Characterization of synthesized Sn-doped polyaniline

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Abstract

In the present research work considerable effort have been made to modify the structure of Polyaniline by doping it with p-block metal salt such as Stenous Chloride to study its dynamic electrical and mechanical properties. For this the polymer, polyaniline was synthesized by chemical oxidation polymerization method. In this synthesis aqueous solution of aniline hydrochloride was mixed with aqueous solution of ammonium peroxydisulphate used as an oxidizing agent. Further modifiedpolyaniline was synthesized by doping it with Sn^{2+} ions solution. The reaction was stirred for 24 hours with a magnetic stirrer to get product as a precipitate. The resulting products were vacuum filtered and the precipitate was washed with copious amounts of triply distilled water to remove impurities. The polymers, PANI, Sn-doped PANI were dried in desiccators over night and again dried in oven at 40 – 45^0 C. The synthesized compound samples were further characterized by FT-IR and NMR spectral analysis which shows doping in the polymeric structure.

Key words: Pyrrole, Ammonium peroxydisulphate, Polyaniline, Stenous Chloride, distilled water etc.

Introduction:

Polymers have traditionally been considerd good electrical insulators and a variety of their applications have been relied on their this insulating property. However researchers have shown that certain class of polymers which are conjugated (those that possess an extended pi- conjugation along the polymer backbone) exhibit semi conducting behavior. They are electrically conductive which makes their use as metal replacement materials of some interest.

Electronically conducting polymers such as polyaniline (PANI), polythiophene (PTh), polypyrrole (PPy) have become the subject of increased research interest due to a great variety of applications in many fields such as electrochromism, electroluminescence, sensors and energy storage systems, OLEDs etc. Among these conducting polymers special interest has been focused on polyaniline (PANI) due to its excellent thermal and environmental stability combined with relatively high level of electrical conductivity. Extensive studies on theoretical modeling have demonstrated that Polyaniline differs from other conducting polymers because of the important role of phenyl rings along with the presence of nitrogen heteroatom within the conjugation path.

The conducting properties of polyaniline can be made to vary over a very wide range starting from insulating to semiconductor and towards metallic by varying concentration of dopant. In the present

contribution polyaniline is subjected to structural modification by doping it with one of the d-block metal salt solution containing Sn^{2+} ions to study its dynamic electrical, mechanical and optical properties. Polyaniline and modified polyaniline was synthesized by chemical oxidative polymerization method which is further characterized by FTIR and H^1 NMR spectral analysis.

Experimental Methods:

All the chemicals are of A.R.Grade, monomer aniline hydrochloride,oxidizingagent ammonium persulphate and zinc chloride were used in the present work.polyaniline was synthesized by chemical oxidation polymerization method.the aqueous solution of 0.2 M aniline hydrochloride was prepared.To this solution aqueous solution 0.25M ammoniumperoxydisulphate was drop by drop added with vigorousstirring.It was observed that as soon as the monomer mixture was added to the solution, the colour changed almost instantaneously and the solution becomes dark green/black in colour.The reaction was carried out at room temperature. The reaction was stirred for few hours by magnetic stirrer. This reaction mixture was allowed to stand for 24 hours in order to complete polymerization process. The resulting product was vacumm filtered. The precipitate was washed with copious amount of distilled water until the washing was clear. The polymer obtained was dried in dessicator overnight and again dried in an oven at 40^0 C. In this way polymer was synthesized meanwhile for the preparation of Sn doped polyaniline during polymerization process in different reaction mixture with 0.1 M solutions of both dopants were added drop wise with constant stirring and the procedure is repeated as above.

The synthesized sample of PANI, Sn and Co doped PANI were further characterized by FTIR and NMR spectral analysis.

Result and Discussion:

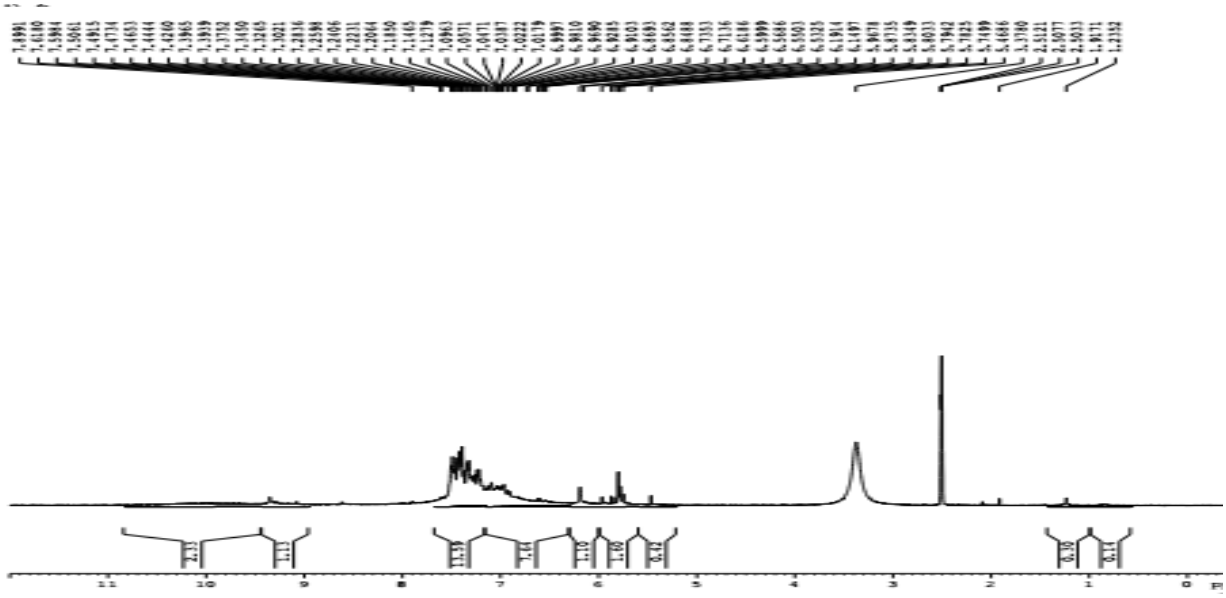
1) **FTIR spectral analysis :-**

In FTIR spectra of Sn-doped polyaniline shows six principle bands at 3315, 3020, 1460, 1142, 955.32 cm^{-1} representing N-H, C=C-H, C=C, C-N and C-C respectively.the band below 900 cm^{-1} reveals C-H bending vibrations.

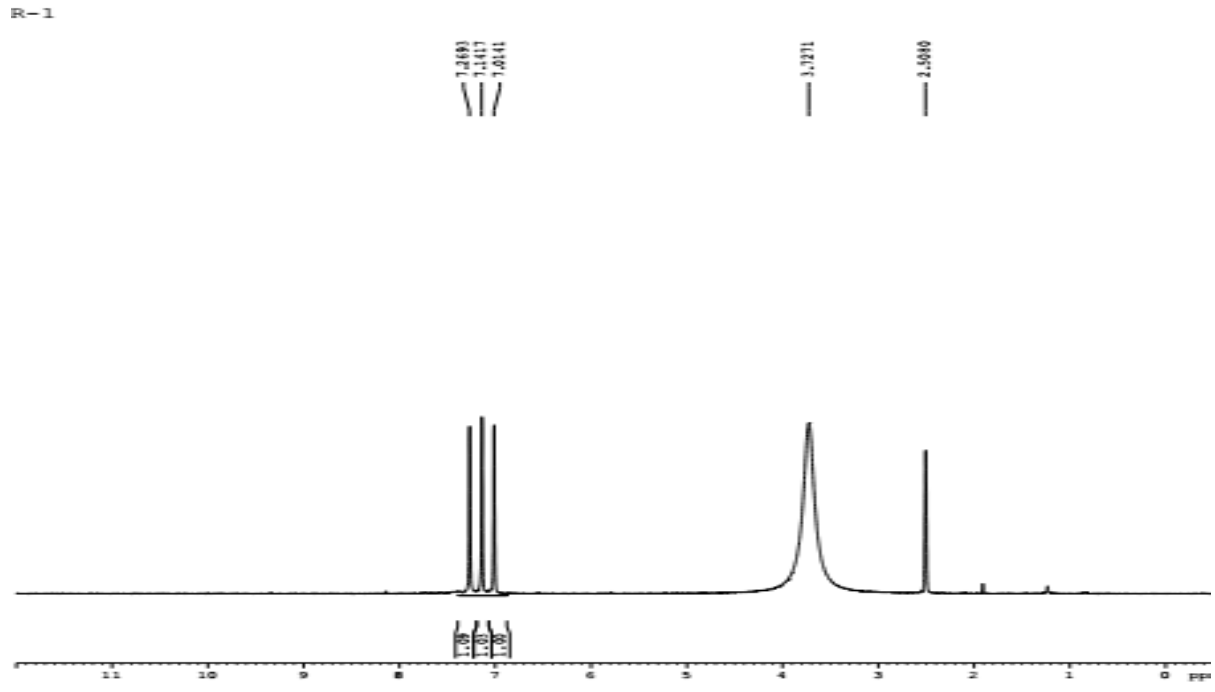
The FTIR spectrum of Sn-doped polyaniline reveals that there is interaction between Sn and Polyaniline and also confirms formation of polymeric structure and increase in extensive pi-conjugation

2) **H^1 NMR spectral analysis :-**

H^1 NMR spectrum of PANI, Sn doped PANI is shown in the following figure.



a) NMR spectrum of polyaniline



b) NMR spectrum of Sn-doped polyaniline Top of Form

From the NMR spectrum of PANI is observed that three signals of δ7.3031 ppm, δ 7.1754 ppm, δ 7.0427 ppm indicates the presence of aromatic character, signal at δ 3.7271 ppm attributed to N-H bonding. In NMR spectrum of Sn-doped PANI δ 6.5325 ppm toδ 7.3031 ppm indicates presence of aromatic character and peak at δ 3.3780 ppm indicates presence of N-H proton.

In case of conjugated organic polymers delocalization of electrons is possible due to extensive pi-conjugation along the polymeric structure. Conducting polymers have very low HOMO-LUMO band gap. This band gap controls electronic and optical properties of conducting polymers. A reduction in HOMO-LUMO band gap increases the conductivity of the polymers. The IR and NMR spectra reveals increase in extensive pi- conjugation in polymeric chain responsible for variation in electrical property of the material.

Conclusion:

FTIR spectra of Sn-doped polyaniline shows six principle bands representing N-H, C=C-H, C=C, C-N and C-C stretching vibrations. The FTIR spectrum of Sn-doped polyaniline reveals that there is interaction between Sn and Polyaniline and also confirms formation of polymeric structure and increase in extensive pi-conjugation

Above discussion about NMR spectral analysis of PANI, Sn-doped PANI and it has been found that peaks are shifted towards lower δ value. This indicates the doping of Sn in polyaniline.

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