Preface

The Thesis reports charge transport studies on conducting polymers, polymer-carbon nanotube composites and organic semiconductor devices. Conducting and semiconducting polymers consisting of π-conjugated chains have attracted considerable attention as they combine the optoelectronic properties of semiconductors with mechanical properties and processing advantages of plastics. The chemical/electrochemical/photodoping of these semiconducting polymers can tune the Fermi levels and conductivity in a controlled way, and hence the properties of devices can be easily tailored to suit in several applications. Carbon nanotube (CNT) is another another novel promising material for electronic/optoelectronic applications. Lately there has been a great interest in developing composites of polymer and CNTs to utilize the advantages of both CNTs and polymers. The inclusion of CNTs in polymers improves the mechanical, electrical and thermal properties since the aspect ratio (ratio of length to diameter) is very large, as well its density is rather low.

The Thesis consists of 6 chapters. First chapter is a brief introduction of general and transport properties of conducting polymers and polymer-carbon nanotube composites. In Chapter 2, the sample preparation and experimental techniques used in this work are discussed. The charge transport in poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) is presented in Chapter 3. Chapter 4 focuses on the transport measurements in the polymer-CNT composite samples. Chapter 5 elaborates the ac and dc characterization of organic field-effect transistors (OFETs). And chapter 6 presents the conclusion and future directions of the work that has been presented in the Thesis.

Chapter 1: In the scientific and technological revolution of the last few years, the study of high performance materials has been steadily increasing including the study of carbon-based materials. Conducting polymers have special properties that are interesting for this new technology. The charge transport in conjugated polymers is important to optimize the performance of devices. The discovery of CNTs with exceptional thermal, mechanical, optical, electrical and structural properties has facilitated the synthesis of new type of nanocomposites with very interesting properties. Nanocomposites represent a guest-host matrix consisting of easily processible functionalized conjugated polymer as host, incorporating CNTs as fillers with versatile electronic and magnetic properties, which provide a wide range of technological applications. To optimize their electrical properties it is essential to understand the charge transport mechanism in detail.

Chapter 2: The multi-wall carbon nanotubes (MWNTs) grown by thermal chemical vapor deposition (CVD) are mixed with a 1:1 mixture of 98% H_2SO_4 and 70% HNO_3 to produce sulfonic acid functionalized multi-wall carbon nanotubes (s-MWNTs). The s-MWNTs are dispersed in a solution of Nafion by ultrasonication and then cast on a glass substrate and slowly dried by moderate heating to obtain the composite films. Polyaniline (PANI)-MWNT composites were obtained by carrying out the chemical synthesis of nanofibrilar PANI in the presence of CNTs. This water dispersible PANI-MWNT composite contains well segregated MWNTs partially coated by nanofibrilar PANI. The ac and dc charge transport measurements suggest hopping transport in these materials. OFETs are fabricated with pentacene, poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene)(PBTTT) and poly(3-hexylthiophene) (P3HT) as active materials. A novel technique is used to characterize the ac photoresponse of these OFETs.

Chapter 3: Charge transport studies on PEDOT-PSS have been carried out and found that it correlates with the morphology. The dc conductivity of PEDOT–PSS shows enhanced delocalization of the carriers upon the addition of dimethyl sulfoxide (DMSO) and this is attributed to the extended chain conformation. PEDOT-PSS is known to form a phase-segregated material comprising highly conducting PEDOT grains that are surrounded by a sea of weakly ionic-conducting PSS and a wide variation in the charge transport properties of PEDOT-PSS films is attributed to the degree of phase-segregation of the excess insulating polyanion. The magnetotransport and temperature dependent ac transport parameters across different conducting grades of PEDOT-PSS processed with DMSO were compared. Depending on the subtle alterations in morphology, the transport at low temperatures is shown to vary from the hopping regime (Baytron P) to critical regime of the metal-insulator transition (Baytron PH510). There is a significant positive magnetoresistance (MR) for P–films, but this is considerably less in case of PH510-film. From the low temperature ac conductance it is found that the onset frequency for PH510 is nearly temperature independent, whereas in P type it is strongly temperature dependent, again showing the superior transport in PH510. The presence of 'shorter network connections' together with a very weak temperature dependence down to ~ 5 K, suggest that the limitation on transport in PH510 arises from the connectivity within the PEDOT-rich grain rather than transport via the PSS barriers.

Chapter 4: DC and AC charge transport properties of Nafion s-MWNT and PANI-MWNT composites are studied. Such a detailed investigation is required to optimize the correlation among morphology and transport properties in these composites towards applications in field-effect transistors, antistatic coating, electromagnetic shielding, etc. The conductivity in Nafion s-MWNT shows a percolative transport with percolation threshold p_c = 0.42 whereas such a sharp percolation is absent in PANI-MWNT composite since the conduction via PANI matrix smears out the onset of rapid increase in conductivity. Three-dimensional variable range hopping (VRH) transport is observed in Nafion s-MWNT composites. The positive and negative MR data on 10 wt. % sample are analyzed by taking into account forward interference mechanism (negative MR) and wave-function shrinkage (positive MR), and the carrier scattering is observed to be in the weak limit. The electric-field dependence, measured to high fields, follows the predictions of hopping transport in high electric-field regime. The ac conductivity in 1 wt. % sample follows a power law: $\sigma(\omega) = A\omega^s$, and s decreases with increasing temperature as expected in the correlated barrier hopping (CBH) model. In general, Mott's VRH transport is observed in PANI-MWNT samples. It is found that the MWNTs are sparingly adhered with PANI coatings, and this facilitates inter-tube hopping at low temperatures. The negative MR of MWNT-PANI composites suggest that the electronic transport at low temperatures is dominated by MWNT network. AC impedance measurements at low temperatures with different MWNT loading show that ac conductivity become temperature independent as the MWNT content increases. The onset frequency for the increase in conductivity is observed to be strongly dependent on the MWNT weight percentage, and the ac conductivity can be scaled onto a master curve given by $\sigma(\omega) = \sigma_0[1 + k(\omega/\omega_0)^s]$.

Chapter 5: Organic field-effect transistors (OFETs) based on small molecules and polymers have attracted considerable attention due to their unique advantages, such as low cost of fabrication, ease of processing and mechanical flexibility. Impedance characterization of these devices can identify the circuit elements present in addition to the source-drain (SD) channel, and the bottlenecks in charge transport can be identified. The charge carrier trapping at various interfaces and in the semiconductor can be estimated from the dc and ac impedance measurements under illumination. The equivalent circuit parameters for a pentacene OFET are determined from low frequency impedance measurements in the dark as well as under light illumination. The charge accumulation at organic semiconductor–metal interface and dielectric–semiconductor interface is monitored from the response to light as an additional parameter to find out the contributions arising from photovoltaic and photoconductive effects. The shift in threshold voltage is due to the accumulation of photogenerated carriers under SD electrodes and at dielectric–semiconductor interface, and also this dominates the carrier transport. Similar charge trapping is observed in an OFET with PBTTT as the active material. This novel method can be used to differentiate the photophysical phenomena occurring in the bulk from that at the metal-semiconductor interface for the polymer.

Chapter 6: The conclusions from the various works presented in the thesis are coherently summarized in this chapter. Thoughts for future directions are also summed up.