CHAPTER 1

Introduction

This chapter presents an overview of the exciting and emerging field of conducting polymers with an emphasis on conducting polymer nanostructures. The basic characteristics, introduction of charge carriers, charge transport and influence of disorder on the charge transport of conducting polymers have been discussed. Towards the end, the chapter outlines the scope of the thesis and statement of the thesis problem.

1.1 Conducting polymer

Silicon and similar inorganic semiconductors have conquered the electronics world since the dawn of electronics. Silicon has become an inevitable part of our day-to-day life ranging from home appliances to electronic gadgets employed for entertainment and communication. Traditionally, polymers have been used as passive components, as insulators or in packaging. The concept of polymers as insulators faded away only after the ground-breaking discovery of high conductivity in polyacetylene, an organic conjugated polymer, in the year 1977 by A.J. Heeger, A.G. MacDiarmid and H. Shirakawa [1]. The conductivity of polyacetylene could be increased by more than seven orders of magnitude upon iodine doping. The three pioneers A.J. Heeger, A.G. MacDiarmid and H. Shirakawa were awarded the year 2000 Nobel Prize in Chemistry for the discovery and development of conducting polymers. This discovery opened up new areas of research in the field of organic conjugated polymers and the opportunity for organic polymers to serve as active material in electronics. Although, the initial emphasis was on the conducting properties of these
polymers, later many new materials were developed, which were designed and implemented in a range of applications. Conducting polymers are also known as 'synthetic metals' as they combine the electrical and optical properties of metals with the processing advantage of polymers. These polymers have now become a promising class of technologically important materials serving both fundamental and commercial purposes. The last four decades have witnessed fascinating progress in this field stimulated by the diverse technological applicability of these materials in areas such as molecular electronics [2], electrodes for redox supercapacitors [3, 4], electrochromic displays [5, 6], sensors [7, 8], actuators [9, 10], electromagnetic shielding [11, 12] and non-linear optics [13]. Some of the most significant conducting polymers are shown in Figure 1.1.

![Chemical formulae of some important conducting polymers.](image)

The key feature of a conducting polymer is the presence of conjugated bonds i.e., double bonds alternating with single bonds along the polymer chain.
This special conjugation in the chains enables the electrons to delocalize throughout the chain making it conductive.

The conjugated polymers can become conductive only on doping, which means removal or addition of electrons. Doping allows the loosely bound electrons to move across the polymer chains producing electric current. The conductivity of a material is determined by the number of charge carriers and mobility. In polymers, these parameters are determined by the chemical structure and doping. The relationship between chemical structure and conductivity, especially the concept of doping, charge carriers and their transport are discussed in the following sections.

1.1.1 Band structure

The ground state electronic configuration of the six electrons in a carbon atom is $1s^2 2s^2 2p^2$, which gives four valence electrons in the one 2s- and three 2p-orbitals. These orbitals exhibit different hybridization i.e., $sp$, $sp^2$ and $sp^3$, each possessing a unique spatial character in different carbon materials. In conventional polymers i.e., 'plastics', the carbon atom is in $sp^3$ hybridization and all the valence electrons are paired; hence they do not conduct electricity. In conducting polymers, the carbon atom is in $sp^2$ hybridization which is a mixture of one s- and two p-orbitals. Three of the four valence electrons are in the three $sp^2$-orbitals while the fourth electron is in the remaining unhybridized 2p-orbital i.e., the $2p_z$-orbital. The $sp^2$-orbitals from different carbon atoms lying on the molecular plane form strong covalent bonds called $\sigma$-bonds, which form the backbone of the polymer. The $p_z$-orbitals which are orthogonal to the molecular plane mix to give weak covalent bonds called $\pi$-bonds. The $\pi$-bonds form a delocalized electron density above and below the molecular plane which are responsible for the conductivity of the polymer, as the charge carriers move through these bonds. Figure 1.2 shows the $\sigma$- and $\pi$-bonds in a simple organic molecule ethylene ($C_2H_4$).
In a molecule with two $sp^2$-hybridized carbon atoms, the interaction between the $p_z$-electrons results in the formation of two molecular orbitals depending on the sign of the wavefunction of the orbitals – bonding with lower energy ($\pi$) and antibonding with higher energy ($\pi^*$). Without an excitation, the
\( \pi \)-orbitals are occupied and the \( \pi^* \)-orbitals are unoccupied. Increasing the carbon atoms in a molecule increases the number of molecular orbitals. When multiple molecules are considered, the energy levels merge to form bands analogous to that of inorganic semiconductors, with the edge of the valence band corresponding to the Highest Occupied Molecular Orbital (HOMO), and the edge of the conduction band corresponds to the Lowest Unoccupied Molecular Orbital (LUMO). Infinite number of \( sp^2 \)-hybridized carbon atoms in a chain will lead to the overlapping of the infinite atomic orbitals brought together. Energy splitting results in the formation of molecular orbitals packed densely with infinitesimal energy difference. This would lead to the formation of bands of states without a band gap (energy difference between HOMO and LUMO) i.e., a one-dimensional metal. However, in reality this is not a stable state and undergoes Peierls distortion [15], forming a gap between the bonding and the antibonding states as that of semiconductors. The difference between the energy of HOMO and the energy of LUMO is the energy gap \( (E_g) \) of the polymer which is generally in the range of 1.5 - 4 eV. Figure 1.3 is a schematic depiction of the formation of HOMO and LUMO in conducting polymers.

1.1.2 Doping and charge carriers

Conducting polymers in its undoped or neutral state are semiconductors with the \( \pi \)-electrons bound to the \( \pi \)-orbitals creating an alternation of single and double bonds. Conductivity i.e., delocalization of charge along the polymer backbone is achieved by the introduction of charge carriers (addition or removal of electrons) by a process called ‘doping’. Typically ‘dopant’ substances are neutral molecules, or inorganic and organic salts that can form ions. Introduction of the dopant species (in non-stoichiometric amount) significantly changes the structural, electronic, magnetic and optical properties of conducting polymers [16]. The conductivity of these polymers can be increased dramatically from the semiconducting range \( (10^{-10} - 10^{-5} \text{ S/cm}) \) to that
in the metallic range (1 - 10^4 S/cm) by increasing the concentration of dopant. The doping process in conducting polymers is completely different from that of semiconductors because the dopants do not substitute the host atoms but remain in the interstitial positions between the chains. The dopants through a redox process can either oxidize to create a positive charge or reduce to create a negative charge on the chain. Conducting polymers can also undergo a non-redox doping – the protonic acid doping, where the number of electrons along the polymer backbone remain constant, but results in a redistribution of electronic energy levels.

Doping in conducting polymers may be achieved by two distinct processes – chemical and electrochemical doping. In chemical doping, the polymer is exposed to an oxidizing agent such as iodine vapors [17] or a reducing agent, viz., alkali metal vapors [18]. In electrochemical process, doping is achieved by applying oxidizing or reducing voltage to the neutral polymer in an electrochemical cell [19]. The most important feature of conducting polymers is that the doping process is reversible i.e., the polymer can be made neutral by a 'de-doping' process unlike that in case of semiconductors. The charge carriers introduced as a result of doping are stabilized by altering the conjugation over several monomers. The charge together with the distortion in the structure of the polymer constitutes a single charge carrier. Depending upon the structure of the polymer backbone, its degeneracy and level of doping, the carriers may be solitons, polarons and bipolarons which are nothing but charged defects [20]. The carriers can move along the polymer chain by rearrangement of double and single bonds in the conjugated system upon application of electric field. The different carriers have different spin orientations which can respond to an applied magnetic field [21]. The charge neutrality of the doped polymer chains is balanced by the dopant counterions. These counterions play a major role in the charge conduction mechanism. Figure 1.4 shows a schematic of the formation of different types of charge carriers in conducting polymers and the corresponding modifications in their band structure.
Formation of polarons and bipolarons in poly(p-phenylene) and solitons in trans-polyacetylene

Neutral polymer chain

Polaron

Bipolaron

Poly(p-phenylene)

Trans-polyacetylene

e

e

Electronic band structure of conducting polymers (CPs) in the neutral and doped states

Figure 1.4: Molecular structures of conducting polymers illustrating the formation of charge carriers, viz., solitons, polarons and bipolarons. A schematic representation of the modifications in the band structure of conducting polymers as a result of the creation of charge carriers upon doping is also illustrated [25].

Removal of an electron via oxidation from a non-degenerate polymer [for example, poly(p-phenylene)] creates an unpaired electron with spin $\frac{1}{2}$ (free radical) and a spinless positive charge (cation). The radical and the cation are coupled to each other via a local bond deformation (rearrangement), creating a polaron which appears in the band structure as localized electronic state located symmetric to the band edges [21, 22]. The lower energy state is occupied by a single unpaired electron as depicted in Figure 1.4. On further oxidation, dications are created in the polymer. The second electron can be removed either from the polaron or from the remaining neutral portion of the polymer chain. In the former case, the free radical nature of the polaron is lost and a dication is created, which comprises of two positive charges coupled with lattice distortion. This dication together with the lattice distortion is termed as
bipolaron, which is a spinless defect [23, 24]. Removal of an additional electron from the neutral portion of the polymer chain would result in the formation of two polarons. However, the formation of a bipolaron is energetically favorable as it produces a larger decrease in ionization energy, as compared to that in the formation of two polarons. These new empty bipolaron states are also located in the band gap symmetric to the band edges. Additional localized bipolaron states are created with further doping, which eventually overlap to form continuous bipolaron bands at high enough doping levels (Figure 1.4). Thus the presence of these carriers creates new energy levels between HOMO and LUMO, hence narrowing the band gap in conducting polymers.

When trans-polyacetylene (trans-PA), a degenerate conducting polymer is oxidized, a polaron is formed (Figure 1.4). Further oxidation of PA leads to the formation of solitons. The ground state of trans-PA is two-fold degenerate i.e., the ground state has two equivalent ways of arranging the single and double bond alteration. Thus the bonding configurations on either side of the polaron differ only by a reversed orientation of the conjugated system and are energetically equivalent resonance forms. This in turn creates isolated, non-interacting charged defects that form domain walls separating two phases of opposite orientation but identical in energy. Such defects are called solitons, which results in the formation of new localized electronic states that appear midway in the energy gap. As the doping level increases, these states overlap to form soliton bands [26].

1.2 Charge transport in conducting polymers

1.2.1 Disorder in conducting polymers

Doping creates charge carriers which are delocalized along the polymer chain. These carriers can move upon the application of an electric field producing an electric current. However, the transport on a macroscopic length is quite complex and is controlled by a variety of phenomena. According to theoretical prediction, the π-electron system of a conjugated polymer makes it straight and
rigid. However, in reality, a polymer chain consists of a number of separated conjugated segments due to the presence of kinks, twists, or chemical defects which destroys the π-conjugation along the same chain. Conjugation length is defined as the mean length of the conjugated segments. As a result, the chains cannot be aligned throughout the whole length, and hence exhibit partial crystallinity [27]. The crystalline regions are interconnected by amorphous regions and the typical size of the crystalline regions varies in the range of 10 - 50 nm [28]. The different local arrangements and distribution of lengths of the conjugated segments modify their energy giving rise to locally varying polarizabilities and dipole interactions between the neighboring chains [29].

All these effects collectively tend to localize the charge carrier. Inhomogeneous distribution of the polymer chains, grain boundaries and morphology has also been found to affect the macroscopic transport. The factors which dictate the macroscopic transport are generally accounted for in the term ‘disorder’. Disorder arises mainly due to simple and cheap processing methods commonly employed, inhomogeneous doping and partial crystallinity. Disorder can be energetic or structural (positional). As the local energy levels are determined by the local structure and the conjugation length, structural disorder often results in energetic disorder [30]. The energetic disorder is generally approximated by a Gaussian density-of-states (DOS), with the standard deviation of the Gaussian giving a characteristic energy width of $\sigma \approx 0.1$ eV [30].

### 1.2.2 Role of disorder on charge transport

Due to π-electron delocalization along the chain, the conducting polymers were initially regarded as one-dimensional semiconductors. The dynamics of π-electrons along the one-dimensional chain were first studied by Su, Schrieffer and Heeger (SSH) [31]. The SSH model is a simple tight binding model developed for polyacetylene neglecting the Coulomb interactions and disorder effects. Although this model might be valid for single isolated chains or highly
ordered and stretch oriented polymer systems as supported by some experiments, the common conjugated polymer systems are highly disordered. It is therefore not possible to draw a one-dimensional semiconductor picture of these polymers.

Disorder inhibits the translational symmetry and causes the formation of localized states in the band gap [27]. Hence, the concept of band conduction by free carriers does not apply in these disordered polymers. For propagation of current, the carriers trapped in the localized states need to be released. The conduction involving localized states occurs by two processes: phonon-assisted hopping and direct tunneling. Tunneling occurs when the electronic wavefunctions of the two localized states adequately overlap, whereas the phonon-assisted hopping occurs when the charge carriers trapped in the localized states absorb a phonon and classically jump into the next available site. This usually leads to a very low carrier mobility typically in the range of $10^{-6} - 10^{-3}$ cm$^2$/V.s. This mechanism of hopping was originally proposed by Mott [32] and Conwell [33] to explain the temperature dependence of dc conductivity in compensated semiconductors which was later applied to all disordered materials. The Mott's variable-range hopping (VRH) model is oversimplified as it ignores the electron-electron interactions or an energy dependent DOS. Various other models proposed to account for the observed conduction mechanism in disordered materials considering the electron-electron interaction effects [34], tunneling between conducting domains [35] and even superlocalization effects, where the electronic wavefunctions decay much faster than that in localized states [36, 37] are also applicable to conducting polymers. In fact, most of these models have severe limitations and are valid only in certain temperature regimes or systems.

Mott's hopping model i.e., VRH model is found to be valid in most of the conducting polymer systems. Hopping transport depends on the tunneling probability between two sites as well as on the probability of absorbing phonons that provide necessary energy for hopping [38]. Therefore, disorder in
position (structural disorder) and energy of hopping sites has a large influence on the mobility of the carriers and are thus crucial to hopping transport. Although, Mott’s VRH model successfully explains the temperature dependence of dc conductivity, it fails to explain the field dependence of charge mobility which is more commonly known as the Poole-Frenkel (PF) mobility behavior [39]. The uncorrelated Gaussian disorder model (UGDM) [40] and the subsequent correlated Gaussian disorder model (CGDM) [41], which assumes a Gaussian DOS taking into consideration both the structural and energetic disorders, are the most used theoretical models to explain the observed PF mobility behavior.

1.2.3 Metal-insulator transition

The transport properties depend on various microscopic variables which may simultaneously be expressed in energy parameters, viz., electron-lattice interaction, electron-electron interaction (electron-hole interaction), bandwidth and the random disorder potential [42]. The relative strength of the bandwidth and the disorder potential gives rise to an interesting phenomenon in conducting polymers – the metal-insulator transition (MIT). If the disorder potential is large enough than the bandwidth potential, the states become localized. The system will then be a ‘Fermi glass’ insulator although there is no gap in the DOS [43]. However, this insulating behavior is due to the position of the Fermi level ($E_F$) in a region of localized states and the conductivity is zero at 0 K. When the disorder is sufficiently reduced, the localized and the extended states are separated by the mobility edge ($E_c$) and the MIT is defined by the position of $E_F$ with respect to $E_c$ i.e., the system becomes metal and insulator for $E_F$ being situated in a region of extended states and localized states, respectively [44]. This transition is called the Anderson’s disorder-induced MIT. A finite conductivity is expected when the Fermi level is at an energy such that the electronic states are extended.
Mott extended the Anderson transition for the case of interacting electrons which was a limitation in the case of Anderson’s assumption of independent electrons. It enlightens a regime where the independent picture approximation, inherent to both Bloch and Anderson pictures, fails due to electron-electron interaction. According to Mott's consideration, a transition from extended to localized states occurs only when the correlation energy (on metallic side) exceeds a critical value compared to the bandwidth [45]. The main idea behind Mott’s transition is that the correlation energy under particular conditions can force a solid to have an insulating ground state when the independent electron approximation picture wrongly classifies it as a metal [46]. However, in reality, MIT in disordered solids is neither a pure Anderson nor a pure Mott one. This type of complex phenomenon cannot occur from a single mechanism, but arises from a number of competing and complementary mechanisms involving a close interplay between two main mechanisms – electron-electron interaction and weak localization (disorder) [45]. The localization-interaction model [47] takes into account these two factors providing a framework to understand these effects in a better way.

1.3 Conducting polymer nanostructures

Nowadays, functionalized nanomaterials with the typical size in the range of 1 - 100 nm have been receiving immense attention due to their substantially improved properties and consequent enhanced performance in devices. Nanostructuring of conducting polymers has recently emerged as a new branch of nanotechnology directed to creation of new smart materials. Conducting polymer nanostructures are a special subclass which not only retain the unique characteristics of conducting polymers, such as π-conjugated polymeric chain, metal-like conductivity and reversible physical properties by a novel doping/de-doping process, but also possess the characteristics of nanomaterials i.e., large surface area, size- and quantum-effects. The nanoscale dimension of these polymers increases the merits in designing and developing efficient
devices and brings in the prospect of a range of enhancements which cannot be acquired by their bulk counterparts. Different nanostructures of conducting polymers such as nanofibers, nanowires, nanoparticles, nanotubes, nanosheets, nanoflowers and urchin-like structures have been synthesized using a number of techniques like micellar and reverse micellar polymerization, interfacial polymerization, rapid mixing polymerization, seeding polymerization, microemulsion polymerization, electro-spinning, and polymerization in the presence of soft- and hard-templates [48-55].

Of late, conducting polymer nanostructures have been successfully used as efficient sensors where the nanodimension offers large specific surface area and porosity increasing the response time of the sensor [56, 57]. These materials have also found applications in actuators [58, 59], as anticorrosion protective layers [60], field emission displays [61], memory devices [62] and flash welding [63].

1.4 Polyaniline (PANI)

Polyaniline (PANI), a heteroatomic non-degenerate conducting polymer is an extensively studied conducting polymer owing to its various favorable characteristics. The interest in this unique conducting polymer is rekindled due to its attractive doping and de-doping characteristics, environmental and thermal stability, and reasonably high electrical conductivity. These features are coupled with simple synthesis, inexpensive monomer and easily tunable morphologies (nanoparticles, nanofibers and nanotubes) that depend on the reaction conditions [64]. These are the key factors for choosing PANI as a material of study in the present thesis.

PANI is different from the family of \( \pi \)-conjugated polymers as it possesses some unique features. It can be regarded as an ‘A-B’ type copolymer with amine (\(-\text{NH}-\)) and imine (\(=\text{N}-\)) segments in the repeat unit [65]. Unlike other heteroatomic conducting polymers like polypyrrole (PPY) and polythiophine (PT), the heteroatom nitrogen occupies the primary sites in the
chain backbone. Therefore, it has asymmetric charge conjugation with benzene rings and nitrogen atoms in the conducting path [66]. The benzene rings either flip or rotate altering the electron-phonon interactions and consequently affect the charge transport. PANI exhibits three oxidation states ranging from fully oxidized to fully reduced forms. Figure 1.5 shows the different oxidation states of PANI which are: (a) leucoemeraldine base (LB)-fully reduced form, (b) emeraldine base (EB)-half oxidized and half reduced, and (c) pernigraniline base (PB)-fully oxidized form.

![Chemical structures of PANI oxidation states](image)

Figure 1.5: The different oxidation states of PANI, (a) leucoemeraldine base - fully reduced, (b) emeraldine base - half oxidized and half reduced, and (c) pernigraniline base - fully oxidized [45].

Although all the oxidation forms are insulating, the EB form can be made electrically conducting by doping with protonic acid of pH < 3. The protonic acid doping makes PANI unique among the conducting polymer family, since the transition from an insulator to a conductor is done without the addition or the removal of charge carriers, but only with a rearrangement of the electronic energy levels after protonation. Through protonic acid doping, the emeraldine base form of PANI is transformed to emeraldine salt (ES) form increasing the conductivity of the material by 9 - 10 orders of magnitude, which makes PANI ideal for the study of the insulator-metal transition [67]. Variations of the
doping level can induce considerable differences in the transport properties of the deduced PANI salts, providing us with a variety of systems on both sides of MIT for investigation. Protonation (or proton doping) can be achieved directly during synthesis or by exposing the already formed polymer to either gas or solution or even powdered acids. Maximum doping is achieved when half of the nitrogen sites on the chain are protonated. Proton doping is a non-redox doping which is significantly different from redox doping that involves partial addition (reduction) or removal (oxidation) of electrons to or from the polymer backbone [68]. The EB form of PANI can be recovered by treating the ES form by aqueous alkali causing de-protonation (de-doping).

![Diagram of doping in PANI]

Figure 1.6: Schematic representation of doping in PANI. The EB form of PANI is doped with protonic acid to form the conducting state [67].
The EB form of PANI consists of amine (–NH–) and imine (–N–) sites in equal proportions. Protonation occurs at the imine nitrogen sites (–N–) in preference \[69\] which gives the bipolaron (cation) form. Figure 1.6 shows the protonation of EB form of PANI. Thus complete doping would mean the formation of a bipolaron (cation salt) lattice i.e., one bipolaron per repeat unit contained in the quinoid structure. This bipolaron is unstable and undergoes dissociation and proportionation to form two polarons which is a polysemiquinone radical cation. Although theoretical studies have predicted that a bipolaron lattice is energetically favorable over a polaron lattice \[70\], it is widely accepted that polarons are the charge carriers and that they are responsible for high conductivity in PANI \[71, 72\]. It has been proposed that the Coulombic interactions and dielectric screening together with the local disorder act to stabilize the delocalized polaron lattice in PANI \[73\]. However, it is also accepted that bipolarons do exist in PANI but are small in number and are not associated with the conducting regions \[73\].

1.5 Scope of the thesis and statement of the thesis problem

As the nature of transport in conducting polymers is determined by a variety of factors such as inter-chain interaction, electron-phonon interaction, Coulomb interaction, screening, lattice stiffness, extent of disorder and extent of conjugation length; theoretical modeling becomes even more complicated. The application of conducting polymers in various solid state devices such as solar cells \[74\], field-effect transistors \[75\], organic light emitting diodes \[76\], Schottky junctions \[77\], electromagnetic interference shielding \[78\], electrodes for redox supercapacitors \[79\], sensors \[80\] and molecular electronics \[2\], have also led the scientific community to investigate the transport mechanisms in much detail. The revelation of the nature of charge carrier and transport processes in conducting polymers is a widely open research problem both from the fundamental and application viewpoint. Many familiar concepts related to
conventional conductors such as the MIT in disordered materials, hopping and/or tunneling conduction, appear to be applicable for these polymers [81]. However, no single unanimous model is so far available that can completely describe the prevailing conduction processes occurring through the presence of non-linear excitations like solitons, polarons and bipolarons formed as a result of doping. The reason is that these polymers have one-dimensional polymer chains which make the conduction highly anisotropic, and the maximum attainable conductivities are limited by the small size of the crystalline regions over which the chains are aligned [82].

In recent times, conducting polymer nanostructures have attracted increasing attention because of their distinctive optical, electronic and mechanical properties, resulting in promising applications in electronic and optoelectronic nanodevices [83-85]. Although, the last decade has witnessed fascinating developments in the field of conducting polymer nanostructures, both in terms of basic science and technological standpoint [86-89], the transport mechanism in these nanostructures still remains poorly understood. A thorough understanding of the charge transport mechanism of the conducting polymer nanostructures is very much important for successful fabrication of sophisticated nanodevices. It is well recognized that nanostructures of conducting material dictate their physical properties. When a large proportion of the constituent atoms are present on the surface of a nanoparticle, then unique electronic and optical properties result. It is known that conducting polymers contain nanodomain components of much higher conductivity than that of the bulk [90], suggesting that nanodimensional control of structures will improve the conductivity of these polymers [91]. As the synthesis of these nanostructures is controlled at the nanoscale, the level of order is improved in the conducting polymer nanostructures [92]. More recently, it has also become apparent that both disorder and nanocrystalline structures are critical to the charge transport properties of conducting polymers [93-95]. Besides charge transport, thermal or heat transport is also an important
property of conducting polymers which has not been explored so far. Thermal transport of conducting polymers is very much important both from the fundamental and application point of view. It gives information regarding thermal management for use of these materials as efficient devices. The nature and mechanism of heat transport in conducting polymers even in the bulk form has not been studied in detail, with only a few reports on the experimental determination of thermal conductivity of polyacetylene [96], polypyrrole [97] and polyaniline [98].

Considering the above mentioned facts, we consider polyaniline (PANI) among the family of conducting polymers as the material of interest in the present thesis as it has many versatile properties (discussed in section 1.4), which makes it one of the most promising candidates for research as well as for application purposes. Moreover, stable nanostructures of PANI, namely, nanoparticles, nanofibers and nanotubes can be synthesized using the chemical oxidative polymerization method. The prime objectives of the present thesis are the study of electrical and thermal transport along with the magnetic measurements of different nanostructures of PANI varying the level of doping, dopant type and temperature, with a view to gain deeper understanding into the mechanism and nature of carriers involved in charge and heat transfer in these PANI nanostructures. In order to achieve the objectives, the following methodology was employed:

1. Different PANI nanostructures, viz., nanofibers, nanoparticles and nanotubes have been synthesized by interfacial polymerization and self-assembly methods.

2. High resolution transmission electron microscopy studies have been carried out to study the morphology, shape and size of the nanostructures.

3. X-ray diffraction studies have been conducted to investigate the structure and degree of crystallinity.
4. Fourier transform infrared spectroscopy and Raman spectroscopy have been recorded to investigate the conformational variations, chemical interactions and vibrational assignments.

5. Electrical transport measurements, viz., dc conductivity, magnetoresistance and current-voltage characteristics have been performed to understand the charge conduction mechanism.

6. Magnetic property measurements, viz., magnetic susceptibility and field dependence of magnetization have been done to understand the magnetic behavior of the charge carrying species.

7. Thermal transport property i.e., thermal conductivity measurements and thermodynamic property i.e., specific heat measurements have been made to understand the nature of heat carrying modes and heat transfer mechanism.