Conduction Mechanism study of Polyphenylene Sulfide doped with Ferric Chloride

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Abstract:

An investigation was carried out to examine the conduction mechanism in poly-phenylene sulfide doped with Ferric Chloride [PPSFC] Films of ($674\mu m$) thickness. The electrical properties were measured for aluminum / polymer / aluminum structure over temperature range (20-70 ^{0}C) .The mechanism conduction at low field region is hoping mechanism, while at the high fields Schottky effect mechanism was observed. The activation energy was estimated to be (0.35eV).

Introduction:

Nowadays the electrical properties studies are important because of their wide range of applications in technology and industrial. An analytical technique, namely transmission electron microscopy (TME), has been widely used for studying the form and structure polymers or composite systems containing polymers [1].

Polymeric materials are well known as insulating materials suitable for many industrials application,[2,3] such as (coatings adhesion ,course, fibers, …, etc) .Conduction in polymers has been extensively studied with some conflict of interpretation. The conduction mechanism in polymers has been determined at both low and high field strength [4]. Conduction mechanism in polymer is a complex process and still not fully understood until now. Many experiments have been performed to identify the type of conduction mechanism but unfortunately experimental results and their interpretations appeared to vary among different investigators, there were found that ionic conduction mechanism is the dominated process in polyvinyl chloride (PVC) [5], while space charge limited current (SCLC) is the dominant mechanism in polyvinyl acetate (PVAC) [6]. There are two mechanisms such as tunneling and hopping effect are demented subsequently with in creasing film thickness, they are thermally assisted hopping with high thickness and tunneling with low thickness,[7]. In the present paper the electrical properties for the poly (phenylene sulfide) doped with Ferric chloride [PPSFC] disk have been studied, in the temperature rang (20-70 ^{0}C). Conduction mechanism has been identified with base of current – voltage and current – temperature measurements together with its variation with film thickness. It is well known that at low voltage hoping mechanism is a predominated one, where Schottky effect was observed at higher voltage.

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Experimental Procedure:

Poly phenylene sulfide (PPS) was prepared by the reaction of P-dichloro benzne with sodium sulfide in the polar solvent at about 250 ^{0}C. The polymer is highly crystalline with a T_m of about 2900^{0}C [8]. The sample was doped with $FeCl_3$ (3%) compressed under 10 ton to obtain disk thickness (674μm). Aluminum metal is deposited by evaporation method on upper and lower surface of the specimen. On the other hand disks thickness were determined by measuring the capacitance of film does not depend on their thickness [9]. Similar micrometer model (KAFC). Inserting the disk in a circuit consisting of DC source, electrometer, and voltmeter carried out electrical measurements. The specimen was mounted in a cell in a sandwich configuration fixed by platinum electrodes cited above with pressure contact. [10]. The specimen was enclosed in grounded aluminum screen box with temperature controller system. The sample temperature was measured with thermocouple placed near the sample Regulated voltages ranging from 1 V to 100 V were supplied by a power supply type phywe 2592. The current was measured by electrometer measuring amplifier type D53200 L.H. Co. .All experiments were performed under ambient laboratory conditions [relative humidity (50-53%)].Currents were measured after a period of time. The upper value of applied electric field is unfortunately limited by the electrical breakdown under atmospheric conditions.

Results and discussion:

The (current-voltage) characteristics were measured at different temperatures (20,40,50,70 ^{o}C). Systematic increase was observed with increasing the applied voltage for different temperature up to the breakdown voltage as shown in fig. (1). At the low field region (1-10V), The current shows ohm behavior, which indicates that thermally generated charge carriers are effected by the current limit [11]. The bulk conductivity of the polymer film in the ohmic region was equal to 4510^{-13} S.cm^{-1} at room temperature. The conductivity versus the resprocal of the temperature (1/T) is shown in figure (2). The conductivity increased two orders for temperature variation form room temperature to 70 ^{o}C with activation energy about 0.35 eV. It is clear from the figure that increasing temperature lead to increase conductivity, that mean polymer has a conductivity of a positive temperature coefficient which is identical to the characteristics of semiconductor materials, this behavior was also noticed in previous new polymers synthesized in our laboratories for electronic application [12]. The most probable conduction mechanism in this study was estimated on the basis of voltage and temperature dependence of steady state current. The relationship between ($\log\sigma$ & $10/T^{1/4}$) and ($\log\sigma$ & $10/T^{1/3}$) as show in figure (3) & (4) respectively confirms the hoping mechanism process [13]. Figure (5) shows the relationship between logarithmic current and the square root of applied field at different temperature. At high field region the curves showed a clear fit to a straight line, quit nicely and display the familiar schottky emission characteristics. These data lead us to speculate that the expected mechanism "Schottky effect or Poole –Frenkel effect "may be more distinct one interpreted experimental result regarding charge transport-Schottky emission depends strongly on the barrier between metal and polymer and should vary with the metal work function. Poole-Frenkel emission (internal Schottky effect) describes the electron transfer by a mechanism of field-enhanced thermal excitation of trapped –electrons into the conduction band of the solid [14].

The Frenkel expression is given by [15]

$$I = I_0 \exp [(\beta E^{1/2} - e\phi)/KT] \qquad \ldots\ldots\ldots\ldots(1) \qquad \text{where}$$

$$\beta = (e^3/\pi \epsilon_o \epsilon)^{1/2} \qquad \ldots\ldots\ldots\ldots(2)$$

$$\alpha_f = \beta_f/KT \qquad \ldots\ldots\ldots\ldots(3)$$

E, eϕ, $\epsilon_o\epsilon$ are the applied electrical field, the work function of metal-polymer interface and the polymer dielectric constant.

The only different between equation 1 and original schottky equation is that [16]
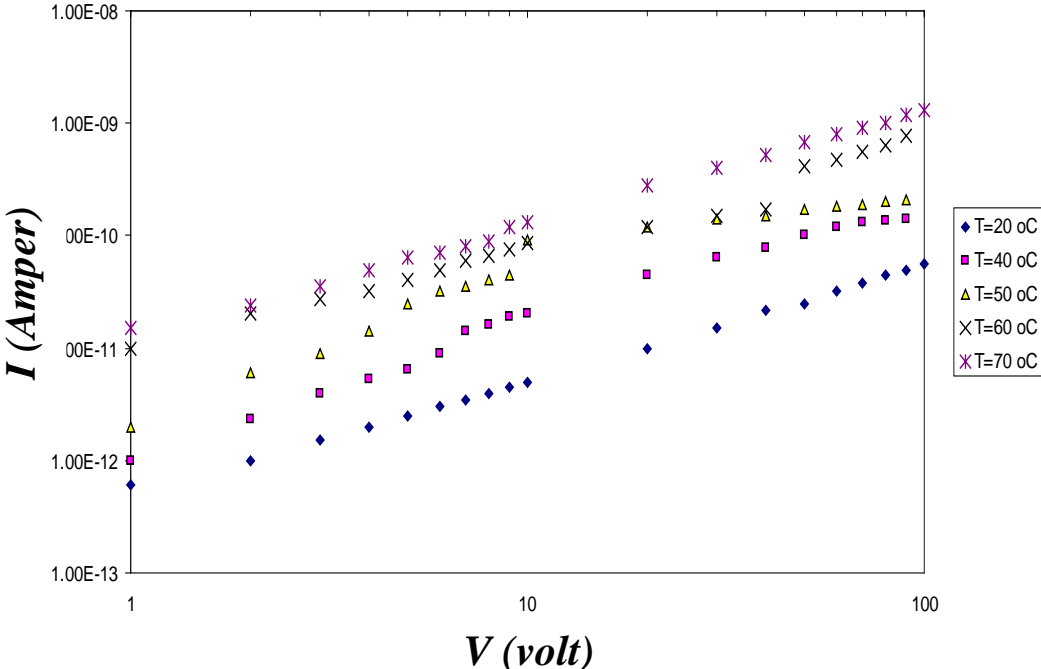
$\alpha_f = 2\alpha_s$ ……………..(4)

the theoretical values of α_f and α_s along with experimental values measured from the slop of Figure (5) are listed in the following table :

α_{exp}	α_s	α_f	
			20
0.0634	0.0630	0.126	□ 0.0590 0.0593 50 / 50
60	0.055	0.0549	0.1818
70	0.039	0.0388	0.0776

the experimental values of α for the examined films indicated that schottky effect is a dominated process mechanism, the values or electrical field was calculated via $E = \gamma v/d$ for plane parallel electrodes with ignoring the fringing effects, where any deviation from the planarity of the electrodes in the form of small protuberances changes the value of effective field that is ($\gamma=1$) . [17].

The emission work function $e\phi_o$ is calculated from equation 1 after being modified to the following formula:

$$\frac{\partial(\log I)}{\partial(1/T)} = T_0 E_0^{\frac{1}{2}} \frac{\partial(\log I)}{\partial E^{\frac{1}{2}}} + \frac{e\Phi_0}{2.3K} \qquad ....(5)$$

where T_o and E_0 are temperature and voltage at which voltage and temperature measurements were taken respectively.

The experimental value of $\partial \log I / \partial E^{1/2}$ at constant temperature and $\partial \log I / \partial (1/T)$ at constant voltage are substituted in equation (5) to get $e\phi_o=0.313$ for aluminum /PP SFC/ polymer interface.

From the relationship between $\log I_o/T^2$ versus reciprocal temperature (Richardson Plot), $e\phi_o$ about 0.396 eV was also estimated (which is nearly equal to that value calculated from eq. (5) as shown in figure (6), where I_o represent the extrapolation of current value to zero applied field.

Figure (7) shows the variation of $\Delta\phi$ versus applied electrical field, where a linear relationship has been observed. Although both poole-Frenkel and Schottky emission yield a straight lines on plots of Log I versus $E^{1/2}$ over the employed direct analysis to distinguish between them (based on comparing α's constants) was assisting by other criteria based on possible electrode effect

Other possible mechanism which explains the transfer of the charge carriers involving tunneling and ionic mechanism were also tested. Tunnneling is not applicable in our study because it requires very thin filmes and current independence of temperature. Fig.(8) shows the plot of $\ln(\sigma T^{1/2})$ versus 1/T the data does doesnot fit well to straight line relationship which indicates evidently that ionic conduction at amorphous phase can also be excluded form the expected mechanisms [18]. Moreover the I-V characteristics of the film dose not obey the general ionic equation [19]. Space charge limited current were also tested but they were excluded form our analysis.

Fig.(1): The plot of (log*I*-Iog*V*) characteristics of AL / PPSFC/ AL at different temperature (20,40,50,60 and 70 °C).
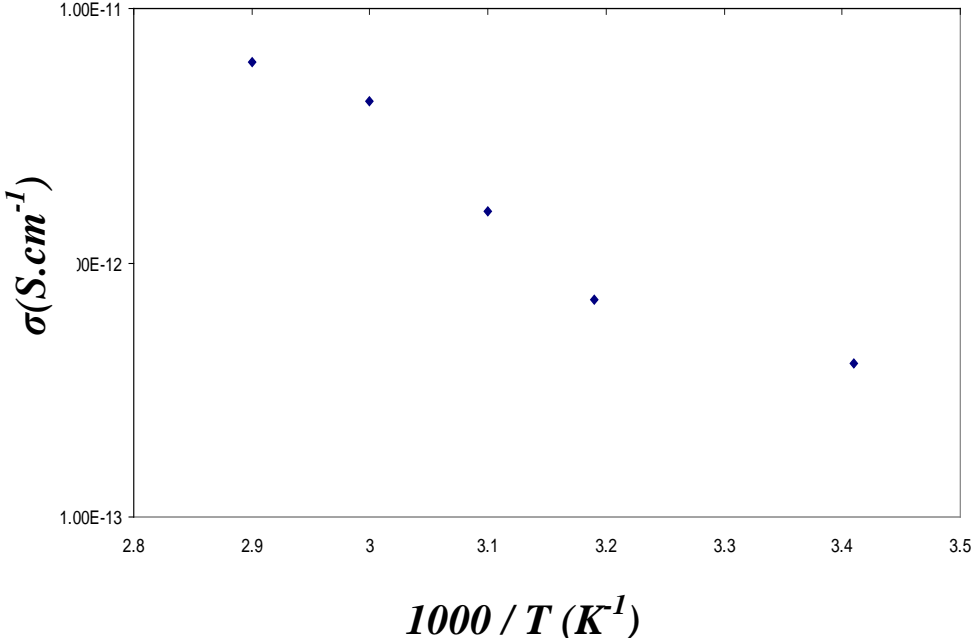

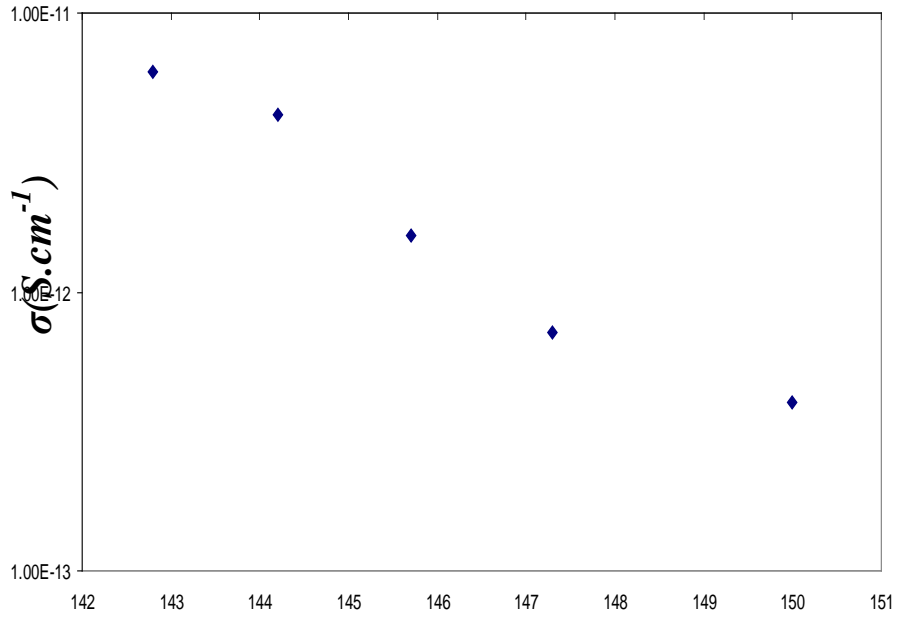**Fig.(2): The variation D.C. conductivity with reciprocal temperature.**

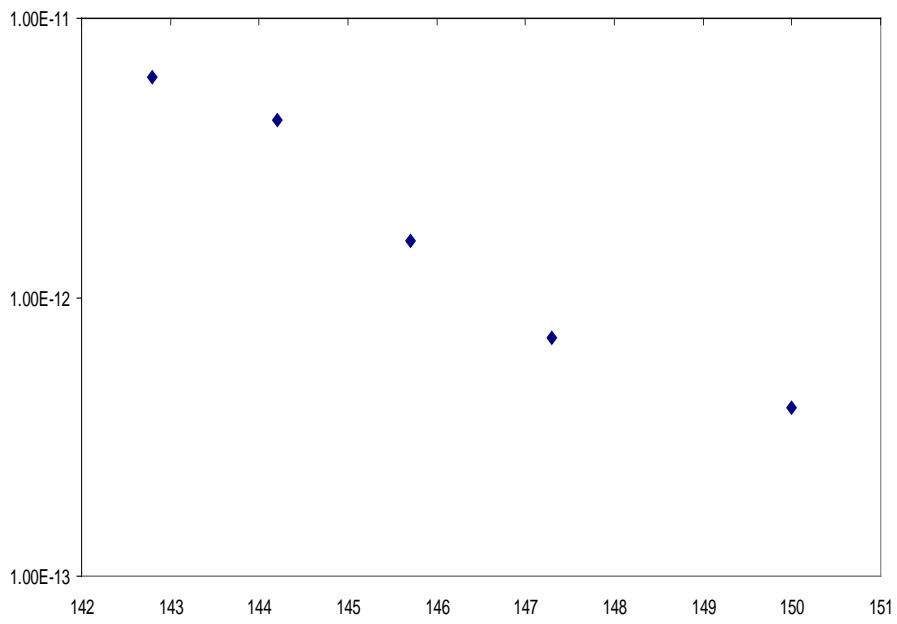**Fig.(3): The variation of D.C. conductivity with $(1000 / T^{1/3})$.**

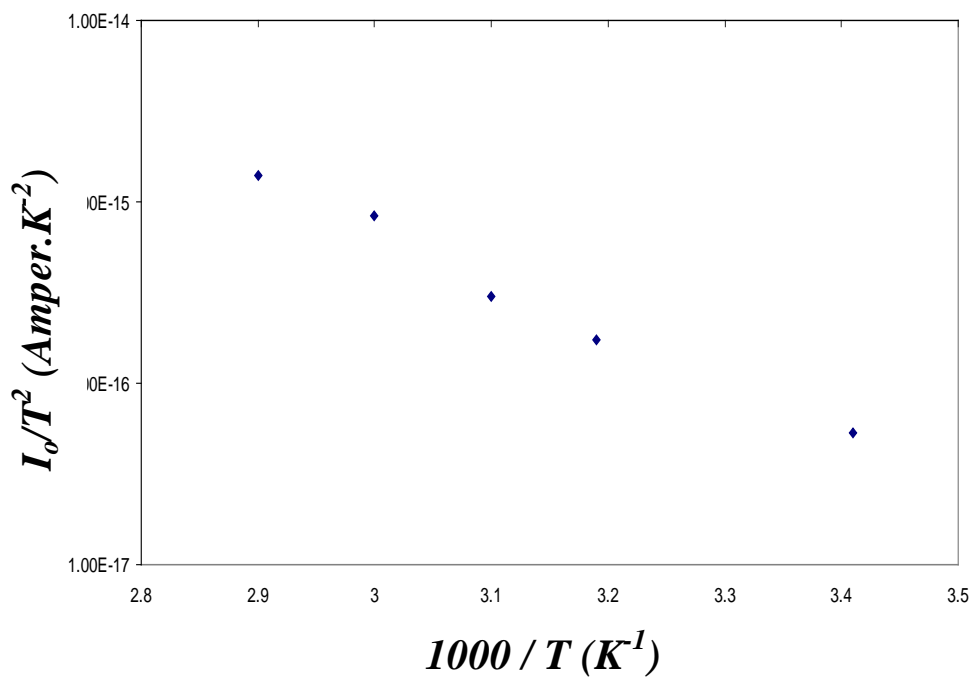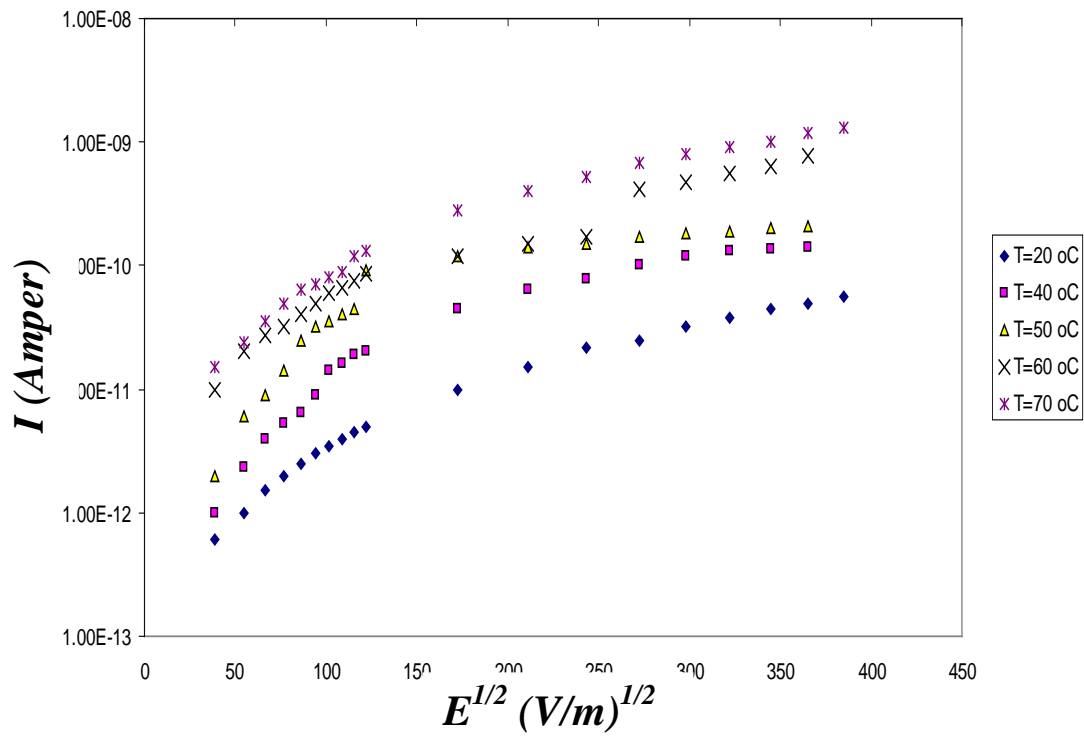**Fig.(4): The variation of D.C. conductivity with $(1000 / T^{1/4})$.**

Fig.(5): plots of (logI-E$^{1/2}$) for AL / PPSFC/ AL at several temperature (20,40,50,60 and 70 ^{o}C).

Fig.(6): The relation of I$_{o}$/T^{2} ratio with reciprocal temperature.
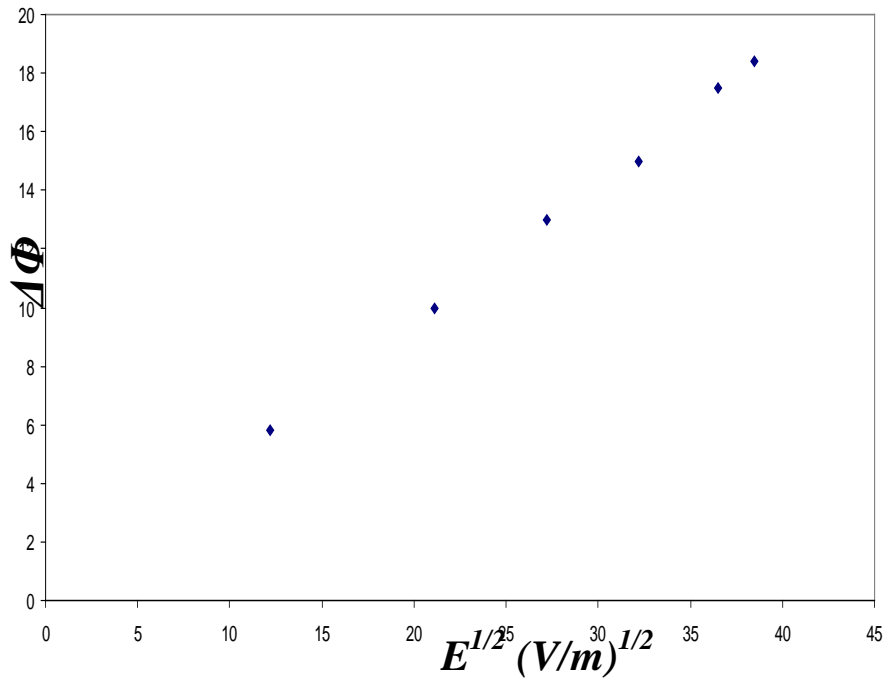
Fig.(7): The relationship between the lowering potential barrier V$_{s}$ E$^{1/2}$ for (Polyphenylne sulfied doped with Ferric chloride polymer)film measured at room temperature.
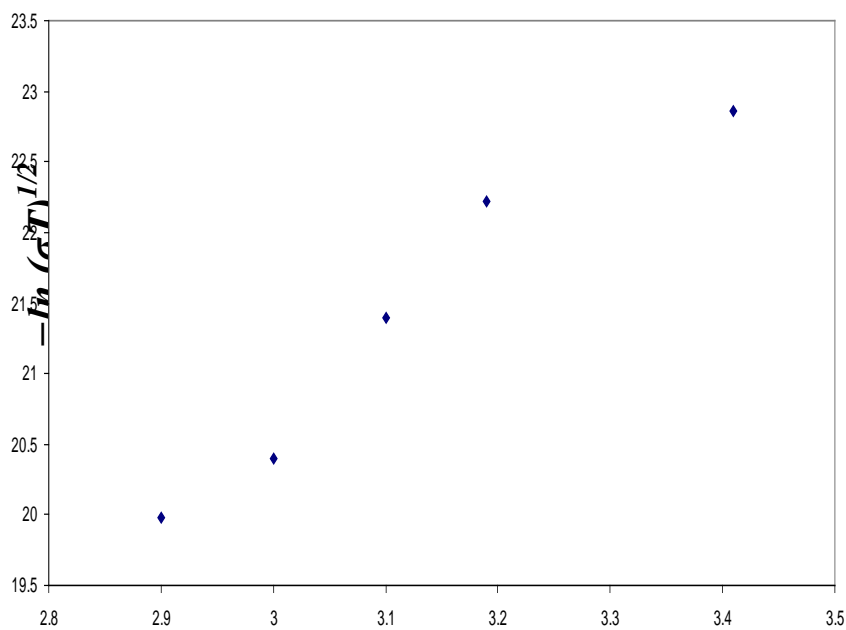

Fig.(8): The variation of   ln(σT)$^{1/2}$ with reciprocal tempretuare.

Conclusion:

The d.c electrical conductivity measurements of Polyphenylne sulfied doped with Ferric chloride polymer filme synthesized by condensation polymerization is of abut 1.4510^{-13} ($S.cm^{-1}$) at room tempreture , Hopping mechanism was shown in low field wilel schottky mechanism effect was shown to be the dominant process at the high electric field. The height of potential barrier between the polymer electrode interface was found to be 0.2529 eV with activation energy of 0.35eV, suggesting the possibility of using this polymer as insulated gate electrode in construction polymer field effect transistor.

References:

1.   A.E. Woodward, "Atlas of polymer Morphology", Munich, Vienna, New York: Hanser, 1989.
2.   H. Block, Advances in polymer science, springier verlag: New York, Vol.33, No.94, 1979.
3.   D.A. Seanor, Electrical properties of polymers, Academic Press: New York, 1982.
4.   W.A.S. Abdw Ghafor, W. Z. Manookien and G. A. Adam, "Iraqi of polymers" Vol.1, No.1, 1997.
5.   M. Kosaki, K. Sugiyama and M. Ieda, Journal of applied physics, Vol.42, No.9, 1971.
6.   J. Chutia and K. Barua, J. phys. Dept.: Appl. Phys., Vol.13, No.9, 1980.
7.   A.Q. Abdullah, W.A.S. Abdual Ghafor, S. Sh. H. Al-La'ibi, Iraqi polymers, Vol.3, No.1, 93-104, 1999.
8.   L.C.Lopez and G.L.Wilkes, J. Macromol Sci. Rev. Macromol Clem. Phys., Vol.C29, No.83, 1989.
9.   S. Hirota, U. Itoh. Thin solid films, Vol.165, No.337, 1988.
10.   W.A.S. Abdul Ghafor, H.F. Hussein & A.M. Haddad, Basrah J. science, A, Vol.19, No.1, 49-58, 2001.
11.   W.A.S. Abdul Ghafor, W.Z.Manookien & G.A.Adam, Tobe Published in J. of Education College – Mustanseria university, 1990.
12.   M. Narkis, A.Ram & Z.Stein, Polymer engineering and science, Vol.18, No.8, 1978.
13.   A.M.Saleh, N.M.Amar & R.D.Gould, The fourth international conference on physics of condensed matter, Amman-Jordan, 108, 2000.
14.   W.A.S. Abdul Ghafor, Journal of polymer science: Part B: Polymer Physics, Vol.38, 2507-2514, 2000
15.   Y.Ohmori, K.Muro & M.Onoda, JPN .J. Appl. Phys, Vol.13, No.646, 1992.
16.   J.Fraenkel, Phys Rev, Vol.45, No.647, 1938.
17.   W.A.S. Abdui Ghafor, A. Hadad, Basrah J Sci. C, Vol.15, No.129, 1997.
18.   J.M. Margolis,"conducting polymers and plastics" Chapman and Hall LTD, 1989.
19.   D.A. Seanor, "Electrical Properties of polymers", Academic press Inc, New York, 1982.

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