Journal of Atomic, Molecular, Condensate & Nano Physics
Vol. 5, No. 2, pp. 159–193, 2018
ISSN 2349-2716 (online); 2349-6088 (print)
Published by RGN Publications
http://www.rgnpublications.com

DOI: 10.26713/jamcnp.v5i2.842

Conducting Polymers: Concepts and Applications

Topical Review

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Abstract. The developments in the field of electrically conducting polymers have grown very rapidly since the discovery and there is a very sharp increase in conductivity when intrinsically insulating organic conjugated polymers are doped with oxidizing and reducing agents. An overview of technological developments involving conducting polymers clearly indicates that the field expands at unprecedented rates. The manuscript first introduces the *conducting polymers* (CPs), conducting mechanism, concepts of doping and briefly introduces main applications. Different types of CPs, their unique properties and synthesis is discussed. The present review will help the effective implementation of conducting polymers in different fields, which directly depends on the degree of understanding of their behaviour and properties.

Keywords. Conducting polymers; Doping; Conduction mechanism; Applications

PACS. 72.80.Le

Received: February 28, 2018 **Accepted:** March 27, 2018

1. Introduction

Polymers are simply very large molecules (macromolecules) that are made up of smaller molecules (monomers) that can be linked together in various ways, resulting in a range of what we call microstructures (e.g. linear chains, branched chains, densely interconnected networks etc.). Until about 48 years ago the notion that plastics could be made to conduct electricity would have been considered to be absurd. Polymers insulate and do not conduct electricity and so electric wires are coated with polymers to protect them and us from short circuits but in 1977, Hediki Shirikawa, Alan Macdiarmid, and Allan Heeger on polyacetylene [1] reinforced the then emerging concept of organic materials behaving not as traditional insulators but as metals or semiconductors. This was particularly exciting because it created a new field of research on the boundary between chemistry and condensed matter physics, and because it created a number of opportunities. This review article critically reviews development in this field, the methods employed so far to improve the electrical conductivities of conducting polymers and applications.

The genesis of the field can be traced back to the mid 1970s when the first polymer capable of conducting electricity– polyacetylene - was accidently prepared by Shirakawa [2]. The subsequent discovery by Heeger and Macdiarmid [3] that the polymer would undergo an increase in conductivity of 12 orders of magnitude by oxidative doping quickly reverberated around the polymer and electrochemistry communities, and an intense search for other conducting polymers soon followed. The target is a material; which could combine the processibilty, environmental stability, and weight advantages of a fully organic polymer with the useful electrical properties of a metal.

The term "conductive polymer" elicits two quite different definitions. The first and most well known (Category I) encompasses polymers filled with the conductive materials such as carbon black, metal flakes or fibers, and so on [4–8]. The major practical function of the polymer matrix is to serve as a "glue" to hold the conductive elements together in a solid entity. The interest in such material derives from the low cost, light weight, mechanical durability, and ease of processabilty of the polymer component, in concert with reasonably good bulk conductivity. The second definition applies to polymers [9, 10] whose backbones are responsible for the generation and propagation of charge carriers (Category II). Potential advantages include variable conductivity by controlling the extent of oxidation or reduction, the ability to dictate the nature of the majority carriers, and facile cycling between conductive and insulating states. In this review article we will focus on the Category II conductive polymers. These conductive polymers can offer attractive advantages over Category I materials, although formidable problems like poor processabilty, poor mechanical properties, and (most problematic) environment instability must be solved before they can enjoy widespread utility.

2. Requirements for Conducting Polymer Systems

The outermost shell of electrons in a material contains the valence electrons and these can be placed in the valence band that defines their lowest energy states. In order to conduct, an electron must obtain sufficient energy to promote it to the conduction band. It is generally recognized that for an organic polymer to support electronic conduction, the polymer must contain an overlapping set of molecular orbitals to provide reasonable carrier mobility along the polymer chain. Conducting polymers are usually polyconjugated structures, which are insulators in the pure state but when treated with an oxidizing or a reducing agent can be converted into polymer salts with electrical conductivities comparable to metals.

The essential structural characteristic of all conjugated polymers is their quasi-infinite π system extending over a large number of recurring monomer units (Figure 1). This feature results in materials with directional conductivity. The extended π system of conjugated polymer are highly susceptible to chemical or electrical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to systematically control the electrical and optical properties with a great deal of precision.

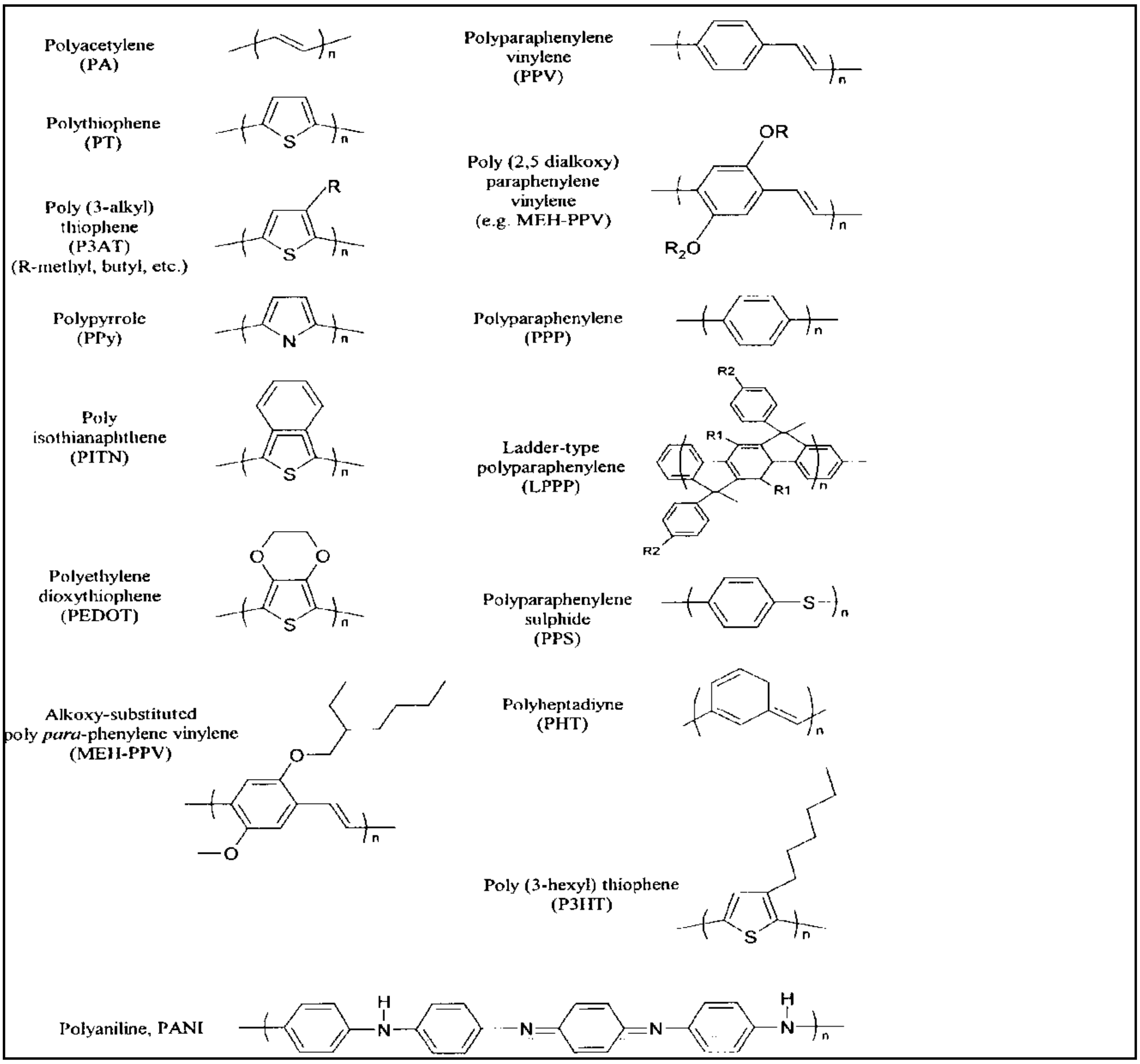


Figure 1. Structure of some conducting polymers

Conjugated polymers in their non-doped state are in fact intrinsic semiconductors whose band gap depends not only on the chemical constitution of the conjugated backbone but also on the nature of the substituent's attached to the main chain. Thus optical and electronic properties of the conjugated polymers can be varied to a very large extent by appropriate functionalization. Most extensively studied area of the application of undoped conjugated polymers is the fabrication of the polymeric light-emitting diodes, i.e. electronic devices which exploit the phenomenon of electroluminescence. Electroluminescence of conjugated polymers and more precisely poly(p-phenylene vinylene) was first reported by Burroughes et al. [11] in 1990. These undoped conjugated polymers can also be used in the fabrication of a large variety of other devices like organic field-effect transistors. Polymer LEDs show attractive characteristics, including efficient light generation, with great potential for commercialisation. Again the polymer interests in polymers is in their potential use for rapid, low-cost processing using film-forming polymer solutions. Like the conductive polymers, the semi-conductive polymers obtain their properties from their conduction-molecular orbitals and valence molecular orbitals, i.e., bonding π and antibonding π^* orbitals, respectively.

In electro-chemical light emitting cells, the semi-conductive polymer could be surrounded asymmetrically with a hole-injection electrode on one side, and a low work function, electron injecting metal contact like aluminum, magnesium, calcium etc. on the other side. The emission of light is then the result of radiative charge carrier recombination in the polymer as electrons from one side and holes from the other recombine.

Conducting polymers are conjugated polymers, namely organic compounds that have an extended p-orbital system, through which electrons can move from one end of the polymer to the other. In conjugated polymers, the bonding leads to one unpaired electron (the π-electron) per carbon atom. Moreover, π-bonding, in which the carbon orbitals are in the sp^2 pz configuration and in which the orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization along the backbone of the polymer. This electronic delocalization provides the “highway” for charge mobility along the backbone of the polymer chain. Electronically conducting polymers are extensively conjugated molecules, and it is believed that they possess a spatially delocalized band-like electronic structure. 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.

3. Doping

The concept of doping is the unique, central, underlying, and unifying theme which distinguishes conducting polymers from all other types of polymers [12, 13]. During the doping process, an organic polymer, either an insulator or semiconductor having a small conductivity, typically in the range 10^{-10} to 10^1 S/cm, is converted to a polymer which is in the ‘metallic’ conducting regime (-1 to 10^4 S/cm). The controlled addition of known, usually small (≤ 10 per cent) non-stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone.

Both doping and un-doping processes, involving dopant counter-ions which stabilize the doped state, may be carried out chemically or electrochemically [14]. Transitory doping by methods which introduce no dopant ions are also known [15]. By controllably adjusting the doping level, a 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. Conducting blends of a (doped) conducting polymer with a conventional polymer (insulator), whose conductivity can be adjusted by varying the relative proportions of each polymer, can be made [16, 17]. This permits the optimization of the best properties of each type of polymer. Trans-$(CH)_X$ and the emeraldine base form of polyaniline are used in Figurer̃effig2 to illustrate the increases in electrical conductivity of many orders of magnitude which can be obtained by doping.

In the“doped” state, the backbone of a conducting polymer consists of a delocalized pi 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 non-conjugated backbone, as in polyaniline (leucoemeraldine base form), which becomes truly conjugated only after p-doping, or a non-conjugated structure as in the emeraldine base form of polyaniline which becomes conjugated only after protonic acid doping.

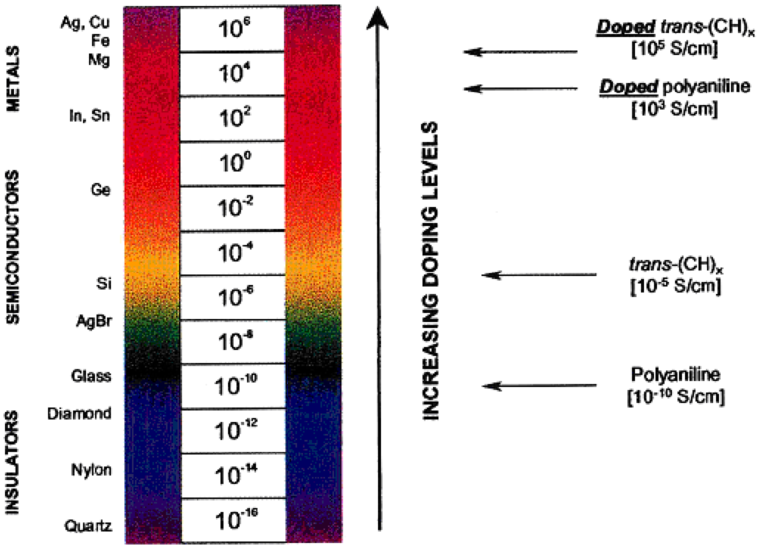


Figure 2. Effect on conductivity of polyacetylene and polyaniline after doping (figure taken from Nobel Lecture, 2000 by Alan G. MacDiarmid)

3.1 Redox Doping

By changing the number of electrons associated with the polymer backbones by the means of chemical or electrochemical processes one can easily perform p- and/ or n-redox doping and can vary the conductivity. In oxidation process polymer could either lose an electron from one of the bands or it could localize the charge over a small section of the chain. Localizing the charge causes a local distortion due to a change in geometry, which costs the polymer some energy. However, the generation of this local geometry decreases the ionization energy of the polymer chain and increases its electron affinity making it more able to accommodate the newly formed charges. This method increases the energy of the polymer less than it would if the charge was delocalized and, hence, takes place in preference of charge delocalization.

The oxidative doping of polypyrrole proceeds in the following way. An electron is removed from the system of the backbone producing free radical and a spinless positive charge. The radical and cation are coupled to each other via local resonance of the charge and the radical. In this case, a sequence of quinoid-like rings is used. The distortion produced by this is of higher energy than the remaining portion of the chain. The creation and separation of these defects costs a considerable amount of energy. This limits the number of quinoid-like rings that can link these two bound species together. In the case of polypyrrole it is believed that the lattice distortion extends over four pyrrole rings. This combination of a charge site and a radical is called a polaron. This could be either a radical cation or radical anion. This creates a new localized electronic states in the gap, with the lower energy states being occupied by a single unpaired electrons. The polaron state of polypyrrole are symmetrically located about 0.5 eV from the band edges. Upon further oxidation the free radical of the polaron is removed, creating a new spinless defect called a bipolaron. This is of lower energy than the creation of two distinct polarons. At higher doping levels it become possible that two polarons combine to form a bipolaron. Thus at higher doping levels the polarons are replaced with bipolarons. The bipolarons are located symmetrically with a band gap of 0.75 eV for polypyrrole. This eventually, with continued doping, forms into a continuous bipolaron bands. Their band gap also increases as newly formed bipolarons are made at the expense of the band edges. For a very heavily dope polymer it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metallic like conductivity. This is shown in Figure 3.

Conjugated polymers with a degenerate ground state have a slightly different mechanism. As with polypryyole, polarons and bipolarons are produced upon oxidation. However, because the ground state structure of such polymers are twofold degenerate, the charged cation are not bound to each other by a higher energy bonding configuration and can freely separate along the chain. The effect of this is that the charged defects are independent of one another and can form domain walls that separate two phases of opposite orientation and identical energy. These are called solitons and can sometimes be neutral. Solitons produced in polyacetylene are believed to be delocalized over about 12 CH units with the maximum charge density next to the dopant counterion. The bonds closer to the defect show less amount of bond alternation than the bonds away from the centre. Soliton formation results in the creation of new localized electronic states that appear in the middle of the energy gap. At high doping levels, the charged solitons interact with each other to form a soliton band which can eventually merge with the band edges to create true metallic conductivity. This is shown below in Figure 4. Polyacetylene, poly p-phenylene, polyhetrocyclic polymers (polythiopene, polypyrrole, polyfuran and their dervatives) and other polyconjugated systems with no strong basic centres in their backbone usually undergo the redox-type doping.

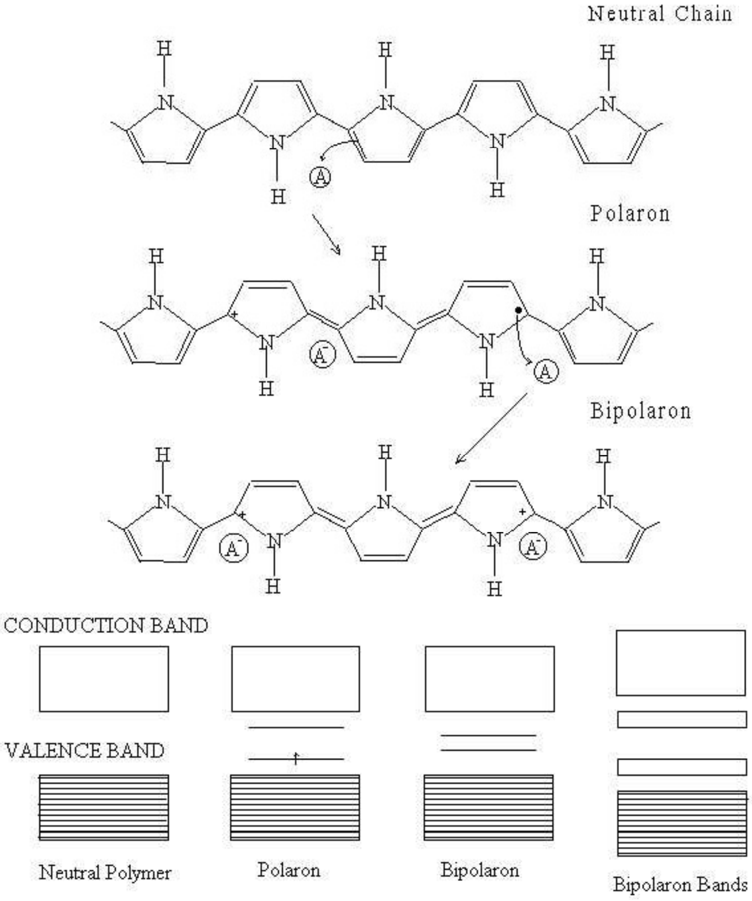


Figure 3. Mechanism of conductivity in polypyrrole: formation of polaron and bipolaron

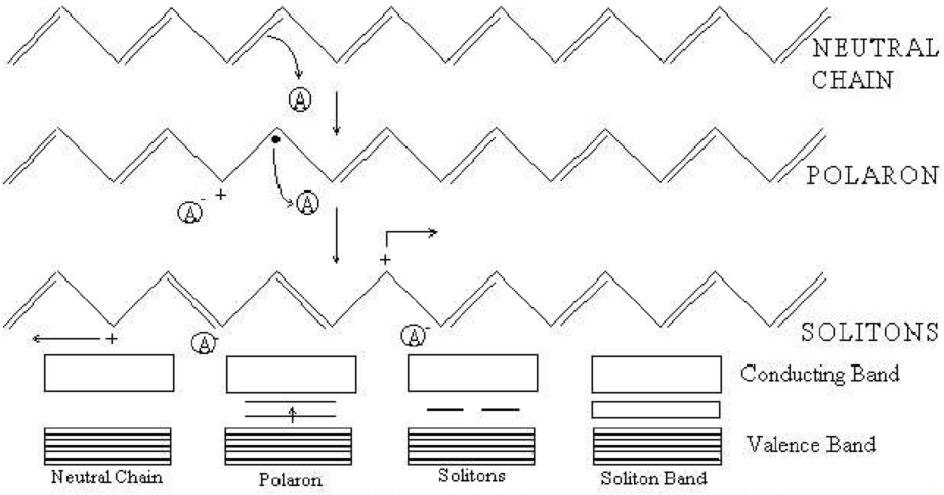


Figure 4. Solitons formation in polyacetylene

Historically, first doping agents used were halogens (Br_2 and I_2) and arsenic pentafluoride (AsF5) (18). They were used in the late 1970s for doping of polyacetylene. Among them the most popular is $FeCl_3$ [19] which is incorporated into the polymer matrix in the form of $FeCl^{-4}$ as shown by Mossbauer spectroscopy [20]. Other popular doping agents involve strongly or mildly oxidizing acids like $HClO_4$, H_2SO_4 [21].

Shirkawa and his co-workers [1] reported that the conductivity of semiconducting polyacetylene (PA) films increases many orders of magnitude when exposed to vapours of halogens, great efforts have been made to produce similar high conducting polymers. Both electron acceptors and donors react with polyacetylene, resulting in highly conducting derivatives [13]. The main step of doping is the oxidation or reduction of neutral PA molecules to polycations or polyanions:

$$(CH)_X + Ox_1 \rightleftharpoons (CH)_x^+ + Red_1$$

$$(CH)_X + Red_2 \rightleftharpoons (CH)_x^- + Ox_2$$

where Ox_1 and Red_2 denotes the oxidant and reductor, while Red_1 and Ox_2 are derivatives after the charge transfer.

Doping can also be carried out by electrochemical methods where the electrons of the electrodes are the oxidizing or reducing agents:

$$(CH)_X - e \rightleftharpoons (CH)_x^+$$

$$(CH)_X + e \rightleftharpoons (CH)_x^-$$

Electrochemical doping is usually carried out in non-aqueous solutions (acetonitrile, propylene carbonate, etc.) containing quaternary amine salts of monovalent anions such as ClO_4^-, BF_4^-, PF_6^-, etc. as the electrolyte. During the doping the polymer is being oxidized at the anode and in the same time the dopant anions, originating from the electrolyte, are inserted to the polymer matrix. Electrochemical doping can be performed either at constant current or at constant potential.

The most extensively investigate p-doped polyacetylenes are the halogen derivatives. The preparation and the conductivity of chlorine-, bromine-, and iodine- doped PA were published in 1977 [1, 12]. A series of metal chloride, bromide, and iodide derivatives of PA have been prepared by Shirakawa and Kobayashi [22] and Billaud et al. [23] in various solvents and the maximum dopant concenteration in most cases was dependent on the type of solvent. The n doping of PA is carried out by strong reducing agents; the known dopants are alkali metal and tetraalkylammonium ions. Different solvents [13, 24–31] have been found to affect alkali metal doping, and an increase in conductivity may be explained [13] by a decrease of the binding energy of the solvated alkali metal ions in PA due to the inclusion of the solvent.

There can be Doping involving no dopant ions such as for example, when trans-$(CH)_x$ is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap, this is called photo-doping [32]. Charge-injection doping is most conveniently carried out using a metal/insulator/semiconductor configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. Applications of an appropriate potential across the structure can give rise, for example, to a surface charge layer, the 'accumulation' layer which has been extensively investigated for conducting polymers [33, 34].

3.2 Non-Redox Doping

In non-redox doping the number of electrons associated with the polymer backbone does not change during the doping process. The energy levels are rearranged during doping when polyaniline emeraldine base is treated with aqueous protonic acids then a nine to ten order magnitude increase in conductivity is obtained resulting in protonated emeraldine base [35–37].

4. Synthesis of Conducting Polymers

Polyacetylene and polyphenylene are the simplest models and can be regarded as sequence of either vinylene or phenylene units. However, even these very simple systems can be put together in quite a variety of ways to create a number of structurally different materials, so the task of those engaged in the synthesis of conjugated organic polymers ought to be to provide as wide a variety of well-characterized materials as possible for the detailed investigations of their electrical properties. In this section we will mention some of the standards methods to synthesis the conducting polymers:

In synthesis, there are mainly two main lines of approach (Figure 5), the first could reasonably be called the direct route and second approach is designated the indirect approach. The direct route represents the classical approach to polymer synthesis in which an appropriate monomer is converted directly into a conjugated polymers via either an addition or a condensation process.

One of the disadvantages of the direct approach stems from the experimental observation that some of structurally simplest conjugated polymers, for example, like polyacetylene and poly-para-phenylene, are essentially insoluble and intractable materials and this observation brings several practical difficulties. The main advantage of the indirect route is an increased flexibility in the design of synthesis. Thus, the precursor polymers may be formed by addition or condensation polymerization procedures, but the second stage may be accomplished by a variety of different reactions.

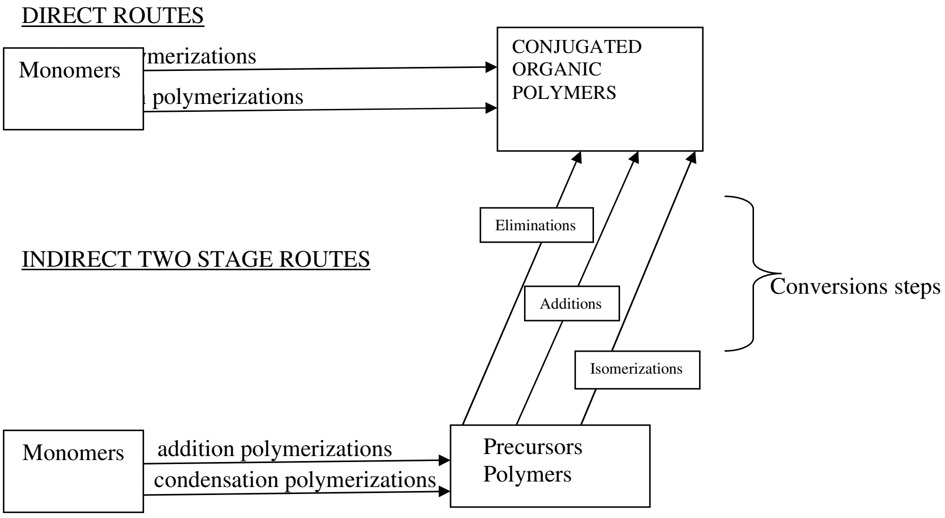


Figure 5. Outline of possible routes to conjugated organic polymers

5. Different Conducting Polymers: Synthesis, Structure and Applications

Among the many polymers known to be conductive, polyacetylene, polyaniline, polypyrrole, polythiopene, poly(phenylene sulfide) and poly(phenylene vinylene) have been studied the most. In this section, we will discuss these polymer's structure, synthesis and their applications along with few other known conducting polymers.

5.1 Polyacetylene

Polyacetylene(PA)is an organic polymer with the repeat unit $(C_2H_2)_n$ (Figure 6). The high electrical conductivity discovered for these polymers beginning in the 1960's accelerated interest in the use of organic compounds in microelectronics.

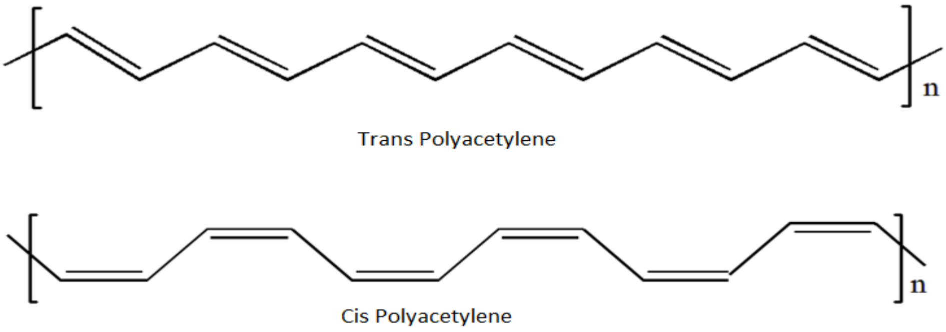


Figure 6. A segment of cis- and trans-polyacetylene

Natta was the first to carry out extensive investigations into direct polymerization of acetylene[38], they reported [39] that bubbling acetylene gas through a solution of Ziegger catalyst in a hydrocarbon solvent resulted in the precipitation of trans-polyacetylene as a semi-crystalline red powder. A major breakthrough in the investigation of polyacetylene resulted from the work of Ito et al.; they discovered that exposing the surfaces of solutions of Zieger catalysts to an atmosphere containing acetylene resulted in the formation of films of polyactylene at the liquid-gas interface [40]. The most widely used technique for preparing films of polyacetylene, after that described by Shirakawa et al., uses a catalyst developed by Luttinger [41]. The main advantage of this technique is that the requirement for regrous exclusion of moisture normally associated with Zieger catalyst is circumvented. Although the Shirakawa and Luttinger techniques appear to have found most favour with the majority of research groups investigating polyacetylene, there are many other catalyst which are effective in this process. It is now well known that catalyzed reactions of acetylene may yield a variety of products and that many of the primary products are themselves fairly reactive compounds [42]. An early example [43] used a catalyst generated from the reaction of phenylmagnesium bromide with ferric chloride in diethylether; acetylene was introduced as a saturated solution in benzene.

Both the cis and trans forms can be prepared as silvery, flexible films, which can be made either free standing or on a variety of substrates, such as glass or metal, with thickness varying from 10^{-5} to 0 cm [40]. The trans isomer is the thermodynamical stable form. Any cis/trans ratio can be maintained at low temperatures, but completely isomerization from cis- $(CH)_x$ to trans-$(CH)_x$ can be accomplished after synthesis by heating the film to temperatures above 15°C for a few minutes [44, 45]. X-ray studies [46, 47] show that the $(CH)_x$ films are highly crystalline. Because of bond alteration tans-$(CH)_x$ is a semiconductor with an energy gap of about 1.5 eV [48, 49]. The discovery that polyacetylene can be doped after synthesis [50–52], at room temperature, and with a variety of dopants makes it fundamentally different from conventional covalent semiconductors. The ability to dope $(CH)_x$ after synthesis using chemical or electrochemical techniques is due to a combination of its open morphology [40, 53, 54] with associated high surface area and weak interchain binding which allows diffusion of the dopant ions between the polymer chains. The electrical conductivity of polyacetylene can be varied in a controlled manner over 12 orders of magnitude through chemical or electrochemical [55–57] doping. Conductivity values of about 10^5 S/CM have already been reported [58–60,62]. Controlled electrochemical doping and undoping have been demonstrated [52], and prototype rechargeable batteries have been constructed using $(CH)_x$ as both the active cathode and anode [55–57]. Photovoltaic phenomenon have been observed in hetrojunctions [63], schottky barrier junctions [63, 64], and photoelectrochemical [65] junctions. Thus, although these and other potential applications will require considerable future work before ultimate technological value can be determined, the properties appear promising.

5.2 Polyphenylenes

Poly(p-phenylene)

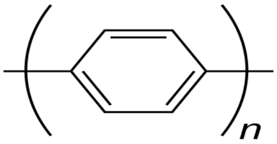


Figure 7. Poly(p-phenylene)

Poly(p-phenylene) (PPP) (Figure 7) is very attractive polymer for many reasons. High conductivity for example of the order of 500 S/cm can be achieved upon doping with AsF5 [66]. Following batteries based on doped PA [67], formulation of rechargeable based on doped PPP has been demonstrated [68]. Polyparaphenylene consists of benzene rings linked in the para position, Crystallographic data on oligomers indicate that carbon-carbon bond lengths within the rings are about 1.40 Å, and those between rings are tilted are about 1.51 Å [69–71]. In the solid state two successive benzene rings are tilted with respect to each other by ~23°. This torsion angle constitutes a compromise between the effect of conjugation and crystal-packing energy, which favour a planar structure, and the steric repulsion between orthohydrogen atoms, which favours a nonplanar structure [72]. The band gap in PPP is 3.4 eV [66], that is, about twice that of trans-PA.

Many well-known reactions have been attempted in order to arrive at high molecular weight, all-para-linked polymer [73–75]. None have been truly successful on both accounts. Various para-dihalobenzenes have been condensed with alkali metals [76] or with copper powder [77], but generally only low molecular weight products, sometimes with structural irregularities were obtained. The Ullmann reaction, however, is particularly useful for preparing substituted polyphenylenes [78–82]. Perhaps the most successful and economical method for preparing PPP is the oxidative coupling reaction of benzene reported by Kovacic and co-workers [83–87]. Several electrolytic methods [88–94] have also been used to prepare polypheneylene. The electrolysis of phenylmagnesium bromide in ether afforded about a 0.1 % yield of polymer [88].

The properties of polyphenylene are to a certain extent dependent upon the method used to prepare it. Acceptor doping of PPP is usually accomplished by exposing either powders or preformed pellets to AsF_5 gas at pressure of up to 450 Torr at room temperature or below using vacuum line techniques [66, 95, 96]. Donor doping with alkali metals is usually accomplished with the aid of an appropriate electron transfer agent such as napthalene (as the alkali metal naphthalide) in an appropriate solvent such as tetrahydrofuran. Electrochemical doping of PPP is performed in a similar fashion to that used for polyacetylene [68]. However, unlike polyacetylene, which has initial undoped conductivities of 10^{-7}-10^{-5} S/cm, PPP is much less conductive in its virgin form (10^{-15}-10^{-10} S/cm). Doping also induces dramatic changes in the optical spectra of PPP [95]. Another feature of poly(p-phenylene) which is similar to PA is its capability to be either acceptor or donor doped by electrochemical means [69, 97]. PPP possesses many attributes like the reversible nature of electrochemical doping, high electronic conductivity, ionic mobility, insolubility, structural integrity, and high voltage, which makes this polymer to be actively explored as an electroactive cathode and anode material in rechargeable batteries.

Poly(m-Phenylene)

Poly(m-phenylene) is a fusible and soluble polymer and is unlikely candidate to form conducting complexes [98]. However, upon doping with AsF_5, a conducting complex of conductivity of the order of 10^{-3} S/cm is formed [99, 100], this is due to the dopant-induced carbon-carbon bond formation resulting in a polymer with an extended orbital system.

5.3 poly(p-Phenylene Sulfide)

poly(p-phenylene sulfide)(PPS) (Figure 8) was the first nonrigid, not fully carbon-backbone-linked polymer made highly conducting upon doping [101, 102]. Several authors have reported the crystal structure of PPS e.g. Tabor et al. [103], who performed X-ray studies on oriented films. They proposed an orthorhombic unit cell with $a = 8.67\,\text{Å}$, $b = 5.61\,\text{Å}$ and $c = 10.26\,\text{Å}$, with space group Pbcn. This structure received confirmation by successive studies of Lovinger et al. [104] and Uemura et al. [105]. Jurga [106] found that the structure of PPS depends on sample preparation conditions. New insight into the PPS structure was given by Napolitano et al. [107]. They found that samples of PPS obtained by different thermal and mechanical treatments exhibited a crystal structure equivalent to that proposed by Tabor et al. [103]. X-ray diffraction data indicate that adjacent phenyl rings are nearly perpendicular [108]. Despite this conformation, the bandwidth of the highest occupied band is relatively large, 1.2 eV. Although PPS has been made by many processes, two of these, the Edmonds-Hill process [109] and the Lenz process [110], stand out as being perhaps the most successful. The Edmonds-Hill process involves condensation of a dihalogenated aromatic with Na_2S in N-methylpyrrolidone at high temperature and provides polymers with aromatic rings linked in known positions. The Lenz process is useful in preparing unsymmetrically substituted polyarylene sulfides regiospecifically.

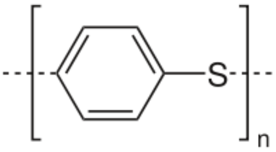


Figure 8. poly(p-phenylene sulfide)

The bandwidth for the highest occupied band of a hypothetical perpendicular conformation of poly(p-phenylene) is only 0.2 eV and the large IP (6.3 eV) limits the p-type dopants to strong acceptors such as AsF_5 it has been demonstrated that exposures of PPS to AsF_5 at room temperature causes substantial changes in the backbone structure of the polymer [111]. The dopant appears to predominantly induce the formation of carbon-carbon bonds bridging the sulphur linkages to form thiopene rings and leading to polybenzothiopene structure, and this chemical modification enhances the conductivity of the complex from about 0.01 to 3 S/cm.

5.4 Polypyrrole

Among the conducting polymers known to date, ones based upon Polypyrrole (PPy) (Figure 9) have attracted special interest because of their high conductivity, their ease and high flexibility in preparation, their stability and good mechanical properties. Potential technological applications such as in electronic and electrochromic devices [112–114], counter electrode in electrolytic capacitors [115], sensors [116–118], chromatographic stationary phases [119], light-weight batteries [120], membrane separation [121] consequently, have attracted a great deal of attentions in recent years and this is currently one of the most active areas of research in polymer science and engineering at present.

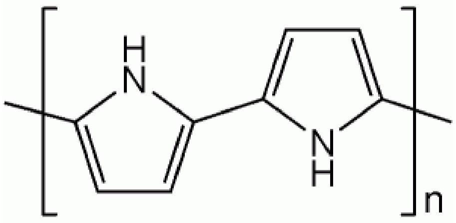


Figure 9. Polypyrole

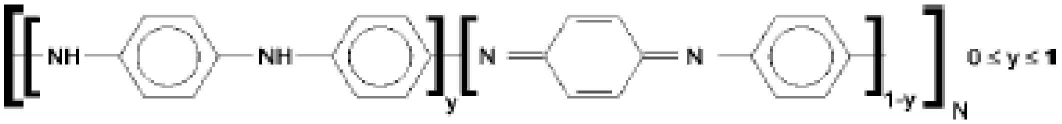
The attractiveness of the polypyrrole systems stems from several factors. Although initially the most important factor was undoubtedly the chemical and thermal stability of these polymers relative to $(SN)_x$ and $(CH)_x$, the ease of preparing was also appealing. As was first reported by Italian chemists, pyrrole monomer is very readily polymerized to give a black conducting powder [122]. This chemistry is particularly facile, taking place with a large number of oxidizing agents, and can even be observed taking on the outside of pyrrole down which the monomer has been allowed to flow. The resulting conducting powder have been referred to as pyrrole black for many years. The polymerization can take place electrochemically [123] as well as chemically [124]. Good quality films were first obtained by Kanazawa et al. [125] and Diaz et al. [126] using a modification of the electrochemical technique pioneered by Dall'Oli et al. [123]. PPy is one of the few electronically conducting polymers that can be prepared in aqueous solutions [127]. Polypyrrole (PPy) and a wide range of its derivatives may be prepared by simple chemicalor electrochemical methods [128–134, 139]. Chemical polymerisation is a simple and fast process with no need for special instruments. Bulk quantities of polypyrrole (PPy) can be obtained as fine powders using oxidative polymerisation of the monomer by chemical oxidants inaqueous or non-aqueous solvents [130–132, 135] or by chemical vapour deposition [133]. However, the use of chemical polymerisation limits the range of conducting polymers that can be produced since only a limited number of counter ions can be incorporated. The chemical polymerisation of pyrrole appears to be a general and useful tool for the preparation of conductive composites [136, 137] and dispersed particles in aqueous media [138, 139]. Iron (III) chloride has been found to be the best chemical oxidant and water is the best solvent for chemical polymerisation with respect to desirable conductivity characteristics [130, 136]. The electrochemical approach for making electroactive/conductive films is very versatile and provides a facile way to vary the film properties by simply varying the electrolysis conditions (e.g. electrode potential, current density, solvent, and electrolyte) in a controlled way. Alternatively, the variations in the properties of polymer can be made in the selection of themonomer or the electrolyte. Furthermore, the electrosynthesis allows an easy control of the thickness of the polymers. Also because of the good solubility of pyrrole monomer in a wide range of solvents, pyrrole is easily electropolymerised in both aqueous [140] and non-aqueoussolvents [141, 142]. The polymerisation reaction is very complicated and the mechanism of electropolymerisation is still not fully understood. The generally accepted mechanism [141–147], is that in the first step the neutral monomer is oxidised to aradical cation followed by aromatisation and oxidation of the dimer. As the dimer, on account of its greater conjugation, is more easily oxidised than the monomerunder the given experimental conditions, it is immediately reoxidised to the cation.

The electrical conductivity of PPy conductive polymers is one of the most important properties for analytical applications. PPy is a conducting polymer which has a nondegenerate conduction band in the ground state polaron and bipolarons are the dominant charge carriers in these polymeric conductors, the mechanism of conduction in PPy has not been yet conclusively established because of the persistent structural disorder of the polymer [148]. The most widely accepted view of conductivity in these systems involves charge transport along the polymer chains, as well as hopping of carriers [149,150] (holes, bipolarons, etc.) The electrical conductivity of PPy is the product of two important factors, the number of carriers (e- or holes) and charge carrier mobility. Higher mobilities will occur with more crystalline, better oriented, defect free materials. Increasing the doping level will increase the density of charge carriers. The conductivity decreases with falling temperature just like that of semiconductors. In contrast, the conductivities of typical metals,like silver, increase with falling temperature [151]. The electrical conductivity of the PPy films are strongly influenced by the preparation conditions such as the nature/concentration of electrolyte or counterion [152, 153], doping level [154] current density [155], synthesis temperature [155, 156] and solvent [157]. It has been indicated [152] that highly conducting PPy films with an electrical conductivity higher than 500 S/cm have been prepared with the electrochemical method by selecting suitable polymerisation conditions. It has also been found that the preparation method also affects the properties of the produced films. For example the use of a pulsed potential technique in the growth of PPy films leads to an enhancement in electrical conductivity,molecular anisotropy and surface smoothness as compared to equivalent films synthesised by constant potential mode. The electrical conductivity of the produced polypyrrole films are also affected by synthesis temperature [158–160, 162]. Polypyrrole synthesised at lower temperature exhibits longer conjugation length, structural order, fewer structural defects, and higher conductivity. The doped PPy film has high mechanical strength and conductivity, but its strength or conductivity decreases remarkably after undoping [154]. Munstedt *et al*. [163, 164] have reported that by a treatment of PPy with NaOH solution the conductivity of all PPys drops with time. Sodium hydroxide, treatment also caused severe embrittlement of the films.Scanning electron microscopy (SEM) investigations of PPy has also showed that the surface morphology of the ppy changes with base or acid treatment [165].

Owing to the high conductivity and thermal stability ofPPy the conducting polymer, the electroactive nature or the switching properties of PPy have been utilized as the basis of most proposed applications such as sensors, separationdevices and rechargeable batteries. The electroactive behaviour of the film is unique because it is an example of a redox polymer reaction which is accompanied by a change in the electrical properties of the film from an insulator to an electrical conductor involving both electron and ion transport within the film [166, 167]. Because of the low oxidation potential of PPy conducting polymers, there dox reactions of PPys are more sensitive to the oxygen than those polymers that are more difficult to oxidise. The PPy conducting polymers, unlike polythiophenes which a restable in air even in the dedoped state, are less stable in their reduced or undoped form (PPyo) and autoxidation in the dedoped state proceeds very fast and irreversibly to produce a dark film [166, 168, 169]. The undoped PPy reacts easily with O_2, resulting inoxidation of the polymer and lowering the mechanical strength. In contrast to the oxidisedstate, the reduced state of PPy films is unstable to oxygen and water. Polypyrrole is also sensitive to moisture because this leads to leaching of the counterion and thus to a decrease in conductivity. This can be avoided by using appropriate hydrophobic or polymeric counterions (e.g., camphor sulphonic acid or poly (styrenesulfonic acid)). Aging and thermal stability of PPy conducting polymers in air and solutions have been the focus of some researchers [169–174]. Exposure of conducting polymers to elevated temperatures is known to induce changes in the molecular structure. The changes may be related to the interaction between the charged polymer backbone and the counterion, or the thermal stability of the counterion and the charged polymer itself. It has been reported [175, 176] that conductivity of polypyrroles doped with arylsulfonates exhibit excellent stability in inert atmospheres but are slightly less stable in the presence of dry or humid air.

5.5 Polyaniline

Polyaniline (PANI) represents one of the most important conducting polymers and received lot of attention due to its controllable electrical conductivity [177], environmental stability [178], and interesting redox properties associated with the chain hetroatoms [179]. The PANI family of polymers has been recognized as an interesting and unusual members of the class of π-electron containing conducting polymers. Unlike many others members of this class viz; polyacetylene, polypyrrole, and polythiopene — whose electronic properties are well understood solely on the basis of their conjugated carbon backbones, in PANI a nitrogen hetroatom is incorporated between constituent phenyl (C_6H_6) rings in the backbone. The chemical flexibility provided by the nitrogen hetroatom allows access to several insulating ground states that are distinguished by their oxidation state. PANI exists in a variety of forms which differ in their oxidation level. The general formula describing PANI chain is



where y gives the average oxidation degree. The three stable forms of PANI are in correspondence to the values $y = 0$ (leucoemeraldine base, LB), $y = 0.5$ (emeraldine base, EB), and $y = 1$ (pernigraniline base, PNB).

Polyaniline was first known in 1835 as "aniline black", a term used for any product obtained by the oxidation of aniline. A few years later, Fritzches [180, 181] carried out the tentative analysis of the products obtained by the chemical oxidation of this aromatic amine. Thereafter, Lethe by [182] discovered that the final product of anodic oxidation of aniline at a platinum electrode, in aqueous sulphuric acid solution, is a dark brown precipitate. Subsequent investigators [183–186] have verified these results, and similar observations have been made during the oxidation of aqueous hydrochloric acid solutions of aniline [187]. Bucherer [188, 189] proposed a phenazene type structure which is more complex, contrary to the presentday understanding. Green and co-workers's proposed a linear octameric structure, of the quinone-imine type in the para-position, for the product obtained by the chemical oxidation of aniline.

Polyaniline is known to be crystalline, and a highly conducting state is accomplished by simple protonation of the imine nitrogen atoms in the emeraldine base backbone. Protonic doping does not change the number of electrons in the polymer chain structure, and its conductivity depends on the pH of the solution. Polyaniline has good environmental stability

[190]. Polyaniline has a chemically flexible –NH-group in its backbone which is responsible for interesting chemistry and physics [191]. Polyaniline is synthesized by both chemical and electrochemical processes in aqueous medium. The quinoid, benzoid, and diimine form an insulator, doped by dilute aqueous protonic acid to a metallic regime (compressed pellet) to give a corresponding iminium salt. The polymer is not oxidized during the doping process. This represents a new type of p-doping phenomenon in conducting polymers. Both these forms of polyaniline are stable in the presence of air or water. The doping process is reversed by treatment with aqueous alkali [192]. Polyaniline was prepared electrochemically by using the acid eutectic mixture NH4Fp2.35HF (PANI-F) in aqueous H_2SO_4 at different pH (PANI-S or PANI-N in Na_2SO_4 is added) [193]. Polyaniline was also prepared by electrochemical oxidation of aniline in an acidic medium. The pure polymer thus obtained was doped with iodine [194]. Polyaniline was polymerized using a static electrochemical cell and a fluidized bed electrode reactor (both static and fluidized beds), respectively, to form thin films on plates by using particular substrates [195]. Conducting polyaniline was synthesized in aqueous 1.0 M oxalic acid containing 0.1M aniline by electrochemical and chemical oxidation [196]. Different modes of the electrochemical synthesis of polyaniline are possible on an aluminum surface in H_2SO_4 electrolytes containing catalytic amounts of H_2IrCl_6 and its salts (e.g., K_2IrCl_6) [197]. Electrically conducting polyaniline (PANI) doped with heteropolyanions (HPA) of Keggin structure was synthesized by electrochemical polymerization. Cyclic voltammetry showed reversible redox systems from the polymer itself and from the immobilized HPA. Electrocatalytic studies of PANI electrode modified by HPA in the electroreduction reaction of bromate were performed by Barth et al. [198]. Chemically synthesized PANI is a precipitated product from an aqueous solution containing typical reagents: ammonium peroxydisulphate (persulphate), acids like hydrochloric, sulphuric, nitric or perchloric, and aniline. This direct route representsthe classical approach to polyaniline synthesis in which, aniline, the monomer, is converted directly to a conjugated polymer by a condensation process. One of the disadvantages of this direct approach stems from the experimental observation that an excess of the oxidant and higher ionic strength of the medium lead to materials [199–201] that are essentially intractable. Many variations of the synthesis of PANI have appeared in the literature [202–206]. Four major parameters affect the course of the reaction, and the nature of the final product. These are: (1) nature of the medium, (2) concentration of the oxidant, (3) duration of the reaction, and (4) temperature of the medium.

The novelty of the polyaniline is that it has a symmetrical conjugated structure, having extensive charge delocalization, resulting from a new type of doping of an organic-polymer salt formation rather than oxidation which occurs in the p-doping of all other conducting polymer systems. PANI differs from earlier studied conducting polymers such as polyacetylene and polypyrrole in that the electronic state of PANI can be controlled through both variation in the number of electrons and in the number of protons per repeat unit The redox activity of PANI is pH-dependentin aqueous medium. It has been established that the electroactivity of PANI ceases in aqueous media of $pH > 4$ [201]. On the other hand, the electrochemical behaviour of PANI, investigated in an aprotic solvent, such as propylene carbonate,in the presence of 1M lithium perchlorate as supporting electrolyte demonstrates two purely electronic processes [207]. However, these redox processes also vanish, if a small amount of 2,4,6-trimethyl pyridine (a strong base) is added to the system [208]. Furthermore, the dramatic effect of conductivity of PANI upon variation of pH (changing pH from 0 to 6 decreases electrical conductivity, σ, by six orders of magnitude) [209] clearly demonstrates that besides, the dopants (counterions), the presence of protons invariably has a pronounced effect on the conductivity. In a recent study [210], evidence is provided which proves that the emeraldine base form of polyaniline is doped by protonic acids to the metallic conducting regime by a process involving neither oxidation nor reduction of the polymer, thereby introducing a new concept of doping to the conducting polymer field. In brief, proton-induced conductivity in polyaniline is a remarkable physical phenomenon demanding explanation. The conductivity of chemically and electrochemically synthesized PANI is dependent on a number of parameters. For example, temperature [209, 211–213], protonation/pH [209, 210, 214–216], humidity [215, 216], oxidation state [215] and counterion [215] exert major influences on the conductivity of PANI. Besides, temperature of synthesis pressure [217], and duration of compression of PANI powders also have a considerable influence on the conductivity of PANI. The ability of polyaniline to store a considerable charge through the redox process has led to proposals for both non-aqueous [218, 219] and aqueous batteries [220]. The massive capacity of 145 Ah/kg, and the self discharge (with separator) rate of about 8% after 90 days make the polyaniline-lithium battery more attractive for new types of technological applications. The oxidized state, PANI films are coloured and highly conductive; while in the reduced state, they are optically transparent with low conductivity. In fact, colouration and conductivity are associated with the doping of the films. Two applications of PANI in Photo electro chemical cells have been studied to date: protection against photocorrosion of inorganic semiconductors [221], and photoresponse of junction PANI film [222]. Polyaniline and modified polyaniline have been shown to exhibit catalytic activity [223, 224]. The multiple colour changes of polyaniline films [225] on electrodes and chromatic reactions of polyaniline solutions in different pH rangesare the bases for development of PANI as an indicator. The use of polyaniline solution as redox indicator is also investigated [226]. Unlike other conducting polymers such as polypyrrole and polythiophene, PANI has a unique feature that the equilibration by acid solution imposes the anion in the polymer. PANI has been investigated very extensively theoretically [227–231].

5.6 Polythiopene

Polythiophene and its derivatives (Figure 10) in particular have been the subject of many recent studies [232–241].

Usually, two techniques have been used to synthesize polythiopene and derivatives: chemical and electrochemical procedures. Thiopene, furan, and selenphene have been polymerized with a variety of initiators: sulphuric acid [242], iron (III) chloride, and Ziegler catalyst [243]. However, experimental data show that with an acidic pter, polythiopene consists of alternating thiopene and tetrahydrothiopene units [244,245]. Yamamoto et al. [246] synthesis using catalytic coupling of the Grignard reagent of 2,5-dibromothiopene or 2,5-dihalogenothiopene by nickel salt. Kossmehl and Chatzitheodorou [247] have also synthesized poly (five-membered hetrocycles) by bringing together the monomer or the dimer and the complex AsF_5. Several results have been published on the electrochemical synthesis of polythiopene and its derivative [248, 249].

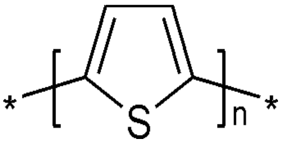


Figure 10. Polythiopene

Polythiopene and its derivatives are insoluble and infusible [250, 251] and their densities, determined by the flotation techniques, lie in the range 1.4-1.6 g/cm^3. The oxidation potential values of substituted polythiopenes show a decrease when electron-donating groups are substituted on positions 3 and/or 4 [252]. These variations confirm that the polymer formation results from the coupling of radicals derived from the supporting salt [253]. The ultraviolet-visible absorption spectra of polythiopene and its derivatives are generally characterized by an intense broad band with a maximum which varies with the length of the polymeric chain [250, 254, 255], this length being connected with the structure of the monomer and the synthesis method. Polyhetrocycles can be doped with either the donor [256] or acceptor [248] group, but owing to the high air sensitivity of the adduct; only polymers doped with acceptor groups have been extensively studied. Polythiopenes and its derivatives are being extensively used in display devices. The reversible doping-undoping processes of polyhetrocycles make them good candidate for secondary battery electrodes [257, 258]. They have been also used in photovoltaic applications: the conversion of solar energy in electricity with the undoped semiconducting polymers as the photoactive material [259], and protection against photo corrosion or photoelectrochemical cells by grafting thin conducting polythiopene films on the surfaces [260]. These polymers are also used for protection of small band gap semiconductors against photodegradtion [261], also a lot of work has been devoted to the physicochemical properties of metallic clusters or aggregates, owing to their interesting applications in the field of catalysis [262].

Polythiopene [poly (2,5-thienylene)] (PT) is usually synthesized from di-halogenated thiopene by utilizing a transition metal catalyzed dehalogenation polymerization [263]. This process leads, however, to a polymer of quite low molecular weight [264], implying a chain length of only 6-15 monomer units.

5.7 Other Conducting Polymers

Poly(Phenylene Vinylene)

A composite polymer of polyphenylene and polyacetylene, is also conductive when its doped with AsF_5 [265]. In contrast to either polyphenylene or polyacetylene, maximum conductivity levels achieved with poly (phenylene vinylene) were considerably lower (3 S/cm), perhaps not surprising in light of the low degree of polymerization in the starting polymers. The calculated bandwidth (VEH technique) of the highest occupied π band of poly (phenylene vinylene) is about 2.8 eV [266].

Polydiacetylenes

Polydiacetylens are usually produced via a solid-stae reaction of single crystal, substituted diacetylenes RC≡C-C≡CR [267, 268]. under favorable packing conditions, which are dominated by R groups, a single crystal polymer with highly one-dimensional electronic properties is obtained.

The properties of PDAs were reviewed in 1985 by Bloor [269]. Substantial interest in PDAs has ensued since then, and a wide array of research efforts have uncovered new properties and insights. The forms in which PDAs can be structured are numerous: bulk singlecrystals [269], multilayer films [270, 271], monolayer films in both the Langmuir [271] and self-assembled [272] form, vesicles suspended in liquids [273], and as nanocomposite components integrated into inorganic host matrices [274]. Properties of substantial interest include their high nonlinear optical susceptibility [275], ultrafast optical response [276], and strong structural anisotropy imposed by the highly aligned, linear backbones. However, the most deeply investigated aspect of PDAs are the chromogenic transitions they exhibit.

Polymethineimine

Although a large number of polymers with conjugated carbon-nitrogen backbones do exist, the unsubstituted polymethineimine, $(CH{=}N)_x$, has been synthesised by Wohrle et al. [277]. By ab-initio quantum chemical calculations Karpfmen suggested an alternating structure like trans-PA and this suggests the possibility of soliton excitations along the chain [278]. The ionization potential value of polymethineimine is predicted to be order of 8eV which is ~3.3 eV higher than polyacetylene.

Polyvinylene Sulfide

Polyvinylene Sulfide (PVS), (-CH=CH-S), is the simples conjugated polymer based on sulfur, carbon, and hydrogen. Its saturated counterpart, polymethylene sulfide, (CH_2-S), has been known for a quite long time [279]. As expected, polymethylene sulfide leads to an IP value larger than 7 eV and a highest occupied bandwidth of the order of a few tenths of an electron volt.

6. Methods for Designing Tailor Made Conducting Polymers

Doping often results in chemical instability and poor processibilty in conducting polymers, in literature there has been various attempts to design low band gap conducting polymers, while maintaining their stability and processibilty. In this section we will discuss some of the standard methods employed so far for designing conducting polymers with low band gap.

Substituents determine whether electropolymerization occurs or whether soluble products are formed.Effect of substituents on the band structure of PA has been investigated by many researchers like, fluorinated polyacetylens [280], highly conductive new aniline copolymers containing butythio substituents have also been successfully prepared [281] with conductivity of the order of 1S/cm. Substitution of thiophene monomers with appropriate 3-substituents induce a "push-pull" effect on the n-electrons of their respective polymers and change the electrical conductivity of the polymer [282]. Thus, the electrical conductivity of poly(3-methylthiophene) is 100 times greater than that of polythiophene. Sometimes, substitution may decrease the conductivity of the polymer but resulting polymer may have high electronic affinity and may be more stable for example, polypyrrole films which are substituted with alkyl groups in the 1-position of the monomer units electrooxidize anodic of polypyrrole by ca. 800 mV. As a result, these films are more oxygen stable. However, 1-alkyl-substituted films are less electrically conducting than the parent polypyrrole, an effect attributed to steric constraints imparted by the bulky substituents. For example, while polypyrrole has an electrical conductivity of ca. 100 S/cm, 1-methyl, 1-ethyl, or 1-n-propyl polypyrroles have conductivities of only 10^{-3} S/cm [283]. Thus by substituents, one can improve the solubility, bandgaps and increase polarizabilty and improve other properties of conducting polymers.

Copolymerization is also very effective technique used so far in literature to design new conducting polymers. Cyclodiborazane-dithifulvene copolymers [284], copolymers of fluorine, and phenothiazine-quinoline coplymers [285]. Copolymers of aniline and pyrrole have also been reported [286–289] and which show good conductivity and better solubility. Tuning electronic properties to a particular value is easily possible by synthesizing periodic co-polymers. The electronic properties of the hypothetical thiopene copolymers: poly (thienylenecyclopentadienylene) (PThS), poly (thienylene-oxocyclopentadienylene) (PThOPD) and poly (thienylenethiocyclypenta-dienylene) (PThTPD) have also been theoretically investigated [290]. Novel carbazole-based co-polymers [291] with different co-monomers have been synthesized.

By using ladder polymerization technique, one can also design low-band gap new conducting systems. The electronic properties of polyacene, polyacenacene, polyphenanyhrene, polyphenanthro-phenanthrene and polyperinapthalene ahve been investigated by many theoreticaians [292, 293]. Using semiemperical methods ground state and excited state properties for phenylene oligomers are being investigated [294] and thiopene polymers have been synthesized with decreased band gap-values [295]. Various other polymers like poly (aroylene benzimidazoles), polyepoxyloxanes [296], and ladder polymers with thienylene [297] units have been studies. Unique new ladder polymer (polyindenoindenes) consisting of condensed succession of six- and five-membered conjugated carbon rings have been synthesized [298]. These polymers are candidate for new materials with unique electronic properties.

7. Current Applications and Future Challenges

The new devices made of conducting polymers are going to be used in every phase of life on earth, as well as in space Compared to other existing technologies, conducting polymers are lightweight, take up less space, and are less expensive to manufacture. They are also flexible, and in many cases unbreakable. These characteristics make them excellent for use in space vehicles, for human or robotic exploration and satellites. For example, the flexible and lightweight nature of these devices would be suitable to introduce built-in computers in space suits, with associated sensors to monitor the health of astronauts while they perform extra-vehicular activities. These devices could also be beneficial for tele-medicine in space due to their flexible nature that can follow the contours of the body. Conducting Polymer actuators are also being explored to be used in micro-robots, for un-manned space missions utilizing micro-satellites. To further qualify these devices for use in the harsh environment of space, more testing is needed to determine reliability, with regard to ionizing radiation, solar UV, and extreme temperatures. Apart of the use of conducting polymers in the light weight and rechargeable batteries [67, 299, 300], solid state batteries [301, 302] and in light emitting diodes, conducting polymers are expected to find places in molecular electronics. Recently, Hudak presented report on quantitative evaluation of conducting polymers (polypyrrole and polythiophene) as active materials for the positive electrode in rechargeable aluminium batteries operating at room temperature [303]. Prakash Sengodu et al. reviewed recent advances in synthetic methods and functions of conducting polymer in hybrid composites and their application in lithium ion batteries [304].

Conjugated polymers in the nondoped and doped conducting state have an array of potential applications in the microelectronics industry. Conducting polymers are effective discharge layers as well as conducting resists in electron beam lithography, find applications in metallization (electrolytic and electroless) of plated through-holes for printed circuit board technology, provide excellent electrostatic discharge protection for packages and housings of electronic equipment, provide excellent corrosion protection for metals, and may have applications in electromagnetic interference shielding [305]. Wu et al. developed ultralight, high-performance electromagnetic interference (EMI) shielding graphene foam (GF)/poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) composites [306]. Intrinsically conducting polymers, especially PANI and PPY, are most promising alternative candidates for EMI shielding due to their lightweight, which is of critical importance in aerospace applications, corrosion resistance, ease of processing, and tunable conductivities [307].

The chemical properties of conducting polymers make them very useful in sensors [308]. A large number of gas sensors use conducting polymers (CPs) because they offer great design flexibility [309, 310]. They can form selective layers in which the interaction between the analyte gas and the conducting matrix generates the primary change of a physical parameter in the transduction mechanism. Jiri Janata et al. recently discussed that sensors based on chemical modulation of electronic properties of CPs resulting from their interaction with gases and concluded that the 'tunability' is an important bonus of CPs that aids the preparation of a variety of sensing layers but it can be troublesome where performance independent of ambient factors is desired [308]. There are few recent reviews which deal with fundamental and technological incentive for ICP composite sensors and the sensing properties [311–313].

Highly intimate contact between an electrode and a living neuron is strongly desired by both basic neuroscientists and engineers seeking to develop more effective neural prostheses. Conducting polymer coatings have been proposed a way to improve the intimacy of the cell-electrode connection. A nanostructured "fuzzy" polymer coat increases electrode surface area, lowering the electrical impedance [314]. Polymer coatings can also contain biomolecules to attract neurons and promote their adherence to the electrode [315]. It has been found that conducting polymer poly-(3-(2-ethylhexyl)-thiopene) (EHPT) is able to significantly increase the current across a lipid bilayer [316]. N.K. Guimard et al. presented a demonstration on the significant impact of conducting polymers in the biomedical field [317].

Conducting polymer nanostructures have received increasing attention in both fundamental research and various application fields in recent decades. In the past decade, conducting polymers nanostructures have become a rapidly growing field of research, because they display new properties related to their nanoscale size and have greatly improved the performance of devices [318–324]. Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. Compared to metals, organic conductors can be expensive requiring multi-step synthesis. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis. One of the major problems with conducting polymers is the non-processibility by solvent or multitechniques. Most of them are insoluble in common solvents and undergo degradation before reaching the melting point. Also they have poor mechanical strength and are environmentally unstable. Many researchers have succeeded in overcoming these problems [325–327] and are generating polymer composites and blends which can show better stability and mechanical strength [328, 329].

Factors driving market growth include increasing acceptance of conductive polymers in automobile and diesel sectors, and growing demand for high-performance, lightweight, and low cost materials for electrical and electronics product components and devices. Much research will be needed before many of the above applications become a reality. The stability and processibilty both need to be substantially improved if these polymers are to be used in the market place.

Challenges arise due to the sensitivity of the polymers to variations in their fabrication, time and temperature dependent effects, and nonlinearity of their coupled mechanical, physical and chemical properties. It is also of importance that conducting polymers perform their functions in dynamic environments over a wide range of temperatures and frequencies. Besides the experimental investigations required to address the outlined problem areas, there is a need to advance computational material science of conducting polymers. It is important in this regard that modelling and simulation are treated as an integral part of design and manufacturing processes.

Competing Interests

The author declares that he has no competing interests.

Authors' Contributions

The author wrote, read and approved the final manuscript.

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