

Investigations on the mechanism of carrier transport in plasma polymerized pyrrole thin films

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ABSTRACT

Plasma polymerization is found to be an excellent technique for the preparation of good quality, pinhole-free, polymer thin films from different monomer precursors. The present work describes the preparation and characterization of polypyrrole (PPy) thin films by ac plasma polymerization technique in their pristine and *in situ* iodine doped forms. The electrical conductivity studies of the aluminium–polymer–aluminium (Al–polymer–Al) structures have been carried out and a space charge limited conduction (SCLC) mechanism is identified as the most probable mechanism of carrier transport in these polymer films. The electrical conductivity shows an enhanced value in the iodine doped sample. The reduction of optical band gap by iodine doping is correlated with the observed conductivity results.

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1. Introduction

Polypyrrole (PPy) was first recognized as an electrical conductor by Kanazawa et al. and it was synthesized by electrochemical oxidation of pyrrole [1]. Even though the polymerized form of this material is widely studied, the electrical transport properties of this material are not completely understood. Most of the studies on PPy that appeared in literature are on its electrochemically synthesized form. There are some reports on the ionic conductivity and the charge transfer mechanism in PPy [2]. The conductivity of PPy is found to be in the range of 200–500 S/cm in its PF₆ doped form. The dc conductivity of PPy is a function of preparation conditions, nature of dopants and temperature. The disorder induced localization and the metal insulator transition in PPy is also reported [1,3]. Plasma polymerization is an easy and inexpensive technique for the preparation of PPy thin films. The optical and electrical properties of PPy films prepared by radio frequency (rf) plasma polymerization techniques is thoroughly described by Kumar et al. [4]. In the present work we have chosen plasma polymerization at 50 Hz (alternating current ac) as a complementary technique for the preparation of PPy thin films. Plasma polymerization in general is a technique for producing polymer-like organic materials in the form of thin films with the aid of a plasma discharge. The plasma discharge energizes and dissociates the monomer molecules into

neutral particles and reactant fragments in the form of electrons, ions and free radicals. The product of recombination of these fragments on a substrate is a highly branched and cross linked three dimensional network—a plasma polymer. However by optimizing the plasma parameters viz. Yasuda parameters [5], the extent of branching and cross linking in the plasma polymer can be controlled.

Being a dry method, plasma polymerization is suitable as a polymer thin film deposition technology in the microelectronics industry. Plasma polymerized films have a variety of applications as low dielectric constant (*low-k*) intermetallic coatings [6,7], surface modifications, barrier coatings, dielectric photoresist and wave guiding films for microelectronics and photonics [8]. The nature of the carrier transport mechanism in the plasma polymer film is highly significant as far as its applications as both passive and active components in microelectronics and optoelectronics are concerned. Hence in the present work attempts have been made to analyse in detail the dc conduction mechanism in pure and iodine doped samples of PPy prepared by ac plasma polymerization.

2. Experimental

2.1. Preparation of thin films

PPy thin films were prepared by ac plasma polymerization technique and the schematic of the plasma reaction chamber is given in Fig. 1. The set-up consists of two stainless steel electrodes, each of diameters 0.23 m and placed 0.04 m apart. Ultrasonically cleaned glass substrates were used for polymer thin

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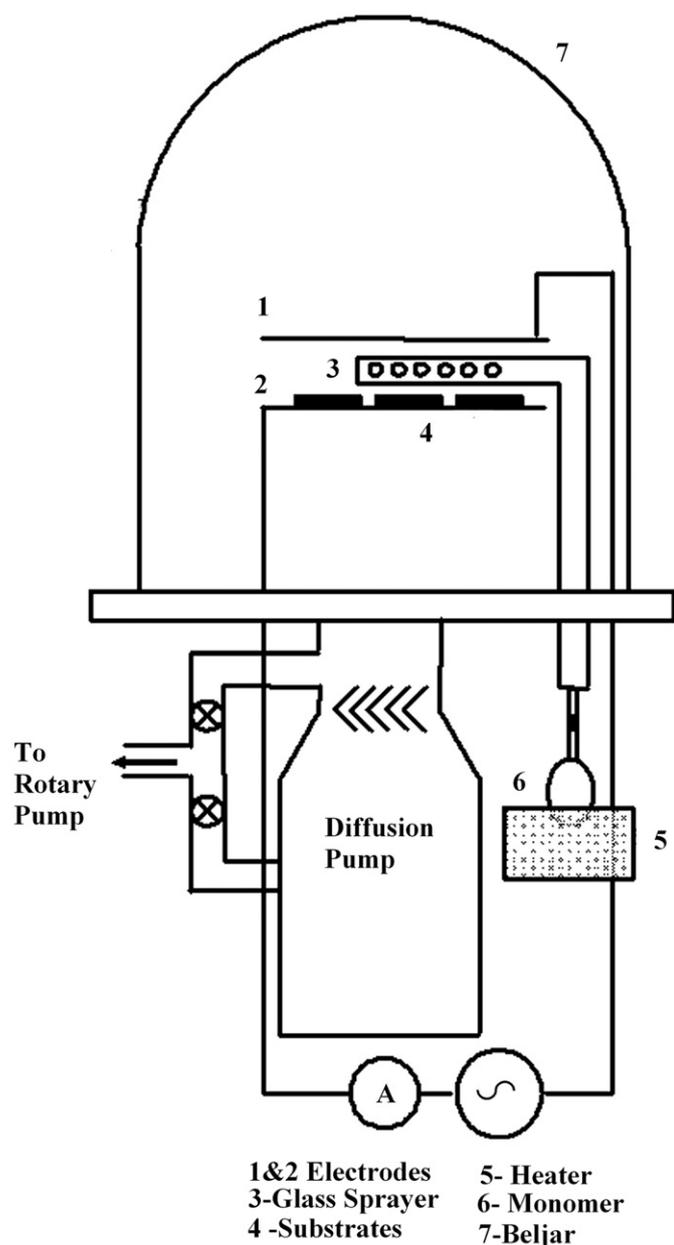


Fig. 1. Set-up for ac plasma polymerization.

film deposition. The glow discharge chamber was evacuated using a rotary pump at a pressure of 0.2 Torr. Plasma discharge was obtained in the chamber by applying an ac voltage of 1000 V of frequency 50 Hz between the electrodes and the current was kept at 70 mA. Monomer was injected into the glass chamber at the region between the electrodes by means of a glass sprayer. The flow rate was carefully controlled using a needle valve.

2.2. In situ doping of iodine

Iodine doping was carried out by introducing iodine vapour into the plasma polymerization chamber along with the monomer vapour by means of a separate glass feed through. The introduction of iodine vapour into the chamber was carried out in such a way that the introduction of dopant gas did not affect the vacuum inside the vacuum chamber. The thin films prepared in the iodine atmosphere were heated at 340 K for about an hour in a vacuum of 10^{-5} Torr for expelling the part of the iodine that was not incorporated in the polymer matrix.

2.3. Preparation of metal–polymer–metal structures and J – V studies

To study the current density–voltage (J – V) characteristics metal–polymer–metal (m–p–m) sandwich structures were prepared. This m–p–m configuration was of the form aluminium–PPy–aluminium with an effective area of $2.5 \times 10^{-5} \text{ m}^2$. The electrodes were deposited on a conventional vacuum thermal evaporation unit at a pressure of 10^{-5} Torr. The Al electrode thickness was about 100 nm. The detailed description of the preparation of m–p–m structure is reported elsewhere [6].

For the electrical conductivity studies, m–p–m structures were placed in a home-made conductivity cell. A bias voltage in the range 1–60 V (step 1 V each) was applied and the current flowing through the films was measured using an automated Keithley 236 Source Measure Unit (SMU). All the measurements were taken under a dynamic vacuum of the order of 10^{-2} Torr.

2.4. Film thickness measurements and UV–vis absorption studies

Thickness of the samples was measured by a Dektach 6M thickness profiler. Ultraviolet–visible (UV–vis) spectra of pure and iodine doped PPy films were recorded using Jasco 570 UV–vis–NIR spectrophotometer. The absorption coefficient (α) was calculated from the spectrum by dividing the αd value obtained from the UV–vis measurement by the film thickness (d) and it was plotted against the photon energy for pure and iodine doped PPy thin films. The band gap (E_g) values of the thin films were obtained from the Mott plot by plotting the $(\alpha hv)^{1/2}$ vs. hv and then extrapolating the linear portion of the plot to $(\alpha hv)^{1/2} = 0$. The dielectric constant of the pure and doped thin films was measured using an HP 4192A LCR Meter in a dynamic vacuum of 10^{-2} Torr by suitably placing the samples in a home-made conductivity cell.

3. Results and discussions

3.1. UV–vis absorption studies

The photon absorption in many amorphous materials is found to obey the Tauc relation [8], which is of the form

$$\alpha hv = B(hv - E_{opt})^n \quad (1)$$

where α is the absorption coefficient, hv the photon energy, B a constant and the index n is connected with the distribution of density of states [9,10].

The plasma polymers at high energies exhibit a linear relationship given by the relation

$$(\alpha hv)^{1/2} = B(hv - E_{opt}) \quad (2)$$

Plots of $(\alpha hv)^{1/2}$ vs. hv is given in Fig. 2. This plot is called Mott plot and the transition energies were evaluated from this plot. The linear portion of the plot when extrapolated to the energy axis corresponds to the threshold of optical absorption. From this band gap energy is calculated. The optical band gap of pure PPy is found to be 1.75 eV. In the iodine doped samples the optical band gap is found to be 1.35 eV. The decrease in the optical band gap can be correlated with the increase in electrical conductivity of the films. A probable reason for this enhancement is that the hole density of the polymer is increased by the doping of iodine. The iodine doping attracts the electrons from the molecular orbitals and produces a sublevel gap or additional level in the band structure, and due to the incorporation of iodine, the band gap between the $\pi \rightarrow \pi^*$ state decreases as a result of increase in the length of the conjugated π system [11]. This is the reason for the modification of the Mott plot in the doped sample. Similar results were reported in

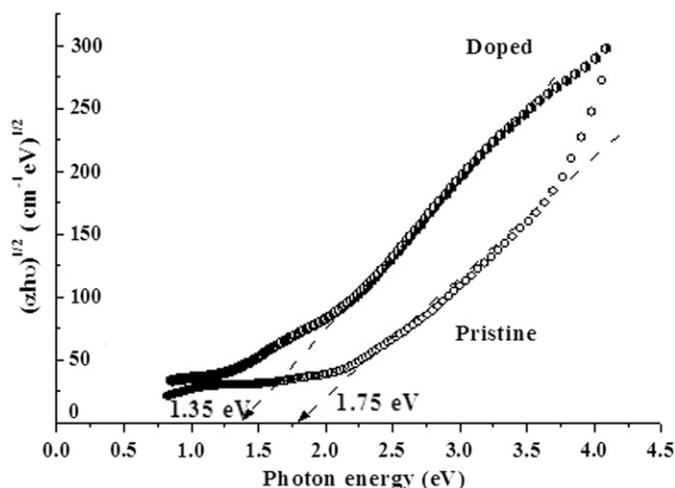


Fig. 2. Mott plot for the calculation of the band gap of pure and *in situ* iodine doped PPy thin films.

polythiophene thin films [12]. The high conductivity of doped polymer films can be attributed to the formation of a charge transfer complex between the pyrrole ring and the oxidative dopant iodine. Some transition energy levels are developed in between the optical band gaps due to the local defects created in the polymer when it is doped. These defects can be charged defects that participate in conduction. The absorption peak obtained at almost 1.35 eV in the doped samples indicates the presence of bipolarons, as reported in the case of plasma polymerized polythiophene thin films by Silverstein and Visoly-Fisher [12].

3.2. Current density–voltage (*J*–*V*) studies

The *J*–*V* characteristics of the polymer thin films are depicted in Figs. 3(a, b) and 4(a, b). The thicknesses of the films are indicated in these figures. The *J*–*V* characteristics at room temperature show a non-ohmic behaviour at higher voltages and an ohmic behaviour in the low voltage region for both pure and *in situ* iodine doped PPy films. It is observed that there is no breakdown of the samples even at higher voltage (60 V) for both pure and iodine doped films. The conductivity values show an order of enhancement in the doped film. The doping of iodine increased the amorphous nature and the enhancement of the irregularities of the polymer thin film, which leads to low mobility and diffusion of the carriers in the polymer matrix. Due to this the enhancement of electrical conductivity is not very much pronounced in the doped films, when compared to the electrochemically doped pyrrole structures given in Table 1.

The double log(*J*–*V*) plot of the films shows space charge limited conduction (SCLC) with a linear behaviour at low bias voltages and a nonlinear behaviour at higher voltages. The equation of conductivity will follow Ohm's law at lower voltages:

$$J = \mu n_0 e \frac{V}{d} \quad (3)$$

where *e* is the electronic charge, *V* the voltage applied, *d* the inter-electrode distance or the film thickness of the sample film and μ the mobility of the carriers [13]. Here the thickness of the film has a prominent role in the value of *J* as in the case of voltage dependence according to the relation

$$J = e\mu N_v \left(\frac{\epsilon_r \epsilon_0}{ePkT_t} \right)^L \frac{V^{L+1}}{d^{2L+1}} \quad (4)$$

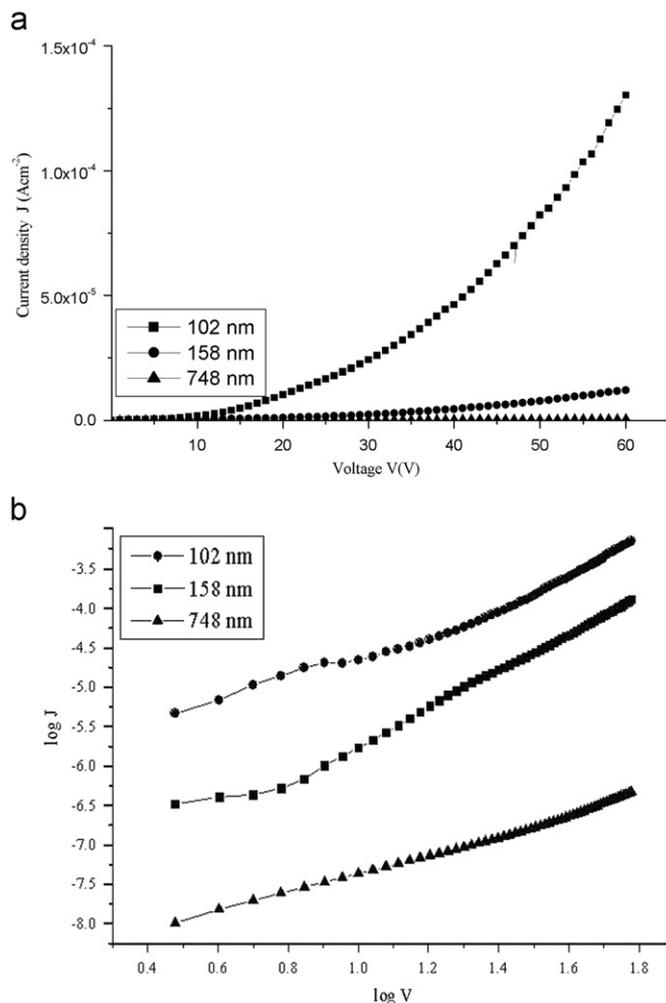


Fig. 3. (a) *J*–*V* characteristics of plasma polymerized pyrrole thin films in the pure form. The thickness of the films is indicated. (b) Double log(*J*–*V*) plots of plasma polymerized pyrrole thin films in the pure form. The thickness of the films is indicated. The value of V_c for the film of thickness 102 nm = 8 V, and for 158 nm = 15 V. For a thin film of thickness 748 nm, such an abrupt increase in current is not observed.

Here *P* is the trap density per unit energy range at the valence band edge, ϵ_0 is the permittivity of free space (8.85×10^{-12} F/M) and $\epsilon_r = 2.92$ in pure PPy and 2.62 in iodine doped PPy, which were calculated from the capacitance measurements. In this equation, *L* is the ratio T_t/T where *T* is the ambient temperature and T_t is the temperature parameter describing the exponential trap distribution. The change over from the ohmic to SCLC conduction takes place at a particular voltage V_c known as transition voltage given by

$$V_c = \left(\frac{P}{N_v} \right)^{1/L} \frac{eN_t d^3}{\epsilon_0 \epsilon_r} \quad (5)$$

Here it is found that the value of V_c depends on the thickness of the film. The values of V_c for PPy thin films of different thicknesses are indicated in the *J*–*V* characteristics. At voltages above V_c , the electron current sharply increases from the ohmic behaviour. For films of larger thickness a sudden transition from ohmic to SCLC is not observed and in that case diffusion of charge carriers in between the electrodes should also be taken into account. Generally the transition from SCLC to trap filled limit (TFL) is an extremely sharp transition [15]. A more gradual increase is observed in the present case. The absence of a sharp increase in the current indicates that the carrier transport in PPy can be

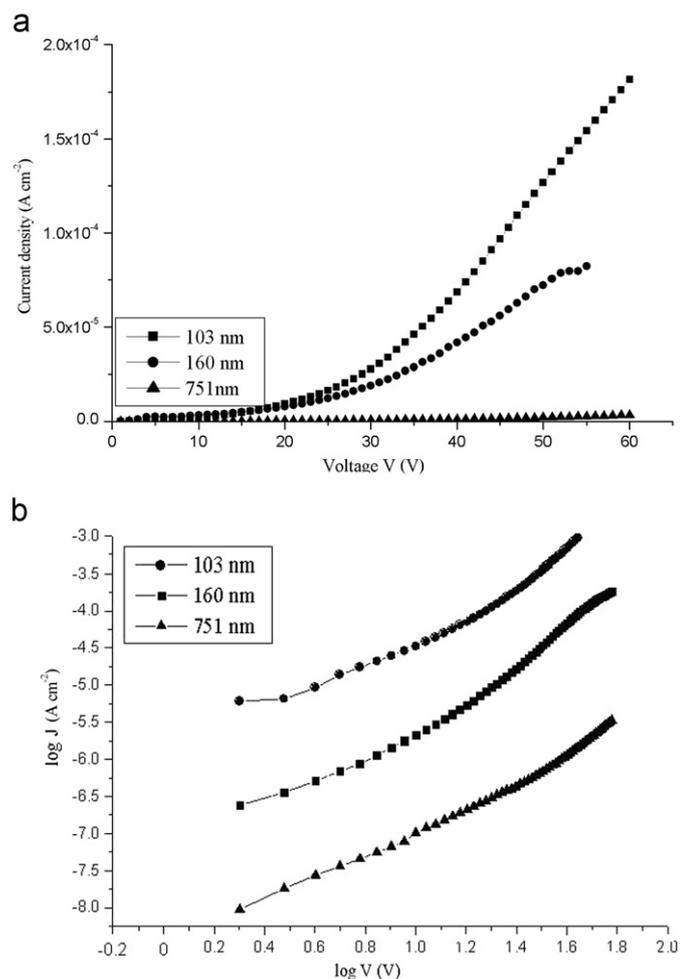


Fig. 4. (a) J - V characteristics of plasma polymerized pyrrole thin films in the iodine doped form. The thickness of the films is indicated. (b) Double $\log(J$ - $V)$ plots of plasma polymerized pyrrole thin films in the iodine doped form (inset). The thickness of the films is indicated. The value of V_c for the film of thickness 103 nm = 7 V, and for 160 nm = 9 V. For a thin film of thickness 751 nm, such an abrupt increase in current is not observed.

Table 1

Electrical conductivity of PPy prepared by chemical, rf and ac plasma polymerized forms. Their references are cited.

	Preparation technique	Conductivity (S/cm)
1	Electrochemical synthesis (PPy-PF3)	200–500 [16] 100–500 [3]
2	Pyrrole microtubes	10^{-1} – 10^2 [17]
3	Chemical preparation	$(3-5) \times 10^{-4}$ [18]
4	Paratoluene sulfonate doped PPy	32–365 [19]

regarded as trap free. Due to this, a sharp increase in current after the space charge region, which is characteristic of a trap filled conduction mechanism, has not been observed in both pristine and doped films even at high voltages (60 V).

At voltages greater than V_c , the SCLC current density is given by the Mott–Gurney relation

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_p \frac{V^2}{d^3} \quad (6)$$

where $\epsilon_0 \epsilon_r$ is the permittivity of the polymer, μ_p the hole mobility and d the thickness of the film. From the slope of the $\log J$ - $\log V$ plot (Figs. 3(b) and 4(b)), it is to be observed that the current density J depends quadratically on the voltage V , which is

characteristic of SCLC, and after this region the quadratic dependence of J on V changes to a trap filled limit (TFL) with slope > 2 . The slope of the graph found in the high voltage region is about 3, and an abrupt increase in current is not observed as reported in Refs. [14,15].

The thickness dependence of the space charge limited current follows the relation $j \propto d^{-n}$ where n is a parameter that depends on the trap distribution and is equal to or greater than three in the presence of traps. The $\log J$ vs. $\log d$ plots of pure and iodine doped films are given in Figs. 5 and 6, respectively, for voltages 4, 10 and 25 V. These plots provide an idea of the dependence of current density on the thickness for PPy films. The slope of the plot for different voltages is shown in Figs. 5 and 6. These values confirm that space charge limited conduction is the prominent carrier transport mechanism in the high voltage region in the case of PPy films [14].

It can be seen from the literature that PPy prepared by techniques other than plasma polymerization exhibits a dc electrical conductivity greater than that of the plasma polymerized thin films. A few reported values of the electrical conductivity of PPy, prepared by different techniques in different forms are

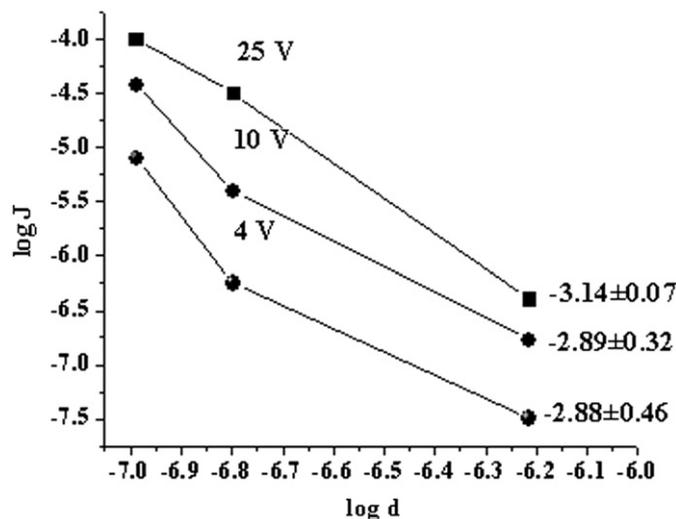


Fig. 5. $\log J$ vs. $\log d$ (thickness) plot of pure PPy.

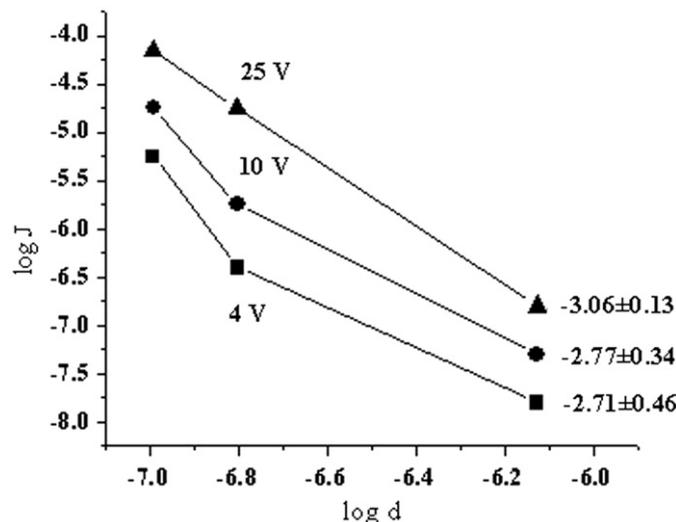


Fig. 6. $\log J$ vs. $\log d$ (thickness) plot of iodine doped PPy. The values of the slope of the plot are indicated.

given in Table 1. It can also be seen that the value of dc conductivity of rf plasma polymerized thin films reported by Sakthi Kumar et al. [4] is less when compared to the dc electrical conductivity of the ac plasma polymerized pyrrole thin films reported in this paper.

4. Conclusions

Investigations on the electrical and optical properties of plasma polymerized pyrrole thin films were carried out. The electrical conductivity studies have revealed that the dominant carrier transport mechanism in these thin films is SCLC. An electric field induced enhancement of the conductivity is also observed. It is noted that the band gap of the pure samples shows a higher value when compared to the iodine doped ones. The decrease in band gap and the enhancement in conductivity are explained on the basis of an enhanced hole density and the presence of charge defects due to the incorporation of iodine into the polymer matrix.

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