Synthesis, identification and study of electrical conductivity of the doped poly 0- amino phenol

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Abstract

Poly o- amino phenol was doped with several types of doping materials which are 4 (4- hydroxy phenyl azo) benzene sulfonic acid, 2,5- dimethyl benzene sulfonic acid, NaCl, $BaCl_2.2H_2O$ $AlCl_3$. The polymer was identified by FT- IR and UV- Visible spectroscopy.

The ionic conductance of poly o- amino phenol doped with 4(4- hydroxy phenyl azo) benzene sulfonic acid, 2,5- dimethyl benzene sulfonic acid, NaCl, $BaCl_2.2H_2O$, $AlCl_3$, was studied as a function of weight of the dopant compounds .It was noted an increase of conductance of poly o- amino phenol by doping with 4(4- hydroxy phenyl azo) benzene sulfonic acid, 2,5- dimethyl benzene sulfonic acid, the conductance became equal to $0.019488ohm^{-1}$.

:
4(4- hydroxy phenyl azo) benzene sulfonic acid, 2,5- dimethyl benzene sulfonic acid,
.NaCl, $BaCl_2.2H_2O$ $AlCl_3$.

FT- IR spectroscopy

. UV- Visible spectroscopy

4(4- hydroxy phenyl azo) benzene sulfonic acid, 2,5- dimethyl benzene sulfonic acid,
. $0.019488ohm^{-1}$

Introduction

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].

Conducting polymers such as polyacetylene, poly thiophene, and poly aniline (PANI) are semiconductors in their pure form but become highly conducting upon doping. A variety of electronic and electro- optical devices such as p-n and Schottky diodes, thin- film transistors, and light – emitting diodes based on thin polymer films [3].

The field of conducting polymers has attracted the interest of many academic and industrial researchers. The properties of these organic polymers have led to use them in various application, such as anti- static and anti- corrosion coating materials, sensors, batteries and super capacitors, light emitting diodes, electro chromic devises and trans parent electrode materials [4].

Electrically conducting polymers combine the electrical properties of metals and semiconductors and the processing and performance advantages of organic polymers, these are highly conjugated systems which are made conducting either by addition of electron donor or acceptor, dopants [5].

Recently, polymers have been synthesized chemically or electrochemically by using ortho- NH_2 [6,7] and –OH [8] groups substituted anilines. Unlike other derivatives of aniline, both the amine hydroxyl substituents in these two monomers can be oxidized. In chemical polymerization, various redox reagents were used in acidic medium, e.g., cupric chloride, barium manganate, ammonium persulfate, sodium dichromate, etc. and the polymers formed had ladder structures.

Due to this ladder structures, the polymers were insoluble in organic solvents resulting in both poor processability and conductivity. Althougth m- amino phenol as a monomer had been used very little and due to many controversies on polymerization mechanism and properties of the final polymer product, it was reported that poly m- amino phenol synthesized from acidic medium is insoluble in organic solvents even after dedoping. [9].

In this communication we report the synthesis of poly ortho amino phenol by oxidative polymerization using ammonium persulfate as an oxidative initiator in aqueous NaOH medium and doped with 4(4- hydroxyl phenyl azo) benzene sulfonic acid, 2,5 – dimethyl benzene sulfonic acid, NaCl, $BaCl_2.2H2O$, $AlCl_3$, was studied as a function of weight of the dopant compounds.

Method

Preparation of the compound 2,5- dimethyl benzene disulfonic acid by

the reference [10], and preparation of the compound 4(4- hydroxy phenyl azo) benzene sulfonic acid by the reference [11].

Preparation of poly (o- amino phenol)

The polymer poly (o- amino phenol) was synthesized with 9.81 gm of o- amino phenol in 150 ml of NaOH (0.6 M) and takes 30.78 gm of ammonium per sulfate in 75 ml of water then stirred for 5 hrs. in 31°C.

Spectroscopy

The absorption spectra in the UV- Visible range (200-800) nm were studied with a Helios Alpha spectrophotometer UVA, No 102024 in ethanol solvent with quartz cell.

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).

Results and Discussion
Identification of the synthesized compounds
Infrared spectroscopy (IR)

The chemical structures of poly o- amino phenol were identified using FT-IR analysis. Table (1) shows the absorption bands of the active groups.

The main functional groups and their FT-IR frequencies of the poly o- amino phenol are presented in table 1, and fig (1).

For the poly o- amino phenol the peak at 3409 cm^{-1} is due to (O-H) stretching, in phenol, and the peaks at 3136, 3149 cm^{-1} due to (N-H) sym. And asym., the peaks at 1461, 1577 cm^{-1} due to (C=C) aromatic ring stretching vibrations the peak at 1112 cm^{-1} due to C-O, the peak at 852 cm^{-1}

due to CH out of plane deformation.

Ultraviolet - Visible spectroscopy (UV)

The UV- Visible spectrum of the poly o- amino phenol was recorded at room temperature using UV-Visible analysis in water as a solvent, and is shown in fig (2).

It was that the resulting poly o- amino phenol can completely dissolve in water, since the strong alkalinity can affect the electric structure of main chains of poly o- amino phenol due to doping and de- doping, water was selected as a fundamental solvent for recording the electronic absorption spectra of obtained poly o- amino phenol. Usually the position of absorption peak, corresponding to the n $\longrightarrow$ π^* transition, 298 nm, and $\pi \longrightarrow \pi^*$ in 428 nm.

Measurement of the electrical conductivity

The electrical conductivity properties are tabulated in Table (2). As indicated in Table (2), in the doped form, the polymer was highly conductive, whereas the undoped state of the polymer had a low conductivity level:

Emeraldine base (insulator) $\longleftrightarrow$ Emeraldine salt (conductor)
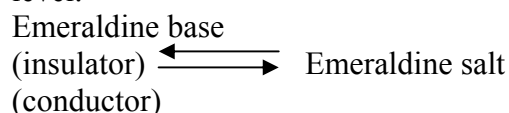
ES is a stable, delocalized polysemiquinone radical cation with a half- filled polaron conduction band and is accompanied by an increase in the conductivity. The electrical conductivity depends mainly on the number and mobility of the charge carriers and can be correlated with the chemical composition and morphology, the type, the extent of the crystallinity, and the tacticity each play a role in evaluating the electrical properties of polymers.

Table (1) the main functional groups and their FT-IR frequencies of the prepared compounds (in cm⁻¹)

C-H	C-O	C=C	C-H	N-H	O-H	Samples
852	1112 In phenol	1461, 1577	2862	3136 sym 3149 asym.	3409	Poly o- amino phenol

Table (2) Room temperature conductance values of poly o- amino phenol doped with different organic sulfonic acid and the salts.

Wt of Dopant materiat (gm)	Higher conductivity (G)	Dopant materiat
0.03	0.019488	4(4- hydroxy phenyl azo) benzene sulfonic acid
0.03, 0.07, 0.1	0.019488	2,5- dimethyl benzene sulfonic acid
0.1	0.025488	NaCl
0.03-0.1	0.022988	$BaCl_2.2H_2O$
0.05	0.023988	$AlCl_3$
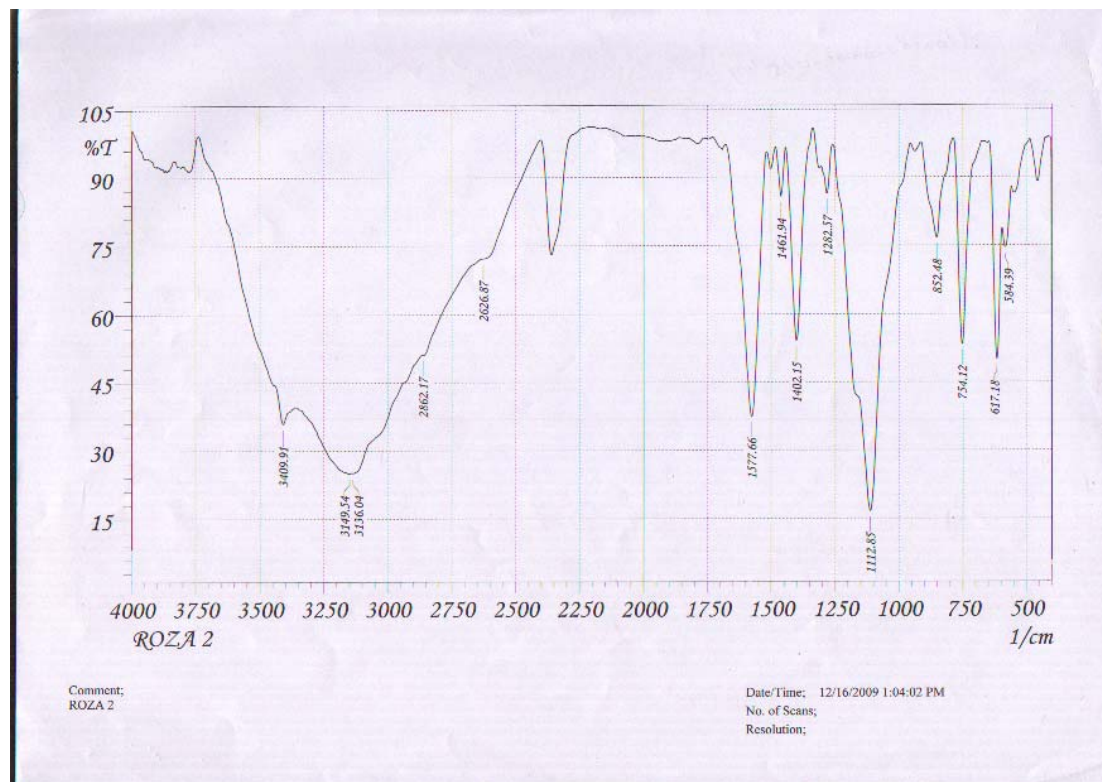
Fig(1) :- FT-IR of poly o- amino phenol
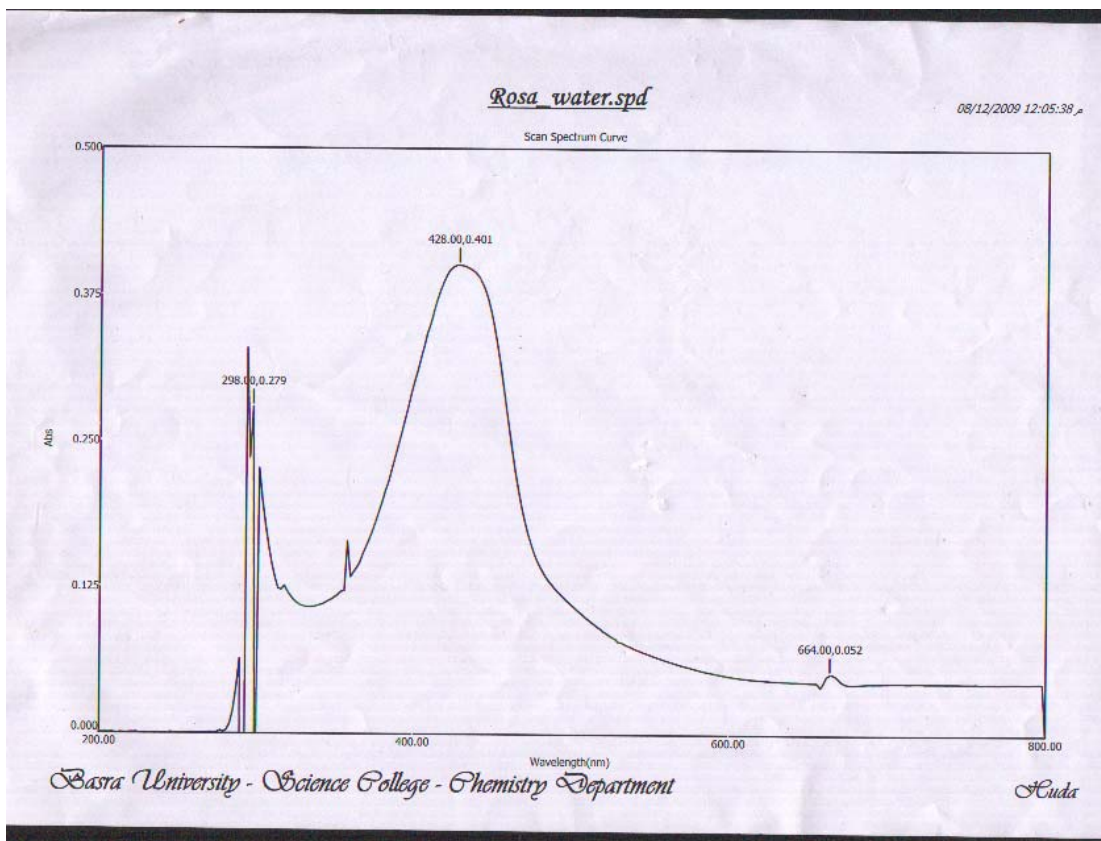
Fig(2) :- UV-VISIBLE of poly o- amino phenol

The electrical conductivity of poly o- amino phenol was higher than that of the other polymers in their self-doped and doped forms, however, they were conducting after doping. 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 o- amino phenol. 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 o- amino phenol, , 4(4- hydroxy phenyl azo) benzene sulfonic acid, 2,5- dimethyl benzene sulfonic acid NaCl , BaCl$_2$.2H$_2$O, AlCl$_3$, were doped with poly o- amino phenol 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) gm using water as solvent. The conductivity values of the samples were plotted against the amount of weight in the feed and showed in figs (3-7). 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 a maxima for 0.1 gm. 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 gm equivalents to poly o- amino phenol.

The electric conductivity increase markedly on doping with suitable electron acceptors.

In is seen from fig (3) that the electric conductivity increase with in 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 π electrons along the polymer chain, therefore, be noted that the conductance was higher and is equal to (0.19498) ohm^{-1} in (0.03) gm.

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 o- amino phenol is shown in Figures (3-7) .Is apparent that the conductance of the poly o- amino phenol increases as the weights of the dopant material increases. In Figure (3) it should be noted that the conductance was higher and is equal to (0.019488) ohm^{-1} in (0.03) gm, while in Figure (4) it should be noted that the conductance was equal to (0.019488) ohm^{-1} in (0.03, 0.07,0.1) gm, while in Figure (5) it should be noted that the conductance was equal to (0.025488) ohm^{-1} in (0.1) gm, while in Figure (6) it should be noted that the conductance was equal to (0.022988) ohm^{-1} in (0.03- 0.1) gm, while in Figure (7) it should be noted that the conductance was equal to (0.023988) ohm^{-1} in (0.051) gm.

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. The conductance of poly o- amino phenol was higher than that of the other polymers in their self- doped and doped forms. Poly o- amino phenol doped with NaCl , BaCl$_2$.2H$_2$O, AlCl$_3$, had highest electrical conductance in its self- doped, with respect to poly o- amino phenol.

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 o- amino phenol when was doped with 4(4-hydroxy-phenyl azo) benzene sulfonic acid, and 2,5 – dimethyl 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 o- amino phenol doped with 4(4-hydroxy-phenyl azo)benzene sulfonic acid, and 2,5 – dimethyl benzene sulfonic acid have low in conductance compare with poly o- amino phenol doped with NaCl ,BaCl$_2$.2H$_2$O, AlCl$_3$, have higher conductivity.

The values of conductance at room temperature of poly o- amino phenol doped with organic sulfonic acid and the salts are listed in table 2.
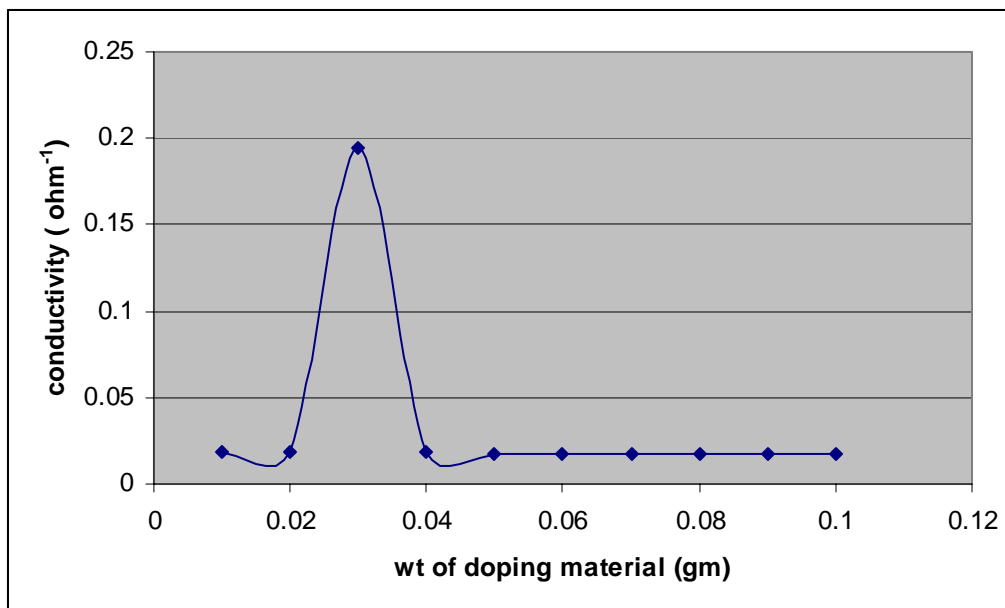
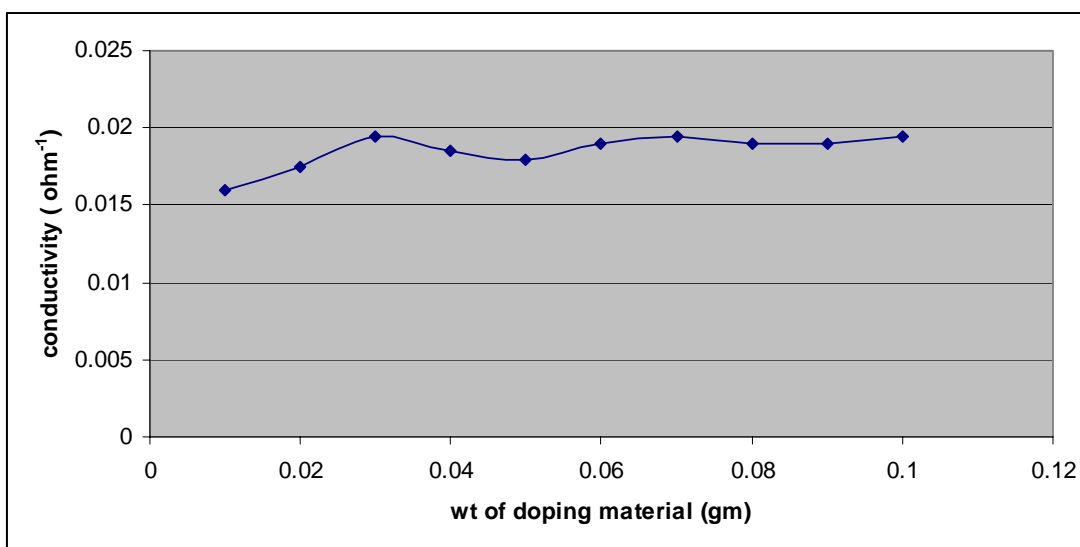**Fig (3) Effect of   4(4- hydroxy phenyl azo) benzene sulfonic acid on conductance of poly o- amino phenol**

Fig (4) Effect of   2,5 – dimethyl benzene sulfonic acid on conductance of poly o- amino phenol
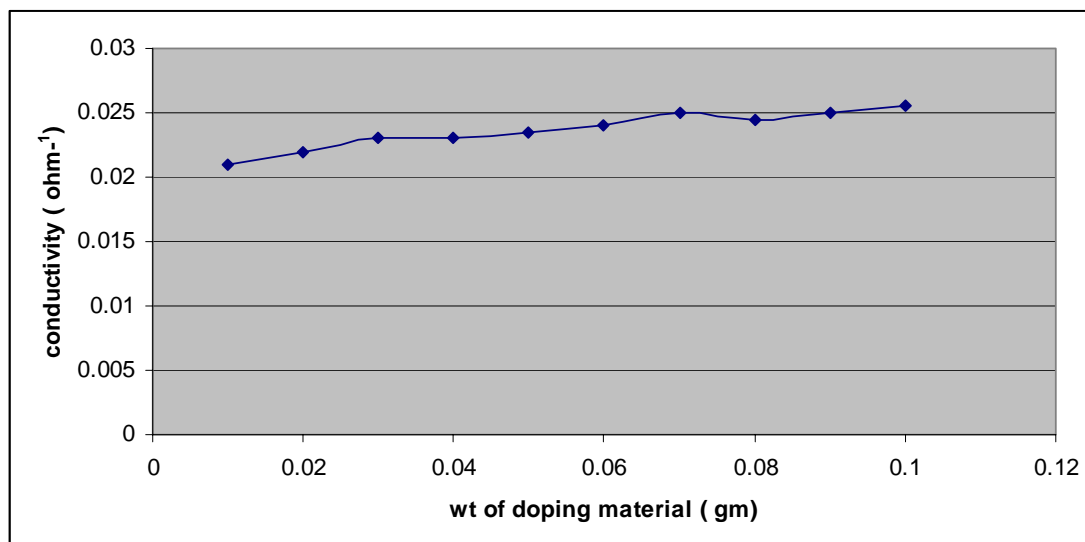
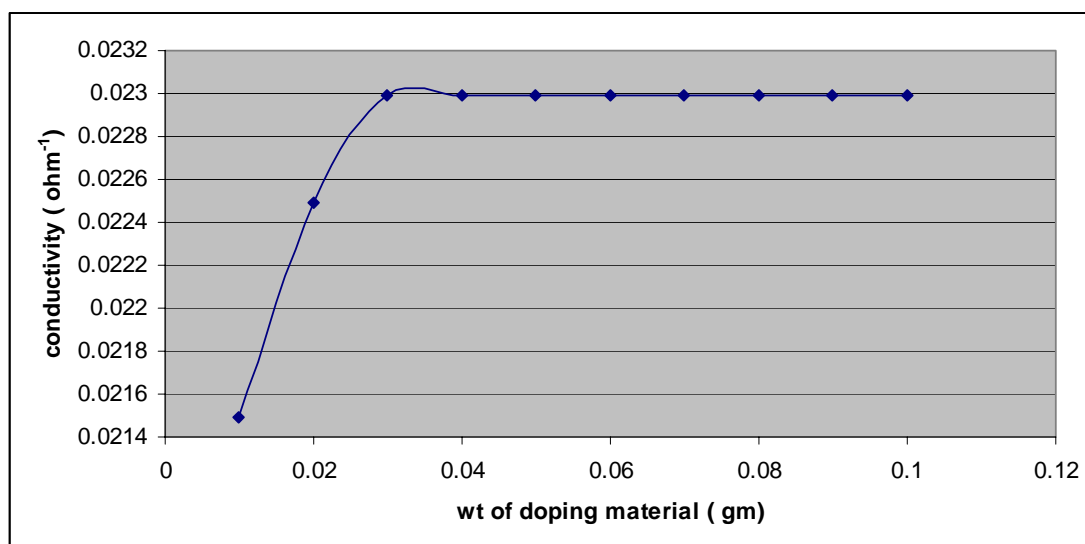**Fig (5) Effect of NaCl on conductance of poly o- amino phenol**

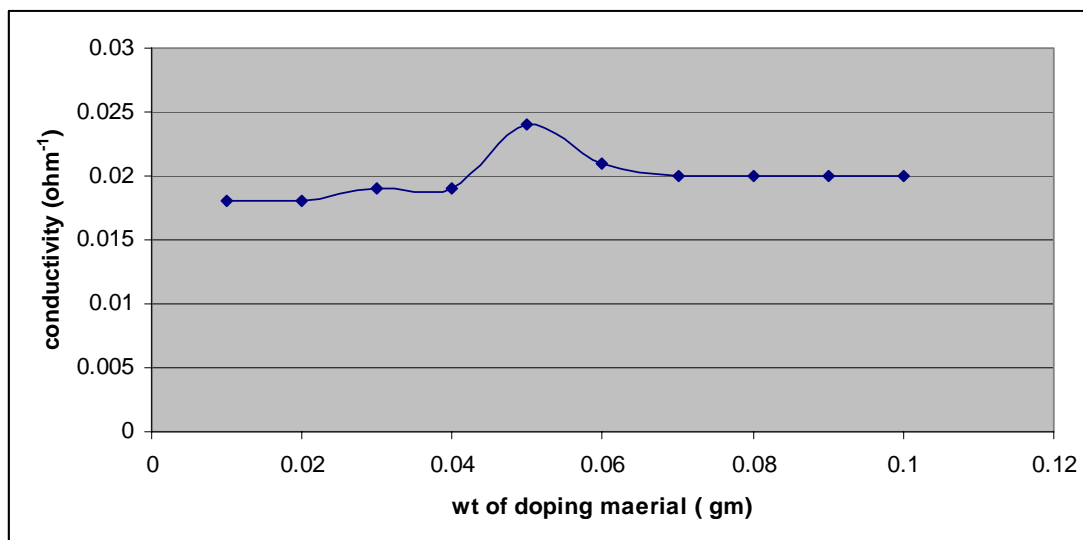**Fig (6) Effect of BaCl$_2$.2H$_2$O on conductance of poly o- amino phenol**

Fig (7) Effect of AlCl₃ on conductance of poly o- amino phenol

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