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Synthesis of Polyaniline without Metal Doping and Its Characterization

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ABSTRACT
Polyaniline is widely study conducting polymer due to its applications in several devices such as biosensor, Gas sensor & Solar cell. This deals with synthesis and characterization of Polyaniline. The characterization has been divided into three categories viz. transmittance by UV-Visible spectroscopy (UV-Vis-NIR V670JASCO), Fourier Transform Infra-Red (FITR) and X-ray diffractometry (XRD) and the various results obtained have been explained. The optical measurements were made from UV-Visible spectrophotometer at normal incidence light wavelength & Fourier transform infrared (FTIR) spectrograph confirmed the presence of functional groups and also the interaction between the polymer chains.

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Introduction

The change in physico - chemical properties of Polyaniline (PANI) and its derivatives occurring in response to various external stimuli have been used in different applications e.g. in organic – electrodes, sensors and actuators [1-3]. Other uses are based on the combination of electrical properties typical of semiconductors with material parameters' characterization of polymers. The examples being the electrochromic devices [4], plastic microelectronics systems [1,2] , tailor made composite systems [5,6] and smart fabrics [7]. The establishment of the physical properties of PANI, prepared under different conditions is thus of fundamental importance. The study of electrical property of polymeric materials has become interesting area of research because these materials have great potential application. Most of the polymeric materials are poor conductors of electricity because they don't have free electrons to participate in the conduction process. The Polyaniline is widely study conducting polymer due to its applications in several devices such as biosensor, Gas sensor & Solar cell. Polyaniline (PANI) is an important conducting polymer due to its facile synthesis, environmental stability, and controllable physical and electrochemical properties by oxidation and protonation . PANI has been used in cathode materials of the lithium secondary batteries.

Experimental

Synthesis and Characterization of Polyaniline without metal doping

The basic material required was prepared through chemical synthesis and typical characterization were made, in different samples, as described in the following

Chemical Synthesis of Polyaniline (PANI)

Chemical synthesis requires three reactants: aniline, an acidic medium (aqueous or organic) and an oxidant. The more common acids are essentially hydrochloric acid (HCl) and sulfuric acid (H2SO4). Ammonium persulfate ((NH4)2S2O8) was used as an oxidant. However, the more popular synthesis is run with a 1 mol aqueous hydrochloric acid solution (pH between 0 and 2), ammonium persulfate as oxidant with an oxidant/aniline molar ratio ≤1.15 in order to obtain high conductivity and yield. The solution temperature is comprised between 0 and 2 ◦C in order to limit secondary reactions. The duration of the reaction varies generally between 1 and 2 hr. The experimental part consists of adding slowly (even drop by drop) the aqueous ammonium persulfate solution to the aniline/HCl solution, both solutions being pre cooled to nearly 0 ◦C. The mixture is stirred for about 1 hr. The obtained precipitate is removed by filtration and washed repeatedly with HCl and dried under vacuum for 48 hr .The obtained material is polyemeraldine salt: polyemeraldine hydrochloride (PANIHCl), green colored. To obtain polyemeraldine base, polyemeraldine hydrochloride is treated in an aqueous ammonium hydroxide solution for about 15 hr. The obtained powder is washed and dried.

Results and Discussion

UV- Visible spectrum

The UV-Visible spectrum of chemically synthesized PANI without metal doping, when dissolved in 1-methyl 2-pyrrolidene (NMP) was recorded with the reference cell containing NMP alone taking the help of a JASCO spectrophotometer, model V-670. Fig. 1 shows the UV-Visible spectrum, thus recorded , for the PANI samples as above. Two absorption peaks of good oscillator strengths are clearly seen in the optical absorption spectrum at 330 nm and 633 nm. These are characteristic of emeraldine base form of PANI [8]. It thus seems that deprotonation of salt had occurred in the PANI samples before recording the spectrum. This is in conformity with the studies of Pruneau et al [8] who have reported that a large excess of NMP leads to the deprotonation of dissolved PANI salt to the emeraldine base form, due to C = O groups in NMP forming hydrogen bonds with the dopant and thus withdrawing the proton of PANI. It may be mentioned that no deprotonation

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has been reported for solvents of different type, such as methanol and acetonitrite [9].

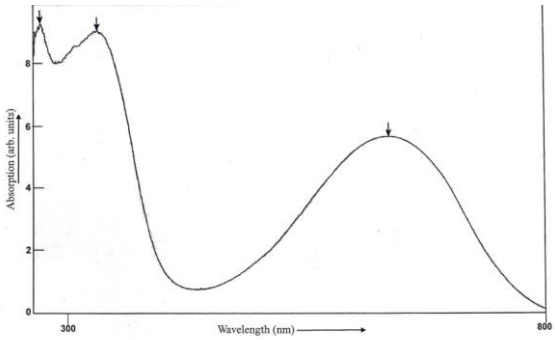

Figure 1: UV- Visible absorption spectra of PANI without any metal doping

The 330 nm band can now be assigned to π – π* transition in the benzenoid structure [10]. The absorption in the visible range, at 633 nm, is ascribed to excitation formation in the quinoid rings [11]. Finally, the highest energy shoulder peak at 270 nm may be attributed due to π – π* charge transfer in aniline monomer [12] left over in the solution after the polymer formation. It may be mentioned that the present optical absorption recordings were for PANI dissolved in NMP, wherein it had got deprotonated and thus no polaron assisted peaks [13] could be expected.

Fourier Transform Infra-Red

The technique of FITR (Fourier Transform Infra-Red) provides information about the chemical bonding or molecular structure of materials, whether inorganic or organic. It is thus an indispensible tool for the structural characterization of conducting polymers too. The frequencies and intensities of various vibration bands exhibited by a given PANI sample thus uniquely characterize it. In the present paper, the FITR spectra were recorded from 400 cm^{-1} to 4000 cm^{-1} with a 510P Nicolet FTIR spectrometer with 4 cm^{-1} resolution. The spectra were recorded in discs made from the powder forms of PANI with KBr powder.

Fig. 2 Shows the FITR spectrum of chemically synthesised PANI without any metal doping. The curves in the fig. show the vibration bands at 3425, 1625, 1555, 1290, 1140, 1090, 790 cm^{-1}. These values are the characteristics of polyaniline chain and in agreement with theoretical predictions [14]. The 3425 cm^{-1} band is assigned to stretching vibration of secondary amine. The 1625 cm^{-1} band is due to C = C double bond associated with benzenoid structure. The 1920 cm^{-1} vibration may be linked to stretching associated with normal C-N linkage. The vibration at 1140 cm^{-1} is also due to C = N vibration but in the structure B – NH = Q and is indicative of protonation of PANI. Finally, the vibrations at 1090 cm^{-1} and 790 cm^{-1} may be attributed to C – H aromatic in plane and out of plane vibrations of para – linked phenyl rings in PANI.The results as above thus also support the conclusions arrived at by Polk et al [15] on protonation doping of PANI.

X-Ray Diffraction

A diffraction pattern is a distribution of scattered intensity as a function of scattering angle. X- ray diffractogram taken for the PANI sample, using CuKα radiation (λ = 1.5420 A°) on a Rigaku instrument is shown in Fig. 3. This exhibits peaks at 2Θ values 9.5° , 14.0°, 20.5°, 27.0° and 29.5°.

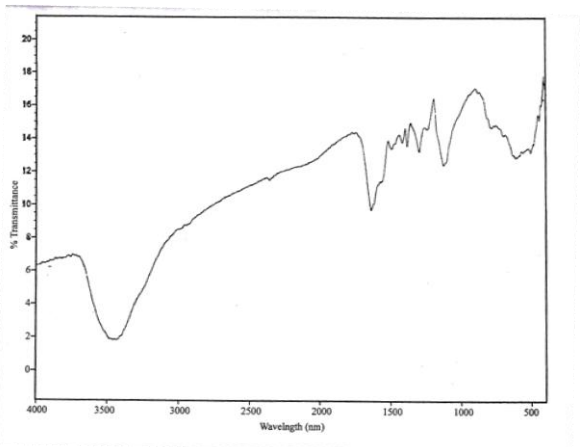

Figure 2: FITR spectra of PANI without any metal doping

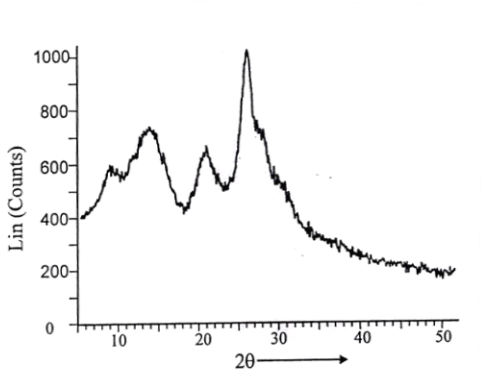

Figure 3: X- ray diffractogram for PANI without any metal doping

Sharma et al [16] have recently reported X-ray runs for their PANI films and reported peaks at 2Θ values of 15.53°, 20.52°, 25.41° and 27.08°. In the present work, however, three additional peaks reported by Sharma et al [16] were broad enough to be seemed only as shoulders of their main peak. Further, it seems that the peaks at 9.50°, 14.0° and 20.5° were quite broadened not to be observed apparently in this work.

In our observations, X- ray peak at 2Θ value of 25.0° is the strongest. As higher order reflections should naturally possess decreased intensities relative to the main peak, the major portion of the present protonated PANI sample corresponds to a crystalline order corresponding to 2Θ as 25.0° with the 'd' value of 3.56 A°. This distance is thus the interchain distance or close-chain distance between two close chains [17]. The 2Θ values of 9.50°, 14.0° and 20.5° must accordingly represent some other ordered arrangements of PANI or oligomers. It may be mentioned that Murugesan and Subramanian [18] have also reported d-spacing for conducting polyaniline with SO_4^{-} trappings to be 3.708 A°, which close to the value obtained as above.

Conclusions

The present optical absorption recordings were for PANI dissolved in NMP, wherein it had got deprotonated and thus no polaron assisted peaks could be expected. The

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results as above also support the conclusions arrived on protonation doping of PANI. The values of 2Θ represents the ordered arrangement of Polyaniline (PANI) oligomers.

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