Study of Some Electrical Properties of poly alpha naphthyle acrylate doped with Ioden(I_2)

ISSN–1817–2695

H. K. Ibrahim

Department of physics, College of Education, University of Basrah, Basrah, Iraq

((Received 10/3/2009, Accepted 23/2/2010))

Abstract

The electrical properties investigation for poly alpha naphthyle acrylate doped with Ioden (I_2) films was carried out for films prepared by cast method.

Conduction processes were analysed through measuring (Current – Voltage) and (Conductivity – temperature) relationships in the voltage and temperature ranges (1-120) V and (308 -373) K respectively.

The resistance of the doped films is found to have a negative thermal coefficient. The activation energy at temperature (308 -373)K was about (0.6)eV is found from the ohmic region of the dark (current – voltage) characteristic. The conductivity at temperature 308 was equal to 5.57×10^{-12} ($S.cm^{-1}$).

The deviation from ohm's law has been analysed in term of the available conduction theories, ionic conduction mechanism was concluded.

Key words: electrical properties, d.c conductivity, Ionic conduction mechanism

Introduction

The use of polymers for electronic applications is widespread and expanding rapidly [1-4]. The electrical behavior of polymers is reviewed and discussed by many authours [5-7] .The conduction mechanism of polymers is not fully understood and usually characterized as a complex process depending not only charge transfer in the bulk, but also across the polymer-metal interface at the electrode [8] .The conductivity of polymer (σ) was calculated by the following relation:**[9]**

$$\sigma = \frac{1}{R}\cdot\frac{d}{A} \quad .... \quad (1)$$

Where : R is the bulk resistance of the polymer.
d is the thickness of the polymer.
A is the area of the electrode.

The activation energy (E_a) was calculated by using Arhenus equation [10]:

$$\sigma = \sigma_o e^{-E_{a.c}/KT} \quad .... \quad (2)$$

Where; σ_o: constant, $E_{a.c}$: activation energy, T: absolute temperature and K:Boltzman constant.

The conduction mechanism type Schottky is found in many polymers such as Poly (pyromellitic-1,2 Naphthylene diamine)(PPND) [11] and Fe-doped $BaTiO_3$ **[12]** .

The hopping conduction mechanism was observed in poly (phthalocyanine) (PC)[13], Amorphous Heavy – Hydrogenated silicon.[14] and (PPAB) terminated by phenylene diamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$[15]. The Space charge limited current mechanism (SCLC) is observed in poly alpha naphthyle acrylate (PNA) doped with Lithium chloride (LiCl)[16]. Tunneling conduction mechanism is the dominant one in the very thin films such that thickness ~ 3.5nm [17].The Ionic conduction mechanism was observed in Plasticized poly(methylmethacrylate)/poly(vinylidene fluoride) [PMMA/PVdF] blend polymer electrolytes [18], $LiClO_4$/PEO/PCL Ternary Blends [19], single crystals of $KTiOPO_4$[20].and (PPAB) terminated by phenylene diamine doped with $K_2Cr_2O_7$ [21] .

In the present study the electrical properties of poly alpha naphthyle acrylate doped with Ioden (I_2) have been investigated by measuring (current – voltage) and (conductivity – temperature) characteristics. The conduction mechanism in the polymer film has been identified.

Experimental Procedure

Poly alpha naphthyle acrylate (PNA) was synthesized used condensation polymerization adopting to method previously reported. [16]

Figure (1) shows the expected structure of the polymer under the present study .

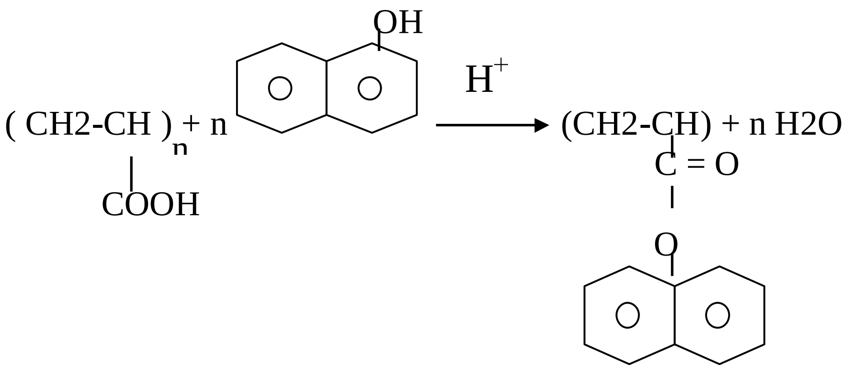

Fig (1): The expected chemical structure of polymer.

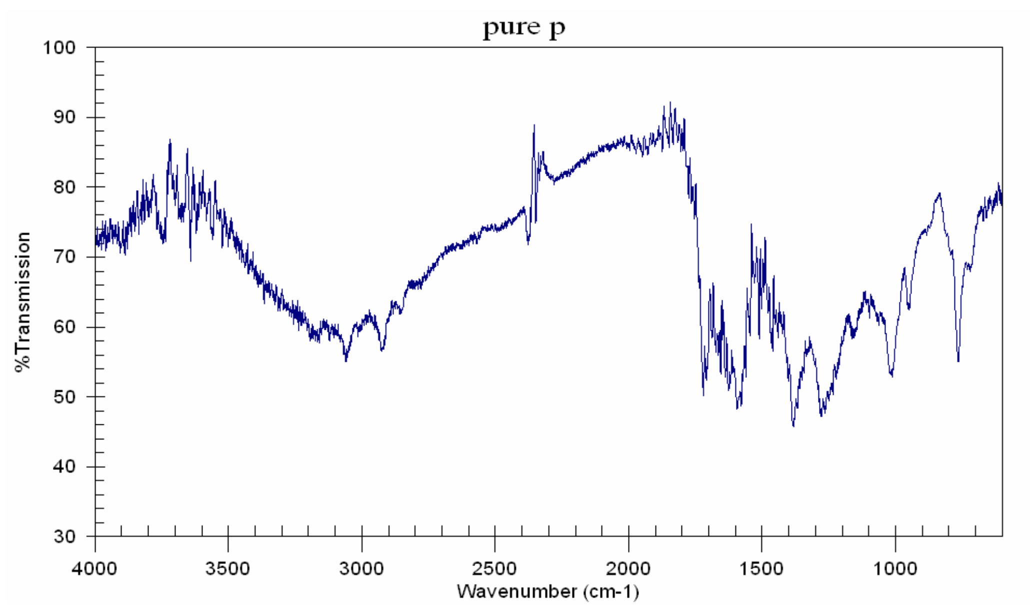

Fig (I) IR spectrum of polymer PNA

0.1M of polymer(0.1081 gm) is first dissolved in Dimethyl Formamide (DMF) with stirred at room temperature for (4 – 6) h. 0.1M of Iodene (I_2) (0.1269gm)dissolved in (DMF) ,then the dopant was added to the polymer with ratio 1:4 (dopant: polymer). The stirred solution was cast on the substrates cited horizontally to get a homogeneous thickness.

The solvent is allowed to evaporate slowly at room temperature followed by vacuum drying. Current process was applied to the samples as a final process via increasing the temperature in the rate 10 C° /hr up to 90C°, then cooled gradually up to the room temperature. For good ohmic contact alluminium circles with radius 1 mm were deposited on the upper face of the polymer sample using evaporation method under vacuum 10^{-4} Torr.

The samples of Al/polymer/Al structure are kept in dark and shielded box to avoid stray capacitance The current is measured by using amplifier model D-53200 with digital voltmeter model Philips PM 2522 .

Results and Discussion

In order to obtain the reproducible results, the electrical properties of the polymer films have been investigated with measuring the steady state current .Steady state measurements are necessary to apply due to the existence of absorption currents.

Fig(2): shows the relationship between current passes across the sample and time measured after applied voltage 10(volt) in room temperature .The steady current was recorded after 5 min from applying the voltage and adopted for all measurements.

The (I – V) characteristics of the film with thickness ~ (15μm) was measured in the voltage range (1- 120) V and temperature (308 – 373) K as shown in Fig (3). It can be observed, that the current was increase with increasing of temperatures and voltages for all measurements. It can be observed from Fig(3) that, the current shows ohmic behavior at low field region (1-30) V, and greater than 30 V the current rise as voltage increasing and the deviation from ohms law can be determined by different conduction mechanisms that are possible to take place in solid polymers. By using Fig (3) and equation (1) one can be determined the bulk conductivity of polymer films in the ohmic region at different temperatures .The bulk conductivity of polymer found to be 5.57×10^{-12}(S.cm^{-1}) at temperature 308 K. The relation between conductivity and the reciprocal of absolute temperature (10^3/T) is shown in Fig (4), the conductivity was decreased with increasing of (10^3/T) that reflect the polymers under study have the negative resistance coefficient.

The activation energy of polymer at temperature (308 – 373) K in the ohmic region was calculated from the slope of the straight line in Fig (4) and using Arhenus equation (equ.2) it is found to be (o.6 eV) . The injected electrode carriers are greater than thermally generated charges. That is clearly from the non ohmic behavior, therefore, different conduction mechanisms could occur to explain the charge transfer.

Tunneling mechanism is not applicable in our investigation because it requires very thin films and current is independent on temperature.

Fig (5): shows the plot of -Ln ($\sigma T^{1/2}$) versus (10^3/T), where ionic conduction mechanism can be expected to occur if data shows linear dependence [22]. Moreover, the (I –V) characteristics obey the general ionic equation (hyperbolic sine relation ship) as shown in fig (6) and the experimental data are well fit to the ionic conduction mechanism. The relationship between (σ, $10^3/T^{1/4}$) as shown in fig (7) is not confirm the hopping mechanism process(see ref 13 and 15).

The experimental data are not fit to the variable range hopping equation (see ref 13 and 15).

$$\sigma = \sigma(T) \exp\left(\frac{T_3}{T}\right)^{1/(d+1)} \quad \text{..........} \quad \text{...(3)}$$

Where d indicates the dimensionality (d=3) and

$$T_3 \quad \alpha \quad \left[a^d N\left(E_f\right)\right]^{-1} \text{..........} \quad .(4)$$

Where N (E_f) is the density of state and (a) denotes the localization length.

Fig (8): shows the plot of I versus $E^{1/2}$ for film at several temperatures. The non linear relationship at high field gives a clear evidence that neither Schottky nor Poole –Frenkel effect mechanism could be speculated to explain the results. The Schottky expression is given by [23].

$$I = I_o \exp\left[\alpha_{sch} E^{1/2} - \frac{e\Phi}{KT}\right] \text{.............}(5)$$

The theoretical values of α_{sch} and α_{PF} are calculated from the following relations:

$$\alpha_{sch} = \frac{1}{K_B T} \sqrt{\frac{q^3}{4\pi \in_o \in}} \text{..........} \quad .(6)$$

$$\alpha_{PF} = 2\alpha_{sch} \quad \text{……………..}(7)$$

Where E is the applied field,

Φ**:** the work function of the polymer metal interface,

e :The charge on an electron,

$\in_0$: The permittivity of free space

$\in$: The high frequency relative dielectric constant

The experimental values of α can be obtained from the slope of fig (8) measured in the high field region. The theoretical values of α_{sch} and α_{PF} can be calculated from equations (6) and (7) and the values are listed in Table I.

Table I: shows the experimental and theoretical values of Schottky and Pool–Frenkel.

T (K)	ε	α_{exp}	α_{sch}	α_{PF}
308	27	2.399×10^{-3}	2.749×10^{-3}	5.498×10^{-3}
323	29.7	8.98×10^{-3}	2.499×10^{-3}	4.998×10^{-3}
333	32.4	2.958×10^{-3}	2.321×10^{-3}	4.642×10^{-3}
353	37.8	8.519×10^{-3}	2.027×10^{-3}	4.054×10^{-3}
373	43.2	3.241×10^{-3}	1.794×10^{-3}	3.588×10^{-3}

From the Table (I) one can conclude that the Schottky and Pool – Frenkel mechanism are excluded from this study.

Moreover, the relation between (10/V) and (I/V^2) as shown in Fig (9) not gives minimal local end therefore we excluded this mechanism from this study (see ref 7).

Conclusion

The d.c electrical conductivity measurements of poly alpha naphthyle acrylate (PNA) doped with Ioden (I_2) to be 5.57×10^{-12} ($S.cm^{-1}$) at room temperature . Ionic conduction mechanism effect was shown to be dominant process. Temperature dependent conductivity with a activation energy at temperature (308 – 373) K about (0.6 eV) and positive thermal coefficient was observed in all temperature ranges. The polymer became nearly a semiconductor after it dopes by Ioden (I_2).

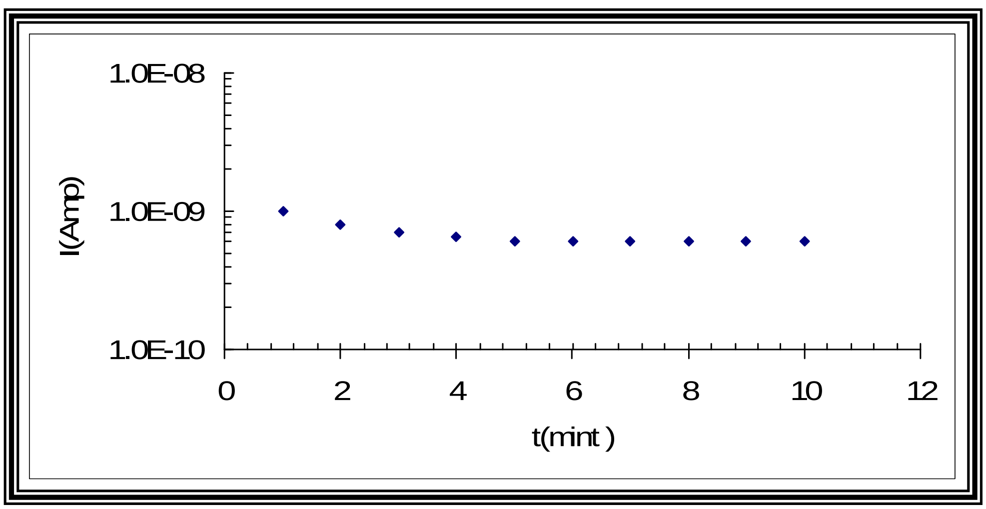

Fig (2): The time dependence of current at 308K and 10 V.

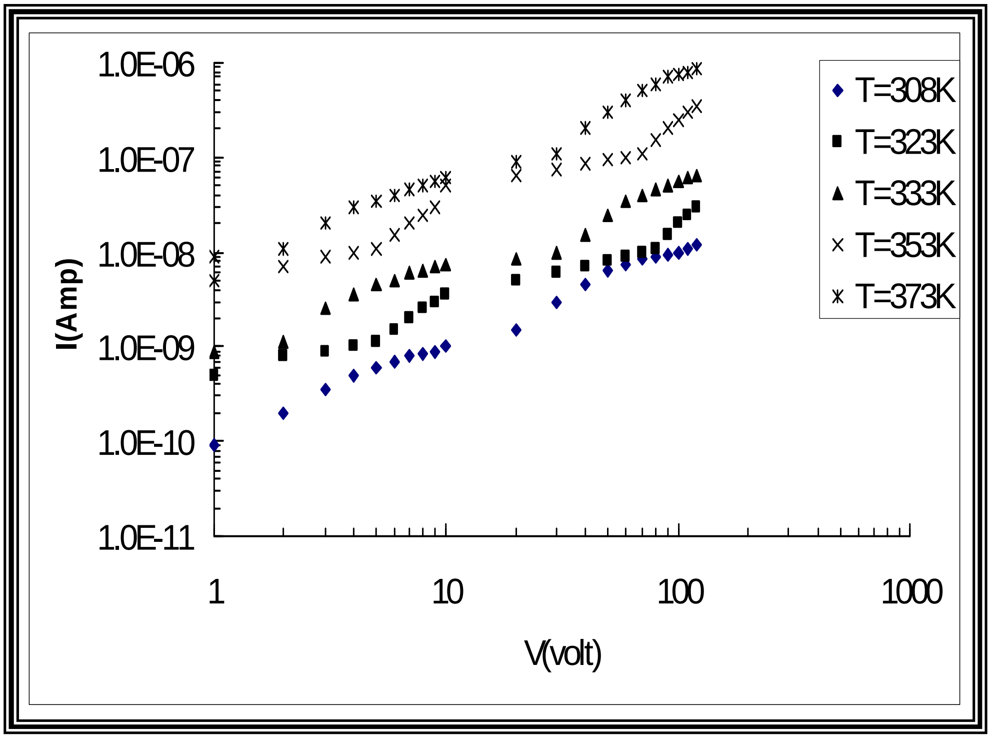

Fig (3): The relationship between current and voltage at different temperatures.

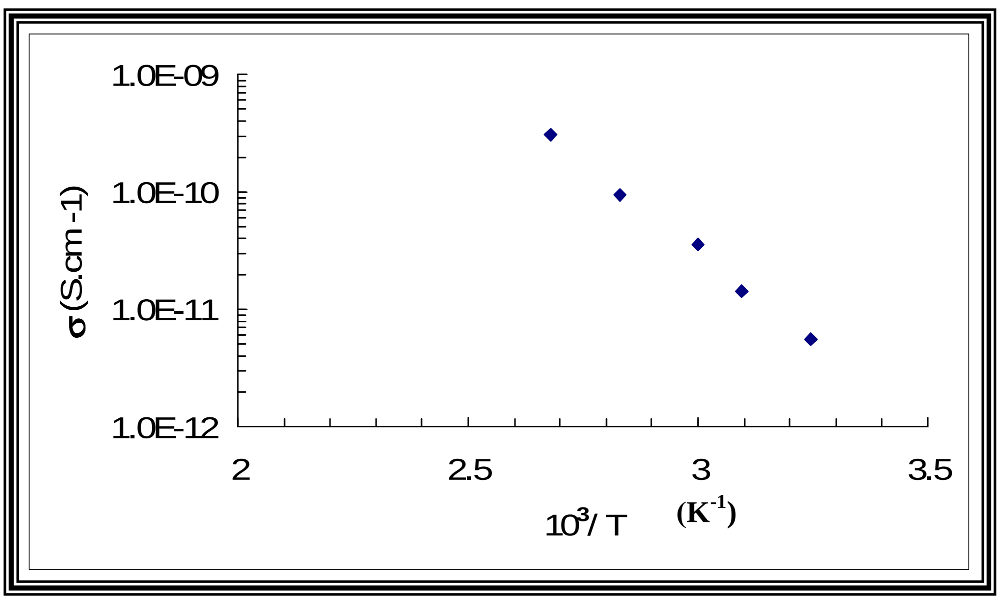

Fig (4): The relationship between conductivity and (10^3/T)

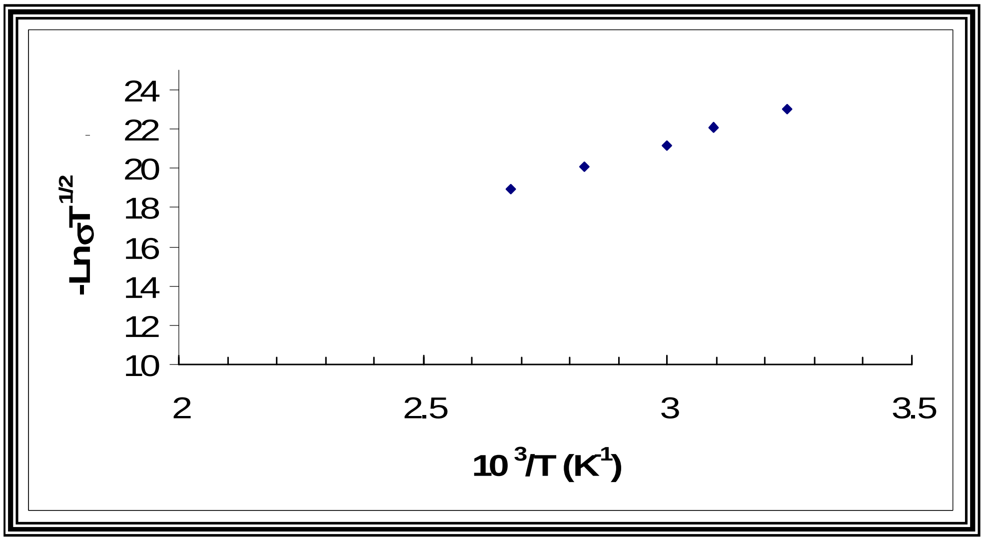

Fig (5): The relationship between –Ln (σT) Vs (10^3/T) for ionic conduction test.

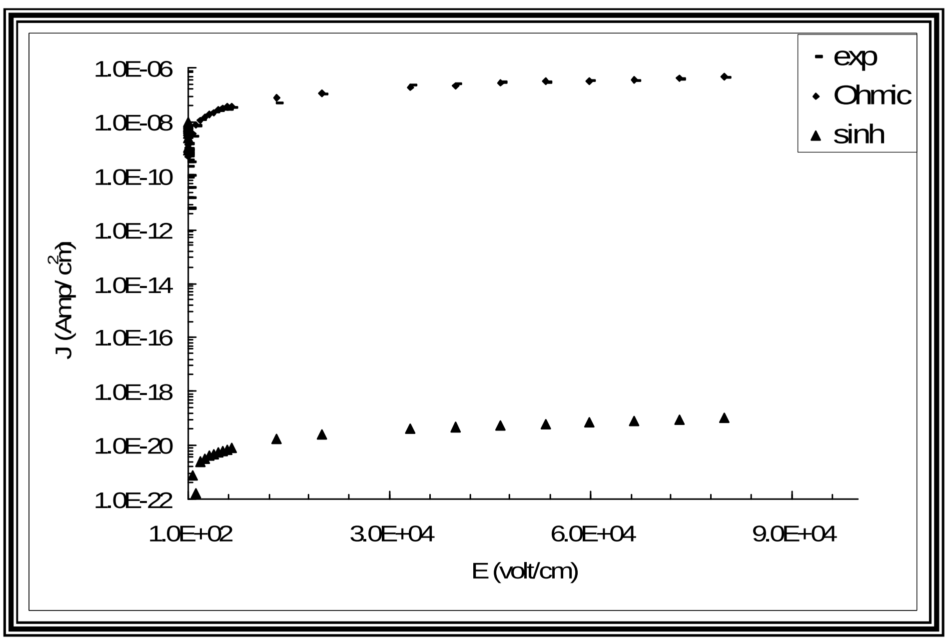

Fig (6): Current density as a function of electric field

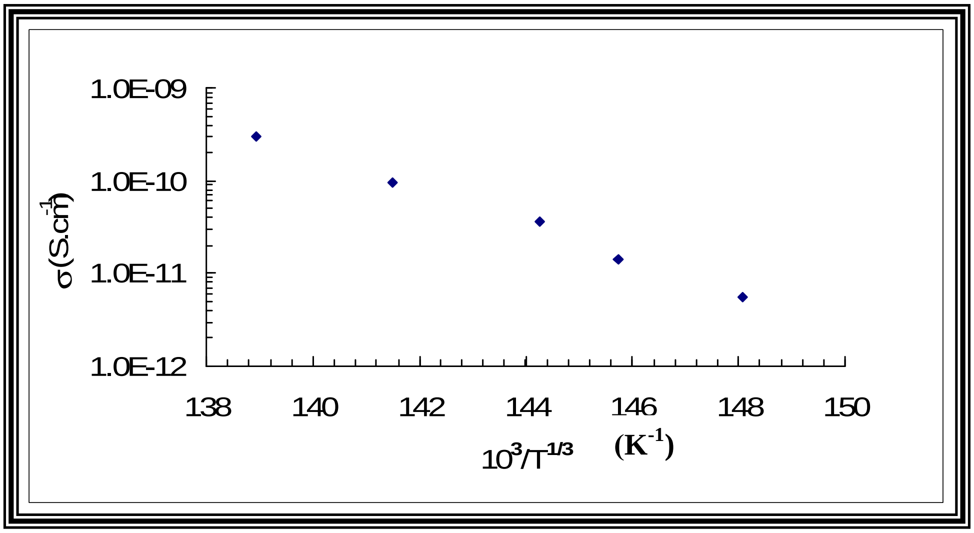

Fig (7): The relationship between conductivity and ($10^3/T^{1/3}$)

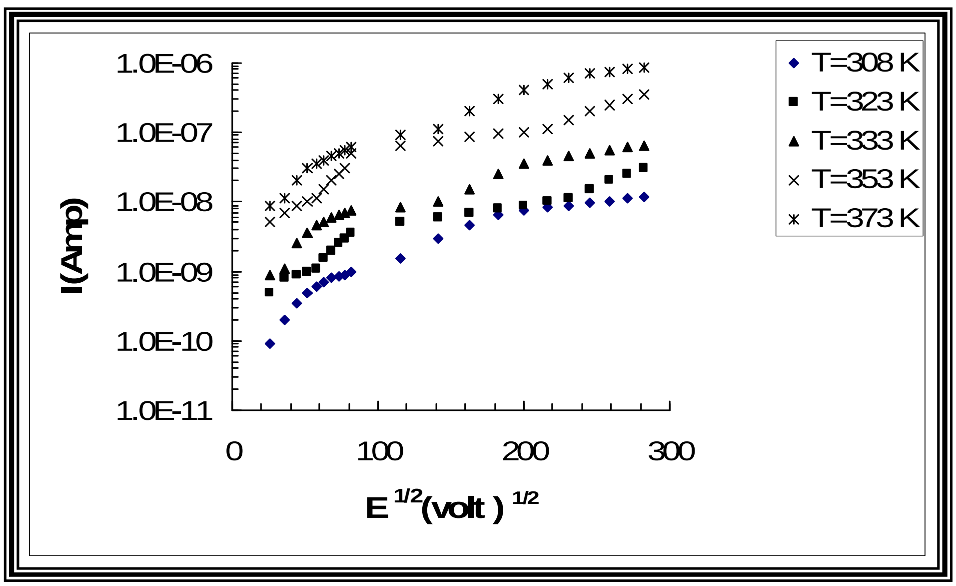

Fig (8): The relationship between current and $E^{1/2}$ at different temperatures.

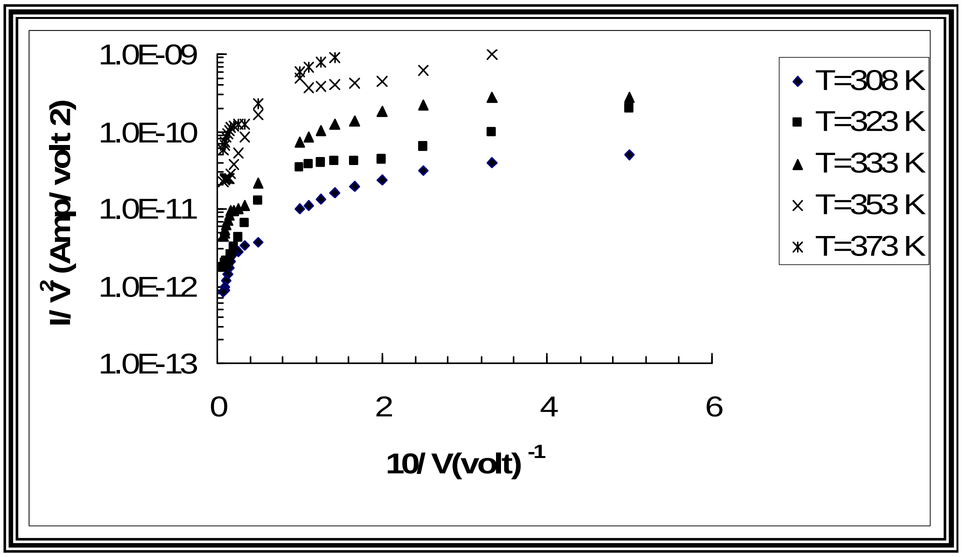

Fig (9): The relationship between (10/V) and (I/V^2)for the polymer doped with Ioden (I_2).

References

1. T. Q. Nguyen, J. wa, and R. Kuzel, Science 288(2000) p 652-656.
2. D. Schlettwein, H.Tada and S. Mashiko, Langmuir,16 (2000)2872.
3. G. Harasanyi, Sensor Review, 20 (2000) p 98-105.
4. C.D. Dimitrakopoulos and D. J. Mascaro, IBM. J. RES and DEV,45(20001)P11.
5. S. Kuniyoshi, M.Lizuka ,K. Kudo and M.Harper IEICE Trans.Electron E83-C,7(2000)P1111.
6. W. A. S. Abdul Ghafor, H. F. Hussien and H. Abdul Gallel. J. Basrah Researches Vol. 28 pant 4 (2002) pp 114 – 121.
7. H. K. Ibrahim "Study of the electrical mechanism and the dielectrical properties of the doped films of the poly (P – Aminobenzal-dehyde terminated by phenylene diamine" MSC. thesis Phys. College of education. Basrah University (2006).
8. W. A. S. Abdul Ghafor, W. A. Hussien, A. M. Haddad and G. A. Adam. Basrah J. Science , C, vol. 18 No.2 (2000) PP 131 – 144.
9. D. A. Seanor,"Electrical properties of polymers" Academic Press N. Y. (1982)
10. F. E. Karasz "Dielectric properties of polymer" Plenum press, N.Y.(1972)P.15.
11. W. A. S. Abdul Ghafor. Iraqi Polymer J. Vol. 1 No. 1 (1996).
12. N. Maso, H. Beltran, E. cordoncillo and P. Escribano. Journal of Materials chemistry Vol.5 No2. (2006).
13. H. F. Hussien. J. Basrah Researches Vol. 28 part 3 (2002) pp 126 – 135.
14. K. Ohno, K. Murayama and A. Matsuda JPn J. Appl. Physics. Vol. 44 part 1 (2005) pp 4764 – 4769.
15. H. K. Ibrahim J. Basrah Researches Vol. 33 No.2(2007) pp 66 – 75.
16. S. A. Ali "Study of the effect of some dopants on electrical conduction mechanism of poly alpha naphthyle acrylate" MSC. thesis

phys.college of education. Basrah University (2005).

17. S. Hirota and U. Itoch, Thin Solid Films, Vol. 165, (1988) P. 337.
18. S. Rajendran, O. Mahendran and T. Mahalingam. Europeam polymer Journal vol. 38 (2002) pp 49 – 55.
19. C. Y. chiu, H. W. chen, S. W. Kou, C. F. Huang and F. C. chang. J. American chem. Society (2004).
20. B. Mohamadou, F. Brehat, B. Wynck and P. Simon. J. of physics No. 3 (2006) pp 9489 – 9501.
21. H. K. Ibrahim and K. I. Ajeel. J. Basrah Researches Vol. 33 No.1(2007) pp 1 –11.
22. C. K. Chaing, G. T. Davis and C. A. Harding J. Solid state Ionics Vol. 18 (1986) P. 300.
23. W. A. S. Abdul Ghafor, Iraqi J. of polymer Vol. 38 (2000) pp 2507 – 2517.

الخلاصة

تم في هذا البحث دراسة الخواص الكهربائية للبوليمر بولي الفا نفثايل اكريليت (PNA) المشوب بمحلول اليود (I_2) المحضر بطريقة الصب. تم قياس ميزة التيار –الفولتية) وكذلك (التوصيلية – درجة الحرارة) في مدى من الفولتيات ودرجات الحرارة V(120 –1) و K(373 – 308) على التوالي.

أظهرت الدراسة أن مقاومة الاغشية المشوبة تمتلك معامل حراري سالب وأن طاقة التنشيط المحسوبة من خلال تحليل ميزة (التيار – الفولتية) عند المنطقة الاومية كانت قيمتهاeV(0.6).في حين كانت قيمتها للغير مشوب(0.95 eV). تم حساب التوصيلية الكهربائية الحجمية عند مدى درجات الحرارة وكانت

قيمتها في درجة الحرارة الغرفه $5.57\times10^{-12}(S.cm^{-1})$ وهذا يعني ان التوصيلية ازدادت بمقدار خمسين مرة تقريباعند التشويب باليود ,بالاضافة الى ذلك فقد كان تأثير درجة الحرارة واضحا في زيادة التوصيلية الكهربائية حيث ازدات التوصيلية بمقدار مئة مرة تقريبا عند مدى درجات الحرارة المحصورة بين K(373 – 308).

تم تحليل الانحراف عن السلوك الاومي من خلال نظريات التوصيل الكهربائي في البوليمرات الصلبة وقد وجد بأن آلية التوصيل من النوع الايوني هي الاكثرمطابقة في وصف النتائج العملية.