J. Mater. Environ. Sci. 3 (1) (2012)50-56
ISSN : 2028-2508
CODEN: JMESCN

Synthesis, identification and study of electrical conductivity of the doped poly p- anisidine

Roza A. Salih*
***Chemistry department /College of Science / Basrah University, Basrah- Iraq**

Received in 25 Apr 2011, Revised 15 Sept 2011, Accepted 15 Sept 2011.
* Corresponding author: E-mail address: **rozachemistry@yahoo.co.uk**; Tel: +9647803164728

Abstract

Poly p- anisidine doped with 4(4- hydroxy phenyl azo) benzene sulfonic acid, 4 - hydroxy- m-benzene disulfonic acid, 3- chloro- 4- hydroxy benzene sulfonic acid, $BaCl_2.2H_2O$, $AlCl_3$, and NaCl, The polymer is identified by FT- IR and UV- Visible spectroscopy. The ionic conductance of poly p- anisidine doped with 4(4- hydroxy phenyl azo) benzene sulfonic acid, 4 - hydroxy- m-benzene disulfonic acid, 3- chloro- 4- hydroxy benzene sulfonic acid, $BaCl_2.2H_2O$, $AlCl_3$, and NaCl, was studied as a function of weight of the dopant compounds , it is noted an increase of conductance of poly p- anisidine by doping with 3 - chloro- 4- hydroxy benzene sulfonic acid equal to 0.011996 ohm^{-1} .

Key words: Synthesis, identification, electrical conductivity, poly p- anisidine

1. Introduction

The need for new materials with potential properties has always been the driving power for the progress in several areas of the science and technology. There are so many new materials coming up for several technological oriented applications. The conducting polymer is one of the most promising new classes of materials, being used for several applications. The combination of electrical, chemical and electrochemical properties of conducting polymers may lead them to be used in many technological applications [1-9].

Conductive polymers have been proposed for a wide variety of applications, including organic electronic devices, electro chromic displays, and sensors. As the interest in these technologies has advanced, so has the need for materials with enhanced or tailored properties.

This is, of course, a multi- faceted problem that can be approached from many angles, including manipulating the physicochemical properties of the materials through synthetic chemistry or post- polymerization modification [1].

The use of electrically conductive polymers has been limited in the past due to such deficiencies as poor mechanical properties and environmental and thermal instability .it has been shown that composite structure using an insulating polymer as the host matrix improves the physical and chemical properties of conductive polymers [2].

Poly(*o*-anisidine) is an important conjugated conducting polymer. It is relatively easy to be prepared. The major problem of its successful utilization is poor mechanical properties like lower conductivity and poor solubility in common organic solvents. Recently much progress has been made to improve these poor mechanical properties by using different organic acids as dopant or stabilizer. This dopant, like organic acid and acrylic acids, is introduced by simple secondary doping or by blending the polymer with doping species such as acrylic acid. This chemical oxidative polymerization method provides polymers better solubility in common organic solvents such as *m*-cresol, NMP, DMF, *etc*. These polymers also have better conductivity, which is very important from application point of view, because conductivity of polymer changes on exposing the polymer materials to ammonia vapors or other gases like H_2S the chemical oxidative synthesis of electrically conducting and organically soluble acrylic acid doped poly(*o*-anisidine). This reaction is unique since the polymer obtained has maximum solubility in common organic solvent directly without the need for a post doping process step, which involves conversion of salt phase to base form of the polymer [3].

The field of conducting polymers has attracted considerable attention due to their fascinating electrical and optical properties that are used in many technological applications . Polyaniline is one of the most explored conducting polymers because of its applications in a wide range including electrochromic devices, light-emitting diodes , lightweight batteries and corrosion protection . However, the practical applications of polyaniline have been limited due to harsh chemical conditions in the synthesis and purification procedure that often lead to an inflexible polymer. To address this problem and improve processability, a diverse set of modified polymerizations have been investigated . The enzyme horseradish peroxidase (HRP) in the presence of hydrogen peroxide catalyzes the polymerization of phenol and aromatic amines . For the polymerization of aniline a unique enzymatic approach (HRP as a catalyst and H_2O_2 as an oxidizing agent) was recently developed. This polymerization has been carried out in presence of a polyelectrolyte template such as poly(4-styrene sulphonate) (SPS) or poly(vinylphosphonic acid) (PVP) under mild conditions in aqueous pH 4.3 buffer. The other approach that may improve the poor processability of polyaniline is to produce its corresponding composites or copolymers. Accordingly, on the polyaniline-type copolymers pioneering . The copolymerization of aniline and *o*-anisidine was performed by chemical oxidation. It was observed that in the chemical polymerization the amount of *o*-anisidine incorporated in the copolymer chains are more than aniline monomers due to the higher reactivity of the former [4].

2. Method

Preparation of the compound 4 - hydroxy- m-benzene disulfonic acid, 3- chloro- 4- hydroxy benzene sulfonic acid was achieved by the reference [5], and preparation of the compound 4(4- hydroxy phenyl azo) benzene sulfonic acid was achieved by the reference [6].

Preparation of poly (p- anisidine)

The polymer p- anisidine was synthesized by dissolving 11.3 g of p- anisidine in 100 ml of HCl (1.5 M), the mixture was cooled at 5°C, 22.8 g of ammonium per sulfate was taken in 100 ml of HCl (1.5 M) and cooled then added to the first solution for 80 min. then remained in water bath (0- 10) °C for 4 hr.

Spectroscopy

The absorption spectra in the UV- Visible range (200-800) nm were studied with a Helios Alpha spectrophotometer UVA, No. 102024 in chloroform and water as solvents with a quartz cell. All spectra were recorded in the wavelength range of 300- 800nm.

FT-IR spectra on KBr pellets were recorded with a FT-IR 8400S spectrophotometer model (2000) from SHIMADZU Japan.

Electrical conductivity

The ionic conductance (G) was measured at room temperature, by using conductivity instrument (Konduktoskop E 365B Metrohm Herisau).

2. Results and Discussion

Identification of the synthesized compounds

Infrared spectroscopy (IR)

The chemical structure of poly p- anisidine was identified using FTIR analysis. The main functional groups and their FT-IR frequencies of poly p- anisidine are presented in fig (1).

The optical absorption spectrum of synthesized poly p- anisidine are shown in Figures (2,3) . The spectrums were recorded in water and chloroform solutions. They were recorded using UV-visible spectrophotometer.

The FTIR spectroscopy was used for structural characterization of synthesized poly p- anisidine. The FTIR spectrum of synthesized poly p- anisidine is shown in Figure (1). It was recorded in the wave number range 4000-500cm^{-1} on the FTIR-8400.

The peak at 3068 cm^{-1} represents to C-H aromatic , The peak at 1514 cm^{-1} corresponds to benzaid and quinoid ring. The band at 1454 cm^{-1} represents the presence of C=C aromatic. The peak at 1305 cm^{-1} corresponds to aromatic amine. The band at 1259 cm^{-1} represents to C-O aromatic. The band at 1026 cm^{-1} represents the C-O-C. The band at 1100 cm^{-1} indicates the presence of C-N-C. [7].

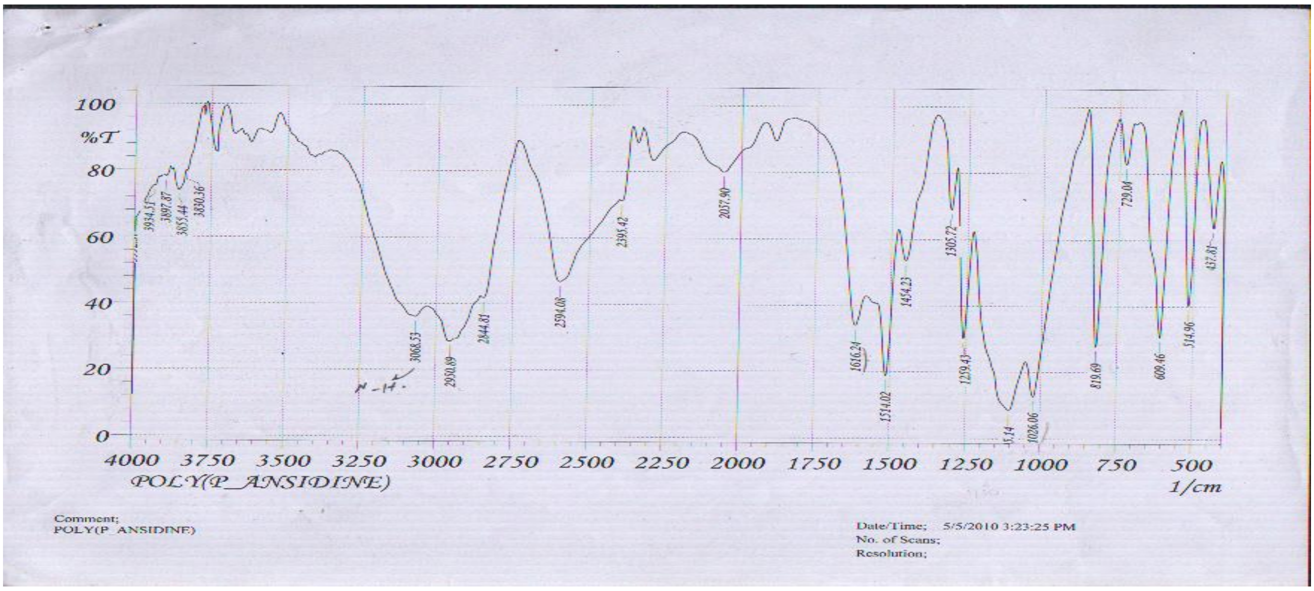

Fig 1 :- FT – IR of poly p- anisidine

Ultraviolet - Visible spectroscopy (UV)

The UV- Visible spectrum of the poly P- anisidine was recorded at room temperature using UV-Visible analysis in water and chloroform as solvents, and is shown in Figs (2,3)

In n $\longrightarrow$ □* transition, the absorption band to shorter wave – length by increasing the polarity of the solvent, the ground state is more polar as compared to the excited state. The hydrogen bonding with solvent molecules takes place to lesser extent with the carbonyl group in the excited state, the solvent used also effects the fineness of absorption band in UV spectrum, if the dielectric constant of the solvent is high, there will be stronger solute- solvent interactions. Due to this, vibrational and rotational energy states of molecules increase. The peak is appearing at about 268 nm for H_2O, and in chloroform in 294 nm [7].

Measurement of the electrical conductivity

The electrical conductivity properties are tabulated in table (1). As indicated from the table, in the doped form, the polymer was highly conductive, whereas the undoped state of the polymer had a low conductivity level:

Emeraldine base (insulator) $\longrightarrow$ **Emeraldine salt (conductor)**

ES is a stable, delocalized poly semiquinone radical cation with a half- filled polaron conduction band and is accompanied by an increase in the conductivity. The electrical conductivity depends mainly on the number and mobility of the charge carriers and can be correlated with the chemical composition and morphology, the type, the extent of the crystallinity, and the tacticity each play a role in evaluating the electrical properties of polymers.

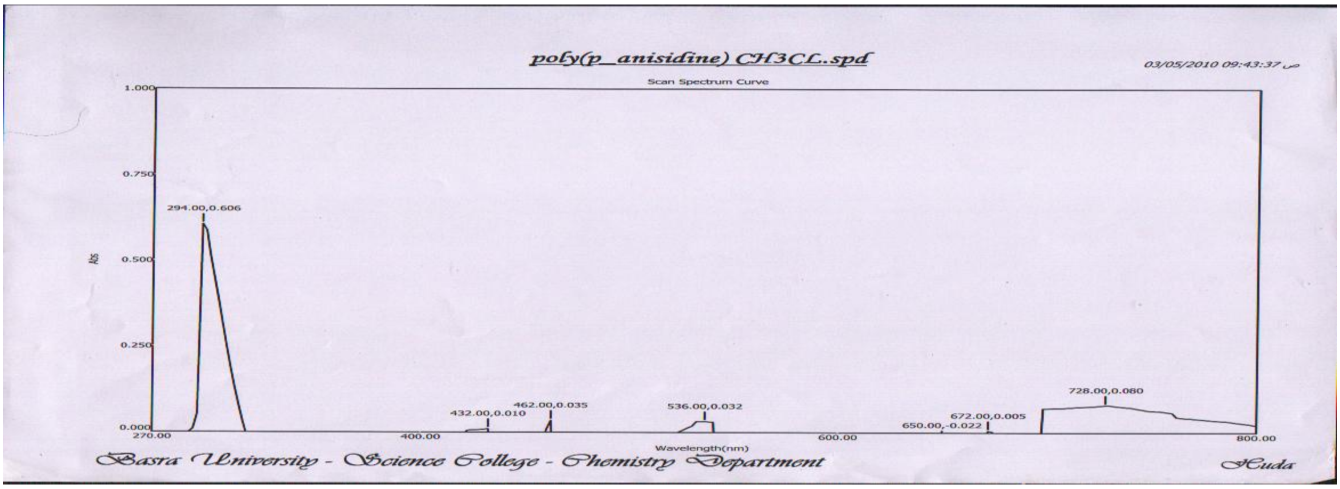

Fig. 2. UV-VISIBLE of poly p- anisidine

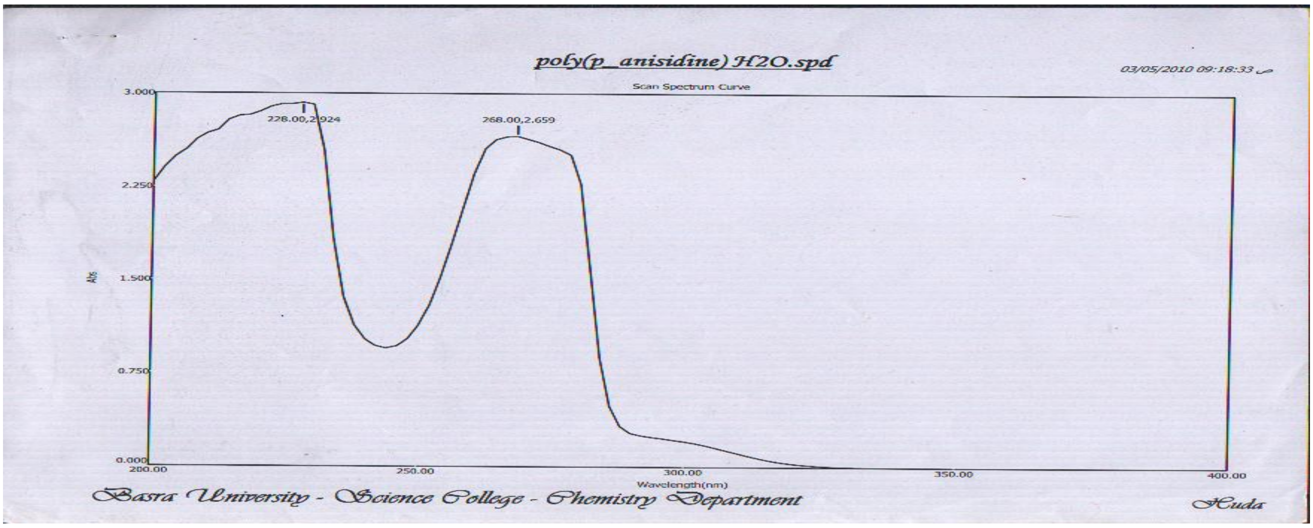

Fig. 3. UV-VISIBLE of poly p- anisidine

Table 1. Room temperature conductance values of poly p- anisidine doped with different organic sulfonic acid and the salts**.**

Wt of Dopant material (g)	Higher conductivity (g) ohm^{-1}	Dopant material
0.01	0.00239	4(4- hydroxy phenyl azo) benzene sulfonic acid
0.08-0.1	0.002596	4- hydroxy – m- benzene disulfonic acid
0.04	0.011996	3- chloro- 4- hydroxy benzene sulfonic acid
0.01	0.002819	$BaCl_2.2H_2O$
0.08, 0.09	0.00946	$AlCl_3$
0.09-0.1	0.01096	NaCl

The long side chain exerted a strong steric effect on the doping process, making it more difficult for 4 (4-hydroxy phenyl azo) benzene sulfonic acid to protonate the amino group. This could have resulted from the decreasing doping level of poly p- anisidine . Furthermore, it may be that with the bonding of the side group, the distance between the two main chains increased, and this made interchain polaron or bipolaron doping more difficult.

In order to investigate the effect of amount of dopant on the conductivity of the poly p- anisidine, 4(4-hydroxy phenyl azo) benzene sulfonic acid, 4 - hydroxy- m-benzene disulfonic acid, 3- chloro- 4- hydroxy benzene sulfonic acid, $BaCl_2.2H_2O$, $AlCl_3$, NaCl, The polymer is, were doped with poly p- anisidine at various weight in the feed (0.01, 0.02, 0.03, 0.04,0.05,0.06,0.07,0.08,0.09,0.1) g using water as solvent. The conductivity values of the samples were plotted against the amount of weight in the feed and showed in figs (4-9). It is very clear from the plots that the conductivity of doped samples increase with increase in the amount of dopant in the feed it attained maxima for 0.1 g. It suggest that minimum of the dopant is required to obtain high conductivity of doped samples. Therefore, for comparing the doping ability of these structurally different dopants, the amount of dopant was fixed 0.1 g equivalents to poly p- anisidine, the electric conductivity increase markedly on doping with suitable electron acceptors.

In is seen from fig (4) that the electric conductivity decrease with the amount of 4(4- hydroxy phenyl azo) benzene sulfonic acid, the composition of the polymer strongly influences the electric conductivity, and the electric conductivity is strongly influenced by the extent of the delocalization of □ electrons along the polymer chain, therefore, be noted that the conductance is equal to (0.00239) ohm^{-1} in (0.01) g.

The ionic conductance (G) of the prepared compounds was measured in the water as solvent. The influence of weight of dopant material on the conductance of the poly p- anisidine is shown in Figures (4-9) .Is apparent that the conductance of the poly p- anisidine increases as the weights of the dopant material increases. In Figure (4) it should be noted that the conductance was decrease and is equal to (0.00239) ohm^{-1} in (0.01) g, while in Figure (5) it should be noted that the conductance was equal to (0.002596) ohm^{-1} in (0.08-0.1) g, while in Figure (6) it should be noted that the conductance was equal to (0.011996) ohm^{-1} in (0.04) g, while in Figure (7) it should be noted that the conductance was equal to (0.002819) ohm^{-1} in (0.01) g, while in Figure (8) it should be noted that the conductance was equal to (0.00946) ohm^{-1} in (0.08, 0.09) g, while in Figure (9) it should be noted that the conductance was equal to (0.01096) ohm^{-1} in (0.09, 0.1) g,

The electrical conductance depends mainly on the number and mobility of the charge carriers and can be correlated with the chemical composition and morphology, the type.

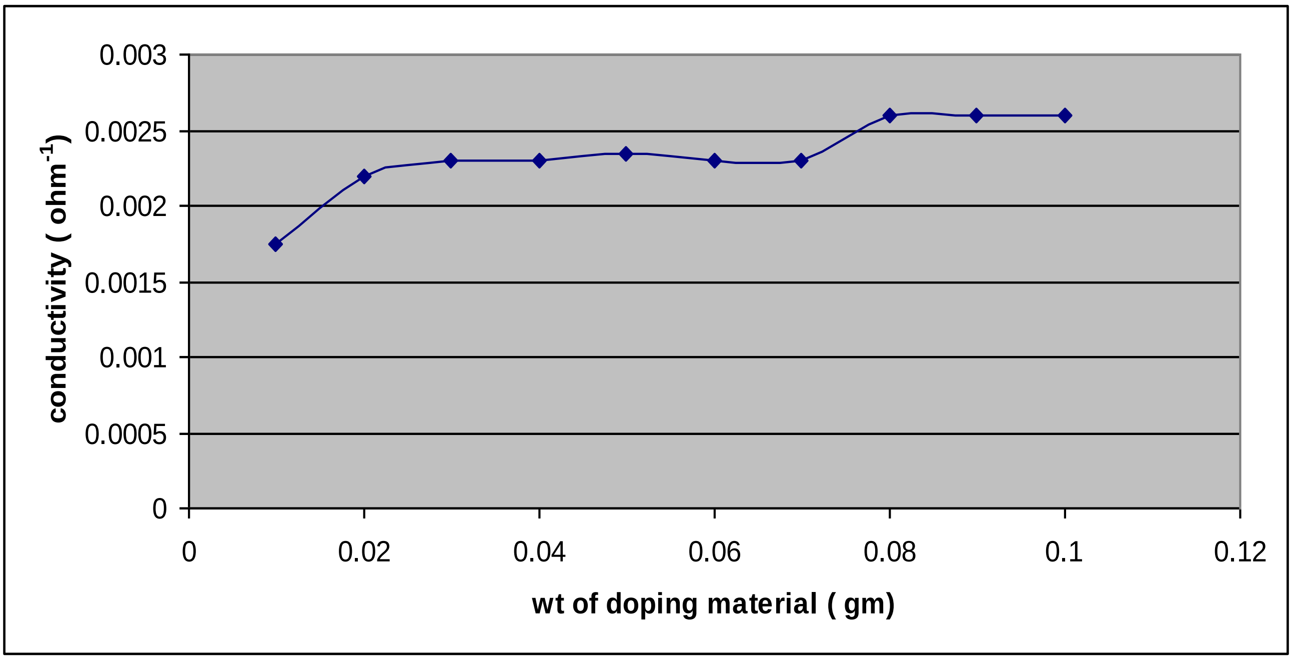

Fig. 5. Effect of 4- hydroxy- m- benzene disulfonic acid on conductance of poly p- anisidine

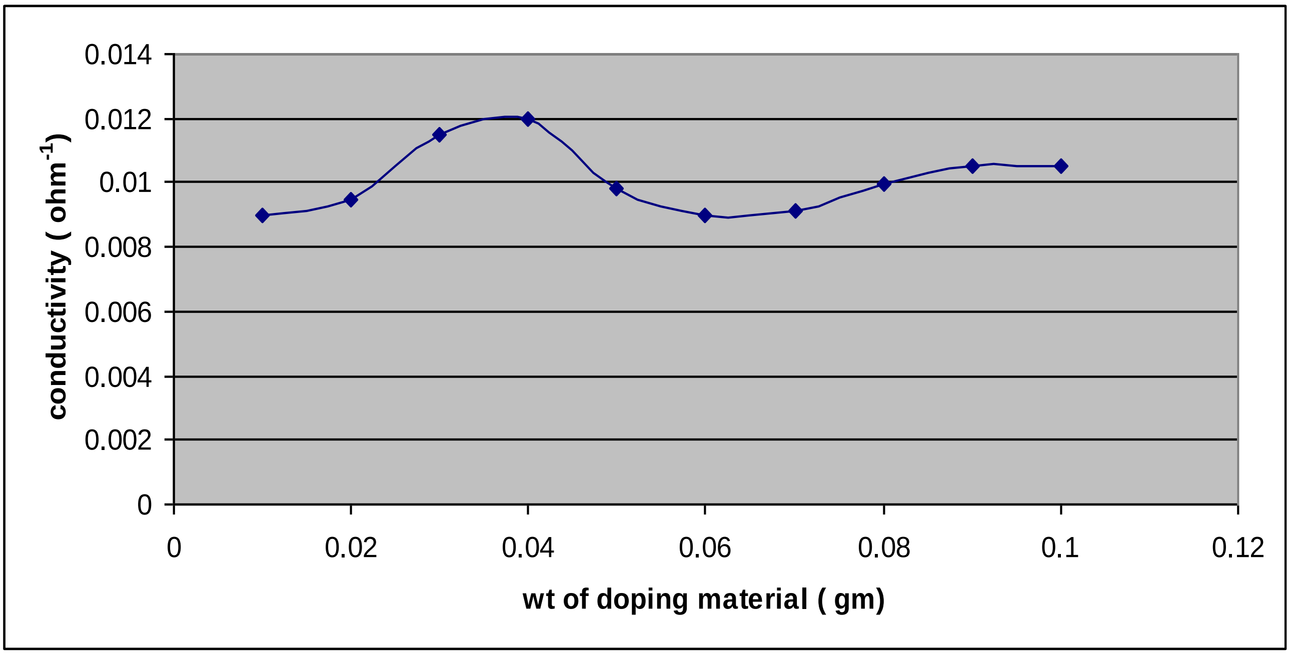

Fig. 6. Effect of 3- chloro- 4- hydroxy benzene sulfonic acid on conductance of poly p- anisidine

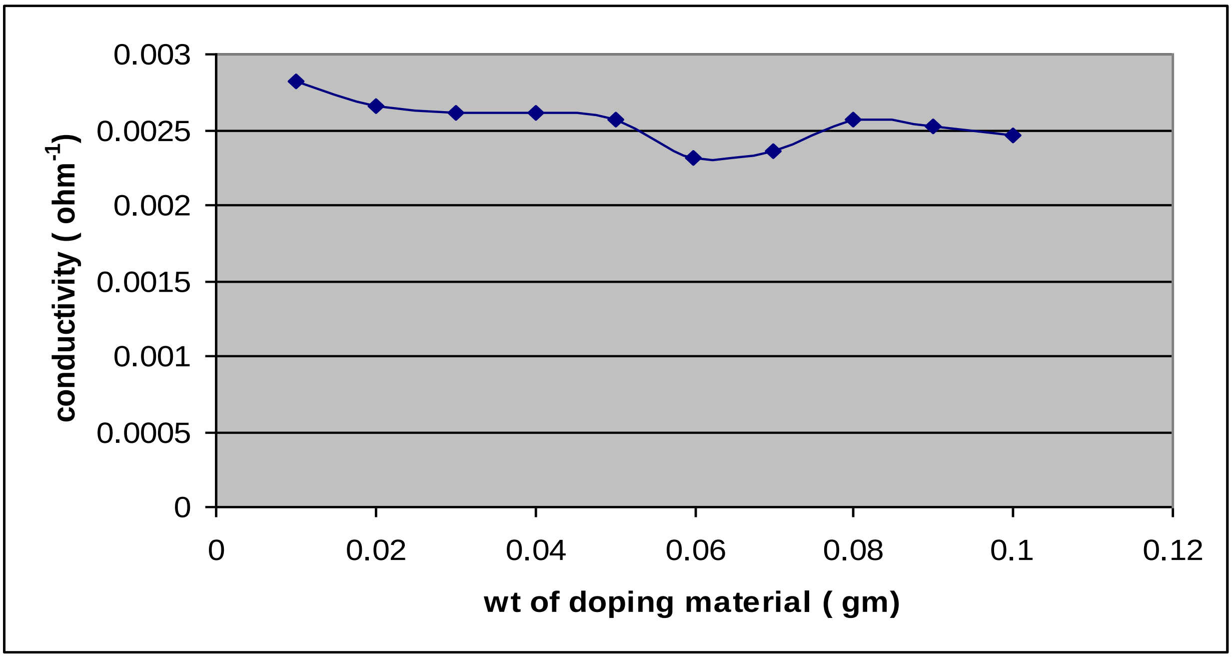

Fig. 7. Effect of $BaCl_2.2H_2O$ on conductance of poly p- anisidine

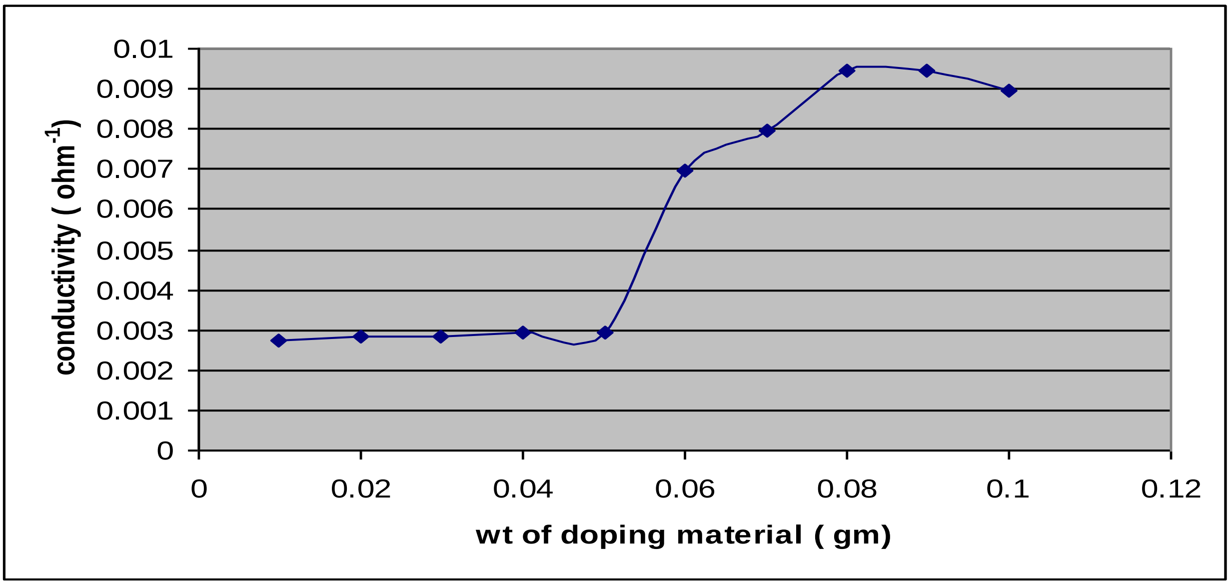

Fig. 8. Effect of $AlCl_3$ on conductance of poly p- anisidine

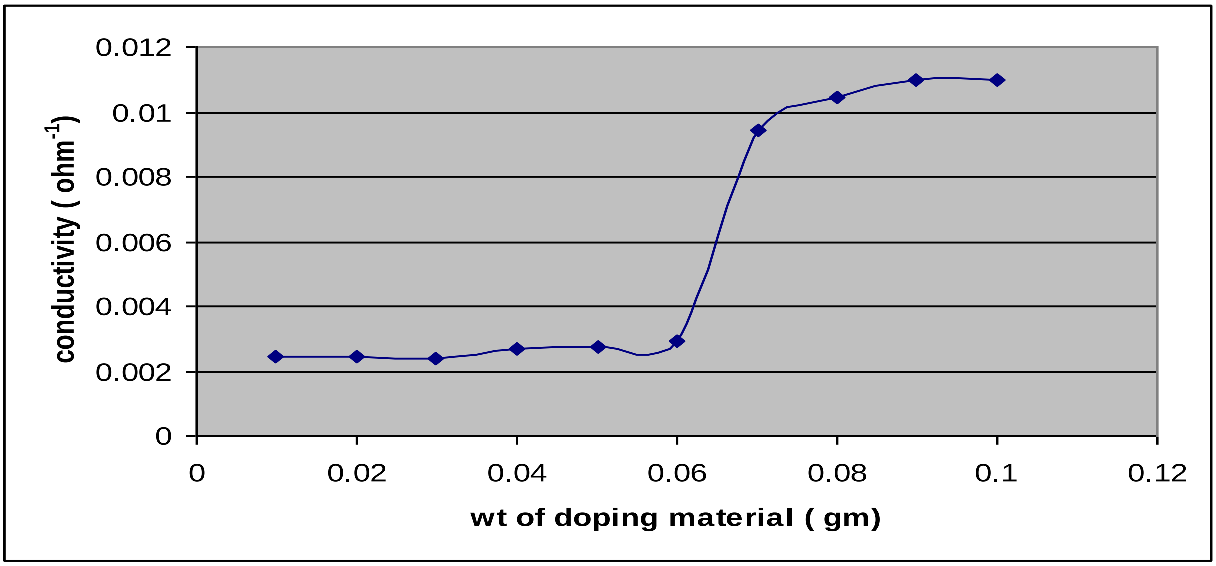

Fig. 9. Effect of NaCl on conductance of poly p- anisidine

The long side chain exerted a strong steric effect on the doping process, making it more difficult for 4(4-hydroxy-phenyl azo) benzene sulfonic acid. This could have resulted from the decreasing doping level from poly p- anisidine when was doped with 4(4-hydroxy-phenyl azo) benzene sulfonic acid, . It may be that with the bonding of the side group, the distance between the two main chains increased, and this made interchain polaron or bipolaron doping more difficult. The conductance of poly p- anisidine doped with 4(4-hydroxy-phenyl azo)benzene sulfonic acid, have low in conductance compare with poly p- anisidine doped with NaCl, $BaCl_2.2H_2O$, $AlCl_3$, have higher conductivity.

The values of conductance at room temperature of poly p- anisidine doped with organic sulfonic acid and the salts are listed in Table 1, shown above.

Conclusion

The Poly p- anisidine was synthesized by chemical polymerization method, 4(4- hydroxy phenyl azo) benzene sulfonic acid, 4 - hydroxy- m-benzene disulfonic acid, 3- chloro- 4- hydroxy benzene sulfonic acid, $BaCl_2.2H_2O$, $AlCl_3$, and NaCl were used as dopants during the polymerization process. 3- chloro- 4- hydroxy benzene sulfonic acid shows the higher conductivity for the polymer by using 0.04 g. which reached to 0.011996 $ohm^{-1.}$

References

1. Skotheim,T. A. R., Elsenbaumer, J. R. (Eds.). *Handbook of conducting Polymers*, Marcel Dekker, New York. (1998) 1097.

2. Jung, F. K., Katherine, H., Michael, K. S. II. *Mat. Res. Soc. Symp. Proc*. (2002) 708.

3. Seneme, K., Zuhal K., Atef, Q. *Turk. J. Chem*. 27 (2003) 417- 422.

4. Vasant, Ch., Ganesh, S. *Chemistry & Chemical Technology*. 3(2) (2009) 95 -99.

5. Nabid, M.R., Zamiraei, Z., Sedghi, R. *Iranian Polymer Journal*, 19 (9) (2010) 699-706.

6. Kahol, P.K., Satheesh, K.K., Geetha, S., Trivedi, D.C. *Synthetic metals*, 139 (2003) 191-200.

7. Jayakanna, M., Anilkumar, P., Sanju, A. *European polymer journal*, 42 (10) (2006) 2623- 2631.

8. Sharma, Y.R. *elementary organic spectroscopy*, priciples and chemical applications. (2007) 356.

9. MacDiarmid,A. G. *Synth. Met.* 84 (1997) 27.