Organic Electronics 52 (2018) 288–294

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Electric field activated nonlinear and disorder-induced charge transport in doped polymer devices

Motiur Rahman Khan*, K.S.R. Koteswara Rao, R. Menon

Department of Physics, Indian Institute of Science, Bangalore, 560012, India

ARTICLE INFO

Keywords:
Charge transport
Organic semiconductor
Nonlinear
Variable range hopping
Scaling

ABSTRACT

In the present study, temperature dependent conductivity and field dependent nonlinear transport are adopted to provide insight into the charge transport in poly(3-methylthiophene) polymer thin film devices that are electropolymerized at different temperatures. The samples obtained at different temperature show relative disorder quantified by the conductivity ratio, $\sigma_r = \sigma$ (84 K)/σ (300 K) which is further correlated with the morphology of the samples. Charge transport in each sample is governed by variable range hopping mechanism and the parameters like density of states at the Fermi level [$N(E_F)$], average hopping distance (R) and average hopping energy (W) have been estimated. Electric field activated nonlinear transport is described by multistep tunneling model of Glazman-Matveev (GM model) over four separate channels of conduction. It is concluded that the field dependent conductivity has a 'field-scale' in all the samples where the conductivity converges to a single master curve in the temperature range of observation. The results obtained from the conductivity ratio and temperature dependent conductivity are strongly supported by electric field dependent conductivity and nonlinear exponents.

1. Introduction

Charge transport in organic semiconductors and conducting polymers has been quite contentious and triggered several debates in the last few decades [1–3]. The diversities in synthesis process introduce different kind of disorder that lead to the localization of carriers like polarons, bipolarons etc., created by doping or impurity [4,5]. Although organic semiconductors have been researched as an emerging class of materials for their executable applications in various fields owing to their multifaceted properties, the conduction mechanism operating the devices is yet to be addressed in detail [6,7]. Conducting polymers synthesized by electrochemical methods have been the focus of early research. The electrical and mechanical properties of the electrochemically prepared polymers depend on many different factors such as electrolyte or doping anion, solvent, substrate electrode, synthesis current or potential etc. [8–10]. Apart from these material parameters, conditions like synthesis temperature, de-doping current and pH values of the electrolyte can vary the structural and energetic disorder together with the surface morphology finally affecting the charge transport mechanisms [11,12]. To understand the basic physics and to improve the device performance, efficiency, charge transport studies in these polymers are important. Apart from the intrinsic electronic properties of the polymeric materials, other factors such as the metal electrode work function, surface morphology of the polymer, polymer-metal interface and the electrode geometry, etc., also have major influence on the charge transport properties [13,14]. Doping dependent charge transport has been widely studied in conducting polymers. A transition in transport mechanism from bulk-limited to contact-limited has been observed at different doping levels by several groups [15–17]. Electric field dependent charge transport studies along with the temperature provide more insights about the transport phenomena [18]. In highly doped polypyrrole, metal-insulator transition is observed by just applying pressure which leads to change in disorder of the sample [19]. In recent reports, efforts are made to understand the effect of disorder on transport in polymer devices, wherein disorder was tailored through de-doping time and temperature in the course of electropolymerized [20–22]. We have reported recently that effect of injection barrier on transport properties in poly(3-methylthiophene) [P3MeT] devices could be observed for certain doping and trap concentrations [23]. Therefore, the carrier density and disorder play a vital role in charge transport among localized and delocalized states often leads to a wide range of possibilities like variable range hopping, interpolaronic hopping, tunneling, etc. [8,24,25]. The detailed reports on the temperature, field dependent studies, effect of synthesis temperature on the disorder and transport properties in conducting polymers are lacking, although some reports have shown the change in

* Corresponding author.
E-mail address: mrkhan.iisc@gmail.com (M.R. Khan).

http://dx.doi.org/10.1016/j.orgel.2017.10.039
Received 1 September 2017; Received in revised form 19 October 2017; Accepted 28 October 2017
Available online 02 November 2017

morphology with temperature of synthesis [26–29].

In the present study, P3MeT polymers were synthesized electrochemically at different temperatures and the role of disorder on the charge transport is investigated. The effect of synthesis temperature on charge transport properties has been studied. Current-voltage (*I–V*) and dc conductivity measurements were performed as a function of temperature on different P3MeT samples to investigate the disorder induced by varying the temperature of synthesis. The role of disorder on the charge transport is studied and explained by fitting the experimental data to Mott's variable range hopping model. While VRH could explain the low field linear conductivity, the high field nonlinear behavior is analyzed and GM model is found to be quite suitable. An effort is made to construe the role of electric field on the disorder and nonlinear behavior of charge transport in case of each sample. The correlation between the morphology and charge transport properties is examined through the granular structure and roughness of the polymer films. Such a comprehensive study of conductivity as a function of temperature and electric field could be instrumental in determining the charge transport in P3MeT system, also correlates well with the disorder and film morphology.

2. Materials and methods

To obtain electrochemically polymerised poly(3-methylthiophene) samples, a solution was prepared in propylene carbonate solvent containing 3-methylthiophene monomer and tetrabutylammonium hexafluorophosphate ($TBAPF_6$) of 0.12M concentration each. $TBAPF_6$ served as electrolyte as well as dopant (PF_6^-). High purity chemicals were obtained from Sigma Aldrich. The solution was purged with high purity nitrogen gas for 30 min prior to the electropolymerisation. RF sputtered platinum coated (100 nm) glass substrates were used as working electrodes and a thin stainless steel sheet was used as counter electrode. Prior to the synthesis, the electrodes were cleaned with triple distilled water, acetone, isopropyl alcohol and then dried in oven at 120 °C. Polymer thin films were synthesized in a two terminal electrochemical cell on Pt electrodes in the nitrogen ambience by applying 2 mA/cm^2 of current for 3 min. The samples PDT1, PDT2 and PDT3 were prepared at synthesis temperatures of 30 °C, 0 °C and −30 °C respectively by applying 2 mA/cm^2 current for 3 min. The de-doping is carried out for 15 s with 0.5 mA/cm^2 current in opposite polarity for all the samples. All films were cleaned with propylene carbonate to remove the excess electrolyte and monomer present on the sample surface followed by drying in vacuum for 12 h. The thickness of all the films were measured by atomic force microscopy (AFM) and found to be ~ 1 μm.

To carry out the electrical measurements, semi-dried silver paste was used as the top contact, while Pt served as the bottom contact to the polymer films. Temperature dependent *I–V* measurements were performed with a source meter (model Keithley 2400) and electrometer (model Keithley 6514) interfaced to a computer in a custom-made cryostat dipped in a liquid nitrogen bath down to 84 K. A calibrated Pt resistance thermometer (Pt100) along with the Lakeshore DRC91C were used as temperature sensor and controller. The dc conductivity measurements were performed using a constant current source (model Keithley- 220) and the voltage was measured through an electrometer (model Keithley- 6514). The current values were typically in the range of 1–10 μA, chosen to avoid any sample heating at low temperature. Atomic force microscopy (AFM) measurements were carried out on all the polymer films just after drying, using NT-MDT, Russia. The morphology of all the samples were analyzed from scanning electron microscopy (SEM) using ZEISS instrument.

3. Results and discussion

The AFM images for all the films exhibited granular morphology, while granular size and surface roughness reduced with temperature of synthesis (Fig. 1).

This was further supported by SEM images wherein PDT3 exhibited more continuous and smoother surface morphology compared to PDT1 and PDT2 (Fig. 2).

However, the inter layer stacking in vertical direction and change in length of polymer chain with synthesis temperature might affect the transport properties. This has been further explored in the following detailed transport studies. The de-doping current and time are taken less to avoid their effect on electrical characteristics and also to investigate the temperature effect on the same. Temperature dependent current-voltage characteristics for all the devices are shown in Fig. 3 down to 84 K. Their symmetric behavior with different top and bottom electrodes proves the Ohmic contact and declaims the contact-limited transport possibility. The PDT1 shows the least temperature dependence in current, which is otherwise pronounced in PDT2 and PDT3. Due to high current at room temperature all measurements are done up to 1 V. Further analysis using log-log plots of *I–V* characteristics revealed Ohmic conduction at low voltages for all the devices, while at higher voltages nonlinear behavior is obtained (in log-log scale). This substantiates that power law behavior or any type of space charge limited conduction (whether trap free or trap limited) is not the driving force in the charge transport in these devices.

For further investigation of transport mechanism, temperature dependent resistance measurements are performed on all the films as shown in Fig. 4. It is observed that change in resistance with temperature is maximum in PDT3 and decreases with increasing the synthesis temperature (PDT3 > PDT2 > PDT1). The conductivity ratio $\sigma_r = \sigma\,(84\text{ K})/\sigma\,(300\text{ K})$ is calculated for all the samples.

The σ_r is used to quantify the relative disorder, which further helps to classify the different transport regimes in conducting polymers [19,30,31]. The temperature dependent resistance for PDT3 reflected a monotonic decrease with temperature accompanied with increment in the conductivity ratio for all the devices. The conductivity ratio σ_r is 8, 27 and 97 for PDT1, PDT2 and PDT3 respectively, indicating that PDT3 is highly disordered among all the samples. Contrarily, some reports have found less disorder and high in-plane conductivity in polypyrrole synthesized at lower temperatures [19]. Therefore, to investigate the effect of synthesis temperature on electrical properties, further efforts are made to fit the conductivity with Mott's 3D VRH model.

Charge transport in organic semiconducting polymers is mainly governed by hopping and tunneling processes. The presence of structural and electronic defects helps in carrier transport in such systems [1]. Upon doping in organic semiconductors, polarons are created which are responsible for conductivity and it can be shown by electronic structure calculations for polymer chains considering electron-phonon interaction. Phonon-assisted hopping of charge carriers between localized states in conducting polymers is the dominant transport mechanism usually observed at intermediate temperatures and mainly attributed to inter-chain transport. Although there are many studies on transport, variable range hopping (VRH) model has been most successful to explicate transport mechanism in conducting polymers [1,19,30,31].

The conductivity in this model as predicted by Mott and Davis is given by Refs. [32,33]

$$\sigma(T) = \sigma_h \exp\left[-\left(\frac{T_0}{T}\right)^m\right] \tag{1}$$

where σ_h is the highest limit of conductivity, T_0 is Mott's characteristic temperature for the material and the exponent $m = 1/(1 + d)$ is considered as the signature of the VRH in which d gives the dimensionality of the charge transport in the material.

The measured temperature dependence of dc conductivity for all P3MeT samples is fitted to 3D VRH model, shown in Fig. 5.

However, deviations from VRH model were apparent and exhibit a direct relationship with synthesis temperature; 290 K in PDT1, which is 272 K for PDT2 and 267 K for PD3. Mott's parameters can be calculated