

Synthesis of conducting polymer, polyaniline doped with monobasic organic acid (benzoic acid) by chemical oxidation and its characterization.

V.T.Bhugul

Department of Engineering chemistry & polymer chemistry,
College of Engineering & Technology Akola, India.

Abstract: Conducting polymers has been observed as frontier area of research and prospective materials for technological applications since last decade. The polymerization mechanism, processability, and transport mechanism are the point of academic and scientific attractions. Among the conducting polymers polyaniline (PANI) possesses exceptional properties to be considerable for application in diodes, Field effect transistors, Solar cells and Gas sensors. In this work PANI was synthesized in the form of emeraldine salt by the chemical oxidation method using Ammonium peroxydisulphate as an oxidizing agent adding Benzoic acid as dopant. The synthesized PANI was subjected to the physico-chemical characterization by X-ray diffraction, photoluminescence and FTIR Spectroscopic study. From the XRD pattern it was observed that interfacial polymerization offers a peak at a 2θ value of 22.9° with d spacing value 3.88\AA . Photo luminescence spectrum of the synthesized PANI shows an emission peak at 421 nm with band gap value 2.95 eV . FTIR absorption peaks representing the surface bonding of PANI and their vibrational modes were also observed.

Key words : PANI, chemical oxidation, XRD, FTIR.

Introduction: In the modern world, plastic and electrical devices are always tightly integrated together. However, it was in 1977 that an electrically conductive, quasi one-dimensional organic polymer, polyacetylene was discovered [1]. During the past 20 years, a variety of different conducting polymers have been developed [2,3]. Excitement about these polymeric materials is evidenced by the fact that the field of conducting polymers has attracted scientists from such diverse areas of interest as synthetic chemistry, electrochemistry, solid state physics, materials science, polymer science, electronics and electrical engineering [4,5]. Among the conducting polymers, polyaniline is emerging as the material of choice for many applications. It is typically phenylene based polymer having a chemically flexible $-\text{NH-}$ group in the chain flanked either side by phenylene ring. The protonation, deprotonation and various physico - chemical properties of polyaniline are due to presence of this group. Polyaniline (PANI) is a unique and promising candidate for potential applications because of its stability in air and solubility in some organic solvents. It also exhibits dramatic changes in its electronic structure and physical properties on protonation. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known since 1862 as aniline black. The interest in this conducting polymer stems from the fact that many different rings and nitrogen-substituted derivatives can be readily synthesized and that each of the derivatives can exist in several different oxidation states which can in principle be "doped" by a variety of different dopants either by non-redox processes or by partial chemical or electrochemical oxidation. These properties, combined with the fairly high conductivity after doping, their ease of synthesis and processing, satisfactory environmental stability, simple doping by protonic acid, its polymerization proceeds with high speed and the resulting salt is quite stable and show relatively high level of conductivity.

Generally PANI exists in three forms namely Leucoemeraldine, Pernigraniline and Emaraldine. In the Emaraldine form, it exists in insulating state [Emaraldine base (EB)] and conducting state [Emaraldine salt (ES)] with conductivity (σ) around 10^{-10}S/cm and 10^{-1}S/cm respectively. Emaraldine salt form is obtained upon protonation of Emaraldine Base with protonic acids i.e., oxidative doping. In this work synthesis of PANI in emeraldine salt form by chemical oxidation method using Ammonium peroxydisulphate as an oxidizing agent and doping with Benzoic acid was carried out and its characterization was done by X-ray diffraction, photoluminescence and FTIR spectroscopic studies. In this work PANI is prepared by chemical oxidative polymerization doped with monobasic organic acid such as benzoic acid.

2. Experimental:

Synthesis of polyaniline by chemical oxidation:

In the synthesis process, 244 mg of benzoic acid and 930 mg of aniline were dissolved in 200 ml deionized water with magnetic stirring at room temperature for half an hour. After that 10 ml aqueous solution of ammonium peroxdisulfate (APS) was added to the above mixture in one portion. The resulting solution was stirred for another 20 minute to ensure complete mixing. The reaction was then allowed to proceed without agitation for 24 hour at room temperature. Finally, the products were washed with deionized water and ethanol until the filtrate became colorless, and then dried in air at room temperature. The XRD pattern is recorded with help of Rigaku (Ultma-IV) diffractometer by using CuK α X-rays of wave length 1.54 \AA . Photoluminescence (PL) spectra were recorded on a RF-5301 spectrometer excitation wavelength 421nm at room temperature. Fourier transform infrared (FTIR) spectrum was recorded by Fourier Transform Infrared Spectrophotometer (Shimadzu IRAFFINITY 1-S).

3. Results and discussions

3.1 XRD analysis:

The X-ray diffraction pattern of PANI emeraldine salt form (Figure 1) shows a sharp peak at $2\theta=22.90$. The interplanar distance value obtained is 3.88 \AA . The average crystallite size is calculated by Debye Scherer equation, $D = k\lambda / \beta \cos \theta$, Where, K is the shape factor (0.89); D is the average crystallite size; λ is the wavelength of X ray radiation used (1.54 \AA); β is the full width at half maximum; θ is the diffraction angle.

Average crystallite size value obtained is 1.398nm [6, 7]. Generally polymers are considered to be amorphous, but here the synthesized polymer showing crystalline structure due to its fiber nature and planar nature of benzenoid and quinoid functional groups.

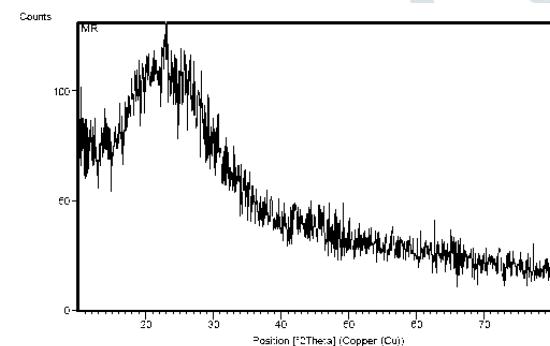


Figure.1 XRD Pattern of PANI emeraldine salt

3.2 Photoluminescence analysis

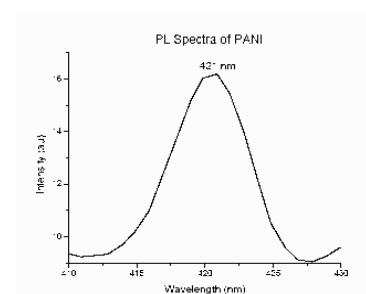


Figure.2 PL Spectrum of PANI emeraldine salt

Photoluminescence is the light emission from any form of matter after the absorption of photons. They undergo emission over a wide range from the violet to the red. They can also be combined in several different forms to produce white light. One category of organic material with PL properties is organic polymers. Photoluminescence emission peak obtained in the present study for polyaniline is 420nm as shown in Figure 2. This peak arises due to transitions from the polaronic band to the π band structures of PANI. The direct band gap energy of PANI is found as 2.95eV.

3.3 FTIR analysis:

Fourier transfer infrared spectrum of PANI shows all the major peaks of benzoic acid doped PANI. The distinct absorption bands represent the characteristic bands of PANI [8]. The FTIR spectrum of PANI is as shown in Figure 3. In the

spectrum the band observed at 3429.43cm^{-1} is due to O-H stretching vibrations. The polymer shows the absorption bands at 2922.17 and 2852.73cm^{-1} were due to asymmetric C-H and symmetric C-H stretching vibrations. The band at 1653cm^{-1} was attributed to C-C stretching mode vibrations. The bands at 1581.63 and 1506.41cm^{-1} were attributed to C-H stretching on aromatic ring. The absorption peak observed at 1301.95cm^{-1} was attributed to C-N stretching of primary aromatic amines. The characteristic peak at 1238.30cm^{-1} is due to C-N stretching mode vibrations. The peak at 1149.57cm^{-1} was attributed to quinonoid unit of PANI. The characteristic peak at 1041.56 cm^{-1} is due to $-\text{SO}_3\text{H}$ mode. The peak at 829.40 cm^{-1} attributes due to the out of plane hydrogen deformation of aromatic rings in PANI unit sequences [9].The bands at 696.30cm^{-1} and 590.23 cm^{-1} were attributed to aromatic ring and also the peak at 507.28 cm^{-1} corresponds to C=N amino quinone mode. The above characteristic peaks confirm the formation of PANI.

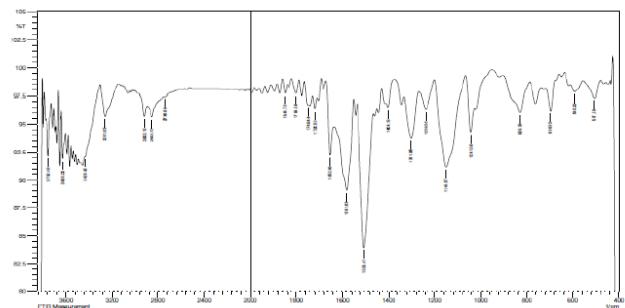


Figure. 3 FTIR Pattern of Polyanilineemeraldine salt

Conclusion:

In this work PANI emeraldine salt was synthesized by chemical oxidative polymerization method .The synthesized polymer was characterized by XRD, PL and FTIR spectroscopic techniques. The X- ray diffraction pattern of PANI emeraldine salt form shows a sharp peak at $2\theta=22.9^{\circ}$ and d-spacing value obtained is 3.88 \AA . The PL analysis shows the PANI emission peak at 420 nm with direct band gap value obtained is 2.95eV . The FTIR characteristic peaks obtained confirm the formation of PANI.

References:

- Y.W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, A.G. MacDiarmid, Journal of the American Society, 100,1113 (1977).
- T.A. Skotheim, Handbook of Conducting Polymer, Marcel Dekker, New Jersey,(1981).
- C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E.J. Louis, S.C.Gau and A.G. MacDiarmid, Phys. Rev. Lett.39 (1977) pp.1098
- Ram M K, Yang O, Lahsangarh V and Aldissi M. CO Gas Sensing from Ultrathin Nano- Composite Conducting Polymer Films. Sensors and Actuators B., 2005, 106:750-757.
- Liu G and Freund M S. New Approach for the Con-trolled Cross-Linking of Polyaniline: Synthesis and Characterization. Macromolecule., 1997, 30: 5660-5665.
- Cheng-Ho Chen. Thermal and morphological studies of chemically prepared emeraldine- base- form polyaniline powder. Journal of Applied Polymer science., 2003, 8: 2142-2148.
- Gupta K K, Jasnal M, Agarwal K. Sol-gel derived titanium dioxide finishing of cotton fabric forself cleaning. Indian Journal of fiber and Textile research., 2008, 33:443- 450.
- Sariciftci N S, Kuzmany H, Neugebauer H, Neckel A. Structural and electronic transitions in Polyaniline: A Fourier transforms infrared spectroscopic study. J. Chem. Phys., 1990, 92:4530-4537.
- Draman S F S, Daik R, Ahmad M. Synthesis and studies on fluorescence spectroscopy of CSA-doped polyaniline solution in DMF when exposed to oxygen gas. Malaysian Polym.J., 2009, 4: 7-18.