

DC Conduction in Electrochemically Synthesized Polypyrrole Films

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DC conductivity measurements were performed by modified four-probe rig on electrochemically synthesized polypyrrole films at a temperature range of -30°C to 120°C . Conductivity increased with temperature. The temperature dependence of conductivity was very high for lightly doped polymers, decreasing as the doping level increased. The model used to describe the conduction process was the conduction model originally developed for amorphous silicon by Mott and Davis. When applied to conducting polymers, it assumes that electron transport originates from localized or fixed states within the polymer chain. The charge transfer between the chains takes place by hopping, referred to as phonon-assisted hopping, between two localized states. Plots of DC conductivity versus temperature can be parametrized by Mott's Variable Range Hopping conduction model. The DC conductivity of polypyrrole films doped from light to intermediate levels with p-toluene sulphonic acid were measured in the temperature range of 77K to 300K. The localization length of localized electrons was assumed to be 3\AA , which is approximately equal to the length of the pyrrole monomer. Mott parameters of polypyrrole films doped with p-TS were evaluated at 300K and 10K. Results were found to be consistent with the Mott's requirement that $\alpha R \gg 1$. Theoretical values of α and $N(E_F)$ have been determined at approximately 10^8 cm^{-1} and $10^{19}-10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$, respectively. Hence according to Mott parameters determined by the experimental data for the p-TS doped polypyrrole samples, Mott parameters are seen to have a better agreement with those expected from disordered systems, particularly for lightly doped samples, indicating the suitability of Mott's model to these samples. The average hopping distance R decreased from 16\AA to 4.4\AA with the increase in the doping level from 0.006 M to 0.03 M at 300K, whereas at 10K, R decreased from 37\AA to 10\AA over the same dopant range.

Introduction

Until recently, polymers and electrical conduction were thought to be mutually exclusive. However, this view was proved to be incorrect with the synthesis of conducting polymers in the 1970's. Unusual properties of these polymers have led to extensive research resulting in better understanding and numerous commercial applications. Conductive polymers can be made by filling an insulating polymer matrix with conducting particles such as carbon black, metal flakes, or metallised fibres, or by chemical and electrochemical synthesis methods to produce intrinsically conducting polymers. The conductivity of the former is provided by

the filler material, and the function of the polymer matrix is to hold the material together in one piece. These conductive composites often replace metals when light weight, toughness, shapeability and corrosion resistance are required for the application. However, a considerably high concentration of the conducting filler is required to achieve acceptable levels of electrical conductivity, thus giving rise to poor mechanical properties in these composites. Conductivity in these materials is not an intrinsic property of the polymer chains but a property of the material as a whole.

The term "Intrinsically Conducting" refers to a polymer the conductivity of which is a property originating from its own electronic structure. A common feature of intrinsically conducting polymers (ICP) is the alternation of the double and single carbon bonds along the polymer backbone, referred to as π -bond conjugation. The conductivity is due to four conditions in their molecular organization: namely, the existence of charge carriers, an overlap of molecular orbitals to aid carrier mobility, π -bond mobility and charge hopping between polymer chains¹.

Intrinsically conducting polymers possess the unique property of wide ranging modification of their conductivity by the variation of electrolyte dopant anion concentration during electrochemical polymerization. Undoped conjugated polymers are insulating. However, conductivity can be increased by incorporating dopant counterions during polymerization. Small concentrations of the dopant anion results in semiconducting polymers with significant band gaps, whereas high dopant concentrations give rise to highly conducting polymers. That is why highly doped conducting polymers are often referred to as "synthetic metals"².

Although unstable, the most conductive polymer is polyacetylene. Conductivities up to 10^4 S/cm have been reported by Shirakawa³ et.al. Pure polyacetylene is the most semiconducting. Conductivity is achieved by chemical doping with an oxidizing agent such as iodine. The most stable polymers among ICPs are Polyheterocycles (polypyrrole and polythiophene). These polymers consist of five-membered cyclic ring molecules with a nitrogen or sulphur heteroatom. Pyrrole or thiophene monomers are ideally linked at $\alpha-\alpha'$ positions (lowest energy bonding) which provides free π -bond mobility.

Most ICPs are unprocessable. Therefore, physical properties of the polymer are determined at the synthesis stage. For example, the electrical, dielectric, microwave and morphological properties of the polymer can be tailored by adjusting synthesis parameters such as dopant and monomer concentration, dopant type, synthesis time, synthesis temperature and electrolyte pH. Ideally, the electrical properties of a metal would combine with the chemical and mechanical properties of a thermoplastic to produce a processible, tough and highly conducting polymer. In reality, most conducting polymers are unprocessable and possess poor mechanical properties when compared with conventional materials. However, significant developments have been made in the synthesis of soluble derivatives of ICPs and in the in situ synthesis in conventional thermoplastics⁴.

Experimental

Polypyrrole (PPy) films were galvanostatically synthesized with a range of p-toluene sulphonate (p-TS) dopant concentrations in a single compartment cell⁵.

DC conductivity measurements at a temperature range of 70K to 300K were made with a modified four probe rig similar to that described in ASTM D4496-87. A constant current was applied to the outer electrodes from a Keithley model 224 constant current source and potential drop between the inner electrodes was measured with a Keithley model 197 digital multimeter. The multimeter was interfaced to an IBM XT computer via an IEEE 488 bus for automated data collection. Impedance-phase measurements were made over a frequency range of 100 Hz to 1 MHz with a Hewlett-Packard 4194A Gain-Phase Analyzer. Electrical

contacts were made through gold electrodes, sputtered on polypyrrole films to achieve ohmic contacts.

The resistance of the sample was determined by the impedance-phase data ($Z - \theta$)

$$R = |Z| \cos \theta \quad (1)$$

Conductivity was then determined by

$$\sigma = \frac{1}{\rho} \frac{A}{RL} \quad (2)$$

where A is the cross-sectional area, L is the length, R is the resistance, ρ is the resistivity and σ is the conductivity of the polypyrrole film.

Results and Discussion

Although metallic behavior such as high reflectivity in the microwave region has been observed in highly doped conducting polymers⁶, the temperature dependence of conductivity was similar to that of amorphous semiconductors. In contrast with metals, conductivity increased with temperature (Fig. 1). The temperature dependence of conductivity was high for lightly doped polymers, decreasing as the doping level increased.

Conducting polymers are amorphous with short conjugation lengths. Therefore, it has been suggested that electrical conduction takes place by charge hopping between polymeric chains. A model used to describe the conduction process is the one originally developed for amorphous silicon by Mott and Davis⁷. When applied to conducting polymers, it assumes that electron transport originates from localized or fixed states within the polymer chain. The charge transfer between the chains takes place by hopping, referred to as phonon assisted hopping, between two localized states. Lattice vibrations enhance this process of tunneling from one localized state to another. Plots of DC conductivity versus temperature can be parametrized by Mott's Variable Range Hopping conduction model. The DC conductivities of polypyrrole films doped from light to intermediate levels with p-toluene sulphonic acid were measured in the temperature range of 70K to 300K. Temperature dependence of dc conductivity as a function of $T^{-1/4}$ can be seen in Figure 2.

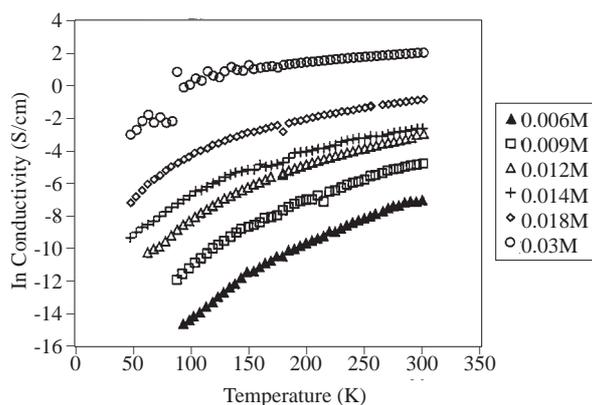


Figure 1. Variation of DC conductivity of polypyrrole films with temperature

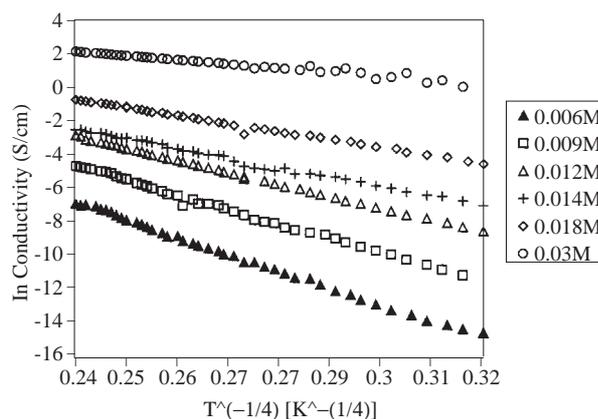


Figure 2. Natural log of DC conductivity vs Temperature ($T^{-1/4}$) for polypyrrole films with different doping levels

Most conducting polymers showed a temperature dependence of DC conductivity consistent with the

Variable Range Hopping Conduction process, obeying the following relationship:

$$\sigma = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right] [S \text{ cm}^{-1}] \quad (3)$$

where Mott's parameters are listed as follows:

$$\sigma_0 = e^2 R^2 v_{ph} N(E_F) \quad (4)$$

$$T_0 = \frac{\lambda \alpha^3}{k N(E_F)} [K] \quad (5)$$

$$R = \left[\frac{9}{8\pi \alpha k T N(E_F)} \right]^{1/4} [cm] \quad (6)$$

$$W = \frac{3}{4\pi R^3 N(E_F)} [eV] \quad (7)$$

where

σ	=	conductivity of sample at temperature $T(K)$
σ_0	=	pre-exponential factor ($S \text{ cm}^{-1}$)
T_0	=	characteristic temperature (K)
e	=	electronic charge ($1.602 \times 10^{-19} \text{C}$)
k	=	Boltzmann's constant ($8.616 \times 10^{-5} \text{ eV K}^{-1}$)
R	=	average hopping distance (cm)
v_{ph}	=	phonon frequency ($\approx 10^{13} \text{ Hz}$)
$N(E_F)$	=	density of localized states at the Fermi level ($\text{cm}^3 \text{ eV}^{-1}$)
λ	=	dimensional constant (≈ 18.1)
α	=	coefficient of exponential decay of the localized states (cm^{-1})
W	=	hopping activation energy (eV)

Taking the natural logs of both sides of Eq. (3), the following relationship is obtained:

$$\ln \sigma = \ln \sigma_0 - (T_0)^{1/4} (T)^{-1/4}. \quad (8)$$

As seen in Figure 2, the straight line nature of the $\ln \sigma$ vs $T^{-1/4}$ plots justifies the validity of Eq. (3) for the polypyrrole samples studied here.

Pre exponential factor σ_0 and temperature T_0 were calculated from the slopes and y -intercepts of the plots in Figure 2. Mott's parameters were calculated by substituting the values of σ_0 and T_0 , determined from Figure 2, into the Eqs. (4 to 7)⁸, which relate σ_0 and T_0 to Mott's parameters. The localization length of localized electrons was assumed to be 3 Å, which is approximately equal to the length of the pyrrole monomer. Mott parameters of polypyrrole films doped with p-TS, evaluated at 300K and 10K, are listed in the following table.

Results were found to be consistent with Mott's requirement that $\alpha R \gg 1$. Theoretical values of α and $N(E_F)$ have been determined as approximately 10^8 cm^{-1} and $10^{19} - 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$, respectively⁹. Hence, by referring to Mott parameters determined by using the experimental data for the p-TS doped polypyrrole samples (Table 1), it can be seen that Mott parameters, particularly for lightly doped samples, had a better agreement with those expected from disordered systems, indicating the suitability of Mott's model to these samples. The average hopping distance R decreased from 16Å to 4.4 Å with the increase in the doping level from 0.006 M to 0.03 M at 300K, corresponding to about 5 to 1.5 monomer units, respectively, whereas at 10K, R decreased from 37Å to 10Å over the same dopant range, corresponding to about 12 to 3

monomer units. Maddison et.al.¹⁰ have observed a similar trend in a study of temperature dependence of electrical conductivity of p-TS doped PPy films with the hopping distance ranging between 4-5 Å at 300K and 9.5-12.2 Å at 10K. However, such a difference in the magnitude of $R(T)$ values between the results presented here and that of Maddison et.al. is reasonable as PPy films synthesized by Maddison et.al. had higher concentrations (0.1M p-TS) of the dopant, corresponding to higher conductivity levels than the films used in this work. The results indicated agreement with the Variable Range Hopping model for charge transport in polypyrrole over a wide temperature and doping range. Mott parameters for lightly doped samples had a better agreement with those expected from disordered systems, indicating the suitability of the model particularly for these samples.

Table 1. Mott parameters for p-TS doped polypyrrole films for $T = 300\text{K}$ and $T = 10\text{K}$.

$p - TS[M]$	$\sigma_0[S\text{cm}^{-1}]$	$T_0[K]$	$N(E_F)$ [$\text{cm}^{-3}\text{eV}^{-1}$]	$R(300\text{K})$ [cm]	$R(10\text{K})$ [cm]	$W[eV]$
0.006	2.5×10^7	1.0×10^8	7.0×10^{20}	1.6×10^{-7}	3.7×10^{-7}	0.0089
0.009	6.5×10^6	5.2×10^7	1.3×10^{21}	1.3×10^{-7}	3.1×10^{-7}	0.0763
0.012	1.0×10^6	2.4×10^7	2.9×10^{21}	1.1×10^{-7}	2.6×10^{-7}	0.629
0.014	4.6×10^4	9.5×10^6	7.4×10^{21}	8.7×10^{-8}	2.0×10^{-7}	0.0497
0.016	3.4×10^4	4.8×10^6	1.5×10^{22}	7.3×10^{-8}	1.7×10^{-7}	0.0419
0.03	8.4×10^3	6.6×10^5	1.1×10^{23}	4.4×10^{-8}	1.0×10^{-7}	0.0255

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