1.1 Conducting Polymers

Materials are generally classified as insulators, semiconductors, conductors and superconductors based on their electrical properties. A material with conductivity less than $10^{-7}$ S/cm is regarded as an insulator. Metals have conductivity larger than $10^{3}$ S/cm whereas the conductivity of a semiconductor varies from $10^{-4}$ to $10$ S/cm depending upon the degree of doping. It was generally believed that plastics (polymers) and electronic conductivity were mutually exclusive and the inability of polymers to carry electricity distinguished them from metals and semiconductors. As such, polymers were traditionally used as inert, insulating and structural materials in packaging, electrical insulations and textiles where their mechanical and electrically insulating properties were paramount. In fact, any electrical conduction in polymers was generally regarded as an undesirable phenomenon. The breakthrough happened in the year 1977 when, somewhat accidentally, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa, discovered that plastics that are generally referred to as insulators can, under certain circumstances, be made to behave like metals [1]. This path-
breaking discovery of high conductivity in polyacetylene in 1977 resulted in a paradigm shift in thinking and opened up new vistas in chemistry and physics [1-4]. Their work was finally rewarded with the Nobel Prize in Chemistry in 2000 for the discovery and development of electronically conductive polymers [5-7].

After the initial discovery in 1977, the field of electronically conducting polymers has surmounted to such heights that it is far ahead of what could have been envisaged when the field was in its formative years. A variety of other conducting polymers and their derivatives were discovered in the subsequent years after the discovery of conductivity in polyacetylene [8-18]. Investigation of electrical conduction properties of conducting polymers was the prime focus of research in the early years [19-24]. Gradually, research in the field of conjugated polymers surpassed the limits of studying conduction processes in doped conjugated polymers and optical properties, electroluminescence and other physical properties of conjugated polymers were being investigated [25-30]. In recent years, distinct development has also been made in understanding of the structure-property relationships for many of the conducting polymers [31-37]. This fascinating progress rate has been stimulated by the field’s fundamental synthetic novelty, importance to interdisciplinary research and to the emerging technological applications of these materials in different areas such as molecular electronics [38], electrodes for redox supercapacitors [39, 40], electrochromic displays [41, 42], chemical sensors [43], actuators [44-46], electromagnetic shielding [47-49] and non-linear optics [50].

Intrinsically conducting polymers (ICPs) are completely different from other conducting polymers in which a conducting material such as metal or carbon powder is dispersed in a non-conductive polymer [51]. These polymers often referred to as conjugated polymers belong to a totally different class of polymeric materials with alternate single-double or single-triple bonds in their main chain and are capable of conducting electricity when doped. ICPs, similar to other organic polymers, usually are described by $\sigma$ (sigma) bonds and $\pi$ (pi) bonds. While the $\sigma$ electrons are fixed and immobile due to the formation of covalent bonds between the carbon atoms, the remaining $\pi$-electrons can be easily delocalized upon doping. Fig. 1.1 shows the molecular structures of some of the
popular intrinsic conducting polymers that have been synthesized during the last few decades and applied in different application areas. In the next few sections and sub-sections of this chapter, we present a state-of-the-art literature survey of the historical developments in the field of conducting polymers with a special focus on the different characteristic properties of conducting polymers.

Figure 1.1: Molecular structures of some of the most popular conjugated polymers

1.1.1 Historical developments

Although polymeric materials have been used by mankind since prehistoric times in the form of wood, bone, skin, and fibers, the existence of macromolecules was accepted only after Hermann Staudinger developed the concept of macromolecules during the 1920s, which got him the Nobel Prize in Chemistry in 1953 “for his discoveries in the field of macromolecular chemistry” [52]. This was followed by very important contributions by Wallace Carothers [53] and Noble laureates Karl Ziegler, Giulio Natta and Paul Flory [54] which made the field of macromolecular science popular amongst the scientific community. Because the saturated polymers studied by Staudinger, Flory, Ziegler, and Natta were insulators, they were viewed as uninteresting from the point of view of electronic materials.
The research field of conjugated (conducting) polymers came into focus with the preparation of polyacetylene by Shirakawa and coworkers along with the subsequent discovery of enhancement in its conductivity after “doping” by the group led by MacDiarmid and Heeger [1-4]. The history of conducting polymers, however, dates back to the nineteenth century. Some of the most important representatives in the family of $\pi$-conjugated polymers in non-conducting as well as conducting forms viz., polyaniline (PAni) and polypyrrole (PPy), were already being prepared chemically or electrochemically in the nineteenth century, decades before the existence of macromolecules was even accepted and as such they were not called polymers.

Gas industries in the first half of the nineteenth century prepared aniline from the coal tar residues which later played a pivotal role in the development of organic chemistry and the chemical industry [55]. Soon aniline dyes replaced dyes from natural sources and then coal tar dyes found use in medicine for staining tissues [56]. After the discovery of selective toxicity of these compounds by P. Erlich, the chemical production of medicines was initiated and led to the establishment of the pharmaceutical industry [57]. It was in 1862, when Dr. Henry Lethéby observed that a bluish-green precipitate was formed at the anode during electrolysis of aniline, which became colourless when it was reduced and regained its blue color when oxidized again [58]. Subsequently, Runge [59] in 1834 and Fritzsche [60] in 1840 isolated aniline and observed the appearance of a blue colour during the oxidation of aniline in acidic media. Lethéby’s experiments were repeated and his findings were verified by Goppelsroeder [61], Szarvasy [62] and others. A linear octameric structure was proposed and generally accepted for aniline in the first decade of the twentieth century. The existence of polyaniline (PAni) in four oxidation states was also recognized [63]. A reaction scheme for the electro-oxidation of aniline at a carbon electrode was suggested by Yasui in 1935 [64]. It was almost a century after Lethéby’s observations that Mohilner and co-workers reinvestigated the mechanism of the electro-oxidation of aniline in aqueous sulphuric acid solution at a platinum electrode and characterized polyaniline (PAni) [65]. The first real breakthrough came in 1967, when Buvet and his group established that polyanilines are redox active electronic conductors and
PAAni pellets can be used as electrodes for conductivity measurements [66-67]. However, this discovery did not give rise to great excitement during that time. Diaz and Logan initiated research into polymer film electrodes based on polyaniline in 1980, which is still continuing [68]. However, it was the investigations by MacDiarmid et al. in the mid 1980s [9-13, 69], and, in particular, the discovery of electrical conductivity for its emeraldine salt form that led to an explosion of interest in this fascinating polymer.

Polypyrrole (PPy), on the other hand, was known as “Pyrrole black” and was formed due to the oxidation of pyrrole in air. PPy is an inherently conducting polymer with interesting electrical properties first discovered and reported in the early 1960s [70]. It was followed by the preparation of coherent and free standing polypyrrole films by electrochemical polymerization by Diaz and his co-workers [71, 72]. Thus, it is evident that although the research in the field of conducting polymers seems to have aroused interest of researchers and public alike in the 1970s, these polymers were already known but not as conducting polymers that we know today. Thus, these materials have a long history and, perhaps without any overstatement, a dazzling future.

1.1.2 Primary features of conducting polymers

The ground state of a carbon atom has six electrons arranged as $1s^2 2s^2 2p^2$, which gives four electrons in the outer electronic orbital. In the presence of other atoms (H, O etc.) these levels may hybridize either into sp, sp$^2$ or sp$^3$ orbitals, each possessing their unique spatial character. Fig. 1.2 shows the schematic structure of the simplest three-dimensional (3D), two-dimensional (2D) and the one-dimensional (1D) form of carbon materials. In case of diamond, the carbon atoms are sp$^3$ hybridized whereas in case of graphite and polyacetylene the carbon atoms exhibit sp$^2$ hybridization. Out of these three forms of carbon materials, only the 2D and 1D form are conducting. Diamond, which contains only $\sigma$ bonds, is an insulator and its high symmetry gives it isotropic properties. Graphite and acetylene, on the other hand, both have mobile $\pi$ electrons. Graphite is known to be a conductor while doped polyacetylene shows highly anisotropic metallic conductivity [1].
All the hybridized orbitals in carbon materials are strongly localized, however in case of sp$^2$ we are left with one unhybridized p$_z$ orbital. This p$_z$ orbital is oriented perpendicular to the three sp$^2$ orbitals that are coplanar with angles of 120° between one another (Fig. 1.3). In case of an identically hybridized neighbour C atom with similar orientation, these p$_z$ orbitals will overlap and form a molecular $\pi$ bond. The $\sigma$ bond between the two C atoms (created by two hybridized sp$^2$ orbitals) together with the $\pi$ bond results in a double bond. The stacking of neighbouring sp$^2$ hybridized C atoms, all with their p$_z$ orbitals parallel, results in an alternating single bond, double bond structure as can be seen from Fig. 1.2 (c).

Conducting polymers are different from other polymers primarily because of this framework of alternate single-double carbon-carbon (carbon-nitrogen) bonds in the polymer backbone chain. In this alternating sequence (conjugation
structure), the positions of the double and single bonds may be exchanged with small or no energy difference [73]. All the conducting polymers have a backbone of \( \sigma \)-bonds between carbon atoms that are \( sp^2 \) hybridized leading to one unpaired electron (the \( \pi \) electron) per carbon atom. This allows the overlapping of the remaining out-of-plane \( p_z \) orbitals to form a \( \pi \)-band, which leads to electron delocalization along the backbone of the polymer. This electronic delocalization allows charge carriers to move along the backbone of the polymer chain although the mobility is low. The electronic structure in conducting polymers is determined by the number and kind of atoms within the repeat units i.e., the symmetry of the chains. The characteristics of the \( \pi \)-band, therefore, play an important role for determining the semi-conducting or in some cases metallic properties of conjugated polymers. In their pristine form, most of the conducting polymers are insulating except for polyacetylene \([\text{trans-(CH)}_x]\) that exhibits semi-conducting behavior in the pure form. However, enhancement in the conductivity of conjugated polymers by many orders of magnitude can be achieved through simple chemical or electrochemical oxidation or in some cases reduction by a number of simple anionic or cationic species called dopants [74]. Doped conjugated polymers when in appropriate oxidized or reduced states are semiconductors and in some cases exhibit metallic behavior due to their unique \( \pi \)-conjugation.

1.1.2.1 Doping in conducting polymers

Doping in conjugated organic polymers is something that is responsible for the great scientific and technological importance achieved by these materials since their discovery in 1977. The concept of doping is the unique and central theme that unites all the conducting polymers and differentiates them from all other types of polymers [2, 3, 74]. During the doping process, an organic polymer, either an insulating or semi-conducting polymer could be converted into electronic polymers exhibiting metallic conductivity \((1 - 10^6 \text{ S/cm})\). Although the term “doping” might look familiar but the concept of “doping” in conducting polymers is much different than that in case of inorganic semiconductors. Fig. 1.4 shows a schematic diagram to explicit the difference between the doping mechanisms in inorganic semiconductors and conjugated polymers. In semiconductor physics,
doping describes a process where dopant species present in small quantities occupy positions within the lattice of the host material, resulting in a large-scale change in the conductivity of the doped material compared to the undoped one. The “doping” process in conjugated polymers is, however, essentially a charge transfer reaction, resulting in the partial oxidation (or less frequently reduction) of the polymer. Unlike inorganic semi-conductors, doping in conjugated polymers is reversible in a way that upon de-doping the original polymer can be retained with almost no degradation of the polymer backbone. Another very important difference between the doping in conjugated polymers and that in inorganic semiconductors is that doping in conjugated polymers is interstitial whereas in inorganic semiconductors the doping is substitutional.

Figure 1.4: Schematic diagram showing the difference between the doping mechanisms in inorganic semiconductors and conjugated polymers

One can easily obtain a conductivity anywhere between that of the undoped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer by simply adjusting the doping level. During
doping and de-doping processes a stabilized doped state of the conducting polymer may be obtained using dopant counterions by chemical or electrochemical processes [75]. Conducting polymers can be p or n doped chemically and electrochemically to obtain a metallic state [2, 3, 76, 77]. Doping of conjugated polymers can also be carried out by methods that introduce no dopant ions such as field induced charging [78]. In the doped state, the backbone of a conducting polymer consists of highly delocalized π electrons. Fig. 1.5 presents a chart showing the different methods that have been adopted for doping conducting polymers.

**Doping in conducting polymers**

- Redox doping
  - Redox p-doping
  - Redox n-doping
- Non-Redox doping
  - Redox doping involving no dopant ions
  - Charge-injection doping
  - Photo doping
- Doping by Ion implantation
- Doping by Heat treatment

**Figure 1.5: Different methods for doping conducting polymers**

Doping of conjugated polymers either by oxidation or by reduction in which the number of electrons in the polymeric backbone gets changed is generally referred to as redox doping [74-77, 79]. The charge neutrality of the conducting polymer is maintained by the incorporation of the counterions [80]. Redox doping can be further subdivided into three main classes: p-doping, n-doping and doping involving no dopant ions viz., photo-doping and charge injection doping [77, 81, 82]. Both chemical and electrochemical redox doping techniques can be employed to dope conjugated polymers either by removal of electrons from the polymer back-bone chain (p-doping) or by the addition of electrons (n-doping) to the chain. In chemical doping the polymer is exposed to an oxidizing agent such as iodine vapours or a reducing agents viz., alkali metal.
vapours, whereas in electrochemical doping process a polymer coated working electrode is suspended in an electrolyte solution in which the polymer is insoluble, along with separate counter and reference electrodes. On the application of a potential difference between the electrodes, charges cross into the polymer in the form of electron addition (n-doping) or removal (p-doping) and the appropriate counter ion from the electrolyte enters into the polymer film in order to maintain charge neutrality.

Photo-doping is a process where conducting polymers can be doped without the insertion of cations or anions simply by irradiating the polymer with photons of energy higher than the band gap of the conducting polymer. This leads to the promotion of electrons to higher energy levels in the band gap [83]. However, due to rapid recombination of electrons and holes, photo-doping does not sustain after the irradiation of the polymer is stopped. Charge injection doping is another type of redox doping that can also be used to dope an undoped conducting polymer [78, 84, 85]. In this method, thin film of conducting polymer is deposited over a metallic sheet separated by a high dielectric strength insulator. This metal/insulator/semiconductor structure is used to carry out charge injection in the polymer film. The charges are injected into the conducting polymer without involvement of any dopant ion. When an appropriate potential difference is applied across the structure a surface charge layer is formed in the polymer. The accumulation of charge layer for conducting polymer has been extensively studied and experimental signatures of solitons and mid gap absorption have been observed in injected charge layer in polyacetylene in the absence of dopant ion.

The non-redox doping of conducting polymer is a process of doping conducting polymers in which the number of electrons associated with the polymer chain is kept constant. In fact it is the energy level in the conducting polymer that gets rearranged in the non-redox doping process [86]. The best example of non-redox doping is the conversion of emeraldine base form of polyaniline to protonated emeraldine base (polysemiquinone radical cation) when treated with protic acids [69]. It has been observed that the conductivity of
polyaniline is increased by approximately 10 orders of magnitude by non-redox doping.

Ion implantation and heat treatment methods have also been used to dope conducting polymers. Ion bombardment of polyaniline by 100 KeV Ar⁺ ion and 24 KeV I⁺ at a fluence of 10⁶ ions/ cm² has been reported [87] and it has been observed that upon I⁺ ion implantation the films become environmentally stable showing enhanced conductivity by 12 orders of magnitude. Heat treatment induced doping has been observed for ladder type of conducting polymers [88]. It has been observed that for ladder type of polymers conductivity increases from 10⁻⁸ to 10⁻⁴ S/ cm upon heat treatment, which has been attributed to the improved ordering of the polymer structure and thermally excited charge carriers. However, this technique has rarely been used for doping conducting polymers.

1.1.2.2 Metal-Insulator transition in doped conducting polymers

Metal-Insulator (M-I) transition is one of the most interesting physical aspects of conducting polymers. When the mean free path becomes less than the inter-atomic spacing due to increase in disorder in a metallic system, coherent metallic transport is not possible [89]. When the disorder is sufficiently large the metal exhibits a transition from the metallic to insulating behavior. As a result of this transition which is also known as the Anderson transition all the states in a conductor become localized and it converts into a "Fermi glass" [90] with a continuous density of localized states occupied according to Fermi statistics. Although there is no energy gap in a Fermi glass but due to the spatially localized energy states a Fermi glass behaves as an insulator [90, 91]. It has been found that electrical conductivity of a material near the critical regime of Anderson transition obeys power law temperature dependence [92].

This type of M-I transition has been observed for different conducting polymers viz., polyacetylene, polyaniline, polypyrrole, poly(p-phenylene vinylene) etc. and is particularly interesting because the critical behaviour has been observed over a relatively wide temperature range [93, 94]. In conducting polymers, the critical regime is easily tunable by varying the extent of disorder by means of doping or by applying external pressure and/or magnetic fields [93]. In the metallic regime, the zero temperature conductivity remains finite, and σ (T)
remains constant as $T$ approaches zero [93]. In the critical region, the conductivity follows a power law, whereas in the insulator regime transport occurs through variable range hopping (VRH) among localized states. Although disorder is generally recognized to play an important role in the physics of “metallic” polymers, the effective length scale of the disorder and the nature of the M-I transition are yet central unresolved issues [94-97]. In particular, it has been a matter of in-depth discussion that whether disorder is present over a wide range of length scales or whether the properties are dominated by more macroscopic inhomogeneities. In the former case, the metallic state and the M-I transition can be described by conventional localization physics (e.g. the Anderson transition), while in the latter case, the M-I transition would be better described in terms of percolation between metallic islands [97].

1.1.2.3 Band structure and charge carriers in conducting polymers

A continuous system of strongly interacting atomic orbitals leads to the formation of band-like electronic states. The atomic orbitals of each atom in an inorganic semiconductor or in a metal overlap with each other in the solid state giving rise to a number of continuous energy bands. The electrons provided by each orbital are delocalized throughout the entire array of atoms. The extent of delocalization and the bandwidth are determined by the strength of interaction between the overlapping orbitals. In case of conjugated polymers, the band structure originates from the interaction of the $p$ orbitals of the repeating units throughout the chain. A set of bonding and anti-bonding molecular orbitals is formed by the combination of two or more adjacent $p$ orbitals, in which the electron pairs are shared by more than two atoms resulting in a delocalized $\pi$-band. The bonding $\pi$-orbital is referred to as the highest occupied molecular orbital (HOMO) and the anti-bonding $\pi$-orbital is referred to as the lowest unoccupied molecular orbital (LUMO) [98]. The HOMO and LUMO can be thought to be analogous to the valence and conduction band in case of solid state materials. Fig. 1.6 (a) is a schematic depiction of the formation of HOMO and LUMO in case of trans-polyacetylene. The detailed band structure of polyacetylene and the difference in the band structures of conventional polymers
as compared with conducting polymers has been schematically depicted in the Fig. 1.6 (b, c).

Figure 1.6: (a) Schematic representation of the formation of HOMO and LUMO in polyacetylene due to the presence of a continuous system of strongly interacting atomic orbitals. (b) Difference between band structure of conventional polymer, undoped and doped conducting polymer and (c) Detailed band structure of trans-Polyacetylene showing the energy band-gap and associated parameters.
Unless doped, most of the conjugated polymer systems behave as insulators. Although this property of conducting polymers is very similar to that of semiconductors but the underlying physics is quite different. Three-dimensionally bonded materials have rigid structures owing to their four-fold (or six-fold, etc.) coordination of each atom to its neighbors through covalent bonds [98]. Due to the rigidity of the lattice, charge carriers added to the system are accommodated in the conduction and the valence bands without negligible rearrangement of the bonding. In such systems, therefore, the conventional concept of electrons and holes as the dominant excitations has been followed.

Bonding in conjugated polymers, on the other hand, has reduced dimensionality since the intra-chain interactions are much stronger than the inter-chain interactions between adjacent chains. These polymers therefore have two-fold coordination and are hence susceptible to structural distortion [99]. As a result, the dominant electronic excitations are inherently coupled to chain distortions, and the equilibrium geometry is determined by the occupancy of the electronic levels via electron-phonon coupling [100].

When a conjugated polymer is doped, the accommodation of an added charge becomes much easier if the charge is localized over a smaller section of the chain. The charge can be localized in the conjugated polymer if the reduction in the ionization energy of the chains due to addition of the charged species can offset the elastic energy gained by the system due to the local rearrangement of the bonding configuration in the vicinity of the charge. The nature of charged defects formed on the polymer backbone during doping depends on the structure of the polymer chain. Different types of charged defects have been observed for conducting polymers with degenerate ground state structures such as polyacetylene and for those with non-degenerate ground state structures such as polyaniline or poly (p-phenylene) [101, 102]. Figure 1.7 shows a schematic depiction of the formation of different types of charge carriers in conducting polymers and the corresponding modifications in their band structure.

When an electron is removed from the \( \pi \)-system of a non-degenerate polymer such as poly (p-phenylene) or polyaniline (PAni) via chemical oxidation, an unpaired electron with spin \( \frac{1}{2} \) (a free radical) and a spinless positive charge
(cation) are created as is evident from the Fig. 1.7. The radical and cation are coupled to each other via a local bond rearrangement, creating a polaron which appears in the band structure as localized electronic states symmetrically located within the gap with the lower energy states being occupied by a single unpaired electron [101-103].

Creation of Polarons and bipolarons in poly (p-phenylene) and solitons in trans-polyacetylene

Figure 1.7: Molecular structures of conducting polymers illustrating the formation of the localized defects (charge carriers) viz., polarons, bipolarons and solitons. A schematic representation of the modifications in the band structure of conducting polymers after the creation of these localized defects upon doping is also illustrated.

Further oxidation creates dications in the polymer [Fig. 1.7]. An electron can be removed from either the polaron or 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 comprised of two positive charges coupled through the lattice distortion, creating a new spinless defect known as the bipolaron [104, 105]. Removal of an additional electron from a neutral portion of the chain would create two polarons. Because the formation of a bipolaron produces a larger decrease in ionization energy compared to the formation of two polarons, the former process is energetically favourable. These new empty bipolaron states are
also located symmetrically within the band gap. Further doping creates additional localized bipolaron states, which eventually overlap to form continuous bipolaron bands at high enough doping levels. The case of polyaniline is somewhat different as they have polarons as the major charge carriers. The reason for the non-existence of bipolarons in polyaniline has been elaborated in the section 1.1.3.

In case of conjugated polymers with degenerate ground state structures, the situation is somewhat different. Although, the initial oxidation of trans-polyacetylene also creates polarons, but further oxidation leads to the formation of a different type of charged defects in polyacetylene. Since the ground state of trans-polyacetylene is twofold degenerate, the bonding configurations on either side of the charged defects only differ by a reversed orientation of the conjugated system and are energetically equivalent resonance forms as can be seen from the Fig. 1.7. It in turn creates isolated, non-interacting charged defects that form domain walls separating two phases of opposite orientation but identical energy. Such defects are called solitons, which results in the creation of new localized electronic states that appear in the middle of the energy gap. As doping increases, these states can overlap to form soliton bands [83].

1.1.2.4 Transport processes in conducting polymers

The revelation of the nature of charge transfer and charge transport processes in conducting polymers is the most interesting theoretical problem of this field. It is also of great practical importance, because in most of their applications fast charge propagation through the conducting polymer is desired. In conducting polymers the polymer backbone is extensively conjugated, which makes charge delocalization possible considerably. Various models have likewise been developed to explain the mechanism of charge transport in conducting polymers. Out of the two approaches that are generally employed, one is the delocalized band model in which, the charges and unpaired electrons are assumed to be delocalized over a large number of monomer units [10, 106]. The other one is the chemical model where it is assumed that the charge is localized in the polymer chain [107], or at most only some monomer units.

The macroscopic charge transport in a conducting polymer matrix represents a superposition of the local transport mechanism. The intrinsic
conductivity, which refers to the conduction process along a conjugated chain, can be described in terms of band theory, which is well-established for solid materials. The neutral (reduced, undoped) polymer has a full valence and empty conduction band separated by a band gap. This intra-chain conduction provides very high intrinsic conductivity \[108, 109\].

It is now well accepted that non-intrinsic (interstrand and interfiber) transport processes in conducting polymers occur by the movement of charge carriers from the localized defect states viz., polarons, bipolarons or solitons \[83, 101-105\]. As a result, the theories explaining non-intrinsic charge transport mechanisms in conducting polymer are dominated by thermally activated hopping (or tunneling processes) in which the charge carriers hop across (or tunnel through) barriers created by the presence of isolated states or domains \[110-114\]. These include models such as intersoliton hopping \[110\], interchain hopping of bipolarons \[111\], variable range hopping in three, two and one dimensions \[112, 113\] and charging energy limited tunneling between conducting domains \[114\]. These theoretical models that have been developed for explaining transport phenomena in conducting polymers will be discussed in details in Chapter 2.

1.1.3 Polyaniline: a promising conducting polymer

Although the original work depicting the synthesis of polyaniline (PAni) from anodic oxidation of aniline was “Aniline black” published by Letheby \[58\] in 1862 but unfortunately the electrical properties were not measured at that time. It was MacDiarmid et al. in 1986 who found that aniline monomer in an acid aqueous solution can be chemically oxidized by ammonium peroxydisulfate (APS) to obtain green powder of PAni with a conductivity of \(~3\) S/ cm \[69\]. Since its rediscovery as a conducting polymer, PAni has generally been synthesized by both chemical and electrochemical methods \[75\]. Recently, PAni has also been synthesized using a novel mechano-chemical route \[115\]. PAni has been a highly investigated conducting polymer because of easy synthesis, low-cost, high environmental stability, complex molecular structure and special doping mechanism by oxidation as well as protonation.

Polyaniline (PAni) has a complex molecular structure dominated by its oxidation states. The allowed oxidation states of PAni have been investigated
The general molecular structure shown in the Fig. 1.8 (a) for the base form of PAni was for the first time proposed by MacDiarmid et al. [117] and later confirmed by 13C-NMR [118]. The base forms of polyaniline (PAni) can exist in four different oxidation states depending upon the values of $y$ [Fig. 1.8 (a)]. Leucomeraldine, the completely reduced form of polyaniline, has a structure corresponding to $y=1$ in the general structure as can be visualized from the Fig. 1.8 (b). The completely oxidized form of PAni base can be obtained by substituting $y=0$ in the general structure and is known as Pernigraniline [119]. The half-oxidized or so for that matter half reduced form of PAni is called “Emeraldine base” ($y = 0.5$). PAni may also exist in another oxidation state known as Nigraniline for which the value of $y$ is taken as 0.75.

Figure 1.8: (a) General molecular structure of polyaniline (PAni). The different oxidation states of PAni (b) Leucomeraldine, (c) Emeraldine, (d) Nigraniline and (e) Pernigraniline are depicted in the figure.
Polyaniline (PAni) is unique among the family of \( \pi \)-conjugated polymers because of several characteristic features that it possesses. Firstly, Polyaniline (PAni) is a generalized “A-B” type polymer in which both the carbon rings and nitrogen atoms are within the conjugation path. Thus, in PAni the heteroatoms also contribute appreciably to the formation of \( \pi \) band [120]. The emeraldine form of the polymer is to a large extent different from other \( \pi \) conjugated polymers that have been studied so far because of its charge-conjugation asymmetry [121]. Secondly, PAni is the first example of conducting polymers doped by protons, which was later called “proton doping”. Proton doping in emeraldine does not involve a change of the number of electrons associated with the polymer backbone as shown in Fig. 1.9 [69, 122]. The emeraldine base (EB) form of PAni is an insulator constituted by an equal number of reduced \([-(C_6H_4)\text{-NH}\text{-}(C_6H_4)\text{-NH-}]\) and oxidized \([-(C_6H_4)\text{-N}=\text{(C}_6\text{H}_4)=\text{N-}]\) units having conductivity of the order \(10^{-10}\) Scm\(^{-1}\) but can be transformed into the conducting emeraldine salt (ES) form \([\sigma (295\text{ K})\sim 5\text{ Scm}^{-1}]\), if protons are added to the –N= sites. Thus, the proton doping process is significantly different from redox doping that involves the partial addition (reduction) or removal (oxidation) of electrons to or from the polymer backbone [123].

**Emeraldine Base**

\[
\begin{align*}
\text{H} & \text{N} \text{H} \\
\text{N} & \text{N} \\
\text{N=\text{N}} & \text{N} \\
\end{align*}
\]

Proton doping \(\leftrightarrow +2\text{H}^+\text{A}^-\) \(-2\text{H}^+\text{A}^+\)

**Emeraldine Salt**

\[
\begin{align*}
\text{H} & \text{N} \text{H} \\
\text{N} & \text{N} \\
\text{N}^+ \text{A}^{-} & \text{N}^+ \text{A}^{-} \\
\end{align*}
\]

Figure 1.9: Schematic representation of the conversion of Emeraldine base (EB) into the Emeraldine salt (ES) form of polyaniline upon proton doping.
Initially, it was proposed that proton doping only takes place on the imine segment of the emeraldine base to generate a bipolaron [69, 117]. However, this was not supported by theoretical calculations which ruled out the presence of a bipolaron lattice (spinless) in the emeraldine salt form [121]. Furthermore, a strong ESR signal observed from the proton doped emeraldine base also indicated that instead of spinless bipolarons, polarons were the major charge carriers in emeraldine salt [124]. This controversy was solved later by Epstein et al. [124, 125] who suggested that spinless bipolarons can convert into two spinning polarons. The bipolaron lattice in the emeraldine is destabilized by local lattice distortion and coulombic interactions [126]. MacDiarmid et al. [122] proposed that polarons in emeraldine salt are of semiquinone form. It suggests that the complete protonation of the imine nitrogen atom in the emeraldine base by proton doping results in the formation of a delocalized poly-semiquinone radical cation [69, 122]. The mechanism of proton doping in polyaniline has been investigated in details using in situ UV-Visible, fluorescence and ESR spectroscopy by Wan et al. [127-129], which confirmed that proton doping took place on the imine segment of poly-emeraldine chain. Thus, the molecular structure of the protonated emeraldine base i.e., emeraldine salt is determined by both oxidation and protonation states.

It has also been observed that the crystalline structure of emeraldine can be distinguished between two classes viz., Class I and Class II, which differs in their ordering and compactness [130]. Class I emeraldine that is obtained by direct preparation (synthesis/ precipitation of a salt form) exhibits ES-I crystal structure and the insulating base form is essentially amorphous EB-I. Polyaniline belonging to class II possess ES-II structure in the conducting HCl salt form and EB-II structure in the insulating base form. The emeraldine salt ES-I, is the most compact structure, while the less compact ES-II is obtained by converting crystalline EB-II into a salt form (i.e., by insertion of Cl- anions into a pre-existing crystalline structure). In ES-I the neighbouring columns of chlorine ions are in phase i.e., Cl- ions are at the same level), while in ES-II they are out of phase in the “a” direction i.e., they are shifted by “c/ 2” [130].
The emeraldine base (EB) form of polyaniline (PAni) is soluble in NMP and is generally used to fabricate free-standing films of the emeraldine base. However, the solution processibility of the doped form (ES form) is very poor since it is insoluble in organic as well as aqueous solution. Many methods such as sulfonation or incorporation of N-alkyl-sulfonic acid pendant groups [131, 132], dopant-induced [80], self-doping polymer [133], micro-emulsion polymerization [134], and controlled relative molecular mass [135], have, therefore, been reported for improvement of solubility and processability of PAni.

Polyaniline (PAni) is not only unique in its molecular structure and doping mechanisms but also has unique optical, electrical and magnetic properties, which have been effectively used in several applications areas. Highly conducting form (ES) of PAni is controlled by two completely different processes: protonic acid doping and oxidative doping, while other conductive polymers are affected by their oxidation state alone, resulting in it holding a special position in the field of conducting polymers. PAni has been found to exhibit nonlinear optical properties because of the relatively weak \(\pi\)-binding and the special proton doping process [136]. Magnetic properties of PAni are also interesting in that the magnetic susceptibility changes from a Curie-like to a Pauli-like behaviour as the temperature increases [137]. Moreover, the magnetic properties of PAni are affected by doping structure and degree of protonation, chain structure as well as synthesis conditions [124]. Strong thermo-chromic effect and improved mechanical properties have also been reported for diesters of 4-sulfophthalic acid doped PAni. The development of PAni fiber production techniques have been used to create commercial fibers (PANION) that can be used in solid-state electrochemical devices [138]. PAni has also found applications in diverse areas such as sensors, OLEDs, OFETs, electrodes for supercapacitors, EMI shielding applications etc [48, 139-142].

1.2 Conducting polymer based nanostructured materials

Nanoscience and nanotechnology has emerged as an inimitable and powerful interdisciplinary research area, which has generated several futuristic ideas that are slowly finding important applications in the present day world.
Nanostructured materials (having one of their dimensions less than 100 nm) may be two dimensional (2D) such as quantum well or nanosheets like that of graphene [143], one-dimensional (1D) such as nanofibers or nanowires or nanotubes for that example and zero dimensional (0D) structures such as quantum dots. Nanostructured materials have attracted tremendous interest amongst the scientific community primarily because of their peculiar and fascinating properties, as well as their unique applications. As compared to the bulk counterpart, nanostructured materials exhibit enhanced properties mainly because of their large surface area that becomes extremely important in applications such as catalysis or sensing in which the interaction of the material with the environment is the major criteria determining the efficiency of the device. Another important reason as to why the physico-chemical properties of nanostructured materials are often entirely different from the bulk counterpart is due to the variation in the energy band-gap which leads to a variation in their optical and electrical conduction properties. Fig. 1.10 illustrates the variation in colour of gold with the variation in particle size. Fig. 1.10 (a) shows a gold one-dollar coin depicting the original colour of gold in bulk form whereas the Figs. 1.7 (b-f) show the variation in gold particles with increasing particle size [Fig. 1.7 (b-f)].

Figure 1.10: Variation in colour of (a) $1 gold coin, showing the normal bulk color of gold and (b-f) gold nanoparticles of different colours with increasing particle size (Courtesy: http://www.bluesci.org).

Among different types of nanostructured materials, conducting polymer based nanostructured materials deserve a special mention as they combine the advantage of organic conductors with that of low dimensional materials. These nanostructured materials have some unique properties such as \( \pi \)-conjugated polymeric chains, metal/semiconductor like conductivity, reversible physical
properties by novel doping/de-doping processes. The prospect of these materials being used as molecular wires and nanodevices has made these materials extremely important in nanosciences and nanotechnology. However, the field of conducting polymer based nanostructured materials is still in its infancy and there are several concerns that need to be resolved for realizing the true potential of these nanostructured materials. The first major criteria is the development of simple and efficient methods for the synthesis of conducting polymer based nanostructured materials and the influence of size on the physical properties must be properly investigated. Some sophisticated characterization techniques have to be used or even developed in certain special cases for detailed analysis of the molecular structure and physico-chemical properties of the conducting polymer nanostructures in order to bring out their difference with the bulk and the mechanism underlying their formation. This can help in tailoring the properties of these nanomaterials for specific applications. Tremendous amount of development is also required in the fabrication technology to improve the application of these materials as efficient nanodevices and for future commercial applications.

Conducting polymer based nanostructured materials may be broadly classified into two categories:

(i) Conducting polymer nanostructures such as nanofibers, nanoparticles, nanowires, nanotubes of pure conducting polymers and

(ii) Conducting polymer nanocomposites, which are mixtures of metal / metal oxide / ceramic nanoparticles with conducting polymer at nanoscale or nanoscale mixture of conducting polymer nanostructures with another polymer.

The following sub-sections present a brief overview of these two categories of conducting polymer based nanostructured materials in order to give a better insight into the science and technology of these materials.

1.2.1 Conducting polymer nanostructures

Nanostructures viz., nanofibers, nanotubes, nanoparticles, nanowires etc. of pure conducting polymers have created immense excitement in the scientific community because of their potential in different application. The last two
decades have witnessed tremendous development in the field of conducting polymer nanostructures. There are three main strategies that are generally used for obtaining conducting polymer nanostructures: (a) Templateless synthesis, (b) Template-assisted synthesis and (c) Molecular template-assisted synthesis [144].

Conducting polymer nanostructures have been synthesized using different techniques viz., 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 [145-154]. These materials have also found applications in diverse areas such as chemical and biosensors, memory devices (PAni-MEM), flash welding etc. [155-159].

1.2.2 Conducting polymer nanocomposites

Composite materials are naturally occurring or engineered materials made from two or more constituent materials with significantly different physical or chemical properties as compared to their individual components which remain separate and distinct at the macroscopic or microscopic scale. A common example is “Concrete”, a composite construction material composed of cement (commonly Portland cement) and other materials such as fly ash, slag cement, limestone, granite, fine aggregate such as sand, water and chemical admixtures. Concrete is used more than any other man-made material in the world [160]. However, in the microscopic world, due to the reduced particle size of the components the interface interactions play a pivotal role in composite mixtures and this is especially important for a new class of recently developed materials named, the nanocomposites.

Nanocomposites can be defined as multiphase solid materials having unique physical properties and wide application potential with at least one of the phases constrained by some means to grow more than 100 nm in either one, two or three dimensions that are obtained from molecular level mixing of two or more nanosized objects using an appropriate technique [161]. Depending upon the macroscopic physical structures nanocomposite materials can be classified into three broad categories: (a) Fiberous (b) Laminar and (c) Particulate nanocomposites [162, 163].
Chapter 1: Introduction

The first generation of nanocomposites were the nanocomposite plastics which were homogeneous dispersions of small sized inorganic particles throughout a polymer matrix. These nanocomposites were prepared in the 1970's employing sol-gel technique, however, the inorganic phase in these nanocomposites were in some cases not attached chemically to the organic phase. Nanocomposite plastics found tremendous applications in surface coating technology. The second generation of nanocomposite materials emerged in the 1980's when fine particles, minerals and clay fillers were used as a secondary phase in plastics. During 1990's and beyond, the third generation of nanocomposite materials emerged where polymeric materials were reinforced with nanofibers such as carbon nanotubes, SiC whiskers, colloidal silica, nano-clay particles etc [164].

Nanocomposites of intrinsically conducting polymers (ICPs) are materials that utilize conjugated polymers and at least one secondary component that can be inorganic or organic materials or biologically active species [165]. One can derive exciting novel properties from nanocomposites by successfully combining the characteristics of its parent constituents into a single material. Generally, in polymer nanocomposites the polymeric component is utilized to provide mechanical strength and processibility to the resulting nanocomposite material. However, in case of nanocomposites of intrinsically conducting polymers the secondary components viz., inorganic, biological or organic active species are generally used to enhance the processibility and mechanical strength whereas the functionalities of intrinsic conducting polymers are used for different applications [165]. The properties of the secondary components are also utilized in some applications. In a nutshell, conducting polymer nanocomposites are truly hybrid materials which have excellent physicochemical properties resulting from the synergistic effect of the individual properties of two or more components. Conducting polymer nanocomposites can be broadly classified into three classes depending upon the nature of association between the individual components. These are Inorganic-in-Organic (I-O) nanocomposites, Organic-in-Inorganic (O-I) nanocomposites and Organic-in-Organic (O-O) nanocomposites, which are discussed in the following sub-sections.
1.2.2.1 Inorganic-in-organic (I-O) nanocomposites

Inorganic-in-organic nanocomposites refer to materials in which inorganic nanoparticles are embedded in organic matrix. Thus, in these hybrid materials the organic phase plays the role of a host to an inorganic guest. These nanocomposites not only correlate the world of nanoparticles with that of the macromolecules, but often help in surmounting the processing problems associated with intrinsic conducting polymers (ICPs). Several techniques have been adopted to encapsulate inorganic nanoparticles into the host-conducting polymer matrix, which predominantly includes chemical and electrochemical techniques [166]. The encapsulation is generally done ex-situ where the inorganic nanoparticles are prepared separately and then added to the conducting polymer matrix in different compositions during the polymerization reaction [164-166]. However, in-situ techniques have also been used to synthesize inorganic-in-organic nanocomposites in which the inorganic nanoparticle is synthesized and encapsulated in the conducting polymer matrix simultaneously during polymerization in the same reaction vessel [164-166]. Different conducting polymers viz., polyaniline (PAni), polypyrrole (PPy), polyphenylene vinylene (PPV), poly (3, 4-ethylenedioxythiophene) (PEDOT) have been extensively used as hosts for inorganic metal, metal oxide and ceramic nanoparticles to synthesize inorganic-in-organic conducting polymer nanocomposites [167-171]. Different types of inorganic particles have been encapsulated in conducting polymers by chemical or electrochemical incorporation techniques depending upon the necessity of the application areas where the nanocomposites are intended to be applied. These include metals such as gold (Au) and silver (Ag), metal oxides such as SiO$_2$, SnO$_2$, CeO$_2$, CuO, Fe$_2$O$_3$, Fe$_3$O$_4$, MnO$_2$, BaSO$_4$, Al$_2$O$_3$, ZrO$_2$, n-TiO$_2$, V$_2$O$_5$, WO$_3$ etc. [172-190]. The methods adopted for preparation of the nanocomposites govern the physico-chemical properties such as its colloidal stability, optical, catalytic, electrochemical, magnetic susceptibility, etc., exhibited by these materials. These properties always add new dimensions to the characteristic of the resulting nanocomposite and in most cases are much better when compared to that of the individual components.
1.2.2.1.1 Core-shell nanocomposites

Among the inorganic-in-organic nanocomposites, those having core-shell structures have attracted tremendous scientific interest and have become more popular leading to some interesting aspects of nanocomposite synthesis. During the past decades, various synthetic methods have been developed for the preparation of core-shell conducting polymer nanocomposites with different metal and metal oxide nanoparticles encapsulated in the core of conducting polymers. Depending upon the composition of these nanocomposites several functionalities have also been observed which are quite different from the pure materials.

Figure 1.11: Schematic diagram to illustrate the synthesis mechanism of inorganic-in-organic conducting polymer nanocomposites and core-shell type nanocomposites based on conducting polymers.

Core-shell nanocomposites of polyaniline (PAni) and polypyrrole (PPy) were synthesized in stable colloidal forms with silica (SiO\textsubscript{2}) particles as the core
Colloidal PPy-gold(Au) core-shell nanocomposites have also been synthesized by a template-guided polymerization technique [194]. Fig. 1.11 shows a schematic diagram to illustrate the formation of both general and core-shell inorganic-organic nanocomposites based on conducting polymers from the constituents. Deng et al. reported the synthesis of ferromagnetic and conducting Fe₃O₄-crosslinked polyaniline nanoparticles in core-shell morphology in the presence of magnetic fluid in aqueous solution [195]. Hematite silica polypyrrole (Fe₂O₃/ SiO₂/ PPy) ellipsoidal sandwich composite spheres as well as SiO₂/ PPy ellipsoidal hollow capsules with movable hematite cores were successfully fabricated by hematite (α-Fe₂O₃) olivary particles [196]. A facile and versatile solution route was developed to prepare semiconductor metal oxide nanobelt-conducting organic polymer core-shell nanocomposites by Xu et al. [197]. Polypyrrole-coated silver nanocomposite particles have been synthesized by one-step aqueous chemical oxidative dispersion polymerization of pyrrole using silver nitrate as an oxidant [198]. Electromagnetic functionalized core-shell nanocomposites of polypyrrole (PPy) were prepared by a self-assembly process [199]. Yang et al. prepared novel sunflower-like organic-inorganic composites comprising of spherical silica and smaller conductive polypyrrole particles through an in situ self-assembly polymerization process by choosing chitosan as a modifying agent of silica surface [200]. Polypyrrole (PPy)-coated Ag composites were synthesized through interfacial polymerization technique in the presence of polyvinylpyrrolidone (PVP) by Feng et al. [201]. Monodispersed and uniform core/shell nanocomposites including CuO/ PAni, Fe₂O₃/ PAni, In₂O₃/ PAni and Fe₂O₃/ SiO₂/ PAni were successfully prepared using a double-surfactant-layer-assisted polymerization method [202]. The preparation of CeO₂/polyaniline (CeO₂/ PAni) core-shell nanocomposites via chemical oxidation of aniline using CeO₂ as an oxidant was reported by Chuang and Yang [203]. Synthesis of metallic copper nanoparticles coated with polypyrrole was very recently reported by Kobayashi et al. [204]. The importance of these types of nanocomposites is evident from the amount of work that has been done in recent years regarding the investigation of the synthesis procedures and related properties of the core-shell nanocomposites.
1.2.2.2 Organic-in-inorganic (O-I) nanocomposites

Another type of nanocomposite materials is the organic-inorganic nanocomposites in which the organic polymer is confined into the inorganic layers for a broad range of applications. A large variety of layered inorganic materials possessing well defined and ordered intralamellar space are available. These materials act as hosts and can be easily accessed by foreign species such as polymers yielding interesting lamellar nanocomposite materials. Lamellar nanocomposites can be divided into two distinct classes, intercalated and exfoliated. These two classes of organic in inorganic nanocomposites are discussed in the following sub-sections. Figs. 1.12 (a, b) show the molecular structures of two layered silicates (clays) viz., montmorillonite and kaolinite, respectively that are often used as inorganic hosts for organic polymers.

Figure 1.12: Molecular structure of (a) Montmorillonite and (b) Kaolinite (Courtesy: http://pubs.usgs.gov/of/2001/of01-041/htmldocs/clays/smc.htm)

1.2.2.2.1 Intercalated and exfoliated nanocomposites

Layered silicates have crystal structures with two dimensional spacings in the nanometer range as seen from Fig. 1.12. Clay-Polymer nanocomposites have recently attracted a great deal of attention as they offer enhanced mechanical and thermal properties as compared to conventional materials. These nanocomposites can be subdivided into primarily two groups: intercalated and exfoliated nanocomposites.

Polymers intercalated into low-dimensional host lattices form an attractive class of organic-in-inorganic nanocomposites since intercalation can combine
properties of both the guest polymer and the inorganic host in a single material [205]. In the case of intercalation, the organic component is inserted between the layers of clay such that the inter-layer spacing is expanded, but the layers still bear a well-defined spatial relationship to each other. These compounds also serve as model systems for understanding the effect of confinement of the guest on properties in relation to those in bulk [206, 207]. In recent years, there has been extensive study of the factors such as exchange capacity of the clay, the polarity of the reaction medium and the chemical nature of the interlayer cations (e.g. onium ions). Fig. 1.13 shows a schematic diagram of the different types of clay-polymer nanocomposites.

![Schematic diagram of different types of layered organic-inorganic nanocomposites](image)

**Different types of nanocomposites**

- **Conventional**
- **Intercalated**
- **Ordered Exfoliated**
- **Disordered Exfoliated**

Figure 1.13: Schematic diagram of different types of layered organic-in-inorganic nanocomposites
In exfoliated nanocomposites, the polymer chains alternate with the inorganic layers in a fixed compositional ratio and have a well-defined number of polymer layers in the intra-lamellar space. In an exfoliated structure, the layers of clay completely separate out and the individual layers are distributed throughout the organic matrix. The number of polymer chains between the layers is almost continuously variable and the layers stand >100 Å apart and these nanocomposites are interesting for their superior mechanical properties. Okada et al. prepared new molecular scale nanocomposites from saturated polymers (Nylon-6 and other plastic) exfoliated in clay layers [208]. These products show extraordinary mechanical strength compared to that expected by simple mixing of the individual components. Because of these enhanced properties, they find extensive applications in automobile, and furnishing industries. Exfoliated nanocomposites can again be divided into ordered and disordered exfoliated nanocomposites; the major difference being that the former can be detected by X-ray diffraction and the latter is X-ray amorphous.

Despite their relatively large molecular weights, electroactive polymers can play the role of intercalated guest molecules inserted within the van der Waals gaps of layered inorganic phases resulting in a special class of intercalative nanocomposites that are expected to have novel multifunctional properties useful for opto-electronic and electrochemical devices. Both polymer electrolytes and electronically conducting polymers have been used as the organic guests in clay based organic-inorganic hybrid nanocomposites. Recently, many related investigations have reported the use of polymer/clay nanocomposites in solid-state electrolytes, where the intercalated or exfoliated state of MMT plays an important role in ion conduction in these electrolytes [209, 210]. Several conducting and non-conducting organic polymers have successfully been inserted into highly oxidizing hosts via intercalation by the groups of Kanatzidis, Nazar, Buttry, and Gomez-Romero et al. [211-214]. Conducting polymers viz., Poly (3, 4-ethylene dioxythiophene) has also been intercalated in different layered compounds such as V$_2$O$_5$, VS$_2$ and MoO$_3$ [164, 215-217] and has been applied as electrodes for Lithium batteries.
1.2.2.3 **Organic in Organic (O-O) nanocomposites**

Organic-in-organic (O-O) nanocomposites form another class of nanocomposite materials in which an organic polymer having functionality acts as a guest material for another polymeric host with superior mechanical properties. Generally, insulating polymers having superior mechanical strength and processibility such as poly (methyl methacrylate) [PMMA], polyvinyl alcohol (PVA) etc. are used as host materials [218, 219]. Conducting polymer nanofibers and nanotubes in both conducting and non-conducting forms have been extensively used as guest materials in these types of nanocomposites. Insulating polyaniline (PAni) nanofiber reinforced gel polymer electrolytes have been found to show better ionic conductivity than the pristine polymer electrolyte [220]. Carbon nanotube and nanofiber reinforced polymer composites have been extensively studied and the resulting nanocomposite has been found to have much better mechanical strength and stability with the added advantage of being conducting [221-225]. This class of nanocomposites can be extremely helpful for minimizing the processibility related problems associated with conducting polymers and hence can have potential applications in device fabrication.

1.3 **Swift heavy ion (SHI) irradiation of conducting polymers**

Ion beams have become an integral part of numerous surface processing schemes and in the modification of surface layers of solids [226, 227]. Swift heavy ion (SHI) irradiation causes exotic effects in different classes of materials which otherwise cannot be generated by any other means. Swift heavy ion irradiation has already been used as an efficient tool for enhancing the physico-chemical properties of conducting polymers such as conductivity, electrochemical stability, sensing properties etc. [228, 229]. The primary phenomena associated with the interaction of ion beam and polymers are cross-linking, chain scission and emission of atoms, molecules and molecular fragments [230, 231].

An important parameter used to characterize the energy transfer from ion to the target is the energy loss $\Delta E / \Delta x$ (eV/Å), defined as the energy deposition per unit length along the ion track. The value of $\Delta E / \Delta x$ varies with varying ion
energies. When an energetic ion interacts with a polymer, depending upon its energy, it can lose its energy in two main processes viz., by interacting with the target nuclei (Nuclear Energy Loss) and by interacting with target electrons (Electronic Energy Loss), which are discussed in the following sub-sections.

1.3.1 Nuclear energy loss

Nuclear energy loss ($S_n$) arises from collisions between the energetic ion and the target nuclei, which causes atomic displacements and phonons [232]. When the colliding particle imparts energy greater than certain displacement threshold energy ($E_d$) to a target atom it can displace. $E_d$ is the energy that a recoil atom requires to overcome the binding forces and to move a distance more than the atomic spacing away from its original site. Since the nuclear collision occurs between two atoms with electrons around their nuclei, the interaction of an ion with a target nucleus is treated as the scattering of two screened particles. The incident ion primarily undergoes nuclear energy loss ($S_n$) at low energies (~1KeV/nucleon) [233]. The nuclear energy becomes important when an ion slows down to approximately the Bohr radius (orbital electron velocity, $2.2 \times 10^6$ m/s). Therefore, the maximum nuclear energy loss occurs near the end of the ion track for high energy ions. Nuclear energy loss is derived with the consideration of momentum transfer from the incident ion to the target atom and the interatomic potential between them.

1.3.2 Electronic energy loss

Electronic energy loss ($S_e$) arises from the electromagnetic interaction between the positively charged ion and the target electrons. Electronic energy loss can be explained by primarily two mechanisms: one mechanism is called glancing collision (inelastic scattering, distant resonant collisions with small momentum transfer) and the other is known as knock-on collision (elastic scattering, close collisions with large momentum transfer) [232]. Both glancing and knock-on collisions transfer energy in two ways: electronic excitation and ionization. At high energies ($\geq 100$ KeV/nucleon) the incident ion primarily undergoes electronic energy loss ($\mathrm{d}E / \mathrm{d}x_e$), and if the films are sufficiently thin compared to
the stopping range of the ion, the electronic energy loss is reasonably uniform throughout the film thickness [233].

1.3.3 Latent tracks

On their way through matter, energetic ions lose energy and induce a continuous trail of excited and ionized target atoms. Due to their highly charged state, associated with a high energy transfer, heavy ions are especially suited to create cylindrical zones of irreversible chemical and structural changes. These zones have a diameter of only a few nanometers and are known as latent tracks. Formation of tracks in polymers can be explained on the assumption that particles lose energy during its passage through the matter in two ways: (i) along the trajectory, the energy yield being large, all chemical bonds are broken and (ii) in the neighboring of the trajectory, only the bonds between the monomer units are broken [232, 233].

1.4 Conducting polymers for biomedical applications

Research on conducting polymers for biomedical applications intensified greatly with the discovery that these materials are compatible with many biological molecules such as those used in biosensors in the 1980s. By the mid-1990s conducting polymers were also shown to modulate cellular activities, including cell adhesion, migration, DNA synthesis and protein secretion via electrical stimulation [234-237]. Recently, conducting polymers are also being considered for a range of biomedical applications, including the development of artificial muscles [238], controlled drug release [239] and the stimulation of nerve regeneration [240]. Low cytotoxicity and good biocompatibility of these materials are also evident from the growth of cells on conducting polymers and from the low degree of inflammation seen in test animals over a period of several weeks [241]. Electrochemical actuators using conducting polymers have been developed by several investigators [238, 242-244]. Actuation properties of conducting polymers have been used to release drugs from reservoirs covered by thin PPy bilayer flaps upon application of a small potential to the PPy [245]. Actuator devices based on conducting polymers have great potential as actuators for many biomedical applications, such as steerable catheters for minimally invasive
surgery [246], micropumps and valves for labs-on-a-chip [247, 248], blood vessel connectors and microvalves for urinary incontinence [249]. With respect to drug delivery applications, electrical stimulation of CPs has been used to release a number of therapeutic proteins and drugs such as NGF [249], dexamethasone [250, 251] and heparin [252]. Treatment of the inflammatory response of neural prosthetic devices in the central and peripheral nervous systems requires precise and controlled local release of anti-inflammatory drugs at desired points in time [251], which can be obtained using specially designed conducting polymers nanostructures. Martin and his group demonstrated that individual drugs and bioactive molecules can be released from polypyrrole and PEDOT nanotubes at desired points in time by using electrical stimulation [251]. Conducting polymers such as polypyrrole and polyaniline have been extensively investigated for tissue engineering applications [249, 253]. Conducting polymers augmented with biological moieties have also been considered to offer advantages for neural probe applications [249, 254, 255]. There have also been some investigations regarding the antioxidant activity of conducting polymers especially polyaniline (PAni) and polypyrrole (PPy) [256, 257].

1.5 Sensors based on conducting polymers

Sensors are very important devices in industry for quantity control and online control of different processes. In order to measure parameters such as temperature, pressure, vacuum, flow etc. physical sensors were used. However, in some special cases such as the detection of evolution of hazardous gases during industrial processes which are very harmful for the environment, chemical sensors are required. Chemical sensors based on metal-oxides have, therefore, been synthesized for detection of various toxic gases produced during industrial processes that destruct the environment [258]. However, the metal-oxide sensors suffer from a major drawback in spite of being selective. Sensors based on metal-oxides generally operate at very high temperature, which is not desired for detecting hazardous chemicals evolving from industrial processes [259]. In order to overcome this problem the active layer of sensors have been replaced by conducting polymers viz., polypyrrole (PPy), polyaniline (PAni), polythiophene (PTh) and their derivatives since early 1980s [260]. Conducting polymers are
redox active materials and when doped these materials exhibit changes in their colour, volume, mass, conductivity, ion permeability and mechanical strength [126]. Detecting the variations in any one of these physical properties indirectly allows the detection of the analyte responsible for provoking the physical change in the conducting polymer. As compared to the commercially available metal-oxide sensors, conducting polymer based sensors have many improved characteristics such as high sensitivities and short response times at room temperature. Another advantage of sensors based on conducting polymers is that they can easily be synthesized by chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivations [259]. Conducting polymers also have good mechanical properties, which permit simplistic manufacture of sensors [259]. As a result, enormous interest has grown amid the scientific community intended for sensors fabricated from conducting polymers. In the following sub-sections we discuss briefly about chemical and biosensors based on conducting polymers. A description of the different types of configurations and sensing principles used for conducting polymer based sensors has also been presented.

1.5.1 Chemical sensors

Chemical sensors based on conducting polymers have attracted tremendous interest in the scientific community primarily because of the fact that they can be easily fabricated and can operate at room temperature. Chemical sensors based on conducting polymers have been used to detect several types of chemicals either in gaseous form or even in liquid form at room temperatures [261-268]. Several synthesis techniques have also been adopted for fabricating conducting polymer based chemical sensors that include spin-coating, dip-coating, drop-coating, solution casting and Langmuir-Blodgett techniques [259]. Although the chemical sensors based on conducting polymers exhibit very high sensitivity and fast response time they suffer from very poor selectivity [269]. The selectivity of chemical sensors can be, however, improved by several methods. One such method is the use of ion selective membranes as a layer over the conducting polymer sensors [270]. The ion selective membrane allows only a specific analyte to interact with the conducting polymer and produce detectable
change in its physico-chemical properties. Another alternative is using conducting polymer based biosensors in which a reactant specific biomolecule is immobilized in the polymer matrix. Details of biosensors based on conducting polymers have been discussed in the next section.

1.5.2 Biosensors

The first biosensing device was created by integrating an enzyme into an electrode [271]; since then, there has been a lot of progress in monitoring and diagnosing biologically important metabolites such as glucose, hormones, neurotransmitters, antibodies and antigens for clinical purposes. Biosensors represent a new trend budding in the clinical diagnostic technology. A biosensor is a device that comprises of a biological sensing element either intimately connected to or integrated within a transducer [249, 272]. The sensing element interacts with the analyte of interest producing a chemical signal that is transmitted to the transducer, which ultimately transforms the input into an electrical signal. Enzymes, tissues, bacteria, yeast, antibodies/antigens, liposomes, organelle etc. are some of the biocomponents that have been used as biochemical transducers [234, 272, 273]. These recognition biomolecules incorporated within a biosensor possess tremendous specificity towards a particular analyte but have some severe problems regarding their stability. These biomolecules are extremely vulnerable to extreme conditions such as temperature, pH and ionic strength and generally have short lifetime in solution [274]. This led to the development of the concept of immobilization of these biomolecules in a suitable matrix; however, immobilization of biomolecules against the environmental conditions results in decreased enzyme activity [275, 276]. The activity of immobilized molecules not only depends upon the surface area, porosity and hydrophilic character of immobilizing matrix but also upon the reaction conditions and methodology chosen for immobilization [272].

Conducting polymers have been extensively used as transducers that integrate the signals produced by biological sensing elements such as enzymes. Biosensors based on conducting polymers viz., polypyrrole (PPy), polyaniline (PAni), polythiophene (PTh) have been extensively used for the estimation of metabolites such as glucose, urea, cholesterol etc. in blood that is of immense
importance in clinical diagnostics [234, 235, 277-284]. Depending on how the 
chemical signal is sensed and transmitted, biosensors can be divided into several 
categories: amperometric (measures current), potentiometric (measures potential), 
conductometric (measures change in conductivity), optical (measures light 
absorbance or emission), calorimetric (measures change in enthalpy), and 
piezoelectric (measures mechanical stress).

Conducting polymers offer many important features that make them 
potential candidates as electrodes for miniaturized biosensors. Firstly, electro-
deposition of conducting polymer films can be utilized to localize a biologically 
active molecule of any geometry and size in the conducting polymer electrodes 
which is appropriate for the fabrication of multi-analyte micro-amperometric 
biosensors [285]. Secondly, the chemical structures of conducting polymers are 
flexible and the electronic and mechanical properties can be modified according to 
the requirements. In fact, the polymer itself can be modified to bind protein 
molecules [286]. Another advantage offered by conducting polymers is that 
electrochemical synthesis allows direct deposition of the polymer on the electrode 
surface, while simultaneously trapping the protein molecules [287]. Thus, the 
spatial distribution of the immobilized enzymes, the film thickness for the 
conducting polymer based electrodes can be modified and the enzyme activity 
can be modulated by changing the state of the polymer.

However, the most crucial problem associated with the manufacture of 
conducting polymer based biosensors is the stable immobilization of enzymes 
without compromising their activity [272]. As such several physical and chemical 
techniques have been adopted for the immobilization of enzymes in conducting 
polymer matrices. As compared to some of the conventional procedures used to 
immobilize enzymes viz., physical adsorption, entrapment, cross-linking and 
covalent binding in gels and membranes, electrochemical techniques have been 
preferred for immobilizing enzymes in conducting polymer matrices [272].

1.5.3 Sensor configuration and sensing principles

Sensors based upon conducting polymers may have different 
configurations and sensing principles. In this section we will briefly discuss about 
the most common types of configurations that are widely employed for
conducting polymer based sensors with a special emphasis on piezoelectric sensors based on conducting polymers, which forms a major part of the work carried out in the present thesis.

Conducting polymer based sensors have been used in different configurations but the principle of sensing an analyte by conducting polymers depends primarily upon the fact that these polymers are redox active and can exhibit significant variations in their physico-chemical properties during doping and de-doping processes. The main sensing principles of these types of sensors can be summarized as follows [259]:

a) Redox reactions with the analytes.

b) Partial charge transfer reaction with the analytes.

c) Catalytic oxidation is also sometimes the mechanism if a catalyst is incorporated in the conducting polymer matrix.

d) Acid/base reactions.

e) Absorption of the analyte in the conducting polymer matrix can change the properties of the material and make the analyte detectable.

f) Swelling of the conducting polymer upon physical interaction with the analytes can also changes the properties of the polymer film and thereby changes the resistivity, mass etc. of the film.

Figs. 1.14 (a-e) depict the schematic configurations of different types of conducting polymer based sensors. The most common type of conducting polymer based sensors is the Chemiresistor, which are resistors with their electrical resistance sensitive to the chemical environment [288-290]. In chemiresistors contact is made between one or several pair of inter-digitated electrodes [291, 292] and the conducting polymer film used to sense the analyte. The change in the resistivity of the conducting polymer film upon exposure to different types of chemical or biochemical analytes is detected and the signal obtained is used to detect the analyte.

Organic thin-film transistors and diodes have also been applied in sensing field [293, 294]. In general, a thin-film transistors (TFTs) based upon conducting polymers consist of a active layer of the polymer in contact with two electrodes ("source" and "drain"), and a third electrode ("gate") which is separated with the
active layer by an insulating film. The analyte can be sensed by detecting the variations in the source-drain current of the device. Diodes fabricated using conducting polymers are also often used in sensing applications [295]. Exposing the conducting polymer diodes to chemical species capable of changing the doping level of the conducting polymer leads to remarkable variations in its effective barrier height, current density and rectification ratio. Thus in comparison with chemiresistors, transistors and diodes provide more parameters for measurements and hence are much more efficient as sensors.

Figure 1.14: Schematic diagrams of some of the configurations of conducting polymer sensors (a) Inter-digitated chemiresistor, (b) Thin film transistors based on conducting polymers (c) IGFETs, (d) Fiber optic sensors and (e) electrochemical sensors based on conducting polymer electrodes.
Electronic configuration of conducting polymers can change upon doping by different chemical agents and can be easily detected by UV-Vis and NIR spectroscopy [296]. New absorption bands corresponding to the formation of polaron and bipolaron can be observed in the absorption spectra; whereas some existing bands might disappear during dedoping. Based upon this principle, optical sensors with conducting polymers as active layers have also been developed for sensing different chemical and biomolecules [297-299]. In some cases fiber optic cables have also been used for detection of analytes at long distances [300-302]. Surface-plasmon resonance (SPR) is another optical technology that has been sometimes applied for detection of chemicals in gaseous forms [303, 304]. In case of a SPR sensor, the minimum in the reflectance curve shifts upon exposure to the analyte, which indicates the existence of the analytes. Although the sensitivity of these types of sensors is high but the detecting procedures are complicated.

Electrochemical sensors using conducting polymer working electrodes have also been used for detection of chemical and biochemical analytes. Electrochemical sensors are devices that extract information about sample from measurement of some electrical parameter. It is easy to categorize them according to the measured electrical parameter, because the three are linked together by the Ohm's Law. In “potentiometric sensors", the potential difference is measured. If the parameter of interest is current, then “amperometric sensors” are used and if we measure resistance or conductance we talk about “conductometric sensors“. For sensing gases using these type of sensors the general configuration is somewhat modified and a divided electrochemical cell is used with conducting polymer/metal/Nafion as the working electrode [305-307]. The supporting electrolyte usually is an inorganic acid to provide H⁺ ions for ionic conductance in Nafion film.

However, in the present thesis, we have employed piezoelectric sensors modified by conducting polymers to sense different analytes. The basic scientific principles of these types of sensors have been elaborated in the following section with a state of the art literature survey on the development of piezoelectric
sensors in general and conducting polymer modified piezoelectric sensors in particular.

1.5.3.1 Piezoelectric sensors

Piezoelectricity is a phenomenon exhibited by crystals which don't have a centre of symmetry. It is a phenomenon in which electric polarization (i.e. charge) is induced in the material upon the application of a stress. Conversely, it is the development of an induced strain that is directly proportional to an applied electric field. Different types of materials have been found to show the piezoelectric effect which includes crystals such as quartz and Rochelle salt, and ceramics such as barium titanate (BaTiO$_3$), PZT etc [308]. However, we will restrict our discussion to piezoelectric crystal sensors only as these types of sensors have been used in the present work.

A piezoelectric quartz crystal resonator is a precisely cut slab from a natural or synthetic crystal of quartz. Piezoelectric crystal sensors are passive solid-state electronic devices, which can respond to changes in temperature, pressure, and most importantly, to changes in physical properties at the interface between the device surface and a foreign fluid or solid. Such changes in physical properties include variations in interfacial mass density, elasticity, viscosity and layer thickness. The incorporation of various chemically sensitive layers has enabled the transition from the microbalance to the mass sensors and resulted in explosive growth in piezoelectric sensors in recent years. This type of sensor operates by observation of the propagation of an acoustic wave through the piezoelectric crystal. The variations in the acoustic wave propagation can be correlated to the amount of analyte captured at the surface that can be used to sense the analyte. The frequency and resonant resistance of the piezoelectric crystal under the influence of the analyte are measured [308]. However, these parameters are influenced by a large number of parameters as mentioned above. A selective sensor is obtained when a sensor surface is coated with selectively interacting thin film. Piezoelectric crystal sensors are generally available in two configurations: surface acoustic wave (SAW) and quartz crystal microbalance (QCM-B) sensors.
1.5.3.1.1 SAW sensors

The standard design for a SAW sensor is shown schematically in Fig. 1.15 [308]. This configuration is usually repeated on the same piece of quartz. Hence, one side can be the reference and the other the sensing element. The second side is often coated with a polymer, or similar material, showing selectivity toward the analyte under investigation. The electrodes take the form of IDTs etched on the surface of the quartz by photolithography technique, out of which one is the transmitter IDT which transmits the surface acoustic wave (SAW) and the other is the receiver IDT that receives the signal. Since this device deals with the variation in surface acoustic waves the name SAW sensors have been given.

![Figure 1.15: Configuration of a SAW sensor](image)

An input radio frequency (RF) voltage is applied across the transmitter IDTs, which induce deformations in the piezoelectric substrate. These deformations give rise to a Rayleigh surface wave confined within one acoustic wavelength of the surface. The wave traverses the gap between the two arrays of IDTs and when it reaches the receiver IDTs, the mechanical energy of the wave is converted back into an output RF voltage. The input and output is connected via an RF amplifier and when the gain in the loop is greater than unity, the circuit oscillates. When a mass arising from a coating or gas is adsorbed on the surface, there is a shift in the SAW device resonant frequency. This phenomenon allows the SAW device to be used as a gas sensor as the frequency shift is proportional to the mass shift. Conducting polymers both in bulk and nanostructured forms have
been used as active layers of SAW sensors for sensing different analytes, which confers these types of sensors with sensitivity towards a specific analyte [309-311].

### 1.5.3.1.2 Quartz crystal microbalance sensors

A quartz crystal microbalance (QCM) consisting of a thin quartz disk with electrodes plated on it and one of its surface coated with a conductive polymer can be seen in Fig. 1.16 [259]. Internal mechanical stress is produced in a piezoelectric material upon the application of an external electrical potential. The oscillating electric potential applied to the QCM induces an acoustic wave that propagates through the crystal and meets minimum impedance when the thickness of the device is a multiple of a half wavelength of the acoustic wave. A QCM is a shear mode device in which the acoustic wave propagates in a direction perpendicular to the crystal surface [312].

![Figure 1.16: Configuration of a quartz crystal microbalance sensor device](image)

Deposition of a thin film on the crystal surface decreases the frequency in proportion to the mass of the film. If the surface of the quartz crystal electrode is coated by a material capable of interacting with the environment of interest, a sensor sensitive to this component can be constructed. The performance characteristics of the QCM sensor such as selectivity, response time and reversibility depend on the chemical nature and physical properties of the coating material. The sensitivity of these types of sensors is very high and they can detect very low concentrations of analyte accurately, since a small change in mass of the quartz crystal brings about remarkable change in its frequency and resonant resistance. These types of sensors, once calibrated, can also be used not only to detect a particular analyte but also to detect the amount of analyte in terms of
mass change of the quartz crystal oscillator, since this type of device can also act like a microbalance. Quartz crystals, coated with different coatings including conducting polymers viz., polypyrrole (PPy), polyaniline (PAni) and their composites, have been used for determination of various compounds [313-322].

1.6 Scope of the thesis and statement of the thesis problem

Conducting polymers are recently being considered for different biomedical applications such as artificial muscles, drug delivery, stimulation of nerve regeneration, tissue engineering etc. Conducting polymers have been found to be potential antioxidants. They have also attracted applications as competent sensing material for various organic vapours, hazardous gases, humidity and warfare stimulants due to their applicability at room temperature. Conducting polymer based nanostructured materials offer the advantages of low dimensionality and enhanced surface to volume ratio that makes them promising materials in biomedical applications and also as sensors. Polymers are highly radiation sensitive materials and irradiation can cause useful modifications in the polymer which cannot be achieved by other means. Irradiation can lead to several interesting physico-chemical modifications in conducting polymer nanostructures leading to the enhancement in their performance.

Considering the above mentioned critical review, the present work aspires to achieve a deeper insight into the synthesis and physicochemical properties of conducting polymer based nanostructured materials. Although swift heavy ion (SHI) irradiation has been used as a tool to tune the properties of conducting polymers, the effects of SHI irradiation upon conducting polymer based nanostructured materials have not been properly elucidated. One of the prime focuses of the present work is the detailed investigation of the effects of SHI irradiation upon the structural, morphological, conformational, optical and charge transport properties of the conducting polymer based nanostructured materials. The present work also emphasizes on the application potential of these nanostructured materials in the field of biomedical science as biocompatible.
antioxidants and in the field of chemical sensors as sensitive active layers for quartz crystal microbalance sensors.

In order to fulfill the aforesaid objectives the following systems have been chosen for investigation in the present work:

- Polyaniline (PAni) nanofibers synthesized using interfacial polymerization technique have been chosen because of ease in synthesis, processibility, environmental stability and the unique and exciting properties that polyaniline (PAni) offers as a conducting polymer.

- Another system investigated in the present work viz., PAni nanofiber reinforced PVA nanocomposites have been synthesized by in-situ rapid mixing polymerization technique that has been developed with a view to apply these materials in sensing applications.

The above mentioned material systems have been irradiated with 90 MeV O$^{7+}$ ions using the 15 UD Pelletron accelerator installed at Inter University Accelerator Centre (IUAC), New Delhi. The materials have been irradiated at normal beam incidence and at different fluences viz., $3 \times 10^{10}$, $3 \times 10^{11}$ and $1 \times 10^{12}$ ions/cm$^2$ with a view to investigate the fluence dependent variations in the physico-chemical properties of the above mentioned materials.

Both the pristine and SHI irradiated materials have been investigated using sophisticated analytical tools. Electron microscopy has been used to study the morphology and structural details of the nanostructured materials. X-ray diffraction studies have been carried out to investigate the degree of crystallinity, domain length and strain in the nanostructured materials. The conformational variations in the materials have been studied using vibrational spectroscopy employing Micro-Raman ($\mu$R) and Fourier Transform Infrared (FT-IR) spectroscopy. UV-Visible spectroscopy has been used to study the optical properties of the pristine and irradiated samples. Dielectric spectroscopy and ac conductivity studies have been carried out with a view to study the relaxation processes and charge transport mechanisms of the samples.

The antioxidant activity and biocompatibility of polyaniline (PAni) nanofibers have been investigated using specific biochemical assays. Swift heavy ion irradiation effects on the antioxidant activity and biocompatibility of these
materials have also been studied. Quartz crystal microbalance coated with PA
nanofiber reinforced PVA nanocomposites have been fabricated for sensing
analytes viz., free radicals and hydrochloric acid in solution. Different parameters
associated with these sensors viz., sensitivity, response time and linearity have
also been studied in the present work.