Calculation of Some Electrical Properties of Poly Vinyl Alcohol Grafted with Eosin Dye (PVA-g-Ei)

Ali Q.Abdullah, A.Shawi, and Harith A.Hassan
Department of Physics, College of Science, University of Basrah
Basrah-Iraq

ISSN –1817 –2695
((Received 21/12/2008 , Accepted 25/3/2009))

Abstract

The electrical conducting mechanism of newly synthesized polymer by condensation polymerization, poly vinyl alcohol grafted with Eosin dye (PVA-g-Ei) have been investigated. Electrical measurements including (current-voltage) and (conductivity-Temperature) characteristics at a range of temperature (313-368)K .The result shows that the sample has semiconductor behavior as its conductivity increases with the increasing temperature and the value of dark conductivity at R.T estimated from Ohmic region was about $1.04x10^{-13}$S/cm .The energy required to move electrons from valance band to conduction band can be estimated which about 0.52eV.The deviation from Ohmic law has been analyzed in terms of variable range hopping (VRH) conduction theories. Thermal properties were also studied to estimate the bipolar contribution to thermal conductivity of polymer.

Keywords:Polydye mechansim,Electrical properties, Polyvinyl alcohol graft, Eosin dye conduction.

Introduction

Over the last decades thin polymer films have attracted an increasing interest for application in micro-electronic industry and in optical component due to their ease of processing, low dielectric constant ease of chemical modification, customization, light weight and high strength [1, 2] . The electrical conduction of thin polymer films have been extensively studied in recent years to understand the nature of charge transport in these materials that [3] .Synthesize polymer dye hybrid materials ,in which one can take advantage of the properties of each component individually and ,also reach synergistic properties between them[4,5].

Experimental

A-Synthesis of new polymer

A three-neck reaction flask equipped with thermometers ,mechanical stirrer and condenser , was charged with 1 mol of commercial Eosin dye provided by Fluka without any purification ,0.01 mol of poly vinyl alcohol (PVA) provided by Aldrich Mw(110,000-106,000) ,100 ml Dimethyl Sulfoxid (DMSO) provided by BDH Ltd. Co. as a solvent and three drops of Phosphoric acid(H_3PO_4) provided by Fluka as catalyst . The reaction mixture was stirred and heated to 383K for 7hr's then the reaction mixture was evaporated by rotary evaporate to remove the solvent under reduced pressure 0.1mmHg for 24hr's at R.T .The reaction equation was shown in Figure(1).

The polymer was structurally characterized by using FT-IR type Shimadzu8400s FT-IR spectroscopy and Elemental Microanalysis (C H N) type 2400 Perkin Elmer Co. The FT-IR spectrum of PVA-g-Ei as shown in Figure (2) shows that the most important bands for functional groups which are listed in Table (1) .The most important peaks of the spectrum are found at $1710cm^{-1}$related to carboxyl ester group that indicates that reaction between PVA and Eosin dye occurred [6].

Table (1): The location of the most absorption bands for (PVA-g-Ei)

Functional Groups	Wave number(λ^{-1})cm^{-1}
C-O	1030
C-H(band)	1450
C=O(stretch)	1650
C=O(stretch)(ester)	1710
C-H(stretch)(Aliph.)	2950
C-H(stretch)(Aromatic)	3075
O-H(stretch)	3500

The results obtained are shown in Table (2) .A reasonable agreement between the determined and calculated data was found .

Table (2):The quantitative elemental analysis data of PVA-g-Ei

Polymer	Found			Calculated		
	C%	H%	N%	C%	H%	N%
PVA-g-Ei	36.54	1.24	----------	37.95	1.29	----------

B-Thin films preparation

Aluminum substrates which used to study electric conduction mechanism of (PVA-g-Ei).The polymer was cleaned by immersing in cleaning solution[10%$K_2Cr_2O_7$+H_2SO_4][7] then ultrasonically in distilled acetone,deionized water .After the cleaning substrates polymers as thin film have been deposited on aluminum substrates (as a lower electrode) at normal equilibrium condition using cast method from solution technique[8]. The substrates were kept in a vacuum desiccators over gel for 24hr's, after that .The films were transferred to an evacuated oven with temperature raised gradually up to 323K by a rate 10^oC/h and kept at this temperature for 24hr's to complete curing then cold gradually to R.T.Finally ,all substrates transferred to the chamber of in a varian model 3117 to evaporate the upper aluminum electrodes under vacuum 10^{-5}torr at circular shape with area $0.03cm^2$.The sample and electrodes were enclosed in ground copper screen box ,and an oven whose temperature was controlled by . proportional controlled .,and a regulated voltage range from (1-120V) were supplied by power supply model hp 6443B .The current was measured by Ammeter model MEGOHMMETER(IM6)at the range (10^{-12}-10^{-4}A) and voltmeter model SC-MultiLOGGER IWATSU Electric Co.LTD.The sample temperature was measured with a thermocouple placed near the sample. The thermocouple consist of copper and constantan connected wires connected together in two junctions, one of these immersed in fix reference point (ice – water mixture 0^oC) while the other was connected to specimen .The thermocouple are connected to a voltmeter A schematic diagram of electrical properties measurement is shown in Figure(2).

Electrical measurements

The electrical measurement of PVA-g-Ei was measured at steady state condition .In order to obtain the reproducible results as shown in Figure(3) .Steady state measurement are necessary to apply due to the existence of absorption current [9] .Figure(4) shows the relationship between current and applied voltage at different temperature range (313-368K).At law voltage (≤10V) Ohmic conduction mechanism was observed clearly which indicates that the charge carriers are thermally generated , and charge carriers which are effected by current limits [10] ,from the Ohmic region the dark conductivity can be estimated at R.T which will be about $1.04x10^{-13}$S/cm .At high applied voltage (≥10V) non-Ohmic behavior can be noticed which indicates that the injected electrode carriers are greater than the thermally generated charge .Figure(5)shows the temperature dependence of the conductivity of the sample which indicates that it is fitted to Arrhenius exponential equation [11] :

$$\sigma_{dc} = \sigma_o e^{\frac{-Ea}{K_B T}} \quad \text{..... (1)}$$

Where :σ_o is the pre –exponential rate corresponding to 1/T=0,Ea is the activation energy ,K_B is the Boltzmann's constant and T is absolute temperature. The polymer has a semiconductor behavior where the conductivity increases with increasing temperature due to delocalized π-electrons ,from the Figure it can be estimated the activation energy (Ea) from the slope of the straight line, it found to be about 0.52eV .Mott's conduction mechanism variable range hopping(VRH) ,which was successfully applied to this polymer according to the equation [12]:

$$\sigma = Ae^{-BT^{\frac{-1}{n}}} \quad \text{..... (2)}$$

Where A,B and n are constants ,the value of the exponent (n)determined the nature of the conduction mechanism .Experimentally ,DC conductivity measurement carried out for this sample which shows that the temperature dependence of the DC conductivity obeys lnσ(T) versus $T^{-1/4}$ in Figure(6), which is consistent with a charge transport process governed by theory of (VRH) that has been successfully used in describing the transport properties in a variety of disorder semiconductors. In this study another possible conduction mechanisms such as ionic ,space charge limited current,Schottky and Poole-Frenkel effect and tunneling were also studied to identify the proper investigation .Figure(7)shows the relationship between –ln(σ T) and 10^3/ T , where the linear relation can exclude the ionic mechanism from our speculated [13] .The possible existing of Schottky or Poole –Frenkel effect can be investigated from the relationship between current and square root of electric field ($E^{1/2}$) .A nonlinear behavior was obtained at high electric field as shown in Figure (8) ,also (current –voltage) characteristics does not obey the general space charge limited current .Moreover, the range of thickness for films under study were out of range satisfying tunneling mechanism[14].

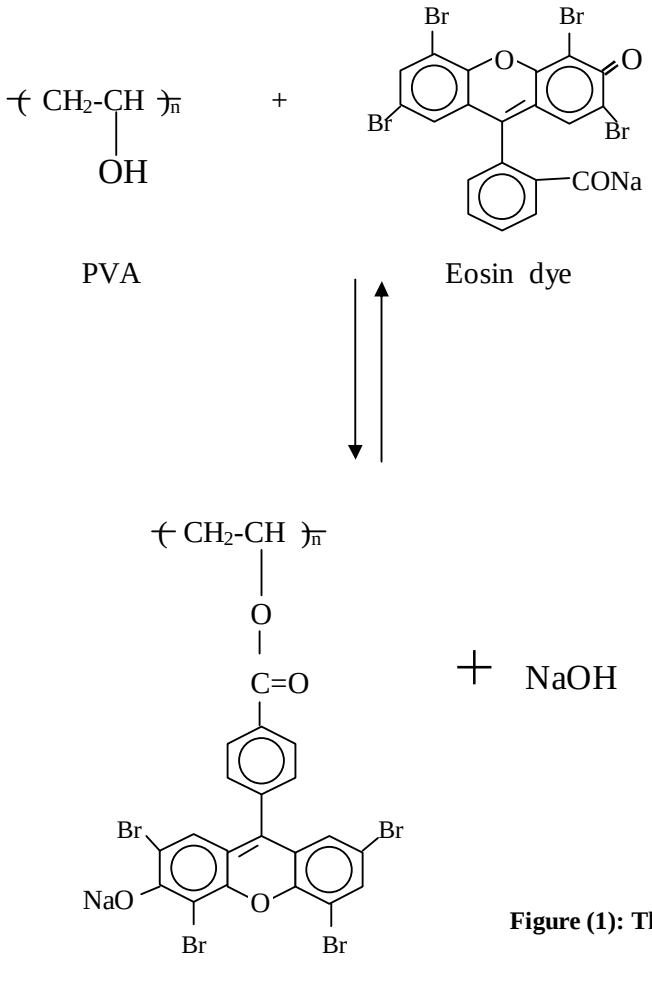
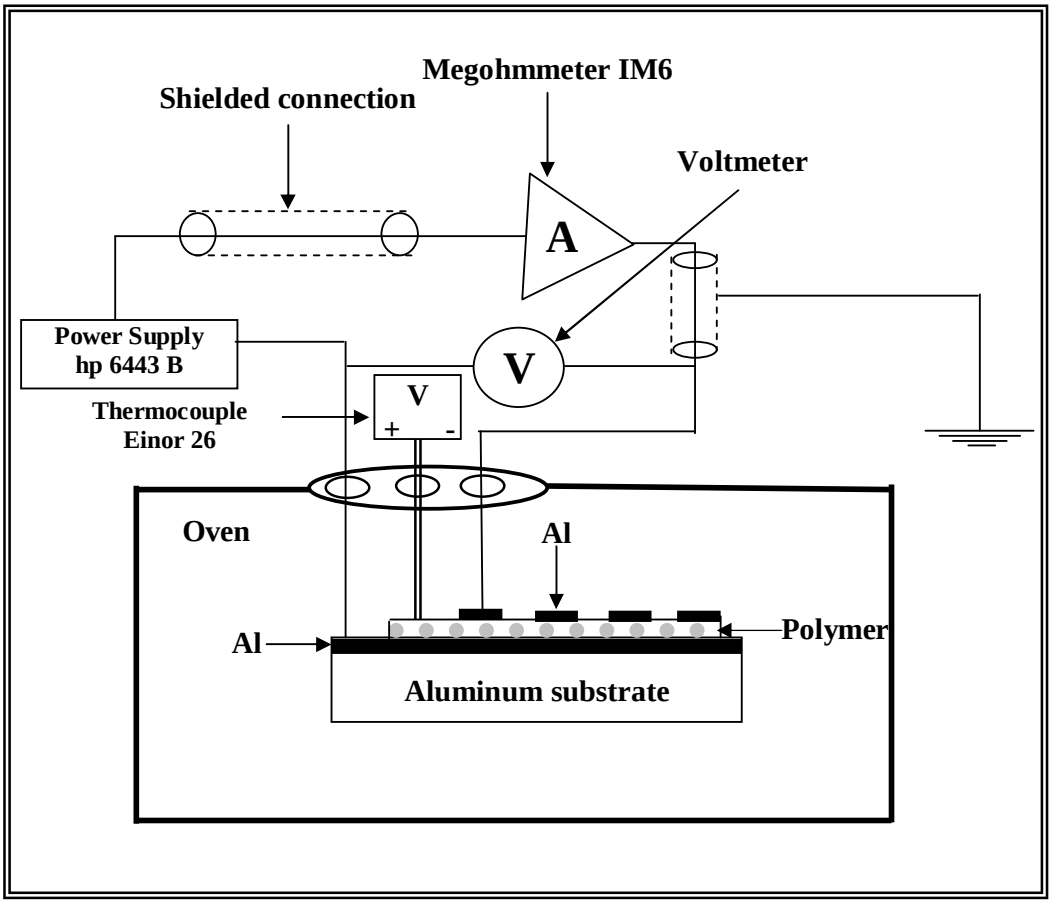
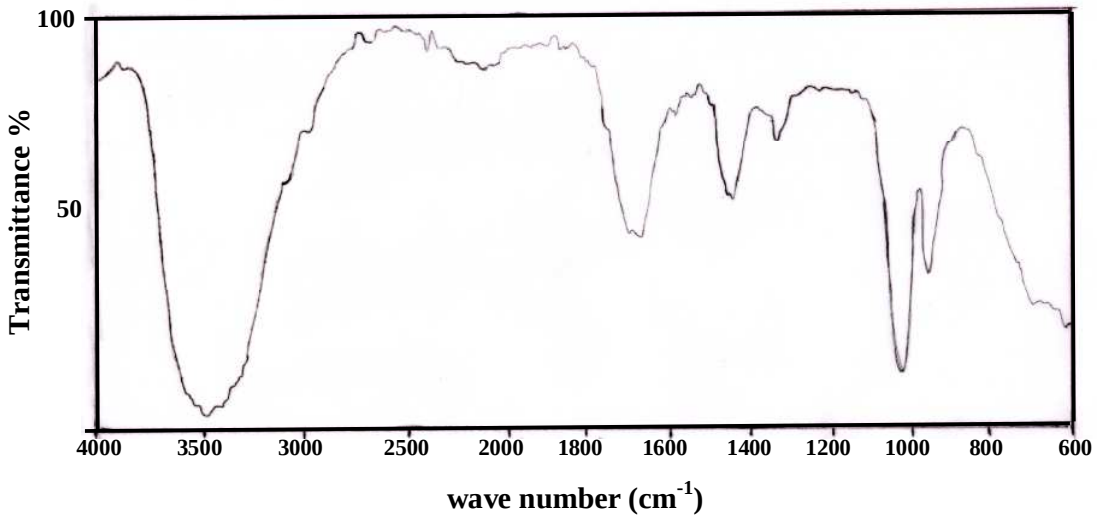


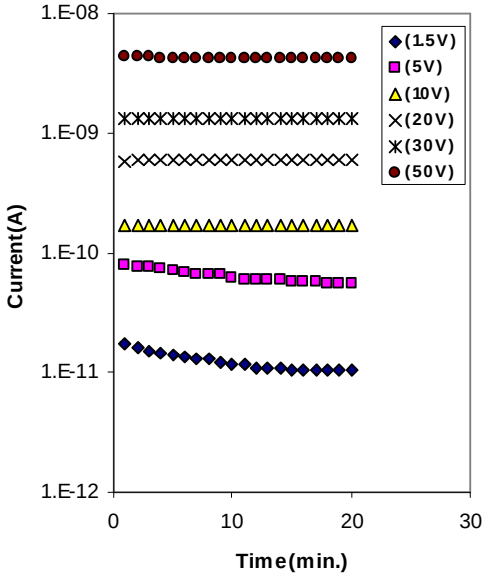
Figure (1): The diagram structure reaction of PVA-g-Ei.



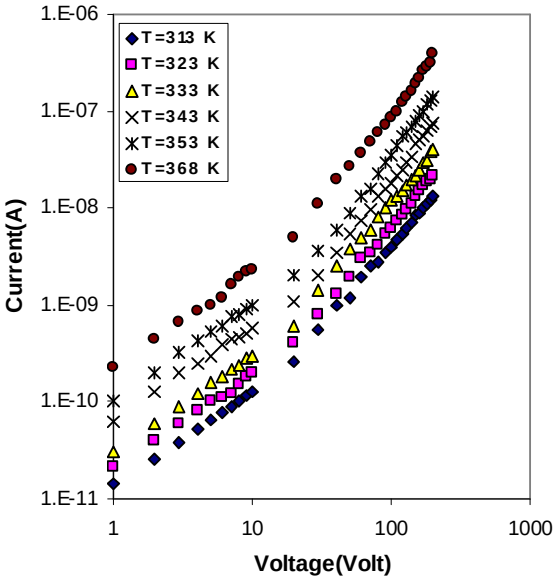
Figure(2): Schematic diagram of the electric circuit measurement



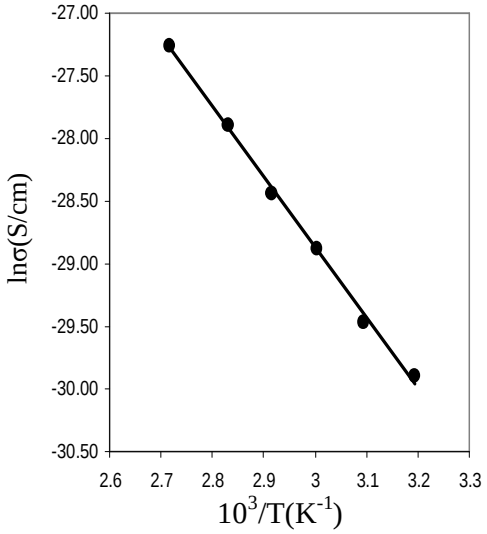
Figure(3):The FT-IR spectrum of PVA-g-Ei .



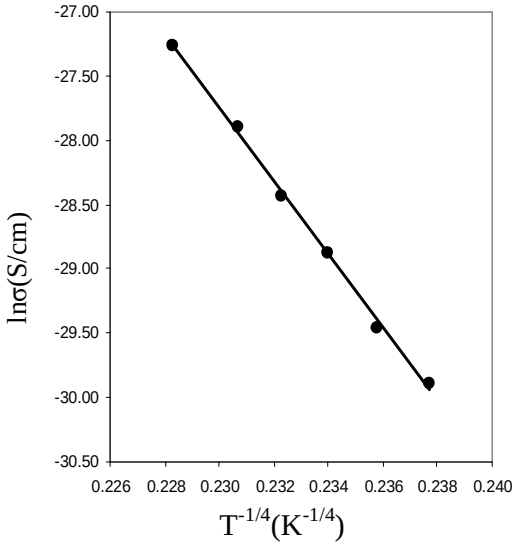
Figure(4):The relationship between current and time at different voltage (1.5-50V).



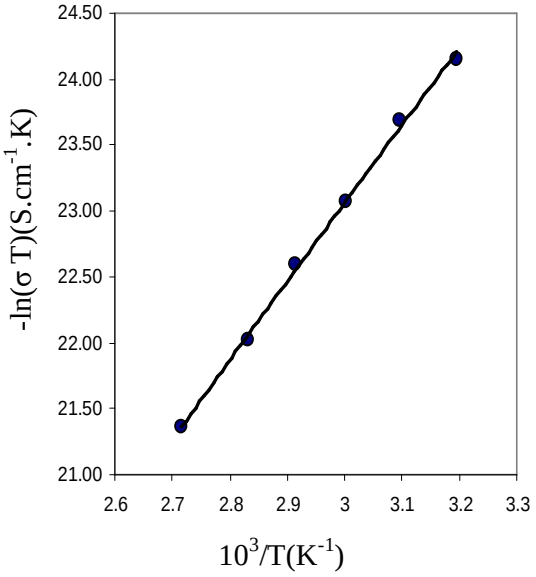
Figure(5):The (current-voltage)characteristics at different temperature range (313-368)K.



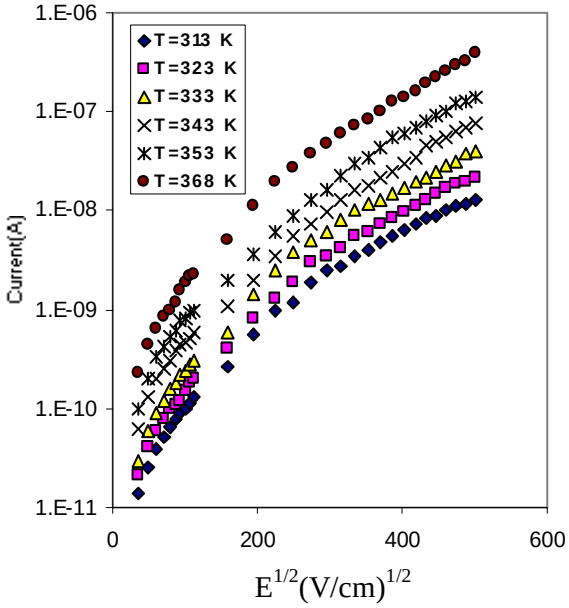
Figure(6):The relationship between lnσ(T) and $10^3/T$.



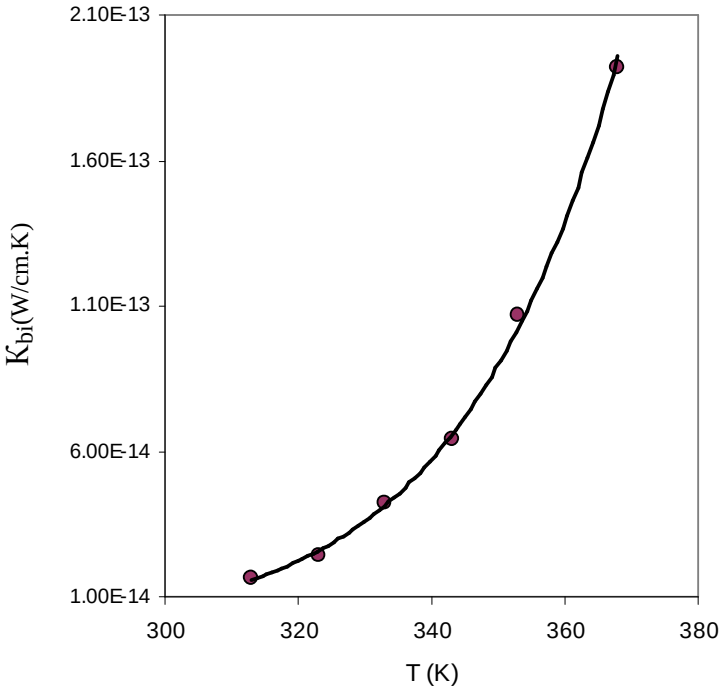
Figure(7):The relationship between lnσ(T) and $T^{-1/4}$.



Figure(8):The relationship between –ln(σ T) and 10^3/ T .



Figure(9):The relationship between current and square root of electric field ($E^{1/2}$) .



Figure(10):The variation thermal conductivity versus temperature of PVA-g-Ei .

Thermal measurement

The value of the activation energy (Ea) obtained from the electrical conductivity measurement made it possible to estimate the bipolar contribution to thermal conductivity .The thermal conductivity was calculated using the equation [15]:

$$\kappa_{bi} = (\frac{3\pi^3}{4}) L\sigma T (\frac{E_a}{K_B T} + 4)^2 \qquad \ldots (3)$$

Where the Lorentz number L is define as:

$$L = \frac{\pi^2}{3(\frac{K_B}{e})^2} = 2.45\times10^{-8} \qquad \ldots. (4)$$

The calculation value of κ_{bi} of sample is given in Figure(9) .The mechanism of heat transfer in this sample can be due to phonon bipolar κ_{bi} . It was seen that the values of κ_{bi} are low in the investigated temperature range, since the sample has a semi conducting property of electrons and contributions of phonons .

Conclusions

The electrical properties of new polymer (PVA-Y- Eosin) films had been carried out. It is shown that this polymer has a simeconducting property. Its conductivity is in the order of magnitude 10^{-13}S/cm. The DC electrical conductivity of the polymer shows typical Arrhenius -type dependence on temperature and its behavior can be explained by means of hopping conduction mechanism. The current voltage characteristics for the polymer could be interpreted in terms of both Schottky and Pool -Frenkel effects.

References

[1]-R.Kulish and H.Franke,J.Appl.Phys.,71,3123,(1992).

[2]-C.Y.Chao and L.J.Guo,J.Vac.Sci.Technol.,B,20,2062,(2002).

[3]- N.Ch Nagaraj,V.Subba Reddy, A.K.Shorrma and V.V.R.Narasimhae Rao,J.Power Sources,112,326,(2002).

[4]- S.Bezerra C. Silva,J.Augsto and P. Siva.,Mat.Res.,.6,.3,(.2003),

[5]-J.Liu,T.Fan and J.Lv,J.Opt,A:Pur Appl.Opt,9,(2007).

[6]-R.Silvertein ,G.Bassler and E.Morrill,"Spectrometric Identification of Organic Compunds",John Wiely & Son,N.Y.,(1981).

[7]- A.I.Vogel,"Practical Organic Chemistry",Lowe and Brydone Ltd., London, (1972) 53.

[8]-M. Kaneko and D.Wohrle"Polymer-Coated Electrodes:New Materials for Science and Industry",Advance in Polymer Science,Speringer-Verlage Berlin Heidelberg,84, (1988) 147.

[9]-J.I.Kroschwitz,"Electrical and Electronic Properties of Polymer,A State of the Art Compendium ,Wiley ,Newyork,140,(1988).

[10]-A.Q.abdullah,K.M.Ziadan and S.Sh.Al-Labia,Iraqi J.Polym.,11,2,84,(2007).

[11]-F.Yakuphanoglu,M.Aydin,N.Arsu and M.Sekerci,Физика И Техника полпророводников,38,486,(2004).

[12]-N.F.Mott,E.A.Davis,"Electronic Process in Non-Crystalline Materials,Clarendon Press,Oxford,(1971).

[13]-C.K.Chaing,G.T.Davis and C.A.Harding,Soild State Ionic,18,300,(1986).

[14]-A.Q.A.Al-Assadi" SYNTHESIS AND STUDY OF OPTCAL AND ELECTRICAL PROPERTIES FOR SOME NEW POLYMERS DERIVED FROM ORGANIC DYES AND THEIR PROMISING APPLICATIONS AS LIGHT –EMITTING DIODES" Ph.D Thesis ,Unversity of Basrah,College of Science,Basrah,Iraq,(2007).

[15]-A.A.Abd El-Rahman,M.El-Desoky,A.El-Wahab,A.El- Sharkawy,J.Phy.Chem, 60,119,(1999).

المستخلص

درست الخواص الكهربائية لأغشية رقيقة من البولي فنيلين الكحول والمطعم بصبغة الايوسين العضوية مرسبة على أقطاب من الألمنيوم . حللت القياسات الكهربائية والتي تتضمن العلاقة بين التيار والفولتية والعلاقة بين التوصيلية ودرجة الحرارة في المدى بينK (313-368) . أثبتت النتائج أن البوليمر يسلك سلوكا كمادة شبه موصلة حيث تزداد التوصيلية مع ازدياد درجة الحرارة وقيمة التوصيلية هي بحدود 10^{-13} S/cm

كما تم حساب طاقة التنشيط للبوليمر ووجد أنها تساوي 0.52 eV. درست ميكانيكية انتقال حاملات الشحنة للبوليمر المحضر حيث كانت من نوع الانتقال الالكترونية بالقفز عند المجالات الواطئة فضلا عن ذلك فان التوصيلية الحرارية للبوليمر قد تمت دراستها في مدى درجات الحرارة المذكورة أعلاه.