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A Review: Conducting Polymers and Their Applications.

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ABSTRACT

During the past two decades, both fundamental and applied research in conducting polymers like polyaniline, polyacetylene polythiophene and polypyrrole has grown enormously. Conducting polymers are unique due to its ease of synthesis, environmental stability and simple doping/dedoping chemistry. polyaniline is one of the most studied conducting polymers of the past 50 years. The most common chemical synthesis of polyaniline is by oxidative polymerization with ammonium per sulfate as an oxidant. Conducting polymers owing to its ease of synthesis, remarkable environmental stability and high conductivity in the doped form has remained thoroughly studied due to their varied applications in fields like biological activity, drug release systems, rechargeable batteries and sensors.

Keywords: Doping, Effect on conductivity, conducting polymers, applications

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INTRODUCTION

Perhaps the first modern example of polymer science is Henri Braconnot's work in the 1830s. He and his coworkers developed derivatives of the natural polymer cellulose, producing new, semi-synthetic materials, such as celluloid and cellulose acetate. The term “polymer” was firstly coined by Berzelius. Friedrich Ludersdorf and Nathaniel Hayward discovered that the addition of sulfur to raw natural rubber (polyisoprene) helped in the prevention of material from becoming sticky. In 1844 Charles Goodyear received a U.S. patent for vulcanizing natural rubber with sulfur and heat. This process strengthened natural rubber and prevented it from melting with heat without losing flexibility and also important in formation of water proofed articles. It also facilitated practical manufacture of such rubberized materials. Vulcanized rubber represents the first commercially successful product of polymer research. The first synthetic polymer, a thermosetting phenol-formaldehyde resin called Bakelite [1] was prepared by Leo Baekeland. In spite of some significant advances in synthesis and characterization of polymers, a correct understanding of polymer molecular structure emerged in.

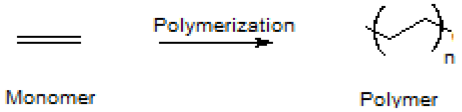
Despite significant advances in polymer synthesis, the molecular nature of polymers was not understood until the work of Hermann Staudinger in 1922 [2]. Prior to Staudinger's work, polymers were understood in terms of the association theory or aggregate theory, which originated with Thomas Graham in 1861. Graham proposed that cellulose and other polymers were "colloids", aggregates of molecules of small molecular mass connected by an unknown intermolecular force. Hermann Staudinger was the first to propose that polymers consisted of long chains of atoms held together by covalent bonds. It took over a decade for Staudinger's work to gain wide acceptance in the scientific community, work for which he was awarded the Nobel Prize in 1953.

The World War II era marked the emergence of a strong commercial polymer industry. The limited or restricted supply of natural materials such as silk and latex necessitated the increased production of synthetic substitutes, such as nylon [3] and synthetic rubber [4]. In the intervening years, the development of advanced polymers such as Kevlar and Teflon have continued to fuel a strong and growing polymer industry.

The growth in industrial applications was mirrored by the establishment of strong academic programms and research institutes. In 1946, Herman Mark established the Polymer Research Institute at Brooklyn Polytechnic, the first research facility in the United States dedicated to polymer research. Mark is also recognized as a pioneer in establishing curriculum and pedagogy for the field of polymer science. In 1950, the POLY division of the American Chemical Society was formed, and has since grown to the second-largest division in this association with nearly 8,000 members.

Synthetic polymer materials such as nylon, polyethylene, teflon and silicone have formed the basis for a further development in polymer industry and there was significant development in rational polymer synthesis [5]. Most commercially important polymers today are entirely synthetic in nature and produced on large scale. Synthetic polymers find applications in nearly all industries and area of life [6]. Polymers are widely used as adhesives and lubricants, as well as structural components for products ranging from children's toys to aircraft [7]. These have been employed in a variety of biomedical applications ranging from implantable devices to controlled drug delivery [8]. Polymers such as poly (methyl methacrylate) find application as photo resistivity materials used in semiconductor manufacturing and low dielectrics for use in high performance microprocessors [9]. Recently, polymers have been employed as flexible substrates in the development of organic light emitting diodes for electronic display [10]; lithium – ion polymer batteries are useful in laptop, mobile etc [11]. In early 1990s, new electroactive polymeric (EAP) materials have been found to be highly attractive for biomimetic applications such as biologically inspired intelligent robots.

Interlinking of many units has given the polymer its name, poly meaning 'many' and mer meaning 'part' (in Greek). Polymers are complex and giant molecules and are different from low molecular weight compounds. These big molecules or 'macro-molecules' are made of much smaller molecules [12]. The small molecules, which combine to form a big molecule, can be one or more chemical compounds. The individual small molecules from which the polymer is formed are known as monomer (meaning, single part) and the process by which polymer is formed are known as 'polymerisation' [13, 14].



The macromolecule is a synonym for a high molecular weight polymer whereas the lower molecular weight products with relatively small number of repeating units in the molecular structure should preferably be called oligomers (Greek Oligo = few), just to distinguish them from polymers [15].

The polymeric materials may be of hard and tough nature, e. g., plastic or may be elastomers of good strength and elongation. These may also be in the form of fibers and resins possessing variety of applications [16]. Depending on the effect of heat they may be of thermosetting and thermoplastics [17].

When only one species of monomer is used to build a macromolecule the product is called as a homopolymer [18]. A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species, which commonly used to describe polymers which contain two or more different types of mer or repeating units [19].

Polymerization process

There are two fundamental polymerization mechanisms. Classically, these have been differentiated as addition polymerization and condensation polymerization [20]. In the addition process, no by product is formed, whereas in condensation process, a low molecular weight by product (e.g., HCl, H_2O etc.). Addition polymerization takes place via free radical mechanism involving various steps like chain initiations, chain propagation and chain termination [21, 22].

Free radical polymerization [23] is carried out by four different processes e.g. bulk or mass polymerization, solution polymerization, suspension polymerization and emulsion polymerization. Bulk and solution polymerization are homogeneous processes but some of these homogeneous systems become heterogeneous with progress of polymerization due to the polymer formed being insoluble in its monomer (bulk polymerization) or in solvent used to dilute the monomer (solution polymerization) [24]. Suspension and emulsion polymerization are essentially heterogeneous type containing a large proportion of solvent (H_2O) acting as dispersion medium for the immiscible liquid monomer [25].

Most of the polymers with heteroatoms (O, N, S) in the chain are produced by condensation or step wise polymerization reactions. It includes esterification, amidation, urethane formation, aromatic substitution etc. Stepwise polymerization of suitable monomers can produce polyurea, polyurethane and polyimide films [26, 27].

Doping of Polymers

Conductive polymers generally exhibit poor electrical conductivity ($\sigma \leq 10^{-12}$ S/cm) in the virgin state and behave as insulators. These virgin polymers need to be treated with a suitable oxidizing or reducing agents to remarkably enhance their conductivities to the metallic region. This phenomenon has been termed as “doping”. Doping can be simply regarded as the insertion or ejection of electrons. Doping processes result in dramatic changes in the electronic, electrical, magnetic, optical and structural properties of the polymers [28]. Doping of polymeric semiconductors is different from that in inorganic or conventional semiconductors.

The inorganic semiconductors have three dimensional crystal lattice and on incorporation of specific dopant, n-type or p-type in ppm level, the lattice becomes only highly distorted [29]. The dopant is distributed along specific crystal orientations in specific sites on a repetitive basis. Whereas, doping of conducting polymer involves random dispersion or aggregation of dopants in molar concentrations in the disordered structure of entangled chains and fibrils. The dopant concentration may be as high as 50%. Also incorporation of the dopant molecules in the quasi one dimensional polymer systems considerably disturbs the chain order leading to reorganization of the polymer. Doping process is reversible and it produces the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counterions which stabilize the doped state, may be carried out chemically or electrochemically [30].

Doping of inorganic semiconductors generate either holes in the valence band or electrons in the conduction band. On the other hand, doping of polymer leads to the formation of conjugation defects, viz. solitons, polarons or bipolarons in the polymer chain. The ultimate conductivity in polymeric semiconductors depend on many factors, viz. nature and concentration of dopants, homogeneity of doping, carrier mobility, crystallinity and morphology of polymers [31]. By controllably adjusting the doping level, conductivity anywhere between that of the non-doped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained. In the doped state, the backbone of a conducting polymer consists of a delocalized system. In the undoped state, the polymer may have a conjugated backbone such as in trans- (CH)x which is retained in a modified form after doping, or it may have a nonconjugated backbone, as in polyaniline (leucoemeraldine base form), which becomes truly conjugated only after p-doping, or a nonconjugated structure as in the emeraldine base form of polyaniline which becomes conjugated only after protonic acid doping [32].

Different types of doping

The expression doping is ambiguous and refers to an uptake into pure material of some other material. This uptake may be diffusion of dopants in to the fibers, a chemical reaction with internal or surface chains or simple adsorption on the surface. Doping is accomplished by chemical methods of direct exposure of the conjugated polymer to a charge transfer agent in the gas or solution phase, or by electrochemical oxidation or reduction. Doping of polymers may be carried out by the following methods.

Redox doping

Redox doping is the most common method of doping. This is also known as oxidative doping and accomplished by removing pi electrons from the conjugated pi electrons system. Polyaniline undergoes p- and/ or n- redox doping by chemical and/ or electrochemical processes during which the number of electrons associated with the polymer backbone changes. p-Doing is accompanied by partial oxidation of the backbone of the polymer. It was first discovered by treating trans- (CH)x with an oxidizing agents such as iodine. p-Doping can also be done by electrochemical anodic oxidation by immersing a trans-(CH)x film in a solution of $LiClO_4$ and attaching it to the positive terminal of a DC power source, the negative terminal being attached to an electrode also immersed in the solution. n-Doping, i.e. partial reduction of the backbone system of an organic polymer, was also discovered using trans-(CH)x by treating it with a reducing agents such as sodium naphthalide [33].

Charge injection doping

Charge injection doping is most conveniently carried out using a metal/insulator/semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator.

Using a field-effect transistor (FET) geometry charge carriers can be injected into the band gap of conjugated polymers [*e.g.* polyacetylene, poly(3-hexylthiophene), P3HT] by applying an appropriate potential on the metal/insulator/polymer multilayer structure [34]. The charge-injection doping does not generate counter ions, allowing a systematic study of the electrical properties as a function of the charge carrier density with a minimized distortion of the material structure.

Non redox doping

Although oxidative doping is available for polyaniline, a more common method of producing doped polyaniline is known as acid- doping (or proton doping). This type of doping differs from redox doping in that the number of electrons associated with the polymer backbone does not change during the doping process [35]. As like the oxidative doping process, doped polyaniline may be produced in one step. The presence of the acid results in the protonation of nitrogen atoms. Once protonated, the polymer chain is now positively charged, and has associated counter- anions. The degree of protonation depends on the oxidation state of the polymer and the pH of the acid solution. The energy levels are rearranged during doping. The emeraldine base form of polyaniline was the first example of the doping of an organic polymer to a highly conductive regime by non redox type doping [36].

Neutral (or undoped) polyaniline exhibits conductivity of the order of 10-10 S/cm; as with oxidative doping, protonic or acid doping can also result in a significant increase in conductivity [37].

Types of doping agents

Dopants may be classified as:

- Neutral dopants: I_2, Br_2, AsF_2, Na, K, $FeCl_3$ etc.
- Ionic dopants: $LiClO_4$, CF_3SO_3Na, BuNClO etc.
- Organic dopants: CF_3COOH, CF_3SO_3Na, p-$CH_3C_6H_4SO_3H$
- Polymeric dopants: Polyvinylsilane (PVS), Polyphenylene sulfide (PPS) etc.

Neutral dopants are converted into negative or positive ions with or without chemical modifications during the process of doping. Ionic dopants are either oxidized or reduced by an electron transfer with the polymer and the counter ion remains with the polymer to make the system neutral. Organic dopants are anionic dopants, generally incorporated into polymers from aqueous electrolytes during anodic deposition of the polymer. Polymeric dopant may applied in polymer in to three different ways: in solid state, in solution and in gel state. In solid state, the conducting form was achieved only through a novel thermal doping method with the increase in temperature and pressure. In solution, the doping process was shown to be dependent on the nature of the solution and also on the molecular weight of the polymer. In the gel form of polymer, a polymeric dopant with a surprising low degree of sulfonation was found to be successful in the doping process.

Doping techniques

Doping in polymers can be carried out by following methods:

- Gaseous doping
- Solution doping
- Electrochemical doping
- Self doping
- Radiation induced doping
- Ion exchange doping

Gaseous, solution and electrochemical doping methods are widely used because of the convenience in carrying out and of low cost. In gaseous doping process, the polymers are exposed to the vapor of the dopant under vacuum. The level of dopant concentrations in polymers may be easily controlled by temperature, vacuum and time of exposure. Solution doping involves the use of a solvent in which all the products of doping are soluble [38]. Polar solvents such as dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), tetrahydrofuran and nitro methane are used as solvents. The polymer is treated with dopant solutions. In the electrochemical doping technique simultaneous polymerization and doping generally occurs. But sometimes this method is used for doping for polymers obtained by other methods also. In this process only ionic type dopants are used as the electrolyte in polar solvents [39].

Effect of doping on conductivity

The doping process involves transfer of the charge to or from the bonding system of the conjugated polymer, leaving the system essentially intact and hence the structural identity of an individual chain preserved. However, vibrational, electronic and other properties of the polymer are strongly altered upon doping as well as its supramolecular structure. The most spectacular result of the doping is the increase of the polymer conductivity over several orders of magnitude. In some cases conjugated polymers reach the conductivity of metals with a negative temperature coefficient which is characteristic of metallic behavior [40]. Doping with acceptor or donor molecules causes a partial oxidation (p-doping) or reduction (n-doping) of the polymer molecule, respectively. As a result positively or negatively charged quasi-particles are created presumably polarons in the first step of doping. When doping proceeds, reaction among polarons take place, leading to energetically more favorable quasi-particles, i.e, a pair of charged solitons (bipolarons) in materials with a degenerate ground state [41]. Thus due to the changes in the environment of the chains, disorders are created from doping. At low dopant concentration, the dopant molecules occupy random positions between the chains. The effect of electronic properties by their coulomb potential and hybridization with the polymer p-orbitals. As polarons produced has long lifetime, they are treated as quasi-particles. Polarons have low mobility, which results in obtaining moderate conductivity at low doping concentration [42].

As the doping level is increased, the concentration of polarons go up and they become crowded together, close enough to form bipolaron. At this point in the doping process, conductivity undergoes a marked increase. Once the radical components of the polarons have combined to form bonds, the remaining charges achieve high mobility along the chain. Example showing formation of polarons –bipolarons in polypyrrole chain is given in the Figure 1.

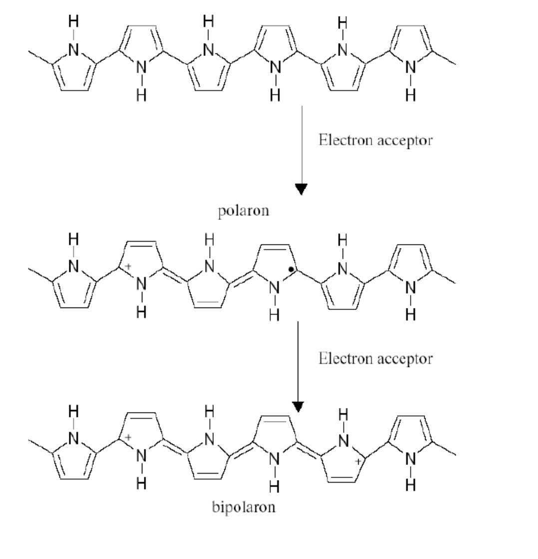


Figure 1: Formation of polaron- bipolaron in a PPy chain

Factors affecting conductivity of polymers

It is only the doping which makes most of the conjugated polymers conducting from their insulating state to semiconducting or conducting. Although the charged species are incorporated by doping, the electrical conductivity is not ionic but electronic. Electronic conductivity of conducting polymers depend upon numerous factors. Significant among these are:

- Nature or chemical reactivity of the dopant
- Process of doping
- Doping level
- Method and condition of polymer synthesis

Chemical reactivity of the dopant is of prime importance to obtain a conducting polymer. Not all dopants are equally capable of oxidizing a polymer chain. Iodine is a dopant for increasing the electrical conductivity of polyacetylene by thirteen orders of magnitude but is too weak to oxidize polypyrrole or polyaniline where as HCl is used to oxidize polyaniline. The electrical conductivity of polyaniline hydrochloride was observed is 4.4 + 1.7 S cm–1. Doping conditions also play an important role. Electrical conductivity usually increases with the doping level due to increase in charge carriers concentration. Rapid increase in mobility of the charge carriers may be responsible for this high rate of increase in conductivity. Development of quantitative model for conduction is hampered by the fact that there are at least three elements contributing to the carrier mobility:

- Single chain or intramolecular transport
- Interchain transport
- Interparticle contact

Electrical conductivity is very much dependent on the method of polymer synthesis, purification of the polymer, physical treatment of the polymer etc. in addition to the nature of the dopants and the process of doping.

Conducting Polymers

Discovery of polymers has given a new dimension to the present era. Polymers known so far as a class of heat sensitive [43], flexible [44] and electrically insulating amorphous materials [45]. Polymers are generally known for their insulating property because of covalent bond present in saturated carbon compounds [46]. Since desirable properties can be conveniently attained by tailoring the polymer structure and also by incorporating additives; scientists have been enthusiastic to explore the possibility of transforming insulating polymers into conducting or semiconducting materials envisaging such special characteristics like low density, ease of fabrication, flexibility of design, low energy and labour requirements for fabrication and processing [47].

In the mid 1970s, the first polymer capable of conducting electricity was reported by Shirakawa to be polyacetylene [48]. The subsequent discovery by Alan Heeger and Alan MacDiarmid that the polymer would undergo an increase in conductivity of twelve orders of magnitude by oxidative doping quickly reverberated around the polymer and electrochemistry communities and an intensive search for other conducting polymers soon followed [49].

In 1976, Alan MacDiarmid, Hideki Shirakawa, and Alan Heeger, along with a group of young students found that conductivity of polyacetylene increased by up to six orders of magnitude when reacted with iodine [50] (from 10^{-4} S/cm to 10^{2} S/cm); this phenomenon, known as doping, is as a result of charge carriers. In addition, it has been discovered that varying the level of doping yielded polymers exhibiting wide range of electrical properties, from insulator or semi-conductor to metal [51]. Although polyacetylene is not stable in air, the fact that it could become conductive upon doping led to further experimentation with other known conjugated polymers [52]. Since 1976, a number of conducting polymers, namely polypyrrole, polythiophene and polyaniline, have become the focus of much study [53]. The importance of conducting polymers is exemplified by the awarding of the 2000 Nobel Prize in Chemistry to MacDiarmid [54], Shirakawa [55] and Heeger [56] for the discovery and development of conducting polymers. This was particularly exciting because it created a new field of research and a number of opportunities on the boundary between chemistry and condensed-matter physics. As the commonly known polymers, in general, are saturated and so are insulators, these were viewed as uninteresting from the point of view of electronic materials [57]. Conducting polymers are polymers containing an extended pi conjugated system, made up of overlap of singly occupied p - orbitals in the backbone of the polymer chain [58]. Although conducting polymers possess a relatively large number of delocalized pi electrons, a fairly large energy gap exists between the valence band and the conduction band (greater than 1 eV), thus these polymers are considered to be semi-conducting. These polymers must be doped (usually meaning altering the number of pi electrons) in order to render the polymers truly conducting.

In conjugated polymers the electronic configuration is fundamentally different, where the chemical bonding leads to one unpaired electron per carbon atom. The orbitals (having one electron in each) on successive carbon atoms along the backbone overlap, leading to electron delocalization along the backbone of the polymer [59]. This electron delocalization provides the highway for charge mobility along the backbone of the polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry, i.e. the number and kind of atoms within the repeat unit, with the result that such polymers can exhibit semiconducting or even metallic properties.

Electrically conducting polymers are designated as the fourth generation of polymeric materials. Electrically conducting polymers are extensively conjugated in nature and therefore, it is believed that they possess a spatially delocalized band-like electronic structure [60]. These bands stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of the band structure of solid-state semiconductors. It is generally agreed that the mechanism of conductivity in these polymers is based on the motion of charged defects within the conjugated framework [61]. The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the polymer respectively. The simplest possible form of conducting polymer is of course the arche type polyacetylene (CH)x. Polyacetylene itself is too unstable to be of any practical value, its structure constitutes the core of all conjugated polymers. Little *et al*. [62] had proposed that properly substituted polyacetylene molecule would exhibit superconductivity at room temperature. The electrical conductivity of the order of 10^{-5} S/cm for trans polyacetylene sample has been reported [63]. Polyacetylene could attain high levels of electronic conductivity when oxidized by suitable reagents initiated a significant research [64]. Since late seventies, a large number of polymers have been added to the list of conducting polymers such as polypyrrole [65], polythiophene [66], polyparaphenylene [67], polyphenylene sulphide [68], polyaniline [69], polyphenylene vinylene etc [70]. Doping the polymers creates new states (donor or acceptor states), which exist within the band gap [71] and are energetically accessible to the pi electrons, resulting in significant increase in conductivity [72]. In fact, the conductivity of doped polymers may be up to ten orders of magnitude greater than that of the neutral (undoped) polymers [73]. The concept of conductivity of conjugated polymers was quickly broadened from polyacetylene [74] to include a conjugated hydrocarbon and aromatic heterocyclic polymers, such as poly (p-phenylene) [75] and polythiophene [76]. The conductivity of various doped and undoped polymers, some common semiconductors and metals are presented in Table 1.

Table 1

MATERIAL	CONDUCTIVITY (S/cm)
Gold, Silver, Copper	~10^{6}
Doped trans- polyacetylene	~10^{5}
Doped polyaniline	~10^{1}
Germanium	~10^{-2}
Silicon	~10^{-6}
Undoped trans- polyacetylene	~10^{-6}
Undoped polyaniline	~10^{-10}
Glass	~10^{-10}
Quartz	~10^{-12}
H2SO4 doped polyaniline	~10^{-8}
Dodecylbenzene sulfonic acid-doped Polyaniline	~10^{-8}

As the conducting polymers may be doped to various degrees, there is an element of control in doping level, hence the conductivity. This ability to tailor the polymer's electrical properties exemplifies the versatility of conducting polymers. Conductivity of conductive polymers compared to those of other materials [77], from quartz (insulator) to copper (conductor) is shown in Figure 2.

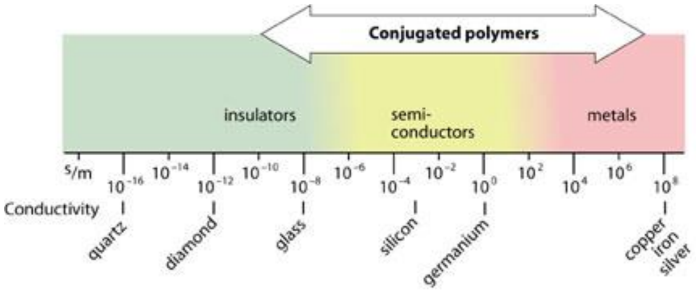


Figure 2: Conductivity of different materials

Types of Conducting Polymers

Conducting polymers can be classified in to different types on the basis of conduction mechanism that renders electrical conductivity to polymers.

- Conducting polymer composites
- Organometallic polymeric conductors
- Polymeric charge transfer complexes
- Inherently conducting polymers.

A brief description of the first three type of conducting materials have been given here. However, the present study deals with the inherently conducting polymers, therefore, a detailed discussion have been done for this type of conducting material.

Conducting Polymer Composites

Conducting polymer composites are mixture or blends of conductive particles and polymers. Various conductors have been used in different forms together with large number of conducting and engineering plastic [78]. Various conductive fillers have been tried such as carbon black, graphite flakes, fibers, metal powders etc. The electrical conductivity of the compound is decided by the volume fraction of the filler. A transition from insulating to non-insulating behavior is generally observed when volume fraction of conductive filler in the mixture reaches a threshold of about 25%. The various polymers, which have been used as major matrix, are typically polypropylene (PP), nylon, and polyvinyl chloride (PVC) etc [79].

Organometallic Polymeric Conductors

This type of conducting materials is obtained by adding organometallic groups to polymer molecules. In this type of materials, the d- orbital of metal may overlap orbitals of the organic structure and thereby increases the electron delocalization [80]. The d - orbital may also bridge adjacent layers in crystalline polymers to give conducting property to it. Metallophthalocyanines and their polymers fall in this class of polymeric material. These polymers have extensively conjugated structures. The bridge transition metal complexes form one of the stable systems exhibiting intrinsic electrical conductivities, without external oxidative doping. Polyferrocenylene is also an example of this type of polymer. These materials possess strong potential for future applications such as molecular wires, antistatic foils and in fibers [81].

Polymeric Charge Transfer Complexes

Polymeric charge transfer complexes (PCTC) are formed when acceptor like molecules are added to the insulating polymers [82]. There are many charge transfer complexes reported in the literature, e.g., CTC of tetrathaifulvalene (TTF) with bromine, chlorine etc. is a good conductor [83]. The reason for high conductivity in polymeric charge transfer complexes and radical ion salts are still somewhat obscure [84]. It is likely that in polymeric materials, the donor–acceptor interaction promotes orbital overlap, which contributes to alter molecular arrangements and enhanced electron delocalization [85].

Inherently Conducting Polymers

Research in the field of inherently conducting polymer started nearly three decades ago when Shirakawa and his group found drastic increase in the electrical conductivity of polyacetylene films when exposed to iodine vapor. The highest crystalline variety of the polyacetylene showed electrical conductivity of the order of 10^{-5} S / cm and was in all possibility the trans-form of polyacetylene [86]. Leading on from this breakthrough, many small conjugated molecules have been polymerized, producing conjugated polymers, which were either insulating or semiconducting in the oxidized or doped state. The electronic properties of conjugated polymers are due to the presence of electrons. The conjugated polymers are studied as the intrinsically conductive polymers. The conductivity in such polymers arises due to a special type of metallic bonding in which valence electrons are completely delocalized and move almost freely through the crystal lattice. This delocalization of electrons may occur through the interaction of π-bonded electrons in a highly conjugated chain or by a similar interaction of π-electrons with nonbonded electrons of electron rich hetero atoms (e.g., S, N etc.) in the backbone. For this the molecular structure of the backbone should be planar. There should be no torsion at the bonds, which would decrease the delocalization of the electron system [87]. Some examples of conjugated polymers are shown in Figure 3.

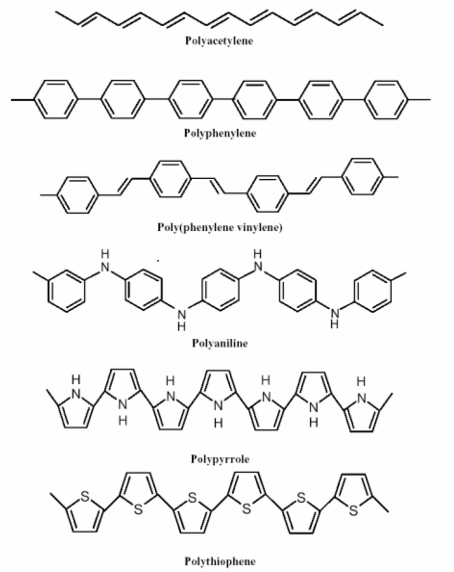


Figure 3: Different Conducting polymers

Polyacetylene, polythiophene, polypyrrole, poly (p- phynlene vinylene) are commonly used conducting polymers. These polymers are costly, less stable mechanically after doping and difficult in processing. Therefore, here polyaniline (PANI) is selected for study because polyaniline owing to its ease of synthesis, remarkable environmental stability and high conductivity in the doped form, has remained one of the most thoroughly studied conducting polymers.

Polyaniline (PANI)

The monomer aniline was obtained first time in 1826, from the pyrolytic distillation of indigo and was called “Krystallin” because it produced well formed crystalline salts with sulfuric and phosphoric acid. In 1840, Fritzsche also obtained a colorless oil from indigo, called it aniline from the Spanish word añil (indigo), and oxidized it to polyaniline (PANI). From the early 20th century on, occasional reports about the structure of polyaniline appeared in the literature. In recent years, the study of polyaniline exploded and currently a vast literature on the synthesis, properties, and applications of polyaniline exists.

Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. Since the early 1980s, polyaniline has captured the intense attention of the scientific community.

Amongst the family of conducting polymers and organic semiconductors, polyaniline is unique due to its ease of synthesis, environmental stability and simple doping/dedoping chemistry. Although the synthetic methods to produce polyaniline are quite simple, its mechanism of polymerization and the exact nature of its oxidation chemistry are quite complex. Because of its rich chemistry, polyaniline is one of the most studied conducting polymers of the past 50 years. Polymerized from the aniline monomer, polyaniline can be found in one of three idealized oxidation states [88]:

- **Leucoemeraldine** – white/clear and colorless
- **Emeraldine** – green for the emeraldine salt, blue for the emeraldine base
- **Pernigraniline** – blue/violet

Leucoemeraldine is the fully reduced state of polyaniline. Pernigraniline is the fully oxidized state with imine links instead of amine links. The emeraldine form of polyaniline, often referred to as emeraldine base (EB) is neutral, if doped it is called emeraldine salt (ES), with the imine nitrogens protonated by an acid. Emeraldine base is regarded as the most useful form of polyaniline due to its high stability at room temperature and the fact that, upon doping with acid, the resulting emeraldine salt form of polyaniline is electrically conducting [89]. Leucoemeraldine and pernigraniline are poor conductors, even when doped with an acid.

The color change associated with polyaniline in different oxidation states can be used in sensors and electrochromic devices [90]. Though color is useful, the best method for making a polyaniline sensor is arguably to take advantage of the dramatic conductivity changes between the different oxidation states or doping levels [91].

The most common synthesis of polyaniline is by oxidative polymerization of aniline. Aniline has been dissolved in HCl or other acids (dopant) and ammonium persulphate (oxidant) has been added drop – wise and reaction has been continued for few hours.

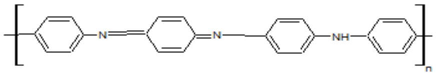


Figure 4: Structure of Polyaniline emeraldine base

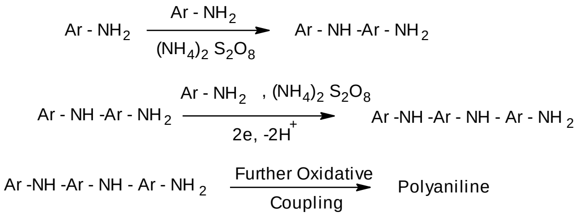
Using special polymerization procedures and dopants, the polyaniline powder can be recovered after polymerization and can be made dispersible and hence useful for practical applications. A three stage model for the formation of emeraldine base has been proposed. In the first stage of the reaction the pernigraniline salt (PS) oxidation state is formed. In the second stage pernigraniline is reduced to the emeraldine salt as aniline monomer gets oxidized to the radical cation. In the third stage this radical cation couples with ES salt [92].

In the doped emeraldine salt form, polyaniline is electrically conductive, which makes it suitable for e.g. manufacture of electrically conducting yarns, antistatic coatings, electromagnetic shielding and flexible electrodes [93]. Another important property is its position in the electrochemical series. Polyaniline is more noble than copper and slightly less noble than silver which is the basis for its broad use in printed circuit board manufacturing (as a final finish) and in corrosion protection [94]. Polyaniline is typically produced in the form of long chain polymer aggregates, surfactant (or dopant) stabilized nanoparticle dispersions, or stabilizer-free nanofiber dispersions depending on the synthetic route. Surfactant or dopant stabilized polyaniline dispersions have been available for commercial sale since the late 1990s [95]. The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties of PANI, allowing its potential applications in various fields. It is an environmentally stable and highly tunable conducting polymer, which can be produced as bulk powder, cast films, or fibers. Due to its low- cost and large- scale production, it has various applications. Much of the structural characterization of polyaniline has taken place in the last 20 years or so, and is fairly well established, although the large number of papers published in the last five years would indicate that polyaniline is still under much scrutiny.

Polyaniline is a typical phenylene based polymer having a chemically flexible –NH group in a polymer chain flanked on either side by a phenylene ring. It can also be defined as the simple 1, 4- coupling product of monomeric aniline molecule. The protonation and deprotonation and various other physico-chemical properties of polyaniline is due to the presence of the –NH- group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions. There are several reports of polyaniline found in the literature over the decades about the structure and constitutional aspect of aniline polymerization [96]. Surville *et al.* [97] reported the proton exchange and redox properties with the influence of water on the conductivity of polyaniline. Polyaniline can be synthesized by both chemical and electrochemical oxidative polymerization. Structure of the polymer was described in terms of degree of order, for example crystalline, semicrystalline, or amorphous [98]. Bulk synthesis of polyaniline nanofibers has led to a highly scalable and commercially applicable form of polyaniline that has been researched extensively since their discovery in 2002 [99]. As synthesis of polyaniline nanostructures is facile and they have been prepared by various methods, polyaniline is an important nanomaterial [100].

Synthesis of Polyaniline

The most common synthesis of polyaniline involves oxidative polymerization, in which the polymerization and doping occurs concurrently, and may be accomplished either electrochemically or chemically. Electrochemical methods tend to have lower yields than that obtained by chemical methods [101]. Synthesis of polyaniline by chemical oxidative route involves the use of either hydrochloric or sulfuric acid in the presence of ammonium persulphate as the oxidizing agent in the aqueous medium. The principal function of the oxidant is to withdraw a proton from an aniline molecule, without forming a strong co-ordination bond either with the substrate / intermediate or with the final product. However, smaller quantity of oxidant is used to avoid oxidative degradation of the polymer formed. Letheby [102] has reported that the propagation of the polymer chain proceeds by a redox process between the growing chain (as an oxidant) and aniline (as a reducer) with addition of monomer to the chain end. The high concentration of a strong oxidant, $(NH_4)_2S_2O_8$, at the initial stage of the polymerization enables the fast oxidation of oligo and polyaniline, as well as their existence in the oxidized form (Scheme 1).



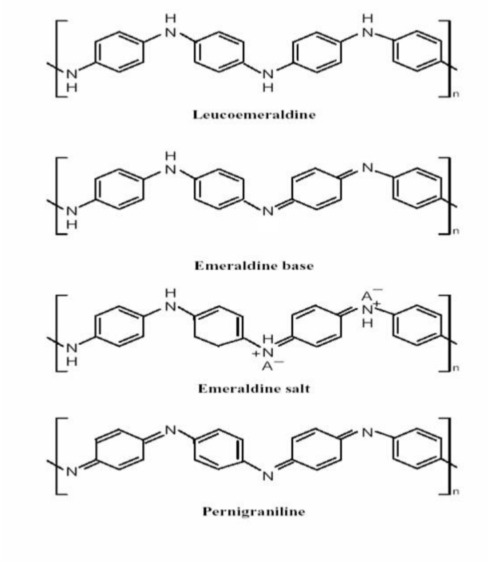
Scheme 1: Formation of polyaniline

Ayad and Whdan [103] studied about the chemical oxidation of aniline with ferric chloride, $FeCl_3{\cdot}6H_2O$ in the HCl aqueous solutions to form polyaniline powder. Qi *et al.* [104] studied about synthesis of PANI/ γ-Al_2O_3 composite by using aniline, HCl, ammonium persulphate and γ-Al_2O_3. Cortés and Sierra [105] obtained maximum yield of polyaniline by carrying out polymerization of aniline at optimum conditions. The temperature, concentration of dodecylbenzensulfonic acid (dopant), concentration of ammonium persulphate (oxidant) and stirring rate were 25°C, 27 mmol, 11.5 mmol and 500 rpm, respectively.

Sarifah *et al.* [106] reported synthesis of camphor sulfonic acid (CSA)-doped polyaniline (PANI) via oxidative polymerization of aniline with ammonium persulfate as the oxidant at 5˚C. CSA has been used as doping agent in order to improve the solubility of the polymer.

Kiran *et al.* [107] studied about aqueous binary dopant ($ZrOCl_2$/AgI) in different ratios such as 1:1, 1:2 and 2:1 (w/w) for chemical doping to enhance the conductivity of synthesized polyaniline (PANI). The doping of polyaniline is carried out using tetrahydrofuran as a solvent. Vivekanandan *et al.* [108] reported the electrochemical and chemical oxidative synthesis of polyaniline using $K_2Cr_2O_7$ as an oxidant and H_2SO_4 as dopant. The conductivity of electro chemically synthesized polyaniline doped with H_2SO_4 at various voltages have been compared with polyaniline synthesized by oxidative polymerization.

Chauhan *et al.* [109] reported that polyaniline-emeraldine bases may be synthesized in aqueous hydrochloric acid HCl / LiCl or CF_3COOH medium by chemical oxidative polymerization with $(NH_4)_2S_2O_8$ as an oxidant. Polymerization of aniline was carried out in a reaction vessel in temperature range from -15°C to 5°C. Aniline was dissolved in HCl / LiCl or CF_3COOH and ammonium persulphate was added dropwise. Then the reaction was continued for 2 hours. The solution was filtered by vacuum filtration and the precipitate was washed with acetone to remove the unreacted aniline. PANI synthesized by this method was formed in its protonated state and it is dark green in color. The precipitate was dried, washed and allowed to equilibrate with an appropriate amount of ammonium hydroxide overnight. This process converted the PANI-ES to PANI-EB form (Scheme 2).



Scheme 2: Different oxidation states of polyaniline

Grafted Polyanilines

In the past few years, aromatic conducting polymers such as polypyrrole, polythiophene or polyaniline have received considerable attention owing to their good electrical, optical and electrochemical properties. However, due to the stiffness of its backbone, polyaniline is almost insoluble in common organic solvents. Consequently, its post synthesis processability is quite difficult. In most cases, the solubilization of a polymer can be achieved through functionalization of starting material with a suitable side chain prior to polymerization. Although polyaniline shows good conductivity (1.2 S cm^{-1}), but it is insoluble in common organic solvents. On the other hand, poly(halogensubstituted aniline)s are soluble in some organic solvents like N-methylpyrrolidinone, dimethylformamide, tetrahydrofuran, dimethylsulfoxide and acetic acid upto 80% v/v, but their conductivity remain low ($\sigma < 10^{-11}$ S cm^{-1}) [110]. Considering these data, the synthesis of a copolymer that combines the conductivity of polyaniline and the solubility of polyhalogenanilines would be of interest. Therefore, the copolymerization of aniline with halogenanilines should lead, upon proper adjustment of the copolymer composition, to a soluble and conducting or semiconducting material. Until recently, this strategy was used only by a few workers for the synthesis of a new aromatic conducting polymer. The chemical copolymerization of aniline and 2, 5-dibromoaniline or 2,6-dibromoaniline by oxidation with $K_2Cr_2O_7$ in H_2SO_4/acetonitrile medium has been carried out [111]. When substituted aniline fraction is increased in the copolymer, the electrical conductivity (σ) decreases; this effect is more important when 2,6-dibromoaniline is used. Thus, the conductivity can be controlled in a broad range, from 1.2 to 10^{-6}–10^{-11} S·cm^{-1} depending on the substituted aniline and the feed ratio. The relation between copolymer compositions and monomer feed molar ratios shows that the aniline is slightly more reactive than dibromoanilines during the copolymerization process. All the copolymers were shown to be more processable than polyaniline [112]. The PANI/Co_3O_4 composites have been synthesized by in situ polymerization in the presence of Co_3O_4 nanoparticles and HCl as the dopant [113].

Yue and Epstein [114] have synthesized self doped polyaniline through the reaction between an emeraldine base form of polyaniline and fuming sulfuric acid. The resulting polymer was a soluble type with ring-substituted sulfonic acid group and having a conductivity of about 0.1 Scm^{-1}. Increased solubility has been reported for alkyl- and alkoxy- substituted polyanilines [115].

A mucopolysaccharide, chitosan has been grafted with polyaniline through oxidative-radical copolymerization using ammonium persulfate in acidic medium [116]. The grafting conditions were extensively studied by varying grafting parameters. All the findings have been investigated and a plausible mechanism for the graft copolymerization has been proposed. Ch-g-PANI exhibited electrical conductivity, which increases with the extent of grafting. Its electrical conductivity is further influenced by pH and showed pH switching electrical conduction behavior when exposed to NH_3/HCl vapors. The application of conducting biomaterial such as Ch-g- PANI in the electronic devices especially for the fabrication of sensor devices would be attractive not only in terms of product cost and environmental safety but also from a materials science point of view [117].

Polyaniline coated conducting fabrics have been obtained by chemical oxidation of aniline by potassium peroxydisulfate on polyester fabrics. Two different acids have been employed to carry out the synthesis (HCl and H_2SO_4), obtaining the best results of conductivity with the latter one. The conducting fabrics have also shown electrochromic properties, changing its color from green yellowish to dark green. The durability of the coating has been evaluated by means of washing and rubbing fastness tests [118].

Conducting polyaniline/γ -Fe_2O_3 (PANI/FE) composites have been synthesized using an *in situ* deposition technique by placing fine-graded γ -Fe_2O_3 in a polymerization mixture of aniline. It has been observed that the conductivity increases up to a composition of 20 wt % of γ -Fe_2O_3 in polyaniline and decreases thereafter. The initial increase in conductivity is attributed to the extended chain length of polyaniline, where polarons possess sufficient energy to hop between favourable sites. Beyond 20 wt % of γ -Fe_2O_3 in polyaniline, the blocking of charge carrier hop occurs, reducing conductivity values. The magnetic properties such as hysteresis characteristics and normalized a.c. susceptibility have also been measured, which show a strong dependence on content of γ -Fe2O3 in polyaniline. Because of superparamagnetic behaviour of these composites, they may find extensive technological applications, especially for absorbing and shielding applications in microwave frequencies [119].

Polyaniline (PANI), N-methyl- and N-ethyl-PANI, 2- and 3-ethyl-PANI as well as 2,6-dimethyl- and 3,5-dimethyl-PANI have been synthesized using ammonium persulfate as catalyst. The chemical structures of the N-methyl- and N-ethyl-PANI have been found to contain quinoneimine units along the polymer chain. In the doped state the N-alkyl-PANIs show the polaronic band transition in the near infra red region of the spectrum, at longer wavelength than doped unsubstituted PANI [120].

Jayanna *et al.* [121] have reported synthesis of polyaniline/$ZnFe_2O_4$ nanocomposites by using a simple and inexpensive one-step in-situ polymerization method in the presence of $ZnFe_2O_4$ nanoparticles. The a.c. conductivity of polyaniline/$ZnFe_2O_4$ nanocomposites has been found to be 0.695 Scm^{-1} at room temperature.

Zhao *et al.* [122] studied about a functional structure made up of $Mn_{0.5}Zn_{0.5}Fe_2O_4$-polyaniline nanocomposites with high dielectric absorbing properties and electromagnetic shielding effectiveness at low frequencies. It has been successfully fabricated through a facile *in situ* emulsion polymerization. Polyaniline (PANI) has been doped with hydrochloric acid to improve its electrical properties and interactions with ferrite nanoparticles. The electrostatic & paramagnetic force and hydrogen bonding strongly bonded or assembled ferrite nanoparticles on the polyaniline surface and improved its thermal stability. The ferrite-grafted polyaniline nanostructures have been demonstrated as a promising functional material for absorbing the electromagnetic microwaves because of a large amount of dipole polarizations in the polymer backbone and at the interfaces of the ferrite nanoparticles and polyaniline nanofibers.

The utilization of conducting polyaniline emeraldine salt (PANI-ES) and intrinsic leucoemeraldine polyaniline (PANI-LEB) for the synthesis of diglycidyl ether bisphenol A - grafted PANI (DGEBA–g–PANI) via anionic copolymerization has been described by Rasid *et al.* [123]. Results obtained indicated that the graft copolymer exhibited higher electrical and thermal conductivities than that of the blend counterpart.

Polyaniline N-grafted with poly(ethyl acrylate) (PEA) has been synthesized by the grafting of bromo-terminated poly (ethyl acrylate) (PEA-Br) onto the leucoemeraldine form of PANI. PEA-Br has been synthesized by the atom transfer radical polymerization of ethyl acrylate in the presence of methyl-2-bromopropionate and copper(I) chloride/bipyridine as the initiator and catalyst systems, respectively. The leucoemeraldine form of PANI was deprotonated by butyl lithium and then reacted with PEA-Br to prepare PEA-g-PANI graft copolymers containing different amounts of PEA via an N-grafting reaction [124].

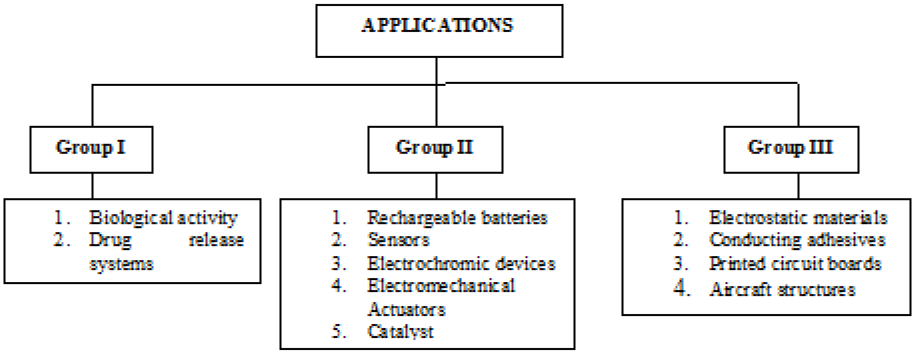
Kanzhu *et al.* [125] has been studied about the synthesis and characterization of poly(ethylene glycol)- grafted expanded graphite/polyaniline (PEG-grafted EG/PANI) as a novel ecofriendly composite material. EG as substrate prepared from expandable graphite has been firstly synthesized by in-situ polymerization at the presence of aniline (An) to obtain EG/PANI, and then graft polymerization with as-prepared PEG-grafted PANI (PEG-g-PANI) composite under no tough conditions.

Polyaniline containing benzo-12-crown-4 small cycle crown ether functional groups in side chains has been synthesized. It has been used to prepare a mixed electron-ion conductor by complexing with lithium salt and doping with dodecyl benzene sulphonic acid(DBSA). The conductivity of the mixed conductor has been tested, using the four-probe method, and its value is as high as 10^{-2}S/cm at room temperature.

Charge Carriers in Conducting Polymer

The mechanism of conduction and behavior of charge carriers in the conducting polymers have been explained using the concept of polarons and bipolarons. Polaron is an excitation that carries a single positive/ negative electron charge. A Bipolaron is a double charged excitation. An exciton is a neutral excited state, which in simplistic way, can be described as carrying a dipole. A radical cation that is partially delocalized over some polymer segment is called a polaron. When electron is removed from the top of the valence band of a conjugated polymer, a vacancy (hole or radical cation) is created that does not delocalize completely, only partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. The energy level associated with this radical cation represents a destabilized bonding orbital and thus has a higher energy than the energies in valence band. This rise is in energy is similar to the rise in energy that takes place after an electron is removed from a filling bonding molecular orbital [126]. If another electron is removed from the already oxidized polymer containing the polaron, than this electron could come from either a different segment of the polymer chain, which create an another independent polaron. Low doping levels give rise to polarons, whereas higher doping levels produce bipolarons. The two positive charges of the bipolaron are not independent, but act as a pair. Both polarons and bipolarons are mobile and can move along the polymer chain by the rearrangement of double and single bonds in the conjugated system that occurs in an electric field. If many bipolarons are formed, say as a result of high doping, their energy can start over lapping at the edges, which creates narrow bipolaron bands in the band gap [127].The energy spacing between the highest occupied and the lowest unoccupied bands is called band gap. The highest occupied band is called the valence band, and the lowest unoccupied band is the conduct ion band. Conducting polymers either have a zero energy band gap or a very low band gap. The band gap controls the electronic and optical properties of the conducting polymers. A reduction in the band gap increases the conductivity of the polymers [128].

Applications



Research shows that conducting polymers exhibit conductivity from the semiconducting range (~10-5 S/cm) right up to metallic conductivity (~10^4 S/cm). With this range of electrical conductivity and low density coupled with low cost polymeric conductor pose a serious challenge to the established inorganic semiconductor technology. There are mainly three groups of applications for organic conducting polymers which are briefly described as follows:

Group I

Biological activity

Polyaniline is a typical phenylene based polymer having a chemically flexible –NH- group in the polymer chain flanked on either side by phenylene ring. The protonation, deprotonation and various other physico-chemical properties of polyaniline due to the presence of this –NH- group.

Polyaniline is different from other conducting polymers in the three important aspects (i) Charge conjugation in polyaniline is not symmetric, that is, Fermi level and band gap are not formed in the centre of the band and hence, valence band and conjugation bands are quite asymmetric, (ii) Both carbon rings and nitrogen atoms are within the conjugation path; this conjugation differes from polypyrrole, whose hetero atoms do not contribute significantly to the π- bond formation and (iii) Electronic state of the polyaniline can be changed through vibration of either the number of electrons or number of protons. An electro active polymer, when oxidized or reduced, displays a significant change in intrinsic electrical conductivity e.g. polyaniline, polythiophene. These are also known as electroconductivve polymer (EP) / conducting electroactive polymer (CEP). The earliest reported application of conducting polymers (CPs) has been the use of free standing polymers as sensor devices. Chemical sensors are analytical devices that convert the chemical potential energy of a targated analyte into a proportionate measurable signal, usually electrical or optical.

There have been a number of reviews on CPs with regard to biomedical applications. The commercially available soluble CPs polyaniline (PANI) grafted to lignin, poly(anilinesulphonic acid) and polypyrrole (PPy) are effective scavengers of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical. This property may be particularly beneficial in tissues suffering from oxidative stress, where the ability to lower the excessive levels of reactive radical species is desirable. This free radical reducing ability of CPs is revealed by efficient scavenging of DPPH radicals, with two and four radicals scavenged per aniline or pyrrole monomer unit during the 30 min test period of the DPPH assay, indicating the potential for CPs to be effective antioxidants when present in biological medium [129 ,130]. The various vitamins and polyphenol free radical- scavenging antioxidants present in beverages, fruits and vegetables are currently of great interest, as these antioxidants may offer protection against various diseases, such as cardiovascular diseases and cancer [131].

The ES forms of the copolymers appear to be more effective than EB forms of the same copolymer. It appears that the presence of an acidic functional group (-COOH) in the polmer chain improves the antibacterial efficacy of the copolymer. Without being bound by theory, the acidic dopants on the molecular chains of copolymers may react with the bacteria (Or other relevant microbial organism) which result in their death. Alternatively, due to electrostatic adherence between copolymer molecules and the bacteria, which carry charges of different polarity, the walls of bacteria may break and the contents of bacteria become exposed or leak out, which cause the bacteria to die [132].

The antimicrobial properties of conductive functionalized polyanilines has been investigated by exploring their interaction with bacterial cells for it has been observed lower concentrations of PANI strongly inhibited the growth of wild-type *Escherichia coli*, *Pseudomonas aeruginosa* and *Staphylococcus aureus* as well as several antibiotic resistant clinical pathogens [133].

Nanofibres of polyaniline combined with fluconazole have been prepared by simple and cost effective sol-gel method using D-10-camphorsulfonic acid (D-CSA) as a dopant and as a surfactant, and ammonium persulfate as the oxidant. The synthesized nanostructured material was dissolved in dimethylsulfoxide at different concentrations and tested for its antifungal properties against *Candida albicans* (ATCC 140503), *Candida tropicalis* (ATCC 13803) and *Candida krusei* (ATCC 34135). The results showed that, compared to nanofiber structured conducting PANI, polyaniline doped with fluconazole have shown higher antifungal activity on all the species tested. It is very much evident that PANI doped fluconazole has considerable enhanced antifungal activity. *C. tropicalis* (ATCC 13803) is more susceptible than *C. albicans* (ATCC 140503) and *C. krusei* (ATCC 34135) [134].

Polyaniline-Zr(IV)sulphosalicylate has also been tested against the various bacterial (*Escherichia coli*, *Bacillus thuringiensis* and *Pseudomonas aeruginosa*) and fungal strains (*Aspergillus nigrus*, *Fusarium oxysporum* and *Penicillium chrysogenum*) and relatively higher activities has been observed than the known antibiotics [135].

Polyaniline Grafted Chitosan (Chit-*g*-PANI) has been tested for its antimicrobial activity against *Staphylococcus epidermidis, Staphylococcus aureus, Staphylococcus pyogenes, Escherichia coli, Candida albicans, Candida tropicalis and Candida krusei*. The results of antimicrobial activity of PANI and Chit-*g*-PANI assessed based on the average diameter of zones of inhibition, which confirms that Chit-*g*-PANI have an enhanced antimicrobial activity compared to PANI. PANI and Chit-*g*-PANI also shows a potent antifungal activity compared to antimicrobial activity [136].

The antibacterial properties of silver/ Poly(methyl methacrylate) (PMMA) nanofiber against both Gram-negative (Escherichia coli) and Gram-positive (Staphylococcus aureus) bacteria were evaluated using minimum inhibitory concentration (MIC), the modified Kirby-Bauer method, and a kinetic test. The MIC test demonstrated that the silver/PMMA nanofiber had enhanced antimicrobial efficacy compared to that of silver sulfadiazine and silver nitrate at the same silver concentration [137].

Azo dyes are known for their medicinal importance and are well recognized for their use as antineoplastics [138], antidiabetics [139], antiseptics [140], antibacterial [141], antitumor [142]. They are known to be involved in a number of biological reactions such as inhibition of

DNA, RNA and protein synthesis, carcinogenesis and nitrogen fixation [143]. Azo dyes are important structures in the medicinal and pharmaceutical fields [144] and it has been suggested that the azoimine linkage might be responsible for the biological activities displayed by some Schiff bases [145]. In addition, Evans blue and Congo Red azo dyes has been studied as HIV inhibitors of viral replications. This effect is believed to be caused by binding of azo dyes to both protease and reverse transcriptase of this virus [146]. The existence of an azo moiety in different types of compounds has caused them to show antibacterial and antifungal activities. In the recent times, exploration of azo dye as antimicrobial agents has received considerable attention [147].

Drug release systems

Another application for conducting polymers is controlled release devices. Ions can be selectively released, as well as biologically active ions such as adenosine 5-triphosphate (ATP) and Heparin. Principle used in this application is potential dependence ion transport. This potential dependence ion transport is an interesting way to deliver ionic drugs to certain biological systems. One can deliver selective ions depending on the requirement [148, 149].

Group II:

This group utilizes the electroactivity character property of the materials. Molecular electronics, Electrical displays, Chemical, biochemical and thermal sensors, Rechargeable batteries and solid electrolytes, Drug release systems, Optical computers, Ion exchange membranes, Electromechanical actuators, 'Smart' structures, Switches.

Rechargeable batteries

Batteries were one of the first areas where conducting polymers promised to have a commercial impact. Conducting polymer batteries were investigated by leading companies like BASF/VARTA and Allied Signal. A number of conducting polymers such as polyacetylene, polyaniline and other polyheterocycles have been used as electrode materials for rechargeable batteries [150].

Sensors

Since electrical conductivity of conducting polymers varies in the presence of different substances, these are widely used as chemical sensors or as gas sensors. In its simplest form, a sensor consists of a planar interdigital electrode coated with conducting polymer thin film. If a particular vapor is absorbed by the film and affects the conductivity, its presence may be detected as a conductivity change [151].

Electrochromic devices

The phenomenon of electrochromism can be defined as the change of the optical properties of a material due to the action of an electric field. The field reversal allows the return to the original state. Conjugated polymers that can be repeatedly driven from insulating to conductive state electrochemically with high contrast color are promising materials for electrochromic device technology. Conjugated polymers have an electronic band structure. The energy gap between the valence band and the conduction band determines the intrinsic optical properties of the polymers. The color changes elicited by doping are due to the modification of the polymer band electronic structure. The electrochromic materials first drew interest in large area display panels. In architecture, electrochromic devices are used to control the sun energy crossing a window. In automotive industry rearview mirrors are a good application for electrochromic system [152].

Electromechanical Actuators

Conducting polymers also change volume depending on their oxidation state. Therefore, it is possible for conducting polymers to convert electrical energy into mechanical work. Conducting polymer actuators were proposed by Geoffrey and coworkers [153].

Catalyst

Conducting polymers show redox property; therefore these are expected to behave as redox catalyst. Several reports have been found in the literature on modification of conducting polymers and their use as catalyst for small organic molecules. Conducting polymers in their various oxidation states interconvert each other, which permits to construct redox cycle for catalytic reactions. The catalytic activity has been revealed to be controlled by doping. Coordination of transition metals to the nitrogen atoms (in case of polyaniline and polypyrrole) affords the complexes, in which transition metals are considered to interact through a conjugated chain. The characteristics of conjugated polymers are reflected on the complexes, which are expected to provide novel catalytic system [154].

Group III

These applications just use the conductivity of the polymers. The polymers are used because of either their lightweight, biological compatibility for ease of manufacturing or cost.

Electrostatic materials

By coating an insulator with a very thin layer of conducting polymer, it is possible to prevent the build up of static electricity. This is particularly important where such a discharge is undesirable. Such a discharge can be dangerous in an environment with flammable gasses and liquids and also in the explosives industry [155].

Conducting adhesives

By placing monomer between two conducting surfaces and allowing it to polymerize, it is possible to stick them together. This is a conductive adhesive and is used to stick conducting objects together and allow an electric current to pass through them [156].

Printed circuit boards

Many electrical appliances use printed circuit boards. These are copper coated epoxy-resins. The copper is selectively etched to produce conducting lines used to connect various devices [157]. These devices are placed in holes cut into the resin. In order to get a good connection the holes need to be lined with a conductor. Copper has been used but the coating method, electroless copper plating, has several problems [158]. This process is being replaced by the polymerization of a conducting plastic. If the board is etched with potassium permanganate solution a thin layer of manganese dioxide is produced only on the surface of the resin. This will then initiate polymerization of a suitable monomer to produce a layer of conducting polymer [159].

Aircraft structures

Modern planes and spacecraft are often made with lightweight composites. This makes them vulnerable to damage from lightning bolts. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft [160].

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