

Spectroscopic Studies of Nano Size Crystalline Conducting Polyaniline

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Abstract: Polyaniline (PANI) was synthesized in Emeraldine form by in situ chemical oxidation method by using Ammonium perdisulphate as oxidizing agent. The XRD pattern indicates that PANI is a semi crystalline solid with d-spacing 4.801 Å and 4.358 Å. The SEM results show that the particle size lies as an average of 80 nm and length 550nm. Similarly the UV-Visible spectra of this polymer indicate two absorption bands at around 320nm and 640nm. These absorption bands are attributed to the transitions of $\pi \rightarrow \pi^*$ and Benzenoid to Quinoid respectively. The FT-IR spectrum of PANI shows strong bands at 3442, 2925, 1598, 1494, 1453, 1176, 1112 and 744 cm^{-1} respectively. ¹H NMR spectrum shows 6 peaks with chemical shifts $\delta = 7.452, 7.468, 7.505, 7.525, 7.604, 7.638$ ppm. The lower three peaks at ($\delta = 7.452, 7.468, 7.505$ ppm) are attributed to the protons related to the ¹⁴N nucleus. These spectral lines intensity ratio lies as 1:1:1. Another three peaks at ($\delta = 7.525, 7.604, 7.638$ ppm) are attributed to the three protons, which are present at CH Benzenoid, NH, CH at Quinoid. The intensity ratio of these spectral lines is 1:2:1. The room temperature ESR spectrum of PANI Emeraldine salt shows an unresolved peak with lande's g factor 2.010 due to polaron.

Key words: Polyaniline (PANI), XRD, FTIR, NMR, ESR.

I. Introduction

Over 30 years ago conjugated polymers were as futuristic new materials that would lead to the next generation of electronic and optical devices. The development of "plastic electronics" devices based on conjugated polymers has evolved the states of these materials from academic curiosity to the rapidly growing new electronic industry. Among these conjugated polymers polyaniline possess excellent thermal and environmental stability. Polyaniline have been used in variety applications like diodes, Field effect transistors, solar cells, memory devices, corrosion resistance and in gas sensors [1]. The polyaniline can be synthesized in to different sizes and shapes like nanofibers, nanorods, nanotubes and in to thin films. Not only tunable morphology, polyaniline can be synthesized with tunable properties like electrical conductivity and optical band gap. The presence of Imines and amine nitrogen functional groups in the polyaniline is the main reason for the tunable properties of polyaniline [Fig. 1] These two peculiar properties have given a lot of importance to polyaniline in nano-electronic and optical devices technology. A morphological and spectroscopic study of these polymers is an important subject to understand the transport phenomena of these conjugated polymers to apply them in electronic industry [2, 3]. Hence we attempted to synthesis the polyaniline nanofibers, and characterization of these synthesized nano-polymers with help of different spectroscopic techniques.

II. Experimental Section

Synthesis of Polyaniline:

Polyaniline was synthesized by *In-Situ* chemical polymerization of aniline in the presence of hydrochloric acid as a catalyst and ammonium peroxydisulphate as an oxidant. For the synthesis, we took 50ml, 1M HCl, and 2 ml of aniline were added into a 250ml beaker equipped with a Teflon coated magnetic stirrer at about 0°C temperature. Then 5 g of ammoniumperdisulphate ((NH₄)₂S₂O₈) aqueous solution in 50ml 1M HCl was drop wise added into the above solution. The polymerization temperature 0° C was maintained for 10 h to complete the reaction. Then the precipitate obtained was filtered. The product was washed successively by 1M HCl followed by double distilled water until the wash solution turned colorless. The product PANI was dried at 60°C for 24h to get powder form PANI. This powder was pelletized with help of hydraulic machine for characterization.

Characterization:

The X-Ray diffraction studies of polyaniline were performed on Phillips XPERT diffractometer with Cu K_α X-ray ($\lambda = 1.54 \text{ \AA}$). Scanning electron microscope (SEM) experiments are performed by employing Hitachi SU 1510 microscope. The Fourier transform infrared (FTIR) spectra were obtained using a Bio-rad FT-IR (model FT-155) spectrophotometer. The samples were mixed with KBr and pressed in to a pellet. The room

temperature optical absorption spectrum of these materials was recorded by employing the Varian spectrometer (model Cary 5E) in the 190nm to 1000 nm wavelength region. The ESR spectra were recorded by using JEOL spectrometer and NMR studies are performed in CFRD Osmania University by employing the Bruker spectrometer.

III. Results And Discussion

The X-ray diffraction pattern of polyaniline emeraldine salt form shows two sharp peaks at $2\theta = 21.10$ and 23.59 . The inter-planar distances are calculated as 42.10 nm and 37.70 nm respectively. The average crystallite size is calculated by Debye Scherer equation $D = [0.89 \lambda] / [\beta \cos \theta]$ respectively, where β is full width of half maxima (FWHM) [Fig.2]. Generally polymers are considered to be amorphous, but here the synthesized polymer is showing crystalline structure due to their fiber nature and planar nature of Benzenoid and Quinoid functional groups [3]. Similarly polyaniline emeraldine base form shows only one peak at 19° . The SEM micrographs reveal that they are actually agglomeration of nanofibers [Fig.3]. The diameter and length of nanofibers are measured as 80 nm and 550nm respectively. Agglomeration is taking place due to the conventional filtration of polymer powder in the synthesis process. The Fourier transform infrared spectra [Fig. 4.1] of Polyaniline nanofibers are also consistent with the existing literature with strong bands at around 1558 and 14690 cm^{-1} corresponds to Benzenoid and Quinoid rings and the remaining bands assigned to their respective functional groups [5] as shown in Table 1.

The UV-Visible spectrum of Polyaniline Emeraldine base form shows two absorption peaks at 325 and 625 nm (Fig.5). These peaks are assigned to the $\pi-\pi^*$ transition and polarons band transitions respectively. Similarly, the UV-Visible spectrum of HCl doped Polyaniline emeraldine salt shows three absorption bands at 340 nm, 440 nm and 800 nm (Fig.6). They are the $\pi-\pi^*$ transition located 340 nm, the polaron- π^* transition at ~ 440 nm and polaron- π transition around 800 nm. This indicates that the synthesized polyaniline have been effectively doped protonic acid. These two features are fingerprint of electronically conducting Polyaniline Emeraldine salt form [6, 7].

Table .1 FTIR peak assignment of polyaniline emeraldine form

S.No.	Peak position cm^{-1}	Assignment
1	3442	O-H Stretching
2	2925	N-H Bending
3	1598	Quinoid deformation
4	1494	Benzenoid deformation
5	1112	C-N=C stretching
6	744	C-H out of plane bending

The room temperature ^1H NMR spectrum of polyaniline shows 6 peaks with chemical shifts $\delta = 7.452, 7.468, 7.505, 7.525, 7.604, 7.638$ ppm (Fig.7). The lower three peaks at ($\delta = 7.452, 7.468, 7.505$ ppm) are attributed to the protons related to the ^{14}N nucleus. These spectral lines intensity ratio lies as 1:1:1. Another three peaks at ($\delta = 7.525, 7.604, 7.638$ ppm) are attributed to the three protons, which are present at CH Benzenoid, NH, CH at Quinoid [8-10]. The intensity ratio of these spectral lines is 1:2:1. The ESR spectrum of PANI Emeraldine salt form at room temperature shows an unresolved peak with lande's g factor 2.010 ($h\nu = g\beta H$). This may be attributed to the half spin polarons which is created in the PANI back bone due to doping of HCl acid. This result is quite supporting the UV-Visible spectra of PANI Emeraldine salt form. As polyaniline is doped, the resonance line amplitude of the positive lobe (I+) is not equal to the amplitude of the negative lobe, (I-). This change in the resonance line shape is due to the skin effect in polyaniline [11, 12].

IV. Conclusion

We synthesized polyaniline nano-fibers by chemical oxidative polymerization method. The morphological studies (XRD, SEM) indicate the radius of polymer fiber is around 80nm and length around 550 nm respectively. The Emeraldine salt form of polyaniline is confirmed with FTIR, UV/Visible and ESR spectra. The proton NMR studies reveals that peak at a triplet is caused by -NH free radical. ESR studies reveal the formation of polarons in polyaniline emeraldine salt form.

V. Acknowledgements

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Figure Captions:

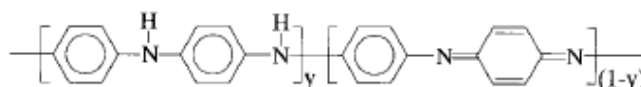


Fig.1. Polyaniline Chemical Structure

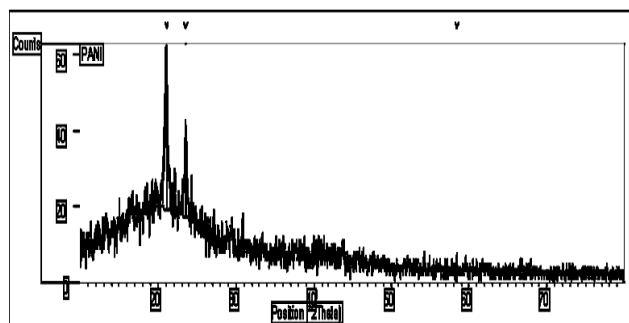


Fig.2 XRD Pattern of Polyaniline

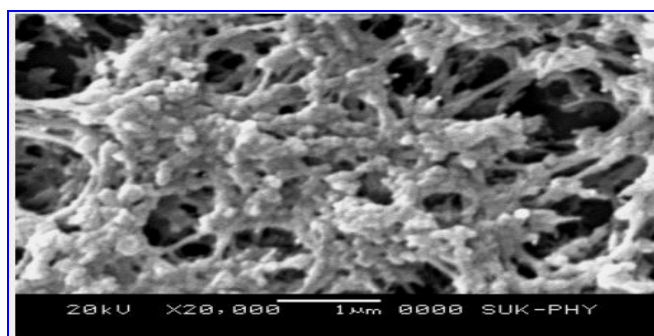


Fig.3 SEM image of Polyaniline

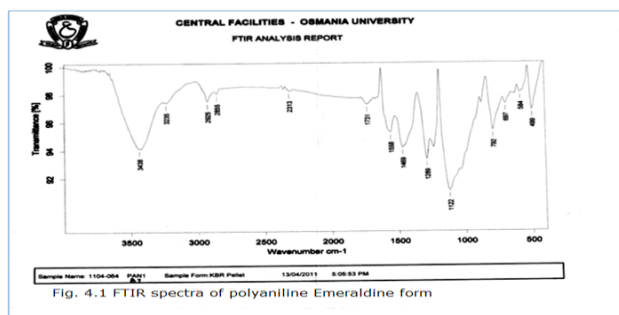


Fig. 4.1 FTIR spectra of polyaniline Emeraldine form

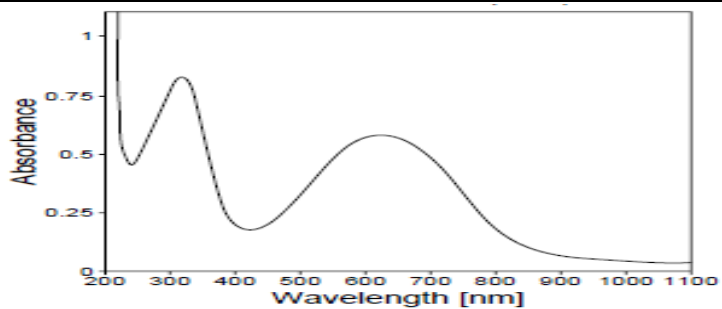


Fig.5 UV/Visible spectra of Polyaniline Emeraldine base form.

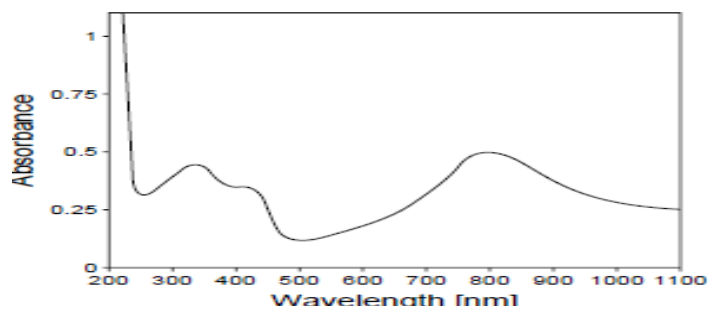


Fig.6 UV/Visible spectra of Polyaniline Emeraldine salt form.

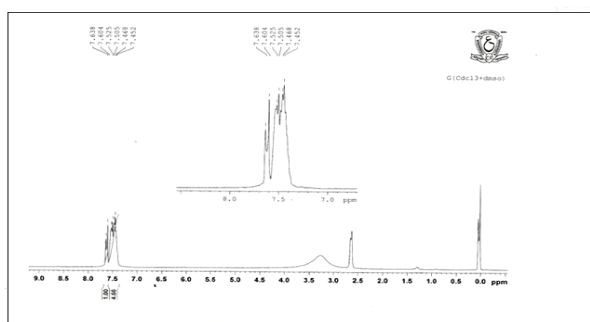


Fig. 7 ¹H NMR spectra of Polyaniline