Electrical Transport and Magnetoresistance of Doped Polypyrrole

Tarek Fahmy, Moustafa T. Ahmed

Abstract— **Different doped samples of conducting polypyrrole (PPy) are prepared electrochemically at different current densities. The electrical transport of conducting polypyrrole is investigated in a wide range of temperature starting from 4.2 K to 300 K. It is observed that, for samples prepared at high current densities, the electrical conduction is dominated mainly by the mechanism based on variable range hopping in a wide temperature range. On the other hand, the magnetoresistance of polypyrrole is investigated in the temperature range from 1.2 K to 4.2 K and magnetic field from H=0 T to H= 10.3 T. It is observed that, PPy sample is characterized by large positive magnetoresistance. This obtained large positive magnetoresistance in the insulating regime is typically expected for VRH conduction**.

Index Terms— **Polypyrrole, Electrical conductivity, Magnetic field, Magnetoresistance.**

I. INTRODUCTION

Conducting polymers have attracted considerable attention for the last three decades. Among the conductive polymers, polyacetelyne, polyaniline, polythiophene, and polypyrrole have drawn considerable interest because of their economical importance, good environmental stability and satisfactory electrical conductivity when doped. Conducting polymers are candidate materials used in commercial applications such as in solar cells, electromagnetic shielding, electrodes for rechargeable batteries, sensors, supercapacitors, corrosion protection and nonlinear optical display devices [1-4].

Conjugated conducting polymer is a class of polymer that can distinguish significant level of electrical conductivity comparable to metals [5]. Among the conducting polymers known to date, ones based upon polypyrrole (PPy) have attracted special interest because of their high conductivity ($10^1 - 10^3$ S/cm), their ease and high flexibility in preparation, high environmental and thermal stabilities. Polypyrrole conducting polymers are easily synthesized using a broad range of electrolytes (as dopant) from aqueous and non-aqueous solvents electrochemically [6,7].

The transport properties of conducting polypyrrole, in which related to free charges become more complicated as the system becomes disordered [8-13]. Polarons is a defect as a result of doping encompasses reaction between pyrrole monomer and dopant whereas free ions come from dopant which does not take place upon polymerization of polypyrrole. The variation of temperature can provide more detail on the behavior of charges and ability to enhance the electrical conductivity [14]. The aim of the present article is to study the electrical transport properties of the conducting polymer.

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II. EXPERIMENTAL WORK

Different doped samples of polypyrrole are prepared electrochemically. Initially pyrrole monomer (Fluka) was distilled twice just before the polymerization process under reduced pressure. The doped polypyrrole films with toluene-4-sulfonate are obtained on the platinum (Pt) foil as anode, with an area of 6 cm^2 (cathode was also Pt foil) in an electrochemical cell containing different concentration of tetraethylammonium toluene-4-sulfonate, $C_{15}H_{27}NO_3S$, (Fluka) and 0.2 M pyrrole and 1% volume of distilled water in acetonitrile (Merck, Germany) as a solvent at room temperature. Different current densities are applied between Pt electrodes placed 1.5 cm apart. Before polymerization the solution was stirred for 20 minutes and then deoxygenated by purging with argon gas for further 2o minutes. After polymerization the free standing films of PPy-TOS are peeled off the electrode and washed several times in pure acetonitrile, then dried under vacuum at room temperature.

III. RESULTS AND DISCUSSION

A. Electrical Conductivity:

The electronic states of conducting polymers are strongly influenced by disorder. Although heavily doped conducting polymers have a metallic density of states at Fermi level (E_f), their transport properties are dominated by disorder which originates from a combination of partial crystallinity (molecular scale disorder) and/or inhomogenous doping.

Figure 1 shows the electrical conductivity of different polypyrrole samples prepared at different current densities in a wide range of temperature starting from 4.2 K to 300 K. It is observed that the room temperature conductivity of as grown sample prepared at current density of 7.5 mA/cm^2, is relatively high~ 47 S/cm and is in good agreement with the earlier reported values [15]. As polypyrrole has a non-degenerate ground state, the spinless carriers are considered to be bipolarons [6]. The relatively high conductivity requires the transverse coupling of polarons into interchain bipolarons for a more efficient coupling between the chains, because many transverse hops from chain to another are necessarily involved in the transport [16]. The only way to build up stable polarons or bipolarons between adjacent chains is to use the dopant center as a bridge. A dopant molecule placed between two polymeric chains can

donate its carrier to the chain as its right as well as to the chain at its left.

It is demonstrated from Figure 1a that, the electrical conductivity increases monotonically with temperature, expressing a semiconductor type behavior. Although relatively conductivity values have been reported for doped polypyrrole, the conductivity of such materials is typically activated and decreases as temperature is lowered. The electrical conductivity of samples prepared at high current densities has weak temperature dependence in the range 100 K to room temperature, whereas, for samples prepared at low current densities, the conductivity drops by more than five orders of magnitude as the temperature is lowered.

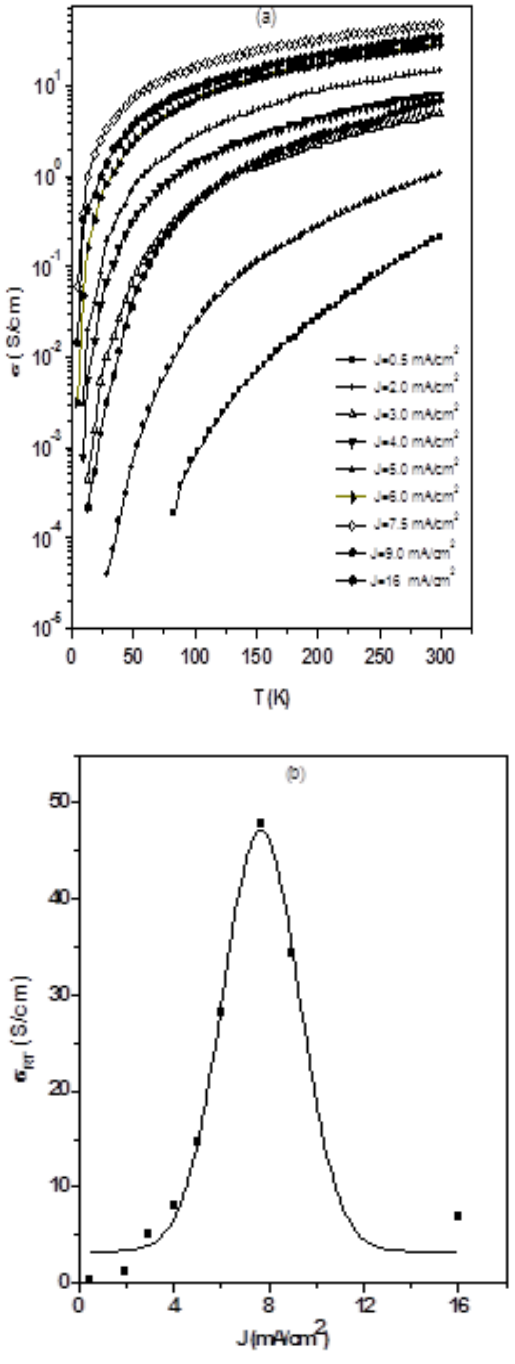
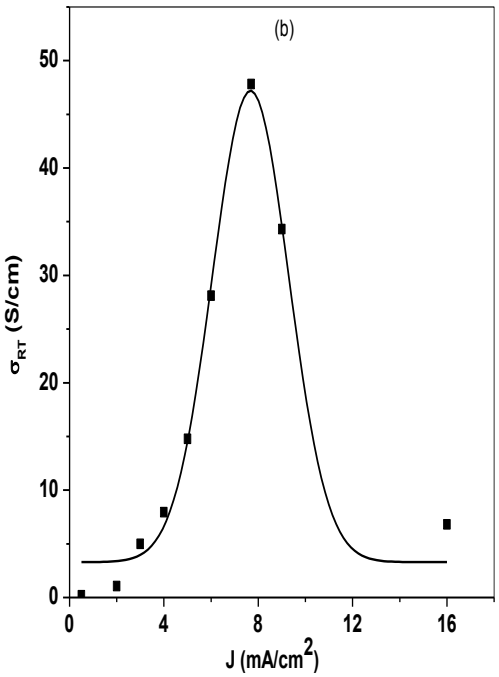


Figure 1:(a) Temperature dependence of electrical conductivity for different polypyrrole samples prepared at different current densities. (b) Room temperature electrical conductivity as a function of current density



The electrical conductivity as a function of different values of current densities is shown in Fig. 1b. It is observed that, the conductivity increases as current density increases up to optimal value of 7.5 mA/cm^2 and then decreases at higher current densities. At lower current densities oxygenation of active sites on the pyrrole ring may occur in preference to the polymerization reaction, resulting in chain termination and thus a low conjugation length. It is also, probable at high current densities that side reaction occurs, which result in lower conjugation lengths and thus higher defect concentration. This leads to formation of potential barriers, inhibiting electrical conduction [17-18].

The early point of view on the nature and mechanism of transport in conducting polymers are similar to amorphous semiconductor [19]. According to this analogy the conduction mechanism of thermal activation, Mott's variable range hopping (VRH) mechanism is used to investigate the electrical conductivity according to the following equation [20]:

$$\sigma = \sigma_0 \exp\left[-(T_0/T)^{1/1+d}\right]$$

Where σ, T and *d* represent the electrical conductivity, temperature and dimensionality, respectively. It seems that it is possible to determine whether the conductivity is 1D or 3D by examining the electrical conductivity temperature dependence as shown in Figure 2. Transport properties reflect the structural disorders, so that the transport occurs by hopping states near E_f. These states reside in the band tails of localized states that extend from the band edges into the energy gap as a consequence of disorder. The hopping probability depends not only on the energy difference between the initial and final states and on the photon spectrum, but also on the overlap of the wavefunctions. Hence, if localization is not very strong, hopping occurs with variable range hopping.

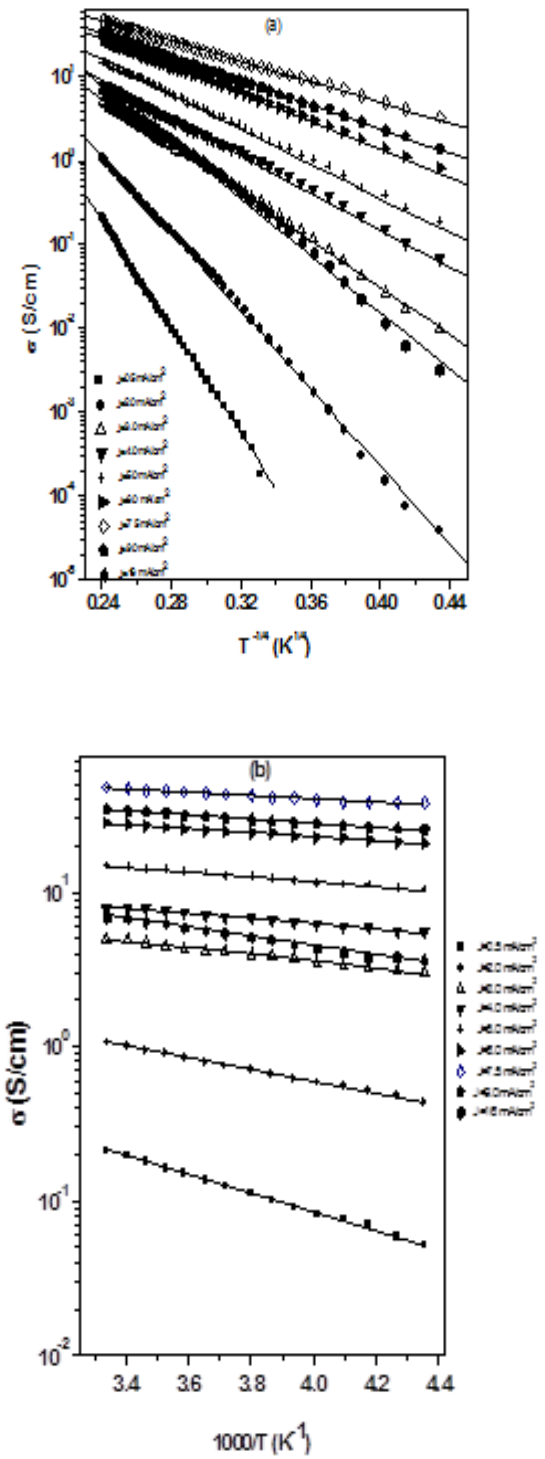
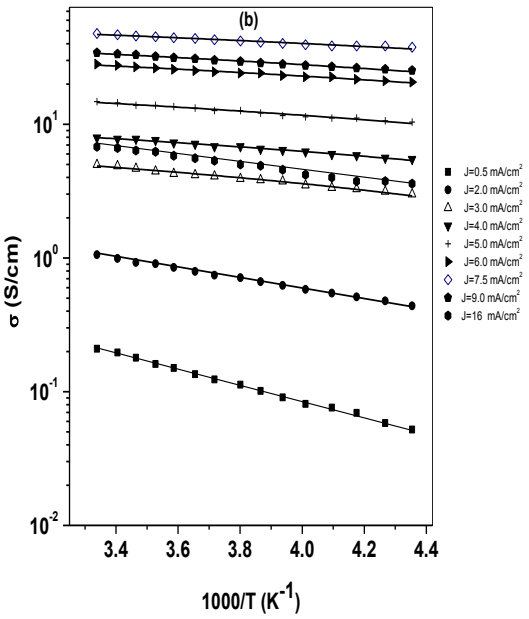


Figure 2: (a) Electrical conductivity versus $T^{-1/4}$ and (b) Arrhenius plot for different polypyrrole samples at different current densities.

Figure 2a shows the Mott plots regarding electrical conductivity of different polypyrrole samples. The complex morphology of PPy (polymer chains, small crystalline regions, fibrils, disturbances effected by the anions), makes it difficult to describe the transport properties by a consistent model within a large temperature range. However, one can observe that the plots obeyed the Mott equation between 18 K and slightly deviation above 200 K. Starting from 200 K and around room temperature, the electrical conductivity fitted Arrhenius equation better than Mott equation suggesting nearest-neighbour hopping as shown in Figure 2b.



By knowing the initial slope of the Arrhenius plot, the activation energy (ΔE) values have been calculated and summarized in Table 1, which serve as simple index of the conductivity behavior. It was found that, the activation energy decreases as the current density increases until the optimal value of 7.5 mA/cm^2 and then increases again. On the other hand, it is found that in Mott's plot the deviation below 18 K was smaller as the current density was higher. Accordingly, for samples prepared at high current densities, the plots are close to the Mott's equation below 18 K, suggesting that the electrical conduction is dominated mainly by the mechanism based on variable range hopping in a wide temperature range.

Table 1

Room temperature electrical conductivity (σ) and characteristic temperature (T_0) from Mott's plot, activation energy ΔE and the initial conductivity σ_0 from Arrhenius plot at different current densities.

J (mA/cm^2)	σ (S/cm)	T_0 (K)	ΔE (eV)	σ_0 (S/cm)
0.50	0.209	$3.2x10^7$	0.047	0.25
2.00	1.057	$9.2x10^6$	0.030	1.22
3.00	4.980	$1.2x10^6$	0.017	5.15
4.00	7.940	$4.3x10^5$	0.014	8.35
5.00	14.77	$3.4x10^5$	0.011	15.45
6.00	28.11	$1.2x10^5$	0.011	29.60
7.50	47.82	$4.2x10^4$	0.009	50.00
9.00	34.30	$8.1x10^4$	0.010	36.75
16.0	6.840	$2.6x10^6$	0.021	7.170

The most interesting observation is the variation of T_0 with the values of current density, values of T_0 are ranged from $3.2x10^7$ to $4.2x10^4$ K relating to different current densities. In addition, it is found that room temperature electrical conductivity has current density dependence. It has been reported that variable range hopping is applicable under the requirement of $(T_0/T)^{1/4} \geq 10$ [21]. In addition, Mott and Davis have pointed out that the variable range hopping occurs in the system in which the wavefunctions are confined in a small space [20]. Therefore small values of $(T_0/T)^{1/4}$ as listed in Table 1 due to the fact that the wavefunctions of polypyrrole is highly delocalized [22]. In addition, it was observed that, for the samples which are prepared at relatively higher current density, the VRH is no longer valid. This may be due to the fact that polarons and bipolarons are mobile along the polypyrrole chain and the charge transport is partly by the mobile polarons and bipolarons, and partly by the hopping electrons [23]. The deviation from the exponent 1/4 which is observed at high temperatures may have various reasons, i.e., spatial inhomogenities, variations of the density of states with energy or lower dimensionality [24].

Magnetoresistance Measurements:

The magnetoresistance (MR) phenomenon defined as $[\rho(H)-\rho(0)]/\rho(0)$ is one of the most important tools used to study the transport properties of conducting polymers. Magnetoresistance has traditionally been a powerful method to probe the mean spatial characteristics of charge transport and scattering processes in metals. As means to know the transport mechanism, the magnetoresistance has been carried out at very low temperatures. The contribution to magnetoconductance due to electron-electron interactions is negative (positive magnetoresistance) and arises predominantly from Zeeman splitting of the spin-up and spin-down. In contrast, the sign of the magnetoconductance associated with localization can be negative or positive depending on whether or not spin-orbit effects are important.

The magnetoresistance has been investigated for conducting polypyrrole in the temperature range from 1.2 K to 4.2 K and magnetic field from H=0 T to H= 10.3 T, as shown in Figure 3. It was observed that, the magnetoresistance increases in the positive direction as the magnetic field increases and the temperature decreases. Since the contribution from electron-electron interaction increases at lower temperatures and higher magnetic fields, the magnetoresistance has a higher value of $\Delta\rho/\rho$ at very low temperature ($\Delta\rho/\rho_{at\ 1.2\ K}$ = 2.21). This high value of $\Delta\rho/\rho$ is characteristic for the insulating regime. The conduction mechanism in this regime is dominated by VRH, where the magnetic field may modify the conduction process via Zeeman shift in the levels relevant to hopping. Electron transfers either between singly occupied levels or between doubly occupied and vice versa are suppressed; this leads to a positive magnetoresistance [25].

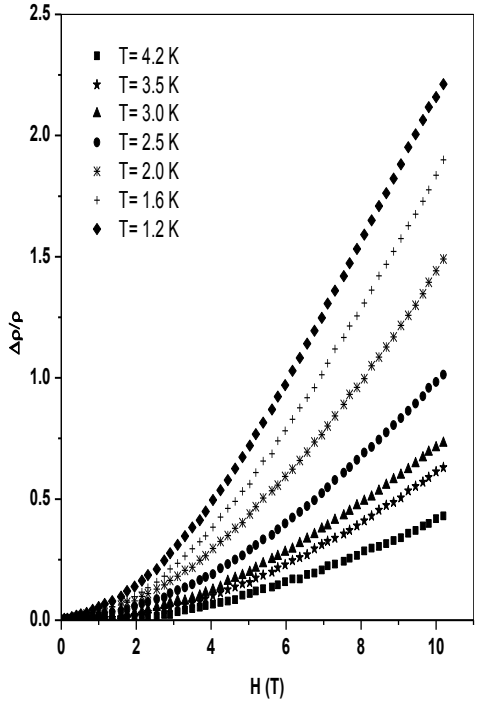
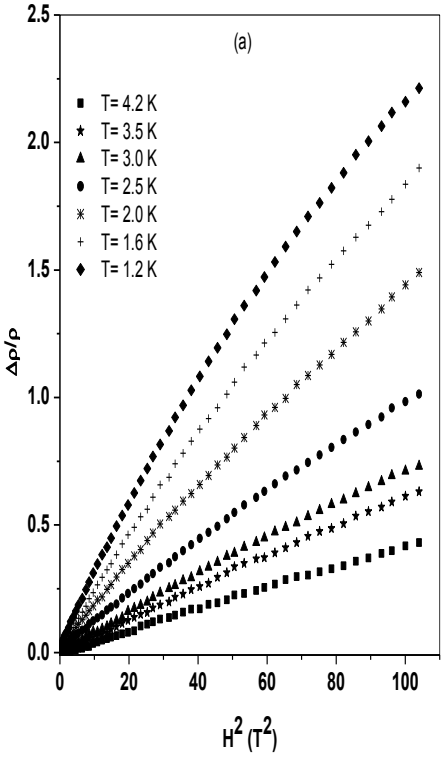


Figure 3. Magnetic field dependence of the magnetoresistance ($\Delta\rho/\rho$) (where ρ is the resistance at H=0T and $\Delta\rho$ is the resistance increament) for conducting polypyrrole sample

Figure 4 displays the magnetoresistance as a function of H^2 at different temperatures. It is observed that, the data are quadratic in H at low fields up to H=4 T, but at high fields tends to saturate. The obtained large positive magnetoresistance in the insulating regime as shown in Figure 3 is typically expected for VRH conduction, since the overlap of the localized state wavefunctions shrink in the presence of the magnetic field, the average hopping length increases.



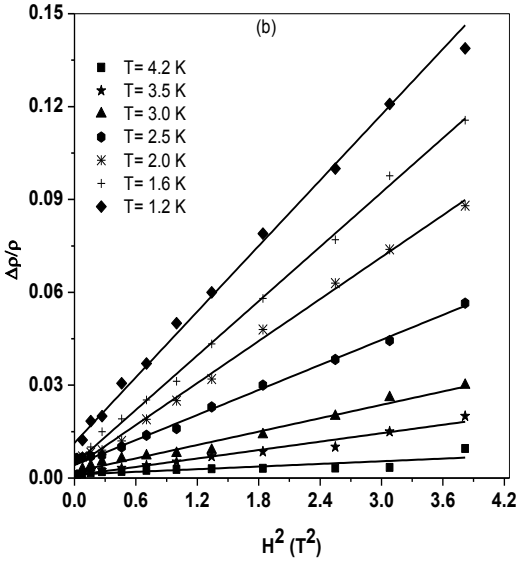


Figure 4: Magnetoresistance of conducting polypyrrole ($\Delta\rho/\rho$) as a function of H^2.

In the insulating regime the localization length can be estimated from the expression of the magnetic field dependence on the resistivity as follow [26-27]:

$$\ln\left[\frac{\rho(H)}{\rho(0)}\right] = t\left(\frac{L_c}{L_H}\right)^4\left(\frac{T_0}{T}\right)^{3/4}$$

where t= 5/2016 for 3D-system, L_c is the localization length and L_H is the magnetic length.

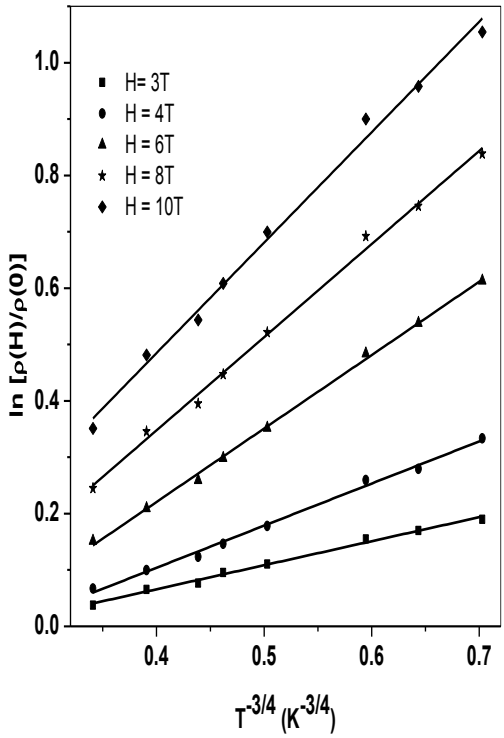


Figure 5: ln $\rho(H)/\rho(0)$ versus $T^{-3/4}$ of conducting PPy sample.

Fig. 5 shows the resistivity dependence on the temperature at different magnetic fields with good fitting to Mott's equation. It was observed that, the characteristic temperature T_0 is increased as the magnetic field increased. The values of localization length and magnetic length are estimated and summarized in Table 2.

Table 2
The values of characteristic temperature, localization length and magnetic length

Magnetic field Strength (T)	T_0 (K)	L_c (Å)	L_H (Å)
3	1.2×10^5	62.49	146.95
4	1.3×10^5	58.56	127.27
6	1.4×10^5	53.79	103.91
8	1.5×10^5	48.92	89.99
10	1.6×10^5	45.01	80.49

IV. CONCLUSION

The electrical conductivity of conducting PPy is investigated in a wide range of temperature starting from 4.2 K to 300 K. It is concluded that, for samples prepared at low current densities has weak temperature dependence in the range 100 K to room temperature, whereas, for samples prepared at low current densities, the conductivity drops by more than five orders of magnitude as the temperature is lowered. In addition, the conduction mechanism of conducting PPy samples is dominated mainly by the mechanism based on variable range hopping in a wide temperature range. On the other hand, the magnetoresistance of polypyrrole sample is investigated in the temperature range from 1.2 K to 4.2 K and magnetic field from H=0 T to H= 10.3 T. It is observed that, PPy sample is characterized by large positive magnetoresistance. This obtained large positive magnetoresistance in the insulating regime is typically expected for VRH conduction.

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REFERENCES

[1] Hui, P.; Lijuan, Z.; Soeller, C.; Travas- Sejdic, J. Conducting polymers for electrochemical DNA sensing. Biomaterials. **2009**, 30, 2132-2148.
[2] Wang, Y. G.; Li, H.Q.; Xia, Y.Y. Ordered whiskerlike polyaniline grown on the surface of mesoporous carbon and its electrochemical capacitance performance. Adv. Mater. **2006**, 18, 2619-2623.
[3] Yang, S.; Lozano, K.; Lomeli, A.; Foltz, H. D.; Jones, R. Electromagnetic interference shielding effectiveness of carbon nanofiber/LCP composites, Compos Part A: Appl Sci Manuf. **2005**, 36 (5), 691-697.
[4] Kachoosangi, R.T.; Musameh, M.M.; Abu-Yousef, I. A.; Yousef, J. M.; Kanan, S. M.; Xiao, L.; Davies, S.G.; Russell A.; Compton, R.G. Carbon Nanotube-Ionic Liquid Composite Sensors and Biosensors. Anal Chem. **2009**, 81(1), 435-442.
[5] Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, A. G.; Heeger. A. J. Synthesis of electrically conducting organic polymers: Halogen Derivatives of Polyacetylene, (CH)x. J. Chem. Soc. Chem. Commun., **1977**, 474, 578-580.
[6] Skotheim, T. *Handbook of conducting polymers*. 2nd ed. Marcel Dekker. 1986.

[7] Benseddik, E.; Makhlouki, M.; Bernede, J. C.; Lefrant, S.; Pron. A. XPS studies of environmental stability of polypyrrole-poly(vinyl alcohol) composites. Synth. Met. **1995**, 72, 237-242.
[8] Migahed, M. D.; Fahmy, T.; Ishra, M.; Barakat, A. Preparation, characterization and electrical conductivity of polypyrrole composite films, Polymer Testing. **2004**, 23 (3), 361-365
[9] Migahed, M. D.; Ishra, M.; Fahmy, T.; Barakat, A. Electric modulus and AC conductivity studies in conducting PPy composite films at low temperature. Journal of Physics and Chemistry of Solids. **2004**, 65, 1121–1125.
[10] Khan, A. Ali.; Paquiza, L. Electrical behavior of conducting polymer based 'polymeric–inorganic' nanocomposite: Polyaniline and polypyrrole zirconium titanium phosphate. Synth. Met. **2011**, 161 (9-10), 899-905.
[11] Foroughi, J.; Kimiaghalam, B.; Ghorbani, S. R.; Safaei, F., Abolhasan, M. Effect of conducting polypyrrole on the transport properties of carbon nanotube yarn, Thin Solid Films. **2012**, 520 (24), 7049-7053.
[12] Gu, H.; Guo, J.; Yan, X.; Wei, H.; Zhang, X.; Liu, J.; Huang, Y.; Wei, S.; Guo, Z. Electrical transport and magnetoresistance in advanced polyaniline nanostructures and nanocomposites. Polymer. **2014**, 55 (17), 4405-4419.
[13] Mativetsky, J. M.; Tarver, J .; Yang, X .; Koel, X.; Loo, Y-L. Structural origin of anisotropic transport in electrically conducting dichloroacetic acid-treated polymers. Organ. Elect. **2014**,15 (2), 631-638.
[14] P. Dutta, S. Biswas, M. Ghosh, S. K De, S. Chatterjee. The dc and ac Conductivity of polyaniline and polyalcohol blends. Synth. Met. **2000**, 122, 455-461.
[15] Mehendru, P. C.; Singh, R.; Panwar, V. S.; Gupta, N. P. Hopping transport and relaxation phenomena in Poly (Vinyl Chloride: Vinyl Acetate: Vinyl Alcohol) terpolymer. IEEE, Trans. Electr. Insul **1986**, EI-21 (3), 297-300.
[16] Zuppiroli, L.; Paschen, S.; Bussac, M. N. Role of the dopant counterions in the transport and magnetic properties of disordered conducting polymers. Synth. Met **1995**, 69(1-3), 621-624.
[17] Satoh, M.; Kaneto, K.; Yoshino, K. Dependences of electrical and mechanical properties of conducting polypyrrole films on conditions of electrochemical polymerization in an aqueous medium. Synth. Met. **1986**, 14(4), 289-296.
[18] Maddison, D. S; Unsworth, J. Optimization of synthesis conditions of polypyrrole from aqueous solutions. Synth. Met **1989**, 30 (1), 47-52.
[19] Epstein, A. J.; Lee, W. P.; Prigodin, V. N. Low-dimensional variable range hopping in conducting polymers. Synth. Met. **2001**, 117(1-3), 9-13.
[20] Mott, N. F.; Davis, E. A. *Electronic Processes in Non-Cryst. Mater*., Clarendon, Oxford, 1979.
[21] Ehinger, K.; Roth, S. Non-solitonic conductivity in polyacetylene Philos. Mag. B 1986; B53: 301-320.
[22] Li, J.; Wang, E.; Green, M.; West, P. E. In situ AFM study of the surface morphology of polypyrrole film. Synth. Met. **1995**, 74 (2), 127-131.
[23] Shen, Y.; Caneiro, K.; Jaconsen, C.; Qian, R.; Qiu, J. Characterisation of the transport properties of conducting polypyrrole films. Synth. Met. **1987**, 18 (1-3), 77-83.
[24] Bender, K.; Gogu, E.; Hening, I.; Schwitzer, D.; Mueenstedt, H. Electric conductivity and thermoelectric power of various polypyrroles. Synth. Met. **1987**, 18(1-3), 85-88.
[25] Kurobe, A.; Kamimura, H. Correlation Effects on Variable Range Hopping Conduction and Magnetoresistance. J. Phys. Soc. Jpn. **1982**, 51, 1904-1913.
[26] Shlovskii, B. I.; Efros, A. L. *Electrical properties of doped semiconductor*, Springer-Verlag, Berlin, P. 212, 1984.
[27] Kim, K. H.; Choi, A.; Park, J.; Hong, S. J.; Park, M.; Lee, I.; Choi, E. S.; Kaiser, A. B.; Choi, T.; Park, Y. W. Magnetoresistance of a copolymer: $FeCl_3$-Doped poly (2,5-dioctyloxy-p-phenylene vinylene-alt-3,4-ethylenedioxythiophene vinylene), Synth. Met. **2014**; 188(1): 30-34