Conduction mechanism of poly (P-Aminobenzaldehyde) terminated by phenylene diamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$

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Abstract

The electrical properties of poly (P-Aminobenzaldehyde) terminated by pheneylene diamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$ films prepared by cast method have been investigated.

The (Current – Voltage) and (Conductivity – temperature) relationships are measured in the voltage and temperature ranges (5-120) V and (288 -348) K respectively.

The resistance of the doped films is found to have a negative thermal coefficient. The activation energy at temperature (288 -348)K about (0.175)eV is found from the ohmic region of the dark (current – voltage) characteristic. The conductivity at room temperature was equal to 2.5×10^{-14} ($S.cm^{-1}$).

The deviation from ohm's law has been analysed in term of the available conduction theories. Hopping conduction mechanism was concluded to be the most probable as interpreting the behavior of charge transport that supplied by injector electrodes.

Key words: Electrical properties, D.C. conductivity, Hopping conduction mechanism

Introduction

Polymeric materials are well known as insulating materials (as an inherent property) and are used widely for many industrial applications [(1)]. Even conductivity polymers in their intrinsic nature are insulators and can be transferred to conductors by suitable doping with strong acceptor or donor agents [(2)].

A great efforts are consumed to control the electrical conductive properties of polymers in an analogous manner to semiconductors taking into account the possibility of combining the desirable physical properties with electronic functions[(3)]. The mechanism of the electrical conduction in polymers is not fully understood and usually characterised as a complex process depending not only charge transfer in the bulk, but also across the polymer – metal interface at the electrode [(4)].

Ionic conduction mechanism was found in LPC series – $LiCF_3CO_3$ complex[(5)], Plasticized poly(methylmethacrylate)/poly(vinylidene fluoride) [PMMA/PVdF] blend polymer electrolytes[(6)], $LiCLO_4$/PEO/PCL Ternary Blends[(7)] and single crystals of $KTiOPO_4$[(8)].

Space charge limited current mechanism (SCLC) is observed in several organic polymers such as polyethylene[(9)] and poly alpha naphthyle acrylate (PNA) doped with Lithium chloride (LiCl)[(10)].

Tunneling conduction mechanism is the dominant one in the very thin films such that thickness ~ 35Å [(11)]. The conduction mechanism type Schottky is found in poly(pyromellitic-1,2 Naphthylene diimide) [PPND][(12)], Fe – doped $BaTiO_3$[(13)] and PPAB terminated by phenylene diamine[(14)]. The conduction mechanism type hopping was observed in (4-Bromo Isatin – $4B_1$) films[(15)], (PPAB – DDS) films[(4)], poly (phthalocyanine) (PC)[(16)], Benzidine terminated poly (P-Aminobenzaldoxime) thin films[(17)] and Amorphous Heavy – Hydrogenated silicon.[(18)]

In the present study the electrical properties of poly (P-Aminoben zaldehyde) terminated by phenylene diamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$ have been investigated based on measuring (current – voltage) and (conductivity – temperature) characteristics. The conduction mechanism in the polymer film has been identified.

Experimental Procedure

Poly (P-Aminobenzaldehyde) terminated by phenylene diamine is synthesized used condensation polymerization adopting to method previously reported. [19]

Figure (1) shows the expected structure of the polymer under the present study (see ref.19).

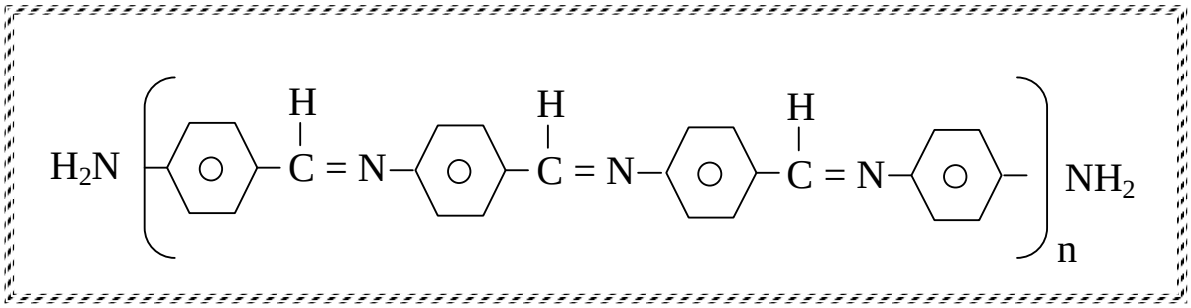

Figure (1) Expected structure of the polymer.

The resulted resin then is doped with $Na_2[Fe(CN_5).NO].2H_2O$. Polymer films with thickness ~ (25µm) were deposited on aluminum substrate using solution cast technique. The thickness is measured by micrometer that range (1-100) µm.

The polymer is first dissolved in Dimethyl Formamide (DMF) with stirred at room temperature for (4 – 6) h. 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 5 C° /hr up to 80C° .

Circular aluminum electrodes with 0.1 cm radius are deposited by evaporation method under vacuum 10^{-4} Torr on the polymer surface using [LABORGERATH UND UAKUIJMTECHNIXD.6980 WERTHEIM/MAIN,HP 150B PUDOLF R.B AND GMBH + CO]

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. the measuring system has a two platinum probes supported on free moving arms cited beside a hot plate. Thermocouple of type cupper constantan is fixed on the top of the sample to measure the temperature, where the temperature was varied by external circuit through temperature controller.

The whole system is cited in vacuum desicater to satisfy that all measurement were carried out under vacuum.

Results and Discussion

The electrical properties of the polymer films have been investigated with measuring the steady state current in order to obtain the reproducible results. Steady state measurements are necessary to apply due to the existence of absorption currents. The absorption current are generally observed in bulk insulating materials [20].

The absorption current decays with time (t) approximately according to the relation. [21]

$$\mathbf{I = Kt^{-n}} \qquad \text{.....1}$$

Where K, n are constants.

Fig (2): Shows the relation between current passes across the sample and time measurement after applied voltage 60 (Volt) and temperature 308K. The steady current was recorded after 4min from applying the voltage and adopted for all measurements.

The (I – V) characteristics of the film with thickness ~ (25µm) was measured in the voltage (5- 120)V and temperature (288 – 348) K as shown in Fig (3).It can be observed , that the current increases with increasing of temperatures and voltages at range (5- 50)V and then saturated at range (50- 120)V in the temperatures 288 K and 298 K .

At low field region (5 -25) V the current shows ohmic behavior which indicates the thermal generated charge carrier which effected by the current limits [22].At voltage greater than 25V the current rise as voltage increasing and the deviation from ohm's law can be discussed by different conduction mechanisms that are possible to take place in solid polymers.

The bulk conductivity of polymer film in the ohmic region was found to be $2.5\times10^{-14}(S.cm^{-1})$ at temperature 288K. The conductivity versus the reciprocal of the temperature ($10^3/T$) is shown in Fig (4). A semi conducting behavior is observed satisfying the negative resistance coefficient of the conductivity; this behavior was also noticed in previous polymers for electronic applications. [23, 24]

The activation energy at temperature (288 – 348) K (the ohmic region) was calculated from slope of the straight line in fig (4) and using Arhenus equation [25]

$\left(\sigma = \sigma_o \; e^{-Ea/KT}\right)$ and found about to be (0.175eV). The non ohmic behavior indicates that the injected electrode carriers are greater than thermally generated charges, therefore, different conduction mechanisms could be occurred to explain the charge transfer. The most probable conduction mechanism in this study was estimated on the basis of voltage and temperature dependence of steady state current.

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 (σT) versus ($10^3/T$), where ionic conduction mechanism can be expected to occur if data shows non linear dependence, on the other hand the plote of -Ln ($\sigma T^{1/2}$) versus ($10^3/T$) as shown in fig (6), where ionic conduction mechanism can be expected to occur if data show linear dependence[26].

Moreover, the (I –V) characteristics do not obey the general ionic equation (hyperbolic sine relation ship) as shown in fig (7), therefore the ionic conduction mechanism is excluded from this study. The relationship between σ and $10^3/T^{⅓}$ as shown in fig (8) confirm the hopping mechanism process. [27]

The experimental data are well fit to the variable range hopping equation .

$$\sigma = \sigma(T) \exp\left(\frac{T_3}{T}\right)^{1/(d+1)} \quad \text{..... ...(2)}$$

Where d indicates the dimensionality (d=3) and

$$T_3 \quad \alpha \quad \left[a^d N\left(E_f\right)\right]^{-1} \text{.....} \quad .(3)$$

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

Fig (9): shows the relationship between current density (J) and films thickness (d), a linear relationship is obtained with slope less than 3. That indicates the space charge limited current (SCLC) mechanism is fails as reliable one to interpret the characteristics.

Fig (10): shows the plot of I versus $E^{½}$ 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[22].

$$I = I_o \exp\left[\alpha_{sch} E^{1/2} - \frac{e\Phi}{KT}\right] \text{.....(4)}$$

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

$$\alpha_{sch} = \frac{1}{K_B T} \sqrt{\frac{q^3}{4\pi \in_o \in}} \text{.....(5)}$$

$\alpha_{PF} = 2\alpha_{sch}$ **……..(6)**

Where E is the applied field,
Φ the work function of the polymer metal interface,
q carrier's charge,

$\in_o$ **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 (10) measured in the high field region. The theoretical values of α_{sch} and α_{PF} can be calculated from equations (5) and (6). 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}
288	18.75	7.75×10^{-4}	3.53×10^{-3}	7.05×10^{-3}
308	22.32	1.5×10^{-3}	3×10^{-3}	6×10^{-3}
318	24.1	2.51×10^{-3}	2.8×10^{-3}	5.6×10^{-3}
328	26.78	1.58×10^{-3}	2.59×10^{-3}	5.1×10^{-3}
338	32.14	1.34×10^{-3}	2.29×10^{-3}	4.58×10^{-3}
348	38	9.11×10^{-4}	2.1×10^{-3}	4×10^{-3}

From the table one can conclude that the Schottky and Pool – Frenkel mechanism are excluded from this study.

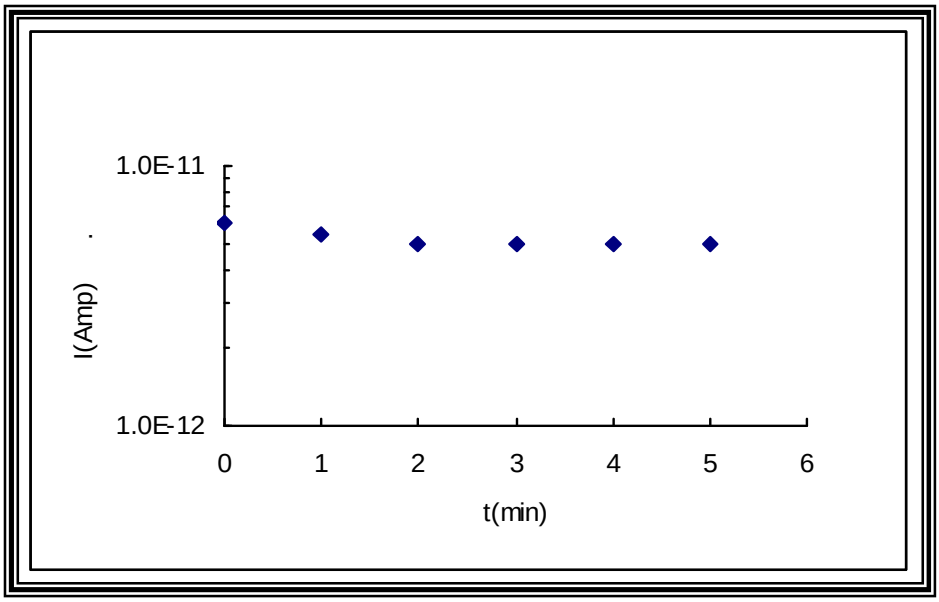

Fig (2): The time dependence of current at 288K and 60 V.

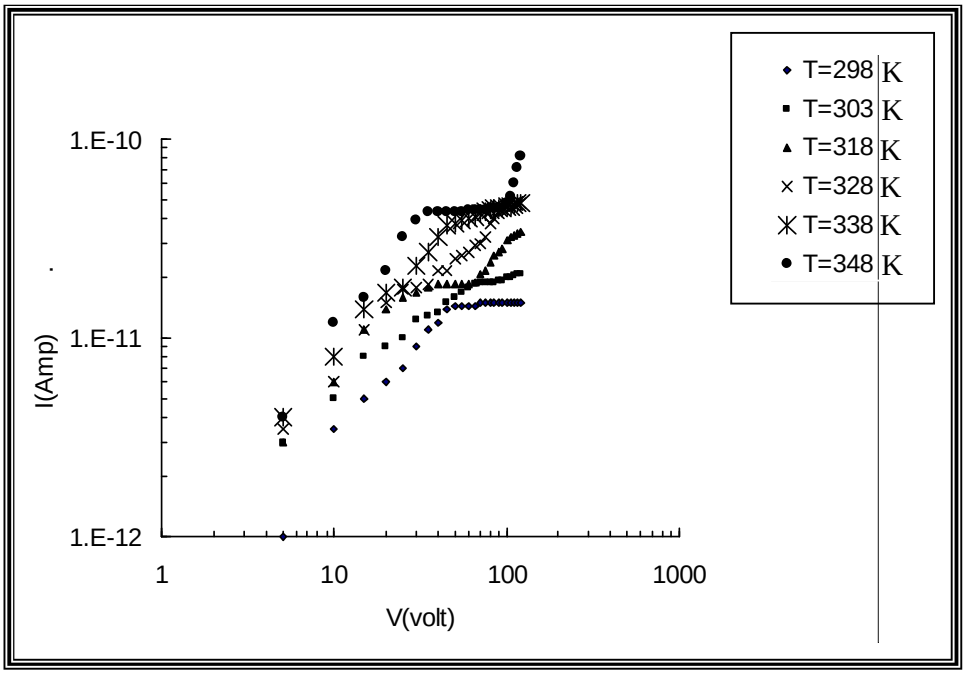

Fig (3): The relationship between current and voltage at different temperatures.

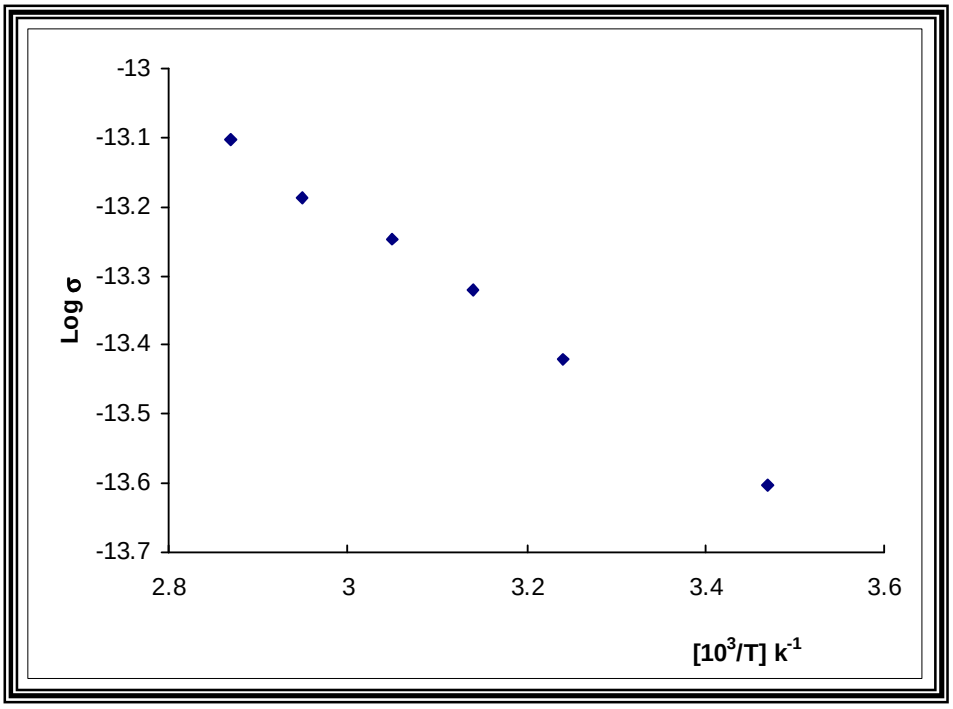

Fig (4): The relationship between conductivity and (10^3/T)

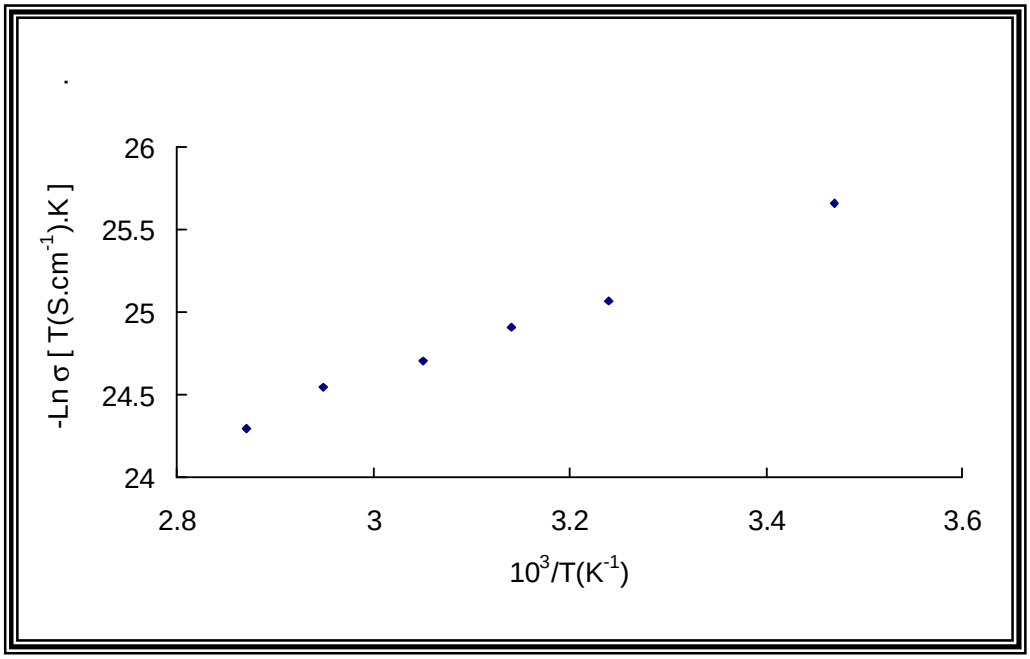

Fig (5): The relationship between –Ln (σT) Vs (10^3/T) for ionic conduction test.

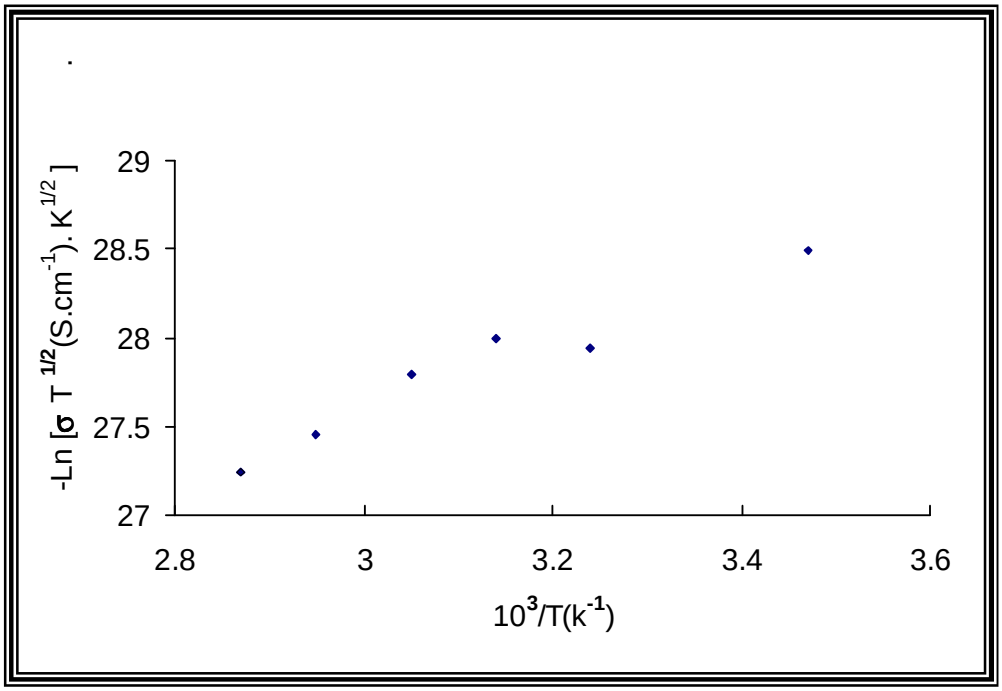

Fig (6): The relationship between –Ln ($\sigma T^{1/2}$) Vs (10^3/T) for ionic conduction test.

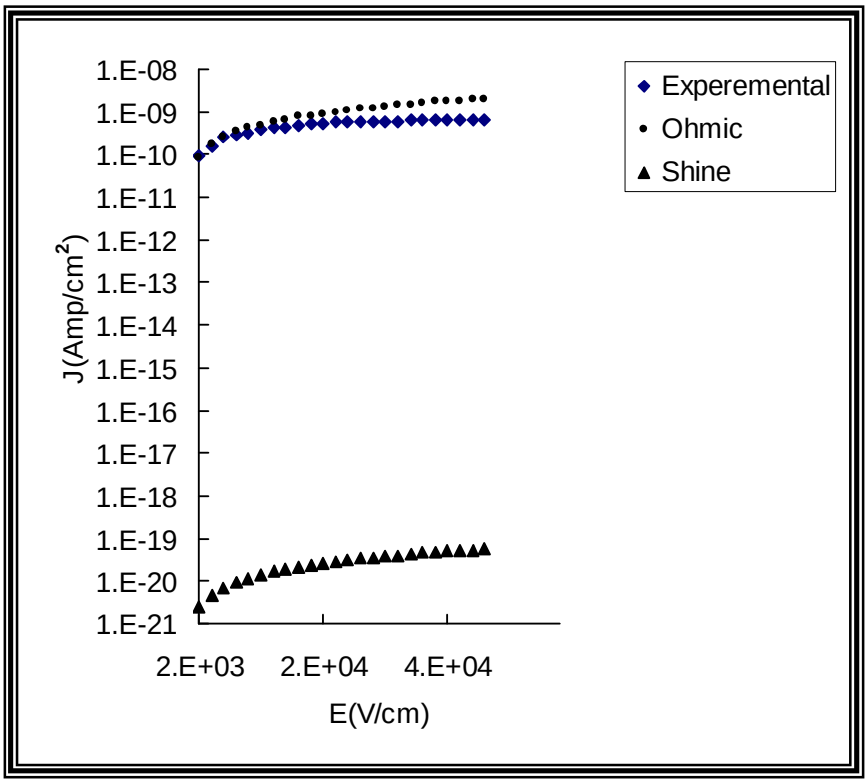

Fig (7): Current density as a function of electric field

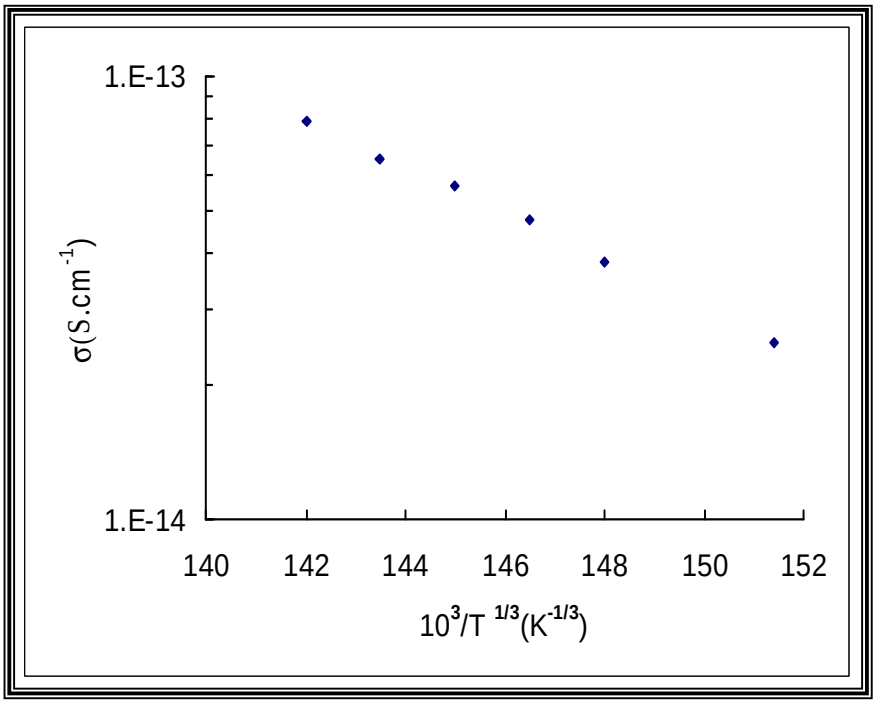

Fig (8): The relationship between conductivity and ($10^3/T^{1/3}$)

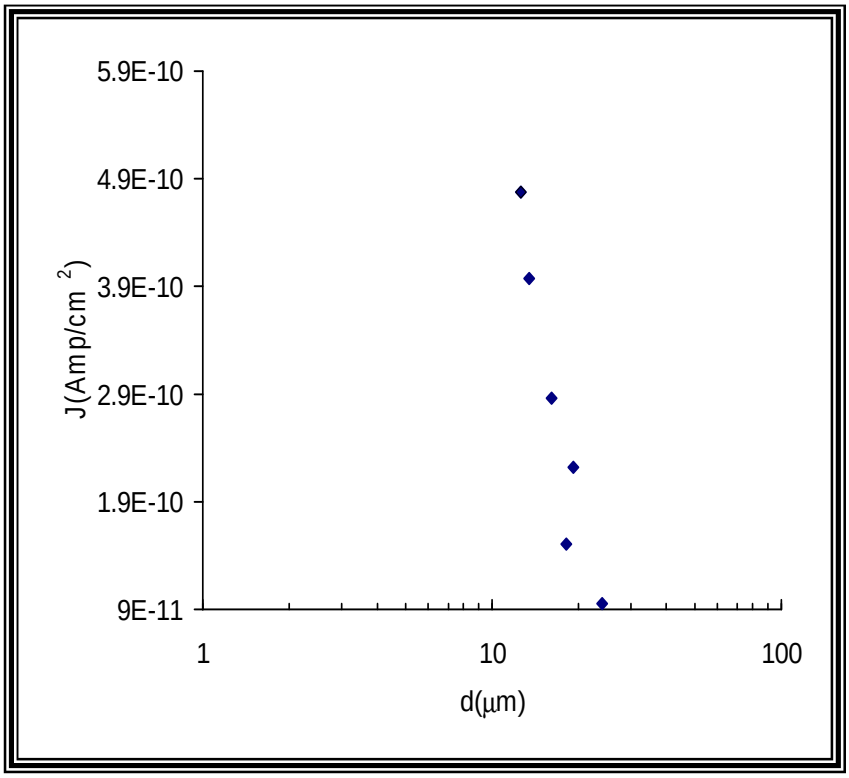

Fig (9): The relationship between current density (J) and thickness (d)

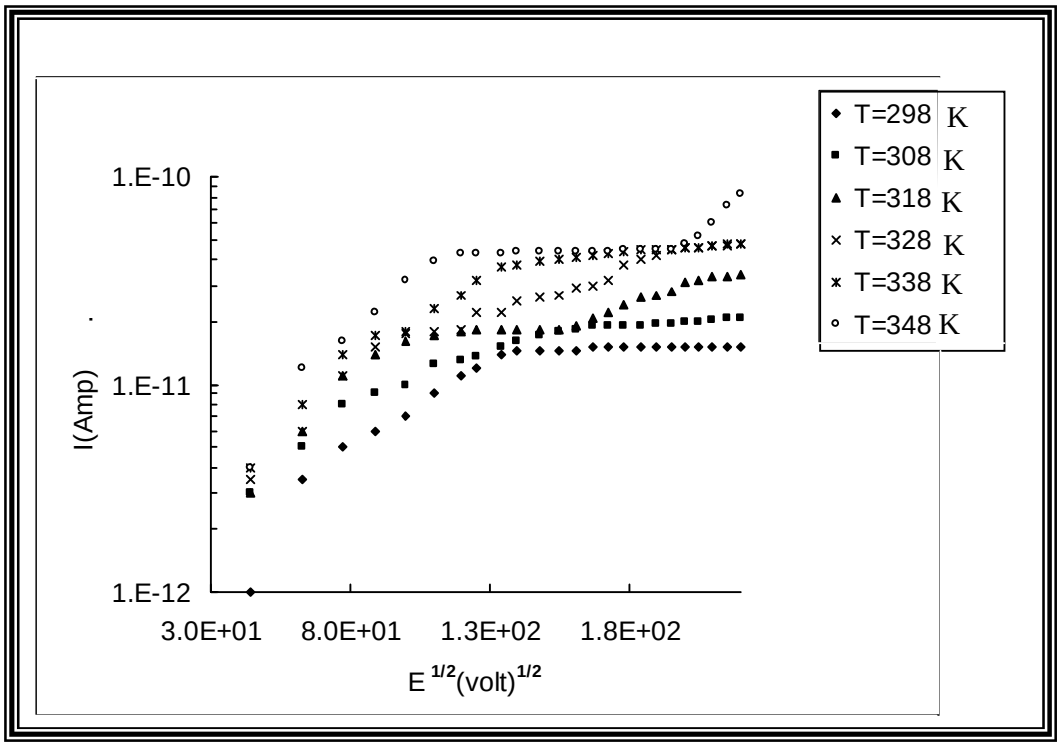

Fig (10): The relationship between current and $E^{1/2}$ for doped polymer film with thickness (25μm) at different temperatures

Conclusion

The d.c electrical conductivity measurements of poly (P-Aminobenzaldehyde) terminated by phenylene diamine doped with $Na_2[Fe(CN)_5.NO].2H_2O$ to be 2.5×10^{-14} $(S.cm^{-1})$ at room temperature . Hopping conduction mechanism effect was shown to be dominant process. Temperature dependent conductivity with a activation energy at temperature (288 – 348) K about (0.175 eV) and positive thermal coefficient was observed in all temperature ranges.The polymer became nearly a semiconductor after it dopes by $Na_2[Fe(CN)_5.NO].2H_2O$.

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الخلاصة

تم في هذا البحث دراسة الخواص الكهربائية للبوليمر بولي (بارا – أمينو بنزلديهايد) ذي النهاية الطرفية ثنائي أمين فنيلين المشوب بمادة خماسي سيانات نتروسيل الحديدوز ثنائي الصوديوم ثنائي جزيئة الماء $Na[Fe(CN)_5].2H_2O$ والمحضر بطريقة الصب.

تم قياس ميزة التيار –الفولتية) وكذلك (التوصيلية – درجة الحرارة) في مدى من الفولتيات ودرجات الحرارة (5 – 120)V و (288 – 348)K على التوالي.

أظهرت النتائج العملية أن مقاومة الاغشية المشوبة تمتلك معامل حراري سالب وأن طاقة التنشيط المحسوبة من خلال تحليل ميزة (التيار – الفولتية) عند المنطقة الاومية كانت قيمتها(0.175)eV. تم حساب التوصيلية الكهربائية الحجمية في درجة حرارة الغرفة وكانت قيمتها $2.5\times10^{-14}(S.cm^{-1})$.

تم تحليل الانحراف عن السلوك الاومي من خلال نظريات التوصيل الكهربائي في البوليمرات الصلبة وقد وجد بأن آلية التوصيل من نوع القفز (الهوي) هي الاكثر في وصف النتائج العملية.