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## Conductivity and thermoelectric power in conducting polypyrrole films

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**Abstract.** The electrical conductivity and thermoelectric power of films of polypyrrole doped with  $\text{BF}_4^-$  have been measured. The electrical conductivity measured in the temperature range 90–300 K follows the variable-range hopping theory proposed by Mott and Davis. However, a variation in the value of the parameter in the exponential expression for conductivity has been observed with film thickness. The magnitude of the thermoelectric power measured in the temperature range 200–300 K is found to be small and p type. The temperature variation in thermoelectric power also obeys the above theory. Some physical parameters such as the density of states at the Fermi level and the hopping distance have been evaluated.

### 1. Introduction

Since the discovery of conductivity in partially oxidized or reduced polyacetylene films by Heeger and co-workers [1], intense experimental and theoretical work on polyacetylenes have continued unabated. However, polyacetylenes are difficult to prepare and are also unstable in air. Subsequent research led to the discovery of a host of conducting polymers, e.g. polypyrroles, polythiophenes and polyanilines, which not only are stable in air but also could be prepared by easy electrochemical as well as chemical means [2–5].

There are striking analogies between polypyrrole and unhydrogenated amorphous semiconductors of the tetrahedrally coordinated type such as a-Ge, a-Si and III-V compounds [6]. A variation in electrical conductivity with thickness has been found for such semiconducting films [7]. It is expected that similar variations might be found in the polypyrrole films. In this paper, we have studied some of the electrical properties such as DC conductivity and thermoelectric power of polypyrrole films doped with tetrafluoroborate ions for several films having different thicknesses.

### 2. Preparation of polypyrrole

#### 2.1. Reagents

Pyrrole (Eastman Organic Chemicals, USA) was distilled at a reduced pressure of 60–70 mm Hg. The central fraction of the distillate was collected and stored in dark under

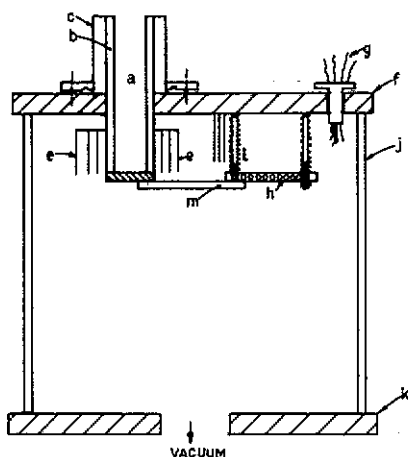
$N_2$  at 263 K. The supporting electrolyte,  $Bu_4NBF_4$  (Fluka), was used without further purification. Nitrobenzene (analytical reagent (AR), S.D. Fine Chemicals) was fractionally crystallized thrice, about one third of the total being thrown away as a liquid each time. It was then washed successively with sulphuric acid (1:1), water, sodium hydroxide and water. Alkali washing was continued until the washings were no longer coloured. It was then dried over anhydrous calcium chloride and fractionally distilled twice under reduced pressure (less than 10 mm Hg) from activated alumina using a packed column 1 m long. The middle fraction was collected and stored in a coloured bottle under a  $N_2$  atmosphere.

## 2.2. Film formation

Polypyrrole films were prepared by electrochemical oxidation of pyrrole on a Pt anode with a constant potential of 2.3 V impressed between the Pt electrodes placed 1 cm apart in a one-compartment cell which contained a solution of pyrrole (0.1 M) and  $Bu_4NBF_4$  (0.1 M) in nitrobenzene. Before polymerization, the solution was deoxygenated by purging with nitrogen gas for 15 min, and electro-oxidative polymerization was carried out with a very slow bubbling of nitrogen just below the solution surface from behind the counter-electrode. For maximum reproducibility, the Pt electrodes were always treated in the same way before each experiment. First, the electrodes were cleaned off the polymer and then immersed in warm chromic acid solution for 30 min. Finally, they were thoroughly washed with double-distilled water. Films of different thicknesses were prepared by varying the polymerization time. After polymerization, the films were washed with acetone, peeled off the electrode surface with a razor blade, washed several times with acetone and dried in vacuum at room temperature for 72 h. For physical measurements, films obtained on the surface of the anode facing the counter-electrode were always used.

## 3. Experimental details

The films of different thicknesses were subjected to electrical conductivity and thermoelectric power measurements starting from room temperature to lower temperatures. The experiments in both the cases, were performed in high vacuum of the order of



**Figure 1.** Schematic diagram of the apparatus for the measurement of thermoelectric power: a, inner cylinder; b, outer cylinder; c, outer coaxial chamber; e, heat shield; f, top plate; g, electrical leads; h, heater; j, Pyrex glass cylinder; k, base-plate; l, brass rod; m, glass slide containing sample.

70  $\mu\text{Pa}$  in a cryostat specially made for this purpose. The necessary set-up is shown in figure 1. The main evacuation chamber was simply a conventional coating unit with the exception that the glass bell-jar was replaced by a glass cylinder  $j$  open at both ends. For thermoelectric power measurements, hot and cold heads were fixed on the aluminium plate  $f$  which was placed on the top end of the glass cylinder. The hot end was made of a thick copper block with holes  $h$  drilled laterally through it for the insertion of heating elements. The copper block was mounted on the aluminium plate with four rods  $l$  made of brass having adjustable nuts and springs which took care of any misalignments regarding mating of the substrate with the hot end. The other end of the substrate  $m$  was at the cold end  $a$  which was fixed. Heat shielding  $e$  of the hot and cold heads was achieved by using alternative plates of mica and Teflon. The samples were mounted on glass substrates using thermally conducting but electrically insulating paints. Measuring leads were attached to the film by silver paste (Acheson Colloids Co., UK) and taken out of the vacuum chamber through proper vacuum seals. Copper-constantan thermocouples were used to measure the temperatures at the two ends.

An integral method was used to determine the Seebeck coefficients (i.e. the derivative of thermo-EMF with respect to temperature) at different temperatures. The temperature of the hot end was kept at constant room temperature by passing a current through the heater whenever necessary whereas the cold end was cooled. A microvoltmeter (model Keithley 177 microvolt DMM) was used to measure the temperature and thermo-EMF.

For conductivity measurements, the samples on glass substrates were mounted on the cold end only. Two thermocouples were attached to the specimens at two different points and the mean temperature was accepted. The experiments were done both during cooling of the specimen and subsequently during heating. In most of the samples the two sets of data agreed closely. However, a mean value was accepted. The resistances of the samples at different temperatures were measured using a constant DC source (Keithley model 224) and nanovoltmeter (Keithley model 181). The standard four-probe technique was used to measure the resistances.

#### 4. Results and discussion

The doped conjugated polymers are termed synthetic metals in view of the high conductivity of these materials, but the temperature coefficient of resistivity is opposite to that of a metal, i.e. the resistivity of these polymers increases with decreasing temperature. The conductivity is generally explained by the variable-range hopping (VRH) model [8] originally proposed for amorphous semiconductors. On the assumption of photon-assisted hopping between localized states the VRH model relates the conductivity  $\sigma$  to temperature  $T$  as

$$\sigma = \sigma_0 \exp[(-T/T_0)^{-1/\gamma}]. \quad (1)$$

The exponent  $\gamma$  in the above equation is connected with the dimensionality of the charge transport in the solid.  $\gamma$  is 4 for three-dimensional and 3 for two-dimensional transport.

For three-dimensional transport (i.e.  $\gamma = 4$ ) [9]

$$T_0 = 24/\pi r_0^3 kN(E_F) \quad (2)$$

$$\sigma_0 = (9/4) \sqrt{3/2\pi} e^2 \gamma_0 \sqrt{r_0 N(E_F)/kT} \quad (3)$$

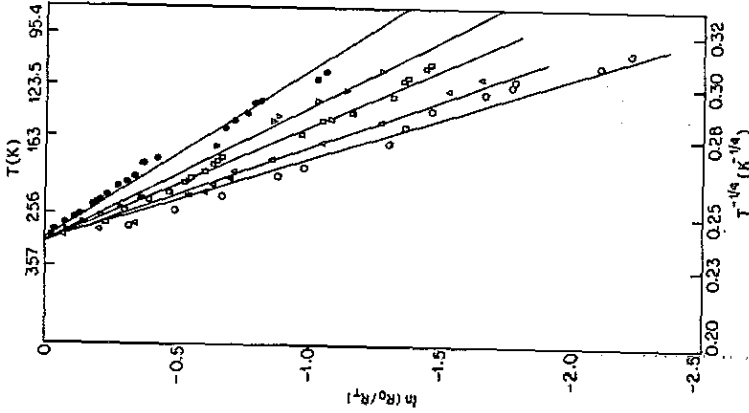


Figure 2. Variation in  $\ln(R_0/R_r)$  as a function of  $T^{-1/4}$  (where  $R_0$  is the resistance at room temperature and  $R_r$  is the resistance at absolute temperature  $T$ ) for films of various thicknesses.  $\circ$ , 32.6  $\mu\text{m}$ ;  $\Delta$ , 38  $\mu\text{m}$ ;  $\square$ , 44.4  $\mu\text{m}$ ;  $\nabla$ , 57.1  $\mu\text{m}$ ;  $\bullet$ , 81.7  $\mu\text{m}$ .

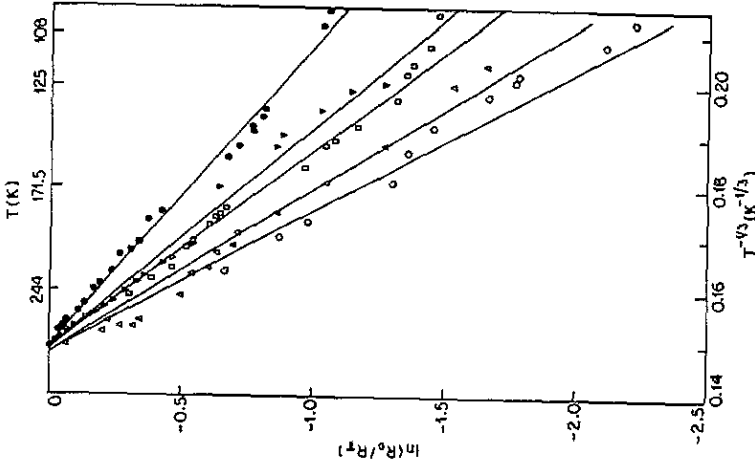


Figure 3. Variation in  $\ln(R_0/R_r)$  as a function of  $T^{-1/3}$  for films of various thicknesses:  $\circ$ , 32.6  $\mu\text{m}$ ;  $\Delta$ , 38  $\mu\text{m}$ ;  $\square$ , 44.4  $\mu\text{m}$ ;  $\nabla$ , 57.1  $\mu\text{m}$ ;  $\bullet$ , 81.7  $\mu\text{m}$ .

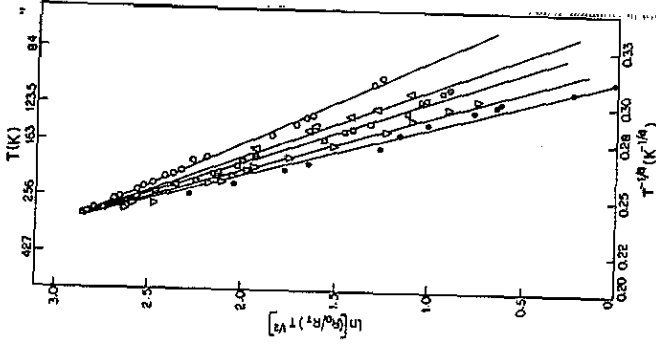


Figure 4. Variation in  $\ln[(R_0/R_r)T^{1/2}]$  as a function of  $T^{-1/4}$  for films of various thicknesses:  $\circ$ , 32.6  $\mu\text{m}$ ;  $\nabla$ , 38  $\mu\text{m}$ ;  $\square$ , 44.4  $\mu\text{m}$ ;  $\Delta$ , 57.1  $\mu\text{m}$ ;  $\bullet$ , 81.7  $\mu\text{m}$ .

where  $r_0$  is the localization length,  $k$  the Boltzmann constant,  $N(E_F)$  the density of states at the Fermi level and  $\gamma_0$  ( $=10^{12}$ – $10^{13}$  s $^{-1}$ ) the molecular vibration frequency. The hopping distance  $R$  has been defined by Mott and Davis [8] as

$$R = [3r_0/2\pi N(E_F)kT]^{1/4}. \tag{4}$$

A similar equation has been proposed by Epstein *et al* [10] using the VRH model:

$$\sigma(T) = K_0 T^{-1/2} \exp[-(T_0/T)^{1/4}] \tag{5}$$

where

$$T_0 = 16/r_0^3 kN(E_F)$$

and

$$K_0 = A[r_0 N(E_F)/k]^{1/2} \gamma_0 e^2 \tag{6}$$

$A$  being a constant.

The conductivity experiment has been done from room temperature down to 90 K. The data have been plotted as  $\ln(R_0/R_T)$  against  $T^{-1/4}$ ,  $\ln(R_0/R_T)$  against  $T^{-1/3}$  and  $\ln[(R_0/R_T)T^{1/2}]$  against  $T^{-1/4}$  in figures 2, 3 and 4, respectively, for five different thicknesses of the polymer film.  $R_0$  is the room temperature resistance and  $R_T$  is the resistance at temperature  $T$ . From the three sets of graphs it is difficult to ascertain the best fitting criterion unless the statistical distribution of the data about the least-squares fitted plot is taken into account. In fact, the correlation coefficients computed with the three sets of data indicate that they are  $-0.9964$ ,  $-0.9970$  and  $-0.9984$  for  $\gamma = 3$ , 4 and Epstein's model, respectively. These values have been quoted for the sample having thickness 81.7  $\mu\text{m}$ . So it seems that the fitting is best with Epstein's formulation (equation (5)). It has already been observed by Roth [11] that  $\gamma$  can have any value between 2 and 4 without changing very much the quality of fit which seems to hold good for our case also. Hence, the slopes  $T_0^{1/4}$  as obtained from equation (1) using  $\gamma = 4$  and equation (5) for samples of different thicknesses have been plotted in figure 5. The plot shows a systematic decrease of  $T_0^{1/4}$  with a saturation at higher thicknesses in both case I and case II. The change in the value of the slope was also observed by Knotek and Pollak [7] for an

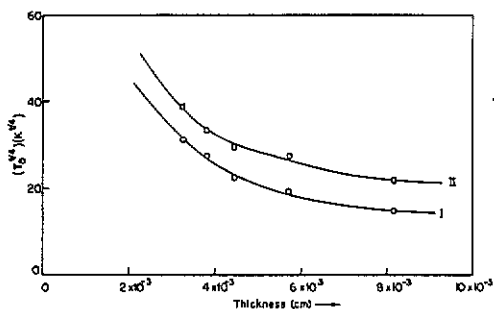


Figure 5. Variation in  $T_0^{1/4}$  with thickness: trace I, from the plots in figure 2; trace II, from the plots in figure 4.

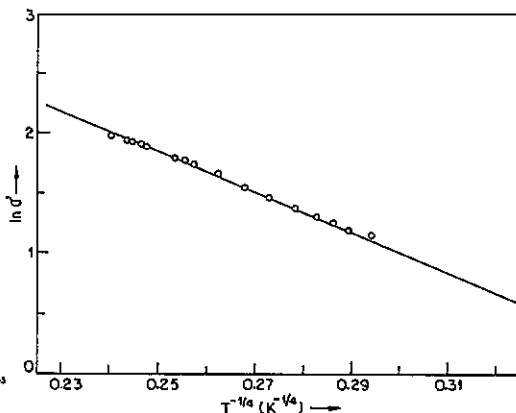


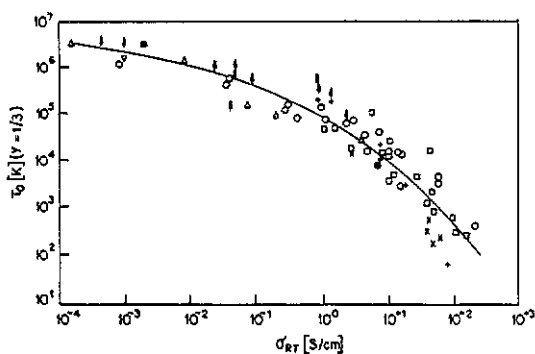
Figure 6. Variation in  $\ln \sigma$  as a function of  $T^{-1/4}$  for a film of thickness 81.7  $\mu\text{m}$ .

**Table 1.** The estimated values of slopes  $T_0^{1/4}$  from figure 5, density  $N(E_F)$  of states and hopping distance  $R$  assuming a localization length  $r_0$  of 10 Å.

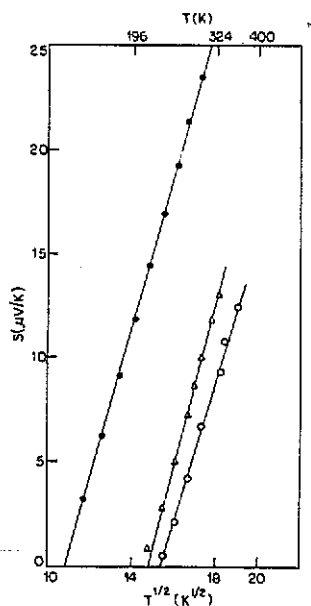
Trace no	$T_0^{1/4}$ (K <sup>1/4</sup> )	$T_0$ (K)	$N(E_F)$ (states eV <sup>-1</sup> cm <sup>-3</sup> )	$R$ (Å)
I	15	50625	$6.8 \times 10^{20}$	18
II	22	234256	$3.09 \times 10^{20}$	21.9

amorphous germanium film with a film thickness less than 500 Å in a  $T^{-1/3}$  plot. However, in this case the slope is independent of thickness in the conductivity plots on a  $T^{-1/4}$  basis for higher thicknesses. The cause of the change in slope with thickness in our case is not due to a dimensionality problem. As  $T_0^{1/4}$  is directly proportional to  $r_0^{-3/4}$  and  $[N(E_F)]^{-1/4}$ , the cause might be due to the variation in either of the two with thickness.

Electron diffraction studies [12] as well as XPS [4, 13] and UPS [14] data show that polypyrrole is highly disordered, producing an apparent localization of states in the band gap. Also from the observation on electrochemical cycling of the films of polypyrrole it is evident that the conductivity is due to spinless carriers, presumably bipolarons. Bredas *et al* [15] have calculated that in polypyrrole the formation of a bipolaron is favoured over two polarons by 0.45 eV and the calculated bipolaron length is about four pyrrole rings. Using the calculation of Bredas *et al* which has been further verified from UPS data [16], we have assumed that the hopping state is delocalized over four rings, i.e. the



**Figure 7.** Universal correlation between the room-temperature conductivity and its temperature dependence for various conducting polymers: □, polyacetylene; ○, segmented polyacetylene; +, polypyrrole; ×, polybipyrrole; △, substituted polypyrrole; ↑, polyaniline; ▽, polythiophene; ■, amorphous silicon; ●, this experiment.



**Figure 8.** Variation in thermoelectric power  $S$  with square root  $T^{1/2}$  of temperature for films of various thicknesses: ○, 38 μm; △, 67.1 μm; ●, 81.7 μm.

localization length  $r_0$  is of the order of 10 Å (the monomer dimension being about 3 Å). Equation (2) can now be used to have an estimate of  $N(E_F)$ . The results have been shown in table 1, where we have used the saturation values of  $T_0^{1/4}$  from figure 5.

The estimated magnitude of  $N(E_F)$  is similar to that obtained from ultraviolet spectroscopy [14], i.e.  $5 \times 10^{20}$  states  $\text{eV}^{-1} \text{cm}^{-3}$ . It is also possible to get an idea of  $\gamma_0$  from equation (3) using the intercept of the curve of  $\ln \sigma$  against  $T^{-1/4}$  (figure 6). The value of  $\gamma_0$  for the film having a thickness of 81.7  $\mu\text{m}$  thus estimated is  $2.37 \times 10^{13} \text{s}^{-1}$ .

It was observed by Roth [11] that there exists a correlation between  $\sigma(300 \text{ K})$  and  $T_0$  not only for polyacetylene treated with various dopants but also for a variety of conducting polymers. He has drawn a universal graph with the experimental points obtained with various polymers (figure 7) corresponding to  $\gamma = 3$ . Since the fit to experimental data does not change very much with the variation in exponent between 2 and 4, a similar universal graph might be drawn for  $\gamma = 4$ . However, as the detailed experimental data of all the materials shown in figure 7 are not available to us, we do not redraw the curve corresponding to  $\gamma = 4$ . Instead, we have chosen to compare the experimental data obtained by us corresponding to  $\gamma = 3$  with this universal curve drawn by Roth. The full circle in figure 7, which fits this curve well, further confirms the universality of the two parameters  $\sigma(300 \text{ K})$  and  $T_0$  as pointed out by Roth.

For disordered semiconductors in which VRH dominates, the thermopower is given by [17]

$$S(T) = (k^2/2e)[d(\ln N)/dE](T_0 T)^{1/2} \quad (7)$$

where the energy derivative of the density  $N$  of states is taken at the Fermi level.

The thermopower  $S(T)$  has been investigated for three films having thicknesses 38, 67.1 and 81.7  $\mu\text{m}$  and is shown in figure 8 in the temperature range 300–200 K as a function of  $T^{1/2}$ . Measurements could not be made below this temperature range, especially for thinner films as the curves show a sudden discontinuity. This was due to the stresses developed across the film which became evident as cracks in the film could be observed on inspection. However, for the thicker film (81.7  $\mu\text{m}$ ), we could go to a slightly lower temperature. The magnitude of the thermopower is found to be very small and p type within the temperature range of measurement. However, the plots are linear within this temperature range. Using the average slope of the plots in figure 8, the value of  $d(\ln N)/dE$  comes to about  $5 \text{ eV}^{-1}$ . At present, there are no other measurements of  $d(\ln N)/dE$  for polypyrrole system. However, the only data available are those for moderately doped polyacetylene which give  $2 \text{ eV}^{-1}$  [17]. This indicates that the above value for polypyrrole is quite plausible.

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