Synthesis of Acid Doped Conducting Polyaniline

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Summary: Conducting polymers have received considerable attention in the fields of nanoscience and nanotechnology. These materials exhibit enhanced properties in a variety of applications, such as chemical sensors, microreactors/ containers and fuel cells. Micro/ nano-materials of conducting polymers also include micro-containers, nanowires, nanotubes, nanobelts, core corona, hollow spheres, and nanofibers. Polyaniline (PANI) is an air-stable conducting polymer and has attracted increased attention for several reasons; monomer is inexpensive, polymerization reaction is simple, and processing is easy. In this study polyaniline was synthesized by the chemical method in acidic medium using H_2O_2, $K_2S_2O_3$ and $K_2Cr_2O_7$ as oxidizing agents. The reaction was studied at three different temperatures and it was found that maximum yield of aniline was obtained at lower reaction temperature. The polymer was characterized by FTIR, UV-Visible absorption spectroscopy, and conductivity (four probe method). The conductivity measurements revealed that PANI prepared in the presence of $K_2Cr_2O_7$ is a better conducting material among other samples.

Introduction

Conducting polymers have received considerable attention in the fields of nano science and nanotechnology [1-2]. These materials exhibit enhanced properties in a variety of applications such as chemical sensors, microreactors/ containers and fuel cells. Conducting polymer materials also include micro-containers, nanowires, nanotubes, nanobelts, core corona, hollow spheres, and nanofibers. Basically conducting polymers combine the advent-ages of plastics, e.g., flexibility and processing from solution, with the advantage of metals or semiconductors [3-4].

Polyaniline (PANI) is an air stable conducting polymer and has attracted increased attention for several reasons; monomer is inexpensive, polymeri-zation reaction is simple, easy processing from solutions into films and environmental stability [5-6]. Also the electric and optical properties of PANI can be reversibly controlled over a wide range by both charge-transfer doping and protonation [7]. The structure of insulating and conducting PANI is shown in Fig. 1 and 2.

Polyaniline can be synthesized by electro chemical and chemical oxidative polymerization methods [8-12]. The chemical oxidative polymeri-zation process is of particular importance since this synthesis is the most feasible route for the production of polyaniline on a large scale [13].

In this paper we are reporting synthesis of polyaniline by chemical method in acidic medium
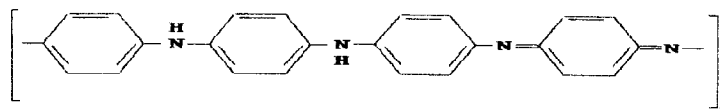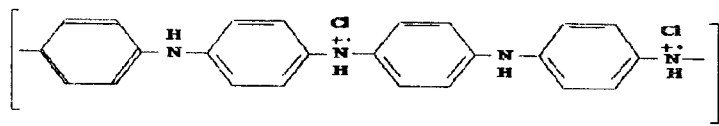

Fig. 1. Insulating emeraldine base from PANI.

Fig. 2. Conducting emeraldine salt from PANI.

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using H_2O_2, $K_2S_2O_3$ and $K_2Cr_2O_7$ as oxidizing agents. The reaction was studied at three different temperatures and it was found that maximum yield of polyaniline was obtained at lower reaction temperature. The polymer was characterized by FTIR, UV-Visible absorption spectroscopy, and conductivity (four probe method). The conductivity measurements revealed that PANI prepared in the presence of $K_2Cr_2O_7$ is a better conducting material among these samples.

Results and Discussion

Table-1 shows percentage yield of PANI, calculated at different temperatures using different oxidizing agents. Table-1 shows that yield of Polyaniline depends on the oxidizing agent as well as the temperature of synthesis. H_2O_2 gives maximum yield as compared to $K_2S_2O_3$ and $K_2Cr_2O_7$. The reason is that H_2O_2 acts as the best initiator and initiates the reaction more rapidly among these oxidizing agents. The initiating capability of $K_2Cr_2O_7$

is low and therefore gives poor yield. Moreover, due to the steric hindrance (bulkiness) of $K_2Cr_2O_7$ is maximum in the used oxidizing agents and can not react easily and therefore gives poor yield. H_2O_2, on the other hand, offers less steric hindrance and can attack on either side of the growing polymer and gives maximum yield.

Table-1: Percentage yield of polyaniline synthesized with different oxidizing agent at different temperature.

Samples	Oxidizing Agents	Yield (%)		
		2 °C	5 °C	8 °C
A	H_2O_2	96%	87%	79%
B	$K_2S_2O_3$	54%	50%	42%
C	$K_2Cr_2O_7$	40%	35%	30%

The lower temperature favors the maximum yield of PANI which is clear from the Table-1. At 2 °C yield is found to be maximum whereas at 8 °C yield is minimum for all the used oxidizing agents.
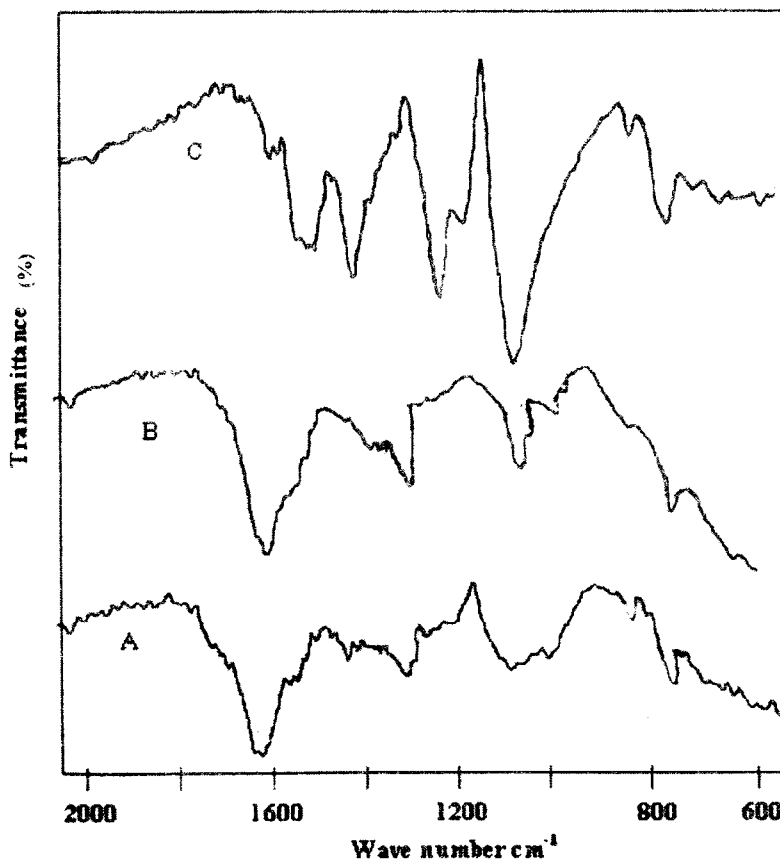

Fig. 3. FTIR spectra of polyaniline samples: (A) sample A, (B) sample B, (C) Sample C

The FTIR spectra of samples of polyaniline are shown in Fig. 4. The band in the region of 1590-1620 cm^{-1} is indicative of the nitrogen bond to benzenoid-quinoid rings and that in the 1280-1350 cm^{-1} region is due to aromatic amine. The band observed in the 1100-1140 cm^{-1} region is the characteristic for conductive PANI and is due to the charge delocalization on the polymer backbone [14]. The intensity of this peak is the measure of the delocalization of the electrons or the conductivity [15]. A very weak band in the region of 900-990 cm^{-1} indicates poly conjugated system.

UV-visible spectra of all the samples are given in Fig. 4. Here λ_{max1} is caused by a π-π^* transitition of aniline and/or anilinium radicals and the λ_{max2} is due to a π-π^* transitition of quinine-imine groups. The color and absorption bands of PANI depend upon the pH of the solution. The spectrum of undoped PANI in DMSO (pH = 6.2) gives two fundamental absorption bands at 323 and 630 nm [16].

At low pH values (pH = 2.7) the absorption band at 630 nm completely vanishes and the band at 435 nm , which corresponds to a π- π^* transition of quinine- iminium ions, and the broad band at about 800 nm, which is due to delocalized free electron states, becomes visible [17].

The pH of 1M HCl doped PANI is very low so the curve in Fig. 4(a) (sample A) gives two absorption bands, one at 328 nm and other at 434 nm. The curve in Fig. 4(b) (sample B) also shows two absorption bands at 320 and 418 nm and in Fig. 4(c) (sample C) absorption bands appear at 322 and 420 nm. It is clear from the comparison of the UV/ VIS spectra of three samples that sample "B" and sample "C" give absorption bands (λ_{max1} and λ_{max2}) about at the same wavelength but λ_{max1} and λ_{max2} of sample "A" shift to somewhat longer wavelength (328 and 434 nm). This shift is most likely due to the increase in the oxidation level of PANI, which increases with the strength of oxidizing agent [18].

Conductivity of different samples of polyaniline is given in following Table-2. All the samples of polyaniline show an increase in voltage

Table-2: Mean Conductivity of Polyaniline samples.

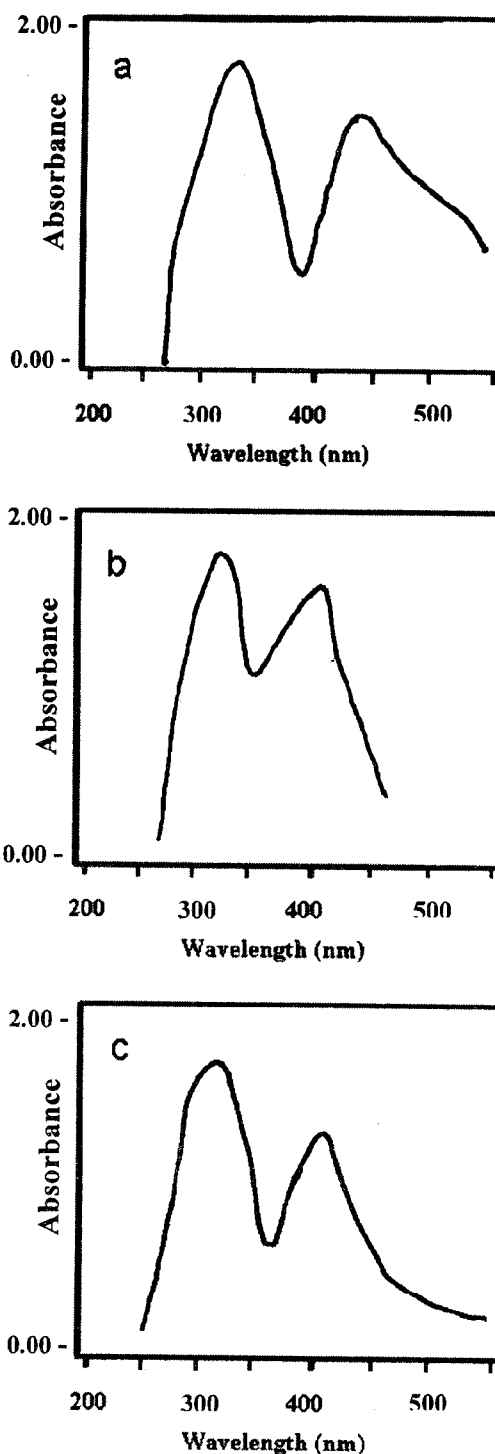| Sample	Mean Conductivity (S cm^{-1})
A	2.004
B	6.60
C	14.67

Fig. 4: UV/Vis spectra of polyaniline samples: (a) sample A, (b) sample B, (c) sample C.

by increasing the current therefore show an ohmic behaviour. It is clear from the Table-2 that the sample "C", which was prepared by using $K_2Cr_2O_7$ as an oxidizing agent, is the best conductor among the three samples and the sample "B", which was prepared by using $K_2S_2O_3$ as an oxidizing agent, is better conductor than sample "A", prepared by using H_2O_2 as an oxidizing agent. The reason is that $K_2Cr_2O_7$ is the strongest oxidizing agent among the above mentioned oxidizing agents with oxidation potential of 1.33 and it creates more active sites (holes) to give maximum conductivity. On the other hand H_2O_2 is weak oxidizing agent with oxidizing potential of 0.88 and it creates least number of active sites among the used oxidizing agents and hence gives minimum conductivity.

The results in this paper show that polyaniline-hydrochloride can be produced with reasonable yield and conductivity by using hydrogen peroxide, potassium thiosulphate, and potassium dichromate as an oxidizing agents. Infrared, electronic absorption, and conductivity measurement results support the formation of polyaniline salts. Maximum yield is obtained in the presence of hydrogen peroxide, whereas maximum conductivity is observed in the samples prepared using potassium dichromate.

Experimental

Material

Aniline (reagent grade) was distilled prior to use and kept under nitrogen. Reagent grade hydrochloric acid (HCl), dimethylformamide (DMF), and acetone was used as purchased. Reagent grade hydrogen peroxide (H_2O_2), potassium persulphate ($K_2S_2O_3$), potassium dichromate ($K_2Cr_2O_7$), and ferrous chloride ($FeCl_2$) was purchased from Merck and used without further treatment.

Sample preparation

In a typical experiment, 5 ml of vacuum distilled aniline was added to 100 ml of 1M aqueous solution of HCl with constant stirring until complete mixing. This mixture was placed in an ice bath at 0 °C. The oxidizing agent (K_2CrO_7, $K_2S_2O_3$, and H_2O_2) was added dropwise under constant stirring to the aniline/HCl solution at 2 °C over half an hour. For oxidizing agent H_2O_2, 0.1 mg of $FeCl_2$ was also added in the aniline/acid solution prior to polymerization. After a few minutes, the dark suspension

became green, indicating a good polymerization. The reaction mixture was placed at 2 °C for about 24 h. At the end, the reaction mixture was filtered under vacuum, the powder was washed with 1M solution of HCl followed by acetone to remove oligomers and other impurities. The polyaniline powder was dried at 50 °C until it reached a constant weight. In this process the polyaniline results in its primary doped form, i.e. emeraldine salt (ES). All samples of polyaniline (A, B and C) were also prepared at 5 °C, and 8 °C. The polymerization yield of all samples of Polyaniline at different temperatures, according to stoichiometric relations with respect to the aniline monomer, was determined.

Characterization

The polyaniline samples were mixed with KBr powder and compressed into pellets, wherein, the polyaniline powder was evenly dispersed. Fourier transform infrared spectra were recorded using FTIR spectrometer (Perkin Elmer A-100).

Electronic absorption spectrum of the polyaniline sample was recorded at ambient temperature using using U-2000 Hitachi spectrophotometer. The solution for the absorption spectrum of polyaniline was prepared by dissolving the sample in dimethyl formamide (DMF) and filtered through Whatman 41 filter paper. Absorption spectrum of the dilute solution was recorded in the range 950–200 nm using a pair of matched 3×10^{-6} m^3 stoppered silica cells of 10 mm path length.

Polyaniline samples were pressed into disks of 8 mm-diameter and ca 2-mm thickness under a pressure of 400 MPa. Resistance measurement of the pellets was carried out by the Four probe method using a Keithley constant current source (MODEL–230) and digital voltmeter (MODEL–195A). Resistance was calculated based on the average of at least three pairs of consistent readings at different points on the pressed pellet. Since, the mean value was used in the calculation of resistance, the total error involved is < 1 %.

Acknowledgement

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