Research Journal of Pharmaceutical, Biological and Chemical Sciences

Synthesis and Characterization of Polyaniline at Different Temperatures.

Omar Melad*.

Chemistry Department, Al-AzharUniversity-GAZA, P.O.Box 1277, GAZA, Palestine.

ABSTRACT

In this work, the synthesis of a conductive polymer which is polyaniline (PANI) was achieved by chemical oxidation of monomer at different temperatures (-3, 0, 6 and 25 º C). Aniline was oxidized in an aqueous medium with ammonium persulphate (APS) as oxidant and 1.0 M HCl. Lithium chloride was used in sufficient amount to prevent the freezing of aniline mixture at low temperatures. The amount of polyaniline obtained is reduced with increasing the temperature. The best electrical conductivity of the polyaniline was obtained at lower temperatures (0,-3ºC). The resulting polyaniline at different temperatures was characterized by FTIR and Uv-Vis spectrometry.

Keywords: Polyaniline, Electrical conductivity, Chemical synthesis, elemental analysis, FTIR, Uv-Vis studies.

Corresponding author

INTRODUCTION

Conducting polymers such as polyaniline, polythiophene, polyphenylene etc. [1-3] have a great interest in the scientific researches because of their electronic properties for use in electronic devices, functional electrodes, electro chromic devices, optical switching devices, sensors, batteries, and fuel cells [3-12]. Polyaniline (PANI) is one of the most studied materials because of its high conductivity upon doping with acids, well behaved electrochemistry, and easy preparation under reproducible conditions by electro polymerization and chemical oxidation of aniline, chemical and electrical stability, and good environmental stability [13-21].Polyaniline is inexpensive to produce, relatively light weight, corrosion resistant, possesses environmental stability, good redox properties and exhibits good matrix adhesion [22]. The electrical and optical properties of polyaniline conducting polymers are highly dependent on the nature of the dopant, the present of substituent and the synthetic conditions (temperature, time, etc) [22]. Polyanilne can exist in three isolated oxidation states, leucoemeraldine, emeraldine, and pernigraniline, among which only emeraldine, salt (ES) is electrically conductive [23]. It can changes the electronic conductivity about (10) orders of magnitude, passing from insulator state (emeraldine base with $\sigma < 10^{-10}$ S/Cm) to metallic conduction (emeraldine salt with $\sigma \sim 10^{-1} - 10^{-2}$ S/Cm), depending upon protonation degree [24-26]. Conducting polymers can be prepared by chemical or electrochemical polymerization. The electrochemical method involves the direct formation of conducting polymers with better control of polymer film thickness and morphology about the mass production by this method is not possible [22,27], while in the chemical polymerization, monomers are oxidized by oxidizing agent or catalyst to produce conducting polymers [9,10], it offers mass production at low cost, for this reason, this makes suitable for use in many productions such as Light Emitting Diode, electrochemical (bio) sensors, conductive textiles and fabrics, etc. [9]. Although the synthetic methods to produce polyaniline are simple, its mechanism of polymerization and the exact nature of its oxidation chemistry are complex and not very well established. In our previous work, the influence of organic solvents on the polymerization of polyaniline using Tetrahydrofuran (THF), N,N-dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) has been studies [28]. In this paper, the synthesis of a conductive polymer which is polyaniline (PANI) wasrealized by chemical oxidation of monomer in acidic aqueous medium at different temperatures (-3, 0, 6, and 25ºC).The effect of variation of temperature on the resulting polyaniline has been investigated using FTIR, Uv-Vis spectroscopy, conductivity measurements and elemental analysis.

EXPERIMENTAL

Materials

Aniline (ANI) (ADWIC, Egypt), Ammonium Persulphate (APS) (WINLAB, UK), Lithium Chloride (LiCl), Hydrochloric acid (HCl 32 %) and acetone. All these materials were used as received without further purification.

Synthesis of polyaniline at different temperatures

Synthesis of (PANI) at - 3 ºC

Lithium chloride (20.8 g, 0.49 mol) was dissolved in hydrochloric acid (125 ml , 1 M). Aniline (5.0 g , 0.054 mol) was dissolved in 75 ml of this solution and cooled to -3° C. Ammonium persulfate oxidant (12.3 g, 0.054 mol) was dissolved in the remaining HCl / LiCl solution and cooled to -3° C. The two solutions were mixed together and left to stand at -3° C for 36 h . The reaction mixture was then filtered, washed, rewashed and dried. The yield obtained is 87.2 %.

Synthesis of (PANI) at 0 and 6 ºC

Lithium chloride (3.0 g, 0.071 mol) was dissolved in hydrochloric acid (143 ml, 1M). Aniline (5.0 g , 0.054 mol) was dissolved in 75 ml of this solution and cooled to 0°C. Ammonium persulfate oxidant (12.3 g , 0.054 mol) was dissolved in the remaining HCl/LiCl solution and cooled to 0° C. (APS) is added drop wise to a solution (ANI solution) at 0ºC. APS solution is added very slowly to prevent the warming of the solution. After completion the addition, stirring is continued for 2 hours by using a mechanical stirred to ensure the completion of the reaction. The time of initial coloration on mixing reactants depends upon the temperature

and protonic acid (HCl). The addition of LiCl solution is to prevent freezing of the mixture.The reaction mixture was then filtered, washed, rewashed and dried. The sequence of coloration is light blue → blue green → coppery tint → green precipitates. The yield obtained at 0 and 6 ºC was 85.4 % and 83.6 % respectively.

Synthesis of (PANI) at 25°C

Aniline (5.0g , 0.054 mol) was dissolved in 75 ml of 1.0 MHCl and kept at 25°C. Ammonium persulfate (12.3 g , 0.054 mol) was dissolved in 70 ml 1 MHCl and also kept at 25° C. The two solutions were mixed together and left to stand at 25° C for 30 minutes. The reaction mixture was then filtered using   a buchner funnel and flask, and the filter cake washed with 800 ml of acetone. The filter cake was stirred in ammonium hydroxide solution (100 ml , 24%) for 1h before refiltering and rewashing with 1000 ml of acetone, followed by drying in oven at 60° C for 48 h. The yield obtained was 48.5%.

During the preparation of PANI at different temperatures, the reaction mixture turned blue as the polymerization had started and the intermediate protonated pernigraniline from PANI was produced. Then it becomes green as pernigraniline was converted in to final product, the emeraldine form of PANI . At 25°C, the reaction was completed within few seconds, at 0 and 6 ^{o}C, the raction was completes in about 1 hour while at least 3 days were needed for the formation of PANI at -3 ^{o}C.

Polymer Characterization

The PANI synthesized at different temperatures (-3, 0, 6 and 25 ºC)were characterized by FTIR spectroscopy (8201 PC SHIMADZU) instrument by KBr pellets, Uv-Vis spectrophotometer (Uv-1601 SHIMADZU), conductivity measurement was done at room temperature using conductivity meter (CM-30 V) and the C,H,N analysis was carried out using EA 1110 elemental analyzed.

RESULTS AND DISCUSSION

FTIR Spectra of Polyaniline Polymerized at Different Temperatures (-3 , 0 , 6 , 25°C)

Table 1 shows the wave number (Cm^{-1}) of the different functional groups of PANI at different temperatures.

Table 1: The wave number (Cm^{-1}) of the different functional groups of PANI at different temperatures

Assignment	-3°C	0°C	6°C	25°C
P-di-subs.arom. rings	824	805	806	797
C-H out of plane bending	1140	1129	1127	1132
C-N stretching of benzenoid ring	1298	1301	1301	1297
N-H stretching	3439	3433	3428	3437
C-N strtching of quinoid ring	1586	1563	1563	1566
C = C stretching of benzenoid ring	1495	1466	1475	1474

Figs. (1 – 4), show the FTIR spectra of polyaniline prepared at -3, 0, 6 and 25°C respectively. The frequency bands ranging between 797 – 824 cm^{-1}represent the para disubstituted aromatic rings through which polymerization proceeds. C – H out of plane bending vibrations appear at average of 1127 - 1140 cm^{-1}and in the average of 602 - 702 cm^{-1}, at 1297- 1301 cm^{-1}represent the C – N stretching indicating secondary aromatic amine groups. 1563- 1585 cm^{-1} and 1466-1495 cm^{-1}corresponding to the quinoidring and benzenoid ring modes, respectively. The presence of these bands clearly shows the polymer is composed of insulating and conducting phase of the polymer. Bands at 3428 - 3431 cm^{-1} corresponding to the N – H stretching bands of free or non- bonding and H- bonded N – H band respectively. From these Figures, at the lower temperature the bond frequency is higher because the bond is stronger, as the temperature increased, the bond becomes weak due to elongation process, therefore the frequency deviate from their standard value.
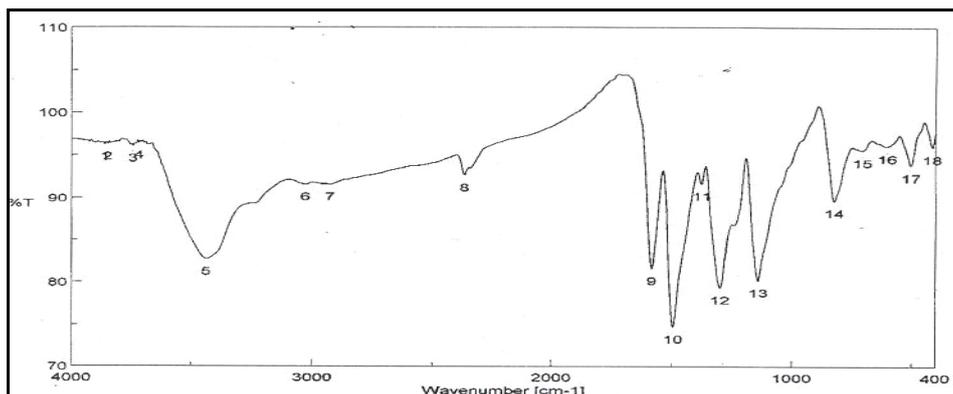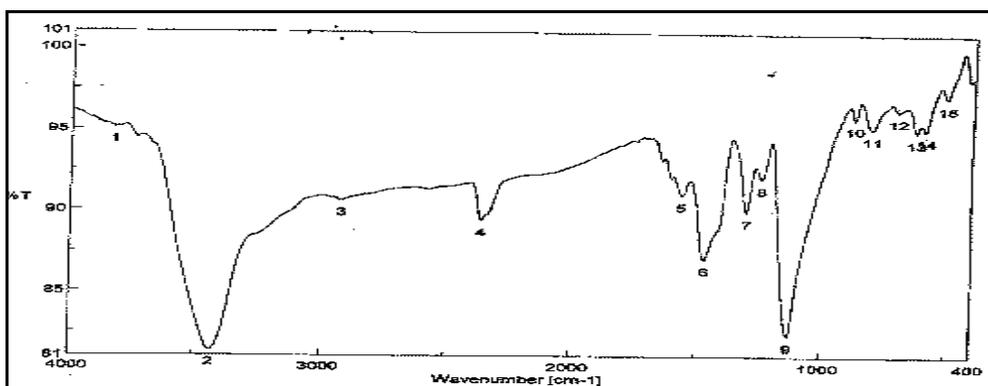
Figure 1: FTIR spectra of polyaniline at -3°C.
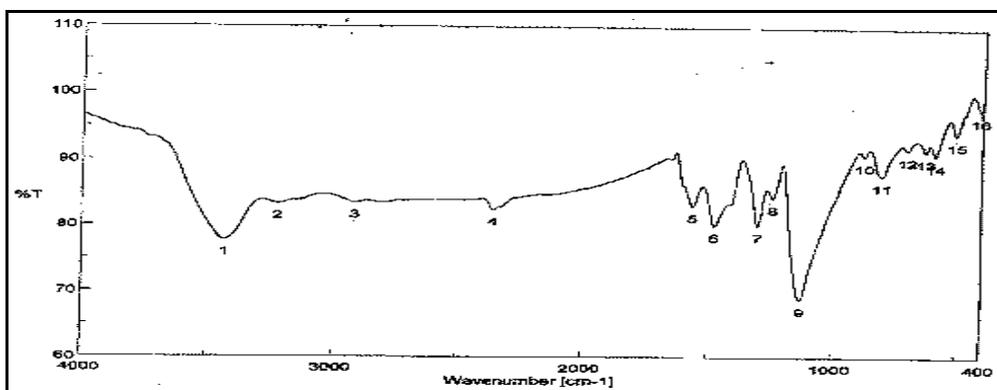

Figure 2: FTIR spectra of Polyaniline at 0°C.
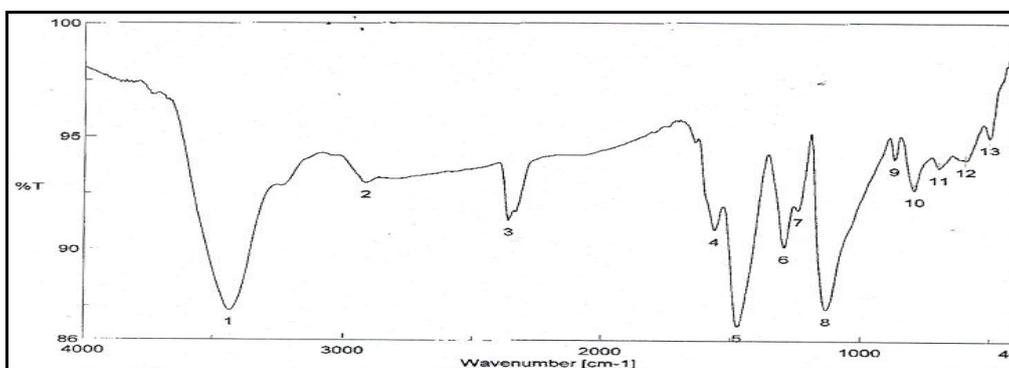

Figure 3: FTIR spectra of Polyaniline at 6 °C.

Figure 4: FTIR spectra of polyaniline at 25°C.

UV-Vis Spectra of Polyaniline at Different Temperatures (-3 , 0 , 6 , 25 ^{o}C)

Table 2: UV-Vis of polyaniline at different temperature (-3, 0, 6, 25°C) in DMF assolvet

Polymerization Temperature °C	λ_{max} (nm) Benzenoid	λ_{max} (nm) Quinoid
PANI at -3°C.	285	590
PANI at 0°C.	290	540
PANI at 6°C.	294	540
PANI at 25 °C.	325	605

From Table.2. as well as Fig.5, two absorption bands are observed between 325, 605 nm corresponding to the Benzenoid$\pi – \pi*$ transition of phenyl ring and quinoidexaction transition (n - $\pi*$) respectively.These peaks show shift to 285 and 590 nm as the temperature decreases.
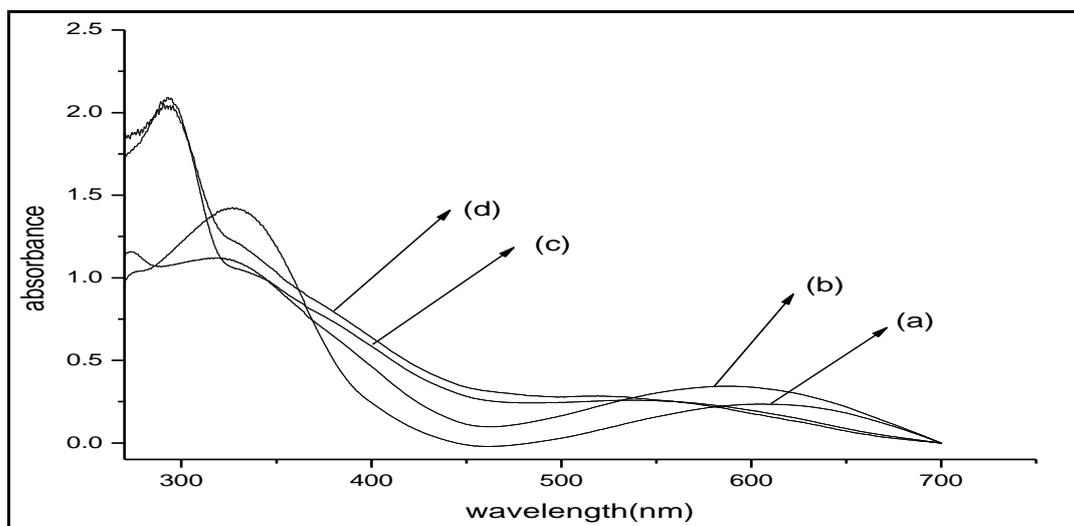

Figure 5: UV-Vis spectra of polyaniline using DMF solvent at
a) 25, b) -3, c) 0,   d) 6°C.

Yield and Conductivitymeasurements of Polyaniline at Different Temperatures (-3, 0, 6 , 25 ^{o}C)

Table 3: Yield (%) and Conductivity measurements of polyaniline at different temperature (-3, 0 ,6 ,25°C)

Polymerization Temperature °C	Yield (%)	Conductivity (S Cm^{-1})
PANI at -3°C.	87.2	3.65×10^{-2}
PANI at 0°C.	85.4	1.60×10^{-2}
PANI at 6°C.	82.6	1.40×10^{-2}
PANI at 25 °C.	48.5	1.80×10^{-3}

From Table.3, the reaction yield is reduced with temperature, this behaviour illustrate in Fig.6 and is in accordance with those observed by other researchers [29,30]. This is due to the fact that over oxidative and the hydrolysis side reactions are stimulated at a higher temperature, the cooling of the reaction temperature allows reducing the degree of hydrolysis of APS [31]., for this reason we conclude that the polymerization of aniline by chemical oxidative method using APS as oxidant should be carried out at very low temperature, since the solubility of APS in aqueous solutions limits the extent of reduction in reaction temperature [32].Therefore the optimum level in this study as shown in Fig.6, ranging between 0 and -3°C for gaining a high yield during PANI synthesis.
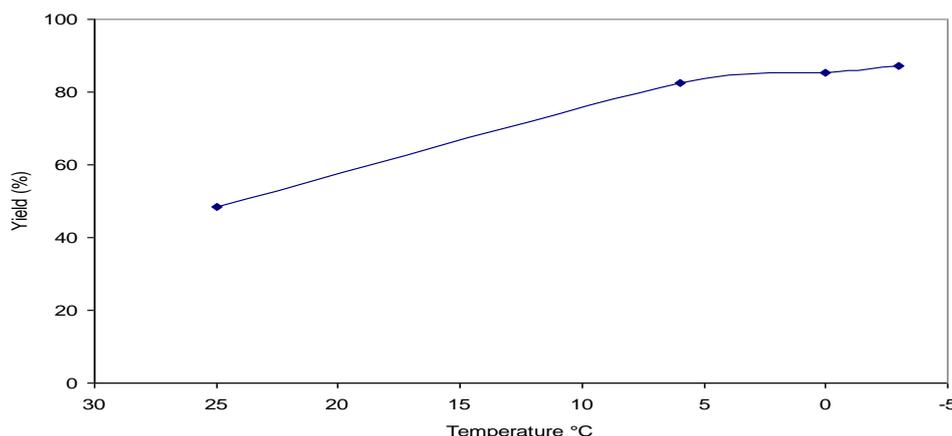
Figure 6: The effect of temperature on the Yield (%) of polyanilne

The measurement of electrical conductivity of PANI have been made at different temperatures(-3, 0, 6 , 25 ^{o}C)**.** Table 3. Showsthe variation in electrical conductivity with temperature. The best electrical conductivity was obtained at the lower temperature between (0 and -3°C) as shown in Fig.7, which is in accordance with the obtained yield results.This behavior may be attributed that at lower temperature, chains are better orderly and have a high molecular mass [33], in other words the amounts of APS as an oxidant at higher temperature is not enough and consequently a conductivity will be decreased, implying an incomplete conversion of aniline to polyaniline at high temperature due to shortage of oxidant may affect the charge hoping within the short oligomers and therefore results in a reduction in the electrical conductivity.
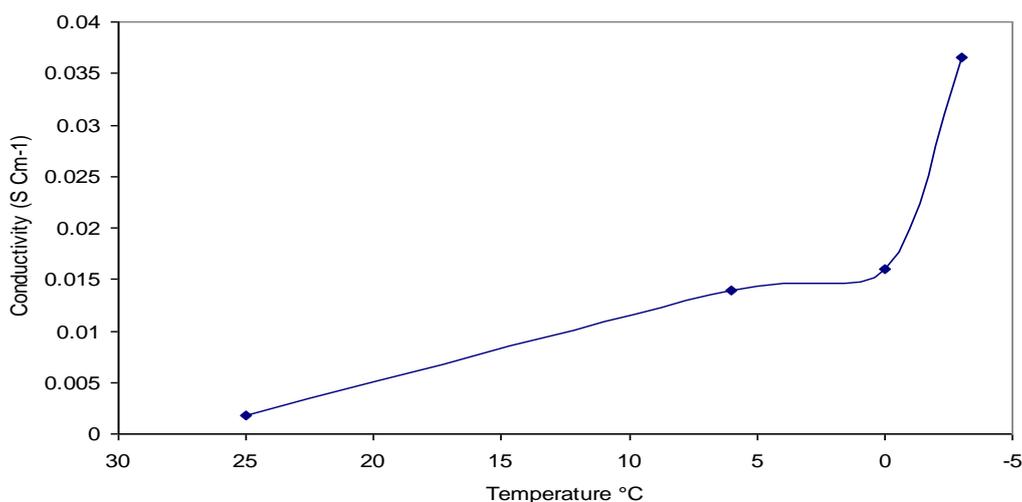

Figure 7: The effect of temperature on the conductivity of polyanilne

Elemental Analysis of Polyaniline at Different Temperatures (-3 , 0 , 6 , 25°C)

The results from elemental analysis of PANI at different temperatures (-3 , 0 , 6 , 25°C) are tabulated in Table.4.

Table 4: Elemental analysis of polyaniline at different temperatures (-3, 0 ,6 ,25°C)

Sample	C%	H%	N%	S%	Total %
	Calculated				
	66.06	4.85	12.84		
	Found				
-3 ^{o}C	54.28	5.32	10.25	1.88	71.73
0 ^{o}C	58.70	4.61	10.29	1.02	74.62
6 ^{o}C	61.89	5.34	11.84	0.46	79.53
25 ^{o}C	63.05	5.14	12.41	0.67	81.27

The presence of oxygen in PANI has been detected by elemental analysis [34]. Our elemental analysis results indicate the presence of oxygen in PANI, which may be attributed to oxygen adsorbed strongly on PANI. This may be due to bound water molecules or, more likely, to partial oxidation of PANI chains. The elemental analysis dataobtained in Table.4. indicate a decrease in the amounts of elements (C,H and N) as the temperature of PANI decreased that means the stability of PANI will be observed at low temperatures.

CONCLUSION

In the present work conducting polymer PANI is prepared by chemical synthesis techniques at different temperatures. From FTIR investigation, higher band frequency is observed at lower temperature, since as the temperature increased, the bond becomes weak due to the elongation process . The $\pi - \pi*$ transitions of aniline and/or anilium radicals and n - $\pi*$ transition of quinine-imine groups were confirmed from the Uv-Vis spectral studies at different temperatures. These peaks show shift to 285 and 590 nm respectively as the temperature decreased. The reaction yield is reduced with temperature due to the over oxidative and the hydrolysis side reactions are stimulated at higher temperature. The best electrical conductivity was obtained at lower temperature (0, -3°C) because at lower temperature, chains are better ordely and have a high molecular mass. The elemental analysis data indicate a decrease in the amounts of elements (C,H and N) as the temperature of PANI decreased that means the stability of PANI at low temperatures was achieved .

REFERENCES

[1]   Diaz AF, Kanazawa KK, Gardini, GP. J Chem Soc Chem Commun 1979; 635 -636.
[2]   Tourillon G, Garnier F. J Electroanal Chem 1982; 135: 173-178.
[3]   Diaz AF, Logan Jl. J Electroanal Chem 1980; 11: 111-114.
[4]   M Angelopoulos. J Res Dev 2001; 45 (1) : 57-76.
[5]   Dinesh D Borole, VR Kapdi, PP Mahaulikar and DG Hundiwale. Chemical Weekly-June 2004.
[6]   R Brown. J Res Dev 1994; 38(4) :379-389.
[7]   B Vercelli, S Zecchin, N Comisso, G Zotti, A Belin, E Dalcanale, LB Roenendaal. Chem Mater 2002; 14: 4768-4774.
[8]   Hua Bai, Gaoquan Shi. Senso: 2007; 7 : 267-307.
[9]   GK Prasad, TP Radhakrishnan, D Sravan Kumar, M Ghanashyam Krishna. Sensors and Actuators B 2005; 106 : 626-631.
[10]   Srivastava A, Singh V, Dhand C, Kaur M, Singh T, Witte K, and Scherer UW. Sensor 2006;6:262-269.
[11]   Nguyen MT, Kassi P, Miller JL, Diaz AF. Macromolecules 1994;27:3625- 3631.
[12]   Prevost V, Petit A, Pla F. Synth Met 1999; 104:79-87.
[13]   Huang JJ, and Kaner BR. J Am Chem Soc 2004; 126: 851-855.
[14]   Catedral MD, Tapia AKG, Sarmago RV, Tamayo JP, and del-Rosario EJ. J Sci Diliman   2004; 16(2) : 41-46.
[15]   Hosseini SH, Dabiri M, and Ashrafi M. Polym Int 2006;55:1081-1089.
[16]   Sharma H. Conducting polymers: polyaniline, its state of the art and applications, thesis, school of physics and materials science M.Sc Thesis 2006.
[17]   Hosseini SH, Simiari J, and Farhadpour B. Iranian Poly J 2009;18(1):3-13.
[18]   Reddya KR, Sina BC, Ryua KS, Nohb J, and Leea Y. J Synth Met 2009; 159 : 1934-1939.
[19]   Vivekanandan J, Ponnusamy V, Mahudeswaran A, and Vijayanand PS. Arch Appl Sci Res 2011; 3(6): 147-153.
[20]   Zareh EH, Moghadam PN, Azariyan E, and Sharifian I. Iranian Poly J 2011;20(4):319-328.
[21]   Bitencourt AS, Barros U, Maria CC, and Leite DS. Int J Anal Chem 2012;116 :1567-1577.
[22]   Jiaxing Huang. Pure Appl Chem 2006;78(1):15-27.
[23]   Harsha SK, Sumedh PS, Xinyu Z, Macdiarmid AG, Sanjeev KM. J Am Chem Soc 2005;127:16770-16771.
[24]   Ali MA, et al. J Eng Sci Technol 2007; 2(1):111-118.
[25]   Detsri E, and Dubas ST. J Met Mater Miner 2009;19(10):39-44.
[26]   Dumitrescu J, Nicolae CA, Maria A, Gabor RA, Grigorescu M, and Mihailescu MUPB. Sci Bull Series A 2009; 71 : 63-72.
[27]   WE Howard, OF Prache IBM. J Res Dev 2001; 45(1) : 115-127.
[28]   Melad O, Alhendawi H, and Fayyad M. Research and Reviews: J Chem 2014;3(4): 40-47.
[29]   Chen CH. J Appl Polym Sci 2002; 85 (7) :1571-1580.

[30]   Cortes MT, Sierra EV. Polym Bull 2006; 56 : 37-45.
[31]   Dyachkova TP, Melezhyk AV, Morozova ZG, Shuklinov AV, Tkachev AG. Transactions TSTU 2012;18: 718-730.
[32]   Cao Y, Andreatta A, Heeger A, Smith P. Polymer 1989; 30: 2305- 2311.
[33]   J Stejskal. Pure App Chem 2002; 74 : 857- 867.
[34]   Shan D, and Mu SL. Synth Met 2002; 126 :225-232.