protonated

by blending with sulphosalicylic acid, salicylic acid and citric acid in the solid state.

EXPERIMENTAL

Materials

N-Methyl pyrrolidone was purchased from Riedel, aniline (Merck) was distilled before use and dimethyl formamide was purchased from Merck.

Polyaniline

Polyaniline was prepared by chemical oxidation of twice vacuum distilled aniline with ammonium peroxodisulphate. Aniline (37.3 g, 0.4 mol) was dissolved in 284 mL of water, then, 280 mL of 1.7 M hydrochloric acid was added to it. The mixture was stirred at room temperature until the precipitated aniline chloride dissolved. The polymerization was started by addition of 400 mL of aqueous 1 M ammonium peroxodisulphate (91.2 g, 0.4 mol) solution at $0-5^\circ\text{C}$. After being stirred for 24 h, the mixture was diluted with water, and the precipitate was separated by filtration, treated with an excess of 1 M ammonium hydroxide, and washed with methanol. Each wash step was carried out until the filtrate became clear colourless. The resulting dark, free-flowing PANI-EB powder was then dried at 70°C for 12 h to remove the remaining moisture and solvent.

Protonic Acid Doping Method

The following functionalized protonic doping acids were used as received unless otherwise indicated sulphosalicylic acid (SSA), salicylic acid (SA) and citric acid (CA) Fluka Chemicals. For the spectroscopic studies, fully doped PANI-ES solutions were prepared by a solution doping method. Our doping process involved first dissolving 10 mg PANI-EB in 10 mL NMP or DMF and vigorously stirred for 2 h at room temperature, then filtrated with $0.5 \mu\text{m}$ filter paper (Whitman). Very little insoluble PANI-EB was observed. To 0.1 mL of PANI-EB solution was added different amounts of SSA; SA, CA dissolved in the same solvents as shown in Tables (1–6). The mixtures were diluted until final volume had been 3.5 mL and

Table 1. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm in various acid (SSA) concentrations in DMF solvent.

SSA Concentration (mol/L)×10 ⁴	PANI-EB Absorption at λ=630 nm	PANI-SSA Absorption at λ=850 nm
0	1.25	0
2.85	0.79	0.037
4.28	0.6	0.27
5.71	0.42	0.68
7.14	0.4	0.77
11.42	0.37	0.91
14.28	0.30	1.10

Table 2. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm in various acid (SA) concentrations in DMF solvent.

SA Concentration (mol/L)×10 ²	PANI-EB Absorption at λ=630 nm	PANI-SA Absorption at λ=850 nm
0	1.18	0
2.57	0.62	0.18
25.7	0.39	0.44
71.42	0.27	0.62
200	0.22	0.77
571.4	0.21	0.92
714.2	0.17	0.99

Table 3. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm in various acid (CA) concentrations in DMF solvent.

CA Concentration (mol/L)×10 ²	PANI-EB Absorption at λ=630 nm	PANI-CA Absorption at λ=850 nm
0	1.1	0
8.57	0.88	0.33
22.85	0.72	0.23
31.42	0.50	0.42
57.14	0.21	0.51
128.57	0.11	0.69
357.14	0.10	0.8
535.70	0.09	1.0

Table 4. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm in various acid (SSA) concentrations in NMP solvent.

SSA Concentration (mol/L)×10 ⁴	PANI-EB Absorption at λ=630 nm	PANI-SSA Absorption At λ=850 nm
0	1.21	0
6.0	0.98	0.12
6.5	0.80	0.37
7.0	0.49	0.65
7.5	0.24	0.70
10.0	0.23	0.76
17.5	0.21	1.0

Table 5. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm in various acid (SA) concentrations in NMP solvent.

SA Concentration (mol/L)×10 ²	PANI-EB Absorption at λ=630 nm	PANI-SA Absorption At λ=850 nm
0	1.19	0
4.28	1.04	0.18
8.57	0.82	0.30
14.28	0.70	0.35
85.22	0.56	0.56
170.70	0.52	0.615
197.84	0.40	0.70

Table 6. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm in various acid (CA) concentrations in NMP solvent.

CA concentration (mol/L)×10 ¹	PANI-EB absorption at λ=630 nm	PANI-CA absorption at λ=850 nm
0	0.94	0
4.28	0.78	0.11
8.57	0.50	0.28
22.85	0.47	0.34
42.85	0.37	0.48
57.14	0.32	0.59

stirred for 10 min. These solutions were placed in a quartz cuvette and the amount of doping protonic acids surveyed in the UV-vis spectroscopy.

Solid State Protonation of Polyaniline Base

PANI-EB and organic acids were mechanically blended with a pestle in an agate mortar for 10 min. Then the mixtures were heated at various temperatures for doping of acids. Then mixtures were cooled to room temperature and their electrical conductivity with four-point probe was measured. The characteristics of components are given in Figures 8, 9.

Spectroscopic Studies

UV-vis Spectroscopy

A Shimadzu spectrophotometer was used to measure the optical absorbency in the wavelength range 300–900 nm of PANI-EB and PANI-ES in DMF and NMP solution.

FTIR Spectroscopy

Infrared spectra were obtained using a Shimadzu-408. Samples were prepared by dispersing the polymer in KBr to form discs.

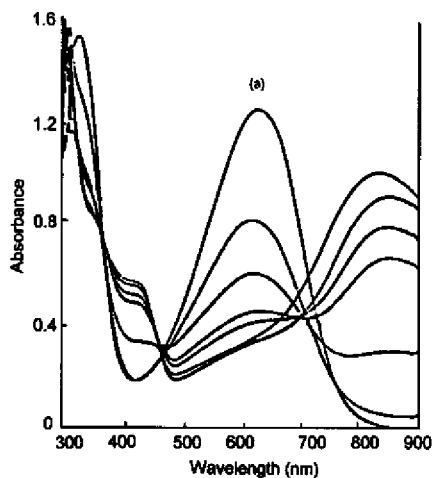


Figure 1. The UV-vis spectra of PANI base and salt (PANI-SSA) solution in DMF in different concentrations of acid.

Electrical Conductivity

Conductivity measurements were carried out by four-point probe method. The blends of polyaniline-acid were compacted into pellets for measurements. The reported conductivity values were the averages of four pair of reading at different parts on both sides of pellets.

All measurements were done in air at room temperature and converted to conductivity by the following equation:

$$\rho = 1/\delta = V/I. \omega. \pi/\ln_2$$

where: ρ =resistivity ($\Omega \cdot \text{cm}$), δ =conductivity (s/cm), V =potential difference (mV), I =applied constant current (mA) and ω =thickness (cm).

RESULTS AND DISCUSSION

UV-vis Spectroscopy

Chain conformation plays a critical role in the properties of polyaniline. The study of the electronic structure of the protonated polyaniline is complicated by the simultaneous presence of different structures. We have investigated this dependence in PANI-EB using UV-vis spectroscopy. PANI-EB has two absorption peaks at 330 and 630 nm. The absorption at 330 nm has been suggested to arise from excitation of the benzene segment including amine structures in polyaniline, where as the peak at 630 nm arise from the quinoid structure including imines. The UV-vis Spectra of PANI doped with SSA in solvent DMF in different concentrations of SSA are shown in Figure 1.

When nitrogen atoms in imine groups are protonated, nitrogen and its neighboring quinoid ring become a semiquinoid radical cation [15], causing a decrease in the exciton absorption peak intensity and generation of the absorption peaks at about 420 and 850 nm due to the presence of polaron/bipolaron [4]. The intensities of these two peaks and the exciton absorption peak 630 nm relative to that of the $\pi \rightarrow \pi^*$ transition at 320 nm also increase and decrease, respectively, with increasing SSA concentrations and

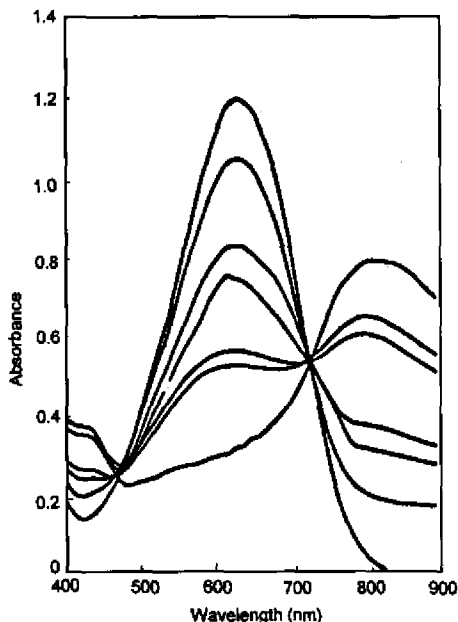


Figure 2. The UV-vis spectra of PANI base and salt (PANI-SA) solution in NMP simultaneous with increasing concentration of acid.

reach to a maximum amount at 0.001428 M. With increasing concentration of SSA there was no changes observed in absorptions. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm versus SSA concentrations in DMF are shown in Table 1.

Decreasing of undoped polyaniline absorption in the 630 nm is proportional to increasing of doped polyaniline absorption in the 850 nm. At high protonation level the 630 nm band completely disappears. In this process quinoid units disappear (to form semi-quinoid structures). Also the absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm versus SA concentrations in DMF are illustrated in Table 2. The most amount of SA for maximum doping PANI in the solution 7.142 M was obtained by UV-vis spectroscopy at $\lambda = 850$ nm. Since SSA is stronger acid than SA, because it contains a sulphonic

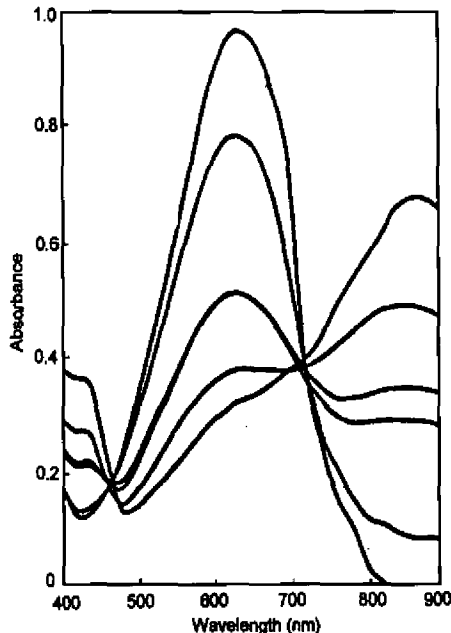


Figure 3. The UV-vis spectra of PANI base and salt (PANI-CA) solution in NMP simultaneous with increasing concentration of acid.

acid group, as a result greater amount of SA is needed for the same level doping of polyaniline.

Citric acid with three carboxylic acid groups was used as dopant. Adding acid solution (DMF) into polyaniline solution, both the 330 nm ($\pi_B \rightarrow \pi^*$) and 630 nm ($\pi_B \rightarrow \pi_Q$) absorptions decrease in intensities. Simultaneously, two new absorptions appear at 420 and 850 nm, which are attributed to polarons/bipolarons in protonated polyaniline. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm versus CA concentrations in DMF are presented in Table 3.

The most amount of CA for completely doping PANI in the solution was obtained by UV-vis spectroscopy at the wavelength of 850 nm. Also, polyaniline was protonated with SSA, SA and CA in NMP as solvent.

The spectra recorded in NMP show a similar

treatment with spectra recorded in DMF. The UV-vis spectra of PANI-SA and PANI-CA are shown in Figures 2 and 3, respectively. The absorption of undoped polyaniline in 630 nm and doped polyaniline in 850 nm versus acid concentrations in NMP are presented in Tables 4, 5 and 6 for SSA, SA and CA, respectively.

Infrared Spectra

The supporting evidence of the protonation could be found in IR spectra. The IR absorption spectra of

polyaniline base, polyaniline sulphosalicylate, polyaniline salicylate and polyaniline citrate is shown in Figure 4. In the spectrum of PANI base the 1302 cm^{-1} band is assigned to the vibration stretch of C-N of secondary aromatic amine and 832 cm^{-1} band to an aromatic C-H. The 1587 and 1503 cm^{-1} modes in the polyaniline base (consistent with quinone and benzene ring deformation) show a red shift to 1572 cm^{-1} , 1490 cm^{-1} in the PANI-SSA and to 1555 and 1487 cm^{-1} in the PANI-CA. In PANI-SA IR spectrum, the 1587 cm^{-1} is not changed and the 1503 cm^{-1} band is shifted to 1487 cm^{-1} .

After protonation of polyaniline with acids, an absorption characteristic of -OH group, at 3485 cm^{-1} for PANI-SSA, at 3454 cm^{-1} for PANI-CA and at 3431 cm^{-1} for PANI-SA have been observed.

Solid-State Blending and Heat Treatment

When powdered polyaniline base is mechanically blended with a solid organic acid, an electrically conducting product is obtained. While the electrical conductivity of the PANI base is of the order of 10^{-9} Scm^{-1} [13], the equimolar mixture (calculated for aromatic units) of the PANI base with SSA shows a conductivity of $10^{-2.44} \text{ Scm}^{-1}$, that its magnitude is several times higher than PANI base.

When the blends were heated to 40, 60, 80, 100 and higher temperature (160 $^{\circ}\text{C}$), the measured conductivity increased several orders in comparison with the room temperature measurement. The heating of equimolar mixtures to 120 $^{\circ}\text{C}$ was found to provide the products with the highest electrical conductivity. Also, the measured conductivity at 25 $^{\circ}\text{C}$ for mixture (ratio molar 1:2) PANI base and CA show increase after heating of blends at 40, 60, 80, 100 $^{\circ}\text{C}$. Heating at 100–120 $^{\circ}\text{C}$ produced sample with lower conductivity compared with treated at 100 $^{\circ}\text{C}$, that is due to sublimation of SA. The appropriate doping temperature of PANI-SSA was 120 $^{\circ}\text{C}$ and PANI-SA and PANI-CA were 100 $^{\circ}\text{C}$.

The plots of conductivity versus temperature for three acids are shown in Figure 5. The plots of conductivity versus time of formation complex between PANI and these acids are shown in Figure 6. The electrical conductivities of the samples are little

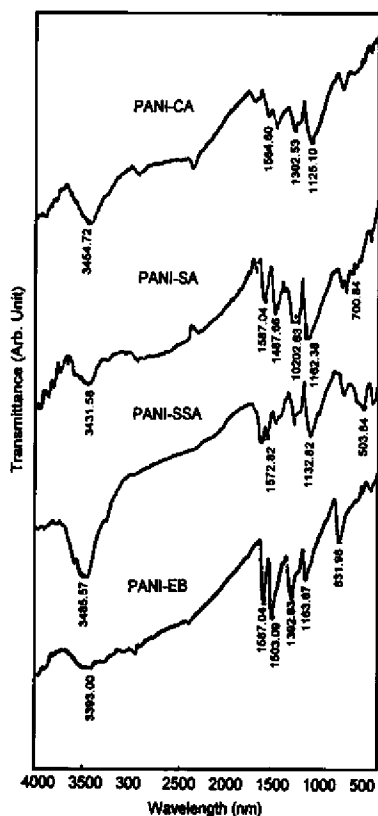


Figure 4. The IR spectra of PANI base, PANI-SSA, PANI-SA, PANI-CA.

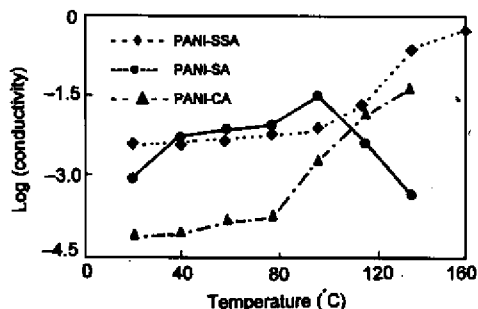


Figure 5. Electrical conductivity versus temperature for thermally doped PANIs by SSA, SA and CA and measured at room temperature.

dependent on the methods of their preparation. Blending components for 40 min were found to be sufficient to obtain an electrically conducting product, and blending for more than 40 min improved the conductivity only marginally.

The temperature to which samples were exposed in this experiment was lower than the melting point of organic acids (mp 120 °C for SSA, 157–159 °C for SA and 153 °C for CA).

During the mechanical blending, protonated polyanilines are produced at the interfaces of the polyaniline base particles with the molecular dopants. In the resulting material, the formed conducting phase continuously diffuses into insulating areas. When heating time is prolonged to 20, 30, 40 min, the measured conductivity at 25 °C increases. The

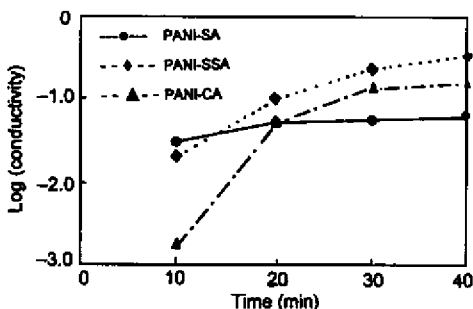


Figure 6. Electrical conductivity versus time of complex formation for thermally doped PANIs by SSA at 120 °C and SA and CA both at 100 °C.

appropriate doping temperature of PANI-SSA was 120 °C and that PANI-SA and that PANI-CA was 100 °C.

CONCLUSION

Polyaniline base can be doped with SSA, SA and CA via protonation of the nitrogens of the imine unit without changing the number of π -electrons in the polymer. The obtained doped polyanilines are soluble in DMF and NMP. We are able to observe for the first time of IR absorption and a noticeable increase in absorbance at UV-vis suggests that conformational changes are a function of the amount of the molar doping level. Also polyaniline base can be protonated with protonic acids by blending of both components in the solid state. The electrical conductivity increased several orders of magnitude after blending of acid and base at different molar proportion and still increased after their heating for 40 min. Besides sulphosalicylic acid, e.g., salicylic acid, citric acid, can also be employed for the solid state protonation of poly-aniline. The extent of protonation can be changed, and thus the electrical conductivity controlled, by varying the composition of blends.

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