CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Natural Rubber [5,6]

Natural rubber can be isolated from more than a thousand different species of plants, the Para rubber tree (Hevea brasiliensis), is practically the sole source of commercial rubber today. The tree is indigenous to the Amazon valley. Natural rubber has been known to the inhabitants of South America for centuries. Christopher Columbus is considered to be the first European to discover it during his second voyage in 1493-1496, rubber was introduced to the western world by Chareles de la Condamine, who sent samples to France from Peru in 1736 and published the result of his observations in 1745. By the end of the eighteenth century, Europe and America were using a few tons of rubber per year. However, users found it difficult to work with solid rubber. Moreover, articles made from natural rubber turned sticky in hot weather and stiffened in the cold.

Two important developments in the nineteenth century enabled these problems to be solved and laid the foundation for the multibillion-dollar modern rubber industry. In 1820, Thomus Hancock invented a machine called the "masticator" that allowed solid rubber to be softened, mixed and shaped. In 1839, Charles Goodyear discovered the process of vulcanization. He found that heating a mixture of rubber and sulfur yielded products that had much better properties than the raw rubber.

The British considered the possibility of cultivating rubber in Asia, the rubber tree arrived in Sri Lanka in 1876 and Malaysia the following year. In 1880 Hevea seeding were widely distributed in Asia. The land used for rubber cultivation and the production of natural rubber has grown steadily as expected since World War II. In 1983, more than 7.5 million hectares of land in the world were under rubber cultivation and about 4 million metric tons of rubber were produced. The Southeast Asia region accounted for about 80 % of the total production. Thailand was the biggest producer, followed by Indonesia and Malaysia. The world production of natural rubber is shown in Table 2.1.

Table 2.1. World production of natural rubber (1993).

Country	**Ton (10^{-3})**
Thailand	1.50*
Indonesia	1.35
Malaysia	1.07
India	0.425
China	0.325
Philippines	0.172
Sri Lanka	0.106
others	0.482
Total	**5.43**

Source : XIRSG, Rubber Statistical Bulletin

* In 1995 Thailand produce 1.7 million tons.

2.1.1 Natural Rubber in Thailand [7-8]

The data from the Industrial Economics & Planning Division, Ministry of Industry showed that in 1992, Thailand produced 1,520,000 tons of natural rubber and exported 1,400,000 tons or 92.1% of total production. The remaining 7.9% was used in the country. Since 1994, Thailand was the biggest producer in world production of natural rubber. The area of Thailand was about 12 million hectares employed for rubber cultivation. In 1995, Thailand produces 1.7 million tons of natural rubber. It is uneconomical to transport preserved field latex over long distances to consumer countries, the normal procedure is to change the latex form before shipment. Therefore, after the natural rubber latex has been collected from the field, it is changed into many forms of rubber, which are showed in Table 2.2.

Table 2.2. The different types of rubber in Thailand 1995.

Types of Rubber	**% wt**
Smoked sheet	66
Block rubber	18.3
Crepe rubber	0.73
Concentrated latex	9.48
Other rubber	5.46

Source : Southern Industrial Economics Center in Thailand

For Natural rubber latex was 60% dry rubber content by concentration method. In 1994, it exported 131,888 tons and the remaining 32,736 tons was used the country. By it exported to USA, Taiwan, German and Singapore.

2.1.2 Properties of Raw Natural Rubber[8]

Natural rubber latex, produced by the tree Hevea brasiliensis, consists of particles of rubber hydrocarbon and non rubber constituents suspended in an aqueous serum phase. The average dry rubber content of latex may range between 30% and 45%. A typical composition of fresh latex is shown in Table 2.3.

Table 2.3 Typical composition of fresh latex and dry rubber.

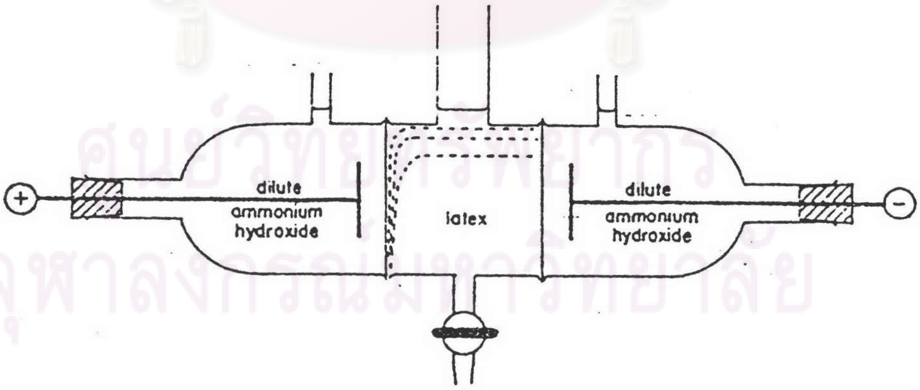
Composition	Latex (%)	Dry Rubber (%)
Rubber hydrocarbon	36.0	93.7
Protein	1.40	2.20
Carbohydrates	1.60	0.40
Neutral lipid	1.00	2.40
Glycolipids & Phospholipids	0.60	1.00
Inorganic constituents	0.50	0.20
Other	0.40	0.10
Water	58.5	-

2.1.3 The Production of Natural Rubber Latex Concentrate [3, 9-10].

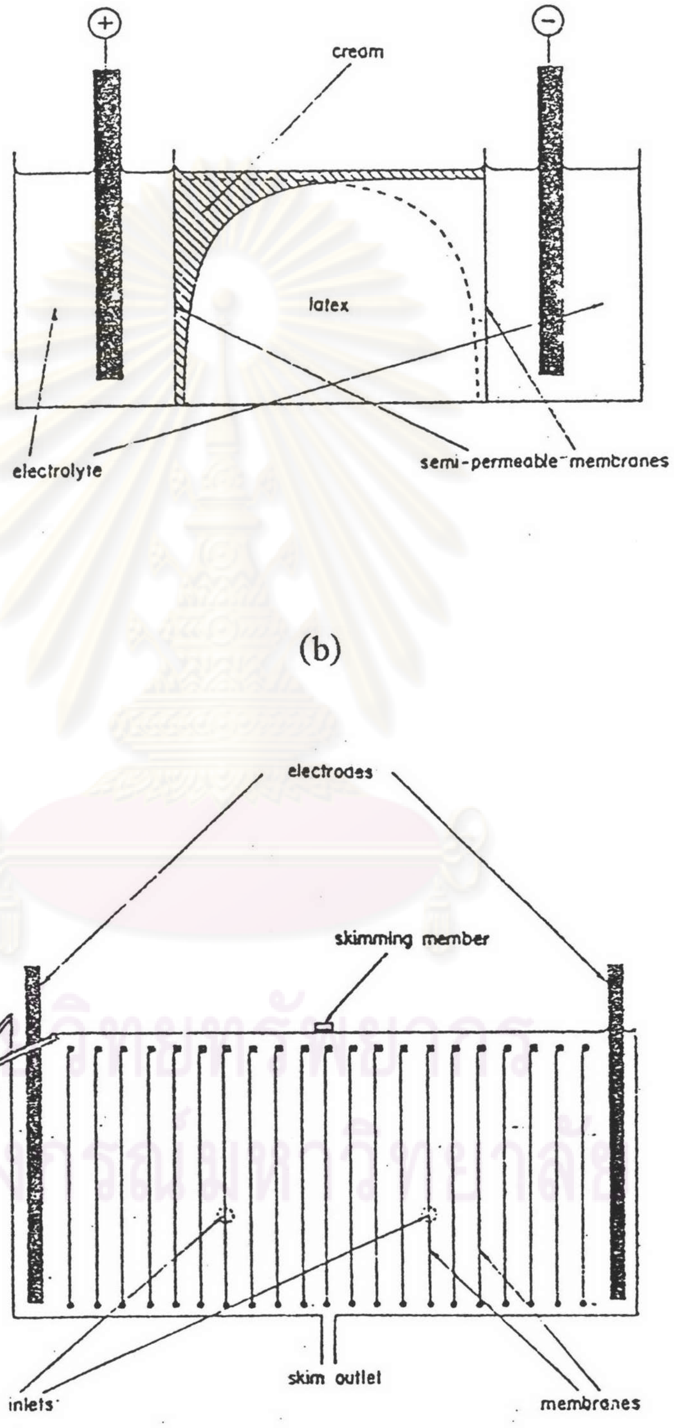
The fresh latex is normally called "field latex", and its average rubber content is 30 percent by weight. This materiel is not utilized in its original form due to its high water content and susceptibility to bacterial attack. It is necessary both to preserve and concentrate it, so that the end product is stable and contains 60 percent or more of rubber. Furthermore, many important latex processes require as a raw material a high-solids latex concentrate of 60% minimal rubber content. Extensive blending of the concentrate latex ensures a specifications.

Of the various methods which have been proposed from time to time for concentrating natural rubber latex, four processes have emerged as of special importance: evaporation, creaming, centrifuging and electrodecantation. The first of these methods involves the removal of water only. Hence the ratio of non rubber constituents (other than water) to rubber remains unaffected by the process of concentration. Also substantially unaffected is the particle size distribution of the latex. On the other hand, three later methods all involve the particle removal of non-rubber constituents relative to the rubber content. The particle size distribution of the concentrate also differs from that of the initial latex, because a proportion of the smaller particles is eliminated at the same time.

The method of concentration by electrodecantation is based upon an observation by Pauli that, when purifying the sols of substances, such as silicic acid, by electrodialysis between vertical semi-permeable membranes, a separation of the sol into strata of different concentration was sometimes observed. The more concentrated layers formed uppermost if the dispersed material was less dense than the dispersion medium, and at the bottom of the vessel if the disperse phase was more dense. This effect is probably the result of the combined influence of electrical and gravitational forces acting upon the dispersed particles. It may be demonstrated in the apparatus illustrated in Figure 2.1(a).



(a)



(b)

(c)

Figure 2.1 Illustrating latex concentration by electrodecantation [3].

The principle of concentration by electrodecantation is illustrated in Figure 2.1(b). The application of a potential difference between the two electrodes causes the negatively-charged rubber particles to move towards the anode. They are intercepted by the semi-permeable membrane, and, provided the potential gradient is not excessive, they deposit at the membrane in an essentially reversible condition. The particles tend to form loose agglomerates in the region of the membrane surfaces, and these agglomerates cream rapidly. A layer of concentrate thus form at the surface of the containing vessel.

An apparatus for the commercial exploitation of the electrodecantation principle has been described by Murphy (1942), and is illustrated diagrammatically in Figure 2.1(c). The rate of separation of latex into cream and skim is increased by introducing a number of semi-permeable membranes between the two electrode compartments. The electrodecantation effect is found to take place simultaneously at each membrane surface, without substantially increasing the current consumption. In this way the effective area of membrane surface can be considerably enlarged. In the apparatus decried by Madge up to 150 membranes are used. It has been found that if the layers of skim and cream are continuously led away, and the volume of latex in the bath maintained constant by the continuous introduction of fresh latex, then the separation may be continued for several days without interruption. Continuous removal of cream also has the advantage of giving a more uniform product. The input rate must be carefully controlled so as to avoid turbulence.

The current consumption is relatively small. According to Stevens (1948), it is of the order of between 20 and 60 Watt hours per pound of 60% concentrate which is produced, assuming the bath to be fed with 35% latex. Voltage gradients are of the order of 1 volt per cm. According to Murphy (1942), a small unit with an effective membrane area of about 100 ft^2 has an output of just over 2 gallons of concentrate per hour. Stevens states that unit with outputs in excess of 7 gallons per hour have been constructed.

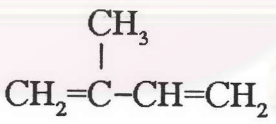
Temperature control of the latex bath is important, because the temperature tends to increase gradually as the process proceeds, due to the dissipation of electrical energy. Increasing temperature has the effect of increasing the electrical conductivity of the bath, thereby causing unnecessary consumption of electricity and promoting the formation of irreversible deposits upon the membrane surfaces. It is therefore desirable to pre-cool the in-going latex if the atmospheric temperature is high.

An important feature of the electrodecantation process is the very small amount of rubber which is contained in the skim Thus this method is especially suitable for the preparation of lattices of low non-rubber content by repeated re-dilution and re-concentration.

2.1.4 The Chemical Formula of Natural Rubber [11, 12].

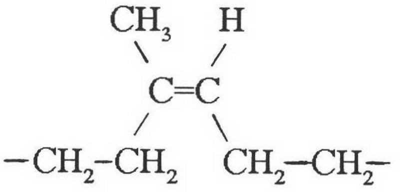
The empirical formula for the natural rubber molecule appears to have been first determine by Faraday who reported his finding in 1826. He concluded that carbon and hydrogen were the only elements present and his results correspond to the formula C_5H_8. While this result was obtained, using a product which contained associated non-rubbery materials, subsequent studies with highly purified materials have confirmed Faraday's conclusion.

The first, isoprene, was found to have the formula C_5H_8, for which Tilden proposed the structure.

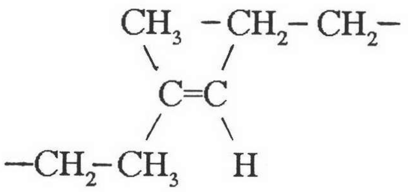


$$CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{C}{-}CH{=}CH_2$$

The linear structure proposed by Pickles provided for the possibility of structure isomerism with both *cis-* and *trans*-repeating units.



Cis-



Tran-

It was known that this is the major hydrocarbon component of both gutta percha and balata (at the time important in belting, submarine cable, golf ball and container applications) was a polyisoprene which when reacted with bromine and ozone gave similar results to those obtained with natural rubber. It was therefore tempting to suggest that one isomer was that of gutta percha and balata and the other that of natural rubber. The earlier work of Staudinger suggested that the *trans*-isomer was natural rubber and gutta percha the *cis*-. However later studies of X-ray fiber diagrams of stretched rubber led Meyer and Mark to the view that natural rubber was the *cis*-polymer, a view reinforced by Bunn (1942) which elucidated the structure and unit cell of the crystalline stretched rubber molecule (Figure.2.2).

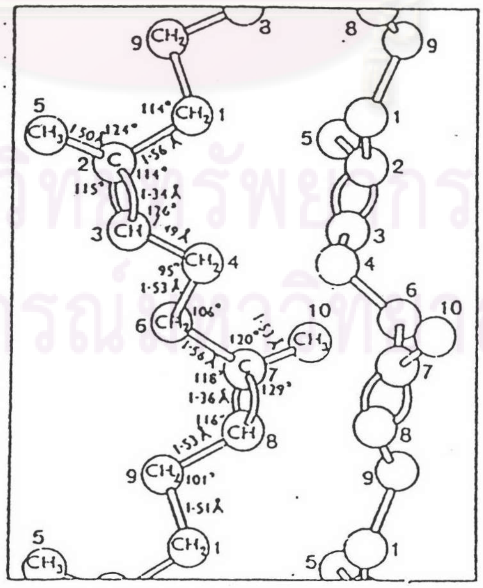
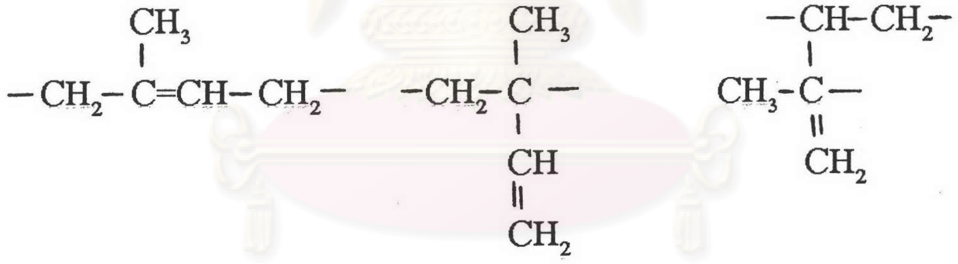


Figure 2.2 Unit cell structure of the natural rubber molecule. (From Bunn,1942.) [12].

The possibility that the natural rubber molecule might contain a mixture of *cis*-and *trans*- groups was considered to be unlikely because such a mixed polymer would have an irregular structure and be unable to crystallize in the manner of natural rubber. Infrared studies have subsequently confirmed that natural rubber was the *cis*-polymer.

Infrared studies have indeed shown for a long while that natural rubber was at least 97% *cis*-1,4- polyisoprene. The absence of measurable amounts of 1,2- structure but an infrared band at 890 $cm^{-1}$was at one time thought to be due possible to the products of a 3,4-structure.



$-CH_2-C(CH_3)=CH-CH_2-$ $\quad -CH_2-C(CH_3)(CH=CH_2)- \quad -CH(C(CH_3)=CH_2)-CH_2-$

1,4- 1,2- 3,4-

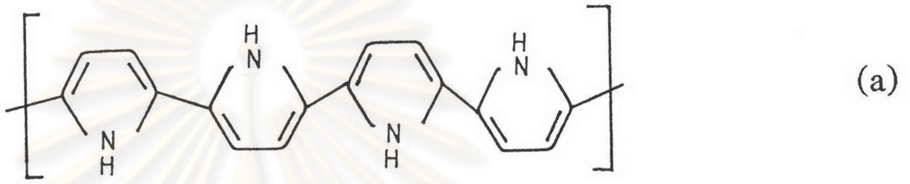
Time-averaging techniques using high resolution NMR which are capable of detecting 3,4-groups at concentrations of less than 0.3% have however failed to establish the existence of any such moiety and have also failed to show up any trace of *trans*-material. The conclusion must therefore be that the molecule is more than 99% *cis*-1,4-polyisoprene. Since all the evidence points to the conclusion that the natural rubber molecule is not obtained in nature by the polymerization of isoprene the absence of detectable pendant groups as would be produced by 1,2- and 3,4-addition is hardly surprising.

2.2 Polypyrrole [2, 13]

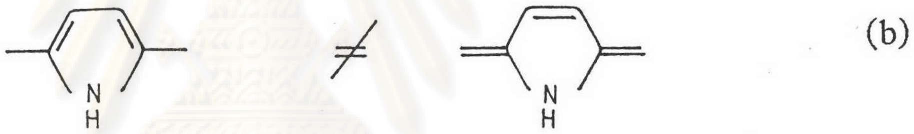
Although polymers of pyrrole have been known for over 50 years, interest in these materials has greatly increased in the past decade because polypyrrole when doped become intrinsically electrically conductive. Efforts are underway to increase processibility of these polymers while maintaining electrical conductivity in ambient conditions

Among the conducting polyheterocylics, the most intensively studied polymers are polypyrrole. Polypyrrole has shown to be a conducting polymer in 1968. It was prepared by oxidation of pyrrole in sulfuric acid. The synthesized polypyrrole was a black powder with room temperature conductivity, of 8 Scm^{-1}. Polypyrrole is another class of electrically active polymer which are thermally and environmentally more stable. The five members ring heterocycles of pyrrole polymerize though α, α'- coupling (2, 5-positon).

The electrophysical properties of polypyrrole are determined by a variety of factors such as the degree of polymerization, nature of dopants and the heteroatom which incorporated into the π- conjugated system of carbon atoms, the band gap was 3.2 eV of polypyrrole. However, the effect of heteroatom on electrical properties of this polypyrrole may not be of that significance because electrical behavior of these highly conjugated polymers was governed by the polymer chain length since defect occur along the π-conjugated system of carbon atom.



Polypyrrole



Two inequivalent structures of the polypyrrole

Figure 2.3 (a) Chemical structure diagram of the polypyrrole.
(b) Two inequivalent structure of the polypyrrole.

Polypyrrole is of current theoretical interest since the two structures (Figure 2.3) sketched are not energetically equivalent. Thus, the coupling of electronic excitations to chain distortions (inherent in such linear conjugated polymers) will lead to polarons and bipolarons as the dominant charged species.

2.2.1 Theoretical Consideration of Conductive Polymer

In order to understand more about conductive polymer, a suitable starting point for consideration is band theory which is the essential basic of concepts for discussion of conduction in molecular solid. Since this thesis prepared polymer by electrochemical polymerization. Thus, effect of oxidation potential of solution was significant in this study. Furthermore, measurement of conductivity was described in section 2.3.

(1) Band Structure [14]

For simplicity, we assume that, one atom provides one atomic s-orbital at some energy, Figure 2.4 (a). When the second atom is brought up, it overlaps the first one and forms a bonding orbital and an antibonding orbital, Figure 2.4 (b). The third is brought up and overlaps its nearest neighbor (and only slightly its next-nearest) and from these three molecular obitals are formed as show in Figure 2.4 (c). The fourth atom leads to the formation of a fourth molecular orbital, and at this stage we can see that the general effect of bringing up successive atoms is slightly to spread the range of energies covered by the orbitals, and also to fill in the range with orbital energies. when N atoms have been slotted on to the line there are N molecular orbitals covering a band of finite width. When N is indefinitely large, the orbital energies are indefinitely close, and form a virtually continuous band. Nevertheless this virtually continuous band consists of N different molecular orbitals, the lowest-energy orbitals in the band bring predominantly bonding, and the highest-energy predominantly antibonding.

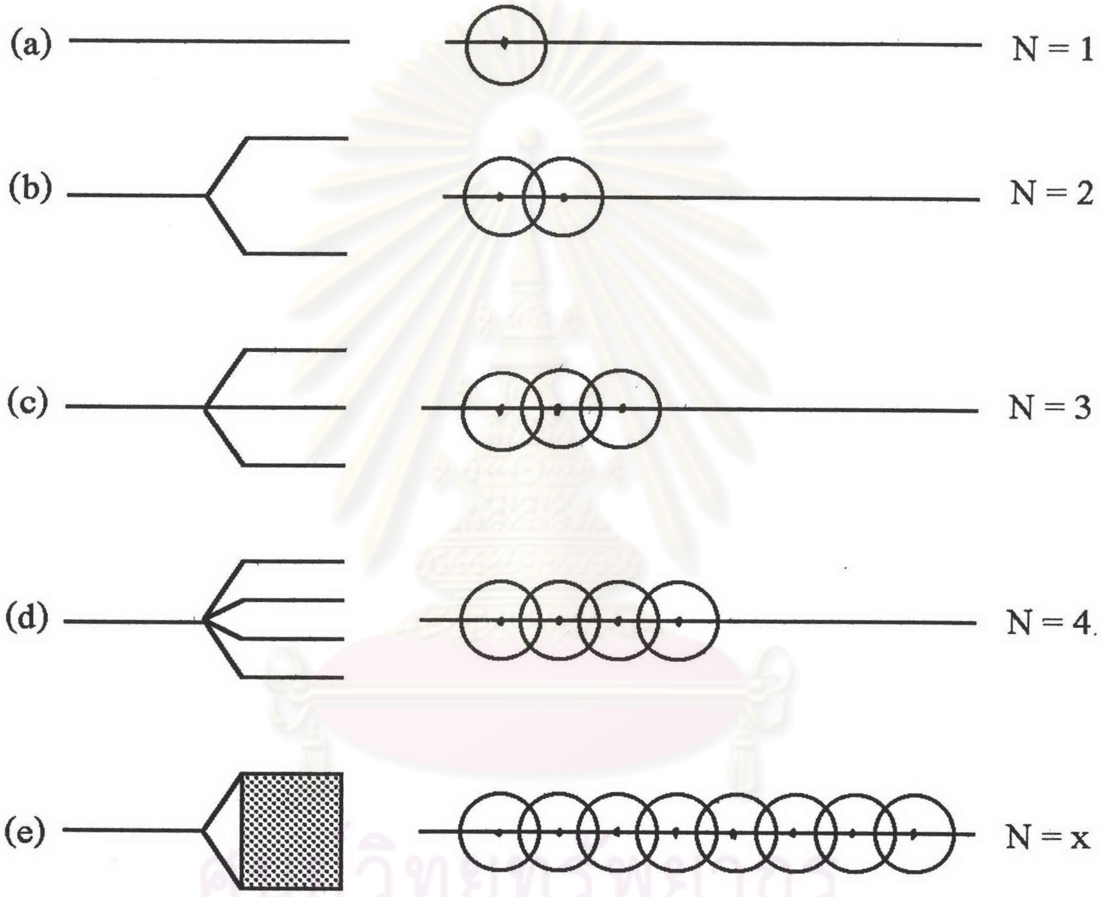


Figure 2.4 The formation of a band of N orbitals by the successive addition of atoms to a line.

The band formed from s-orbitals is called the s-band. If the atoms carry p-orbitals, the same procedure may be followed, and the band of molecular orbitals is called the p-band, Figure 2.5. If the atomic p-levels lies higher than the atomic s-level, the p-band lies higher than the s-band, unless it is so broad (strong overlap) that the band overlap.

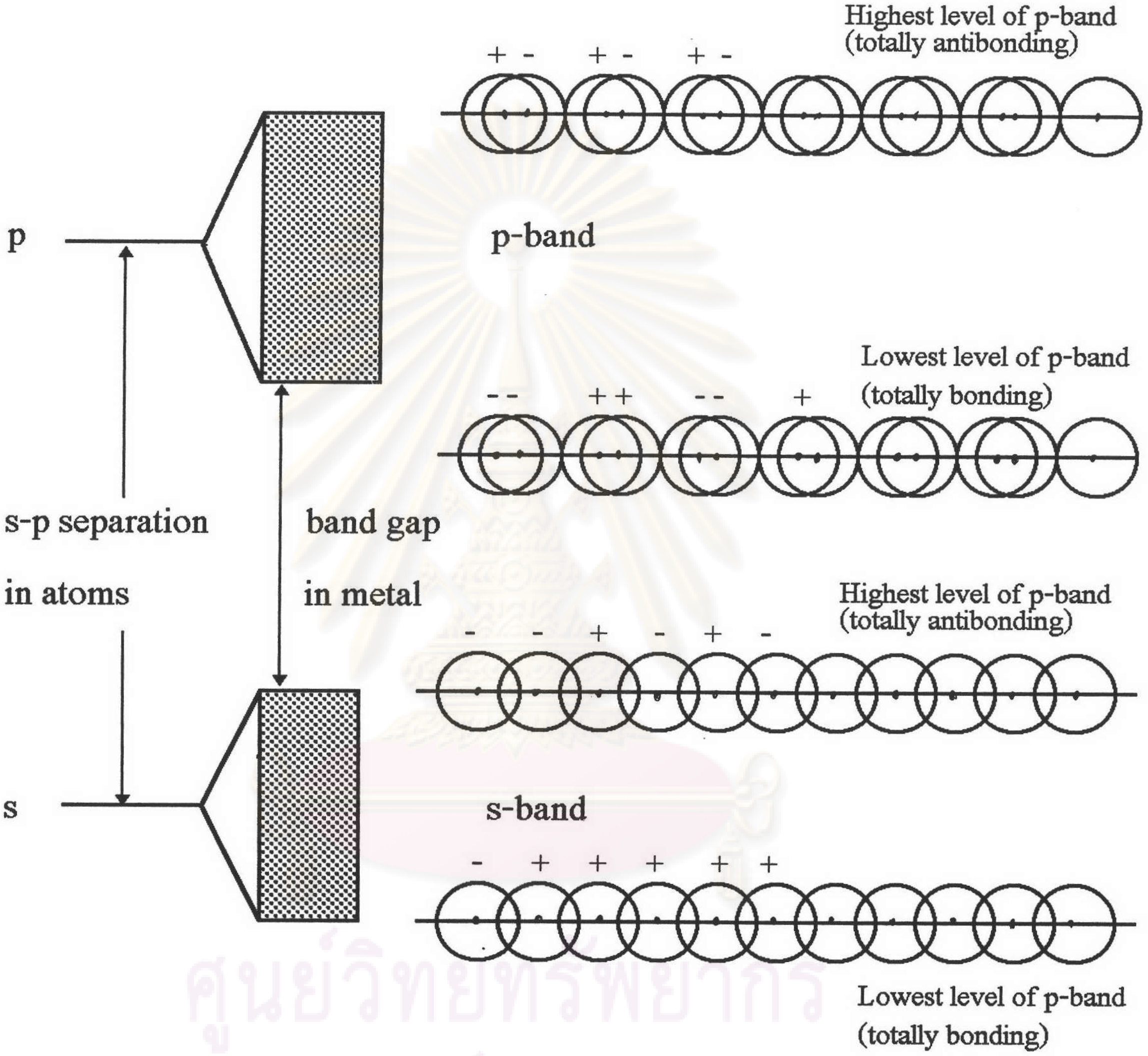
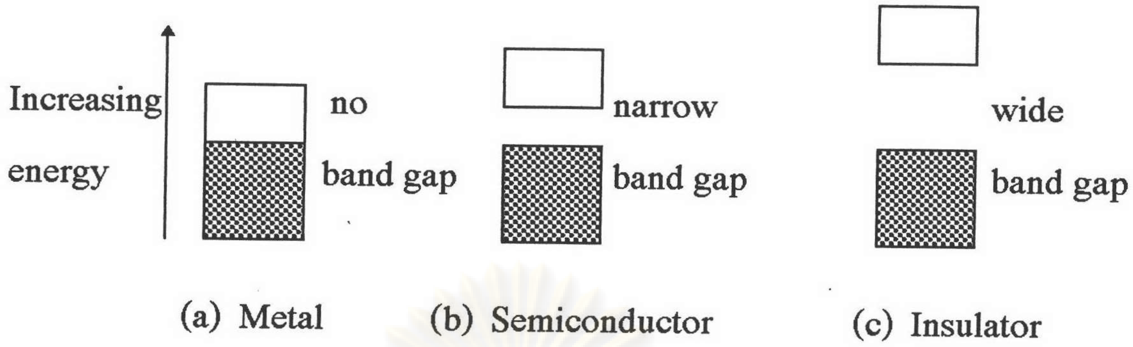


Figure 2.5 S-band, p-band, and the band gap.

(2) Metal, Semiconductor and Insulator [14]

Energy band diagrams may be used to illustrate the differences between metals, semiconductors and insulators. For sample model in metals the electrons completely fill the valence band and partially filled the conducting band . The higher energy conduction band is empty at absolute zero. This is shown in Figure 2.6 (a), above absolute zero, electrons at the top of the highest occupied level can gain thermal energy and move into the low lying empty levels of conductive bands. A substantial fraction of the electrons can be excited into singly occupied energy levels, even at relatively low temperature. Such unpaired electrons contribute to the electrical conductivity of a metal, and the substance is called a conductor.

In semiconductors and insulators, shown in Figure 2.6 (b) and (c), the valence band is completely filled and an energy gap exists between it and the next higher energy band. If the energy gap is wide (large), there is little chance for electrons to be excited into an empty conduction band and the material is an insulator. If there is only a small energy gap, the material is an intrinsic semiconductor, electrons being excited rather easily into the conduction band. If the gap is wide but impurity atoms are added, it may be possible to establish level within the gap that facilitate the movement of electrons into the conduction band. These latter systems are known as impurity semiconductor, or extrinsic semiconductors.



(a) Metal (b) Semiconductor (c) Insulator

☐ EC = Energy levels in conduction band.

▨ EV = Energy levels in valence band.

Figure 2.6 The relationship of energy gaps in the tree types of solids.

(3) Doping of Semiconductors [14-15]

Most technologically important semiconductors are the extrinsic type in which the charge carrier production is determined by trace amounts of impurities or by lattice imperfections. However, with the addition of an impurity (between about 0.1% to less than 1 ppm), the charge carrier type, its concentration and the conductivity of the sample can be controlled.

When the crystal lattice is disturbed by the addition of impurities or even by irregularity in the lattice arrangement, isolated centers are generated. Some centers can contribute electrons to the conduction band of the material. Such defects are called donors or donor centers. If the primary charge carriers are electrons, the material is called an n-type semiconductor. If the centers remove electrons from the chemical bonds, they are called acceptors and produce electron vacancies. These vacancies behave as positive charge carriers in the valence band and are called holes. If holes are the predominant charge carriers, a p-type semiconductor results.

Conducting polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Their electrical conductivity cannot be explained well by simple band theory. For example, simple band theory cannot explain why the charge carriers, usually electrons or holes, in polypyrrole are spinless. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including polarons and bipolarons, have been applied to conducting polymers since the early 1980s.

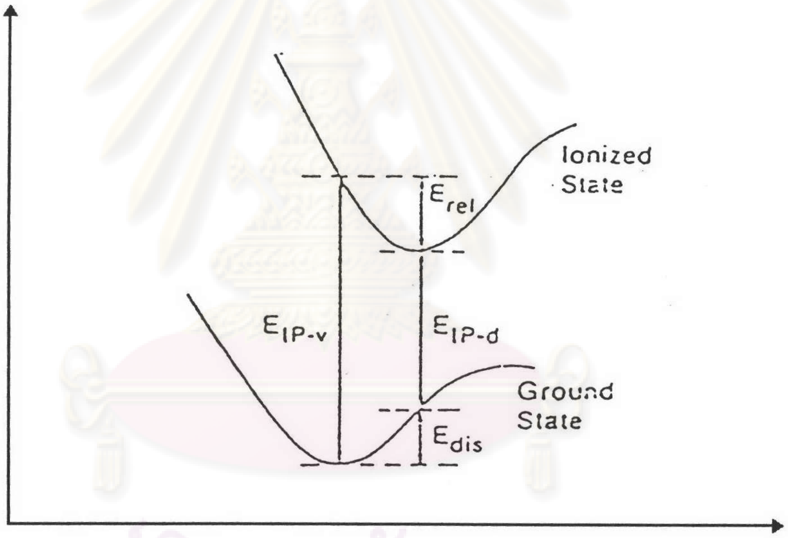
(4) Nature of the Charges Appearing on the Polymer Chain [14-15]

In crystal polymer, the interaction of a polymer unit cell with all its neighbors leads to the formation of electronic bands. The highest occupied electronic level constitutes the valence band (VB) and lowest unoccupied level, the conduction band (CB). The width of the forbidden band, or bandgap (Bg), between the VB and CB determines the intrinsic electronic properties of the material. For all the organic conjugated polymers discussed so far, the band gap is much larger than 1.5 eV so that these materials are intrinsically insulating.

Initially, the high conductivity observed upon doping organic polymers was thought to result from the formation of unfilled electronic bands. It was simply assumed upon p-type or n-type doping, electrons were respectively, removed from the top of the VB or add to the bottom of the CB, in analogy to the mechanism of generation of charge carriers in doped inorganic semiconductors. This assumption was however quickly challenged by the discovery that polypyrrole which can display conductivity does not seem to be associated with unpaired electrons but rather with spinless charge carriers.

In organic molecule, it is usually the case that equilibrium geometry in the ionized state is different from that in the ground state, e.g., the geometry of polypyrrole is aromatic-like but becomes quinoid-like in the ionized state. The energies involved in the ionization process of a molecule are schematically depicted in Figure 2.7. A vertical, Franck-Condon like ionization process costs an energy E_{ip-v}. If a geometry relaxation then takes place in the ionized state, a relaxation energy E_{rel} was gained back. Conceptually, going from the ground state to the relaxed ionized state can also be of in the following way. The geometry of the molecule is first distorted in the ground state in such a way that the molecule adopts the equilibrium geometry of the ionized state. This costs a distortion (elastic) energy E_{dis} (Figure 2.7). For one-electron energy levels of the molecule, this distortion leads to an upward shift $\Delta\varepsilon$ of the highest occupied molecular orbital (HOMO) and a downward shift of the lowest unoccupied molecular orbital (LUMO), as illustrated in Figure 2.8. If we then proceed to the ionization of the distorted molecule, it requires an energy E_{ip-d}.

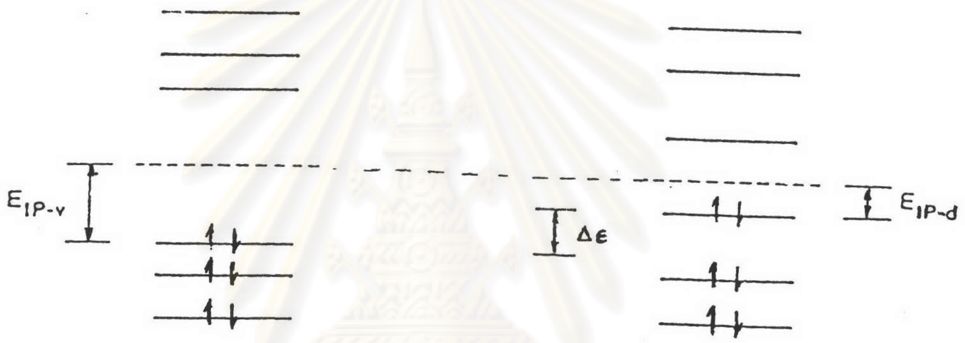
Potentail energy of neigh boring atoms.



Distance between the reacting atom (distance of separation).

Figure 2.7 Illustration of the energies involved in a molecular ionization process. E_{ip-v} is the vertical ionization energy, E_{rel}, the relaxation energy gained in the ionized state, E_{dis}, the distortion energy to be paid in the ground state in order that molecule adopts the equilibrium geometry of the ionized state, and E_{ip-d}, the ionization energy of the distorted molecule.

From Figure 2.7, it is clear that it is energetically favorable to have a geometry relaxation in the ionized state when the quantity $E_{ip\text{-}v} - E_{ip\text{-}d}$ (which actually corresponds to $\Delta\varepsilon$ as can be inferred from Figure 2.8) is larger than the distortion energy E_{dis}; or in other words, when the reduction, $\Delta\varepsilon$, in ionization energy upon distortion is larger than the energy E_{dis} required to make that distortion.

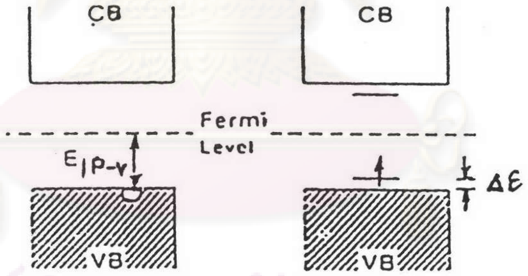


(a) (b)

Figure 2.8 The one-electron energy levels for organic molecule in its ground state electronic configuration.

(a) The equilibrium geometry of the ground state.
(b) The equilibrium geometry of the first ionized state.

In a polymer, or any solid, a vertical ionization process $E_{ip\text{-}v}$ results in creating a hole on top of the valence band; see Figure 2.9 (a). In this case, three remarks can be made. First, by the very definition of the process, no geometry relaxation (lattice distortion) takes place on the chain. Second, the positive charge on the chain is delocalized over the whole polymer chain. Third, the presence of a hole (unfilled level) on the top of the VB leads, as discussed above, to the appearance of a metallic character. This situation corresponds to the initial assumption made about the conduction mechanism in doped organic polymers. However, in an organic polymer chain, it can be energetically favorable to localize the charge that appears on the chain and to have, around the charge, a local distortion (relaxation of the lattice). This process cause the presence of localized electronic states in the gap due to a local upward shift, $\Delta\varepsilon$, of the HOMO and downward shift of the LUMO, Figure 2.9 (b). Considering the case of oxidation, i.e., the removal of an electron from the chain, the ionization energy was lowered by an amount $\Delta\varepsilon$.



(a) (b)

Figure 2.9 Band structure of a polymeric chain in the case of

(a) a vertical ionization process

(b) the formation of polarons

If $\Delta\varepsilon$ is larger than the energy E_{dis} necessary to distort the lattice around the charge, this charge localization process is favorable relative to the band process. It was then formed what condensed matter physicists call a polarons. In chemical terminology, the polarons is just a radical ion (spin 1/2) associated with a lattice distortion and the presence of localized electronic state in the gap referred to as polaron state. The quantity $\Delta\varepsilon$ - E_{dis} (= E_{rel}) corresponds to the polaron binding energy. Calculation (based on Huckel theory with bond compressibility) has indicated that polaron formation is energetically favorable in all the organic conjugated polymers. The polaron binding energy is 0.12 eV in polypyrrole. It must be stressed that in the case of polaron formation, the VB remains full and the CB empty. There is no appearance of metallic character since the half-occupied level is localized in the gap, Figure 2.9 (b)

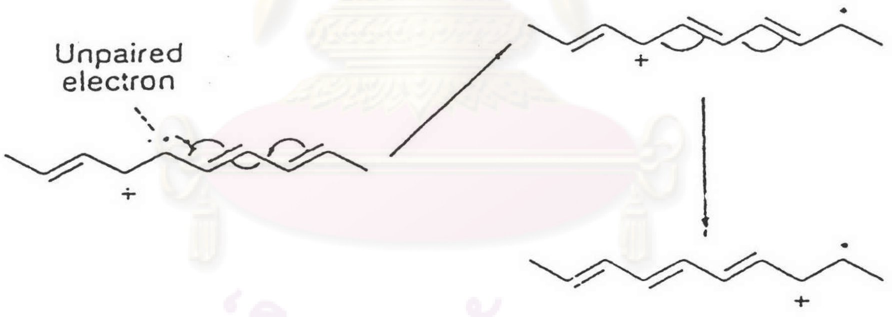


Figure 2.10 A radical cation that is partially delocalized over some polymer segment is called a polaron of polyacetylene.

If another electron is now removed from the already oxidized polymer containing the polaron two things can happen [15]. This electron could come from either a different segment of the polymer chain, thus creating another independent polaron, or from the first polaron level (remove the unpaired electron) to create a special distortion, which solid-state physicists call a bipolaron. A bipolaron is defined as a pair of like charges associated with a strong local lattice distortion. The formation of a bipolaron implies that energy gained by the interaction with the lattice is larger than the Coulomb repulsion between the two charges of same sign confined in the same location. The two positive charges of the bipolaron are not independent, but act as pair.

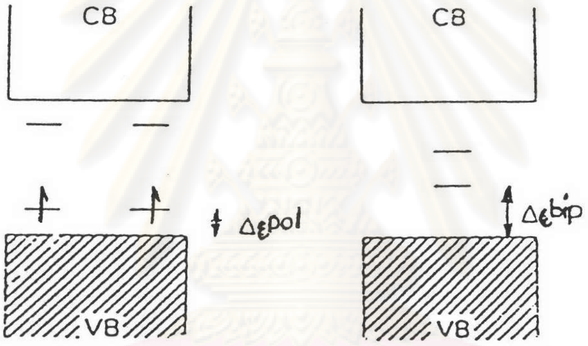


Figure 2.11 Band structure of a polymer chain containing :

(a) two polarons

(b) one bipolaron

The electron band structure corresponding to the presence of two polarons and that of one bipolaron is depicted in Figure 2.11. Since the lattice relaxation around two charges is stronger than around only one charge, E_{dis} for the bipolaron is further away from the band edges than a polaron.

The creating of bipolaron relative to that of two polarons, the calculation for polypyrrole indicate that the distortion energy E_{dis} to form one bipolaron is roughly equal to that of forming two polarons. On the other hand, the decrease in ionization energy is much more important in the bipolaron case ($2\ \Delta\varepsilon^{bip}$) than for two polarons ($2\ \Delta\varepsilon^{pol}$) ; see Figure 2.11. This is the reason why one bipolaron is thermodynamically more stable than two polarons in these systems despite the Coulomb repulsion between two similar charges. Furthermore, the latter is also largely screened by the presence of dopants (counterion) with opposite charge. The bipolaron binding energy [= ($\Delta\varepsilon^{bip}$) - E_{dis}^{bip}] is calculated to be larger than that of two polarons by about 0.45 eV in polypyrrole.

In case of p-(n-) type doping, the bipolaron level in the gap is empty (fully occupied); see Figure 2.11 (b). The bipolaron is thus spinless. The presence of bipolarons on polymer chains result in the possibility of two optical transitions below the bandgap transition : for p-type doping, such as polypyrrole, from the VB to the lower bipolaron level and from the VB to the upper bipolaron level. In the case of polarons, a third absorption is possible below the gap, corresponding to an optical transition between the two polaron levels (Figure 2.11(a)).

Polypyrrole possess a non-degenerate ground state since their ground state corresponds to a single geometric structure which, in this case, is aromatic-like. A quinoid-like resonance structure can be envisioned but has a higher total energy (Figure 2.12). The quinoid structure has a larger electron affinity than the aromatic structure. This explains why, on doping, the chain geometry in these compounds relaxes locally around the charges toward the quinoid structure [17].

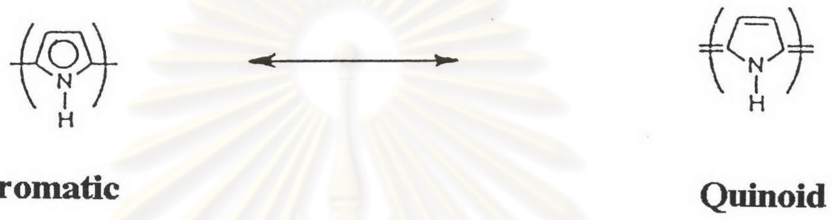


Figure 2.12 Aromatic (ground-state) and quinoid-like geometric structure for polypyrrole.

In summary, conduction by polarons and bipolaron is now thought to be the dominant mechanism of charge transport in polymers. These concepts was dependent on the doping of these polymers, which its data demonstrate that

(i) polarons are formed on the chains at low oxidation level (slightly doped polymer),

(ii) at higher oxidation level, polarons combine to form spinless bipolaron (heavily doped polymer),

(iii) wide bipolaron bands are present in the gap in the highly conducting regime (heavily doped polymer).

However, it should be emphasized that these models were device assuming ideal structure. The actual structure of most conductive polymers, both in the doped and undoped state, are unknown, and all data show that certain polymers have a large number of defects. It shown in Figure 2.13.

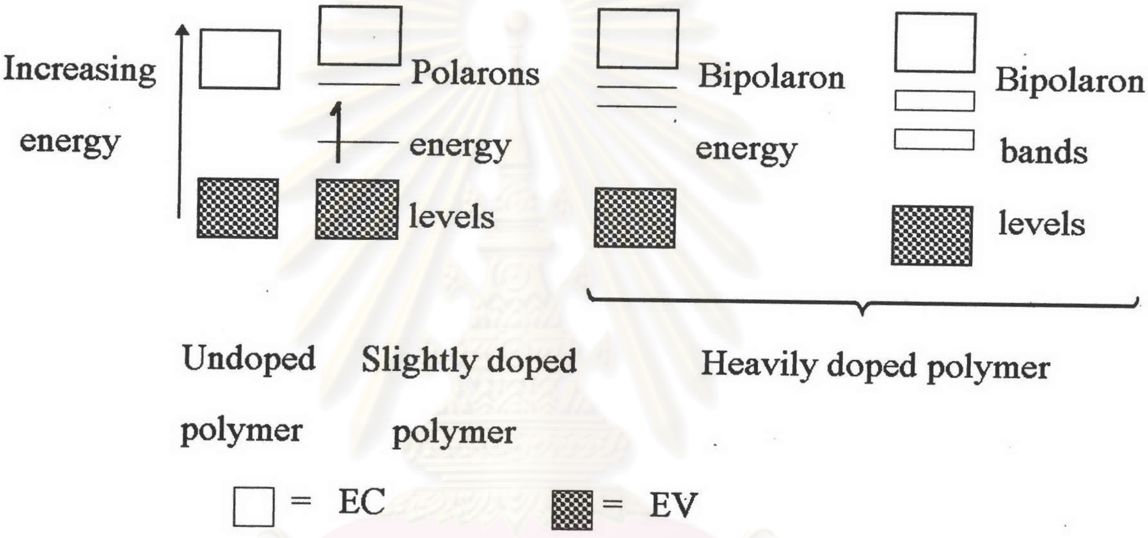


Figure 2.13 The band structure of a polymeric chain in case of polaron energy levels and bipolaron energy levels [19].

2.2.2 The Production of Conducting Polymers

The field of synthetic metals remains an active area for fundamental research in experimental and theoretical solid-state physics as well as organic. and polymer synthetic chemistry. The variety of new conducting polymeric solid have been continuously discovered. The area of synthesis is extremely fast moving and competitive.

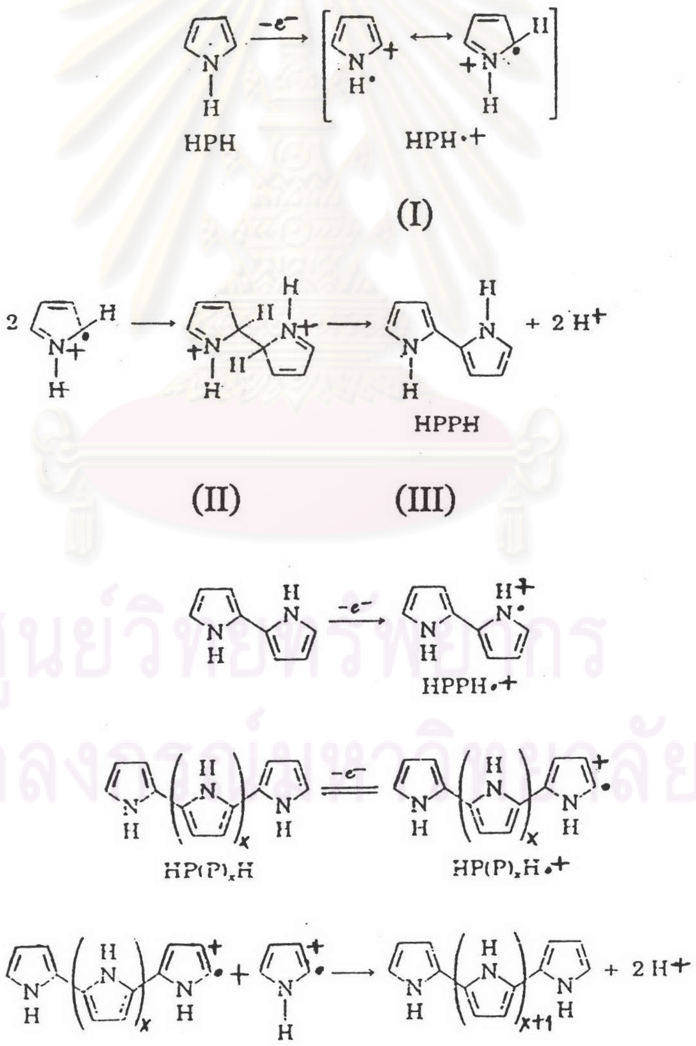
Here, they summarize the major types of synthetic techniques used to prepare polypyrrole.

i) Electrochemical polymerization
ii) Chemical vapor deposition (CVD)
iii) Chemical polymerization

(1) **Electrochemical Polymerization** [4, 16]

Passage of current thought a solution results in the loss of electrons, and compounds are oxidized at the anode. Electrons are gained and compounds reduced at the cathode. This process is referred to as electrochemical polymerization when polymers is formed. Polypyrrole is obtained by the electrochemical polymerization of pyrrole in a solvent such as acetonitrile, tetrahydrofuran, propylene carbonate, or methanol. An electrolyte such as tetrafluoroborate or lithium perchlorate is present, and polymerization is carried out either at constant voltage or constant current.

The mechanism for polymerization involves oxidation of polypyrrole at the α-position to form a radical-cation (I) which undergoes radical coupling to yield the dimer dication (II). The latter loses two protons to yield the dimer (III). The dimer repeats the same reaction sequence-loss of an electron to form a dimer radical-cation, coupling with itself and (I) to form the tetramer-dication and trimer-dication, respectively, followed by two protons loss to yield tetramer and trimer. Propagation to polymer proceeds via repetition of the same sequence, one electron loss, coupling of different-sized radical-cations, deprotonation. This polymerization mechanism bears considerable resemblance to that for the oxidative polymerization of 2,6-disubstituted phenols.



{1}

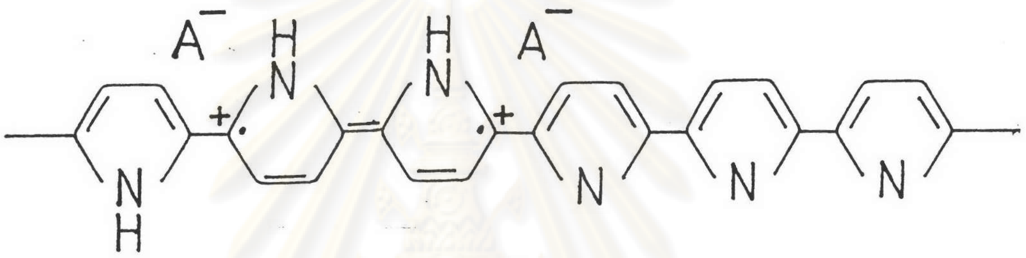
{2}

{3}

{4}

{5}

Electrochemical polymerization, as usually carried out, does not yield the neutral, nonconducting polypyrrole shown in Equation {4} but the oxidized (doped), conducting form. (one can cycle back and forth between the conducting and nonconducting forms, colored black and light yellow, respectively, by reversing polarity.). The doped polymer would have a structure such as (IV),



(IV)

where A^- is the anion of the electrolyte. The doped polymer precipitates out and coats the surface of the anode during polymerization. The polymerization reaction and polymer properties (conductivity and mechanical strength) are dependent on such parameters as identity and concentration of electrolyte, reaction temperature, and current density.

(2) Chemical Vapor Deposition [17]

In 1987, Takeaki Ojio and Seizo Miyata synthesized the conducting composite films of polypyrrole, which can be prepared by exposing polymeric matrix films containing ferric chloride to pyrrole vapor. The composite films are, moreover, highly transparent under the appropriate preparation condition. In that communication, the conductivity and the transparency of polypyrrole composite films by the gas state polymerization was discussed.

Poly (vinly alcohol) was used as a polymeric matrix. $FeCl_3$ was an oxidizing agent for the polymerization. After dissolving PVA and $FeCl_3$ in the water, the solution was casted on a poly (ethylene terephthalate) film substrate. The preparation of polypyrrole-PVA composite films was carried out in a desiccator at -15°C by exposing PVA films containing $FeCl_3$ on the PET film to the pyrrole and H_2O vapors which had been deoxygenated sufficiently. The polymerization period was then dried under vacuum at room temperature. At optimum condition, the composite film shows about 10 Scm^{-1} conductivity.

(3) Chemical Polymerization in Solution [18].

The synthesis of conducting polymer via chemical method is less popular, even though this method allows a simple preparation of large quantities, more covenant and economical. The majority of the chemical synthesis method involves the polymerization and oxidation with oxidative transition metal ions, for example $FeCl_3$, $AgNO_3$, $Cu(NO_3)_2$, $AlCl_3$ and more. The use of other oxidants such as acid, halogens and organic electron acceptors have also been reported. Considerable chemical compositions and reaction stoichiometries for polypyrrole complexes were synthesized from $FeCl_3$, based on the observed chemical compositions of the complex, particularly the [Cl] / [N] ratio. At present time two reaction stoichiometries have been proposed.

$$4\,C_4H_5N + 9\,FeCl_3 \longrightarrow [(C_4H_3N)_4^{+}Cl^{-}] + 8\,HCl + 9\,FeCl_2$$

and

$$n\,C_4H_5N + 2.33\,n\,FeCl_3 \longrightarrow [(C_4H_5N{+}0.33Cl^{-}]_n + 2.33n\,FeCl_2 + 2n\,HCl$$

Recently, polypyrrole obtained from chemical polymerization in solution can exhibit very high electrical conductivity when a suitable solvent is selected and the oxidation potential in the solution is controlled.

2.2.3 General Considerations of Electrochemical Synthesis [19-21]

(1) Electrolytic Conditions

Recognizing that the polymerization reaction proceeds via radical cation intermediates, it becomes apparent that the reaction will be sensitive to the nucleophilicity of the environment in the region near the electrode surface. This then places some limitations of the choice of the solvent and the electrolyte. For this reason, many of reported studies have been performed in aprotic solvents, which are poor nucleophiles. Among these, acetonitrile has been the most commonly used solvent, although a wide variety of other aprotic solvents can be used as long as the nucleophilic character of the solvent is poor. However, certain nucleophilic aprotic solvent, such as dimethylformamide, and hydroxylic solvents can also be used to prepare good films if the nucleophilicity of the solution is reduced using protic acids. This topic is discussed in more detail in the section involving polypyrrole.

With regards to the electrolyte salt, the main considerations are the solubility, degree of dissociation, and the nucleophilicity. For this reason, most of the salts used are tetraalkylammonium salts, since they are soluble in aprotic solvents and are highly dissociated. Although some lithium salts are soluble in aprotic solvents, in general, these salts are highly aggregated. Most sodium and potassium salts are poorly soluble in aprotic solvents. A wide variety of anions can be used as tetraalkylammonium salts, as is discussed below. Good films are typically not produced when the anion is a halide, because halides are fairly nucleophilic and easily oxidized. The highly nucleophilic anions, such as hydroxide, alkoxide, cyanide, acetate, and benzoate, do not produce good-quality films either and instead produce soluble products which color the reaction solution. This is not surprising, since the cyanide anion is known to react efficiently with the electrochemically generated cation of pyrrole.

(2) Electrodes

The best films have been prepared in a divided cell using three electrodes where the counter electrode is separated from the working and the reference electrode. The nature of the working electrode is a critical consideration for the preparation of these films. Since the films are produced by an oxidative process, it is important that the electrode dose not oxidize concurrently with the aromatic monomer. For this reason, most of the available films have been prepared using a platinum, gold or palladium electrode. However, films have been prepared using a variety of semiconducting materials, including tin oxide, n-type polycrystalline silicone, gallium arsenide, cadmium sulfide and graphite.

In the majority of the case, the films are produced so readily that the only serious limitations are the nucleophilic nature of the solution and the nature of the working electrode. In fact, as the case of polypyrrole, films can be produced using a simple two-electrode, undivided cell which is powered by a DC battery.

(3) Effect of Solvent

The solvent has a very strong influence on the outcome of the electro-oxidation reaction. A wide variety of aprotic solvents can be used for the electrochemical reactions of pyrrole, as long as the nucleophilic character of the solvent is poor. Film are not produced in the nucleophilic aprotic solvents such as dimethylformamide, dimethylsulfoxide, and hexamethylphosphoramide, unless the nucleophilicity of the solution is reduced by the addition of the protic acid. Hydroxylic solvents can be used. As we mentioned about the first electropolymerization of pyrrole was performed in aqueous media. The films so obtained are of poorer quality. They are brittle and powdery, with little physical strength, and have lower conductivity values. In solvents with nucleophilic characteristics intermediate between water and the aprotic solvents, such as alcohol and mixed aqueous-aprotic solvent mixtures, films can be prepared with intermediate conductivity values and good physical strengths. The quality of these films can be improved by adding a protic acid to the reaction solution in order to reduce its nucleophilic character.

(4) Counteranion

When in the conducting form, the electropolymerized films contain 10-35% anion (by weight) which is affiliated with the cationically charge polymer chains. The amount of anion found in each film is governed by the level of oxidation of the polymer and is a characteristic of each film. The anion contents for the various films are listed in Table 2.4. This polymer-anion compositional balance of the films actually proves to be quite useful, since the properties of the films can be conveniently altered by changing the anion. Since the anion in the film is incorporated from the electrolyte salt in the preparative solution, the modifications can be made by simply changing the electrolyte salt of the solution.

Table 2.4 Anion content of conducting film [19].

Film	Oxidation Level	Anion Content (%by wt)
Polypyrrole	0.25-0.33	25-30
Polythiophene	0.06	7-25
Polybithiophene	0.22	12
Azulene	0.25	15-28
Pyrene	0.45	-
Carbazole	0.45	21
Indole	0.2-0.3	15-20
Furan	-	26

In the case of the polypyrrole films, a wide variety of anions have been used to prepare thick free-standing films, and can be seen in Table 2.5. The anions listed in Table 2.5 are poorly nucleophilic and permit the formation of good-quality films. Tetraalkylammonium salts were used in the preparation of these films. These films are hydroscopic and will lose 5-7% moisture when dried at 110°C. The level of oxidation of polypyrrole is 0.25-0.32 per pyrrole unit corresponding to one anion for every 3-4 units. The level of oxidation is an intrinsic characteristic of the polymer and is not sensitive to the nature of the anion. The anion, however does influence both the structure properties and the electroactivities of the films. The differences observed between the surfaces is not reflected in the packing structure of the bulk material. Thus, with the exception of one or two of the anions listed in Table2.5, all of the films have similar flotation densities which are in the range 1.45-1.51 g/cm^3. Polypyrrole films containing toluenesulfonate, perchlorate, and fluoroborate anions are hard and strong films and stretch very little (4-5% elongation at break).

Table 2.5 Polypyrrole films with different anion [19].

Anion	Oxidation Level	Density (g/cm^3)	$\sigma(\Omega^{-1}cm^{-1})$
Tetrafluoroborate	0.25-0.32	1.48	30-100
Hexa-fluoroarsenate	0.25-0.32	1.48	30-100
p-Toluenesulfonate	0.32	1.37	20-100
Hexa-fluorophosphate	0.25-0.32	1.48	30-100
Perchlorate	0.30	1.51	60-200
Hydrogen sulfate	0.30	1.58	0.30
Fluorosulfonate	-	1.47	0.01
Trifluoromethyl-sulfonate	0.31	1.48	0.3-1
p-Bromo-benzenesulfonate	0.33	1.58	50

2.3 Electrical Conductivity Measurement by Van Der Pauw Method [22].

Van der Pauw method is one technique for measuring conductivity (σ) of samples which have constant thickness but arbitrary shape. First, four ohms contacts are made at edge of the sample (Figure 2.20). Then applied suitable current (I_{12}) though contacts 1 and 2 and measured potential different (V_{34}) between contact 3 and 4 and find a ratio

$$R_1 = [V_{34}] / I_{12}.$$

Second, I_{23} is applied though contacts 2 and 3 and potential different, V_{41}, is measured thus obtain

$$R_2 = [V_{41}] / I_{23}.$$

From these the conductivity of the sample can be calculated from equation {2.3.1}

$$\exp(-\pi R_1 d \sigma) + \exp(-\pi R_2 d \sigma) = 1 \qquad \{2.3.1\}$$

Where d is the thickness of the sample.

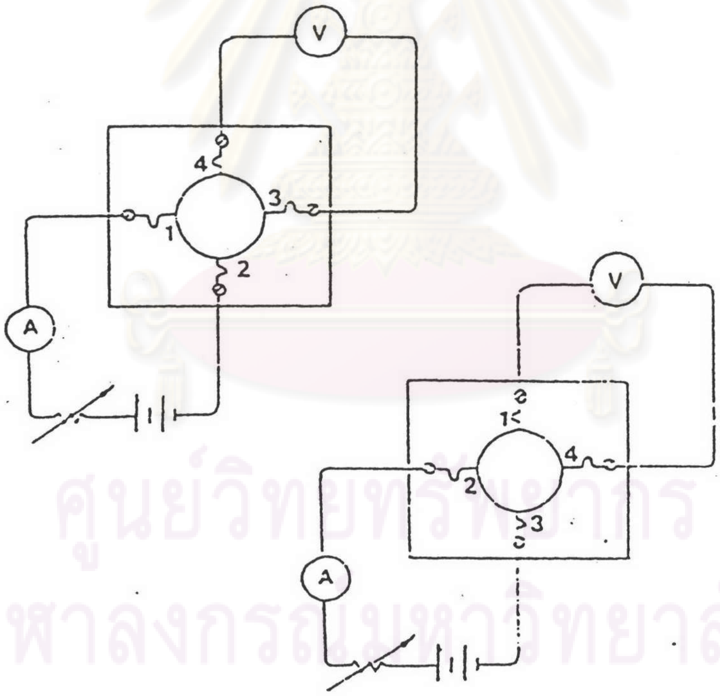


Figure 2.14 Conductivity measurement by Van der Pauw method.

In principle, we can change the current electrodes around, get I_{12}, I_{23}, I_{34}, I_{41} and corresponding potential difference V_{34}, V_{41}, V_{12}, V_{23} respectively. Then calculate σ_1, σ_2, σ_3 and σ_4 from equation {2.3.1} as show in Table 2.6. Finally obtain more accurate conductivity, equation {2.3.2}.

Table 2.6 Various points for applied current.

σ_n	R_1		R_2	
	I	V	I	V
σ_1	I_{12}	V_{34}	I_{23}	V_{41}
σ_2	I_{23}	V_{41}	I_{34}	V_{12}
σ_3	I_{34}	V_{12}	I_{41}	V_{23}
σ_4	I_{41}	V_{23}	I_{21}	V_{34}

$$\sigma = (\sigma_1+\sigma_2+\sigma_3+\sigma_4) / 4 \qquad \{2.3.2\}$$

σ = average conductivity

The main problem in accurate measurement is the contact resistance between the measurement electrodes and the sample. Contact resistance may be reduced by painting electrodes directly on to the surface of the sample instead of relying on pressure contact with metal plates or foils. Suitable paints are silver dispersions or Aquadag (an aqueous dispersion of colloidal graphite).

The accuracy of conductivity measurement by Van der Pauw method depends on the following condition :

i) Size of electrical contact points at edge of the sample should be very small compared with the circumference of the sample.

ii) Sample must have constant density, regular mass and thickness.

iii) Sample must have no broken.

iv) In the case of disc sample, separation distance between each contacts should be approximately the same.

2.4 Literature Survey

Lane and Gardner (1948) studied the resistivities of a series of natural rubber mixings with various loading of acethylene black and quantities of pine tar are given in Table 2.7. Thus at 80 and 100 part loading of acetylene black increases of softener led to lower resistivity, while at the highest loading the reverse was true. The pine tar loading of the last two mixings were, however, beyond those normally encountered.

Table 2.7 Effect of pine tar on resistivity [1].

Acetylene Black (phr)	80	80	80	80	100	100	120	120
Pine Tar (phr)	3	10	15	20	20	30	40	50
Resistivity (ohm cm)	24	20	13	5	10	8	4	7

There are a few references to the use of metals in conductive rubbers. Levina et al. (1960,1961) described the properties of mixings of finely divided iron with small quantities of polyisoprene or polyacrylonitrile. The resistivity attained may be as low as 10^{-1} ohm cm with 20% of metal [1]. It is claimed that flakes of silver, nickel, zinc or stainless steel can be used to impart conductivity to nitrile, neoprene, neutral or silicone rubber.

Natanson et.al (1965) treated natural rubber in solution with colloidal iron within a fraction of a second after the latter was formed by electrolysis [1]. The resulting products are rubber-like if the iron concentration is less than 60% by weight. From 50 to 85% of iron, the resistivity of the material is about 10^{4} ohm cm.

In the patent of multicomponent systems based on polypyrrole [23]. Composition based on polypyrrole are described having incorporated therein a polymer component having one or more segments wherein at least one segment is elastomeric. The polymer is present in an amount of at least about 10 weight percent of the polypyrrole present. The compositions exhibit improved processing properties over those of polypyrrole. Also described is a process for producing the compositions in which a pyrrole compound is electrochemically polymerized in the presence of an at least partially dissolved polymer component having one or more segments wherein at least one segment is elastomeric.

Pyrrole has been grafted onto polystyrene at IBM [13]. Styrene was copolymerized with 4-chloromethylstyrene and then pyrrole monomer used to displace the halide ion. After coating the anode with this polymer, pyrrole was electrochemically grafted onto the polymer by homopolymerization with additional pyrrole in the presence of an electrolyte salt to give a copolymer with a conductivity of 10^{-1} S/cm. The used of surfactant molecules as counterions for pyrrole polymerization in other studies led to films of improved physical characteristics. A patent issued to BASF reveals a method for the continuous preparation of polypyrrole films.

From the preparation of conductive polypyrrole composite film by chemical polymerization in solution [24]. Thin films of conducting polypyrrole were prepared by this method : dipping polyethylene terephthalate film coated with polymethyl methacrylate (PMMA) into pyrrole monomers and then in $FeCl_3$ aqueous solution. The oxidation potential of this solution, which has strong influence on the polymerization, was adjusted to appropriate value by adding suitable polymerization condition, the polypyrrole films obtained possess conductivity as high as 110 S/cm. In the case of long polymerization time, the SEM studies of the films indicate that polypyrrole was not only polymerized on the surface of PMMA, but also penetrated into PMMA to form a strong composite films. It was found that the polypyrrole films obtained in this work were very difficult to undope. This suggests that the prepared films can be used as a conducting surface for electrodeposition of metal on surface of plastic such as PMMA.

A surface active pyrrole, which has a long hydrocarbon chain attached to the 3 position of the pyrrole ring, is used to modify the surface properties of the pores of a porous, crosslinked polystyrene. The latter is prepared starting from a concentrated emulsion of water dispersed in a continuous medium composed of dispersed in a continuous medium composed of styrene, divinyl benzene, a suitable surfactant, an initiator, and the surface active pyrrole. This modified crosslinked porous medium is employed as the host for a polypyrrole composite that is prepared first by imbibing the host with a solution of pyrrole and subsequently with an oxidant solution. The latter plays the role of catalyst for polymerization as well as the role of dopant. The present of the head groups of 3-alkyl pyrrole molecules on the surface of the pores of the host polymer increase the affinity of the surface for pyrrole. The improved wetting thus achieved for the pyrrole solution ensures a higher connectivity among the pyrrole films present on the internal surface of the host polymer and increases the conductivity of the polypyrrole composites, depending upon the solvents employed for pyrrole and oxidant [25].

The used of conductive rubbers as flexible or resilient contact members has been proposed in a number of patents. Further examples of this and other uses of conductive rubbers and plastics described in this section are given in Table 2.8.

Table 2.8 References to various uses[1].

Use	Material	Reference
To sense holes in punched cards	Rubber	West, 1954
Vehicle sensing mat	Rubber	Nutter and Miller, 1955
Railway track signaling contacts	Rubber	Paste, 1957
Rf screens	Rubber	Davis, 1940
Corrosion resistant electrodes for electrostatic precipitators	Rubber or Plastic	Thorpe, 1953