

# **Electrical transport and dielectric relaxation studies of poly(3,4-ethylenedioxythiophene) nanostructures**

## **Abstract**

Conducting polymers have received considerable interest as futuristic materials for the development and production of the next generation electronics and opto-electronics devices since the discovery of highly conducting polyacetylene in 1977. Although conducting polymers exhibit comparable or lower electrical conductivity than that of conventional inorganic materials, they offer unique characteristics such as tunable electronic properties, facile synthesis, light weight, flexibility and low cost. These special properties emanate from the conjugated chain structure of the conducting polymers. The chains interact in a complicated manner and form an irregular network leading to their unique properties, which could be used to fabricate optoelectronic devices such as flexible display, printable organic integrated circuits, organic light emitting diodes, solar cells, keyboards etc. Nanostructure science and technology is a broad and interdisciplinary area of research and development activity which has been growing explosively worldwide for the past few years. The nanostructures exhibit novel optical, magnetic, and electrical properties as compared to their bulk counterparts, which arise due to large surface to volume ratio and quantum confinement effects. Recently conducting polymer nanostructures viz., nanoparticles, nanofibers, nanotubes etc. have received remarkable attention among the scientific community owing to their potential to meet the demand for various technological and biomedical applications. Despite the significant progress in the field of conducting polymer nanostructures, both in terms of fundamental and technological viewpoints, charge transport mechanism in such disordered low dimensional structures has not been fully understood. DC resistivity and magnetoresistance are the primary tool to understand the charge transport mechanism in a material. Impedance spectroscopy is a non-destructive technique to characterize the electrical and charge carrier relaxation behavior of materials under the application of an alternating electric field. The charge transport and charge carrier relaxation behavior are the two fundamental aspects for designing electronic devices. In the present thesis, an

effort has been made to understand the charge transport mechanism in poly(3,4-ethylenedioxythiophene) (PEDOT) nanostructures viz., nanoparticles, nanofibers and nanotubes with systematically varying dopant concentration.

A variety of conducting polymers such as polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh) and poly(3,4-ethylenedioxythiophene) (PEDOT) have been investigated by different research groups due to their diverse properties that can be modified for a given application. Among the family of conjugated conducting polymers, poly(3,4-ethylenedioxythiophene) has emerged as a promising material for diversified applications because of its distinctive properties like high environmental stability, high conductivity at ambient temperature, high optical transparency in doped state and moderate optical band gap (1.5-1.6 eV). The presence of ethylenedioxy group at 3- and 4- position in 3,4-ethylenedioxythiophene (EDOT) monomer restricts the possibility of side chain reactions during polymerization resulting in PEDOT with longer conjugation length.

The present thesis covers the studies on the charge transport and charge carriers relaxation dynamics in poly(3,4-ethylenedioxythiophene) nanostructures. We have synthesized three different poly(3,4-ethylenedioxythiophene) nanostructures, namely, dodecylbenzene sulfonic acid (DBSA) doped nanoparticles, sodium dodecyl sulfate (SDS) doped nanofibers and camphorsulfonic acid (CSA) doped nanotubes by self-assembly method. The structural, vibrational and thermal properties of the synthesized nanostructures have been characterized by high resolution transmission electron microscope (HRTEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), micro-Raman spectroscopy ( $\mu$ -Raman) and thermogravimetric analyzer (TGA). The DC resistivity measurements have been carried out in the temperature range of 5 – 300K to understand the charge transport mechanism. Isothermal magnetoresistance measurements have been performed at different temperatures of 5, 10, 20, 30, 50, 100, 200 and 300 K in the magnetic field ranging from 0 - 8T. AC conductivity analysis has been performed to explore the charge carriers dynamics under alternating electric field. Dielectric properties have been studied to

understand the polarization mechanism and the relaxation dynamics of charge carriers through the framework of impedance and modulus formalisms.

The present thesis contains seven chapters and each chapter is divided into several sections and sub-sections. **Chapter 1** begins with the historical background of conjugated conducting polymers, including their salient features and structures. Different doping mechanisms and formation of charge carriers upon doping have been discussed. Brief discussions about the conducting polymer nanostructures and their various synthesis processes have been presented. The structure, properties, polymerization and doping of poly(3,4-ethylenedioxythiophene) (PEDOT) are briefly summarized. Charge transport mechanism and the factors that affecting the charge transport have been discussed. The scope of the thesis and statement of the thesis problem are presented at the end of the chapter.

The different theoretical models that have been implemented to analyze the results of the research work carried out in the present thesis are discussed in **Chapter 2**. The theories regarding the DC resistivity, magnetoresistance, impedance spectroscopy and AC conductivity have been described. Theory employed to study the thermal degradation kinetics and determine the thermal activation energy has also been discussed at the end of this chapter.

The physico-chemical properties of parent materials and different experimental techniques used for the synthesis and characterization of PEDOT nanoparticles, nanofibers and nanotubes in the present thesis work have been summarized in **Chapter 3**. Contents include the physical properties of the parent materials used for the synthesis of PEDOT nanoparticles, nanofibers and nanotubes viz., monomer (3,4-ethylenedioxythiophene), oxidant ( $\text{FeCl}_3$ ), dopants and solvents. The synthesis routes adopted for the preparation of PEDOT nanoparticles, nanofibers and nanotubes have been presented with block diagram. The different characterization tools viz., HRTEM, XRD, FTIR, micro-Raman spectroscopy, TGA, DC resistivity, AC conductivity and impedance spectroscopy employed in the present thesis work have been briefly described.

**Chapter 4** is devoted to the structural, vibrational and thermal properties of poly(3,4-ethylenedioxythiophene) nanoparticles, nanofibers and nanotubes. The shape and size of the synthesized PEDOT nanostructures are determined by using HRTEM. X-ray diffraction study shows the semi-crystalline nature of PEDOT nanostructures. The degree of crystallinity increases with increasing dopant concentration for all the PEDOT nanostructures, which is attributed to the enhancement of polymer chains ordering in the nanostructures. FTIR and micro-Raman spectroscopy provide information about the different bond vibrations present in PEDOT nanostructures. The Raman spectra of PEDOT nanoparticles and nanotubes show that the  $C_{\alpha}=C_{\beta}$  symmetric stretching deformation band is shifted towards lower wavenumber with increasing dopant concentration, which indicates the conformational transition from benzenoid to quinoid structure. Thermogravimetric analysis reveals the increase of thermal stability of the nanostructures with increasing dopant concentration.

The transport properties of poly(3,4-ethylenedioxythiophene) nanoparticles, nanofibers and nanotubes have been investigated in **Chapter 5**. The temperature dependent resistivity for all the nanostructured systems shows semiconducting behavior i.e. resistivity decreases with increasing temperature in the measured temperature range of 5 – 300 K. From the resistivity analysis, it is observed that the dopant type and dopant concentration have significant effect on the charge transport mechanism. The decrease in resistivity with increasing dopant concentration can be ascribed to the introduction of traps in the highest occupied molecular orbital (HOMO)- lowest unoccupied molecular orbital (LUMO) gap, which increases the hopping rate. The negative slope of reduced activation energy vs. temperature plots indicates that the synthesized samples fall in the insulating regime of the metal-insulator transition. The charge transport in DBSA doped nanoparticles and SDS doped nanofibers follows 3D variable range hopping (VRH) mechanism, whereas a crossover from 3D VRH mechanism to 1D VRH mechanism is observed in CSA doped nanotubes below 10 K. In case of nanotubes the presence of larger bulky cycloaliphatic ring of CSA anion restricts the twisting of polymer chains while it fills up the space between the polymer chains. At low temperatures (< 10 K), the charge carriers have less thermal energy as a result they

cannot make inter-chain hopping due to the absence of chain twisting leading to 1D VRH mechanism in case of CSA doped nanotubes. However, the long alkyl chains in DBSA and SDS cannot restrict the twisting of polymer chains, which leads to random orientation of polymer chains resulting in the 3D VRH mechanism in nanoparticles and nanofibers. The decrease of characteristic Mott temperature ( $T_{\text{Mott}}$ ) with increasing dopant concentration for all the nanostructures can be attributed to the enhancement of polymer chains ordering in the nanostructures (nanoparticles, nanofibers and nanotubes). The smaller value of  $T_{\text{Mott}}$  ( $9.2 \times 10^3$  K) for 1M CSA doped sample leads to smaller value of room temperature resistivity ( $0.04 \Omega \text{ cm}$ ).

The isothermal magnetoresistance (MR) has been measured at eight different temperatures of 5, 10, 20, 30, 50, 100, 200 & 300K in the magnetic field range of 0 – 8 T. The MR values show a transition from positive to negative with increasing temperature for all the nanostructures. The positive to negative cross-over temperature is found to decrease with increasing dopant concentration for all the nanostructures and can be attributed to the increased polymer chain ordering in the nanostructures. The high value of negative MR ( $\sim 3.58\%$ ) in case of 1M CSA doped PEDOT nanotubes indicates the higher delocalization of charge carriers giving rise to the smaller room temperature resistivity of  $0.04 \Omega \text{ cm}$ .

The frequency dependent conductivity exhibits two distinct regimes for all the PEDOT nanostructures: the frequency independent plateau at lower frequency ( $<10^4$  Hz) and a frequency dependent part at higher frequency. The frequency region of constant conductivity extends to higher frequency with increasing dopant concentration and temperature indicating the enhancement of DC conductivity. The frequency independent conductivity is due to the free charges that undergo random diffusion via activated hopping. The frequency dependent conductivity in the higher frequency regime is ascribed to the activation of the trapped charges in the polymeric system. The temperature dependence of universal frequency exponent  $s$  reveals that under AC electric field the correlated barrier hopping (CBH) is the dominating charge transport mechanism in the nanostructured systems. The scaling behavior of AC conductivity at

different temperatures suggests that the conduction mechanism is independent of temperature.

**Chapter 6** presents a comprehensive study on dielectric properties and charge carrier relaxation of poly(3,4-ethylenedioxythiophene) nanoparticles, nanofibers and nanotubes. The dielectric permittivity formalism has been performed to obtain information about the charge carrier polarization. It is observed that all the samples exhibit high values of  $\epsilon'$  and  $\epsilon''$  in the low frequency region that decrease with increasing frequency attaining a constant value at about  $10^6$  Hz. The high values of real part of dielectric permittivity at lower frequencies ( $< 10^4$  Hz) can be attributed to the interfacial polarization effect that arises due to the charge carrier accumulation at the electrode-sample interface. From the fitted plots of real part of dielectric permittivity with Havriliak-Negami (HN) equation it is observed that for PEDOT nanoparticles and nanofibers, the charge carriers follow Debye relaxation, whereas in PEDOT nanotubes they follow non-Debye relaxation. This may be attributed to the strong confinement of charge carriers in case of nanoparticles and nanofibers. Impedance and modulus formalisms are powerful approach to understand the conductivity relaxation dynamics of charge carriers. The imaginary part of impedance and modulus spectra exhibits relaxation peak which shifts towards higher frequency with increasing temperature and dopant concentration for all the nanostructures. The shifting of relaxation peak towards higher frequency indicates the decrease of relaxation time of charge carriers leading to the higher conductivity. The scaling behavior of imaginary parts of impedance and modulus spectra at different temperatures indicates that the charge carrier relaxation in these systems is temperature independent.

Finally in **Chapter 7**, the major conclusions drawn from the present work have been presented. In the end of this chapter, the potential future scope in the field of conducting polymers nanostructures has been highlighted.