CHAPTER II

THEORY AND LITERATER REVIEW

2.1 Introduction to conjugated polymers

The search for conducting polymers began at the end of the 1970s when an increase in conductivity of 12 orders of magnitude was observed in polyacetylene upon charge transfer doping [21]. For their groundbreaking work in this area, MacDiarmid, Heeger, and Shirakawa were awarded the Nobel Prize in Chemistry in 2000 [3]. Excellent introductions into the field of organic electronics are their Nobel lectures [21, 37]. Intrinsic conducting plastic materials and semiconductors, both electron (n-type) and hole transport (p-type) materials with band-like structures, could now be made. Since the early work, many innovative materials in pure form have been developed and characterized for the usage in electronic applications. An overview of the conductivity of different materials from insulators to metals and the span covering organic materials is shown in **Figure 2.1**.

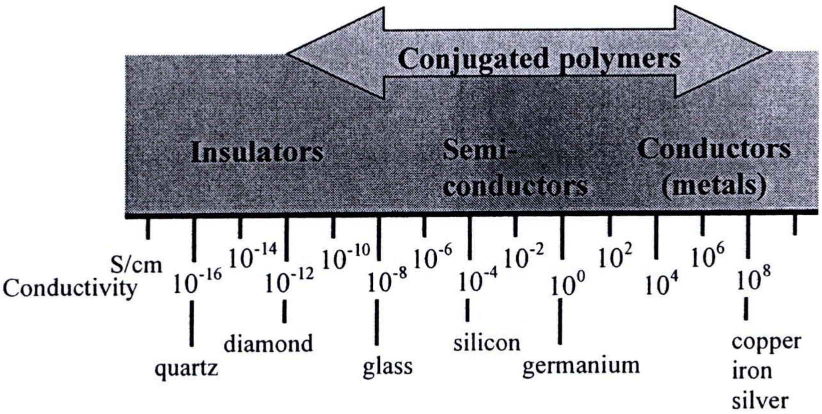


Figure 2.1 Conductivity of different materials.

2.2. Classification of conjugated polymers

Because of the instability of polyacetylene in the environment, the potential of using other types of conjugated molecules as a substitute has been studied. A number of conjugated polymer (CP) chains consisting of only unsaturated carbon atoms in the backbone or carbon atoms with electron-rich heteroatoms or even totally non-carbon atom backbones have since been synthesized [38]. A simple classification of conducting polymers on the basis of chain composition is shown in **Figure 2.2**.

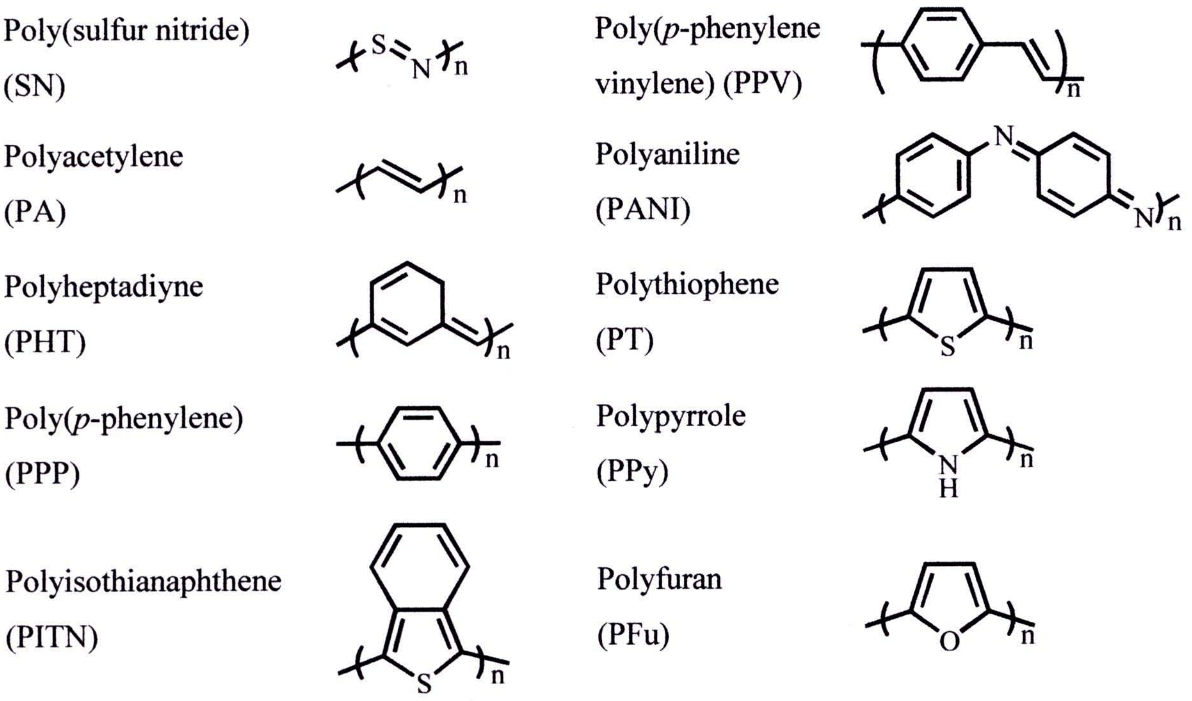


Figure 2.2 Molecular structures of examples of conjugated polymers.

Polyvinylenes, polyarylenes, and polyheterocycles are the major classes of conducting polymers. Polyvinylenes are well known polymers, which have good thermal stabilities and high electrical conductivities [5]. Poly(*p*-phenylene), polyazulene, and poly(*p*-phenylene vinylene) belong to the family of polyarylenes or polyaromatics. Poly(*p*-phenylene) was the first non-acetylenic hydrocarbon polymer that showed high conductivity on doping which was demonstrated in 1980 [39]. This triggered further research for finding other conducting polymers. Many polyheterocyclics also could be added to the list of organic conducting polymers such as polypyrrole, polythiophene, and polyfuran, all having a five membered ring structure with one heteroatom like nitrogen or sulfur or oxygen [40].

Polyacetylene remains the most crystalline conductive polymer but is not the first conductive polymer to be commercialized. This is due to the fact that it is easily oxidized by oxygen in the air and is also sensitive to humidity. Other polymers studied extensively since the early 1980s include polypyrrole, polythiophene (and various polythiophene derivatives), poly(*p*-phenylene vinylene), and polyaniline. Polypyrrole and polythiophene differ from polyacetylene most notably in that they may be synthesized directly in the doped form and are very stable in air. Their conductivities are low, however, only around 10^2 S/cm, but this is enough for many practical purposes [3].

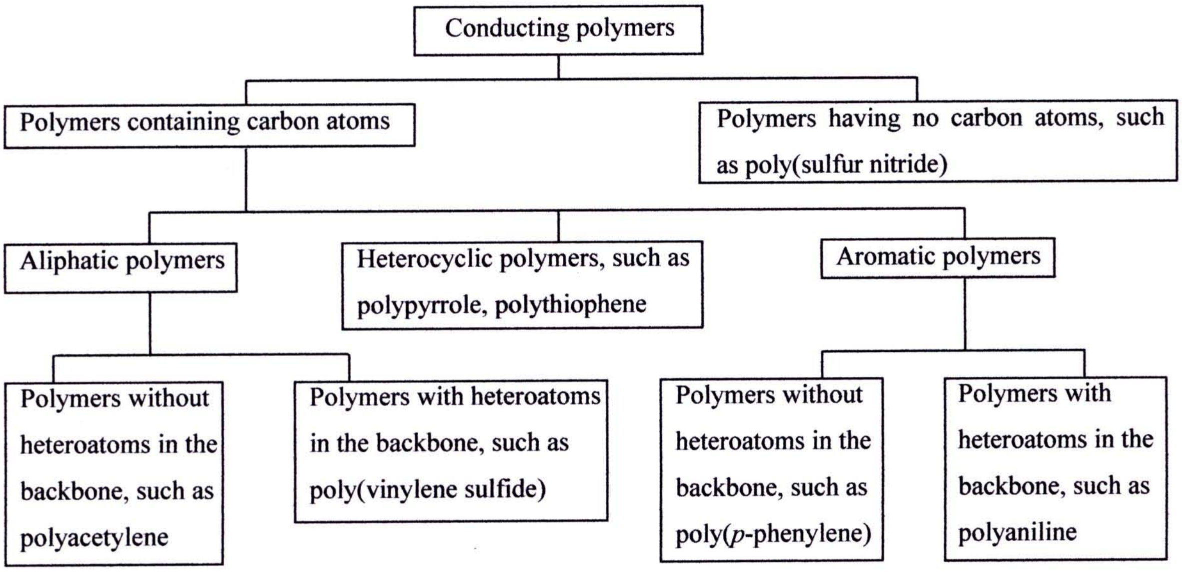


Figure 2.3 Classification of conducting polymers.

2.3 Conjugated polymers: organic semiconductors

Conjugated polymers are organic polymer semiconductors. A conductive polymer is an organic polymer semiconductor, or an organic semiconductor. An organic semiconductor is any organic material that has semiconductor properties. A semiconductor is any compound whose electrical conductivity is between that of typical metals and that of insulating compounds [41].

These polymers consist of alternating single and double bonds, creating an extended π-network. Electron movement within this π-framework is the source of conductivity, **Figure 2.4**, with respect to electronic energy levels and hardly differs from inorganic semiconductors. Both have their electrons organized in bands rather than in discrete levels and their ground state energy bands are either completely filled or completely empty. The band structure of a conjugated polymer originates from the interaction of the π-orbital of the repeating units throughout the chain

Analogous to semiconductors, the highest occupied band (originating from the highest occupied molecular orbital (HOMO) of a single pyrrole unit) is called the valence band, while the lowest unoccupied band (originating from the lowest un occupied molecular orbital (LUMO) of a single pyrrole unit) is called the conduction band. The difference in energy between these energy band levels is called the band gap energy or simply, band gap (E_g). Generally speaking, because conducting polymers possess delocalized electrons in π-conjugated system along the whole polymeric chain, their conductivity is much higher than that of other polymers with no conjugated system. These latter non-conjugated polymers are usually known to be insulators.

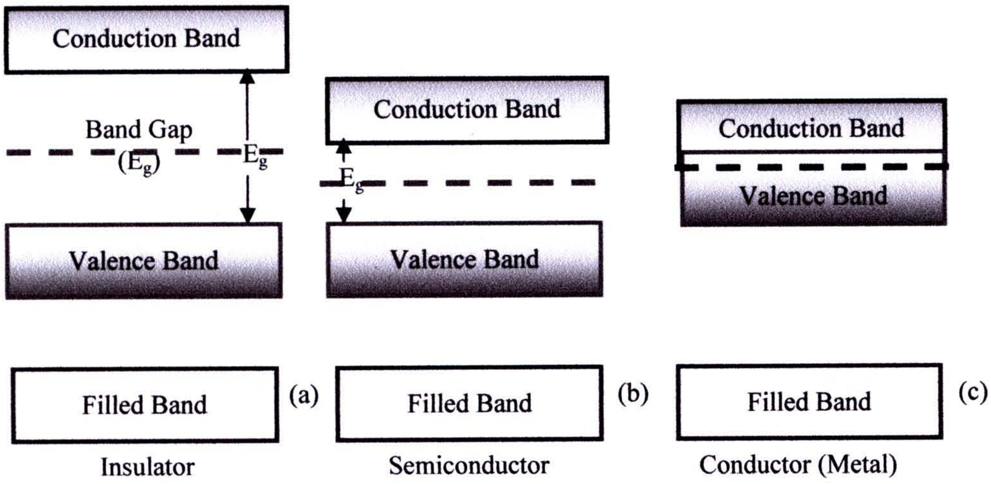


Figure 2.4 Energy band gaps in materials.

The difference between π-conjugated polymers and metals is that in metals, the orbitals of the atoms overlap with the equivalent orbitals of their neighboring atoms in all directions to form molecular orbitals similar to those of isolated molecules. With N numbers of interacting atomic orbitals, there would be N molecular orbitals. In the metals or any continuous solid-state structures, N will be a very large number (typically 1022 for 1 cm^3 metal piece). With so many molecular orbitals spaced together in a given range of energies, they form an apparently continuous band of energies

In insulators, the electrons in the valence band (VB) are separated by a large gap from the conduction band (CB). However, in conductors like metals, the valence band overlaps with the conduction band. In semiconductors, there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperature. The position of the Fermi level which relates to the conduction band is a crucial factor in determining electrical properties.

The conductivity of the metal is due either to partly-filled valence or conduction band, or to the band gap being near zero, so that with any weak electric field the electrons easily redistribute. Electrons are excited to the higher energy bands and leave unfilled bands or hole at lower energy. Metals and conducting polymers exhibit opposite directions of conducting behavior as a function of temperature for metallic materials, (some of which become superconducting below certain critical temperature, T_c) while it generally decreases with lowered temperature for polymeric semiconductors and insulators.

Since π-conjugated polymers allow virtually endless manipulation of their chemical structures; the control of the band gap of these semiconductors is a research issue of ongoing interest. This "band gap engineering" may give the polymer its desired electrical and optical properties. Reduction of the band gap to approximately zero is expected to afford an intrinsic conductor like metal [21].

2.4 Applications of conducting polymers [42]

The extended π-systems of conjugated polymer are highly exposed to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to methodically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state.

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes this electro activity, as shown in **Table 2.1**.

Table 2.1 Applications of conducting polymers.

Group 1	Group 2
electrostatic materials	molecular electronics
conducting adhesives	electrical displays
electromagnetic shielding	chemical biochemical and thermal sensors
printed circuit boards	rechargeable batteries and solid electrolytes
artificial nerves	drug release systems
antistatic clothing	optical computers
piezoceramics	ion exchange membranes
active electronics (diodes transistors)	electromechanical actuators
aircraft structures	smart structures

2.5 Effect of doping

The doping is an addition of an agent into the organic chemical and is expected to improve the conductivity of the polymer. Reversible "doping" of conducting polymers, with associated control of the electrical conductivity over the full range from insulator to metal, can be accomplished either by chemical doping or by electrical doping. Concurrent with the doping, the electrochemical potential is moved either by a redox reaction or an acid base reaction into a region of energy where there is a high density of electronic states; charge neutrality is maintained by the introduction of counter-ions. Consequently, doped conjugated polymers are good conductors for two reasons [21]:

1. Doping introduces carriers into the electronic structure. Since every repeating unit is a potential redox site, conjugated polymers can be doped n-type (reduced) or p-type (oxidized) to a relatively high density of charge carriers.

   p-type

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

n-type

$$(\pi\text{-polymer})_n + [\mathrm{Na}^+(\text{naphthalide})^\bullet]_y \longrightarrow [(\mathrm{Na}^+)_y((\pi\text{-polymer})^{-y}]_n + (\text{naphthalene})^\bullet$$

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

2. The attraction of an electron in one unit to the nuclei in the neighboring units leads to carrier delocalization along the polymer chain and to charge carrier mobility, which is extended into three dimensions through interchain electron transfer.

Disorder, however, limits the carrier mobility and in the metallic state, limits the electrical conductivity. Indeed, research directed towards conjugated polymers with improved structural order and hence higher mobility is a focus of current activity in the field. Charge injection onto conjugated, semi-conducting macromolecular chains, or "doping", leads to the wide variety of interesting and important phenomena which define the field.

2.6 Mechanism of Conductivity [21]

In inorganic semiconductors like silicon or germanium, the strong coupling between the constituting atoms and the long-range order leads to the delocalization of the electronic states and the formation of allowed valence and conduction bands, separated by a forbidden energy gap. By thermal activation or photo excitation, free electrons are generated in the conduction band, leaving positively charged holes in the valence band. The transport of these free charge carriers is described by quantum mechanism.

As we know, most polymers are insulator because their electrons are localized, that is, each of the electrons is attached to its own nucleus. In organic solids, intramolecular interactions are mainly covalent, but intermolecular interactions are due to much weaker Van der Waals and London forces. However, the conducting or semiconducting polymers have the conjugated double bonds. The double bond consists of a σ-bond and a π-bond. The electrons in the σ- bonds form the backbone of the chain, dominating the mechanical properties of the polymers. Due to the π-orbital overlap of neighboring atom of the conjugated structure, the π-electrons delocalize along the entire chain, which provides their semiconducting and conducting properties. The σ-bonds of completely filled, low-lying energy bands have a much larger ionization potential than π-electrons (and a much larger band gap) and thus do not contribute in a major way to the electrical and optical properties. The π-bonds, however, form an energy band in which each carbon atom contributes one electron, and thus the band should be half-filled because of the spin degeneracy. In metals and conventional semiconductors, charge transport occurs in delocalized states. Such a model is no longer valid in low conductivity organic semiconductors, where a simple estimate shows that the mean free path of carriers would become lower than the mean atomic distance. In these materials, the π-electrons are delocalized within a molecule and the carrier transport occurs through hopping of charges from one molecule to another.

Since the π-conjugated system in conducting polymers extends over the whole polymer chain, the conducting polymers can be regarded as one-dimensional polymer semiconductors. In these materials, in addition to direct electron and hole excisions across the semiconductor band gap, the one-dimensional system may support a host of exotic carrier types like solitons (topological defects without charge, with spin ½), polarons (electrons and holes, self-trapped by carrier-lattice interactions) and bipolarons (two carriers with charge of the same sign, bound by lattice distortion).

2.7 Polypyrrole

Pyrrole was known to form a conductive pyrrole black *via* spontaneous polymerization, and its history can be dated back in 1916 [43]. In 1968 [44], it was noted that pyrrole could be electrochemically polymerized using a variety of oxidation agents to give a black conducting powder. It can be synthesized in both aqueous and non-aqueous solution during electrochemical polymerization. Polypyrrole has a relatively high conductivity and environmental stability in the conducting state. It is stable in a wide range of potential range, during thousands of charge-discharge cycles, and under properly selected conditions its response is fast. In contrast to polyaniline it can operate both in acidic and neutral solutions, which makes the polypyrrole electrode attractive for use as sensors material in the bioelectroanalytical chemistry. Polypyrrole is a relatively air stable organic conducting polymer, which suffers from poor processability. The use of new tailor made reactive statistical copolymers for the synthesis of sterically stabilized polypyrrole colloids is described [45]. For all of these reasons polypyrrole has been an interesting material to study.

Pyrrole belongs to the well-known aromatic heterocyclic ring monomers. Polypyrrole's macromolecular structure is generally known to consist of α-α′ linkages, consecutively rotated 180°, and which are believed to create a one-dimensional polymer structure, though there are probably a number of α-β′ linkages, which lead to a two-dimensional polymer structure [46] (**Figure 2.5**).

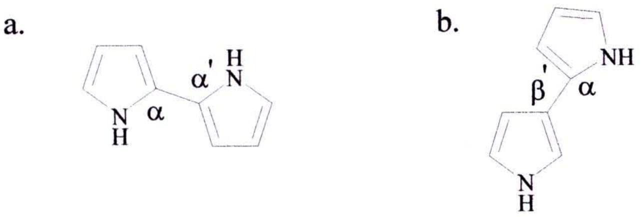


Figure 2.5 Proposed chemical structures for the growth of polypyrrole. (a. α-α′ linkages; b. α-β′ linkages)

In an undoped state, polypyrrole is generally considered to have a so-called benzoid structure and is usually called the neutral state of polypyrrole. Usually conducting polymers in the neutral structure has low (in high crystallinity, 10^{-10}-10^{-6} S cm^{-1}) or no conductivity. Photoexitation or thermal-excitation can only increase very less charge carriers. Removal or addition of electrons from the chain of the polymers to increase the charge carrier can be done by "doping". This "doping" is really a redox process slightly different from doping in conventional semiconductors which can be accomplished through the introduction of impurities. That means "p-doping" or oxidation with an anion accepting the removed electrons from the conducting polymer chain, and "n-doping" with reduction or donation of electrons to the conducting polymer chain. The redox process can be done by chemical electron donators or acceptors, or electrochemical processes.

As doping of the neutral polymer proceeds, the formation of structural and electronic defects will take place. At low concentrations, the first predominant kind of defect will be polaron, which give rise to the formation of two localized states within the band gap, one split off from the top of the valence band (the HOMO level is pushed up in energy), and the other split from the bottom of the conduction band (the LUMO level is pushed down in energy). Further charge transfer from the polymer chain (*i.e.*, higher doping levels) may then proceed either by formation of another polaron or by removal of the single electron in the lower polaron level. In most cases it is found to be favorable to form a doubly charged species-bipolaron.

Figure 2.6 shows the neutral, polaron, and bipolaron structures of polypyrrole, with the corresponding schematic band structures as well as the possible electronic transition for each of them.

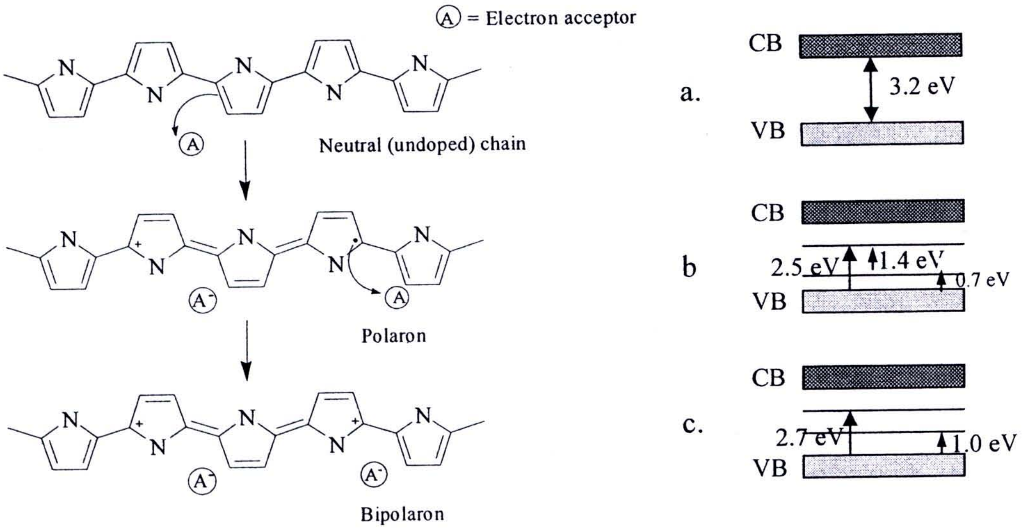


Figure 2.6 Neutral state, polaron and bipolaron structures for lightly and heavily doped polypyrrole, respectively, with their corresponding schematic band structures and the allowed electronic transitions.

For polypyrrole, positively charged polaron and bipolaron have already been illustrated. Negatively charged polaron and bipolaron in practice, they do not exist as polypyrrole cannot be n-doped stable. In an actual conducting polymer structure, the entire constant propagation chain would first have to become nearly saturated with polaron before bipolaron formation commence. This is also supported by spectroelectrochemical studies, at low doping levels, spectra corresponding to polaron are first seen, before bipolaron spectra occur. In UV-VISNIR spectrum of polypyrrole, the single prominent valence-conduction (π-π*) band transition in the pristine polymer (at ca. 388 nm) is accompanied by three additional polaron based transitions at low doping level (ca. 590 nm, 885 nm, 1771 nm), which finally evolve into two bipolaron based bands (ca. 459 nm, 1240 nm) at higher doping level.

In bipolaron structure, the two charges are not isolated on specific monomer units, but rather, are delocalized over several (generally 6 to 8) monomer units, but not the entire constant propagation lattice.

Therefore, at high dopant concentrations the bipolaron, which are spinless, can become mobile under the application of an electric field, thus giving rise to the high conductivity observed in conducting polymers. The gap between two bipolaron bands never goes to zero, thus polypyrrole cannot really reach the metallic state [13].

2.8 Synthesis of Polypyrrole

Polypyrrole can be prepared in various forms, depending on the method used and on the preparation conditions. A general difficulty of the reproducible polypyrrole preparation arises from its complexity. The structure and hence the properties of the resulting polypyrrole are strongly influenced by a number of variable (*e.g.*, the oxidation potential, the monomer concentration, the preparation temperature) that are not perfectly controlled. Therefore, the results on polypyrrole vary widely. Two basic methods are used for the preparation of polypyrrole: chemical and electrochemical synthesis [6, 7, 13]. The chemical synthesis of polypyrrole produces easily arbitrary amounts of polypyrrole in various forms, but its productivity is poor. The electrochemical synthesis of polypyrrole can be conveniently carried out. An advantage of the electrochemical methods is that the preparation process can be simply controlled through the current or the applied potential and the charge consumed. A disadvantage is that polypyrrole can be prepared only in the form of a relatively thin film deposited on the surface of a conducting material, but its films is rather fragile

2.8.1 Chemical Polymerization of Polypyrrole [13]

The chemical synthesis of polypyrrole is based on the chemical oxidation of the pyrrole monomer. Oxidation can take place in a gas phase (oxidation by I_2 vapor) or in an aqueous or nonaqueous solution, generally with oxidants involving $(NH_4)_2S_2O_8$, H_2O_2, and many kinds of salts containing transition metal ions (*e.g.* Fe^{3+}).

The mechanism consists, as a first step, of the oxidation of the monomer to form a radical cation. After the initial oxidation step, there is a coupling reaction, followed by a deprotonation and a one-electron oxidation in order to regenerate the aromatic system. From a mechanistic point of view, there are two unique stages to the coupling reaction (**Figure 2.7**). There is the initial coupling reaction, which involves the coupling of pyrrole monomers to produce the dimeric intermediates, and there is the steady-state coupling reaction, which involves the reaction between the pyrrole monomer and the oligomeric and polymeric intermediates. Considering the coupling reaction in the initial stages of the reaction, the originally formed radical cation could undergo a radical coupling reaction with another radical to form a dimer, or it could react like an electrophile and add to a neutral monomer. Chandrasekhar [7] reports that in a typical chemical polymerization, after initial radical ion generation, rather than a radical-radical coupling as in the generic electrochemical mechanism above, coupling occurs between radical and monomer. This is due to the fact that in the bulk of the reaction environment, where the radical initiators are generated, the concentration of the monomer is in excess, thus radical-monomer combination (generating another radical) is more likely to be the next propagation step after radical generation [7].

For chemical polymerization, the effect of solvent and of the redox potential of the polymerization medium on polymer quality and morphology can be very strong. For example, Miyata and coworkers investigated typical chemical synthesis of polypyrrole using anhydrous $FeCl_3$ as oxidant/dopant in various solvents. They found that while methanol appeared to be the best solvent for optimal conductivity and morphology, the equilibrium redox potential of the solution, controllable via the relative concentrations of the monomer and oxidant and via addition of $FeCl_3$, was a more important determinant of polymer quality. The polymer produced in this way also showed a more ordered, fibrillar morphology, and stretched films.

For polypyrrole, control of morphology, conductivity, doping, and related factors is a little more difficult in chemical polymerizations. Slight changes in temperature, concentration and other factors will yield substantial differences in polymer properties, and even identical synthetic procedures never yielding exactly the same polymer each time.

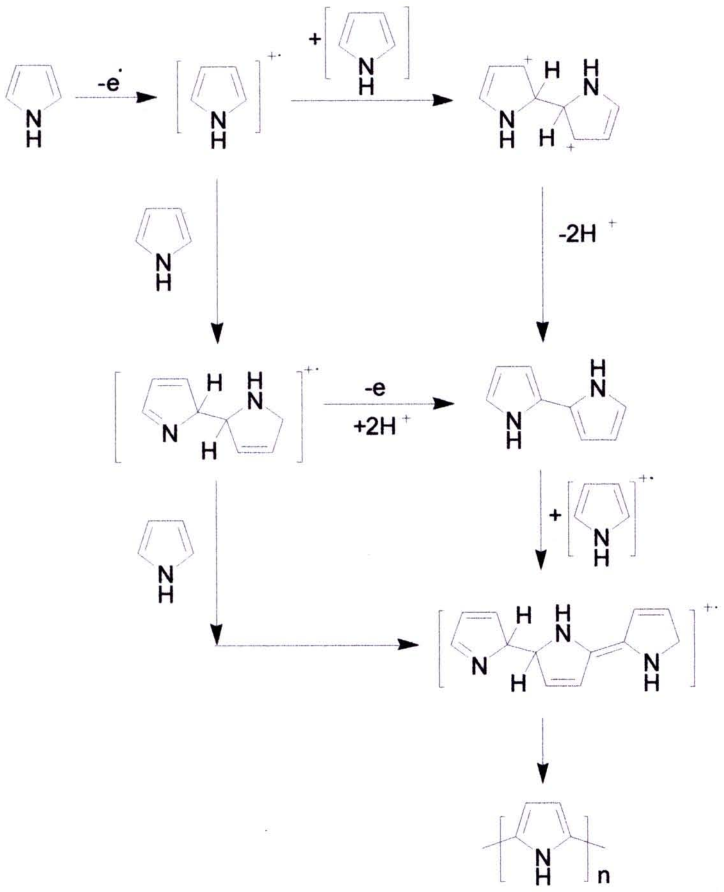


Figure 2.7 Mechanism of chemical polymerization of polypyrrole

Chemical polymerization is a better method for the preparation of a large quantity of polypyrrole because it is free from the restriction of the electrode shape. Except for large amounts of powdery polypyrrole, the deposition of conducting polypyrrole films on conducting, and non-conducting materials, and porous glass is possible by this method. The anions present in the solution are simultaneously incorporated as the polypyrrole dopant during the chemical synthesis.

2.8.2 Electrochemical Polymerization of Polypyrrole

Many mechanisms for the electropolymerization of pyrrole have been made, but the most widely accepted one is that of Diaz *et al* [47]. The electrochemical synthesis of polypyrrole is based on the anodic oxidation of the pyrrole monomer on the working electrode. During the polymerization, the resulting polymeric film is simultaneously oxidized and doped with the anions present in the background electrolyte. The electropolymerization can take place in either aqueous or non-aqueous solutions.

Like chemical polymerization, the initial step is the generation of the radical cation, but in the next step, the mechanism of the electrochemical polymerization is different from the chemical polymerization [21, 48]. The second step involves monomer dimerization by radical-radical coupling, in which two protons are eliminated from the doubly charged dihydromer and a neutral species is formed. As the dimer is more easily oxidized than the monomer because of the increased stability of the formed radical cation, it is reoxidized to the cation and undergoes a further coupling with the monomeric radical cation. **Figure 2.8** gives the pathway of electrochemical polymerization of pyrrole [7]. This pathway shows the following common features:

1. The initiation step is pyrrole radical generation via electrochemical oxidation;
2. Propagation is via
    a). radical-radical coupling;
    b). elimination two protons from the radical-radical intermediate species, then generating the dimer;
    c). electrochemical oxidation of the dimer, generating another oligomeric radical;
    d). combination of this or similar oligomeric radicals with monomer radicals and repeat of steps 2b and 2c, polymer was built up;
3. Termination is via exhaustion of reactive radical species in the working electrode and accompany oxidative or other chain termination processes.

The termination step in polymerization is not clear and different hypotheses have been proposed. Most researches believe that the reaction with water could be one of the reactions that quenches the polymerization.

The final polymer chain a charge of unity for every three or four pyrrole rings; this charge is counterbalanced by the anion of the electrolyte salt. The elimination of the α protons indicated by this mechanism is consistent with the decrease in the pH value of the electrolyte solution during film growth.

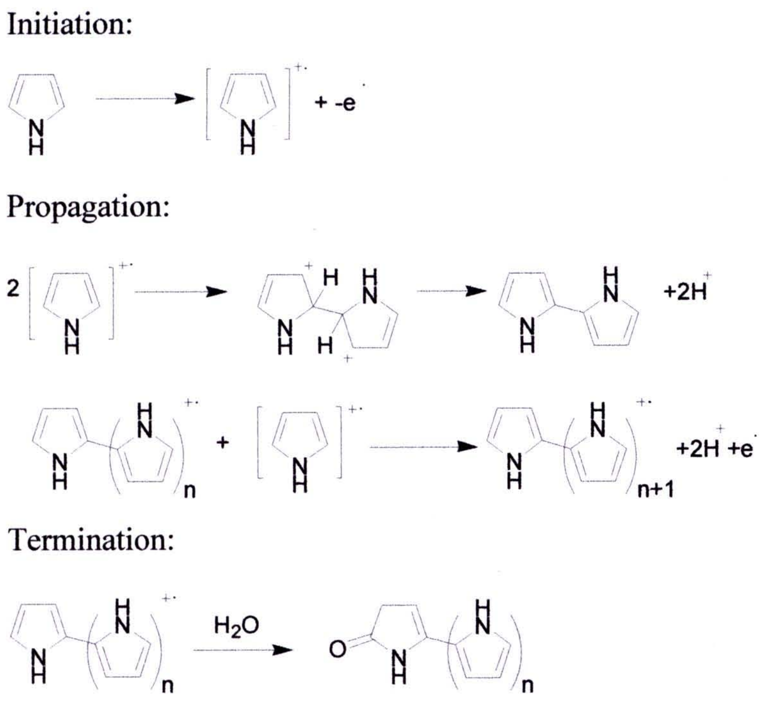


Figure 2.8 Mechanism of electrochemical polymerization

2.9 Conductivity measurement by two point probe technique

Conductivity is a measure of electrical conduction and thus a measure of the ability of a material to pass a current. Generally, materials with conductivities less than 10^{-8} S/cm are considered insulators, materials with conductivities between 10^{-8} and 10^{3} S/cm are considered semiconductors, and materials with conductivities greater than 10^{3} S/cm are considered conductors [21].

In this study, resistivity is determined from a material's resistance (R), which is measured using a two point probe technique. The two point probe technique involves applying voltage (V) across electrodes at the surface of a material and then measuring the change in current (I), according to Ohm's law in Eq. (2.1) [49].

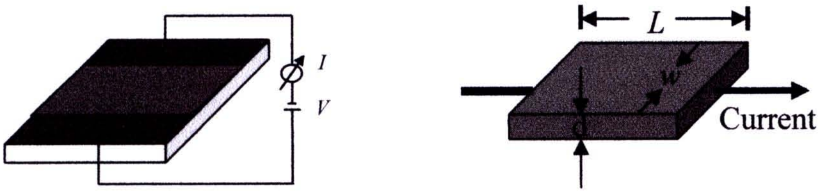
$$R = \frac{V}{I} \tag{2.1}$$

Where: R = Resistance (ohm, Ω)

V = Voltage (volt, V)

I = Current (ampere, A)

Sheet resistance (R) of the films is a common way to express values of thin film resistivity. In general, a two-point probe method (**Figure 2.9**) was chosen to measure the *R* of the film. A model of a conductor film can be depicted as following in **Figure 2.9 (b)**.



(a) (b)

Figure 2.9 (a) two-point probe method for measuring the sheet resistance of thin film; (b) a depicted model of the conductor film with length *L*, width *w*, and thickness d.

This electrical resistance is proportional to the sample's length and the resistivity and inversely proportional to the sample's cross sectional area as shown in Eq. (2.2).

$$R = \frac{\rho\ L}{A} \tag{2.2}$$

Where: ρ □= resistivity (Ω.cm)

A = cross-sectional area or $w \times \mathrm{d}$ (cm^2)

L = length between electrodes (cm)

The electrical conductivity (σ) is the inverse of the electrical resistivity, and is given by Eq. (2.3).

$$\sigma = \frac{1}{\rho} = \frac{L}{RA} \tag{2.3}$$

The units of electrical conductivity in the SI system are siemens per meter (S/m) where the siemens is an inverse of ohm (Ω^{-1}).

2.10 Plasma

As the temperature increases the substance passes from solid to liquid, through gas, to plasma (**Figure 2.10**). The solid, the liquid, and the gas are composed of a very large number of molecules (or atoms). In these phases of matter the heat is an expression of the molecular motion. In these three phases the molecules or atoms are moving as one unit. Plasma is composed of a very large number of free electrons and ions and in this phase of matter the heat is the expression of the separate electron and ion motions. Gas is normally an electrical insulator, that is, electric currents cannot easily pass through it. However, by heating gas to appropriate temperature, physicists found that insulator gas becomes a good electrical conductor. Gas is transformed into plasma which consists of free electrons: the carriers of the electric currents [50].

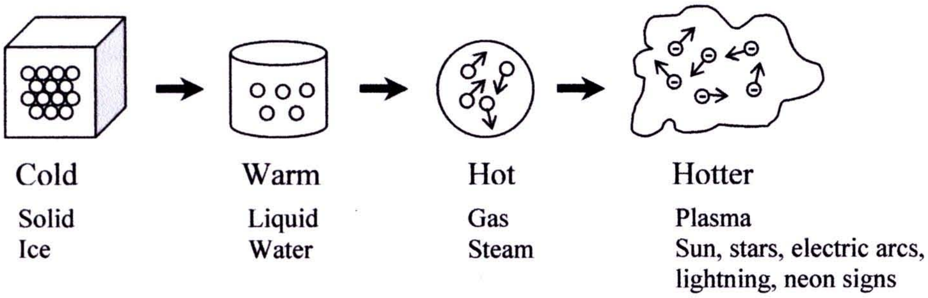


Figure 2.10 The four states of matter; plasma is sometimes referred to as the fourth state.

Plasma is a partially ionized gas containing free electrons, ions, radicals and photons with equal numbers of positive and negative charge carriers. In this situation, plasmas are termed quasi-neutral. Quasi-neutral refers to there being about equal numbers of positive ions and negative electrons in the gas, and thus most of plasmas are electrically neutral. Quasi-neutrality demands that [51]

$$n_i \approx n_e \approx n_s$$

Where: n_i = ion density

n_e = electron density

n_s = plasma density (*i.e.*, the number of particles per cubic meter)

Plasma states can be divided into two main categories: hot plasmas (near-equilibrium plasmas) and cold plasmas (non-equilibrium plasmas). Hot plasmas are characterized by very high temperatures of electrons and heavy particles, both charged and neutral, and they are close to maximal degrees of ionization (100%). Cold plasmas are composed of low temperature particles (charged and neutral molecular and atomic species) and relatively high temperature electrons and they are associated with low degrees of ionization (10^{-4} – 10%). Hot plasmas include electrical arcs, plasma jets of rocket engines, thermonuclear reaction generated plasmas, *etc.* while cold plasmas include low-pressure direct current (DC), Alternating current (AC), radio frequency (RF), microwave (MW) power, and discharges from fluorescent (neon) illuminating tubes. Corona discharges are also identified as cold plasmas.

This research intended to use AC energy to create the plasma, because the energy could give the electric with 50 Hz to generate the plasma. The advantage of this source was the frequency used is lower than others, such as RF and microwave. Besides, the AC source enable the current to alternate flow between two electrodes (the anode and the cathode), when the plasma flowed. In such there is no real cathode or anode since the net flow of charge to either electrode is zero, unlike the DC discharge, and there is no uniquely defined floating potential, either. The electrical particle would then be distributed in the center of two electrodes, instead of one. When the AC reactor is operated, the energy resulted from excess concentration of the particle would not be so high that the thin film would burned.

The energy of the electrons in the plasma produced by a glow discharge is 1-30 eV and their density (10^9-10^{12} cm^{-3}) is dependent on plasma source. For deposition of plasma polymers several types of plasmas can be used, for example; RF, DC, AC, and MW. Possible areas of application of plasma treatment and plasma polymerization are listed below.

1. Electronics (integrated circuits, resistant with a high degree of integration, amorphous semiconductors, etching of fine amorphous ceramics).
2. Electrical engineering (insulators, thin film dielectrics, separators for galvanic elements).

3. Chemical technology (reverse-osmotic, semi-permeable, gas-separation membranes, lubricants, insolubilization).
4. Surface modification (improved adhesion, protective, abrasion-resistant and strengthening coats).
5. Optics (antireflecting and antimisting coatings, improved transparency, optical fibers, laser and optical windows, contact lenses).
6. Textile industry (anti-igniters and antistatic treatment, improved dyeing qualities, hydrophilization, water-repellant properties, anti-creasing).
7. Biomedicine (immobilization of enzymes, organelles and cells, regulation of the release of drugs and pesticides, sterilization and pasteurization, artificial soil, blood vessels, teeth, anticoagulants).

Plasma chemistry includes four types of main reactions: 1) surface reactions of polymers (plasma treatment); 2) plasma polymerization; 3) plasma-initiated polymerization; and 4) plasma reduction .

The individual steps or reactions that are involved in the process of polymer formation in a glow discharge are extremely complex and are dependent on the system. Several important types of phenomena can be identified for the purpose of constructing a general picture of the glow discharge polymerization. This process is represented by the Competitive Ablation and Polymerization (CAP) mechanism schematically shown in **Figure 2.11**. The direct route shown in the figure is referred to as plasma-induced polymerization which is also referred to as plasma-initiated polymerization while the indirect route is referred to as plasma polymerization.

The plasma initiated polymerization comprises exposing a monomer vapor equilibrated with a liquid or solid monomer to a plasma for a short time thereby producing a polymerically active seed and then allowing the polymerically active seed produced in the plasma to come into contact with the surface of the liquid or solid monomer thereby starting polymerization growing in the liquid or solid monomer. Unlike the ordinary plasma polymerization such as the plasma vapor-phase polymerization wherein all the component steps including start of polymerization, growth, migration, recombination, and restart take place in the presence of plasma, the plasma-initiated polymerization occurs in the vapor phase and the subsequent reaction for growth and stop of polymerization occur in the condensate phase. In various fields, [52]such polymers by the plasma polymerization have come to attract growing attention in 1996 to now. The plasma polymerization has been principally used in vapor phase polymerization or applied for surface treatment [53].

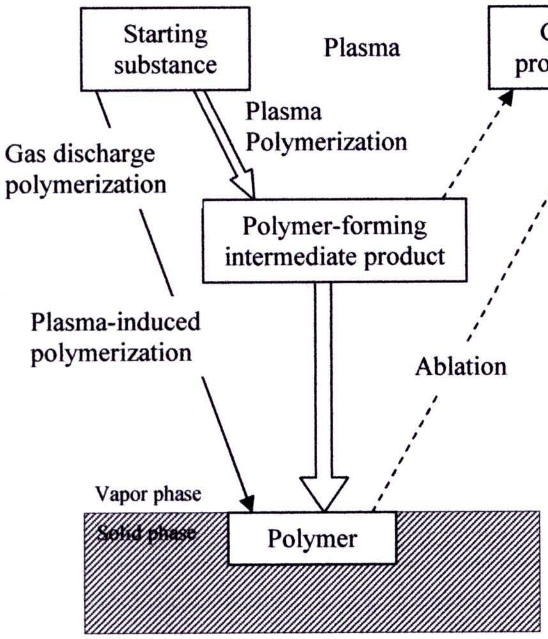


Figure 2.11 General mechanism of gas discharge polymerization.

2.11 Plasma polymerization

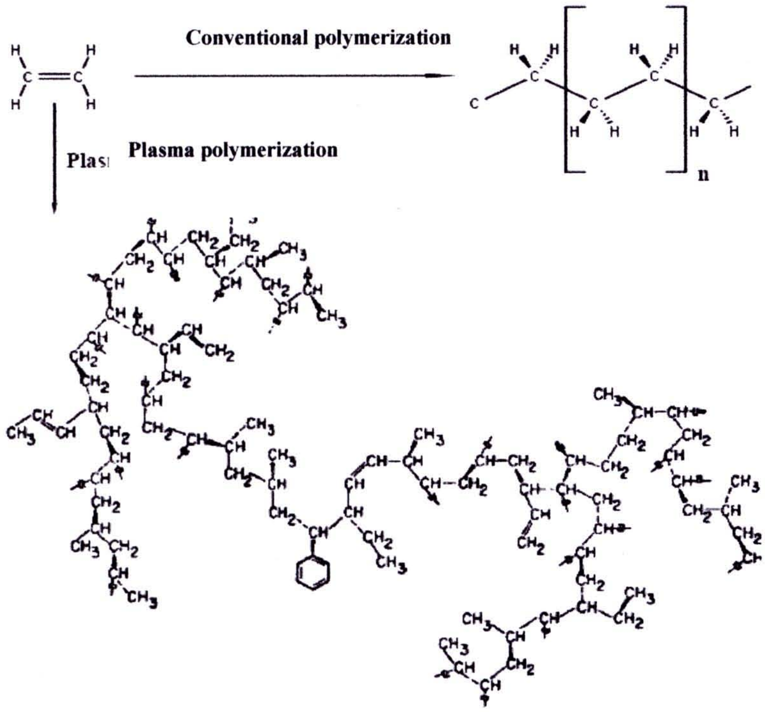
Plasma treatment, which is an electric gas discharge, is typically performed in a vacuum equipment in a pressure range of 0.0075 – 0.075 torr. An electric field, which is [54] applied to the gas under vacuum conditions, causes the acceleration of free electrons. The kinetic energy of the electrons is then high enough for basic reactions like ionization, fragmentation, and excitation of the gas species in the case of the ignition of the plasma, which can be observed by its characteristic visible glow. Atoms and molecules are ionized, excited, fragmented and thus form a highly reactive gaseous mixture, which is able to react chemically with exposed surfaces. The resulting surface properties are mainly dependent on the process gas used and its chemical properties [53].

Plasma polymerization is one of the most important techniques for fabricating thin polymer films (sub-micrometer (μm) range) from almost any organic vapor. Unlike conventional polymers, plasma polymers do not consist of chains with a regular repeat unit (see **Figure 2.12**). The chemical structure and physical properties may be quite different from conventional polymer which is derived from the same starting materials. Plasma-polymerized films are generally chemically inert, insoluble, mechanically tough, thermally stable, and have been used in a wide variety of applications such as permselective membranes, protective coatings, electrical, optical and biomedical films. The process offers several advantages over conventional polymer synthesis, as follows

1. the starting feed gases used may not contain the type of functional groups normally associated with conventional polymerization
2. such films are often highly coherent and adherent to a variety of substrates, including conventional polymers, glasses, and metals
3. polymerization may be achieved without the use of solvents
4. plasma polymer films can be easily produced with thicknesses of 500 °A to 1 μm
5. ultrathin, “pinhole-free” films may be prepared through careful control of the polymerization parameters.

It is possible to tailor the films with respect to specific chemical functionality, thickness and other chemical and physical properties [54].

The mechanism of plasma polymerization of organic compounds is very complex. The overall polymer formation is the consequence of many complex reactions, and the polymer deposition rate as well as the properties of polymers are dependent on many experimental factors such as types of electric discharge, conditions of the discharge, geometrical factors of the reaction vessel, and the properties of substrate upon which a polymer deposits.



Conventional polyethylene (PE)
- Linear
- melting point 130°C
- thermoplastic
- colorless
- composition $(CH_2)_n$
- partly crystalline

Plasma polymerized ethylene (PP-PE)
- (highly) crosslinked
- high density
- amorphous
- pinhole-free
- not meltable (duroplastic)
- unsoluble, unswellable
- colorless-black
- composition CH_x ($x = 0\text{-}2$)

Figure 2.12 Polymer prepared from chemical polymerization compared to that from plasma polymerization method [53, 55].

Consequently, the plasma polymerization cannot be specifically described for the general case. However, a series of recent studies has projected reasonable overall mechanisms of the plasma polymerization of organic compounds, which seem to be able to apply in many cases. The overall mechanisms can be represented by

Initiation:

$$M_i \rightarrow M_i^*$$

$$M_k \rightarrow M_k^*$$

Propagation:

$$M_i^* + M_k^* \rightarrow M_i\text{-}M_k$$

$$M_i^* + M_k \rightarrow M_i\text{-}M_k$$

Where i and k are numbers of repeating units (*i.e.*, $i = k = 1$ for the monomer) and the M* are reactive species which can be ions of either charge, an excited molecule, or a free radical. Although the kind of reactive species that play predominant roles in the plasma polymerization has been a subject of debate for past years, there seems to be no conclusive evidence which enables us to exclude any specific species. Therefore, it seems most reasonable to assume that any energetic and/or reactive species being created in plasma can contribute to the overall polymer formation in plasma [56, 57].

Common techniques developed for the synthesis of thin layer conducting polymers include electrochemical growth on modified electrode surfaces, Langmuir–Blodgett deposition, spin-coating and self-assembly of polyelectrolyte structures. These deposition approaches usually require complex experimental procedures, solubility of the starting materials, and often result in less oriented macromolecular structures. Conducting polymers prepared using conventional polymerization procedures result, in most cases, in the formation of insoluble powdery materials which are difficult to convert into uniform, thin layer, ordered networks. Attempts initiated for the generation of processible conducting polymer structures using chemical derivatives of aniline, pyrrole and thiophene, or by employing chemical modification techniques for altering the structures of conventionally synthesized conducting polymers, have not always generated the expected results. These approaches usually require complex synthetic routes, and the purification of the resulting polymer-containing final products are rather difficult. Solubility can also be a disadvantage in some applications. Deposition of liquid-soluble polyaniline-derivatives (*e.g.* sulfonated-polyaniline) on various substrates, for instance, hardly can be considered for biosensor applications. It is still an unsolved problem to learn how to deposit uniform and insoluble thin conducting polymer layers with good adhesion characteristics on various substrate surfaces, starting from soluble polymeric precursors.

Plasma chemistry was recently considered an alternative for overcoming these drawbacks. Pyrrole, thiophene and aniline were mainly investigated for plasma deposition of conductive (conjugated) polymeric layers since these polymers synthesized by conventional polymerization techniques showed promising electrical behavior [58].

In 1998, Cruz and coworkers [14] used the technique of radio-frequency (RF) plasma polymerization to prepare semiconductive polypyrrole and polypyrrole doped with iodine (PPPy/I_2) thin films on glass substrates. Characterization was done by IR, SEM, thermogravimetry and electric conductivity of polypyrrole films, both undoped and *in situ* doped with iodine. The plasma was produced by electric glow discharges with a resistive coupling mechanism at 13.5 MHz frequency, and 18 W. The synthesis was carried out in a vacuum reactor with reaction times from 60 to 300 minutes. The thickness of the films can be expressed as linear functions of the reaction time under the conditions of synthesis considered. The atomic composition of PPPy and PPPy/I films has N/C ratios which are near the N/C ideal ratio (0.25) taken from the structural formula of the polymers. The N/C ratio and the IR data suggest that the films are made of PPPy and that the monomer rings survive the plasma conditions as observed in other similar synthesis. The results also indicated that the films have enough thermal stability to begin the thermal decomposition at 200 °C. The polypyrrole films were obtained conductivity between $10^{-12} \pm 10^{-9}$ S/cm. The conductivity of the films doped with iodine was between $10^{-9} \pm 10^{-3}$ S/cm.

In 2000, Morales and coworkers [30] synthesized polyaniline and iodine doped polypyrrole by RF glow discharge at 13.5 MHz and an average power of 18 W. The polymers were synthesized as thin films of polypyrrole dope iodine with reactions times of 60, 120, 180, 240, and 300 minutes and as thin films of polyaniline dope iodine with reaction times of 60, 120, 135, and 240 minutes. In polypyrrole dope iodine, the optical band energy had an average value of 1.1 ± 0.1 eV. Iodine doped polyaniline presents different optical band energy that depended on the reaction time and evolved from 0.5 to 1.2 eV.

Subsequently, Morales and coworkers [59] used RF plasma to synthesis aniline-pyrrole bilayer polymers dope *in situ* with iodine at 12 W, and reaction time of 360 minute. There were provide sufficient plasma polymer for XPS analysis, SEM, electric conductivity, and IR characterization of thin films composed of alternating layers of different polymers. The results indicated that the plasma technique was capable of forming chemically bonded layered polymers with several possible combinations. The electric conductivity was studied during heating–cooling cycles (heated uniformly from room temperature to 150°C and cooled again to room temperature) so the dependence of the bilayer polymers on temperature could be observed. The behavior was related with the Arrhenius model, with average activation energies of 0.4 ± 0.1 eV in the heating steps and 0.5 ± 0.1 eV in the cooling steps.

In 2002, Borrós and coworkers [22] synthesized undoped and doped iodine plasma polymerized of pyrrole and thiophene at different power (15, 20, 30 W) and 30 second of reaction time. Structural and morphological characterizations of both undope and dope films were performed using FT-IR, XPS, and AFM techniques. This method produced a polymeric network which retained many of the structural characteristics associated with the original precursor molecule. Nitrogen, sulfur and iodine incorporation into the growing plasma polymer layer drops with increasing glow discharge power due to the weaker C-S, C-N and C-I bond linkages present in the monomer. They discovered that iodine atom in these films could conduct the electricity.

In 2002, Kumar and John [23] did the research on the structural, electrical, and optical properties of plasma polymerized pyrrole and iodine doped pyrrole. A comparative studied of the IR spectra of the monomer and polymer pyrrole gave information that the ring structure was retained during plasma polymerization. Iodine doping considerably increased the conductivity of the polymer film and decreased the optical band gap energy. The optical band gap energy values of plasma polymerized pyrrole films and iodine doped film were 1.3 eV and 0.8 eV, respectively.

After that, Kumar and coworkers [25] synthesized plasma polymerized pyrrole carried out in the presence and absence of iodine, and the resulting films were characterized by optical and electrical means. Films were produced in RF (13.56 MHz) plasma under a monomer vapor pressure of 0.2 Torr and at a current density of 20 mA/cm^2. Their infrared spectra were very similar to each other, suggesting that iodine was neither bonded in any manner to, nor strongly interacted with, the pyrrole polymer chains. Based on their infrared spectra, a chemical structure was proposed for the plasma polymerized pyrrole film (**Figure 2.13**). An analysis of the electronic spectra gave band gap energies of 1.3 and 0.8 eV for the undoped and doped PPPy films, respectively

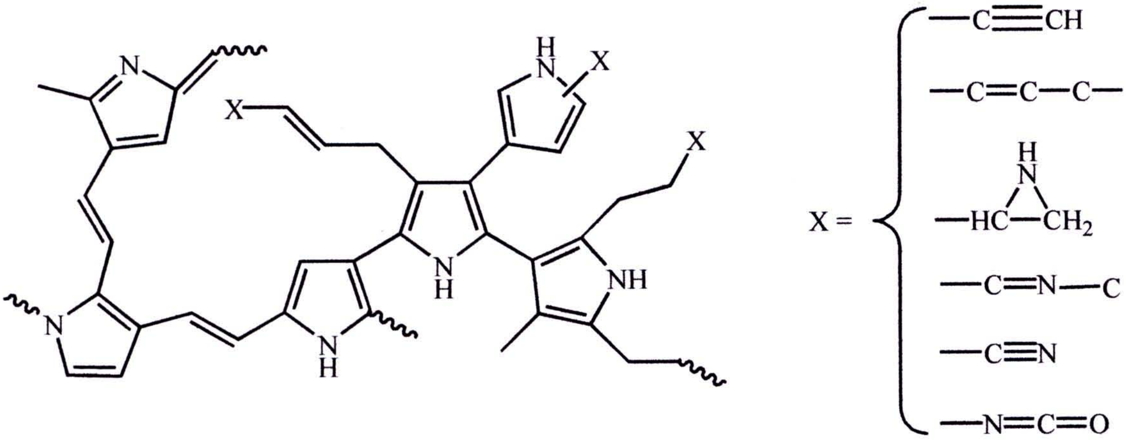


Figure 2.13 Proposed structures of plasma-polymerized polypyrrole.

In 2003, Hosono and coworkers [26] studied the structural and electrical properties of polypyrrole films using RF plasma polymerization process followed by *ex situ* doping technique using 4-ethylbenzenesulfonic acid (EBSA). PPPy films were prepared under a pressure of 26.6 Pa and an average discharge power of 110 W. A comparative was studied with infrared spectroscopy, elemental analysis, and UV–Vis spectroscopy. The conductivity is 4.8×10^{-4} S/cm at 40 °C in the humidity of 60%, which was higher than that for the reported iodine-doped PPPy films measured at the same humidity ($\sim10^{-8}$ S/cm).

After that, Hosono and coworkers [19] studied the effects of the discharge conditions on the structure of PPPy and conductivity of PPPy/EBSA films. Comparative studies of the infrared spectroscopy, elemental analysis and UV–VIS spectroscopy gave information that the some pyrrole rings were remained in the PPPy films prepared with 10, 20 W discharge power, whereas almost all the pyrrole rings were cleaved in the PPPy films prepared with 50, 100 W discharge power and the three-dimensional crosslinked structure. They were proposing structure of films as shown in **Figure 2.14**. However, the difference in the structure of the polymer backbone of the PPPy films does not crucially affect the conductivity. High conductivity was obtained under the wide discharge condition. The electrical conductivity measured at room temperature in the humidity off 40% for the 10, 20, 50, and 100 W of PPPy/EBSA films were 4×10^{-4}, 5×10^{-8}, 2×10^{-5}, and 3×10^{-4} S/cm, respectively.

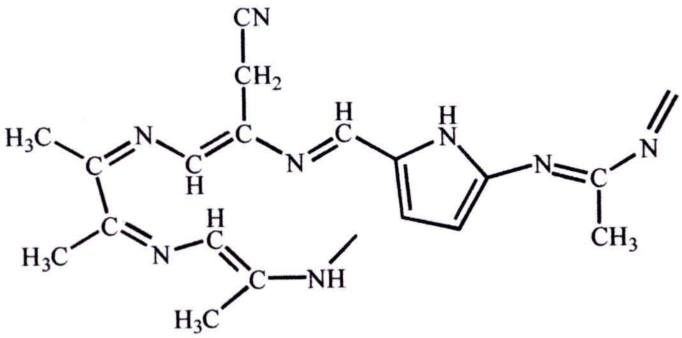


Figure 2.14 Proposed structures of plasma-polymerized polypyrrole.

Subsequently, Hosono and coworkers [27] investigated volatile organic compounds (VOCs) gas sensing properties of PPPy/EBSA films prepared by RF plasma polymerization under a discharge power of 100 W. Upon exposure to VOCs, the resistance of EBSA doped plasma polymerized polypyrrole (PPPy) films decreases. The films exhibit higher sensitivities to polar analyzes such as formaldehyde and acetaldehyde, but showed little response to toluene and benzene. Moreover, the EBSA-doped PPPy films were hardly affected by humidity.

In 2005, Natase and coworkers [35] formed thin films of ferocenne-pyrrole using DC plasma polymerized technique at 6.7 Pa and voltage of 360 V. The reaction time was 480 minute. The polymeric films were characterized by FT-IR, Raman, and AFM. The plasma polymerization with atomizing of the monomer direct to the reaction volume proved to be a useful tool to obtain polymers with a structure similar close to the chemical route. Moreover, the copolymerization of exotic constituents could be made possible with this method.

In 2006, Vásquez and coworkers [32] prepared conducting films of polypyrrole and thiophene dope chlorine by RF (13.5 MHz) plasma polymerization at 12 W and 300 minute duration of polymerization. The synthesis was a hybrid combination of fragmentation, polymerization and doping processes, because some of the reagents participating in the chemical reactions are produced by the decomposition of chloroform molecules by plasma. The characterization of the polymers was carried out by means of SEM, EDS, FT-IR and XPS spectroscopy. The conductivity of the chlorinated polymers resulted in the 10^{-5}-10^{-3} S/cm interval, depending on the environmental humidity. This conductivity is approximately 5 orders of magnitude higher than that of the same polymers synthesized by plasma without doping.

In 2007, Sahin [28] synthesized plasma polymerization of undoped and doped iodine of pyrrole on paper surfaces in order to produce electrically conductive layers using pulsed RF plasma at 10-50 W. The reaction times of film were 1, 5, and 10 minute. An increased in conductivity of all pyrrole-plasma treated papers was observed. The conductivity of PPPy and PPPy /I_2 were 10^{-9} S/cm and 10^{-8} S/cm, respectively.

The aforementioned reports showed that plasma polymerization proves to be an excellent alternative to conventional polymerization of polypyrrole films. Therefore, we would like to explore more into details.