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Direct Current Conductivity Studies on Poly(3-methyl thiophene)

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Abstract

The direct current (DC) conductivity of poly(3-methyl thiophene) was measured in the temperature range of 77–300 K. The observed DC conductivity data were analyzed in the light of Mott's variable range hopping model. Different Mott's parameters such as characteristic temperature (T_0), average hopping distance (R), average hopping energy (W), and density of states at the Fermi level (N [E_F]) were evaluated. By taking the inverse of the coefficient of exponential decay of the localized states involved in the hopping process as 0.5 nm, a realistic value of density of states at the Fermi level (N [E_F]) was obtained that agrees well with the values reported earlier for other conjugated polymers.

Index Entries: Poly(3-methyl thiophene); direct current conductivity; average hopping distance; average hopping energy; density of states; localized states.

Introduction

The electronic properties of conducting polymers have acquired growing importance in the field of material science. There exist a wide variety of phenomena in the charge transport of these materials owing to the fact that the conductivity of these polymers spans a wide range from semiconducting to metallic regime depending on doping. Out of various conducting polymers, the polythiophene family of polymers has emerged as one of the promising candidate materials for device applications, which necessitates the study of their mechanism of charge transport in girth. Poly(3-methyl thiophene) (P3MT) belongs to the polythiophene family of polymers, which

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have good chemical and environmental stability with excellent electronic and optical properties suitable for various device applications *(1)*. The conduction mechanism has been widely investigated in the case of polyacetylene, polypyrrole, polythiophene, polyparaphenylene, polyaniline, and so on. Several theoretical models have been put forward by Su et al. *(2)* and Kivelson *(3,4)* to explain the observed spinless conduction in *trans*-polyacetylene, but none of the existing models account for the conduction processes satisfactorily *(5)*. The polythiophene family of polymers has nondegenerate ground states, and it has been suggested that polarons and bipolarons are the dominant charge carriers. In polypyrrole three absorption peaks at 0.7, 1.4, and 2.1 eV have been observed and have been interpreted in terms of transitions associated with polaron states *(6)*. Several electronic spin resonance and optical measurements on polythiophene and polypyrrole have been reported for determining the nature of electronic excitation in them. In spite of extensive studies of magnetic susceptibility in the polyheterocyclics, it has not been conclusively established whether the electronic charge carriers are polarons or bipolarons *(7)*. For preparing a biomolecular membrane from P3MT, it was thought worthwhile to study the mechanism of charge transport in this system. Very few reports are available on the temperature dependence of direct current (DC) electrical conductivity of polythiophene *(8)*. However, the detailed investigation of charge transport in these systems is lacking. In the present article, we report the DC conductivity measurement on P3MT in the temperature range of 77–300 K. The observed data have been analyzed in the light of Mott's variable range hopping (VRH) model *(9)*.

Materials and Methods

P3MT, having a dopant concentration of 0.2 *M* ferric chloride ($FeCl_3$), has been synthesized by chemical oxidative polymerization technique described elsewhere *(10)*. The synthesis of the polymer has been confirmed by Fourier transform infrared studies *(10)*. The dried powder was ground properly and pressed at a pressure of $\sim 5 \times 10^8$ Pa in a hydraulic press to form pellets. Gold electrodes were vacuum evaporated on both sides of the samples, making an Au-polymer-Au structure for the measurement of DC conductivity. The DC conductivity was measured in the temperature range of 77–300 K with a four-probe as well as two probe techniques using a Keithley 220 constant current source, Keithley 617 electrometer, and Keithley 2000 DMM.

Results and Discussion

The variation in DC conductivity (σ_{dc}) as a function of $10^3/T$, $T^{-1/2}$, $T^{-1/3}$, and $T^{-1/4}$, respectively, is shown in Fig. 1A–D. From Fig. 1A it is obvious that the temperature dependence of σ_{dc} does not follow an Arrhenius-type of behavior. To obtain a better fit, we have analyzed the results in terms of Mott's VRH model *(9)*, in which the DC conductivity shows the temperature

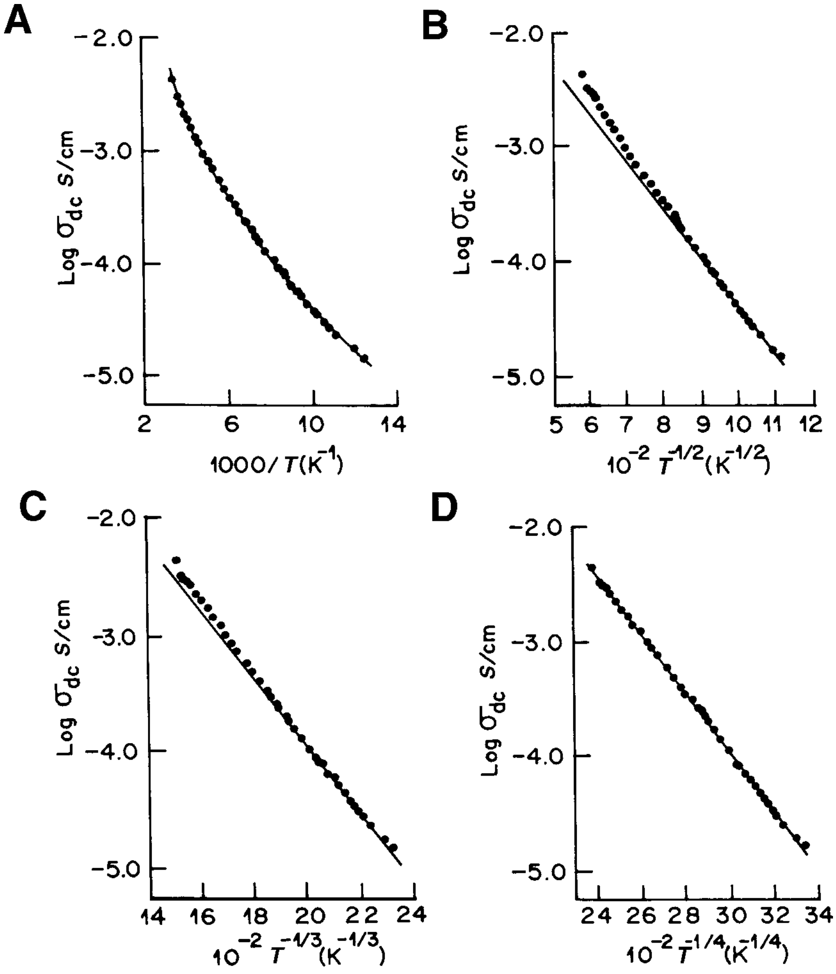

Fig. 1. Plot of log σ_{dc} as functions of **(A)** 1000/T, **(B)** $T^{-1/2}$, **(C)** $T^{-1/3}$, and **(D)** $T^{-1/4}$ for 0.2 M P3MT.

dependence of the type T^{-S}. Here, the parameter $S = 1/(\mathrm{d} + 1)$, in which d is the dimensionality. This gives $S = 1/2$ for one-dimensional, $S = 1/3$ for two-dimensional, and $S = 1/4$ for three-dimensional hopping conduction. The DC conductivity data deviate from the straight-line fit in the high-temperature region for $T^{-1/2}$ and $T^{-1/3}$ (Fig. 1B,C). However, a straight line was obtained in the case of $T^{-1/4}$ (Fig. 1D) over the whole temperature range of 77–300 K, suggesting that electrical conduction is dominated mainly by a mechanism based on three-dimensional hopping conduction, confirming the applicability of Mott's VRH model *(9)* in P3MT. Such a conductivity behavior of P3MT can be assumed to consist of two components, namely, σ_B and σ_H,

$$\sigma = \sigma_B + \sigma_H \qquad (1)$$

in which σ_B (intrachain conductivity) can be described by the mechanism of conduction for the band conduction model and is larger than the σ_H contribution (between the chains). Therefore, the total observed conductivity σ_{dc} of P3MT might be correlated with the conductivity σ_H for the hopping of charge carriers between the chains *(11)*. We consider Mott's relation *(9)* for the DC conductivity as

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \tag{2}$$

In Eq. 2 σ_0 and T_0 are constants and can be expressed as

$$\sigma_0 = e^2 R^2 \upsilon_{ph} N(E_F) \tag{3}$$

and

$$T_0 = \lambda\alpha^3/k_B N(E_F) \tag{4}$$

in which

$$R = [9/8\pi\alpha k_B T N(E_F)]^{1/4} \tag{5}$$

T_0 is the characteristic temperature, σ_0 is the conductivity at infinite temperature, e is the electronic charge, υ_{ph} is a phonon frequency (~10^{13} Hz), and R is the hopping distance between the two sites. λ is the dimensionless constant *(12,13)* and is assumed to be ~18.1, $\alpha(=1/r_p)$ is the coefficient of exponential decay of the localized states involved in the hopping process, k_B is the Boltzmann's constant, and $N(E_F)$ is the density of states at the Fermi level *(12,13)*. The average hopping energy, W, can be estimated by knowing the hopping distance, R, and the density of states at the Fermi level $N(E_F)$ using the following relation:

$$W = 3/4\pi R^3 N(E_F) \tag{6}$$

The value of T_0 has been estimated from Fig. 1D and is ~1.4372×10^7 K. The calculated values of $N(E_F)$, R, and W from the Eqs. 3–6 are 1.169×10^{20} cm^{-3} eV^{-1}, 2.7744×10^{-7} cm, and 0.0956 eV, respectively, after assuming a reasonable value *(8)* of $\alpha^{-1} = 0.5$ nm. The magnitude of the value of $N(E_F)$ is consistent with the values obtained for other conjugated polymers.

The variable range hopping apparently fits the data points in the present investigations (Fig. 1D). The temperature-dependent activation energy (calculated from Fig. 1A), suggests that the variable range hopping can also be qualitatively explained if hopping of polarons is considered. It has been suggested by Holstein *(14)* that for an ordered material having polaronic conduction, the multiphonon processes are gradually replaced at lower temperatures by the processes in which the only contribution to the jump frequency of the polaron is owing to the single optical phonon absorption and emission *(14,15)*. The variation in activation energy for such a process *(14,15)* is given by

$$E'_A/E_A = [\tanh(\hbar\omega_0/4k_B T)/(\hbar\omega_0/4k_B T)] \tag{7}$$

in which $\omega_0 = 2\pi\upsilon_{ph}$, $\hbar = h/2\pi$, E_A is the room temperature activation energy, and E'_A is the activation energy calculated at different temperatures using

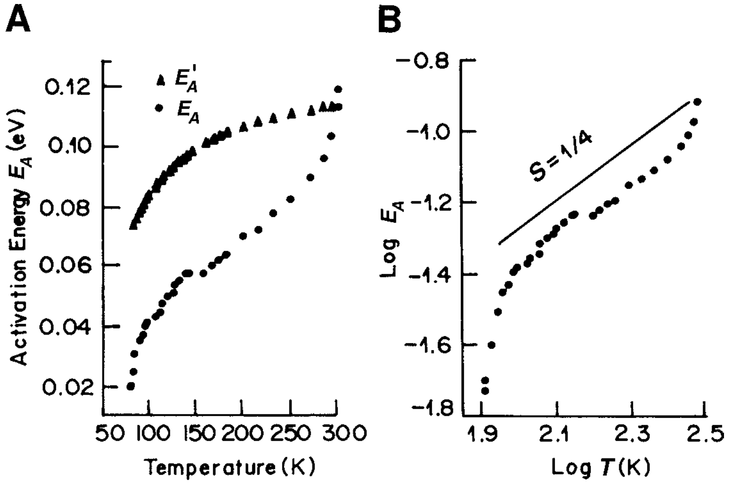

Fig. 2. **(A)** (●) Calculated activation energy E_A as a function of temperature and (▲) calculated activation energy E'_A using Eq. 7; **(B)** (●) calculated activation energy E_A as a function of temperature plotted on a log-log scale. The solid line corresponds to $T^{-1/4}$; slope $S = 1/4$.

Eq. 7 and the value of $\upsilon_{ph} \sim 10^{13}$ Hz. The theoretical plot of the right-hand side of Eq. 7 is shown by a solid line in Fig. 2A. The polaronic hopping conduction can give temperature-independent activation energy where the multiphonon process dominates. However, the temperature-dependent activation energy (Fig. 2A) rules out the above possibility, confirming the existence of a VRH conduction mechanism in P3MT. Similar results have been obtained for other conjugated polymers *(8,12,15)*.

Conclusion

The observed temperature dependence of DC conductivity of P3MT can be explained by assuming that the polaronic hopping conduction is the dominant conduction mechanism as envisaged by Mott's VRH conduction model for disordered systems. The present investigations yielded a realistic value of density of states that agrees well with the values reported earlier for other conducting polymers.

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