

# EFFECT OF OXIDANT CONCENTRATION ON THE CONDUCTIVITY OF POLYANILINE (PANI)

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## Abstract

Conducting polymers can replace metals in a product where electric conduction is the main priority. Polyaniline (PANI) is the most studied conducting polymer among other conjugated families of polyacetylene, polypyrrole and polythiophene. PANI is not conducting polymer itself but can be made conducting when doped and oxidized. Conductivity of PANI can be modified by changing dopant species, oxidant species, oxidant to monomer molar ratio and processing conditions. Effect on conductivity of PANI was studied by varying the oxidant to monomer molar ratio. Different samples were prepared by chemical polymerization technique. Chemical characterization was performed by Fourier-Transform Infra-Red (FT-IR) spectroscopy. Chemical analysis confirmed that prepared PANI-doped-oxidized samples were conducting. The conductivity values were determined by Four-Point probe method. The results suggested that PANI has maximum of conductivity at specific value of oxidant to monomer molar ratio.

## Key Words

Polyaniline (PANI), dopant, initiator/oxidant, FT-IR, Four-Point probe method

## Introduction

Conducting polymers are those organic materials which can conduct electricity just as metals do. In metals free electrons or holes are responsible for electric conductivity. The same charge carriers (electrons and holes) in synthetic organic conducting polymers make them capable to conduct electricity [1]. Conducting polymers act as metals but processing is easier than metals [2]. They find their application in data storage, processing of signals and energy storing devices [3]. Nobel Prize was awarded to MacDiarmid, Heeger, and Shirakawa in 2000 for "The discovery and development of conductive polymers". Then there was boost in research work of discovering the conducting polymers, developing the synthesis techniques and improving the properties. These research works make us familiar with basic chemistry, physics and science of materials and enables us to fulfill the industrial needs [3, 4, 5]. Conducting polymer families of polyacetylene, polypyrrole, polythiophene and PANI are studied mostly. PANI has gained researchers attention because of its improved electrical, optical, chemical, and the mechanical properties. PANI is greenish black conducting polymer and used extensively for electronic applications [3]. A base polymer which has conjugated structure is used and is made conductive when structure is modified by dopants and oxidizing agents. Oxidizing agents oxidize the dopants. Dopants are usually protonic acids and they oxidized the base polymer while reducing themselves. Those oxidizing agents are preferred which result in most conductive and most favorable emeraldine oxidation state. Other oxidized states leucoemeraldine and pernigraniline are not capable of conduction because one is fully oxidized (pernigraniline) and other is fully reduced (leucoemeraldine). Emeraldine is partially oxidized. Charge carriers like electrons, ions, holes, metallic islands, polarons, bipolarons are created by dopants and oxidizing agents [6, 7]. The conduction is devised by four mechanisms. Conductivity of charges in conducting polymers and polymer electrolytes is suggested through formation of polarons and bipolarons [1, 8, 9], formation and charge transfer by metallic islands [10], hopping of ions [8] and ion migration through Schottky and Frenkel defects [11] as shown in Figure-1.

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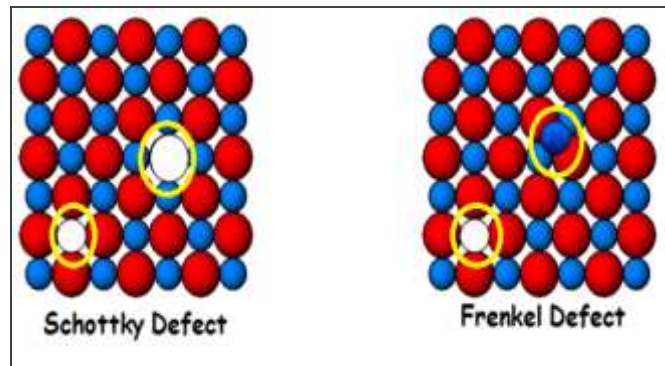


Fig.-1 Migration of ions due to Schottky and Frenkel defects

Conductivity of PANI depends on two parameters. One is the degree of oxidation and the other is degree of protonation [12]. Properties of PANI are dependent on polymerization conditions (pH, temperature and time), concentration of monomer, dopant type and mainly monomer to oxidant molar ratio [13, 14, 15]. So, PANI of modified electrical, optical and chemical properties can be developed [2] and can be used in more advanced applications of sensors, actuators, anti-static coating, membranes, diodes, data and energy storing devices [3, 16, 17]. In this work of research PANI of different electrical and chemical properties was prepared by changing the molarity/concentration of oxidant while using one doping acid HCl with constant molarity. Electrical properties were determined by four-point probe method while chemical characterization is performed by Fourier-Transform Infra-Red (FT-IR) spectroscopy.

### Experimental Materials

Materials supplied by the department were used. Aniline monomer, Ammonium peroxydisulfate (APS) oxidant and doping hydrochloric acid HCl acid were purchased from Akzo Nobel.

### Processing

Chemical polymerization technique was used to synthesize PANI. Aniline monomer was mixed with hydrochloric acid to prepare 0.2M aniline salt (aniline hydrochloride). Oxidant ammonium peroxydisulfate (APS) solutions of different molarity were prepared. Both solutions were mixed and gently stirred for 15 minutes. Then solutions were left at rest for 24 hours for polymerization. The polymerized and protonated PANI is shown in figure-2.

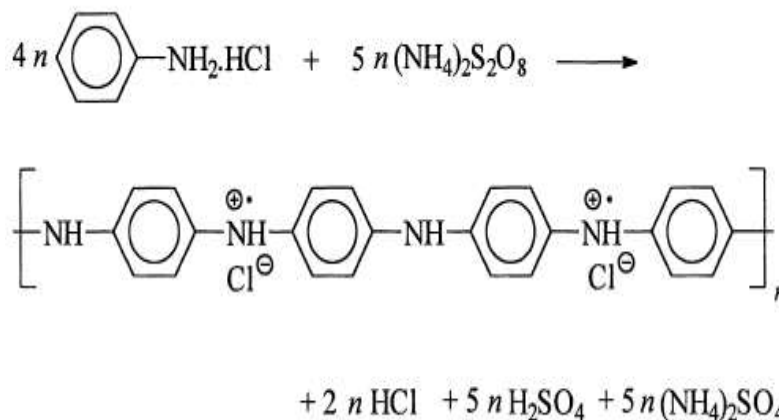


Fig.-2 Oxidation of aniline hydrochloride with ammonium peroxydisulfate yields PANI-hydrochloride

PANI precipitates were taken from filter paper. PANI (emeraldine) powder was desiccated at controlled conditions [18]. The recipes of prepared samples are given in Table-1.

Sr #	Weight of initiator in 50mL water (g)	Molarity of initiator solution (M)	Molarity of aniline-hydrochloride (M)
1	0.799	0.07	0.2
2	1.712	0.25	0.2
3	2.852	0.35	0.2

## Testing and Analysis

### Chemical Characterization

Chemical analysis was completed by Fourier Transform Infra-Red (FT-IR) spectroscopy (Jasco Spectra Manager). FT-IR spectroscopic technique analyzed the presence of functional groups which are responsible for conducting behavior of PANI. Experiments were performed according to FT / IR-4000, 6000 operating manual. Pellets of samples and reference material (KBr) were made. Pellets of samples contain 200 mg of grinded KBr and some fine particles of prepared PANI. While reference pellet contain only 200 mg of grinded KBr. Background spectrogram was recorded by scanning of reference pellet in FT-IR apparatus. Then samples were placed in FT-IR and their spectrograms were recorded. Only PANI peaks were showed in these spectrograms because KBr presence was taken as background of the spectrum. Comparison of standard PANI-HCl spectrogram and scanned results confirmed that the prepared PANI would be conductive.

### Electrical Characterization

Four-probe method finds conductivity of materials at room temperature. Four-point probe method noted voltage difference when a current was passed from test specimen. The resistance to current flow inversely showed the conductivity of PANI. The test specimen was compressed at 700 MPa to make pellet and should have diameter more than 8.4 mm. Pellets of 14 mm diameter were prepared.

### Chemical Structural Analysis

The verification of conducting PANI was analyzed by chemical analysis which was made by comparing the FT-IR results of samples with standard PANI-HCl spectrogram. The Three (3) PANI samples were doped with HCl and oxidized with APS while changing concentration / molarity of APS oxidant / initiator.

The spectrogram of PANI-0.2 Molar HCl-0.07 Molar APS is shown in Figure-3.

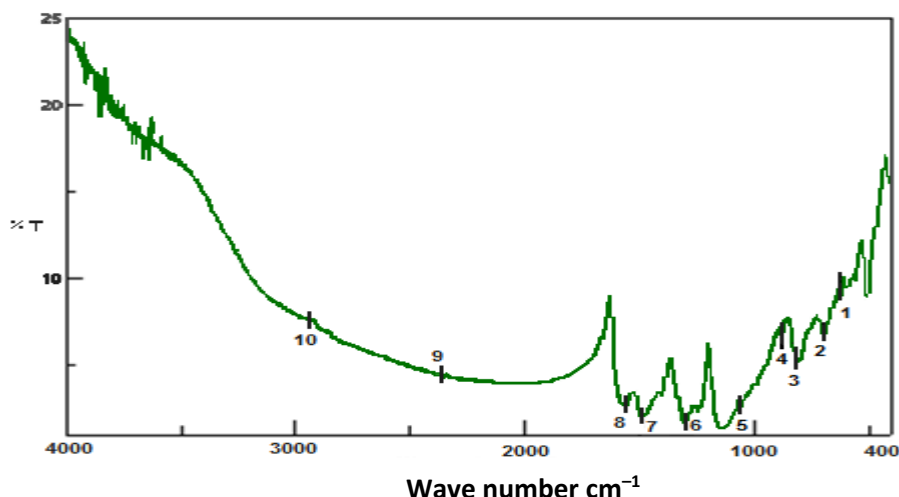


Fig.3 Spectrogram of PANI-HCl sample oxidized by 0.07M of APS with wave number ( $\text{cm}^{-1}$ ) on x-axis and % T (percentage transmittance) on y-axis

In Table-2 the functional groups (and their type of vibration) are shown against respected wave number and a comparison is made between experimental and standard values of wave number.

Table-2 Comparison of experimental PANI-HCl-0.07M of APS Wave numbers with standard PANI-HCl		
Wave number (cm <sup>-1</sup> )	Functional group	Standard PANI-HCl
700.034	CH out of plane deformation	
812.849	Out-of-plane C-H bending	795
880.345	CH deformation	
1055.84	B-NH <sup>+</sup> -B or Qa=NH <sup>+</sup> -B	1104
1296.82	N-H bending	1297
1484.92	N-B-N stretching	1473
1566.88	N=Q=N stretching	1557
2362.37	Amido Group	

Out-of-plane C-H bending, B-NH<sup>+</sup>-B or Qa=NH<sup>+</sup>-B, N-H bending, N-B-N stretching and N=Q=N stretching are responsible for electricity conduction and are in accordance with standard PANI-HCl conducting polymer. Results were noted that a conducting polymer was formed as confirmed by presence of amino and imino groups.

The spectrogram of PANI-0.2 Molar HCl-0.25 Molar APS is shown in Figure-4.

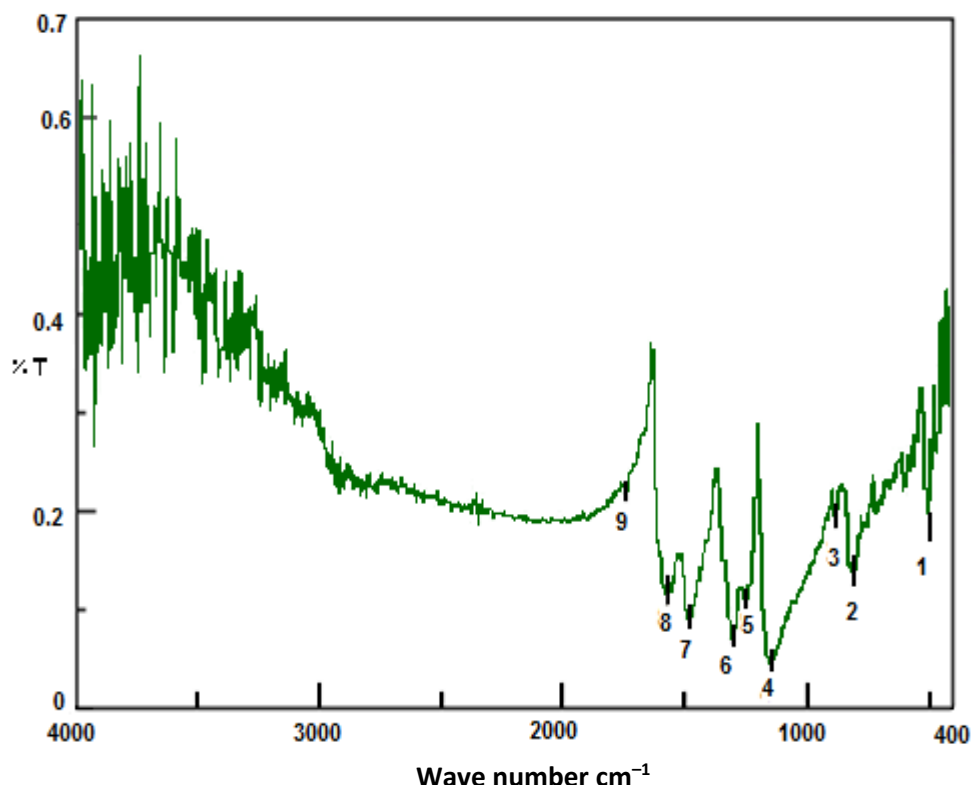


Fig.-4 Spectrogram of PANI-HCl sample oxidized by 0.25M of APS with wave number (cm<sup>-1</sup>) on x-axis and % T (percentage transmittance) on y-axis

In Table-3 the functional groups (and their type of vibration) are shown against respected wave number and a comparison is made between experimental and standard values of wave number.

Table-3 Comparison of experimental PANI-HCl-0.25M of APS wave numbers with standard PANI-HCl		
Wave number (cm <sup>-1</sup> )	Functional group	Standard PANI-HCl
591.08	C-Cl	
812.85	Out-of-plane C-H bending	795
963.52	CH=CH-(trans)	
1138.76	B-NH <sup>+</sup> -B or Q=NH <sup>+</sup> -B	1104
1237.11	C-N stretching	1241
1298.82	N-H bending	1297
1489.74	N-B-N stretching	1473
1562.06	N=Q=N stretching	1557
2362.37	amido Acid	

Out-of-plane C-H bending, B-NH<sup>+</sup>-B or Q=NH<sup>+</sup>-B, C-N stretching, N-H bending, N-B-N stretching and N=Q=N stretching for both experimental and standard of amino and imino functional groups confirmed that prepared PANI was conducting polymer.

The spectrogram of PANI-0.2 Molar HCl-0.35 Molar APS is shown in Figure-5.

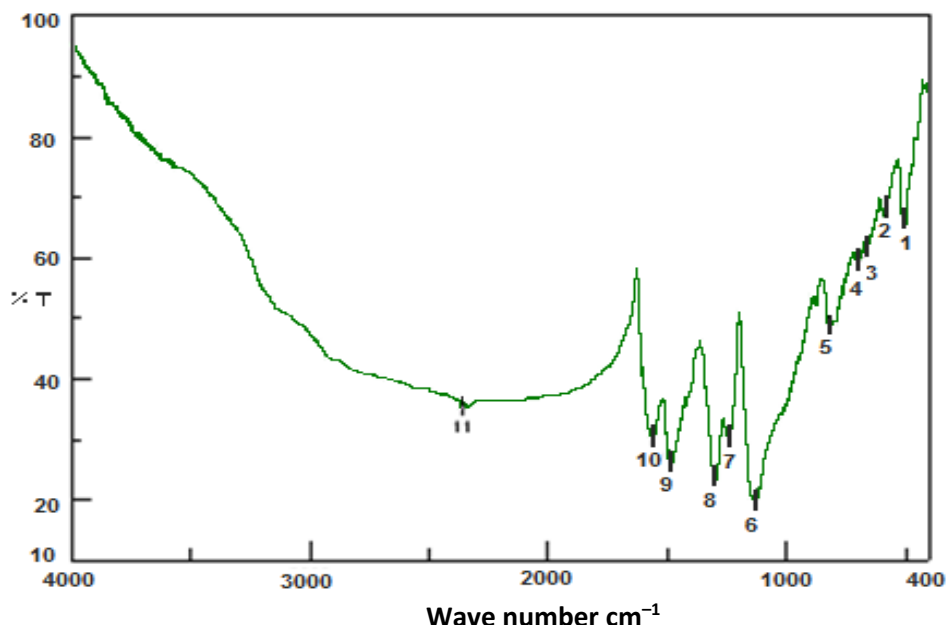


Fig.-5 Spectrogram of PANI-HCl sample oxidized by 0.35M of APS with wave number (cm<sup>-1</sup>) on x-axis and % T (percentage transmittance) on y-axis

In Table-4 the functional groups (and their type of vibration) are shown against respected wave number and a comparison is made between experimental and standard values of wave number.

Table-4 Comparison of experimental PANI-HCl-0.35M of APS wave numbers with standard PANI-HCl		
Wave number(cm <sup>-1</sup> )	Group	Standard PANI-HCl
587.218	amide	
665.321	C-Cl	
701.962	CH out of plane deformation	
821.527	Out-of-plane C-H bending	795
1134.9	B-NH <sup>+</sup> -B or Q=NH <sup>+</sup> -B	1104
1243.95	C-N stretching	1241
1301.72	N-H bending	1297
1483.96	N-B-N stretching	1473
1562.06	N=Q=N stretching	1557

Out-of-plane C–H bending, B–NH<sup>+</sup>–B or Q=NH<sup>+</sup>–B, C–N stretching, N–H bending, N–B–N stretching and N=Q=N stretching at same wave numbers for both experimental and standard of amino and imino functional groups verified preparation of conducting polymer.

The chemical analysis confirmed that conducting form of PANI was prepared. Then exact values of conductivities were noted by Four-Point probe method.

Those boxes in Tables 2, 3 and 4 under “Standard PANI-HCl” are left blank intentionally. When we performed FTIR analysis of our samples and chose about 9 or 10 peaks from each spectra, those peaks are explained with respect to functional groups, but at the same time some of those points (2 – 3 from 9 or 10) varied from standard PANI sample doped by HCl. Comparison is made only to show that we prepared Doped PANI which would have some conductivity value which was further measured by respective method of four point probe method.

### Conductivity Analysis

Four-point probe method found resistivity of samples by using equation 1.

$$\rho = 2a \Pi s (V/I) \quad (1)$$

Where,  $\rho$  is resistivity ( $\Omega$ ),  $a$  is thickness correction factor,  $s$  is spacing between 2 probes,  $V$  is voltage and  $I$  is applied current. The correction factor ‘ $a$ ’ is measured by thickness  $t$ , spacing  $s$ , and diameter  $d$ . The ratio  $d / s$  suggests the thickness correction factor, multiplied by the answer of resistivity. Diameter ‘ $d$ ’ was 14 mm, thickness ‘ $t$ ’ was 1.5 mm, spacing between 2 probes ‘ $s$ ’ was 0.28 mm, ‘ $d / s$ ’ would be 5 (from 14 / 2.8), so, the correction factor “ $a$ ” was 0.7419.

By using the equation (1), the Conductivity [ $S / \text{cm}$  or  $(\Omega \text{ cm})^{-1}$ ] was calculated of PANI samples as given in Table-5.

Table-5 Conductivity values of polyaniline (PANI) samples		
Serial #	Aniline hydrochloride with different APS	Conductivity $(\Omega \text{ cm})^{-1}$
1	0.07 M	$4.98 \times 10^{-12}$
2	0.25 M	$9.27 \times 10^{-6}$
3	0.35 M	$5.31 \times 10^{-10}$

Conductivities values were recorded when samples were dried in oven [8]. Water contents in PANI samples can cause an increase in value of conductivity. There was 5 time increase in conductivity when moisturized PANI samples were tested than dry ones [6, 19, 20]. The varying conductivities for different concentrations of APS initiator were achieved. Each concentration led to different oxidation state of polymer structure while electronic behavior depends on structural disorder and resonance of charges [21, 22]. The conductive inhomogeneous polymer phase can be created by varying oxidant species, oxidant to monomer molar ratio, dopant species and processing conditions (temperature, pH, mixing mechanism) [23, 24]. These modifications lead to such morphology of chains which have charge transitions and hence there will be increased ion transfer (delocalization and hopping-jumping-leaping) [25, 26]. So PANI properties were modified with respect to ratio of oxidant to monomer. The shifting of conductivities is attributed to different oxidation levels. The results cleared that there was increase in conductivities because of increased oxidation and vice versa. The results showed that oxidant to monomer molar ratio of 1.25 have maximum conductivity value as literature suggested that ratio should lie between 1.20 and 1.25 [23].

### CONCLUSION

The conducting PANI was doped with protonic acid HCl and was oxidized by Ammonium Peroxydisulfate APS. The conductivity may change by varying oxidant species, oxidant to monomer molar ratio, dopant acid species and processing conditions (time, temperature, pH, type of mixing). The difference in conductivities may be attributed to the variations in electronic structure (delocalization), number of produced charges/ions, oxidation level and change in

polymer chains morphology. Recent research depicted variations in conductivity by varying oxidant to monomer molar ratio. One sample was prepared with ratio below than 1.25 and one with value above than 1.25. The molar ratio of 1.25 of oxidant to monomer was taken because previous literature suggested that it is the optimized value between reduced and oxidized states. Over oxidation is prohibited because over oxidized form of PANI (pernigraniline PANI even when acid doped) is poor conductor of electricity. On other hand the fully reduced PANI (leucoemeraldine doped with acid) is also poor electricity conducting form. This experimental study revealed that the maximum of conductivity can be achieved when the molar ratio of oxidant to monomer lie between 1.20 and 1.25.

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### **References**

- [1] E. M. Genies, A. Boyle, M. Lapkowski, C. Tsintavis, Polyaniline: A historical survey, *Synthetic Metals*, 36(2), 1990, 139-182.
- [2] J. Stejskal, R.G. Gilbert, Polyaniline (PANI). Preparation of a conducting polymer (IUPAC Technical Report), *Pure Applied Chemistry*, Vol. 74, 2002, 857–867.
- [3] G. G. Wallace, G. M. Spinks, L. A. P. Kane-maguire, and P. R. Teasdale, *Conductive electroactive polymers, intelligent materials systems*, 3rd ed. (CRC Press, Boca Raton, FL, 2008)
- [4] M. Jaiswal, R. Menon, Polymer electronic materials: a review of charge transport, *J Polymer International*, 55(12) (2006)1371-1384.
- [5] C. Weder, Organometallic conjugated polymer networks, *J Inorganic and Organometallic Polymers and Materials*, 16(2) (2006) 101-113
- [6] J. R. Schrieffer, Theoretical concepts of conducting polymers, *J Synthetic Metals*, 43(1-2), (1991) 3307-3366.
- [7] M. Campos, Jr. B. Braz , Mechanism of conduction in doped polyaniline, *J. Phys. D: Appl. Phys.* 30 (1997) 1531-1535
- [8] A. P. Monkman, D. Bloor, G. C. Stevens, J. C. H. Stevens, P. Wilson, Electronic structure and charge transport mechanisms in polyaniline. *J Synthetic Metals*, 29(1) (1989) 277-284.
- [9] V. Luthra, R. Singh, S. K. Gupta, A. Mansingh, Mechanism of dc conduction in polyaniline doped with sulfuric acid. *J Current Applied Physics*, 3(2-3) (2003) 219-222.
- [10] H. H. S. Javadi, F. Zuo, K. R. Cromack, M. Angelopoulos, A. G. MacDiarmid, A. J. Epstein, Charge transport in the "emeraldine" form of polyaniline. *J Synthetic Metals*, 29(1), (1989) 409-416.
- [11] C. Kittel, *Introduction to Solid State Physics* - 8th ed. Wiley, 2005
- [12] J. C. Chiang, A. G. MacDiarmid, Polyaniline: Protonic acid doping of the emeraldine form to the metallic regime, *Synthetic Metals*, 13 (1–3) (1986) 193–205
- [13] Y. Cao, A. Andreatta, A. J Heeger, P. Smith, Influence of chemical polymerization conditions on the properties of polyaniline. *J Polymer*, 30(12) (1989) 2305-2311.
- [14] P. K. Kahol, K. K. S. Kumar, S. Geetha, D. C. Trivedi, Effect of dopants on electron localization length in polyaniline. *J Synthetic Metals*, 139(2) (2003) 191-200.

- [15] JX. Huang, RB. Kaner, A general chemical route to polyaniline nanofibers. *J Am Chem Soc* 126 (2004) 851-855
- [16] I. F. Perepichka, D. F. Perepichka, H. Meng, F. Wudl, Light-emitting polythiophenes. *J Advanced Materials*, 17(19) (2005) 1281-2305.
- [17] D. James, S. M. Scott, Z. Ali, W. T. O'Hare, Chemical Sensors for Electronic Nose Systems, *J Microchim. Acta* 149 (2005) 1–17
- [18] Siddramaiah, *Practicals in polymer science (synthesis and qualitative and quantitative analysis of macromolecules)*. (CBS Publishers & Distributors, 2007)
- [19] W. J. Feast, J. Tsibouklis, K. L. Pouwer, L. Groenendaal, E. W. Meijer, Synthesis, processing and materials properties of conjugated polymers, *J Polymer* 37(22), (1996) 5017-5047.
- [20] H. H. S. Javadi, M. Angelopoulos, A. G. MacDiarmid, A. J. Epstein, Conduction mechanism of polyaniline (PANI): Effect of moisture. *J Synthetic Metals*, 26(1) (1988) 1-8.
- [21] H. H. S. Javadi, M. Angelopoulos, A. G. MacDiarmid, A. J. Epstein, R. H. S. Menon, *Handbook of Organic Conductive Molecules and Polymers*, New York, 1997.
- [22] R.S. Kohlman, A.J. Epstein, T.R. Skotheim, R.L. Elsenbaumer, J.R. Reynolds, Marcel Dekker, *Handbook of Conducting Polymers*, New York, 1997.
- [23] N. Bicak, B. F. Senkal, E. Sezer, Preparation of organo-soluble polyaniline in ionic liquid. *J Synthetic Metals*, 155 (1) (2005) 105–109
- [24] P. K. Kahol, K. K. S. Kumar, S. Geetha, D. C. Trivedi, Effect of dopants on electron localization length in polyaniline, *J Synthetic Metals*, (139) (2003) 191–200  
<http://144.206.159.178/ft/983/183986/4700875.pdf>
- [25] J.P. Pouget, Z. Oblakowski, Y. Nogami, P.A. Albouy, M. Laridjani, E.J. Oh, Y. Min, A.G. MacDiarmid, J. Tsukamoto, T. Ishiguro, A.J. Epstein, Polymer are metals too, *J Synthetic Metals* 65 (1994) 131.
- [26] Y.Z. Wang, J. Joo, C.-H. Hsu, J.P. Pouget, A.J. Epstein, *J Phys. Rev. B* 50 (1994) 16811.