Chapter 1: General introduction and review of earlier works

1.1. Conducting polymers

Polymeric materials in the form of wood, bone, skin and fibers have been used by man since prehistoric time. The twenty-first century is experiencing undoubtedly the use of polymers that move from primarily passive materials such as coatings and containers to active materials with useful optical, electronic, energy storage and mechanical properties. Indeed this development has already begun with the discovery and study of conducting polymers. The importance and potential impact of this new class of material was recognized by the world scientific community when Hideki Shirakawa, Alan J. Heeger and Alan G. MacDiarmid were awarded the Noble Prize in Chemistry in 2000 for their research in this field [1-5].

Organic polymeric molecules are basically compounds of carbon and hydrogen linked by saturated covalent bonds. Their electronic structures do not permit the mobility of the bonding electrons as is the case with metals. So, the organic macromolecules, i.e., polymers behave as electrical insulators due to firm localization of bonding electrons between atoms. On the contrary, metallic atoms in solid state are bound by free electron glue providing ample scope for high mobility of the free electrons rendering them electrically conducting. The polymer scientists got tempted from the mobile free electrons in metals to think of organic molecular architecture having loosely bound electrons for providing electrical conduction. Accordingly, thoughts were driven in polymer scientists for making the firmly bound electrons between atoms in polymer molecular architecture, even though, such macromolecules do not have capability of possessing loosely bound electrons. To create a long path (high way) in saturated carbon chain structure scientists tried to inject electrons or holes into such chains for the purpose of preparing a polymer molecule having electrically conducting behavior. A key discovery that changed the outlook for producing highly conducting polymers was the finding in 1973 that the inorganic polymer polysulfur nitride $(SN)_x$ is highly conducting [6]. The room temperature conductivity of $(SN)_x$ is of the order of 10^3 Scm^{-1}. Below a critical temperature of about 0.3 K, $(SN)_x$ becomes a superconductor [7]. These discoveries were of particular importance because they proved the possibility of generating highly conducting polymers, and stimulated the enormous amount of focus and activity necessary for the discovery of other polymeric conductors. The real breakthrough in the development of conjugated organic conducting polymers was only reached after the discovery of metallic conductivity in crystalline polyacetylene (PAc) films with p-type dopants such as halogens during collaborative research involving Shirakawa, MacDiarmid and Heeger in 1977 [1,2]. A year later, it was discovered that analogous effects could be induced by electron donors (n-type dopant) [8]. Following this work there has been an explosion of activity around characterization, synthesis and the use of conducting polymers in a wide range of fields from electronics to medicine.

1.2. Electronic conducting polymers

In conducting polymers the redox sites are delocalized over a conjugated π system, however, redox polymers have localized redox sites. The redox polymers are well known to transport electrons by hopping or self-exchange between donor and acceptor sites [9]. The redox conductivity is comparatively lower than that of conjugated conducting polymers, likely due to slow electron transport to or from the redox centre. Apart from conjugated organic polymers such as polypyrrole (PPy), polythiophene (PTh) and polyaniline (PANI), the first generation of redox polymers include the following main group materials:

(i) Saturated organic polymers with pendant transition metal complexes such as polyvinyl ferrocene, and metal complexes of polyvinyl pyridine [10].

(ii) Electrochemically polymerized transition metal complexes with multiple polymerizable ligands such as poly [ruthenium (4-vinyl-4'-methyl-2,2'-bipyridine)$_3^{2+}$] [11], poly [iron (4-(2-pyrrole-1-ylethyl)-4'-methyl-2,2'-bipyridine)$_3^{2+}$] [12], and poly [tetra(4-pyrrole-1-ylphenyl) porphyrin [13].

(iii) Saturated organic polymers with pendant electroactive organic moieties [14] such as poly (4-nitrostyrene).

(iv) Ion exchange polymers containing electrostatically bound electroactive ions such as Nafion containing $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) and quaternized polyvinylpyridine containing $Fe(CN_6)^{3-/4-}$ [15].

1.3. Ionic conducting polymers

Ionic conducting polymers (polymer/salt electrolytes) are of great interest because they exhibit ionic conductivity in a flexible but solid membrane. Ionic conductivity is different than the electronic conductivity of metals and conjugated conducting polymers, since current is carried through the movement of ions. They have been critical to the development of devices such as all-solid-state-lithium batteries [16]. The research of Fenton et al. [17], who found ion conductivity in a poly (ethylene oxide) (PEO)–alkaline metal ion complex in 1973, initiated the research and development of solid polymer electrolytes. The considerable potential material as solid ionic conductors was first recognized by Armand [18] in 1979. Since that time there have been intense interests in the synthesis and characterization of these classes of materials, as well as considerable focus on their potential use as solid electrolytes in electrochemical devices such as rechargeable lithium batteries, electrochromic displays, and smart windows [19]. Polymer electrolytes also represent a fascinating class of coordination compounds such as the oxo-crown ethers [20]. Amorphous polymer electrolytes have been studied intensively for 30 years, and although the conductivities have increased substantially over that period, they remain too low ($<10^{-4}$ Scm^{-1}) for many applications. The recently discovered crystalline polymer electrolytes represent a new class of solid ionic conductors and offer a different approach to ionic conductivity in the solid state.

1.4. Intrinsic and doped conducting polymers

Intrinsically conducting polymers (ICP's) offer a unique combination of ion exchange characteristics and optical properties that make them distinctive. They are readily oxidized and reduced at relatively low potentials, and the redox process is reversible and accompanied by large changes in the composition, conductivity, and color of the material. These polymers are made conducting by the reaction of conjugated semiconducting polymer with an oxidizing agent, or a reducing agent or a protonic acid, resulting in highly delocalized polycations and polyanions [21]. The conductivity of these materials can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by the degree of doping and by blending with other polymers.

Recent advances in the field of ICP's have led to a variety of materials with great potential for commercial applications such as rechargeable batteries, light emitting diodes (LED's), photovoltaics, membranes, electronic noses and sensors, etc. Of the many interesting conducting polymers, that have been developed over the past 30 years, PANI, PPy, PTh, poly (p-phenylene) (PPP), and poly (p-phenylene vinylene) (PPV)'s have attracted the most attention.

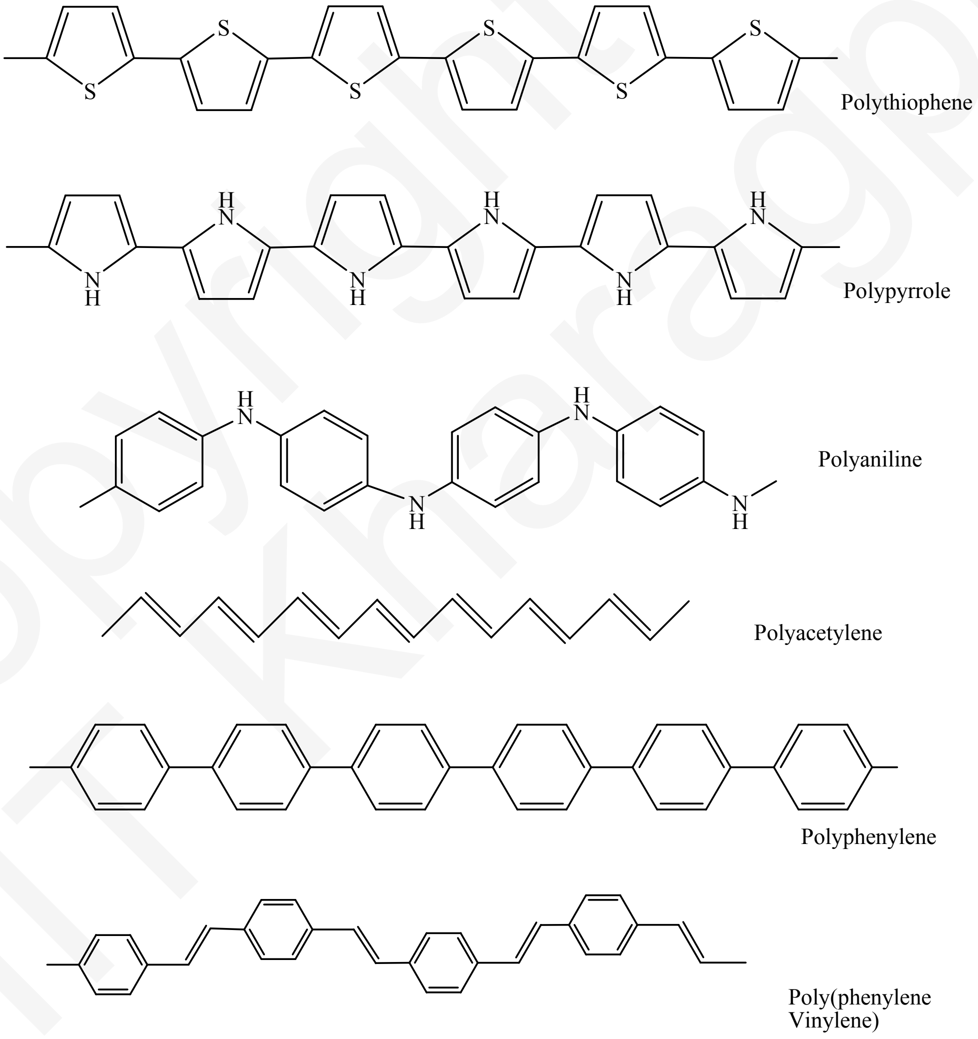


Figure 1.1. Chemical structure of some conducting polymers [9]

Figure 1.1 shows the structure of some conducting polymers in their neutral insulating form. In order to make them electronically conductive, it is necessary to introduce mobile charge carriers into the conjugated system, which is achieved by oxidation or reduction reactions and the insertion of counterions [9]. Dedoped conjugated polymers are semiconductors with band gaps ranging from 1 to several eV, therefore, their room temperature conductivities are low, typically 10^{-8} Scm^{-1} or lower. However, by doping, conductivity can increase by many orders of magnitude. The concept of doping is unique and distinguishes conducting polymers from all other types of polymers [1,22]. During the doping process, an organic polymer, either an insulator or semiconductor having small conductivity, typically in the range of 10^{-10} to 10^{-5} Scm^{-1} is converted to a polymer, which is in a metallic conducting regime (1 to 10^4 Scm^{-1}). The highest value reported to date has been obtained in iodine-doped PAc (>10^5 Scm^{-1}) and the predicted theoretical limit is about 2×10^7, more than an order of magnitude higher than that of copper [1]. Conductivity of other conjugated polymers reaches up to 10^3 Scm^{-1} [2,3,23,24] as shown in Figure 1.2.

1.5. Doping of intrinsically conducting polymers

A wide variety of interesting and important phenomena arise due to charge injection onto conjugated semiconducting macromolecular chains. Doping by reversible charge injection can be accomplished in a number of ways.

1.5.1. Chemical doping by charge transfer

The initial discovery of the ability to dope conjugated polymers involved charge transfer redox chemistry: oxidation (p-type doping) or reduction (n-type doping) [1,2,8], as illustrated with the following examples:

p-type:

$$(\pi\text{-polymer})_n + 3/2\ ny(I_2) \rightarrow [(\pi\text{-polymer})^{+y}\ (I_3^-)_y]_n\ .$$

n-type:

$$(\pi\text{-polymer})_n + [Na + (\text{naphthalide})^{\bullet}]_y \rightarrow [(Na^+)_y\ (\pi\text{-polymer})^{-y}]_n + (\text{naphth})^0\ .$$

When the doping level is sufficiently high, the electronic structure evolves to that of a metal.

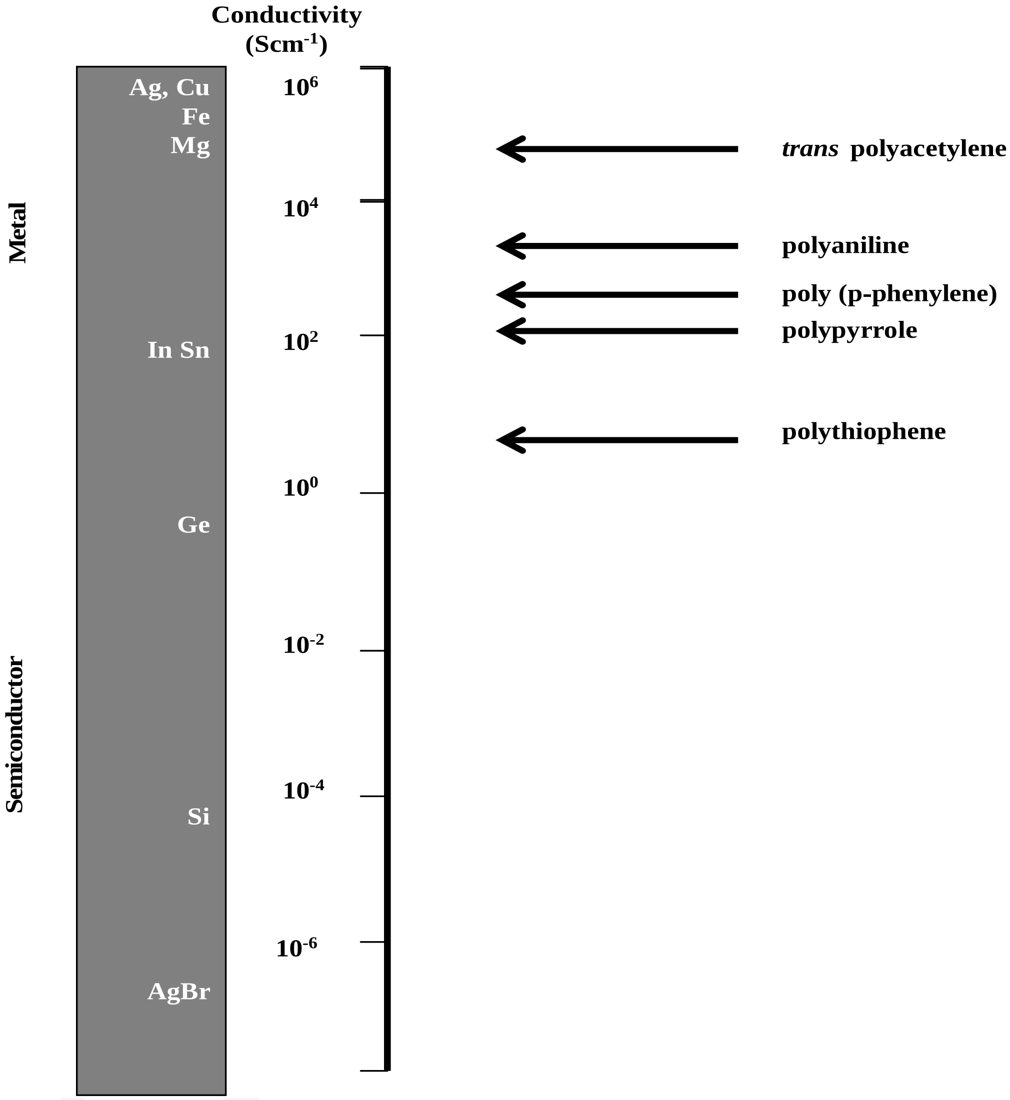


Figure 1.2. Conductivity of some metals and doped conducting polymers [9]

1.5.2. Electrochemical doping

Although chemical doping is an efficient and straightforward process, it is typically difficult to control. Complete doping to the highest concentration yields reasonably high quality materials. However, attempts to obtain intermediate doping levels often result in inhomogeneous doping. Electrochemical doping was invented to solve this problem [25]. In electrochemical doping, the electrode supplies the redox charge to the conducting polymer, while ions diffuse into (or out of) the polymer structure to the nearby electrolyte to compensate the electronic charge. The doping level is determined by the voltage between the conducting polymer and the counter-electrode; at electrochemical equilibrium the doping level is precisely defined by that voltage. Thus, doping at any level can be achieved by setting the electrochemical cell at a fixed applied voltage and simply waiting as long as necessary for the system to come to electrochemical equilibrium. Electrochemical doping is illustrated by the following examples:

p-type:

$$(\pi\text{-polymer})_n + [\mathrm{Li} + (\mathrm{BF_4}^-)]_{\text{solution}} \rightarrow [(\pi\text{-polymer})^{+y}\,(\mathrm{BF_4}^-)_y]_n + \mathrm{Li}\ (\text{electrode}).$$

n-type:

$$(\pi\text{-polymer})_n + \mathrm{Li}\ (\text{electrode}) \rightarrow [(\mathrm{Li}^+)_y\,(\pi\text{-polymer})^{-y}]_n + [\mathrm{Li}^+\,(\mathrm{BF_4}^-)]_{\text{solution}}.$$

1.5.3. Doping of polyaniline by acid-base chemistry

Polyaniline provides a typical example of chemically distinct doping mechanism [26]. Protonation by acid-base chemistry leads to an internal redox reaction and the conversion from semiconductor (emeraldine base) (EB) to metal (emeraldine salt) (ES). The doping mechanism is shown schematically in Figure 1.3. The chemical structure of the semiconducting EB form of PANI is that of an alternating copolymer. Upon protonation of the EB to the ES, the proton-induced spin unpairing mechanism leads to a structural change with one unpaired spin per repeat unit, but with no change in the number of electrons [27,28]. The result is a half-filled band and, potentially, a metallic state where there is a positive charge in each repeat unit (from protonation) and an associated counter-ion (e.g., Cl^-, $\mathrm{HSO_4}^-$, etc.).

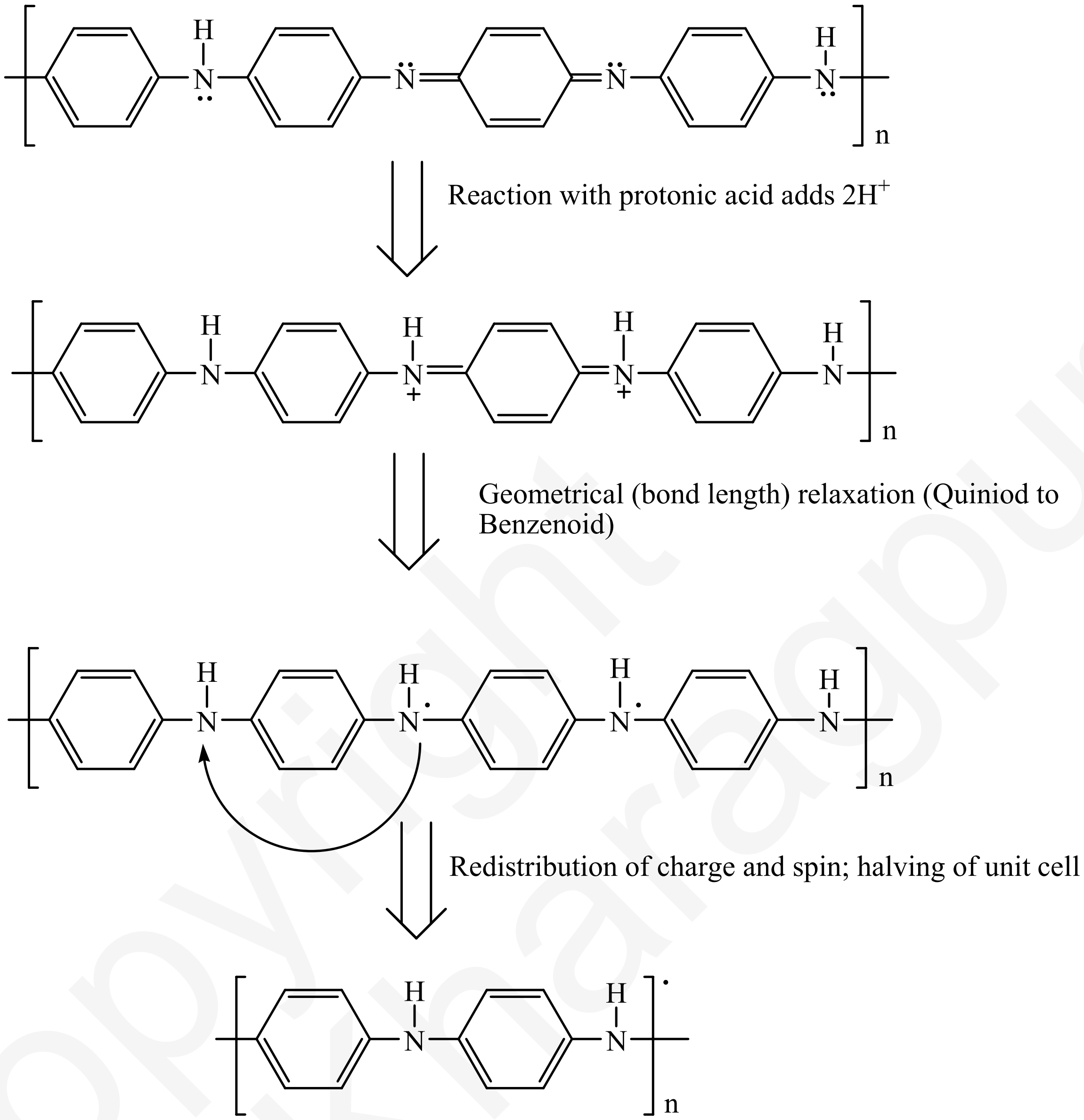


Figure 1.3. Polyaniline doping mechanism [31]

1.5.4. Photodoping

The semiconducting polymer is locally oxidized and reduced by photo-absorption and charge separation:

$$(\pi\text{-polymer})_n + h\upsilon \rightarrow [\{\pi\text{-polymer}\}^{+y} + \{\pi\text{-polymer}\}^{-y}]_n$$

where, y is the number of electron-hole pairs (dependent upon the pump rate in competition with the recombination rate) [29].

Following photoexcitation from the ground state ($1A_g$ in the notation of molecular spectroscopy) to the lowest energy state with proper symmetry ($1B_u$), recombination to the ground state can be either radiative (luminescence) or non-radiative. Some families of conjugated polymers exhibit high luminescence quantum efficiencies (e.g., PPV and PPP and their soluble derivatives), others do not (e.g., PAc and PTh) [30]. A number of mechanisms have been identified that lead to low quantum efficiencies for photoluminescence. Rapid bond relaxation in the excited state and the formation of solitons with states at mid-gap prevent radiative recombination in PAc [31]. The existence of an A_g state or a triplet excited state below the $1B_u$ state favor non-radiative recombination. Inter-chain interactions in the excited state also lead to non-radiative channels for decay [32-34].

1.5.5. Charge injection at a metal-semiconductor (MS) polymer interface

Electrons and holes can be injected from metallic contacts into the π*- and π- bands, respectively:

Hole injection into an otherwise filled π-band

$$(\pi\text{-polymer})_n - y(e^-) \rightarrow [(\pi\text{-polymer})^{+y}]_n.$$

Electron injection into an empty π*- band

$$(\pi\text{-polymer})_n + y(e^-) \rightarrow [(\pi\text{-polymer})^{-y}]_n.$$

In the case of charge injection at an MS interface, the polymer is oxidized or reduced (electrons are added to the π*- band or removed from the π- band). However, the polymer is not doped in the sense of chemical or electrochemical doping, because there are no counter-ions. This distinction becomes particularly clear when comparing charge injection in the polymer light-emitting diode [35,36] (where there are no ions) with that in the polymer light emitting electrochemical cell where electrochemical doping with associated redistribution of ions provides the mechanism for charge injection [37].

Each of the methods of charge injection doping leads to unique and important phenomenon. In the case of chemical and/or electrochemical doping, the induced electrical conductivity is permanent, until the carriers are chemically compensated or until the carriers are purposely removed by “undoping”. In the case of photoexcitation, the photoconductivity is transient and lasts only until the excitations are either trapped or decay back to the ground state. In the case of charge injection at a MS interface, electrons reside in the π*- band and/or holes reside in the π- band only as long as the biasing voltage is applied [30].

Due to self-localization associated with the formation of solitons, polarons, and bipolarons, charge injection leads to the formation of localized structural distortions and electronic states in the energy gap [31]. In the case of "photo-doping", redistribution of oscillator strength associated with the sub-gap infra red absorption and the corresponding bleaching of the interband (π - π*) transition provide a route to non-linear optical response. Real occupation of low energy excited states [31,38] (in the context of perturbation theory) [39] lead to, resonant and non resonant response respectively.

By charge-injection doping at a MS interface, the polymer semiconductor can be used as the active element in thin film diodes [40,41] and field effect transistors (FETs) [42]. Tomozawa et al. [40,41] demonstrated the first example of an electronic device component fabricated by casting the active polymer directly from solution. Dual carrier injection in metal/polymer/metal structures provides the basis for polymer LEDs [36]. In polymer LEDs, electrons and holes are injected from the cathode and anode, respectively, into the undoped semiconducting polymer. Light is emitted when the injected electrons and holes meet in the bulk of the polymer and recombine with the emission of radiation [35].

1.6. Conduction mechanism in conducting polymers

The electronic properties of any material are determined by its electronic structure. The theory that most reasonably explains electronic structure of materials is band theory. Quantum mechanics stipulates that the electrons of an atom can only have specific or quantized energy levels. In a crystal lattice the electronic energy of individual atoms is altered. When the atoms are closely spaced, the energy levels form bands. The highest occupied electronic levels constitute the valence band and the lowest unoccupied levels, the conduction band as shown in Figure 1.4. The electrical properties of conventional materials depend on how the bands are filled. When bands are completely filled or empty no conduction is observed. If the band gap is narrow, at room temperature thermal excitations of electrons from the valence band to the conduction band gives rise to conductivity. This happens in the case of classical semiconductors. When the band gap is wide, thermal energy at room temperature is insufficient to excite electrons across the gap and the solid is an insulator. In conductors, there is no band gap since the valence band overlaps the conduction band and so they exhibit high conductivity [9].

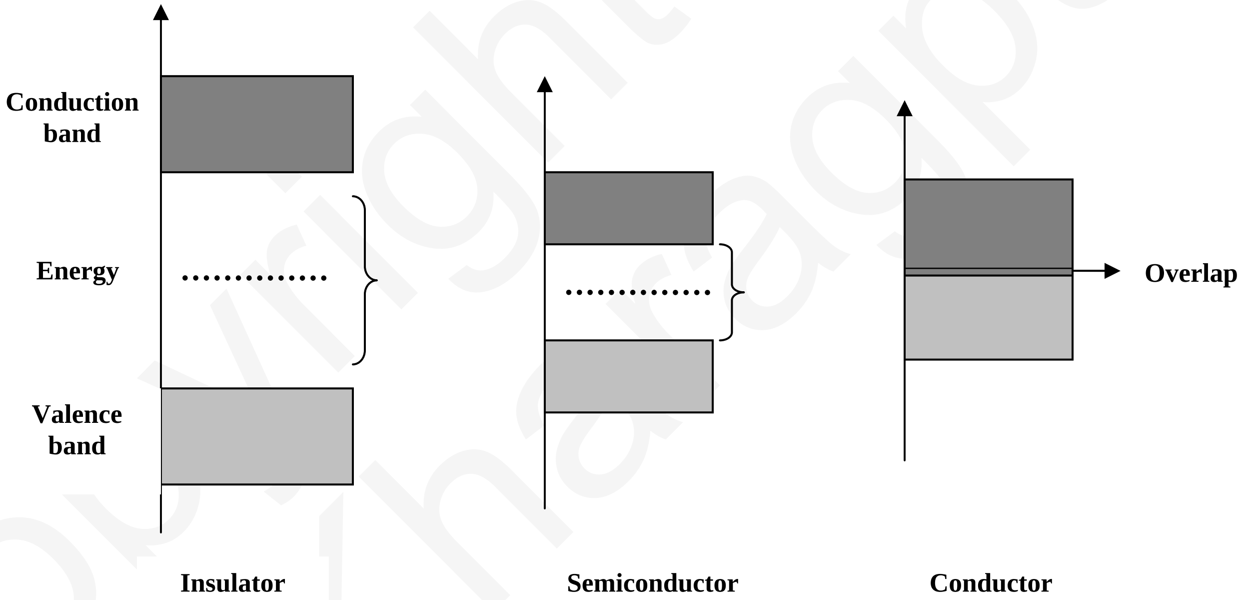


Figure 1.4. Energy band in solid [9]

Conducting polymers are unusual in that they do not conduct electrons via the same mechanisms used to describe classical semiconductors and hence their electronic properties cannot be explained well by standard band theory. The electronic conductivity of conducting polymers results from mobile charge carriers introduced into the conjugated π-system through doping. To explain the electronic phenomena in these organic conducting polymers, new concepts including solitons, polarons and bipolarons

[43-47] have been proposed by solid state physicists. The electronic structures of π-conjugated polymers with degenerate and non-degenerate ground states are different. In π-conjugated polymers with degenerate ground states, solitons are the important and dominant charge species. Polyacetylene is the only known polymer with a degenerate ground state due to its access to two possible configurations. The two structures differ from each other by the exchange of the carbon-carbon single and double bonds. Polyacetylene can exist in two isomeric forms: *cis*- and *trans*- PAc. The *trans*- PAc form is thermodynamically more stable and the *cis*- *trans* isomerization is irreversible [48].

1.6.1. Solitons

Charge storage on the polymer chain leads to structural relaxation, which localizes the charge. The simplest example of the effect of this structural relaxation is the soliton in trans- PAc. The soliton is a domain boundary between the two possible degenerate ground state configurations of *trans*- PAc the "A"phase and the "B" phase as shown in Figure1.5.

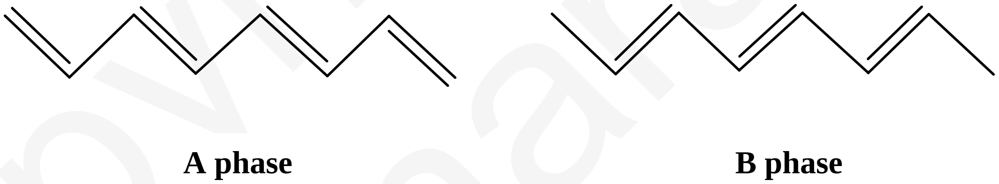


Figure 1.5. Degenerate A and B phases in *trans*-polyacetylene [31]

The chemical structure of the soliton is drawn as an abrupt change from A to B phase as shown in Figure 1.6.

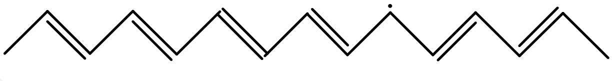


Figure 1.6. Soliton in *trans*-polyacetylene [31]

In agreement with the predictions of the Su-Schriefer-Heeger model [31,43,44] the experimental evidence indicates that the structural relaxation in the vicinity of the domain boundary extends over approximately seven carbon atoms, as illustrated in Figure1.7. The corresponding spin and charge distributions are similarly delocalized.

Figure 1.7. Domain boundary extending over approximately seven carbon atoms [31]

Single occupation of the soliton state neutralizes the electronic charge of the carbon nucleus, while introducing an unpaired spin onto the chain. The localized electronic state associated with the soliton is a non-bonding state at an energy, which lies at the middle of the *n-n** gap, between the bonding and antibonding levels of the perfect chain. On the other hand, the defect is both topological and mobile due to the translational symmetry of the chain. Such a topological and mobile defect is referred to as a soliton [31,43,44]. The term "soliton" refers simultaneously to all three types of solitons; the quantum numbers for spin and charge enter only when referring to a specific type (e.g., neutral solitons found as defects from the synthesis of undoped material or charged solitons created by photoexcitation), and even then, the spin is only implicit. Another feature of the soliton terminology is the natural definition of an "anti-soliton" (AS) as a reverse boundary from B phase back to A phase in Figures 1.6 and 1.7. The AS allows for conservation of soliton number upon doping or upon photoexcitation [30].

1.6.2. Polarons and bipolarons

In cases such as PTh, PPP, and cis-PAc, where the two possible bond alternation patterns are not energetically degenerate, confined soliton-anti-soliton pairs, polarons and bipolarons, are the stable non-linear excitation and the stable charge storage states [49,50]. A polaron can be thought of as a bound state of a charged soliton and a neutral soliton whose mid-gap energy states hybridize to form bonding and anti-bonding levels. The neutral soliton contributes no charge and a single spin, and the charged soliton carries charge of $\pm e$ and no spin; the resulting polaron then has the usual charge-spin relationship of fermions; $q = \pm e$ and $s = 0.5$.

The polaron is illustrated schematically for PPP in Figures 1.8 and 1.9.

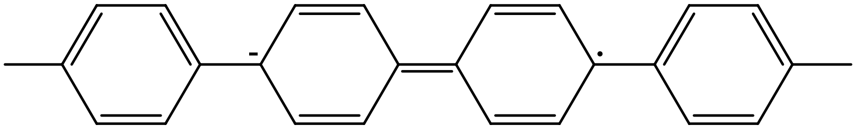
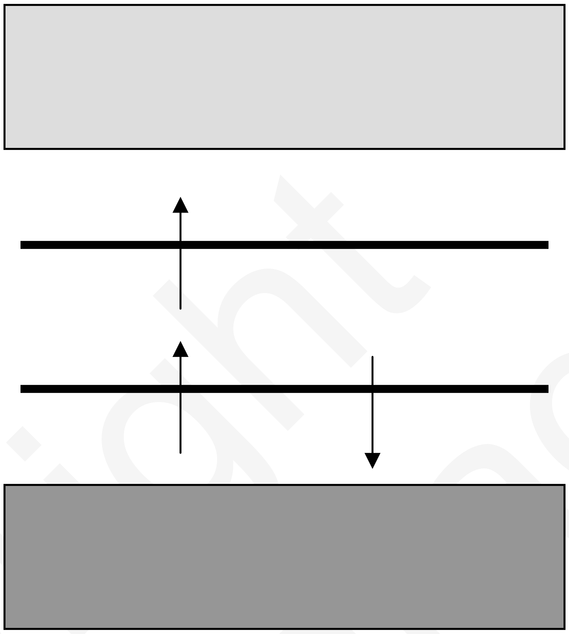


Figure 1.8. Schematic picture of a polaron in PPP [31]



Polaron, s= ½, q= -|e|

Figure 1.9. Band diagram of an electron polaron [31]

The positive (negative) polaron is a radical cation (anion), a quasi-particle consisting of a single electronic charge dressed with a local geometrical relaxation of the bond lengths. Similarly, a bipolaron is a bound state of two charged solitons of like charge (or two polarons whose neutral solitons annihilate each other) with two corresponding mid-gap levels, as illustrated in Figures 1.10 and 1.11 respectively.

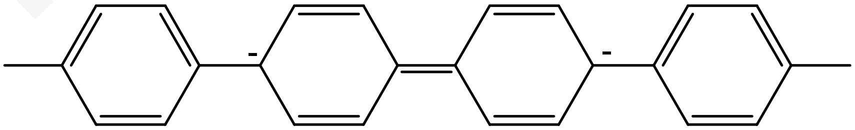
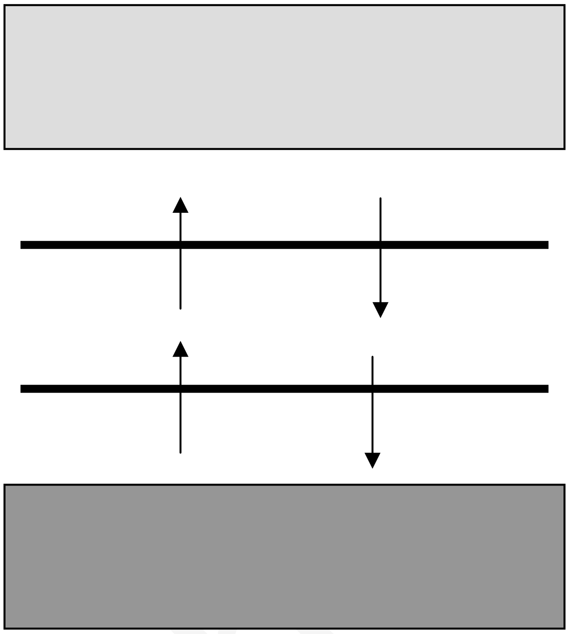


Figure 1.10. Schematic picture of negative bipolaron in PPP [31]



Bipolaron, s= 0, q= -2|e|

Figure 1.11. Band diagram for a negative bipolaron [31]

Since each charged soliton carries a single electronic charge and no spin, the bipolaron has charge ±*2e* and 0 spin. The positive (negative) bipolaron is a spinless dication (dianion); a doubly charged bound state of two polarons bound together by the overlap of a common lattice distortion (enhanced geometrical relaxation of the bond lengths) [30].

1.7. Review of earlier works

Polyaniline is superior compared to other conducting polymers. The thermal stability of PANI is superior to other ICPs. The processability and conductivity of PANI are also fairly good [51]. From economic point of view, PANI is significantly superior to other ICPs because the aniline monomer is less expensive than other monomers used for ICP. The synthesis of PANI is very simple, properties can be tuned easily, and it has numerous application possibilities [52]. PANI has good environmental stability [53,54] and exhibits reversible doping/dedoping behaviour compared to other conductive polymers [55]. All these factors contribute to PANI being superior to other ICPs.

1.7.1. Different methods for the synthesis of polyaniline

Polyaniline can be synthesized by different methods including chemical, electrochemical, template, enzymatic, plasma, photo, and a number of other special methods. The different synthesis methods used to produce PANI are detailed below.

Heterophase polymerization

The heterophase polymerization is used to produce high quality polymers with specially tailored properties from a small to a large volume scale. It includes different methods of polymerization such as precipitation, suspension, microsuspension, emulsion, miniemulsion, microemulsion, dispersion, reverse micelle and inverse polymerizations. In the case of suspension, microsuspension, miniemulsion and microemulsion polymerization methods the monomer is sparingly soluble in water and forms spherical droplets whose size is controlled by a proper choice of the dispersing technique. These droplets are stabilized in an aqueous media through the addition of a surface active agent (stabilizer).

Synthesis of polyaniline colloidal dispersion

Polyaniline is typically produced by the oxidative polymerization of aniline in an acidic aqueous medium and is obtained as a precipitate [56]. Colloidal PANI particles are formed instead of precipitation when a suitable water-soluble polymer such as poly (*N*-vinylpyrrolidone) (PVP) is added to the reaction mixture. Such a process is known as dispersion polymerization [57]. In this process: (a) the monomer is soluble in the reaction medium; (b) the produced polymer is insoluble under the same conditions; and (c) its macroscopic precipitation is prevented by the presence of the so-called steric stabilizer. Such colloids are called dispersions. The colloidal PANI particles have a typical average size of a few tens to hundreds of nanometers and are thus often regarded as nanocolloids. The shape of the particles may be spherical, globular, granular, cylindrical or branched dendritic structures [58].

Direct and inverse emulsion polymerization of aniline

In the emulsion polymerization the monomer is dispersed in an aqueous phase to form a uniform emulsion. The polymerization reaction is carried out by stabilization of the emulsion by a surfactant [59]. For the synthesis of PANI by emulsion polymerization, aniline along with a protonic acid and an oxidant are combined with a mixture of water and a nonpolar or weakly polar solvent, for example, xylene, chloroform, or toluene (sparingly soluble or insoluble in water). In some instances, to form an emulsion with the above systems, a protonic acid such as dodecylbenzene sulfonic acid (DBSA) is employed, which has a substantial emulsifying ability in weakly polar solvents. In addition, the product of the above reaction cannot be isolated directly, since the PANI salt exists in the emulsion along with other by-products. In most cases, the product is isolated by destabilizing the emulsion through the addition of acetone. The PANI salt is then collected and subjected to repeated washing to free it from other constituents [60,61]. With the progress in the development of PANI, different types of emulsions have been prepared for PANI synthesis and accordingly the synthesis methods have different names. The inverse emulsion polymerization process involves the formation of an aqueous solution of the monomer aniline, which is emulsified in a nonpolar organic solvent, for example chloroform, isooctane, toluene, or in a mixture of solvents. The polymerization is then initiated with a water-soluble initiator such as ammonium persulfate (APS), benzoyl peroxide, and so on. The reaction carried out in such a heterogeneous phase has several distinct advantages compared to other methods discussed earlier. The physical state of the inverse emulsion system makes it easier to control the process. Thermal and viscosity problems are much less significant here than those in bulk polymerization. The product of an emulsion polymerization can be used in many instances directly without further separations. During the polymerization, both a high molecular weight and a high reaction rate can be simultaneously achieved. During the course of the reaction, PANI remains as a soluble component in the organic phase. At the end of polymerization the organic phase is separated and washed repeatedly with distilled water. The solution is then treated with anhydrous sodium sulfate or other suitable chemicals to remove the excess water. The viscous organic solution is then added to acetone or other suitable solvent in order to break the emulsion and precipitate the PANI salt [62].

Direct and inverse miniemulsion polymerization of aniline

Miniemulsion is a relatively stable submicron (50–500 nm) dispersion of oil in water prepared through homogenizing the system containing oil, water, surfactant and a co-surfactant. Miniemulsion is stable for a long period of time and exhibits unique polymerization kinetics. The co-surfactants used (1–5%) in miniemulsions are usually low molecular weight compounds such as hexadecane, cetyl alcohol, and so on, which have a poor solubility in water but a good solubility in monomer. Huang et al. [63,64] prepared PANI through the miniemulsion polymerization of aniline using sodium dodecyl sulfate (SDS) as a surfactant and cetyl alcohol as a co-surfactant. Marie et al. [65] prepared PANI both by direct and inverse miniemulsion processes.

Direct and inverse microemulsion polymerization of aniline

A microemulsion is an organized micro-heterogeneous system which provides a large interfacial area and is generally less viscous. Usually, a typical microemulsion system contains water, oil and surfactant, and also often a co-surfactant to stabilize the system. Yang et al. [66] have synthesized PANI by using the microemulsion method with sodium dodecylbenzene sulfonate (NaDBSA) acting as both a surfactant and a dopant. Sun and Gao [67] have managed to functionalize carbon nanotube (CNT) by precipitating metal cations on the nanotube surface from stable inverse microemulsion. These coated CNT particles have a better adhesion with a ceramic or other inorganic matrix, thereby improving both the mechanical and electrical properties of composites.

Reversed micelle polymerization of aniline

A transparent and homogeneous reversed micelle solution is prepared by dissolving the DBSA and an aqueous APS solution in the isooctane through vigorous stirring. The aniline is dissolved in isooctane in order to form a homogeneous solution; the ethanol is added to this system with thorough stirring. The reaction is initiated through the drop-wise addition of solution into the reversed micelle solution. At the end of the reaction a dark green colored DBSA-PANI suspension is obtained. The suspended precipitate is then filtered, followed by washing with methanol and de-ionized water to remove impurities such as APS, free DBSA and un-reacted aniline. The washing is continued until the pH value of the washed liquid reaches 7.0. The PANI obtained from reversed micelle polymerization has comparable or even better conductivity, processability, crystallizability, electrochemical activity, solubility, thermal stability and higher molecular weight compared to the products obtained from other processes [68]. Hu et al. [69] developed a new biomimetic route for the synthesis of a conducting complex of (PANI)/SDS. Hemoglobin was used to catalyze the polymerization of aniline in aqueous micellar solutions of surfactants, such as SDS, hexadecyltrimethylammonium bromide, and polyoxyethylene isooctylphenyl ether (Triton X-100). The micelles formed by strong acid surfactants such as SDS are suitable templates for the enzymatic synthesis of conducting PANI. Yang et al. [70] synthesized the Gemini surfactant containing sodium sulfonate as hydrophilic head group based on nonylphenol. The critical micelle concentration of the gemini surfactant was smaller than that of NaDBSA and SDS, respectively, indicating excellent efficiency of micelle formation and reduced surface tension. Conducting PANI salts were then synthesized by chemical oxidative micellar polymerization of aniline in water firstly using Gemini surfactant as the micelle stabilizer and APS as the oxidant at 0 °C. The stable PANI dispersions were obtained when the molar ratio of the Gemini surfactant to aniline was equal to or above 0.5 used in the polymerization system.

Solution polymerization of aniline

PANI has also been synthesized by solution polymerization of aniline. Aniline has been polymerized in chloroform as a solvent and electropolymerized in acrylonitrile (AN) solvent [71]. Generally, the processability of PANI is very poor due to its poor solubility in all available solvents. Therefore, the PANI prepared through a solution polymerization process has better processability since it is already in a solution [72]. Ito et al. [73] synthesized a water-soluble externally (HC1)-doped conducting PANI by a simple synthetic method where ESs were sulfonated by chlorosulfonic acid in dichloroethane at 80 °C and subsequently hydrated in water at 100 °C. Sulfonating the ES (counter anion $X^- = Cl^-$, SO_4^{2-}, and BF_4^-) or the EB resulted in the production of HCl-doped sulfonated PANI, where HC1 dopant from hydrolysis of chlorosulfonic group exchanged with the original dopant. The degree of sulfonation, namely, sulfur-to-nitrogen ratio, was controlled by adjusting the amount of chlorosulfonic acid. With increasing sulfur-to-nitrogen ratio from 0.65 to 1.3, the solubility in neutral water increased from 22 to 88 g/l and the four-probe conductivity for a compressed pellet decreased from 0.023 to 1.7×10^{-5} Scm^{-1}, showing sulfonation-induced undoping. Adams et al. [74] polymerized aniline at temperatures between 0 and -35 ^{0}C in acid solution containing lithium chloride and using dichromate as oxidant. The optimum temperature to give high molecular weight PANI in the emeraldine oxidation state in good yield was found to be -22 ± 3^{0}C. Majidi et al. [75] obtained films of optically active polyaniline salts (PANI/HCSA) by casting from solutions of emeraldine base doped with (lS)-(+)-camphor-10-sulfonic acid (D-CSA) or (lR)-(-)-camphor-10-sulfonic acid (L-CSA) in various solvents such as N-methyl-2-pyrrolidone (NMP), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO) or chloroform. The mirror-imaged circular dichroism spectra for the salt films derived using D-CSA and L-CSA indicated enantioselectivity in the doping process. The first optically active ring-substituted PANIs, namely poly (o-toluidine)/(+)-HCSA and poly (o-toluidine)/(-)HCSA.were also produced in solution and as films via a similar doping procedure in DMSO. Rahy et al. [76] synthesized PANI nanofiber by using both potassium biiodate, and sodium hypochlorite oxidant and the nanofiber showed high electrical conductivity of greater than 100 Scm^{-1}. The nanofiber product also showed not only a long nano-size fibril structure with average diameter of ~ 50 nm and length of ~ 4 μm but also high crystallinity. It was observed that the nanofibers synthesized using the two oxidants gave both high electrical conductivity and high crystallinity compared to PANI synthesized using commonly known APS oxidant. They also found that dimensional and morphological uniformity of PANI nanofibers were greatly improved when the two oxidants were used. The long length and high crystallinity were probably the contributing factors to have high conductivity. Order of the oxidant addition for the synthesis had no effect on quality of the product.

Interfacial polymerization of aniline

When polymerization reaction is carried out in the interfaces of two immiscible solvents it is known as interfacial polymerization. PANI has been synthesized by an interfacial polymerization technique using a mixture of two immiscible solvents such as water and chloroform in the presence of different acids acting as dopants. The reaction is initiated by an oxidizing agent such as APS, H_2O_2, and so on at room temperature or at any preferable temperature in the presence or absence of a surfactant. The final product is isolated by centrifugation [77]. Chen et al. [78] prepared different shaped PANI through the interfacial polymerization method by simply varying aniline (monomer) to salicylic acid (dopant) ratio. Yongjun He [79] synthesized PANI nanofibers by a methylene chloride/water emulsion solely stabilized by CeO_2 nanoparticles for the first time. The products were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and Fourier Transform Infra Red (FT-IR) spectroscopy. The PANI nanofibers had an average diameter of 65 nm and a length of about 2 μm. PANI /CeO_2 composite microspheres with an average diameter of about 1.3 μm were also obtained. The PANI nanofibers and PANI /CeO_2 composite microspheres could be separated by centrifugation.

Seeding polymerization of aniline

The seeding polymerization is a typical template approach where a foreign material is used as the seed and the polymerization reaction is carried out in the presence of this seed. PANI nanofiber has been synthesized from aniline in the presence of some PANI powder acting as a "seed" using different acid dopants and different solvents. The PANI obtained by this method is similar to a nanofiber with high conductivity. The morphology of this nanofiber depends upon the type of acid used, the acid concentration, type of seed, the solvent used, and the relative amount of seed with respect to solvent.

Metathesis polymerization of aniline

This is a polymerization technique where aniline monomer is not required for the synthesis of PANI. Guo et al. [80] synthesized PANI by heating p-dichlorobenzene at 220 ºC for 12 h with sodium amide in an organic medium such as benzene, when PANI was obtained by a metathesis reaction.

Self-assembling polymerization

The self-assembling polymerization method is carried out in a vapor-phase to obtain an ultra thin film [81]. The PANI thin films are directly grown on the polymeric film substrates by polymerizing aniline monomer in a vapor-phase. Yang et al. [82] prepared molecularly assembled PANI copolymer film from aniline and *m*-aminobenzene sulfonic acid using APS as an oxidant on indium tin oxide (ITO) as a substrate. Zhang and Wan synthesized a PANI nanotube with an 80–200 nm outer diameter and a 20–40 nm inner diameter by the self-assembled method [83].

Sonochemical synthesis of polyaniline

In sonochemical synthesis the polymerization is accomplished with the aid of ultrasonic irradiation. Jing et al. [84,85] synthesized PANI nanofibers with high polymer yields using this technique.

Electrochemical synthesis of polyaniline

The electrochemical synthesis provides a better method of polymerization with a fine control of the initiation and termination steps. The electrochemical reactions are often much cleaner, and the PANI obtained is expected to be in a relatively purer form (as no additional chemicals such as surfactant, oxidant, and so on are used here) compared to that obtained from chemical polymerization. Electrochemical methods are generally employed for the polymerization of aniline under: (i) a constant current (galvanostatic); (ii) a constant potential (potentiostatic); and (iii) a potential scanning/cycling or sweeping. Gupta and Miura [86] synthesized PANI nanowires by electropolymerization on a stainless steel electrode at the potential of 0.75 V vs. saturated calomel electrode. Sung et al. [87] electrochemically synthesized PANI using agar gel as a template (Agar-PANI). The material characteristics and electrochemical behavior of the Agar-PANIs were compared with those of PANI synthesized by means of conventional methods. The electrochemical synthesis was monitored using the cyclic potential sweep (CPS) technique. The dependence of the total deposition charge on the number of cycles was satisfactorily explained with a CPS parameter, *n*, and was consistent with scanning electron micrographs. The electrical conductivity and the bulk density of the Agar-PANI samples were 1.5 Scm^{-1} and 1.53 gcm^{-3}, which were three orders and four times larger respectively than those of the PANI samples prepared by conventional methods. Nekrasov et al. [88] have studied electrochemical polymerization of aniline in the presence of poly(amidosulfonic acid)s of different nature: poly(2-acrylamido-2-methyl-1-propanosulfonic acid) (flexible backbone); poly(*p*,*p*'-(2,2'-disulfoacid)-diphenylene-iso-phthalamid) (semi-rigid backbone); poly(*p*,*p*'-(2,2'-disulfoacid)-diphenylene-tere-phthalamid) (rigid backbone). They also investigated spectral and electrochemical properties of the films obtained, as well as their surface morphology. The matrix polymerization resulted in the formation of interpolymer complexes of PANI and the above-cited polyacids. The acceleration of aniline electropolymerization in the presence of poly(amidosulfonic acid)s was observed due to association of aniline molecules to sulfonic groups of the polyacid and higher local concentration of protons near the polyacid backbone. The rigid-chain polyacids interfere with the normal course of the electropolymerization, which manifests itself in the changes of the shape of time dependence of absorbance and charge. Cyclic voltammetry and spectroelectrochemical experiments showed that the formation of interpolymer complex with rigid-chain polyacids distorts spectroelectrochemical characteristics of PANI. This evidently results from steric hindrances in the formation of quinoid units. Micro- and nano-structures composed of PANI have been prepared by Delvaux et al. [89] by chemical and electrochemical oxidative polymerization of aniline within the pores of particle track-etched membranes. Their morphology has been studied by field-emission SEM. Hollow tubules were formed because PANI initially deposits on the surface of the pore walls. Raman spectroscopy was used to probe the oxidative state of PANI in order to optimize the chemical polymerization conditions with respect to the electrical conductivity. The nanoscopic materials showed an enhancement of the electronic conductivity compared to analogous polymer bulk conductivity. Highly ordered PANI nanofibril arrays were fabricated by Zhao et al. [90] within the pores of porous anodic aluminum oxide (AAO) template membrane by electrochemical polymerization. The packed array of columnar hexagonal cells with central, cylindrical uniformly of AAO template resulted in more ordered and uniform growth of PANI than in films synthesized without spatial restriction. The electrochemical behavior and structure of PANI nanofibrils were examined by cyclic voltammetry and FT-IR spectroscopy. The experimental results indicated that fibrils were composed of PANI. The electrochemical experimental result indicated that the spatial restraint in the pores of AAO membrane was sufficient to induce the formation of more ordered PANI chains in the AAO membrane. Weng et al. [91] facilely synthesized helical PANI nanofibers via a direct electrochemical method without using any template in the presence of D-CSA or L-CSA as the dopant. The helical morphologies of the PANI nanofibers prepared from potentiostatic deposition were confirmed by SEM and TEM. The helical PANI nanofibers induced by d-CSA and l-CSA exhibited mirror-imaged circular dichroism spectra in the ultra violet-visible (UV–VIS) range, indicating the stereochemical selectivity of the electrochemical polymerization. The colors and optical activities of these nanofibers were maintained on an ITO coated electrode with a dedoping/redoping treatment. The optical activities of the helical PANI nanofibers reversibly varied with different oxidized forms, which were easily controlled by the different potentials applied to the nanofibers. Fully sulfonated PANI nano-particles, nano-fibrils and nano-networks were achieved by electrochemical homopolymerization of aniline-2-sulfonic acid by Zhang et al. [92] using a three-step electrochemical deposition procedure in a mixed solvent of acetonitrile (ACN) and water.

Template synthesis of polyaniline

Template-guided synthesis of conducting polymers was first reported by Yang and Sun [93]. In template synthesis the desired material with the required shape is synthesized within the pores of a template and the template is then dissolved, leaving the material with the shape of the pores of the template. The template method has been used both for chemical and electrochemical polymerization in order to obtain conducting polymer nanotubes [94-97]. Template-based methods have attracted great attentions as a viable technology enabling to manipulate a length and a diameter of nanowires [98-101]. The molecular template, in most cases, polyacids such as polystyrene sulfonic acid (PSSA), binds the monomer, for example aniline to form molecular complexes, which are dispersed in water as colloidal particles. Upon polymerization, the aniline monomers form PANI and remain attached to the template to form the template-PANI complex. By choice of the template molecule and the polymerization conditions, stable sub-micron size colloidal particles of PANI-template aggregate can be formed during polymerization. The stabilization against coagulation arises from the Coulomb repulsion between particles, which are a result of the surface charge provided by the extra sulfonic acid groups in PSSA. Very stable dispersions of PANI-PSSA complexes can be made with particle size less than 1 μm [93,102].

One of the interesting and useful features of this method is its effectiveness in the preparation of one-dimensional microstructured or nanostructured PANI with a controllable diameter, length and orientation. However, the disadvantages of the method are: (i) a rather tedious post-synthesis process is required in order to remove the templates; and (ii) the nanostructured polymers may be destroyed or form undesirable aggregates after they are released from the templates [103-105]. Choi et al. [106] reported the self-templating synthesis of PANI nanowires on prestructured aluminum. They emphasized that anodization and electropolymerization could occur at the same time by a single electrochemical process. The method is based on the principle that the anodization of predefined aluminum in H_2SO_4 leads to the formation of highly ordered porous alumina and aniline monomer can be electrochemically polymerized in the formed porous alumina by the anodic reaction. XPS analysis reveals that PANI nanowires prepared in this work are protonated emeraldine. The process of PANI, poly (2-methoxyaniline) (POMA) nanotubes formation was investigated by Mazur et al. [107]. PANI and POMA nanotubes were prepared by chemical *in situ* deposition within the pores of polycarbonate membranes. It was found that the formation of PANI and POMA proceeds by two substantially different mechanisms. In the case of PANI, the polymer is first formed in the polymerization solution (the solution containing the monomer and oxidant, where the polycarbonate substrate is placed), and then it precipitates on/into the membrane. In the case of POMA, the oxidized 2-methoxyaniline molecules are first adsorbed on polycarbonate surface, and then, as a consequence of their accumulation, they recombine to form the polymer.

Enzymatic synthesis of polyaniline

Enzymatic polymerization of aniline to PANI has attracted significant attention because it is carried out under milder conditions, in comparison to those used for chemical polymerization. Horseradish peroxidase (HRP) and soybean peroxidase (SBP) are oxidoreductase enzymes capable of oxidizing aromatic amines in the presence of hydrogen peroxide [108-110]. These enzymes can be derived from non-contaminant renewable sources and have high reaction selectivity to aromatic compounds and they cut down the oxidation by-products to water [111]. For these reasons, peroxidase catalyzed polymerization of aniline is considered to be an environmental friendly route to obtain PANI. Most of the research related to enzymatic polymerization of aniline was carried out using polyelectrolyte templates such as sulfonated polystyrene [112-114], poly (vinylphosphonic acid) [115] and deoxyribonucleic acid (DNA) [116]. These studies have shown that these templates provide a local environment, which promotes *para*-directed, head-to-tail coupling of aniline radicals. This polyanion-assisted polymerization allows the enzymatic syntheses for water-soluble complex of conducting PANI with a well-defined structure at a pH level as high as 4.3 [117]. However, the high degree of complexity between PANI and the polyanion renders it difficult to obtain bulk PANI that is required for specific applications, such as free standing films or fibers [118,119]. Zemel and Quinn [120] have reported that bulk of electrically conductive PANI can be synthesized using HRP as a catalyst, in an aqueous media at pH 3.0. However, under such reaction conditions, the HRP goes through a rapid denaturing process. Thus, to carry out the reaction, a large amount of this enzyme is needed. The problem can be avoided by performing the reaction at a pH above 6.0 in an aqueous medium [121]. When the synthesis of PANI is carried out at a high pH in the absence of an anionic template, a non-conductive material is obtained [122]. The lack of electrical conductivity is attributed to structural defects, such as branched or cross linked chains and phenyl–phenyl couplings, which causes a loss of electronic conjugation of the PANI backbone. SBP is an enzyme with a higher thermodynamic stability than HRP [123] and a better catalytic activity under an acidic environment [124-126]. SBP may, therefore, be used to produce conductive PANI without the use of a template. Unlike chemical oxidation, in enzymatic catalyzed polymerization, the oxidation rate is mainly dependent on the amount and activity of the enzyme [127]. For these reasons, it is useful to prepare PANI colloids in dispersed media, because during chemical polymerization of aniline, the aggregation of the particles takes place during the auto-acceleration period [128]. This, therefore, reveals that the oxidation rate is one of the key parameters to control the morphology of the colloidal particles. In addition, during enzymatic oxidation, no by-products are generated and the contamination of the reaction media with salts is thus avoided [129,130]. Wang et al. [131] obtained PANI fibers spun from water soluble form of PANI, which was enzymatically synthesized. Silva et al. [132] synthesized PANI catalyzed by SBP at 1 °C in either aqueous or partially organic media, as a function of pH or reaction media. Kinetic studies indicated that, unlike chemical polymerization, enzymatic polymerization of aniline showed neither induction period nor autoacceleration. The redox reversibility and chemical structure of the synthesized PANI was strongly dependent on the starting pH of the reaction medium. UV–VIS, FT-IR, wide angle X-ray diffraction (WAXD) and thermogravometric analysis (TGA) analysis were used to explain how the enzymatic reaction conditions influenced both the chemical structure and physical properties of the PANI. Optimum reaction conditions were outlined for the direct enzymatic synthesis of electrically conductive ES with yield as high as 71 %. Silva et al. [133] enzymatically synthesized colloidal PANI particles in aqueous media using poly (vinyl alcohol) (PVA) as steric stabilizer. Hydrochloric acid, p-toluenesulfonic acid (PTSA), and camphorsulfonic acid (CSA) were used as doping agents during polymerization. PANI showed chemical redox reversibility as demonstrated by changes in its electronic absorption spectrum. FT-IR and UV–VIS spectroscopic studies indicate a linear chemical structure of the synthesized polymer, whereas the results from XPS indicate the adsorption of PVA at the surface of the particles. The doping agent used during the enzymatic polymerization of aniline influenced morphology and thermal stability of the synthesized particles. PANI colloids prepared using PTSA showed spherical morphology and a narrow size distribution as shown by SEM and dynamic light scattering. Laccase isolated from *Coriolus hirsutus* was first used by Karamyshev et al. [134] in the synthesis of water-soluble conducting PANI. The laccase-catalyzed polymerization of aniline was performed in the presence of sulfonated polystyrene (SPS) as a template. Laccase shows remarkable advantages in the synthesis of conducting PANI compared to the commonly used HRP due to its high activity and stability under acidic conditions. The characterization of the polyelectrolyte complex of PANI and SPS has been carried out using UV-VIS and FT-IR spectroscopy. Cyclic voltammetry and dc conductivity measurements confirmed that electroactive PANI was synthesized by the laccase-catalyzed polymerization of aniline. Sakharov et al. [135] did enzymatic synthesis of polyelectrolyte complex of PANI and SPS. Royal palm tree peroxidase, which is active and stable under acidic conditions, was used as a biocatalyst. The template polymerization of aniline was carried out in aqueous buffer at pH 3.5. Varying concentrations of aniline, SPS and hydrogen peroxide in feed and the favorable conditions for the production of PANI were determined. Contrary to chemical polymerization of aniline, the role of enzymatic reaction is to control kinetically and proceed under environmental friendly (green) conditions. The production of the electro active form of PANI–SPS complex was confirmed by electron paramagnetic resonance and UV-VIS spectroscopy.

Photo-induced polymerization of aniline

The photo-induced polymerization of aniline involves the photo-excitation of aniline monomer to obtain PANI. PANI has been synthesized by using a laser to irradiate an Au electrode in a solution containing aniline under an applied external bias [136]. Only photons in the UV or visible region are also used to induce polymerization of aniline in an aqueous solution of transition metal salts. The photo-polymerization methods yield a composite material where silver nanowires and microwires are formed along with PANI. The morphology of the conducting polymer is strongly dependent on the excitation wavelength. A more globular morphology is observed for the UV synthesis, whereas a more fibrillar morphology is detected for the visible light synthesis [137,138].

Plasma polymerization of aniline

In plasma polymerization of aniline, the monomer, or a dispersion of monomer-droplets, is first injected directly in the stream of plasma induced by a DC-glow discharge reactor. In the second step, the reactor is specially reconfigured to have a deposition of polymer particles at mild conditions. This is an alternative method for the preparation of different

PANI nanocomposites. The properties of the composites can be adjusted by controlling the dispersed phase. By this process the composites can be easily deposited in a single step on a targeted substrate that has a controlled thickness. It is a solvent free process and a pinhole free coating can be obtained [139]. The plasma polymerization of aniline on different surface functionlized low-density polyethylene (LDPE) substrates was investigated by Wang et al. [140]. The use of acrylic acid graft copolymerized LDPE substrate significantly enhanced the adhesion of the PANI to the substrate over that observed with pristine LDPE. The plasma polymerized PANI was rendered electrically conductive by carrying out the polymerization on a PSSA coated LDPE substrate. Conductivity was induced by acid protonation of the PANI by $HClO_4$. The reaction of the plasma-polymerized PANI with viologen grafted on the substrate under UV irradiation and with $AuCl_3$ and $Pd(NO_3)_2$ in acid solutions was also investigated by them. Plasma polymerization of aniline and *in situ* doping of PANI with iodine was carried out by Bhat and Joshi [141] using radio frequency glow discharge. Thin films of PANI were deposited on platinum and glass. The FT-IR spectrum showed that the aromatic ring was retained under the plasma conditions. The electrical conductivity measurements indicated that the conductivity increased by more than seven orders of magnitude when PANI was doped by iodine. The SEM studies revealed the formation of irregular pentagons on glass substrate while on platinum, a fibrillar network of PANI was obtained. In both the cases a continuous film was obtained. Pure and iodine-doped PANI thin films were prepared by ac plasma polymerization technique by Mathai et al. [142]. Doping of iodine is carried out *in situ* as well as by employing iodine chamber methods. The structural analyses of pure and iodine-doped PANI thin films were carried out by FT-IR spectroscopic studies. Optical bandgaps of these films were evaluated from UV–VIS absorption studies. Direct and indirect transition energy gaps were determined from Tauc plots. The structural changes of PANI upon doping and the reduction of optical bandgap were explained on the basis of the results obtained from FT-IR spectroscopic and UV–VIS absorption studies. An inductively coupled pulsed-plasma reactor was used by Tamirisa et al. [143] to synthesize PANI thin films on several substrates positioned at various distances from the center of the radio frequency (RF) coil. FT-IR results indicated that the chemical composition and structure of the films were very dependent on the substrate's position with respect to the RF coil, there being considerably less aromatic character closer to the coil. The electrochemical behavior of the films in acidic electrolytes was similar to that of small molecule aniline oxidation products; the number of peaks in the cyclic voltammograms varied with the substrate. SEM studies indicated that as the films became thicker, they developed nodules atop a somewhat smoother underlayer. Results from TEM and optical birefringence suggested that the films were not completely homogeneous. The impedance measurements were consistent with relatively rough films possibly containing pinholes. Gong et al. [144] used the radio-frequency plasma polymerization technique to polymerize aniline onto polymer substrates including perfluorinated ethylene propylene copolymer. It was demonstrated that the chemical and physical characteristics of the plasma-polymerized PANI films changed significantly with discharge conditions, indicating the possibility for tailoring the structure and properties of the PANI films by optimizing the discharge conditions. In particular, the contents of quinoid sequences and aliphatic cross linking moieties were found to increase with increasing power input and/or discharge duration. By contrast, the number of free radicals trapped in the PANI films and their mobility were shown to increase with decreasing the power input and/or discharge duration within the plasma conditions covered in the study. Furthermore, a correlation was found between surface hydrophilicity of the resultant plasma-polymerized PANI films and the atomic ratio of C to N.

1.7.2. Polyaniline composite

It is known that undoped state of PANI (insulator) is soluble in common organic solvents, but the conducting form (doped form of PANI) is insoluble in almost all solvents, except concentrated sulfuric acid [145-148]. The lower processability is a major disadvantage of PANI. In order to improve the solubility of the conductive form, some routes are possible to overcome these problems: modification of the polymer chain [149], usage of large anions as dopants [150-154] or by dispersing with suitable insulator polymer matrix [155].

1.7.2.1. Composites produced by polymerization of aniline in dispersion systems

This method, based on experience in aniline polymerization, is conducted at low temperatures (typically 0 – 5 °C) using an appropriate oxidant in the presence of water soluble polymers or tailor-made reactive copolymers [156] (e.g., poly (2-vinyl pyridine-co-p-aminostyrene) [157], PVA [158,159], PVP [160,161], PEO [162], cellulose derivatives [128,163], poly (methyl vinyl ether) [164], etc.). The technique results in sterically stabilized colloidal dispersions of PANI particles of different size (typically from tens to hundreds of nanometers) and morphology. These colloids can be further mixed with film-forming latex particles or with stable matrix polymer dispersions to produce conducting composites [165].

Comparatively, small-molecular surfactants were used for stabilization of ICPs colloids [166]. The polymerization of aniline inside micelles of SDS produced a reasonably stable colloid containing low molecular PANI. This PANI anionic micellar system had a metal–insulator transition from the ES to EB at the unexpectedly high pH of 7–8 [167]. Yassar et al. [168] reported an alternative method to produce conducting colloid latices, through pyrrole emulsion polymerization in sulfonated and carboxylated polystyrene (PS) latices, in which the particles were overcoated by PPy. Wiersma et al. [169] have shown that a critical condition for stability of such latexes is the presence of a chemically grafted non-ionic polymeric stabilizer, such as PEO or hydroxymethylcellulose at latex particles. They used TEM to reveal a 'core–shell' morphology of latex particles (core) coated by the conducting polymer (shell). These coated particles displayed the good film-forming properties of the parent polyurethane (PU) at ambient temperature, despite the fact that the low glass transition temperature (T_g) latex component was encapsulated within the high T_g conducting polymer. The composite films produced had conductivity in the range of 10^{-5}–10^{1} Scm^{-1} [169]. It should be noted that unlike the relatively smooth and uniform morphology of PPy coated latex particles [170,171], PANI overlayers (core) on latex (PS) particles (shell) are rather inhomogeneous [172-174]. Barthet et al. [172] used XPS to examine the surface compositions of the PANI overlayers deposited onto micrometer-sized PVP-stabilized PS latex particles under various synthesis conditions for seven preparations. The thickness of the PANI overlayer was in the range of 2–30 nm, and the conductivity of the coated particles substantially increased with a raise of PANI loading to attain a maximum conductivity 0.17 Scm^{-1} for 9.3 wt% PANI. It has been shown that relatively rapid polymerization at room temperature resulted in the non-uniform PANI coatings and reduced PANI surface yield. Non-uniform PANI coatings were obtained for the polymerization of aniline hydrochloride (AnHCl) in the presence of HCl in the latex medium at ambient temperature (25 ^{o}C), but more homogeneous PANI coatings were obtained at 0 ^{o}C. The maximum PANI coverage was found to be around 57–59%, which was much lower than the surface composition of 94–100% found for PPy deposited onto similar micrometer-sized PS latex [175]. Finally, the improved uniformity of the PANI overlayers prepared using AnHCl in the absence of HCl is consistent with the higher coalescence temperature found for these PANI-coated PS particles in hot-stage optical microscopy studies. The formation of electrostatically bound anilinium cations in the emulsion polymerization of aniline in latices containing polymer particles with surface acidic (sulfonic) groups may be the origin of increased homogeneity of the PANI overlayers observed in these materials. Kim et al. [176] confirmed this supposition for the AnHCl polymerization in PS–PSS latex, reporting that a high concentration of aniline was needed to coat all the core particles uniformly because of a very small size of the PS–PSS core particles (of 30–50 nm in diameter). The conductivity of the produced composite measured on cold pressed pellets increased from 2.6×10^{-5} Scm^{-1} at 3.41 wt% PANI to a maximum of 0.05 Scm^{-1} at 12.3 wt% PANI. In some cases it is important to produce a final conducting composite with good thermostable properties, specifically for melt processing techniques. This suggests that it is preferable to carry out the emulsion aniline polymerization in latex medium in the presence of sulfonic acid than hydrochloric acid [177] to ensure higher thermostability of the composite conductivity. Moreover, the sulfonic acids act both as a surfactant and as a dopant for PANI [178]. Using this approach, Xie et al. [179,180] prepared PANI/SBS [82,83] and PANI/chlorosulfonated polyethylene (CSPE) [181] composites by aniline polymerization in an emulsion comprising of water and xylene containing the elastomers and DBSA. The composites obtained were melt or solution processed. Percolation thresholds were lower for PANI/SBS (10 wt % for melt processed sample and 7 wt % for solution processed sample) than for PANI/CSPE (14 wt % for melt processed samples and 22 wt % for solution processed samples). At the same content of PANI, the conductivity of the solution processed composite was higher than that of the melt processed composite for PANI/SBS, with the reverse observed for PANI/CSPE. The elastomer nature also affected relationships between mechanical properties and the PANI content, as well as the morphological structure of the composites. Thus, for melt processed samples of PANI/SBS, the composites behaved like a thermoplastic elastomer when the PANI content was lower than 12 wt %, with a high elongation (about 600%) and low permanent set (50 %). In the case of PANI/CSPE, a thermoplastic behavior was observed at higher PANI content namely between 12 and 18 wt %, with an ultimate elongation of 400 % and permanent set, 30 %. On secondary doping of the solution processed samples with m-cresol, the conductivity of PANI/SBS increased by two orders of magnitude and that for PANI/CSPE increased by six orders of magnitude [176]. These effects indicate that the interaction of PANI with the elastomers is enhanced for the more polar CSPE.

1.7.2.2. Chemical *in situ* polymerization of aniline in presence of a polymer matrix

Unlike the dispersion systems considered above, there are other methods of chemical polymerization of aniline in the presence of polymer matrix, which do not demand the presence of surfactants in the reaction mixture. Specifically, these are the chemical polymerization of aniline by a variety of methods:

(i) In a solution of aniline and a matrix polymer [182,183]

(ii) At the surface of a polymer substrate dipped in aniline and oxidant solution [184]

(iii) Directly in a polymeric matrix, swelled in aniline and contacting with an oxidant solution [185,186]

(iv) In a polymeric matrix containing an oxidant and contacting with a solution or vapors of a monomer [187,188] etc.

Obviously, it is difficult to find a well-defined boundary between solution polymerization systems and the nanosized dispersion methods reviewed above. This is rather a problem of definitions of true and colloid polymer solutions, and is a topic for discussions of PANI containing systems [189,190]. One may consider that aniline polymerizations follow from case one to another, depending on the polymerization degree and other components of the system. Specifically, this is characteristic for water systems containing water-soluble polymers, e.g., PVA, poly (acrylamide) (PAM), Nafion, and polysaccharides [191,192]. In these systems aniline polymerization was usually carried out at lower temperatures (0–10 °C), but there were some differences in the procedure, especially in the sequence of the addition of reagents to the reaction mixture.

Mechanical studies show that at moderate PANI content (7.75%) the tenacity of PANI/PVA composite films decreased from that of the pure PVA network, probably due to some disruption of the PVA network, with some regain on increased PANI loading. The changes at higher PANI loadings were explained as a direct consequence of a semi-cross linked structure of the matrix polymer, or of a semi-interpenetrating network formed during aniline polymerization [193]. But it seems that one may accept here an additional explanation of these changes via a physico-chemical interaction of PANI and PVA, for the PANI/polycarbonate (PC) composite, characterized by similar behavior [194]. A strong (chemical) interaction between PANI and a soluble matrix polymer can sometimes be formed due to aniline grafting to radicals appearing in the polymer matrix backbone under the action of an oxidant, which in parallel initiates aniline polymerization in the solution. Obviously, this possibility depends on the matrix polymer. Xiang and Xie [195] showed that aniline could be graft copolymerized onto the backbone of PAM in aqueous HCl solution in the presence of APS as oxidant. They dissolved the copolymer PAM-g-PANI in 5 wt% NaOH solution when the molar ratio of aniline/acrylamide in the feed composition was lower than 15. After removal of the salt ions by dialysis and evaporation of the solution, a thin film of PAM-g-PANI was obtained and doped by HCl gas. When the molar ratio of aniline/acrylamide in the feed composition was about 15, the HCl doped thin film of PAM-g-PANI possessed a high conductivity of 8.8 Scm^{-1}. Ghosh et al. [196] investigated a similar system and found that PANI synthesized in an optically clear aqueous solution or dispersion with the support of aqueous PAM (2–5%) showed excellent storage stability, due both to limited grafting of PANI on PAM and to a template effect through hydrogen bonding between segments of the two polymers. When investigating the effect of aniline concentration in the reaction mixture they observed an upper limiting conversion of nearly 75% [196]. Scanning electron micrographs showed that a PANI/PAM composite at low PANI loading (2%) had a little phase separation, but that a minor phase separation appeared for a somewhat higher PANI content (10%), without a gross phase aggregation. The phase morphology of PANI/PAM composites having even 40% PANI content showed a very intimate and uniform distribution of the two phases, without the significant phase aggregation. This highly uniform phase morphology of the PANI/PAM composites is a direct consequence of a mutual interaction between PANI being formed and PAM in the solution during polymerization of aniline, including the establishment of PANI/PAM hydrogen bonding and grafting of PANI on PAM. The PANI/PAM composites showed enhanced thermally stable electrical conductivities (10^{-8}–10^{-1} Scm^{-1}) in comparison to PANI itself [196]. Water insoluble polymers may also be used to produce conducting PANI composites through the solution polymerization method. Specifically, it was demonstrated by the chemical aniline polymerization in PS solution in xylene [197]. It was realized by the addition of the oxidant and DBSA dissolved in xylene to the xylene solution comprising aniline and PS. The electrical conductivity of the separated PANI/PS composites improved with increasing amount of PANI, to reach a value of 0.1 Scm^{-1} at 12 wt% PANI. Due to the fact that DBSA served as dopant, these composites were soluble in a variety of organic solvents (chloroform, xylene, and NMP).

1.7.3. Sensor applications of polyaniline

A sensor is a device that measures a physical quantity and converts it into a signal, which can be read by an observer or by an instrument. The ability of PANI to change the electrical conductivity and color upon exposure to acidic, basic and some neutral vapors or liquids finds its usefulness in the field of sensor, detector and indicator.

1.7.3.1. Heterojunction sensor

Polyaniline-based solid state devices are of low cost and useful in electronics, storage devices and sensors. PANI has been processed into thin film form using different methods including spinning, vacuum sublimation and Langmuir–Blodgett (LB) techniques [198]. These films have been used for the detection of H_2S, SO_2, NH_3, methanol, acetone, etc. and in biosensors as well. Laranjeira et al. [199] fabricated a high quality Si–PANI junction for sensing radiation (γ) and ammonia gas. Joshi et al. [200] reported on the performance of a liquefied petroleum gas (LPG) sensor based on n-CdSe/p-PANI junction fabricated by a simple electrodeposition technique. The junction diode showed the sensitivity to LPG at room temperature (300 K). Dhawale et al. [201] reported the performance of a room temperature (300K) LPG sensor based on a p-PANI /n-TiO_2 heterojunction. Joshi et al. [202] investigated the response of a heterojunction formed with *n*-CdTe and *p*-PANI to LPG using forward bias current measurement at room temperature. Dhawale et al. [203] fabricated a room temperature (300 K) LPG sensor based on n-CdS/PANI thin film heterojunction using simple inexpensive electrodeposition technique.

1.7.3.2. Chemical sensors

Polyaniline is an interesting material for chemical sensors because its conductivity can increase by over 10 orders of magnitude on exposure to doping acids. This process can be reversed by dedoping in the presence of bases. PANI sensors have been used to detect a number of different chemical species including hydrochloric acid, ammonia, organic vapors, and strong reducing agents. Chabukswar et al. [204] utilized chemically synthesized acrylic acid doped PANI as an ammonia sensor. Xie et al. [205] studied the fabrication of PANI based films prepared by LB technique and composite self assembly films and compared their gas sensing properties to nitrogen dioxide. Electrical conductivity and the responses to SO_2–N_2 mixtures of HCl-doped and CSA-doped solvent cast PANI films (PANI/HCl and PANI/CSA) were investigated by Kiattibutr et al. [206]. At a given doping level or with the same number of charge carriers present, electrical conductivity of PANI/HCl films was found to be greater than that of PANI/CSA films due to the more closely packed crystalline domain of the PANI/HCl films, which reflects its greater charge carrier mobility. The lowest detectable concentration was 200 ppm and the response to SO_2 was reversible. Sharma et al. [207] demonstrated the applicability of copper/ PANI nanocomposite as chloroform vapor sensor. The effect of NH_3 gas on the electrical conductivity of four kinds of PANI - insulating matrix polymer blend films was investigated by Matsuguchi et al. [208] for the purpose of preparing a practical NH_3 gas sensor operable near or at room temperature.

The electrical conductivity decreased by exposure of the blend films to NH_3 gas. It was found that the sensing characteristics depended on the kind of dopant species, measuring temperature, matrix polymers, and the solvent used for film preparation. Jain et al. [209] investigated the humidity sensing behavior of PANI doped with different weak acidic dopants. Changes in surface resistivity of the films were monitored as a function of relative humidity. The acidic dopants used were CSA, diphenyl phosphate and maleic acid (MA). Blends of these were formed with styrene–butyl acrylate copolymer for improving the mechanical stability. Films prepared out of styrene–butyl acrylate copolymer with different concentrations of PANI–MA were used for sensing humidity ranging between 20 and 95% relative humidity. The films exhibited almost linear behavior within a chosen range of humidity. Jain et al. [210] reported chlorine gas sensing using PANI as an active layer, which was incorporated in fluorinated ethylene propylene (FEP). The sensor film was made by grafting acrylic acid onto FEP. The film was found to selectively sense chlorine with sensitivity of 45–50% at low ppm levels. Effects of dopants on the correlation between the PANI film resistance and the reduction charge injected to the PANI film in dry ACN solution during electrochemical reduction was investigated by Xu et al. [211] by using the double potential step method. Athawale et al. [212] investigated the sensing behaviour of different aliphatic alcohol vapors such as methanol, ethanol and isopropanol to palladium-PANI nanocomposite. The results showed that the nanocomposite was highly selective and sensitive to methanol vapors. The sensor responded rapidly and reversibly in the presence of methanol vapors. Misra et al. [213] reported a room temperature carbon monoxide sensor obtained by vacuum deposited nanocrystalline PANI thin film. A high sensitivity, selectivity, specificity, and a fast response time have been achieved. Anitha and Subramanian [214] performed a detailed study on the sensing of weakly interacting chlorinated hydrocarbon solvent vapors of CH_2Cl_2 and $CHCl_3$ separately or combined from their solvent mixture (1:1 by volume) by three PANI materials: PANI sulphate, PANI doped with naphthalene sulphonic acid and PANI-PVA blend of 2:1 molar ratio. Each sensor material responded through a decrease in conductivity reversibly and their activities were monitored by normalized conductivity change. Koul and Chandra [215] reported about the conducting PANI-poly (AN–butadiene–styrene) blend films as a sensor material for aqueous ammonia. Tai et al. [216] examined the gas sensing responses of the PANI-titanium dioxide (TiO_2) thin film to NH_3 and CO. The results showed that the response, reproducibility and stability of the PANI/TiO_2 thin film to NH_3 were superior to CO gas. Crowley et al. [217] reported the fabrication and performance of a sensor for ammonia gas analysis, which has been constructed via the inkjet-printed deposition of PANI nanoparticle films. Sensor recovery time, response linearity and sensitivity were all significantly improved by operating the sensor at temperatures up to 80 ^{o}C. The sensor was found to have a stable logarithmic response to ammonia in the range of interest (1–100 ppm). Muthukumar et al. [218] reported a sensor for mercuric ion based on PANI modified with cryptand-222. The transduction process was deprotonation and reprotonation of PANI following the protonation and deprotonation, respectively, of cryptand-222 on binding with mercuric ion. A new chemical gas sensor for NO_2 detection using PANI nanofibers synthesized by an interfacial polymerization method was reported by Yan et al. [219]. The structures of the nanofibers (high surface area, porosity and small diameters) enhanced diffusion of the molecules and oxidative agent into the nanofibers, resulting into high sensitivity and short response time for NO_2 detection. Itoh et al. [220] investigated the aldehyde gas sensing property of MoO_3 with PANI or poly (*o*-anisidine) (PoANIS) thin films. The thin films prepared by the modified process exhibited excellent response of a resistance increase when exposed to formaldehyde and acetaldehyde of several tens ppb because insoluble PANI or PoANIS impurities possessing opposite response of resistance decreased against the hybrids preventing adsorbing onto the surfaces of the hybrid thin films. Srivastava et al. [221] reported multiwall carbon nanotube (MWCNT) doped PANI composite thin films for hydrogen gas sensing applications. The gas sensitivity of these composite films was evaluated by measuring the change in electrical resistance of composite films in presence of hydrogen gas for different pressures at room temperature. The MWCNT/PANI composite film showed a higher sensitivity in comparison to pure PANI and it decreased on increasing hydrogen gas pressure. PANI nanofibers were used for the detection of aromatic organic compounds by Li et al. [222]. The sensor response to aromatic organic compounds was investigated in several hundred ppm ranges. The sensor showed an increase in conductivity, and the maximum response measured at 1000 ppm was several tens of percent. The interaction mechanism was discussed through X-ray photoelectron spectroscopy study. Zeng et al. [223] fabricated humidity sensor based on PANI nanofibres. The sensor responded to low relative humidity (RH) normally by decreasing electrical resistance with increasing humidity. However, at higher RH the sensor reversed its responses by increasing the electrical resistance with humidity. The unique structure of nanofibres, which was more susceptible to distortion during polymer swelling, was responsible for the 'reversed behavior'.

1.7.3.3. Quartz crystal microbalance sensor

A PANI–TiO_2 nano-composite, obtained by combination of chemical polymerization and a sol–gel method, was deposited on the electrode of quartz crystal by Zheng et al. [224]. When analyte vapor was injected into the chamber, gas absorption decreased the frequency of the coated quartz crystal and thereby caused an increase of the frequency difference between the two crystals. The frequency difference change response towards trimethylamine was evident and was recovered by N_2 purgation easily. The calibration curve towards trimethylamine, its long-term stability and selectivity were investigated. The thermal behavior of the sensing characteristics was compared with that of a PANI quartz crystal microbalance (QCM) sensor. Ayad et al. [225] reported a QCM sensor coated with a thin film of PANI EB as a sensitive method for the determination of a number of aliphatic chlorinated hydrocarbons such as carbon tetrachloride, chloroform, dichloromethane, 1,2-dichloroethane vapors. The detection was based on the absorption of the vapors of these organic compounds into the EB film. The work also included the use of a PANI ES film instead of the EB film. It was concluded that the EB film showed higher sensitivity towards the organic vapors than the ES film, which was attributed to the presence of unprotonated amine and imine groups along the PANI chains in the EB form. Xie et al. [226] fabricated a methane gas sensor made by deposition of PANI/PdO thin films on a mass-type QCM device through layer-by-layer self-assembly method. The frequency responses of the PANI/PdO based QCM sensor to methane gas were measured at room temperature and 50 ºC. The PANI/PdO based QCM gas sensor showed a better response at room temperature than that at 50 ºC. PANI chemically coated on the electrode of QCM was developed by Ayad et al. [227] for the determination of phosphoric acid in the liquid phase. The QCM sensor demonstrated a rapid response to the acid with an excellent reversibility. A linear response of the sensor for different concentrations of phosphoric acid was found in the region of 61 M. The conductivity at different concentration of the acid was also determined. Finally, the pH dependence on the electronic absorption of PANI phosphate film was studied, which indicates that the film can be used as a sensor over a wider pH range of 3–12.

1.7.3.4. Optical sensor

Zhe et al. [228] studied the ammonia gas sensing capabilities of the PANI film using absorption spectroscopy method. A significant change was observed in the absorption spectra of the film after it was exposed to ammonia gas. The sensors had a detection limit of 1 ppm (v/v) for ammonia, with a linear dynamic range from 180 to 18 000 ppm. Hu et al. [229] reported optical transmittance changes in PANI coatings originated by their exposure to ammonia gas. Experimental results of the evaluation of the optical response of PANI films obtained by the chemical bath method when they were exposed to low concentrations of aqueous ammonia was reported by Uribe et al. [230]. The optical transmittance of the PANI was measured and analyzed in the wavelength interval of 350–1100 nm to determine its optical sensitivity to different concentrations of ammonia. The PANI films employed as a sensing material for the optical detection of aqueous ammonia had a fast response time and a fast regeneration time of less than 10 s at room temperature.

1.7.3.5. Biosensor

Timur et al. [231] developed thick film electrode based biosensors containing *Trametes versicolor* and *Aspergillus niger* laccases and *Agaricus bisporus* tissues for the determination of phenolic compounds and the measurement was based on oxygen consumption in relation to analyte oxidation. The electrodeposited organic polymer; PANI was used as a matrix for the immobilization in the preparation of thick film sensors. Gerard and Malhotra [232] used electrochemically synthesized PANI film as a matrix for immobilization of glucose oxidase and lactate dehydrogenase enzymes. Amperometric detection of glucose was done by Sharma et al. [233] by using glucose oxidase immobilized PANI film as a working electrode and Ag/AgCl as a reference electrode at a bias voltage of 0.2 V over a physiological range. The electrode carrying glucose oxidase was found to be stable up to 32 days. Suman et al. [234] developed an amperometric enzyme electrode for determination of lactate in serum by immobilization of commercial lactate oxidase from Pediococcus species through glutaraldehyde coupling onto PANI-co-fluoroaniline film deposited on an ITO coated glass plate. The enzyme electrode showed optimum response when operated at 42 °C in 0.05 M, sodium phosphate buffer pH 6.5 for 50 s. The biosensor showed a good performance with a linear response range from 0.1 to 5.5 mM/l. The minimum detection limit of the method was 0.1 mM/l and sensitivity of the sensor was 1.18 μA/mM/l lactate. A biosensor with improved performance was developed by Luo et al. [235] through the immobilization of HRP onto electropolymerized PANI films doped with CNTs. The effects of electropolymerization cycle and CNT concentration on the response of the biosensor toward H_2O_2 were investigated. It was found that the application of CNTs in the biosensor system could increase the amount and stability of the immobilized enzyme, and greatly enhanced the biosensor response. Compared with the biosensor without CNTs, the proposed biosensor exhibited enhanced stability and approximately eight-fold sensitivity. A linear range from 0.2 to 19 μM for the detection of H_2O_2 was observed for the proposed biosensor, with a detection limit of 68 nM at a signal-to-noise ratio of 3 and a response time of less than 5 s.

1.8. Scope and objectives of the present investigation

1.8.1. Scope of the present investigation

Polyaniline synthesized by various methods exists in the conducting ES form. But the ES form is insoluble in common organic solvents. Hence it requires processing for further applications. Conducting polymers are mostly amorphous. So, due to enhanced carrier scattering in the bulk material, the conductivity is very less and thus the efficiency and stability of the device is very poor. Therefore, thin film or surface conducting configuration can be of great help in using those materials for electronic devices. Polyaniline thin films can be fabricated by plasma polymerization technique. The plasma polymerization of aniline monomer results in structures different from those obtained using conventional chemical and electrochemical synthesis methods. This is attributed mainly to the formation of oligomers and substitutions of benzene rings, which result in some $–NH_2$ groups remaining unreacted during the course of polymerization. The level of electrical conductivity is significantly lower than that achievable with chemically synthesized PANI. Thus preparation of conducting PANI thin film by some different method other than plasma polymerization is one area on which some contribution can be made.

Polyaniline based sensors have been used to detect NH_3, H_2, HCl, NO, NO_2, and H_2S in the gas phase. But volatile organic compounds (VOCs), e.g., farnesene, linalool, ocimene, isomeric hexenyl butyrates, 2-methyl butyrate, methyl salicylate, indole and Z-3-hexenyl acetate, etc., released by plants in the environment have not yet been detected using PANI based sensors. Mostly enzyme-based sensors are used to detect VOCs, which are expensive and complex. Thus application of conducting PANI composites for sensing VOCs is another niche area on which I have worked.

1.8.2. Objective

The objective of the present investigation is to synthesize and characterize conducting PANI and PANI-based composite for sensor applications.

1.8.3. Work plan

The following work plan was formulated keeping in view the above objective:

a) Synthesis and characterization of PANI
b) HCl doping of PANI by solution method
c) Iodine doping of PANI by thermal evaporation
d) Preparation and characterization of PANI composite with poly (vinyl alcohol) (PVA)
e) Studies on ammonia sensing by HCl doped PANI film and HCl doped PANI-PVA composite
f) Preparation and characterization of CSA doped PANI-PVA composite
g) Terpene sensing by CSA doped PANI-PVA composite

h) Preparation and characterization of poly (aniline-co-m-aminobenzoic acid) deposited on PVA

i) Ester sensing by poly (aniline-co-m-aminobenzoic acid) deposited on PVA.

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