JOURNAL OF MATERIALS SCIENCE 27 (1992) 210–214

Evaluation of electrical conduction in iodine-doped polypyrrole

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Electrical conductivity of polypyrrole has been measured after doping with different iodine concentrations. A thermally activated electrical conductivity was found which was pseudo-ohmic and increased with doping level. The results can also be fitted by log σ versus $T^{-1/2}$ and log σ versus $T^{-1/4}$ dependences, instead of the Arrhenius log σ versus T^{-1} dependence. From these results it was concluded that within the experimental scatter no significant distinction can be made between these different temperature dependence laws. Hence these data can only enable one to speculate about the true underlying transport model, rather than to draw decisive conclusions. Electrical conductivity results predicting the role of iodine dopant concentration on the conduction process of semiconducting polypyrrole are discussed.

1. Introduction

Conjugated organic polymers have attracted much attention in the scientific community over the past decade because of their unique electronic properties [1]. The electrical conductivity of conjugated organic polymers could be raised from the insulating to the semiconducting and even to the metallic regime by doping with either electron acceptors or electron donors [1, 2]. An essential common feature which induces high electrical conductivity is a reaction of the conjugated π-electron backbone with an appropriate oxidizing or reducing dopant. The delocalization of π-electrons along the conjugated polymer chain is believed to participate in the conduction process. The highly conjugated polyacetylene has a degenerate ground state and the charge-carrying species formed on doping have been described as solitons [3–5]. Polypyrrole, polythiophene and poly(p-phenylene), on the other hand, have a nondegenerate ground state and bipolarons have been considered as the charge-carriers formed on doping [6, 7]. A neutral soliton has a spin $\frac{1}{2}$, while the charge soliton is spinless. Likewise, a polaron has a spin $\frac{1}{2}$, whereas a bipolaron is spinless [1]. These spinless mobile species formed on doping have been considered to be the basis of the conduction process in conjugated polymer solids.

Several conduction mechanisms have been proposed to describe conducting polymers; problems arise from the doping mechanism and from the complexity of polymeric materials, therefore there are some controversies with the analysis and correct interpretation of the conduction process [4]. A theoretical model of Mott's variable range hopping (VRH) conduction can predict transport processes occurring in disordered semiconducting materials [8]. With this model the conductivity–temperature data are best plotted as log σ versus T^{-x}, where σ is the electrical conductivity, T is the temperature and x is a constant ranging from 1 to $\frac{1}{4}$. The $x = \frac{1}{2}$ behaviour evinces a pseudo-one-dimensional conduction [9, 10], whereas $x = \frac{1}{3}$ indicates a two-dimensional conduction [11], and $x = \frac{1}{4}$ predicts a three-dimensional conduction process. Thus an experimental linear log σ versus $T^{-1/4}$ behaviour is taken as a proof of a variable-range hopping in three dimensions, most often suggested for conducting polymers. Sickel *et al.* [12] proposed that the size and the shape of the dopant ions also influence the conduction process and a $T^{-1/2}$ behaviour observed in doped polyacetylene indicates a fluctuation-induced tunnelling conduction. In this conduction process, tiny conducting domains, formed on doping, participate in the delocalization of charge carriers by tunnelling between conducting islands. Structurally, this process resembles a metallic composite (inhomogeneous) system in which metallic particles are embedded in an insulating matrix. It has been thought that the nonuniform doping causes heterogeneity which leads to the formation of nonstoichiometric charge-transfer complexes between the polymer and the dopant. Audenaert *et al.* [13] reported that the conduction process in polyacetylene is affected by the iodine concentrations. Epstein *et al.* [14] investigated the conductivity–temperature characteristics of iodine-doped *trans*-polyacetylene and suggested an intersoliton electron hopping mechanism.

The changes introduced in electrical conductivity are influenced not only by the structure and nature of a dopant but also by the doping concentrations and doping procedures [12]. Dopants also cause morphological as well as structural changes in the polymer matrix [4]. All such factors contribute in determining

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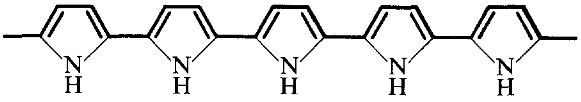
the conduction mechanism in doped conjugated polymers. For the single material polyacetylene, already several mechanisms for transport, namely by variable-range hopping, intersoliton hopping [15] and Sheng-fluctuation-induced tunnelling conduction [16] have been proposed, taking into account one or another aspect of the complicated molecular, crystalline and morphological structures induced on doping. In this regard, polyacetylene is the most extensively studied conducting polymer.

In polypyrrole, bipolarons have been considered to be the fundamental charge-carrying species in the conduction process. Scott *et al.* [17] investigated the transport properties of polypyrrole by employing an electron spin resonance technique. Nechtschein *et al.* [18] analysed the existence of polarons and bipolarons in polypyrrole by simultaneously performing *in situ* electron spin resonance (ESR) and electrochemical experiments. Genoud *et al.* [19] have proposed a different mechanism in oxidized polypyrrole. In a recent study made by the present author [20], magnetic susceptibility measurements carried out on oxidized polypyrrole in the temperature range 6–300 K indicate the possible existence of both polarons and bipolarons. All these studies have been made on electrochemically prepared polypyrrole which was *in situ* doped during the electrochemical polymerization process. Polypyrrole has a very simple structure as depicted below (I). If the heteroatoms were not



incorporated in the conjugated backbone then it could be viewed as a *trans-cis*oid isomer of polyacetylene [1, 4, 21]; therefore the magnetic susceptibility results are similar to those obtained for doped *cis*-polyacetylene [22]. Watanabe *et al.* [23] reported the temperature dependence of conductivity in electrochemically prepared polypyrrole doped with tetrafluoroborate (BF_4^-), and suggested a VRH conduction. To the best of the author's knowledge, the effect of dopant concentration on conduction in polypyrrole has not been studied so far, probably due to problems encountered in controlling the doping level during electrosynthesis. Pristine free-standing films of polypyrrole can be obtained by chemical methods which facilitate quantitative doping and study of the dopant concentration effect on conduction. Therefore, in the investigations reported here, polypyrrole films were grown by a special chemical technique. Studies of the dopant concentration dependence of conduction are reported in this paper. The temperature-dependent conductivities reflect two distinct modes of conduction arising from different iodine concentrations by which the polypyrrole is complexed.

2. Experimental procedure

Polypyrrole films were prepared by the acid-catalysed polymerization process developed by Salmon *et al.* [24]. The details of sample preparation have been discussed earlier [25]. Iodine doping was carried out by exposing thin films to iodine vapour in a vacuum desiccator at room temperature. The iodine concentration was determined at various stages of doping from the weight uptake. The iodine concentration depends upon the exposure (reaction) time and a desired level can be conveniently achieved. The electrical conductivity measurements were performed by a two-probe technique. The current was recorded by a Keithley electrometer (model 610C); the voltage source was a high-voltage power supply (Keithley model 247). The conductivities were measured as a function of temperature and iodine concentration. All measurements were made in a specially designed closed cell equipped with a temperature sensor.

3. Results and discussion

Fig. 1 shows logarithmic plots of current versus voltage for polypyrrole–iodine complexes at various doping levels. The linearity of the plots indicates the ohmic characteristic of the charge-transfer complexes. Non-ohmic behaviour was not observed, even at very high doping concentrations of iodine. The variation of resistivity with reciprocal temperature for polypyrrole–iodine complexes at three different iodine concentrations is represented in Fig. 2. The charge-transfer complexes approximately obey an Arrhenius relationship

$$\rho = \rho_0 \exp(-E_a/kT) \qquad (1)$$

where ρ is the resistivity, E_a the thermal activation energy, k the Boltzmann constant and T the absolute temperature. The log ρ versus $1/T$ curves yield an activation energy of 0.94 eV for 5.4% iodine, 0.90 eV

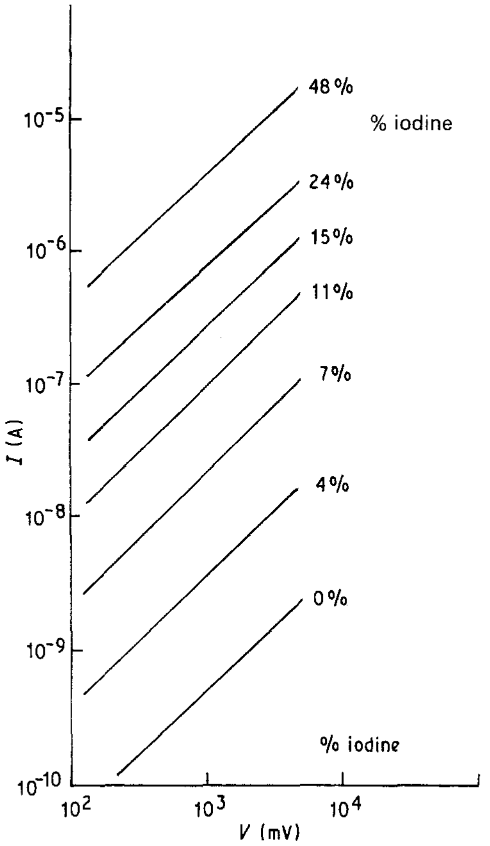


Figure 1 Current–voltage characteristics of iodine-doped polypyrrole samples at different doping concentrations.

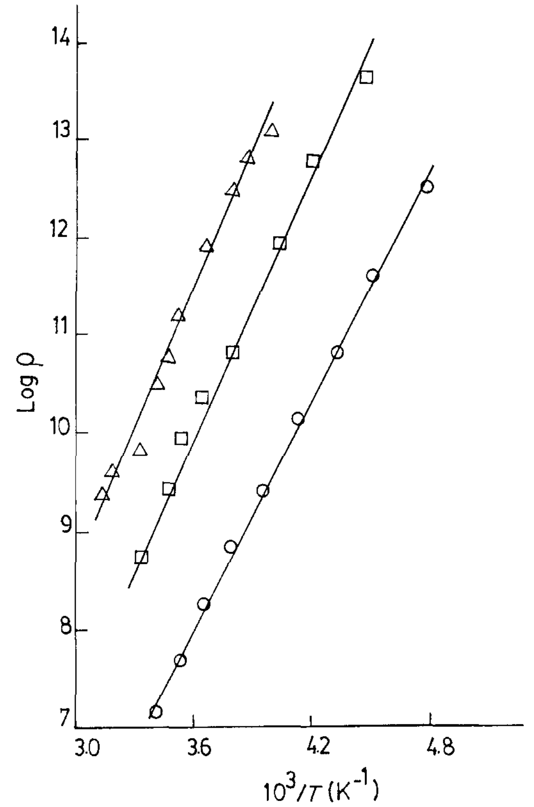


Figure 2 Log resistivity, ρ, versus T^{-1} plots for the iodine-doped polypyrrole samples at three different iodine concentrations to calculate the thermal activation energies. Iodine doping concentrations: (△) 5.4%, (□) 8%, (○) 48%.

for 8.0% iodine and 0.76 eV for 48% iodine by weight. The pristine polymer has an activation energy of 1.0 eV. The activation energy of the conduction process decreases at the higher doping level of iodine which is consistent with the increase in electrical conductivity. The conductivity is strongly temperature dependent and decreases with decreasing temperature. The log ρ versus $1/T$ plots at 5.4% and 8.0% iodine show poor fit, hence the possibility of hopping conduction involving extended states in the band tails is not well supported, but an iodine doping level of 48% substantiates such a conduction process.

Fig. 3 shows conductivity, σ, versus $T^{-1/4}$ plots for three different doping concentrations of iodine. The log σ versus $T^{-1/4}$ behaviour can be attributed to a variable-range hopping conduction process proposed by Mott [8] in which the hopping of charge carriers occurs between the atomic sites. The fit is excellent for 48% iodine concentration, but as the iodine concentration decreases, some deviation from theory takes place, in particular at the 5.4% doping level. When the data are replotted as log σ versus $T^{-1/2}$, which represents the model of metallic islands (Fig. 4), the fit is again excellent for 48% iodine concentration. As the doping level increases from 5.4% to 8.0%, the $T^{-1/2}$ behaviour changes and tends to follow a conduction process similar to that of 48% iodine-doped sample. The present experimental data are well fitted to a log σ versus $T^{-1/2}$ model at low doping level. In the case of 5.4% doping the closest fit is $T^{-1/2}$. At the doping level of 48%, the data do not qualitatively distinguish between T^{-1}, $T^{-1/4}$ and $T^{-1/2}$ models, hence a muddled picture of conduction process develops.

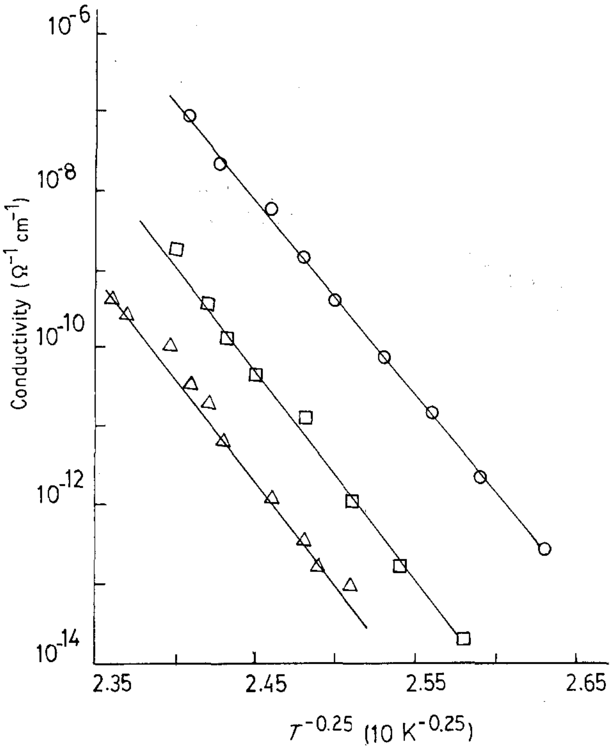


Figure 3 Conductivity, σ, versus $T^{-1/4}$ plots for polypyrrole doped with iodine: (△) $[PY\text{–}I_{0.054}]_x$, (□) $[PY\text{–}I_{0.08}]_x$, (○) $[PY\text{–}I_{0.48}]_x$.

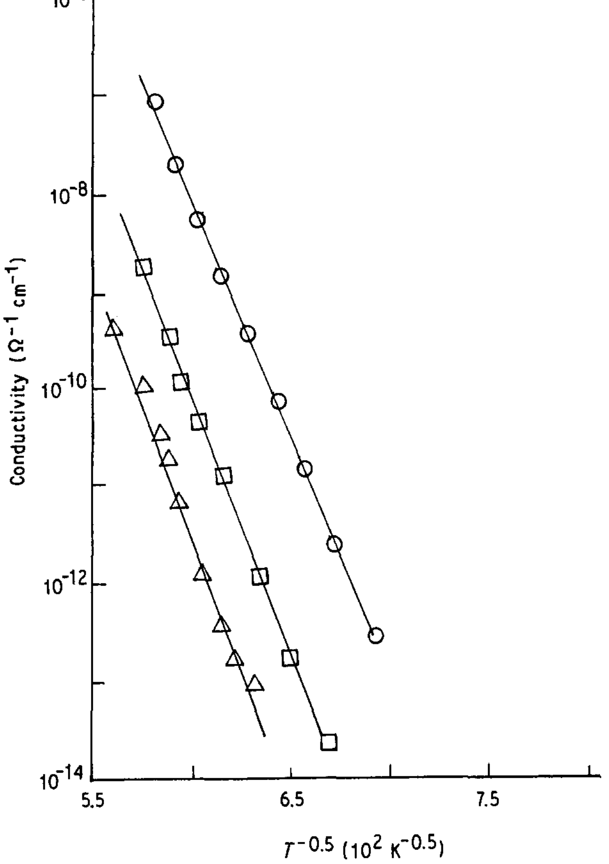


Figure 4 Conductivity, σ, versus $T^{-1/2}$ plots for iodine-doped polypyrrole at three different iodine concentrations: (△) $[PY\text{–}I_{0.054}]_x$, (□) $[PY\text{–}I_{0.08}]_x$, (○) $[PY\text{–}I_{0.48}]_x$.

The temperature dependence of conductivity seems to indicate that conduction occurs through a Sheng-fluctuation-induced tunnelling process [16]. In this mechanism of conduction, the thermally activated energy transfers electrons from one neutral grain to another, with subsequent generation of free charge carriers, and conduction occurs due to tunnelling of electrons and holes from charged grains to neutral grains [26]. In our earlier studies, we found that pristine, as well as $H_2PtCl_6 \cdot 6H_2O$ and $PtCl_4$ solution-doped polypyrrole, demonstrate Mott's VRH conduction model to hold [27]. Likely, the highly doped polypyrrole (48% iodine) also follows the theoretical model of $T^{-1/4}$. It seems that the conduction process is governed by the nature and the concentration of the dopant.

Similar results have been reported for polyacetylene [4]. Diffusion of the dopant into the polymer matrix plays an important role in the conduction process. If the dopant is not distributed homogeneously to electron donor sites, it will cause partial ionization and heterogeneity would create small conducting domains separated by some insulating regions of undoped polymer. In such a system, conduction occurs by carrier transfer between conducting segments rather than by hopping between localized states. This description is especially applicable to composite materials in which conducting (metallic) particles are embedded in an insulating matrix. An example is the carbon–polyvinylchloride composite system [28]. Sheng *et al.* [28] proposed that in composites or inhomogeneously doped polymers, (disorder semiconductors), conduction occurs through a fluctuation-induced tunnelling process. At low doping levels, if dopant species are not uniformly distributed to the electron donor sites, then a conductor–insulator state can easily emerge into the doped polypyrrole. The present data at low doping levels tend to fit into this model, but at higher iodine concentration, the measured conductivity–temperature dependence does not allow us to distinguish between several different models. Epstein *et al.* [30] reported the temperature dependence of conduction of pristine *trans*-polyacetylene and plotted data according to various models, but analysis did not shed any light on the probable conduction mechanism. Also the lightly iodine-doped *trans*-polyacetylene exhibited a similar temperature dependence as the undoped polymer and an intersoliton electron hopping conduction has been suggested. In another study, conduction by variable-range hopping for the iodine-doped polyacetylene has been predicted [31, 32]. Audenaert *et al.* [13] reported that in *trans*-polyacetylene with iodine concentrations of 0.11% and 0.19%, conductivity follows a $T^{-1/4}$ dependence whereas the samples containing iodine levels of 0.03% and 0.29% demonstrate the fluctuation-induced tunnelling conduction process. Therefore, no clear picture emerges in the literature for iodine-doped polyacetylene and this is also true for the present study.

The resistance of a 220 µm thick polypyrrole film containing 8% iodine by weight was measured as a function of voltage in the range 2–300 V (electric field = 0.09–13.6 kV cm^{-1}). Logarithmic plots of the voltage dependence of the resistance are shown in Fig. 5 for several different temperatures. Although the resistance varies strongly with temperature, the voltage dependencies are almost linear, as expected, up to the electrical field of 10^4 V cm^{-1}. Epstein *et al.* [33] reported a linear current–voltage behaviour up to an electric field of 10^4 V cm^{-1} for lightly iodine-doped polyacetylene, whereas non-ohmic behaviour was indicated for heavily doped "metallic" polyacetylene; and these findings suggest that the non-ohmic behaviour is not caused by inhomogeneous doping (i.e. by a formation of metallic islands) but may be due to electron heating. Non-ohmic behaviour of heavily iodine-doped polyacetylene has also been reported by Phillipp *et al.* [34] for iodine concentrations of 14% and 30% with electrical conductivities of 68 and 320 S cm^{-1}, respectively. In the present case, non-ohmic behaviour was not evinced (Fig. 1) up to an iodine concentration of 48%. If the assumptions are made due to the temperature dependence of conductivity ($T^{-1/2}$ behaviour) then these data lead to ambiguity because a non-ohmic behaviour is expected for fluctuation-induced tunnelling conduction.

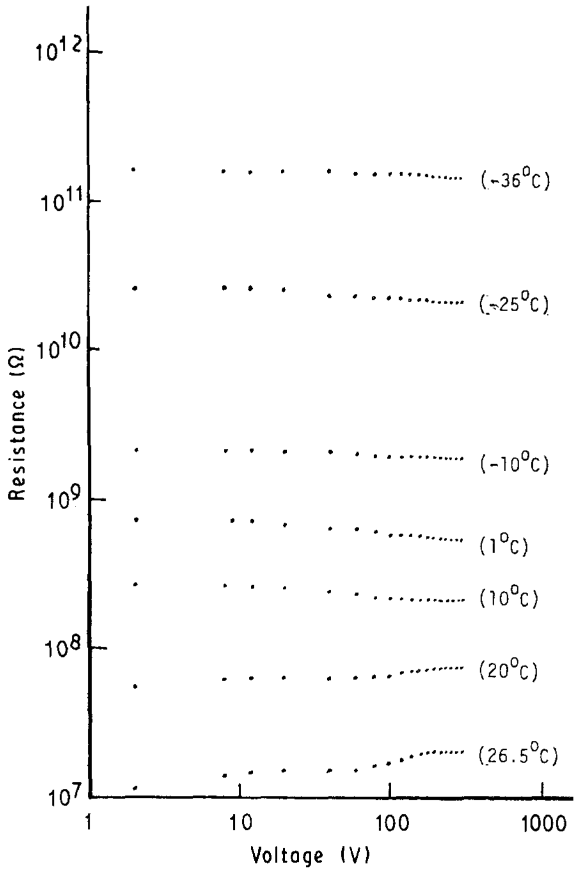


Figure 5 Logarithmic plots of resistance as a function of voltage for $[PY\text{–}I_{0.08}]_x$ sample at different temperatures.

In conclusion the temperature dependence of the conductivity gives evidence for a transport mechanism based on Sheng's fluctuation-induced tunnelling process in lightly iodine-doped polypyrrole, whereas the linear current–voltage behaviour precludes such possibility both in lightly and heavily doped polypyrrole because the magnitude of conductivity is much lower than that of iodine-doped $(CH)_x$. A muddled picture develops from log σ versus T^{-x} ($x = 1, \frac{1}{2}$ and $\frac{1}{4}$) behaviour, but iodine concentration to some extent, plays a significant role in determining the conduction process because the temperature dependence power law changes its exponent as the iodine concentration increases from 5.4% to 8.0%, similar to the situation with polyacetylene.

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Received 28 August 1990
and accepted 28 February 1991