

## CHAPTER II

### THEORETICAL CONSIDERATION AND LITERATURE REVIEW

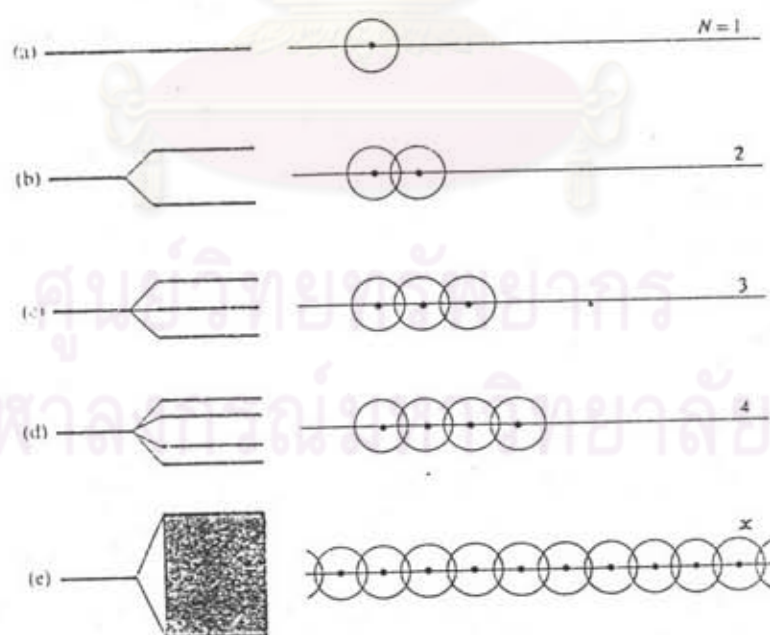
In order to understand more about conductive polymer, a suitable starting point for consideration is band theory which is the essential basis of concepts for discussion of conduction in molecular solid. Since this thesis prepared polymers by chemical polymerization in the solution, thus, effect of oxidation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

#### 2.1 Band theory

##### 2.1.1 band structure [1,24]

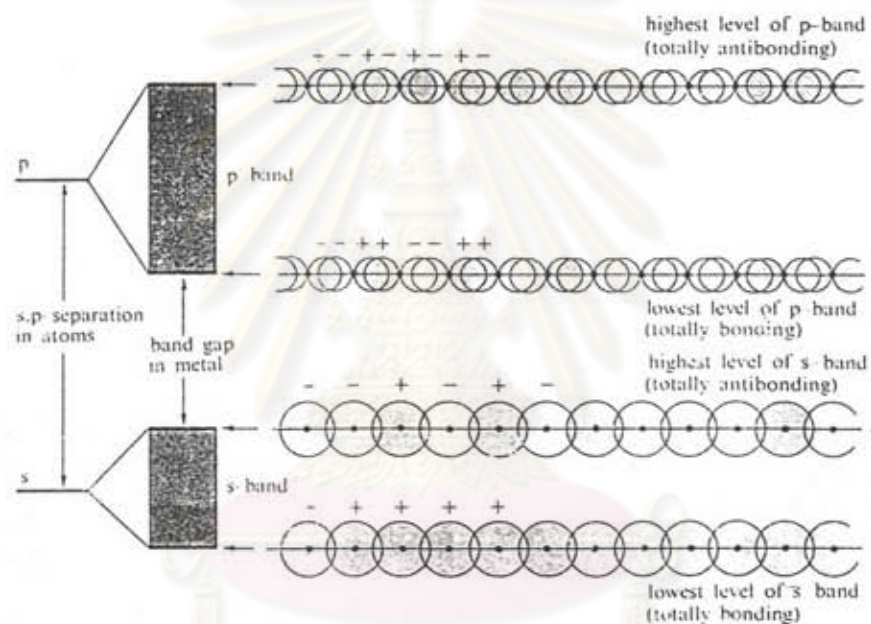
For simplicity, we assume that, one atom provides one atomic s-orbital at some energy, Scheme 2.1(a). When the second atom is brought up, it overlaps the first one and forms a bonding orbital and an antibonding orbital, Scheme 2.1 (b). The third is brought up and overlaps its nearest neighbour (and only slightly its next-nearest) and from these three orbitals three molecular orbitals are

formed as show in Scheme 2.1 (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



Scheme 2.1 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, Scheme 2.2 . 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 bands overlap.



Scheme 2.2 S-band, p-band, and the band gap

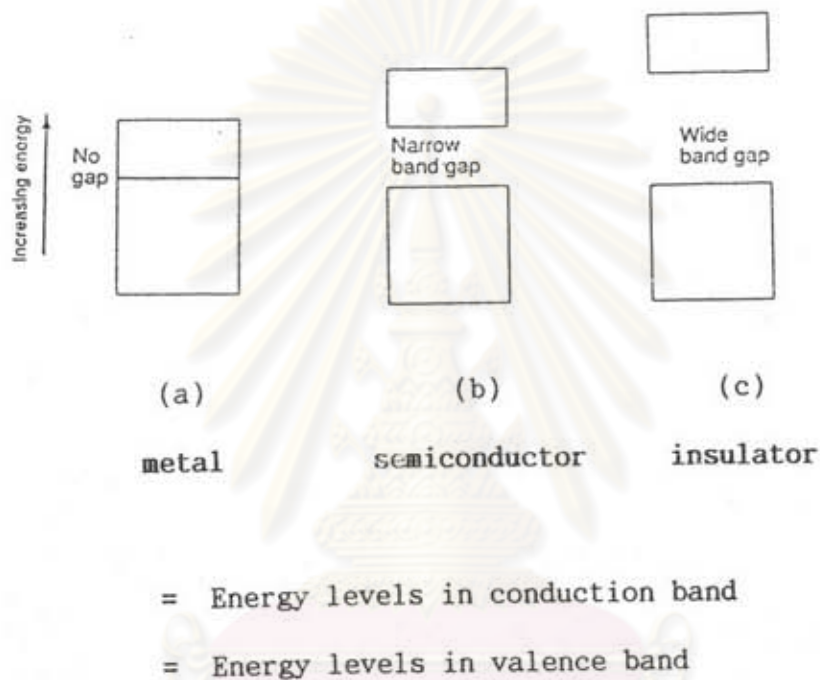
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### 2.1.2 Metal, semiconductor and insulator [24]

Energy band diagrams may be used to illustrate the differences between metals, semiconductors and insulators. In metals the electrons completely fill the valence band. The higher energy conduction band is empty at absolute zero. This is shown in Scheme 2.3(a). There is no energy gap between the valence and conduction bands for metals, 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 conduction 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 Scheme 2.3 (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 semiconductors, or extrinsic semiconductors. [1]



Scheme 2.3 The relationship of energy gaps in the three types of solids

### 2.1.3 Doping of Semiconductors [24-25]

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 polyacetylene and polypyrrole are spinless. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including solitons, polarons and bipolarons, have been applied to conducting polymers since the early 1980s.

#### 2.1.4 Charge storage

The conductivity of organic polymers is drastically increased by doping. This increasing was explained by the following :

##### 2.1.4.1 Nature of the charges appearing on the polymer chain [26-27]

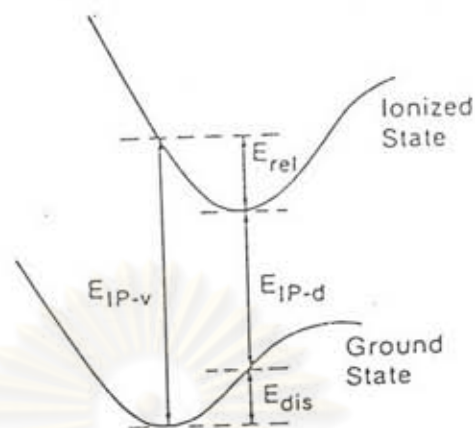
In crystal polymer , the interaction of a polymer unit cell with all its neighbors leads to the formation of electronic bands . The highest occupied electronic level constitutes the valence band (VB) and lowest unoccupied level, the conduction band (CB). The width of the forbidden band, or bandgap ( $E_g$ ), between the VB and CB determines the intrinsic electronic properties of the material. For all the organic conjugated polymers we have discussed so far, the band gap is 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 can display conductivity which 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 Scheme 2.4. 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  $E_{dis}$  (Scheme 2.4). For one-electron energy levels of the molecule, this distortion leads to an upward shift  $\Delta \epsilon$  of the highest occupied molecular orbital (HOMO) and a downward shift of the lowest unoccupied molecular orbital (LUMO), as illustrated in Scheme 2.5. If we then proceed to the ionization of the distorted molecule, it requires an energy  $E_{ip-d}$ .

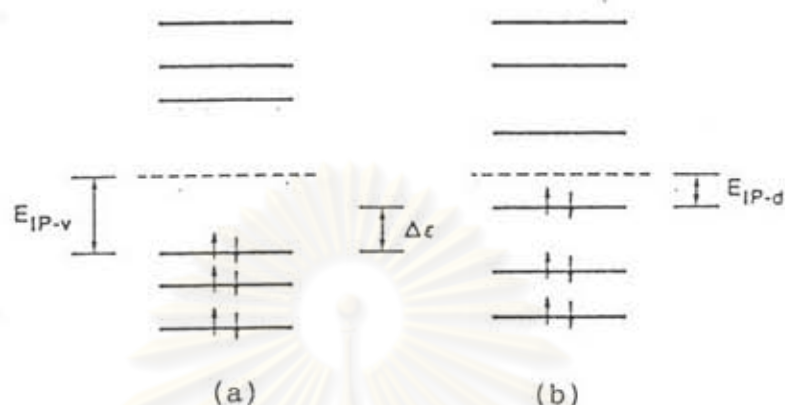




Scheme 2.4 Illustration of the energies involved in a molecular ionization process.  $E_{IP-v}$  is the vertical ionization energy,  $E_{rel}$ , the relaxation energy gained in the ionized state,  $E_{dis}$ , the distortion energy to be paid in the ground state in order that the molecule adopts the equilibrium geometry of the ionized state, and  $E_{IP-d}$ , the ionization energy of the distorted molecule

From Scheme 2.4, it is clear that it is energetically favorable to have a geometry relaxation in the ionized state when the quantity  $E_{IP-v} - E_{IP-d}$  (which actually corresponds to  $\Delta\epsilon$  as can be inferred from Scheme 2.5) is larger than the distortion energy  $E_{dis}$ ; or in other words, when the reduction,  $\Delta\epsilon$ , in ionization energy

upon distortion is larger than the energy  $E_{\text{dis}}$  required to make that distortion.

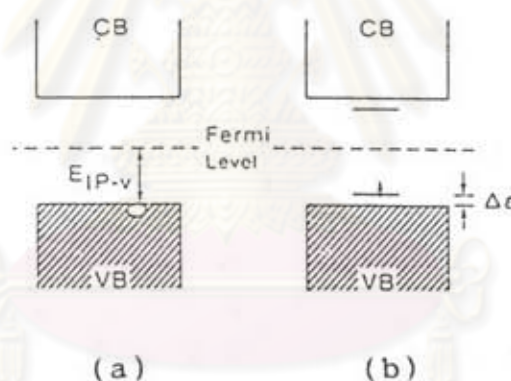


Scheme 2.5 The one-electron energy levels for organic molecule in its ground-state electronic configuration

- (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  $E_{\text{IP-v}}$  results in creating a hole on top of the valence band; see Scheme 2.6(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 causes 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, Scheme 2.6(b). Considering the case of oxidation, i.e., the removal of an electron from the chain, the ionization energy was lowered by an amount  $\Delta\varepsilon$ .



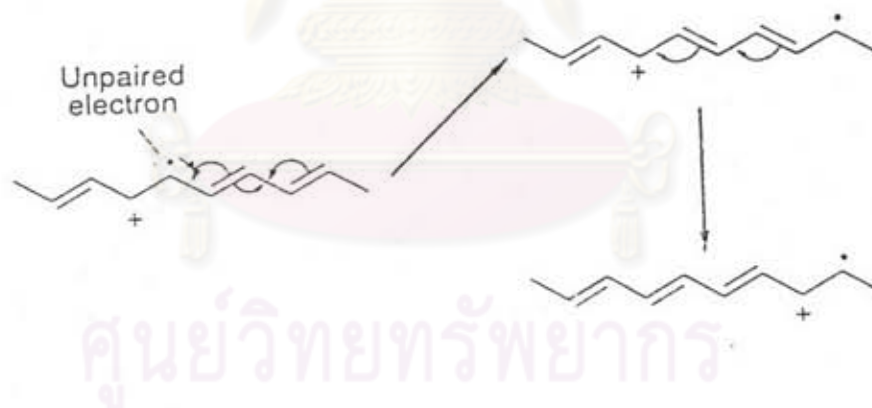
Scheme 2.6 Band structure of a polymeric chain in the case of

(a) a vertical ionization process

(b) the formation of a polaron

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 polaron.

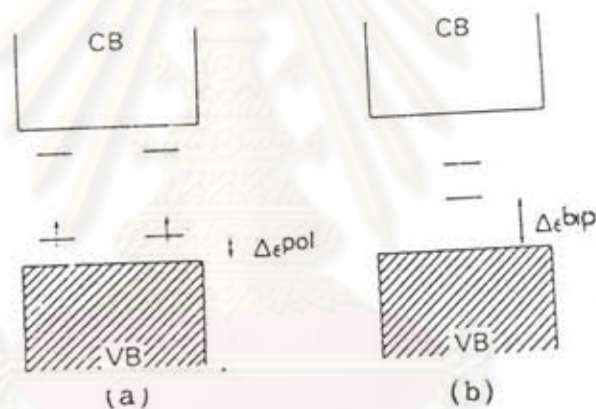
In chemical terminology, the polaron is just a radical ion (spin 1/2) associated with a lattice distortion and the presence of localized electronic state in the gap referred to as polaron state. The quantity  $\Delta\varepsilon - E_{\text{dis}} (= E_{\text{rel}})$  corresponds to the polaron binding 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, Scheme 2.6 (b).



Scheme 2.7 A radical cation that is partially delocalized over some polymer segment is called a polaron

If another electron is now removed from the already oxidized polymer containing the polaron [1] two things can happen : 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 dication, 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.



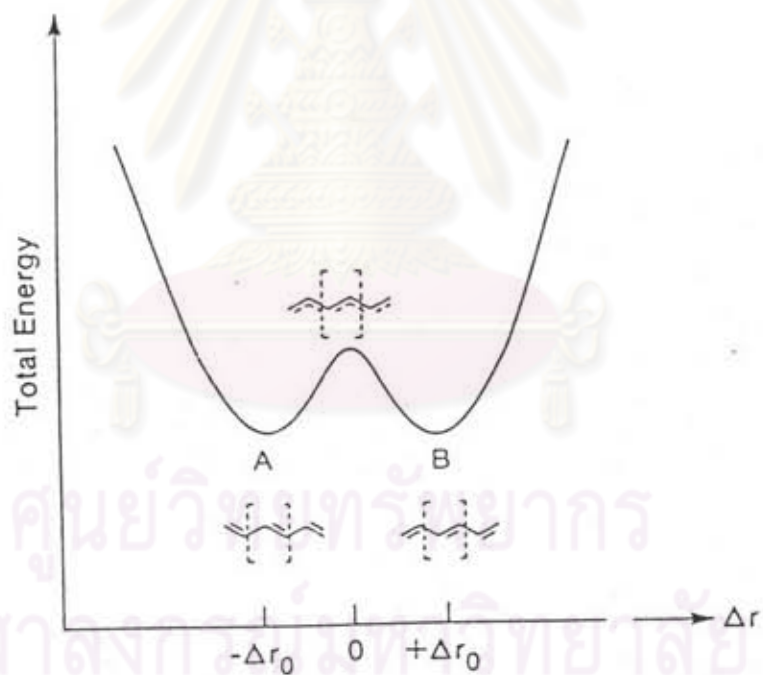
Scheme 2.8 Band structure of a polymer chain containing :  
 (a) two polarons ; (b) one bipolaron

The electron band structure corresponding to the presence of two polarons and that of one bipolaron is depicted in Scheme 2.8 . 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 for a polaron.

In the comparison of the creating of a bipolaron relative to that of two polarons, the calculations for polyacetylene, 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 ( $2 \Delta \epsilon^{bip}$ ) than for two polarons ( $2 \Delta \epsilon^{pol}$ ); see Scheme 2.8. 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 [ $= (2 \Delta \epsilon^{bip}) - E_{dis}^{bip}$ ] is calculated to be larger than that of two polarons by about 0.45 eV in polypyrrole.

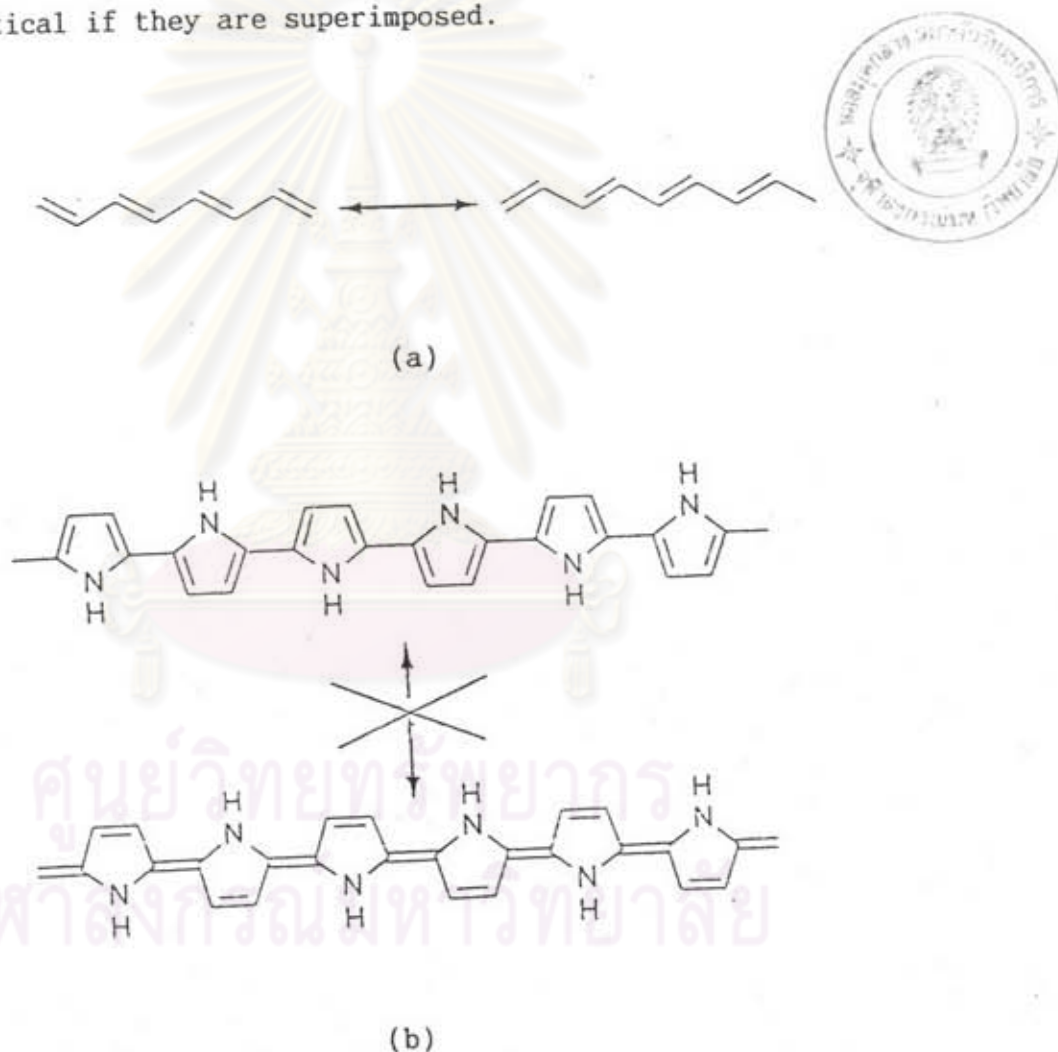
In case of p-(n-) type doping, the bipolaron level in the gap is empty (fully occupied); see Scheme 2.8(b). The bipolaron is thus spinless. The presence of bipolarons on polymer chains result in the possibility of two optical transitions below the bandgap transition: for p-type doping, such as polypyrrole, 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 (Scheme 2.8 (a)).

Trans-polyacetylene is unique so far among conducting polymers because it possesses a degenerate ground state, i.e., two geometric structures corresponding exactly to the same total energy (Scheme 2.9). The two structures differ from one another by the exchange of the carbon-carbon single and double bonds. Experimentally, the degree of bond length alternation  $\Delta r$  (i.e., the difference between the length of a single and a double bond) is  $\sim 0.08$  Å.



Scheme 2.9 Total energy curve for an infinite trans-polyacetylene

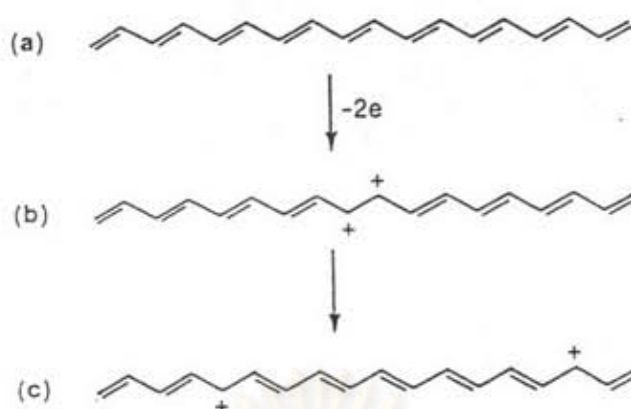
In polyacetylene, which has a degenerate ground state (two equivalent resonance forms), the bipolaron dissociates into two independent cations, which are spinless also and are called solitons. Solitons do not form in polymers with non-degenerate ground state, such as polypyrrole, polythiophene. These polymers are called non-degenerate because their resonance forms are not identical if they are superimposed.



Scheme 2.10 Illustration of resonance forms :

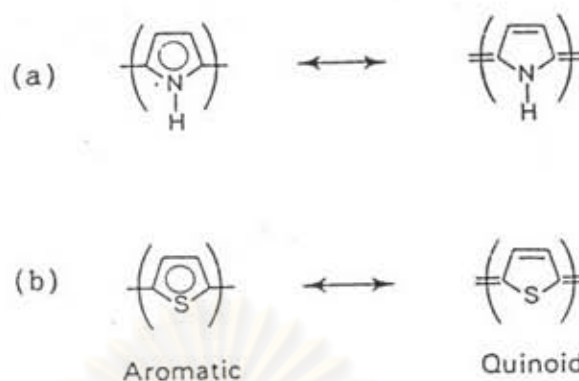
(a) in polyacetylene      (b) in polypyrrole





Scheme 2.11 The formation of two charged solitons on a chain of trans-polyacetylene

As a result of the degeneracy, the two charges forming would be bipolaron in trans-polyacetylene which can readily be separated (Scheme 2.11). This process is favorable because there is no increase in distortion energy when the two charges separate, since the geometric structure that appears between the two charges has the same energy as the geometric structure on the other sides of the charges. Unlike trans-polyacetylene, systems such as polypyrrole or polythiophene possess a non-degenerate ground state since their ground state corresponds to a single geometric structure which, in their case, is aromatic-like. A quinoid-like resonance structure can be envisioned but has a higher total energy (Scheme 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 [25].



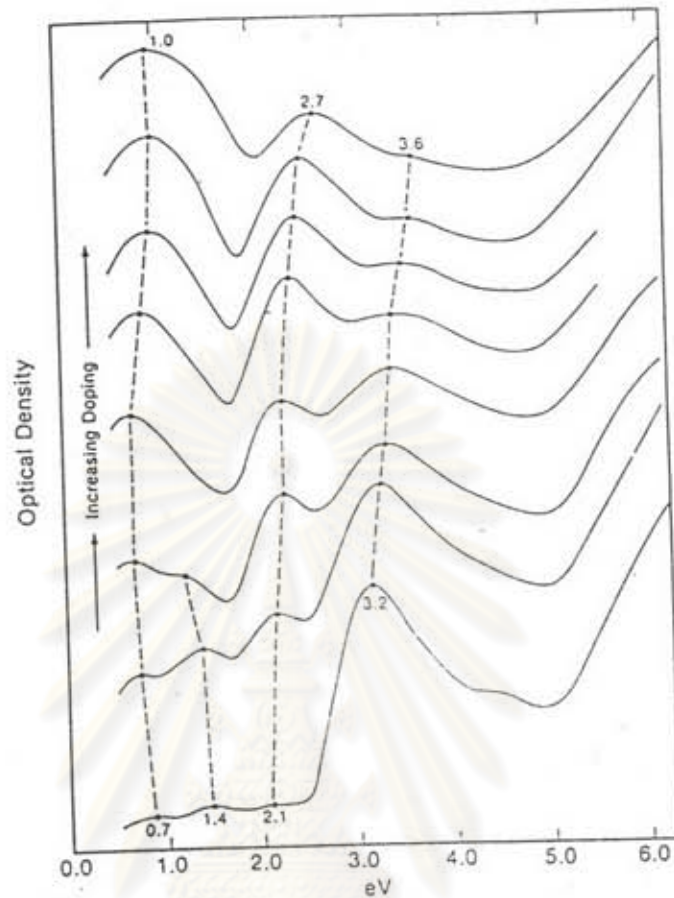
Scheme 2.12 Aromatic (ground-state) and quinoid-like geometric structure for  
 (a) polypyrrole (b) polythiophene

#### 2.1.4.2 Evolution of the Electronic and Transport Properties [28-30]

The state of polarons or bipolaron can be observed and explained by the optical absorption data. A consistent description of the electrical transport mechanism in conducting polymers constitutes a critical problem in the understanding of these materials. Band structure calculations on a deformable polypyrrole chain show that polarons and bipolarons are formed upon doping and the current carriers could be explained by relating charge carriers to doubly charged spinless bipolarons. The localized deformation associated with a polaron or bipolaron consists of lengthening the double bonds and shortening the single bonds.

Yakushi, K. et al. [30] recorded the optical spectra of polypyrrole at various stage of oxidation, From the as-grown highly oxidized to the almost neutral polypyrrole (Scheme 2.13). At low levels of oxidation (lower curve, Figure 2.13), there is a strong absorption maximum at 3.2 eV, associated with the interband  $\pi - \pi^*$  transition. Within the gap region, there are three additional features at 0.7, 1.4 and 2.1 eV. As the level of oxidation increases, the middle 1.4 eV absorption disappears, and the interband transition weakens and shifts to higher energy. In the fully oxidized sample (upper curve, Scheme 2.13), two intense, broad absorption bands are present at 1.0 and 2.7 eV and the interband transition appears as a shoulder at 3.6 eV.

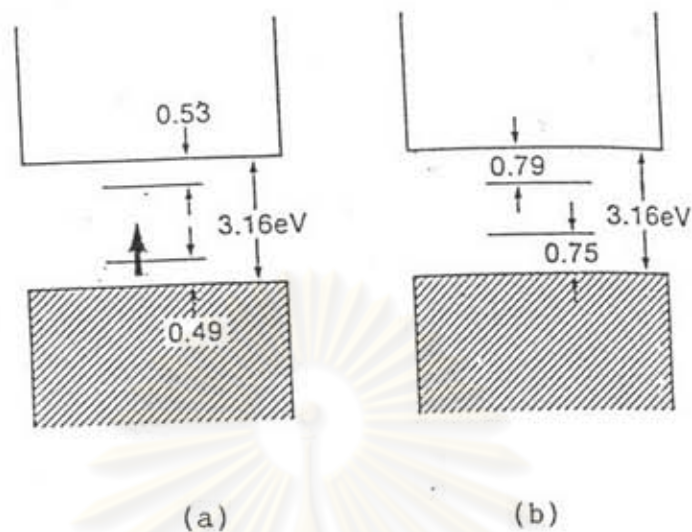
In order to interpret these experimental results, they present a theoretical study of the energetics of polaron and bipolaron formation on polypyrrole chains and the band-structure evolution upon oxidation. The result is to demonstrate that the evolution of the absorption spectra upon oxidation can be fully explained in terms of initial polaron formation and then bipolaron formation on the polypyrrole chains. From the ESR measurements, the theoretical studies of the absorption spectra indicate that bipolarons are the spinless charge carriers in the highly conducting regime of doped polypyrrole.



Scheme 2.13 Evolution of the optical-absorption spectrum of polypyrrole as a function of doping level from bottom curve (almost neutral polypyrrole) to top curve (33 mol % doping level)

Calculation of the energetics of polaron and bipolaron formation on polypyrrole chains are performed using tight-binding Huckel theory with  $\epsilon$  bond compressibility and bond-order-bond lengths relationships. A polaron is formed when the increase in  $\pi$  plus  $\epsilon$  energy due to the lattice deformation is more than that compensated by a lowering in ionization energy, the difference corresponding

to the polaron binding energy. When a single positive charge on the chain, polypyrrole obtain the formation of a polaron with a 0.12 eV binding energy, which difference between the 0.49 eV decrease in ionization energy and the 0.37 eV  $\pi$  plus  $\sigma$  energy needed for the change in geometry. The presence of a polaron on the chain introduces two localized electronic levels in the gap: a singly occupied bonding polaron state, 0.49 eV above the valence band (VB) edge and an empty antibonding polaron state, 0.53 eV below the conduction-band (CB) edge, Scheme 2.14 (a). The polaron states in the gap accounted for the three transitions observed within the gap in very slightly oxidized polypyrrole (lower curve, Scheme 2.13). The first absorption peak at 0.7 eV can be related to a transition from the VB to the bonding polaron state; the peak at 1.4 eV is associated with a transition from the bonding to the antibonding polaron state. Finally, the peak at 2.1 eV corresponds to a transition from the VB to the antibonding polaron state. Exact matching of calculated transitions to the peak in the absorption spectrum should not necessarily be expected, since the experimental data have limited spectral range. Nevertheless, the semiquantitative agreement between calculation and data is quite satisfactory. It must be stressed that the sum of the first two peak energies exactly corresponds to the peak energy for the third transition, as it should be within a one-electron model.



Scheme 2.14 Electronic structure diagrams for a polypyrrole chain containing

(a) low doping level, polaron formation

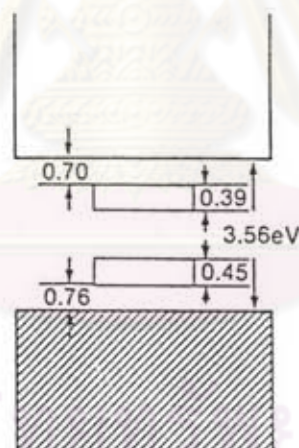
(b) moderate doping level, bipolaron formation

Note that the peak position indicates that the location of the antibonding polaron state is further away from the CB edge than the location of the bonding state from the VB edge. This asymmetric location arises because of the difference nitrogen orbital contribution to the VB and CB state. In the fourth transition, from the bonding polaron state to the CB, should be observed at 3.2 eV. This energy value unfortunately corresponds to the disorder-broadened edge of the band-gap transition.

At higher oxidation levels, polaron state starts interacting. The calculations indicated that two polarons, as they approach each other, become unstable with respect to the pairing of their spins and a doubly charged spinless bipolaron is formed (Scheme 2.14(b)). The geometry relaxation is stronger than in the polaron case (i.e., the geometry within the bipolaron is more quinoid-like than within the polaron), so that the empty bipolaron electronic levels in the gap are 0.75 eV above the VB edge and 0.79 eV below the CB edge (Scheme 2.14(b)). The bipolaron binding energy 0.69 eV means that a bipolaron is favored over two polarons by 0.45 ( $= 0.69 - 2 \times 0.12$ ) eV. Very importantly, the bipolaron bonding state, in contrast to the polaron case, is emptiness. As a result, only two transitions within the gap are now possible. Thus the emptiness of the bonding states in the gap accounts for the loss of the middle 1.4 eV absorption peak when going from slightly oxidized to highly oxidized polypyrrole.

The band structure for a doping level of 33 mol % (per polymer repeat unit) is displayed in Scheme 2.15. The overlap between the bipolaron states leads to the formation of two  $\sim 0.4$  eV (0.45 and 0.39 eV, respectively) wide bipolaron bands in the gap. The bandgap has widened from 3.16 eV in the neutral state to 3.56 eV in the 33 % doped, 0.4 eV larger than in the undoped case.

This is due to the fact that the bipolaron states coming in the gap are taken from the VB and CB edges. This band structure supports the fact that, upon application of an electric field, the spinless bipolarons (which carry two charges) could become mobile at high dopant concentration, where the Coulomb attraction with the counterions is largely screened. This conduction mechanism would be highly unusual in the sense that all bands are either totally filled or empty (as shown in the band structure in Scheme 2.15) and that mobile bipolarons, not electron, transport the current.



Scheme 2.15 Band structure for highly oxidized (33 mol % doping level) polypyrrole, showing the presence of two broad bipolaron bands in the gap



In summary, conduction by polarons and bipolaron is now thought to be the dominant mechanism of charge transport in polymers. These concepts also explain very well the optical absorption changes seen in these polymers with doping, which its data demonstrate that

- i) polarons are formed on the chains at low oxidation level.
- ii) at higher oxidation level, polarons combine to form spinless bipolaron.
- iii) wide bipolaron bands are present in the gap in the highly conducting regime.

However, it should be emphasized that these models were device assuming ideal structure. The actual structures 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.

## 2.2 Oxidation Potential of the Solution

Recently, polypyrrole which obtained from chemical polymerization in solution, can exhibit very high electrical conductivities when a suitable solvent is selected and the oxidation potential of the solution is controlled. Oxidation potentials of oxidant solution were measured using saturated calomel electrodes (SCE) as standards. A platinum wire was

used as a working electrode. To investigate this process further, Machida et al. [12] attempted to find a single measure which affects the electrical conductivity of the synthesized polymers. They have observed that the oxidation potential of the solution plays an important role in the polymerization process and the conductivity of the synthesized polypyrrole. In the equilibrium state the oxidation potential (E) is expressed by Nernst's equation [32] as

$$E = E_0 + (RT/nF) \ln( A_{OX} / A_{red} ) \quad \{2.1\}$$

Where  $A_{OX}$  and  $A_{red}$  are the activities of the oxidant ( $FeCl_3$ ) and reductant ( $FeCl_2$ ) respectively. During this reaction, the  $FeCl_3$  concentration decreases while the  $FeCl_2$  concentration increases. If the reaction rate is not so rapid, they assumed the reaction to be a series of equilibrium step, i.e., a quasistatic process to which equation {2.1} can be applied. According to this equation, the oxidation potential will decrease during the process. To study this decrease in more detail, they gradually added  $FeCl_2$  to 3.5M  $FeCl_3$  in methanol solution, step by step, and measured the oxidation potential of the solution for each step. The results are shown in Figure 2.1, where the filled circles show the experimental values and the open circles show theoretical values calculated by equation {2.1}. In this calculation, the experimental temperature was

$T = 273 \text{ K}$ ,  $n = 1$  and  $E_0 = 420 \text{ mV}$  (versus SCE). The initial ratio  $A_{\text{ox}}/A_{\text{red}}$  for  $\text{FeCl}_3/\text{FeCl}_2$  is calculated to be about 4000, which means that almost only  $\text{FeCl}_3$  exists in the solution initially. This Figure shows good agreement between the theoretical and experimental values.

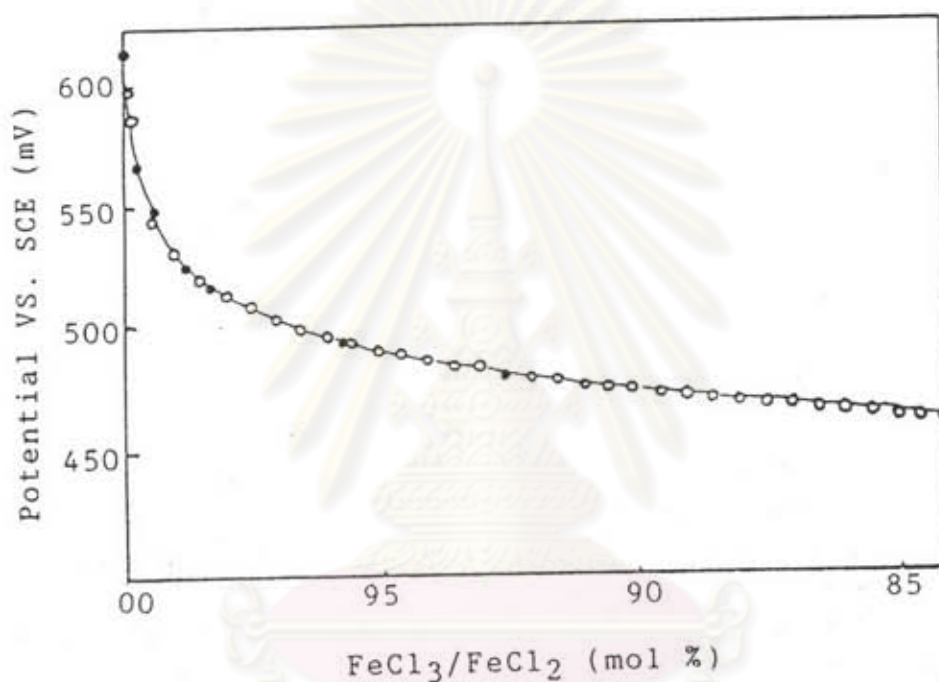


Figure 2.1 The change in oxidation potential of 3.5M  $\text{FeCl}_3$  in methanol solution when  $\text{FeCl}_2$  is added gradually. Open circles denote the theoretical values calculated from eq. (2.1) filled circles show the experimental values

Figure 2.2 shows the change of oxidation potential during the polymerization process. Open and filled circles show the step change of oxidation potential of 2.5 M and 3.5 M  $\text{FeCl}_3$  in methanol solution during polymerization.

Since the oxidation potential decreased during polymerization, it is clear that the conductivity of synthesized polypyrrole depends on polymerization time as well.

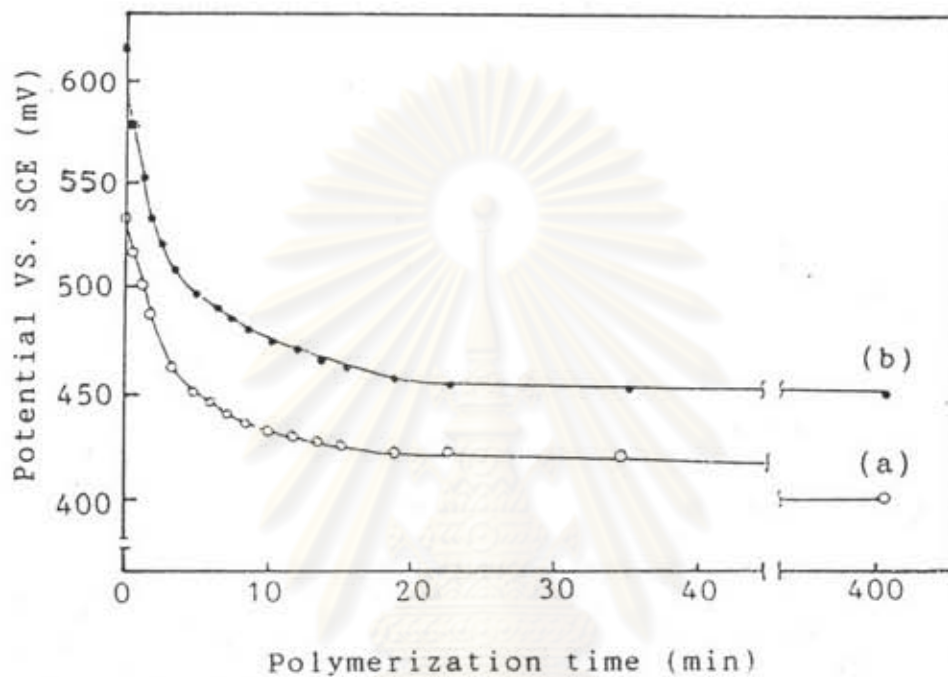


Figure 2.2 The change in oxidation potentials (vs. SCE) of  $\text{FeCl}_3$  in methanol solutions during the polymerization.

(a) 2.5 M  $\text{FeCl}_3$

(b) 3.5 M  $\text{FeCl}_3$

In general the initial oxidation potential of  $\text{FeCl}_3$  solution before the polymerization process depends on the selected solvent. Figure 2.3 shows the conductivity as a function of initial oxidation potential of 2.5 M  $\text{FeCl}_3$  in various solvents. From this result, it is clear that the

oxidation potential of the solution plays an important role in the electrical conductivity of chemically prepared polypyrrole.

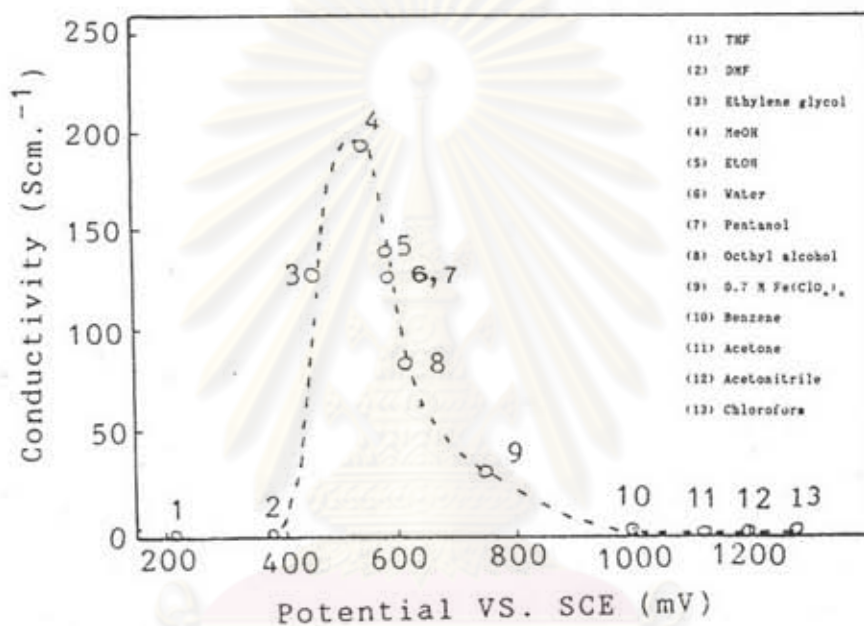


Figure 2.3 The conductivity of prepared polypyrrole when the oxidation potential of the solutions was controlled by changing solvent

## 2.3 Electrical Conductivity Measurement [33]

After synthesis, the electrical conductivity of samples were measured, in this work two measurement techniques were employed:

- i) Van der Pauw method
- ii) Four-point Probe method

Detail of the measurements are described below.

### 2.3.1 Van der Pauw Method

Van der Pauw method is one technique for measuring conductivity ( $\sigma$ ) of samples which have constant thickness but arbitrary shape. First, four ohmic contacts are made at edge of the sample. (Scheme 2.15). Then applied suitable current ( $I_{12}$ ) through contacts 1 and 2 and measured potential different ( $V_{34}$ ) between contact 3 and 4 and got ratio

$$R_1 = |V_{34}|/I_{12}$$

Second,  $I_{23}$  applied through contacts 2 and 3 and measured potential different,  $V_{41}$ , Thus obtained

$$R_2 = |V_{41}|/I_{23}$$

From these the conductivity of the sample can be calculated from equation {2.1}

$$\exp(-\pi R_1 d \kappa) + \exp(-\pi R_2 d \kappa) = 1 \quad \{2.1\}$$

where  $d$  is thickness of the sample.

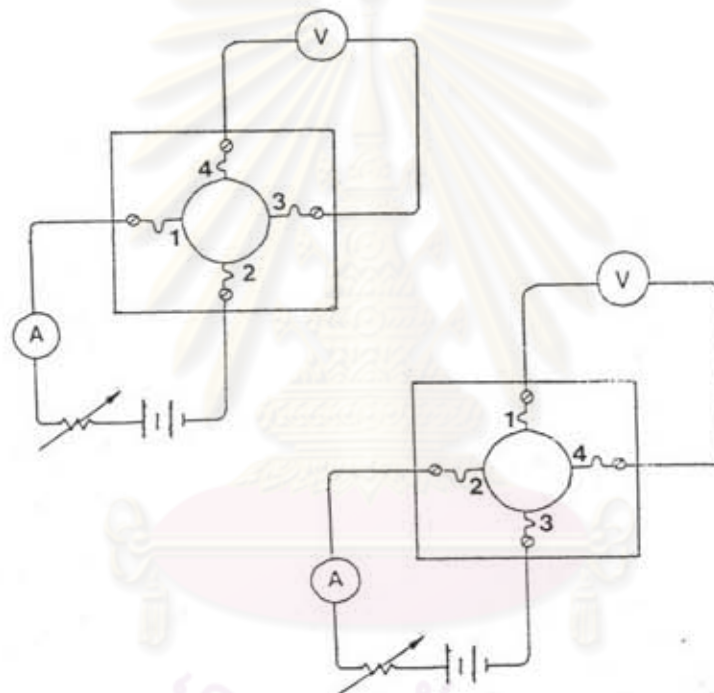


Figure 2.4 Conductivity measurement by Van der Pauw method

In principle, we can change the current electrodes around, get  $I_{12}$ ,  $I_{23}$ ,  $I_{34}$ ,  $I_{41}$  and corresponding potential differences  $V_{34}$ ,  $V_{41}$ ,  $V_{12}$ ,  $V_{23}$  respectively. Then calculate  $\kappa_1$ ,  $\kappa_2$ ,  $\kappa_3$  and  $\kappa_4$  from equation {2.1} as show in table 3.1. Finally obtain more accurate conductivity, equation {2.2}

Table 2.1 Various points for applied current

$\kappa_n$	$R_1$		$R_2$	
	I	V	I	V
$\kappa_1$	$I_{12}$	$V_{34}$	$I_{23}$	$V_{41}$
$\kappa_2$	$I_{23}$	$V_{41}$	$I_{34}$	$V_{12}$
$\kappa_3$	$I_{34}$	$V_{12}$	$I_{41}$	$V_{23}$
$\kappa_4$	$I_{41}$	$V_{23}$	$I_{12}$	$V_{34}$

$$\bar{\kappa} = (\kappa_1 + \kappa_2 + \kappa_3 + \kappa_4)/4 \quad \{2.2\}$$

$\bar{\kappa}$  = 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). In this thesis Aquadag was used.



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

#### 2.3.2 Four-point Probe Measurement

Measurement of conductivity of sample by Four-point Probe method is comfortable and rapid technique but it has some problem about accuracy.

In this method 4 tiny electrodes which lie in straight line and have exactly the same separation distance are prepared to touch the surface sample. The contact between each electrode and sample must be ohmic contact. In the measurement, current ( $I$ ) is applied through contact 1 and 4 and potential different ( $V$ ) across contact 2 and 3 is measured. Then conductivity of the sample can be obtained from equation {2.3}

$$z = \frac{I \pi \ln 2}{d V} \quad \{2.3\}$$

Where  $d$  is separation distance between each contacts

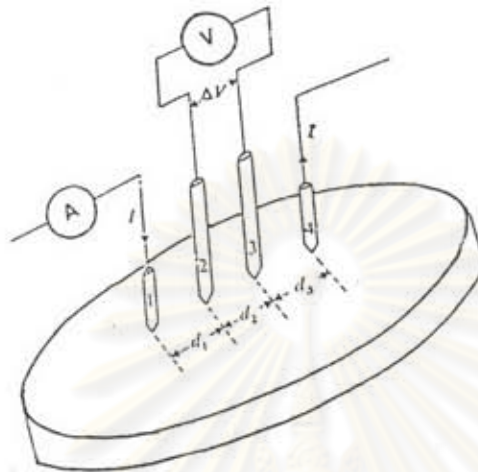


Figure 2.5 Conductivity measurement by Four-point Probe method

The accuracy of conductivity measurement by Four-point Probe method depends on:

- i) The size of the samples must be very large compared with the separation distance between electrodes.
- ii) Thickness of sample must be very small compared with the separation distance between electrodes.

Conductivities of polymer (polypyrrole, polythiophene and poly 3-methylthiophene) in this thesis were measured by both methods, but only conductivities obtained by Van der Pauw method which are more reliable are reported.

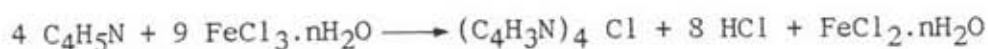
## 2.4 Literature reviews

There are more than 300 reports concerning the synthesis of polypyrrole by electrochemical polymerization and their electrical, morphological and mechanical properties. On the other hand the chemical polymerization of this polymer which is more convenient and economical, and can be used to prepare a large quantity of polypyrrole is not frequently investigated.

In 1977, Jone et al. [quoted in 20] synthesized polypyrrole by the reaction with the oxidants such as hydrogen peroxide or permanganate under acidic conditions. The product was more saturation and after halogen treatment, it had a conductivity of approximately  $10^{-5} \text{ Scm.}^{-1}$

In 1985, Pron et al. [34] prepared polypyrrole by chemical oxidation of pyrrole in ethanol-water solution containing  $\text{FeCl}_3$ . The resultant product was highly conducting ( $\kappa = 10 \text{ Scm.}^{-1}$ ). Elemental analysis was reproducible and gave the following empirical formular  $(\text{C}_4\text{H}_3\text{NCl}_{0.21}\text{O}_{0.30})_x$  with zero or a negligible amount of iron. Nature of oxygen in the obtained polymer was not clear. It might originate from the solution used for the polymerization. The absence of iron and the presence of

chlorine seemed to postulate the following equation for the oxidative polymerization.



In 1986, Kang et al. [35] reported a chemical method for the simultaneous polymerization and doping with halogen such as  $\text{Br}_2$  or  $\text{I}_2$ . The electrical conductivity of the polypyrrole- $\text{I}_2$  complex was in the order of  $10 \text{ Scm}^{-1}$ , while that of the polypyrrole- $\text{Br}_2$  complex is about one order of less magnitude, but both complexes were stable in the atmosphere.

In 1988, Chao and March synthesized [20] polypyrrole powder by the reaction with pyrrole in an aqueous solution or a water-toluene two-phase system. The pressed powder had a conductivity of approximately  $2.7 \times 10^{-2} \text{ Scm}^{-1}$ . All the other metal salts were synthesized from pyrrole with  $\text{FeCl}_3$  produced polymer that had the same organic backbone, morphology and conductivity as the polymer synthesized using  $\text{Fe(III)}$  salt. Regardless of the considerable differences in the reduction potentials of the metal ions, the nature of the anions of the transition metal salt had no effect on the reaction.

In 1989, Machida et al. [14] prepared polypyrrole by chemical polymerization in  $\text{FeCl}_3$  solution, using methanol as a solvent. They found that the oxidation potential of the solution strongly affected the polymerization process and conductivity. Polypyrrole could exhibit electrical conductivity as high as  $200 \text{ Scm}^{-1}$

Maddison and Unsworth [36] prepared polypyrrole (doped with p-toluene sulfoxide in aqueous solution at  $0^\circ\text{C}$ ). The Polymers had a conductivity of approximately  $60 \text{ Scm}^{-1}$

In 1991, Kaneko et al. [37] prepared 3,4-disubstituted polypyrrole films by chemical oxidation with  $\text{FeCl}_3$ . They found that the length of alkyl chains at 4-position of pyrrole ring affected conductivity. A longer chain gave a lower conductivity. On the other hand, the length of alkyl chains of ester group at 3-position did not affect the conductivity so much.

Kucharski et al. [38] studied the interaction between polypyrrole chain and doping anion. They proved that there were strong interaction between the polymer matrix and doping anions. The strength of this interaction can easily be modified by changing the content of water molecules in the polymer. All results suggested that strong deformation was caused by the hydrogen bonding.

The preparation of polythiophene and its derivatives had also been reported by using either electrochemical or chemical synthetic method. Similarly the polypyrrole, at the present time the chemical polymerization method was rare used comparing to electrochemical method.

In 1983 Chung et al. prepare polythiophene by chemical preparation with nickel catalyst. The resulting polymer has relatively low electronic conductivity ( $10^{-4} \text{ Scm}^{-1}$ ).

1983 Tourillon and Garnier synthesized polythiophene and poly-substituted thiophene by electrochemical method, the polypyrrole film (doped with  $\text{ClO}_4^-$ ) had a conductivity of approximately  $10^{-2} \text{ Scm}^{-1}$ . Poly (3-methylthiophene) film (doped with  $\text{ClO}_4^-$ ) had a conductivity of approximately  $10 \text{ Scm}^{-1}$ .

1988 Hotta prepared polythiophene films by electrochemical method (doped with  $\text{ClO}_4^-$  and  $\text{AsF}_6^-$ ). The polymer exhibited the highest conductivity of  $12 \text{ Scm}^{-1}$ , and  $10 \text{ Scm}^{-1}$  respectively.