

Electrical Conduction of Iodine Doped Poly(9-vinylcarbazole) Films

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Abstract: DC electrical conduction of iodine doped Poly (9-vinylcarbazole) (PVK) films was studied at various dopant concentrations and film thicknesses. The current-electric field dependence indicated that the electrical conduction is governed by Schottky mechanism. The conduction in these films increases as the temperature increases with a thermal activation energy $\mathcal{E}_a \sim 0.47$ eV.

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Introduction

The discovery of conducting polymers has opened the door for fabricating devices combining unique optical, mechanical, and electrical properties. The published literature on conducting polymers shows the diversity of substances that can be used. These materials include organic polymers, conjugated polymers, and copolymers [1-6]. Many mechanisms that describe the electrical conduction in these materials have been suggested and investigated [7-11].

Poly(N-vinylcarbazole) PVK is a prototype pendant group polymer. Its electronic properties, for instance the capability to transport optical excitations or charge carries, are all controlled by the dopant rather than the main chain [12]. PVK is a well known photoconducting material, it is an insulator in the dark, and becomes electrically conducting upon exposure to ultraviolet radiation. It has been the subject of considerable research due to its application as a photoreceptor in photocopying technology, and in electroluminescent, photorefractive, and photovoltaic devices [1,6,13,14].

Most research so far conducted on PVK has focused on various photoconductivity measurements. While measurements on DC electrical conductivity of doped PVK are very rare [8]. We believe that doped PVK is a promising material that may offer a good opportunity to researchers to investigate. Much work needs to be done on this material in order to bring insight on various electrical conduction properties such as transport mechanism, conduction mechanism, trapping, the role of dopant molecules, etc. In this article, the effect of doping iodine on the electrical conduction in PVK films was investigated and the results reported below.

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Experimental

PVK with molecular weight equal to 11×10^5 (available from Aldrich chemical Co., USA) was first dissolved in a proper amount of chloroform. The desired weight concentrations of iodine were added to the solution. A homogeneous solution was then obtained by thoroughly stirring this mixture for several minutes. The films were then deposited by spin coating few drops of this solution onto clean indium tin oxide (ITO) electrodes. Then, the samples were heated in an oven at $80\text{ }^{\circ}\text{C}$ for several hours in order to remove residual solvent. Finally, Al back electrodes were deposited by vacuum thermal evaporation. The films thicknesses were estimated by measuring the capacitance of the samples using a digital LCR meter (Tenma 72-960) with accuracy of $\pm 1\%$.

The samples were arranged in sandwich type configuration i.e. electrode–film–electrode structure where a copper lead was pressed to a silver paste dot on each electrode. The DC conductivity measurements of the samples were done in dark, at normal atmosphere, and at various temperatures. The temperature of the samples was measured using a K type thermocouple.

Figure 1 depicts the experimental arrangement used in these measurements.

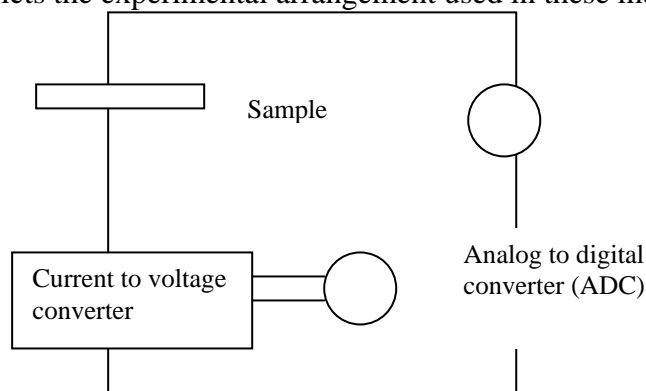


Fig. 1 The experimental setup arrangement.

The current–voltage signals were collected using a MetraByte's DAS-20 data acquisition card interfaced with a computer. Before applying the potential to the sample, the output of the DAC was amplified using a national semiconductor LMI2c1 linear amplifier. This combination insured that the input voltage across the sample can be varied from -30 volt to $+30$ volt. One of the card input terminals was used to measure the voltage across the sample. Another input terminal was used to measure the current passing through the sample via a current to voltage converter.

Result and Discussion

Previous published works indicated that a charge transfer complex CT between PVK and iodine is formed [15-17] upon doping.

A. Current–electric field dependence:

Figure 2 depicts the I–V characteristic curves of poly(9–vinylcarbazole) films doped with 1% iodine at various film thicknesses. At low voltages, the current flowing through the sample increases slowly as the voltage increases. At higher voltages the rate of increasing of current is much faster than that at lower voltages. Moreover, the current flowing through the sample shows a similar behaviour when the polarity is reversed.

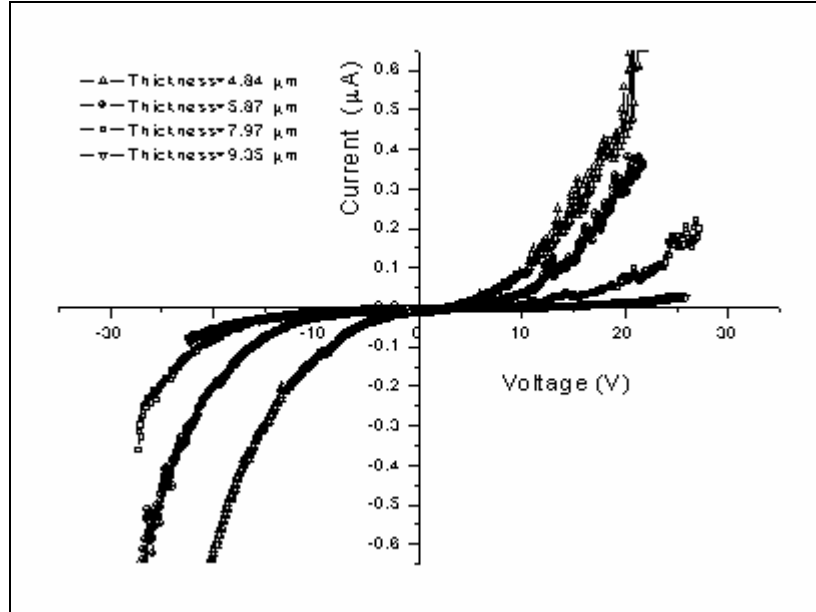
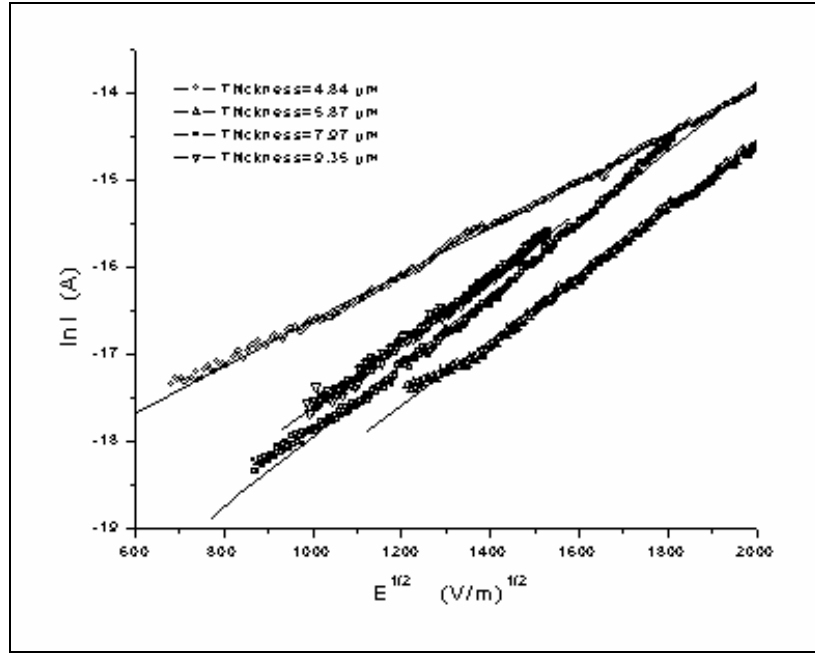
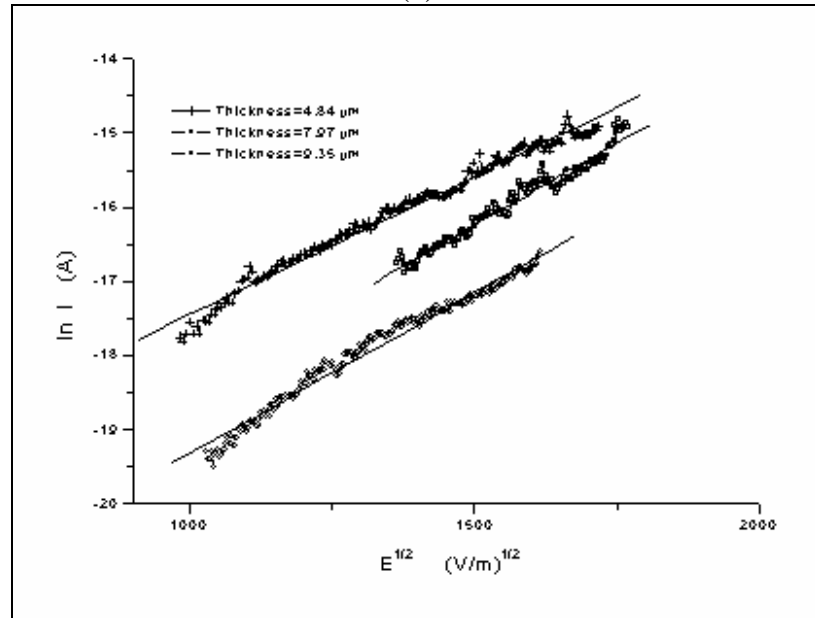


Fig. 2. I-V characteristic curves for PVK films doped with 1.0% iodine.

The relation between the natural logarithm of the current $\ln I$ and the square root of the applied electric field $E^{1/2}$ is shown in Fig. 3, Fig. 4, and Fig. 5. The plots in these figures exhibit linear relationships; a slight deviation from the linear behaviour appears at low applied electric fields. This deviation is, perhaps, due to accumulation of space charges near the electrodes. When the polarity is reversed the relationship between the current and the electric field has the same linear dependence with different slope. The slopes of these lines are shown in table 1 for positive and negative ITO electrode.

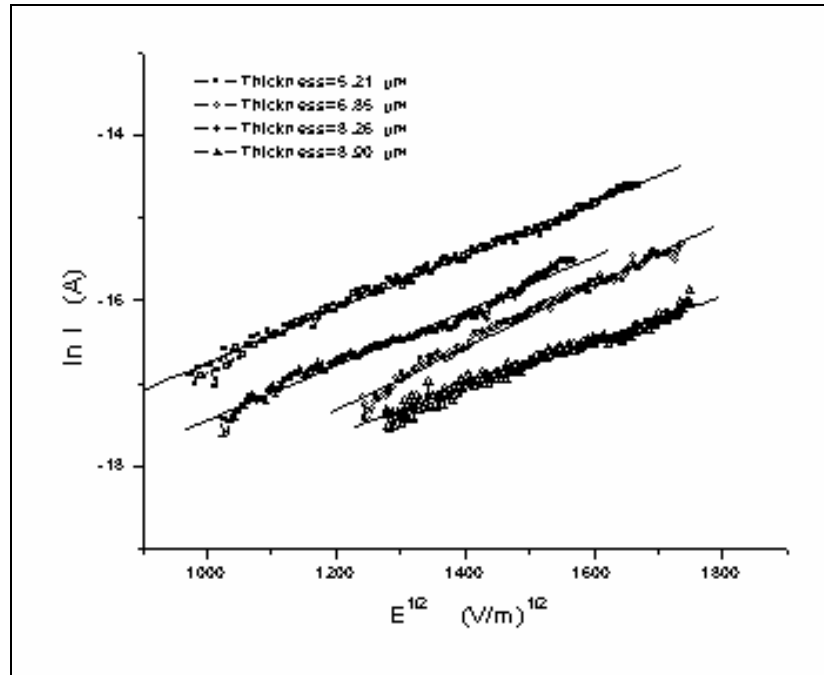


(a)

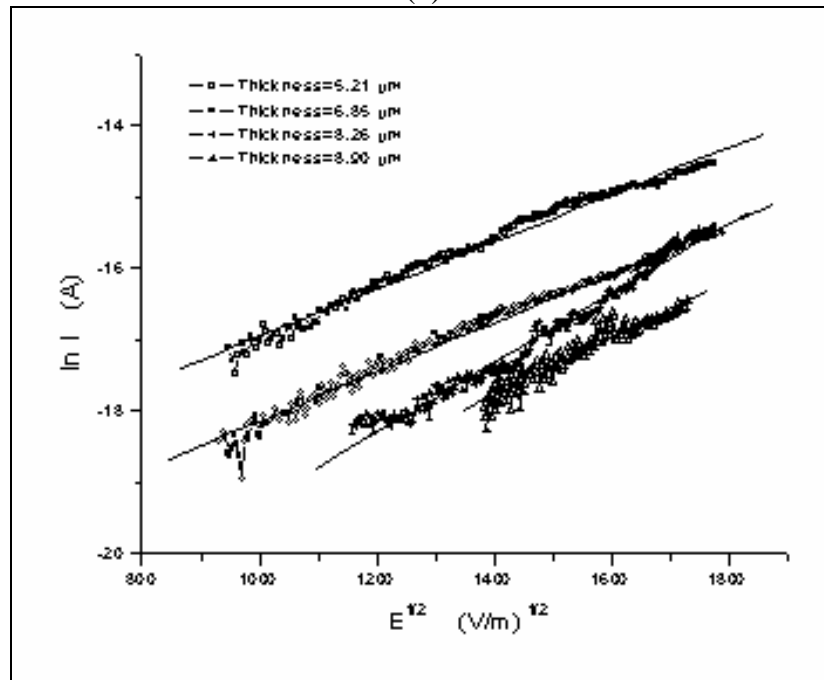


(b)

Fig. 3. Plots of the natural logarithm of the current versus square root of applied electric field for films doped with 1.0% iodine, (a) ITO electrode is positive, and (b) ITO electrode is negative.

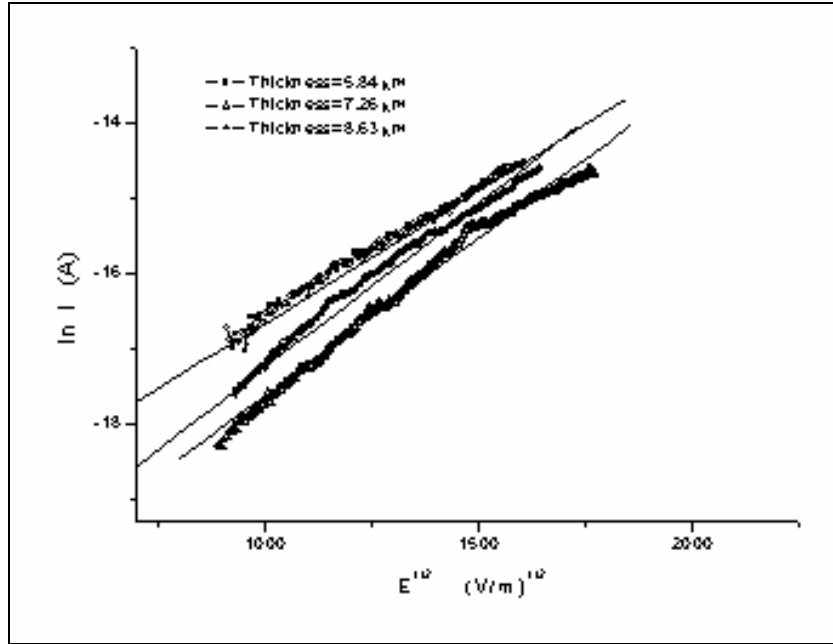


(a)

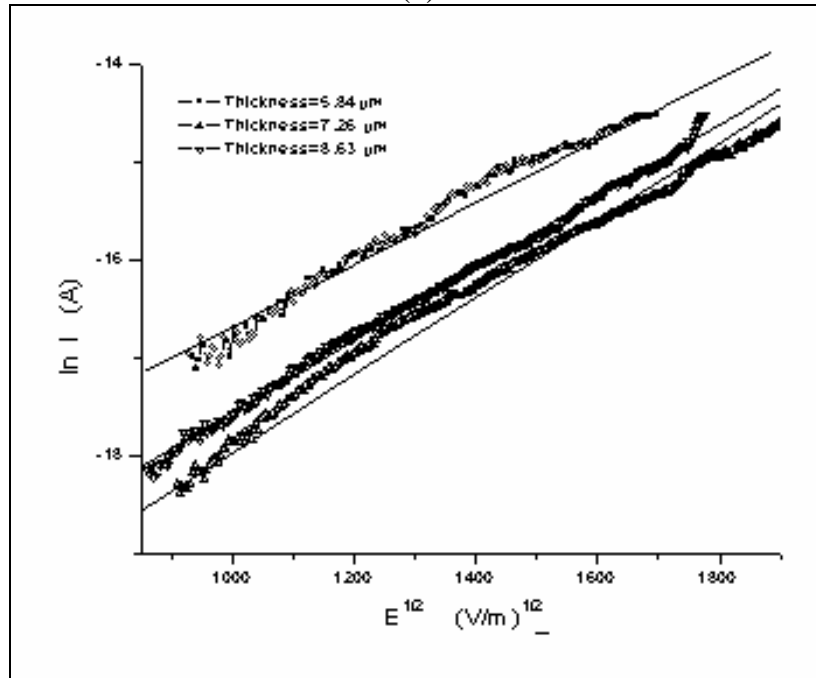


(b)

Fig. 4. Plots of the natural logarithm of the current versus square root of applied electric field for films doped with 2.0% iodine, (a) ITO electrode is positive, and (b) ITO electrode is negative.



(a)



(b)

Fig. 5. Plots of the natural logarithm of the current versus square root of applied electric field for films doped with 4.0% iodine, (a) ITO electrode is positive, and (b) ITO electrode is negative.

Tabel(1): Experimental values of β and slopes of $\ln I$ vs. $E^{1/2}$ lines for iodine doped PVK films at different thicknesses.

Iodine Concentration	Thickness (μm)	Positive ITO electrode		Negative ITO electrode	
		Slope $\times 10^{-3}$ ($\text{Am}^{1/2}/\text{V}^{1/2}$)	β ($\text{V}^{1/2} \text{ m}^{1/2}$) $\times 10^{-5}$	Slope $\times 10^{-3}$ ($\text{Am}^{1/2}/\text{V}^{1/2}$)	β ($\text{V}^{1/2} \text{ m}^{1/2}$) $\times 10^{-5}$
1.0%	4.84	2.49	6.43	3.65	9.43
	5.87	2.74	7.08		
	7.97	4.34	11.21	4.27	11.03
	9.35	3.31	8.55	4.44	11.47
2.0%	5.21	4.29	11.08	3.71	9.58
	6.85	2.06	5.32	3.87	9.97
	8.26	2.59	6.61	5.57	14.39
	8.90	4.08	10.54	5.60	14.46
4.0%	5.84	3.52	9.09	4.21	10.87
	7.26	4.45	11.49	4.48	11.57
	8.63	4.60	11.88	4.62	11.93

B. Conduction mechanism:

The linear current-electric field dependence exhibited in the plots of Fig. 3, Fig. 4, and Fig. 5 can be illustrated by the following relation:

$$I \propto \exp\left(\frac{e\beta E^{1/2}}{kT}\right) \quad (1)$$

where E is the applied electric field, e is the electronic charge, β is a constant characteristic of the conduction mechanism, k is Boltzmann's constant, and T is the absolute temperature. From the behaviour depicted in these figures between $\ln I$ and $E^{1/2}$ the conduction mechanism could be determined.

The linear behaviour of $\ln I$ versus $E^{1/2}$ plots points to an electronic-type conduction mechanism of either Schottky emission mechanism or Poole-Frenkel mechanism [7-11]. The expression for the current density J_{RS} according to Schottky emission is

$$J_{RS} = RT^2 \exp\left(-\frac{e\phi_{BP}}{kT}\right) \exp\left(\frac{e}{kT} \sqrt{\frac{eE}{4\pi\epsilon_s}}\right) \quad (2)$$

where R is Richardson's constant, ϕ_{BP} is the barrier height at the electrode-polymer interface, and ε_s is the dielectric constant. The relation for the current density in case of Poole-Frenkel mechanism is given by

$$J_{PF} = CE \exp\left(-\frac{e\phi_{PF}}{kT}\right) \exp\left(\frac{e}{kT} \sqrt{eE/\pi\varepsilon_s}\right) \quad (3)$$

where C is a constant, and $e\phi_{PF}$ is the depth of the potential well. In order to differentiate between these two conduction mechanisms the values of β were calculated from the slopes of $\ln I$ versus $E^{1/2}$ plots. The theoretical values of β for either Schottky emission or Poole-Frenkel mechanism are given by

$$\beta_{RS} = \frac{1}{2} \left(\frac{e}{\pi\varepsilon_s} \right)^{1/2} \quad (4)$$

and

$$\beta_{PF} = 2\beta_{RS} \quad (5)$$

As seen in table 1, the experimental values of β are larger than the theoretical values of either $\beta_{PF} = 4.38 \times 10^{-5} \text{ V}^{1/2} \text{ m}^{1/2}$ and $\beta_{RS} = 2.19 \times 10^{-5} \text{ V}^{1/2} \text{ m}^{1/2}$. Thus, the comparison between the theoretical and the experimental values of β doesn't reveal which mechanism is involved in the conduction.

Jonscher and Carchano have suggested a proper way to draw a distinction between either Schottky or Poole-Frenkel mechanism [7,10,11]. The distinction between these mechanisms depends on the pre-exponential factors of eq. 2 and eq. 3. These factors are

$$I_{OS} = RAT^2 \exp\left(-\frac{e\phi_{BP}}{kT}\right) \exp\left(\frac{e}{kT} \sqrt{eE/4\pi\varepsilon_s}\right) \quad (6)$$

in case of Schottky mechanism and

$$I_{OPF} = cAE \exp\left(-\frac{e\phi_{PF}}{kT}\right) \exp\left(\frac{e}{kT} \sqrt{eE/\pi\varepsilon_s}\right) \quad (7)$$

in case of Poole-Frenkel mechanism. Where A is the area of the sample, and c is a constant. Therefore, if one takes two electrodes of different work functions forming an asymmetric structure, the current will be very asymmetrical when one reverse the polarities in case of Schottky mechanism. On the other hand, the current remains practically unchanged

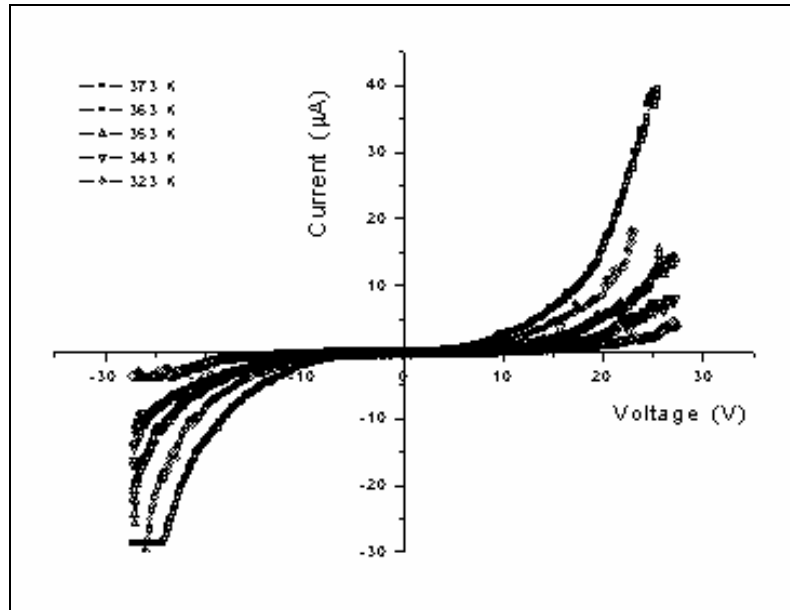
when one reverses the polarities in case of Poole-Frenkel mechanism, which does not depend on the potential barrier between the electrodes and the bulk of the material. From the data listed in table 1 we note that the slopes of $\ln I$ versus $E^{1/2}$ plots changed when the electrodes polarities are reversed. This indicates that the conduction in these films is governed by Schottky mechanism.

C. Activation Energy Measurement:

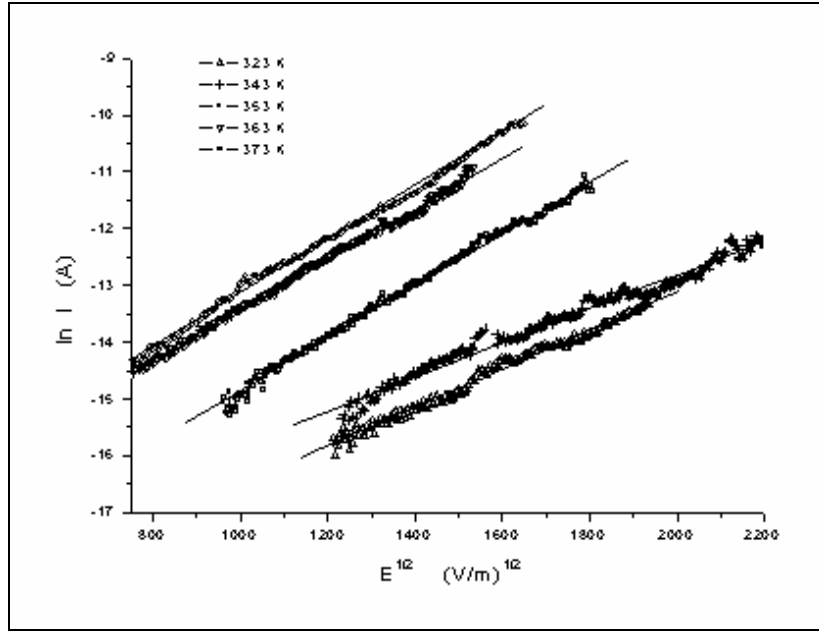
Figure 6.a depicts the variations of the I-V curves with temperature for a sample doped with 1% iodine. This figure illustrates that the DC conduction increases with increasing temperature. The relation between $\ln I$ versus $E^{1/2}$ for the same sample at different temperature is depicted in fig. 6.b. It is clear from this figure that the plots still exhibit the same linear dependence. Figure 7 depicts the variation of the natural logarithm of the DC conductivity $\ln \sigma$ with the reciprocal of temperature. This behaviour indicates that σ obeys the following relation

$$\sigma = \sigma_0 \exp\left(-\frac{\varepsilon_a}{kT}\right) \quad (8)$$

where σ_0 is the maximum conductivity, and ε_a is the activation energy. ε_a is found ~ 0.47 eV.



(a)



(b)

Fig. 6.(a) The dependence of the I-V curves on temperature for a PVK film doped with iodine (b) Plots of the natural logarithm of the current versus square root of applied electric field for films doped with iodine at various temperature.

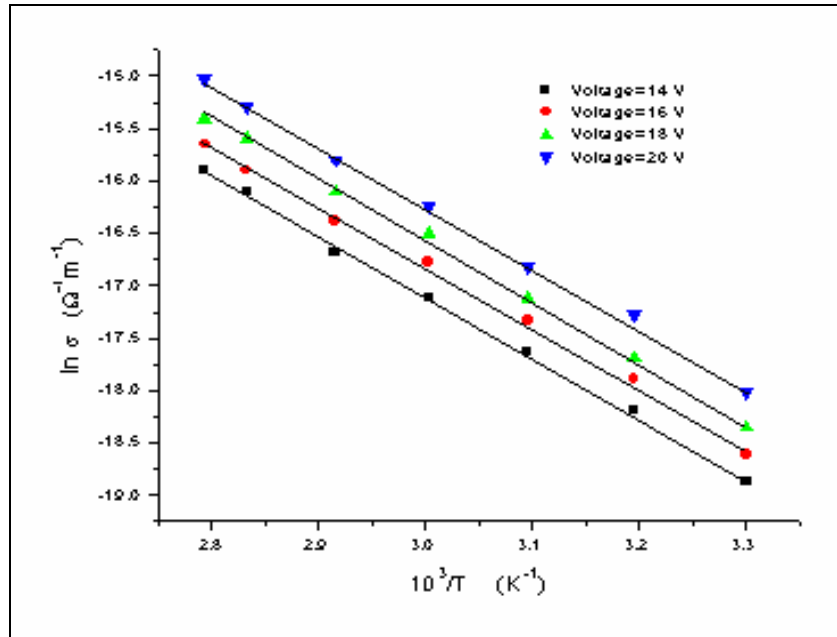


Fig. 7. The natural logarithm of DC conductivity as a function of the reciprocal of temperature ($1000/T$) for a $4.84 \mu\text{m}$ film doped with 1.0% iodine.

Conclusion

DC electrical conduction of Poly (9-vinylcarbazole) (PVK) films doped with iodine was studied at various dopant concentrations and film thicknesses. We found that the electrical conduction in these films is governed by Schottky mechanism. The thermal activation energy ε_a of the DC conduction is ~0.47 eV

References:

1. C. Jonda,; and A. P. R. Mayer, Chem. Mater. **1999**, 11, 2429-2435.
2. A. Kaynak, Materials Research Bulletin. **1998**, 33 No. 1, 81-88.
3. M. Biswas, and S. S. Ray, Synthetic Metals. **2001** 123, 135-139.
4. S. Rajendran, T. Uma, and T. Mahalingam, European Polymer Journal. **2000**, 36, 2617-2620.
5. N. S. Choi, and J.-K. Park, Electrochimica Acta. **2001**, 46, 1453-1459.
6. U. Mitschke, and P. Bäuerle, J. Mater. Chem. **2000**, 10, 1471-1507.
7. R. Bahri, J. Phys. D. **1982**, 15, 677-687.
8. A. A. El Tayyan, and A. Khogali, *Chinese J. of Physics*. **2004**, 42, No. 4I, 392-400.
9. M. Ohring, The Materials Science of Thin Films. (Academic Press, San Diego), Chap. 10, **1992**
10. A. K. Jonscher, and A. A. Ansari, Phil. Mag. **1970**, 23, No. 1981, 205-210.
11. H. Carchano, and M. Valentin, Étude électrique de couches minces de polymère obtenues dans une décharge lumineuse I: Caractérisation électrique sous champ continu. Thin Solid Films. **1975**, 30, 335-349.
12. U. Rauscher,; and H. Bassler, Macromolecule. **1990**, 23, 398-405.
13. G. Yu. Nishino, A. J. Heeger, T. Chen, and R. D. Rieke, Synthetic Metals. **1995**, 68, 243-247.
14. F. Michelotti, F. Bertolotti, E. Cianci, and V. Foglietti, Synthetic Metals. **2000**, 111, 105-112.

15. G. Safoula, K. Napo, J. C. Bernède, S. Touihri, and K. Alimi, *European Polymer Journal*. **2001**, 37, 843-849.
16. S. Touihri, J. C. Bernede, P. Molinie, and D. Legoff, *Polymer*. **2002**, 43, 3123-3129.
17. K. Alimi, G. Safoula, J. C. Bernede, and C. Raibiller, *J. Polym. Sci. Part B: Polym. Phys.* **1996**, 34, 845-851.