

Synthesis , identification and study of electrical conductivity of the doped poly indole trimer

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Abstract :

Poly indole trimer was synthesized and doped with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , 4-hydroxy-3-benzene disulfonic acid as well as 4-(4-hydroxyphenyl azo)benzene sulfonic acid each one alone. In addition to study the identification of poly indole trimer by FT-IR and UV-Visible spectroscopy.

Electrical conductivity of poly indole trimer doped with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , 4-hydroxy-*m*-benzene disulfonic acid and 4-(4-hydroxyphenyl azo)benzene sulfonic acid, was studied as a function of weight of the dopant compounds, it is noted an increase of conductance of poly indole trimer by doping with NaCl , the conductance became equal to 0.02099 ohm^{-1} for 0.1 gm.

Introduction :-

The indole nucleus is one of the most ubiquitous scaffolds found in natural products, pharmaceuticals, functional materials, and agrochemicals. Several indole derivatives that occur in nature possess pharmacological activity. These include the hapalindole alkaloids, which exhibit significant antibacterial and antimycotic activity. Other indole alkaloids are uleine, aspidospermidine, the ibophyllidine alkaloids, brevicolline and numerous tryptamine derivatives which exhibit important biological activities (1) .

As a method of chemically polymerization indole proposes a method including the step of dripping an indole solution into an oxidant solution. This method assumes only the case where indole containing no substituent is used as the raw material . there is no mention of an indole derivative containing a substituent . in addition, the product is a polymer containing indole as a repeating unit, and the publication does not include any description concerning formation of trimer. The unsubstituted and substituted indole trimers produced by the conventional technology have the insufficient cycle characteristic and low adaptability to industrial production. Therefore, the development of indole derivative trimers having a high oxidation- reduction potential, a high oxidation- reduction capacity, and excellent cycle characteristics, as well as the development of a method of industrially producing the indole derivative trimers have been very important problems to be solved in the art.(2)

Conducting polymers have received much attention due to their potential usage in several applications such as biosensor, electrochemical display, corrosion protection, or even rechargeable batteries. Conducting polymers were first discovered in 1976 by MacDiarmid, Shirakawa and Heeger, when they found that the conductivity of polyacetylene increased by up to 6 orders of the magnitude when reacted with iodine (from 10^{-4} S/cm to 10^2 S/cm). This phenomenon is known as doping, and is the result of the formation of a charge carrier in the polymer backbone structure. In addition, by varying the doping level, it was possible to yield polymers exhibiting a wide range of electrical properties, from insulator and semi-conductor to metal.

Conducting polymers can be classed in many categories based on their functional groups and include poly-pyrrole, poly-aniline, poly-thiophene, poly-fluorene, poly-indole, poly-carbazole, polyparaphenylene, poly-paraphenylene-vinylene and poly-acetylene. Conducting polymers possess an extended pi-conjugated system made up of overlapped singly occupied p orbitals in the backbone of the polymer chain. Although conducting polymers possess a relatively important number of delocalized pi electrons, a large energy band gap exists between the

valence band and the conduction band. Thus, these polymers are considered to be semi-conducting, at best. To be conducting, these polymers must be doped creating new states (donor or acceptor state), which exist within the band gap, and are energetically accessible to the pi electron. A large number of doping methods is known to affect the conjugated polymers and includes chemical, electrochemical, photo-doping, chargeinjection. The most common doping method is known as oxidative doping, and is accomplished by removing pi electrons from the conjugated pi system via either chemical or electrochemical oxidation. This method is known as p-doping and results in a positive charged backbone with counterions in close proximity. Another doping method, known as n-doping, injects electrons into the pi system, thereby increasing the number of pi electrons, and producing a negatively charged polymer. Although oxidative doping is available to prepare polyaniline, a more common method of producing doped polyaniline is known as acid doping. This method is non-redox in the sense that the number of pi electrons in the backbone chain remains unchanged. As with the oxidative doping process, doped polyaniline may be produced in one step. The presence of the acid results in the protonation of nitrogen atom. Once protonated, the polymer chain becomes positively charged and is associated with counterions. The degree of protonation depends on the oxidation state of the polymer and the pH of the acid solution. The relative number of imines and amine nitrogen atoms depends on the oxidation state of the polyaniline. When being more basic, the imine sites are more readily protonated than the amine sites. Weak acid, such as acetic acid, is not strong enough to protonate the imine sites, even at relatively high acid concentration (3).

Nitrogen-containing heterocyclic compounds are important components of many natural and synthetic products with wide range of properties. In recent years, there has been renewed interest in the synthetic polymers having nitrogen-containing heterocyclic moieties. For example, poly(N-vinylcarbazole), poly(NVC), is the first and the most widely studied polymeric photoconductor. Recent developments in this field are mostly connected to the applications in polymeric light emitting diodes, organic photorefractive materials, and photovoltaic devices. To manipulate unique electronic and photonic functions of these polymers, it is desirable to establish precise synthetic methods to control molecular weight, polydispersity, topology, composition, and functions. Here, we present controlled synthesis of optoelectronic polymers with complex architectures by reversible addition-fragmentation chain transfer (RAFT) polymerization of functional monomers, such as NVC, N-vinylindole derivatives (NVI, 2MNVIn, 3MNVIn), and N-vinylphthalimide (NVPI). Controlled/living radical polymerization has allowed to synthesize

various functional polymers with predetermined molecular weights, narrow molecular weight distribution, and controlled architectures, such as graft and block copolymers, by a facile approach. Among various controlled radical polymerizations, in this study, we selected RAFT polymerization, because of versatility with respect to monomer type and reaction conditions.(4).

milestone in the history of conjugated polymers has been the single-step electrochemical synthesis of more stable polyheterocycles . Among them, polypyrrole, polythiophene and their substituted derivatives have received a great deal of attention because of their good electrical properties, environmental stability and ease of synthesis . A number of other heterocyclic polymers namely polyindole, polycarbazole, polyfuran, polyisothianaphene, polybithiophene and polyphenazine are also electrically conducting and continue to be developed and studied (5).

Experimental :-

1) Apparatus:

1. UV- Visible Helios Alpha spectrophotometer UVA, No 102024.
2. FT-IR 8400S spectrophotometer model (2000) from SHIMADZU Japan.
3. Conductivity instrument (Konduktoskop E 365B Metrohm Herisau).

2) Chemicals:

1. BaCl₂. 2H₂O Fluka 98%
2. NaCl Merck 99.5%
3. Indole BDH.
4. DMF Fluka 99.5%
5. Ammonium persulfate. BDH. 99%

3) Method:

- 4- hydroxy -m- benzene disulfonic acid prepared according to (6), and 4(4- hydroxy phenyl azo) benzene sulfonic acid prepared as in (7).

Synthesis of poly indole trimer

The polymer was synthesized with 1.4 gm of indole was dissolved in 15 ml of DMF , a 11.4 gm ammonium persulfate in 2.7 ml of H₂O was

added dropwise for 15 min , then the reaction mixture was added to the solution for 60 min, the reaction mixture was left 12 hrs in 50 ° C .

Results and Discussion

Spectrophotometric studies:

Infrared spectroscopy (IR)

The chemical structures of poly indole trimer were identified by using FT-IR spectrophotometer.

Table (1) and Fig (1) shows the main functional groups and FT-IR frequencies of the poly indole trimer. The spectrum shows poly indole trimer giving strong peak at 3191 cm^{-1} is due to cis (N-H), and the peak at 1407 cm^{-1} due to (C=C) in benzene , the peak at 1107 cm^{-1} due to (C-N) in amines (8).

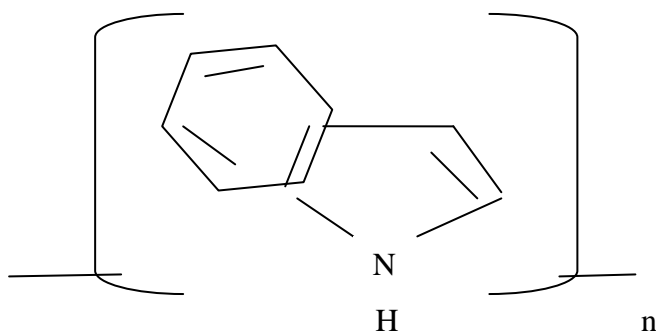
Ultraviolet - Visible spectroscopy (UV)

The UV- Visible spectrum of the poly indole trimer dissolved in chloroform or water was recorded at room temperature by using UV-Visible spectrophotometer shown in Fig (2,3)

poly indole trimer completely dissolve in chloroform and water , these solvents selected as a fundamental solvent for recording the electronic absorption spectra of obtained poly indole trimer. The position of absorption peak, for $n \longrightarrow \pi^*$ transition, appear at 296 nm in chloroform, and 264 nm in water(8).

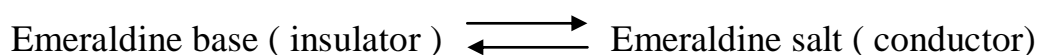
Table (1) The main functional groups and their FT-IR frequencies of poly indole trimer (in cm^{-1})

C-N	C=C	N-H	Samples
1107	1407	3191	Poly indole trimer



Measurement of the electrical conductivity

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



Emeraldine salt (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.

In order to investigate the effect of amount of dopant on the conductivity of the poly indole trimer were doped with $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, NaCl , 4- hydroxy -m- benzene disulfonic acid 4(4- hydroxy phenyl azo) benzene sulfonic acid , poly indole trimer 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 (4-7).

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

It is seen from fig (4) that the electric conductivity increase with in the amount of $BaCl_2 \cdot 2H_2O$, 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 $(0.01699) \text{ ohm}^{-1}$ in (0.06) gm.

The ionic conductances (G) of the prepared compounds were measured in the water as a solvent. The influence of weight of dopant material on the conductance of the poly indole trimer is shown in Figures (4-7) . In Figure (4) it should be noted that the conductance was higher and is equal to $(0.01699) \text{ ohm}^{-1}$ in (0.06) gm, while in Figure (5) it should be noted that the conductance was equal to $(0.02099) \text{ ohm}^{-1}$ in (0.1) gm, while in Figure (6) it should be noted that the conductance was equal to $(0.01949) \text{ ohm}^{-1}$ in (0.1) gm, while in Figure (7) it should be noted that the conductance was equal to $(0.01799) \text{ ohm}^{-1}$ in (0.03) 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 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 indole trimer when was doped with 4(4-hydroxy-phenyl azo) benzene sulfonic acid, and $BaCl_2 \cdot 2H_2O$. 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 values of conductance at room temperature of poly indole trimer doped with organic sulfonic acid and the salts are listed in table 2.

Table 2: Conductance values of poly indole trimer doped with different organic sulfonic acid and the salts at room temperature.

Wt of Dopant material (gm)	Higher conductivity (G)	Dopant material
0.06	0.01699	BaCl ₂ .2H ₂ O
0.1	0.02099	NaCl
0.1	0.01949	4- hydroxy -m- benzene disulfonic acid
0.03	0.01799	4(4- hydroxy phenyl azo) benzene sulfonic acid

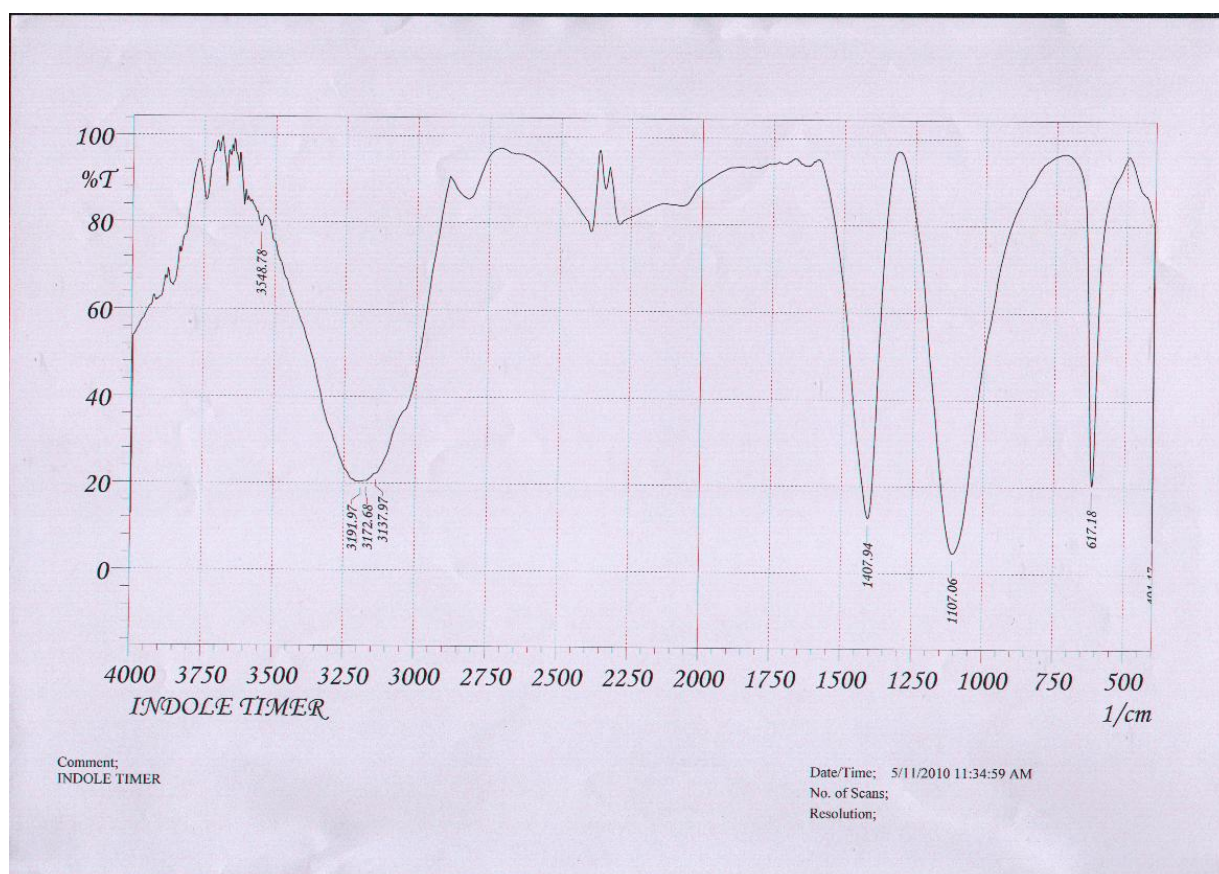


Fig (1) FT- IR of poly indole trimer in chloroform

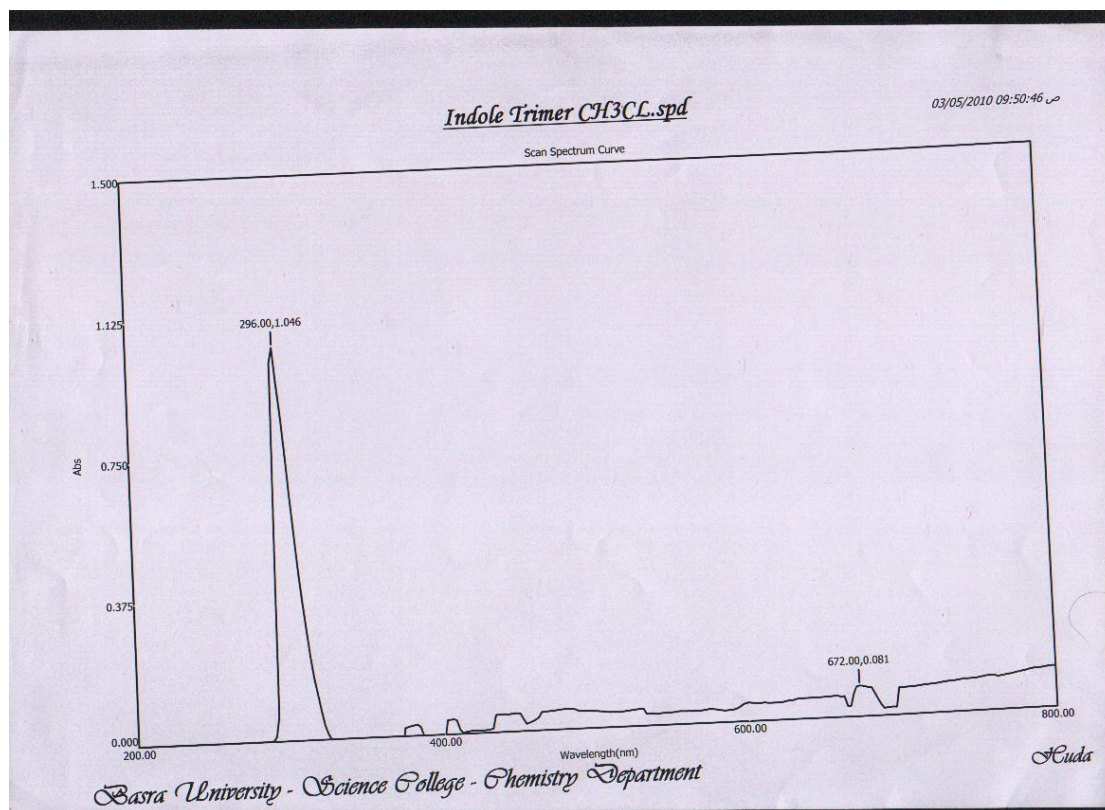


Fig (2) UV- VIS. of poly indole trimer in chloroform

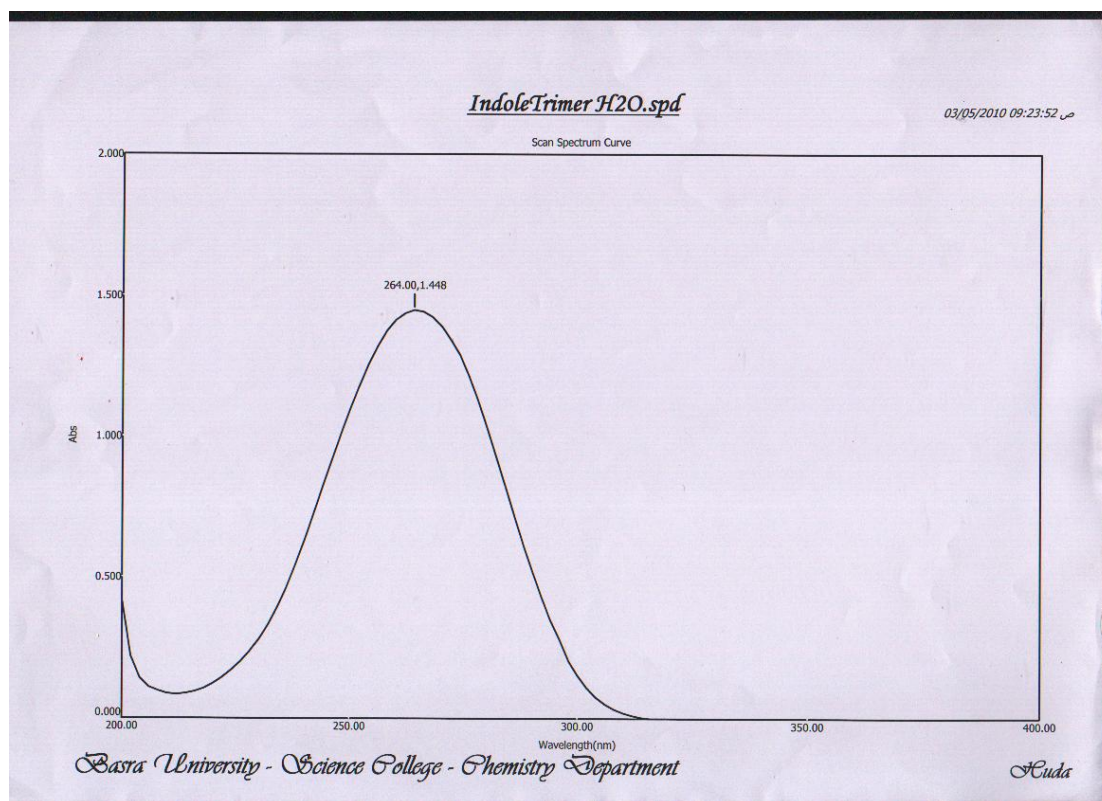


Fig (3) UV- VIS. of poly indole trimer in water

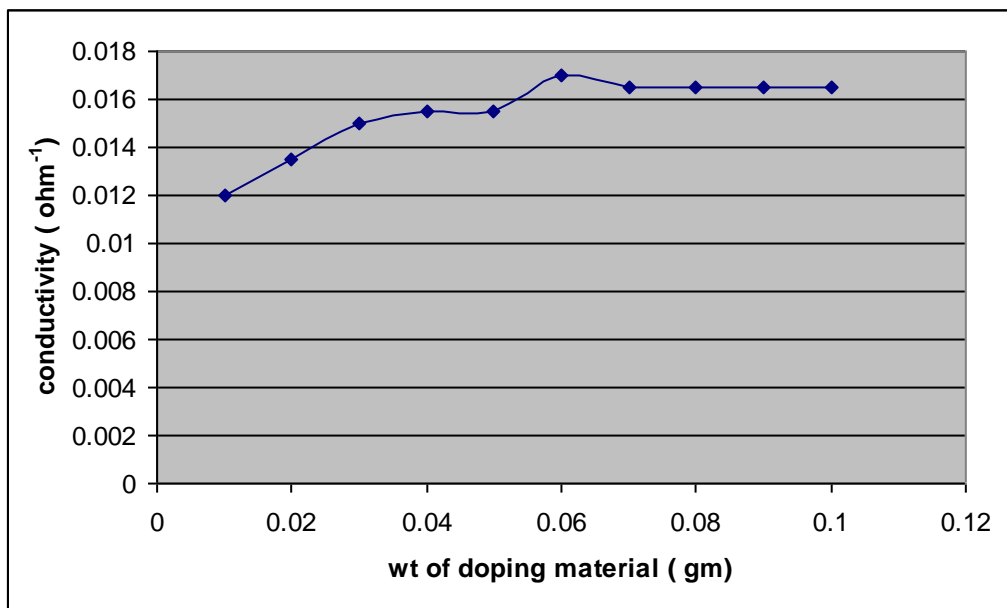


Fig (4) Effect of BaCl₂.2H₂O on conductance of indole trimer

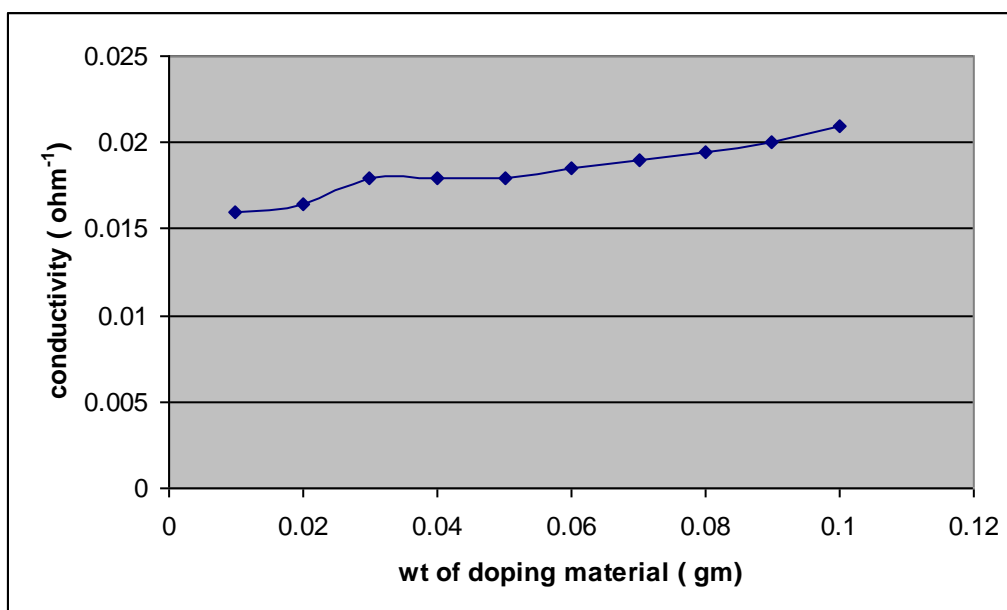


Fig (5) Effect of NaCl on conductance of poly indole trimer

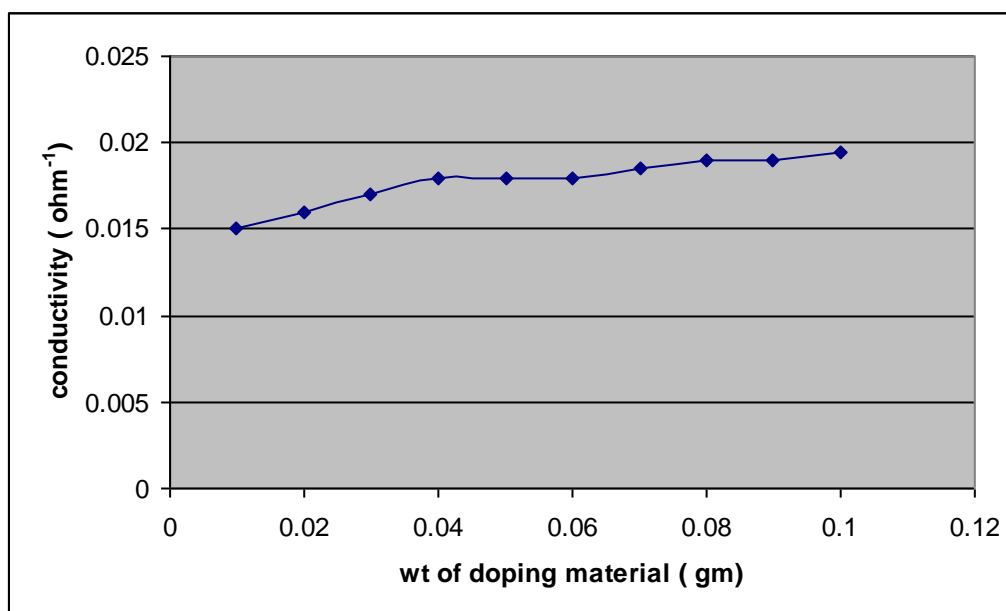


Fig (6) Effect of 4- hydroxy –m- benzene disulfonic acid on conductance of poly indole trimer

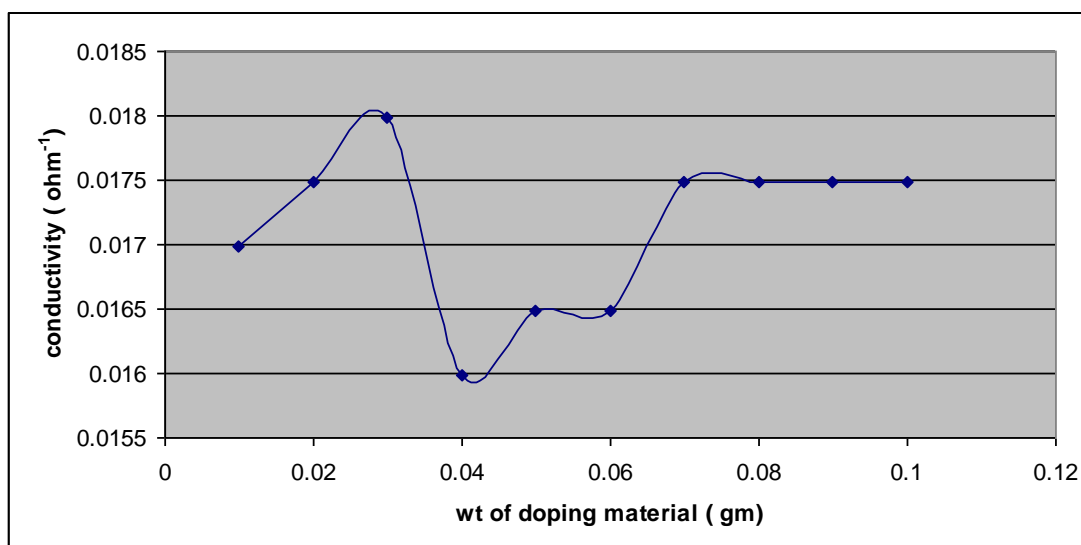


Fig (7) Effect of 4(4- hydroxy phenyl azo) benzene sulfonic acid on conductance of poly indole trimer

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تحضير وتشخيص ودراسة التوصيلية الكهربائية
للبوليمر المشوب poly indole trimer

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حضر البوليمر Poly indole trimer وشوب بعدة مشوبات وهي $BaCl_2 \cdot 2H_2O$ و $NaCl$, و 4-hydroxy-3-benzene disulfonic acid و 4-hydroxy phenyl azo) benzene sulfonic acid (4) كلا على حدة. إضافة إلى ذلك شخض البوليمر poly indole trimer بتقنيتي طيف الأشعة تحت الحمراء FT-IR و طيف الأشعة المرئية وفوق البنفسجية UV-Visible. درست التوصيلية الكهربائية للبوليمر Poly indole trimer كدالة لوزن المادة المشوبة، بالمواد المشوبة المختلفة وهي $BaCl_2 \cdot 2H_2O$ و $NaCl$ و 4-hydroxy-3-benzene disulfonic acid و 4-hydroxy phenyl azo) benzene sulfonic acid (4) وقد أوضحت النتائج زيادة التوصيلية الكهربائية للبوليمر poly indole trimer من خلال تشويبه بالملح $NaCl$ حيث كانت التوصيلية مساوية إلى 0.02099ohm^{-1} وبنسبة 0.1 غرام.