CHAPTER II

THEORITICAL AND LITERATURE SURVEY

2.1 Classical theory for electrical conduction materials

Generally, the conduction mechanism of any conductive solid has been described by using band theory which can explains the mechanism of electrical transport in solid, such as metal, semiconductor, and insulator. The principle of band theory is the main information for explains electrical conduction behavior in those of materials.

2.1.1 The formation of band [17]

Electrical band is built from the addition of atoms to a line in one-dimensional consider. One atom contributes one s orbital at certain energy. This is shown in Figure 2.1(a). When a second atom is brought up it overlaps the first, and forms a bonding and antibonding orbital (Figure 2.1(b)). The third atom overlaps its nearest neighbor (and only slightly the next nearest) and, from this three atomic orbitals, three molecular orbital are formed (Fig 2.1(c)). At this stage, the bringing up successive atoms is to spread the range of energies covered by the molecular orbitals, and also to fill in the range of energies with more and more orbitals. The band is fully filled with N orbital when N is very large. However, the band remains of finite width.
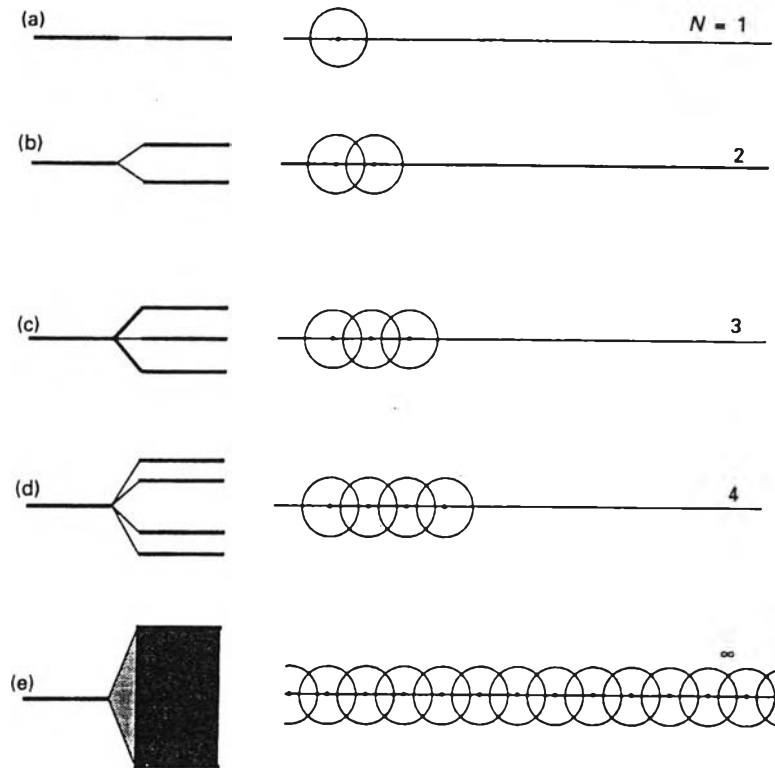
Figure 2.1 The formation of a band of N orbitals

In Figure 2.2, this shows that the s band formed from overlap of s orbitals and p band formed from p orbitals. In this case the s and p orbitals of the atom are so widely spaced that there is a band gap. The different characters of metal, semiconductors, and insulators depend on the width of band gap.

2.1.1.1 Metal

The simple model is shown in Figure 2.3(a). Because the orbital in the bands are so close together, electrons close to the top of the filled orbital. In this case highly occupied molecular orbital (HOMO) is called ' Fermi level '. The empty orbitals are very close in energy to this level. Some of the electrons are therefore very mobile, and give rise to electrical conductivity.
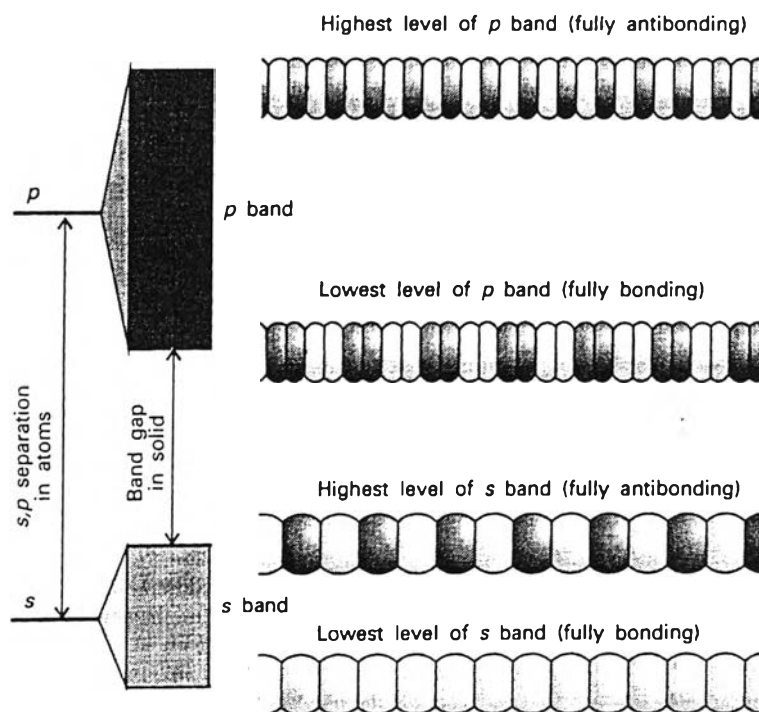
Highest level of *p* band (fully antibonding)

p band

Lowest level of *p* band (fully bonding)

Highest level of *s* band (fully antibonding)

s band

Lowest level of *s* band (fully bonding)

Figure 2.2 The formation of *s* and *p* orbital and the band gap

Increasing energy

(a) Metal — no band gap

(b) Semiconductor — narrow band gap

(c) Insulator — wide band gap

☐ EC = Energy levels in conduction band.
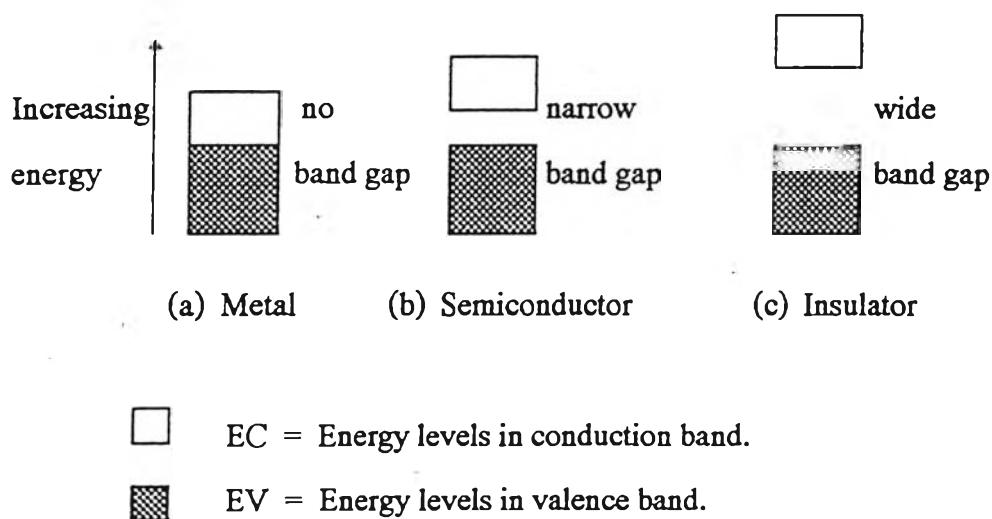
▨ EV = Energy levels in valence band.

Figure 2.3 The relationship of energy gap in the three types of solids

2.1.1.2 Insulator and Semiconductors

In these materials, shown in Figure 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 small, some electrons can be easily excited into the conduction band. This material is a semiconductor. If the energy gap is very large, the chance of electrons to be excited into an empty conduction band is a little, this property can founded in an insulator. When the impurity atoms are added into the materials, although the band gap is wide, it may be possible to establish level within the gap those facilitate the movement of electrons into the conduction band. These systems are called extrinsic semiconductors.

The method that lead the conductivity occurs in materials is called doping. This method is to implant foreign atoms into pure materials. If these dopants can trap electrons, the withdrawn electrons from the filled band, leaving holes which allow the remaining electrons to move (Figure 2.4(a)). This procedure give rise to p-type semiconductivity, the p indicating that the holes are relatively positive to the electrons in the band. Alternately, a dopant might carry excess electrons, e.g., p atoms introduced into germanium, and these additional electrons occupy otherwise empty bands, giving n-type semiconductivity (Figure 2.4(b)), where n denotes the negative charge of the carriers.
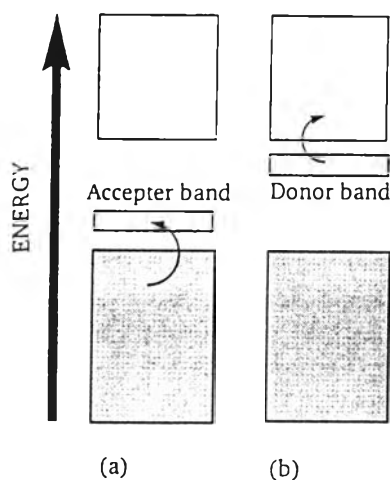
ENERGY

Accepter band   Donor band

(a)   (b)

Figure 2.4 The band diagram for the doping material

Now, we present the concept of electrical conductivity in ordinary materials, which are used in worldwide application for long time. This concept, however, is not quite correct for the new materials, which have long molecular chain, such as polymer. The feature of electrical transport in these materials is very different and complicate from old conductive materials.

2.2 Nature of charge in polymers [18]

2.2.1 The polymeric solid state

A distinguishing feature of polymeric and, more generally, organic materials that exhibit semiconducting electrical behavior is their molecular nature [19]. In the solid state, organic molecules retain their identity and interact weakly as molecular entities through van der Waals or electrostatic forces. For example, in a linear polymer electron interactions within a given macromolecular chain are much stronger than interaction between chains. Therefore, most polymers, the macromolecules are not packed into perfect single crystals.

Although organic polymers seem to exhibit transport and optical properties analogous to those of crystalline semiconductors, but there have the different physical phenomena that obtain from organic polymer in the two cases.

2.2.1.1 Relaxation

This incident occurs when a charge is injected into a polymer, it induces changes in the electronic charge density and atomic positions both on the molecular site that it occupies (intramolecular relaxation) and on neighboring molecular sites (intermolecular relaxation). This phenomenon is called relaxation and leads to a lowering of the energy of the composite system. It called relaxation energy, E_r.

2.2.1.2 Localization

The local or extended nature of charges in polymers is determined by a competition between fluctuations in the local site energies, which tend to localize the charges, and the hopping integrals for intersite charge transfer, which tend to delocalize the charges. This fluctuation-induced localization concept can be defined more precisely by considering the motion of an injected charge along a polymer chain.

These complicated phenomena appear in the polymer chain. They are involved with the different sets of parameters in Hamiltonian model from quantum physics, which can be demonstrated below.

Consider first a simple schematic model for the transfer of an electron (an injected electron) between two states (labelled by i = 1,2) that are centered on

two different molecular sites. The electronic energy of state 1 at site 1 is ε_1 that of state 2 at site 2 is ε_2, when the atomic nuclei are all the rest. Vibration of the molecule affects the energies states with frequencies ω_n (where n = 1,2,...). This coupling between the electronic energies ε_i depends on the positions of the atomic nuclei in the atoms. To lower order, the energies of the states are modified by their overlap that is by the energy associated with the electrons hopping between two states.

By known Hamiltonian model, the system consists of two electronic sites each of which is coupled to a common normal mode spectrum of vibration is:

$$H = H_e + H_v + H_c + H_T$$

The electron energies $\qquad H_e = \varepsilon_1 a_1 a_1^* + \varepsilon_2 a_2 a_2^*$

The vibrational energies $\qquad H_v = \Sigma_n \hbar\omega_n (b_n b_n^* + 1/2)$

The electron - 'phonon' coupling $\qquad H_c = \Sigma_n g_{1n}^2 \hbar\omega_n a_1 a_1^* (b_1^* + b_n)$

$$+ \Sigma_n g_{2n}^2 \hbar\omega_n a_2 a_2^* (b_2^* + b_n)$$

The transfer Hamiltonian $\qquad H_T = t_0(a_2^* a_1 + a_1^* a_2)$

By considering electronic states for the different sites of a crystal lattice one can account successfully for transport properties of many organic crystals. H_e becomes $H_e = \Sigma_i \varepsilon_i a_i^* a_i$ and the vibrational quanta become 'lattice' phonons. If electron-phonon interaction (g_{in}) is neglected, $g_{in}=0$, the electron state displays the full periodicity of the lattice. The width of result energy bands is formed $W = 2zt_0$ where z is the coordination number of the site and is the overlap integrals. However, in the presence of g_{in} the occupations of electron and phonon state are coupled. At low temperature electronic motion still occurs with extended states (localized) built from periodic states. The entity consisting of the localized electron

with its accompanying distortion of the lattice is called a 'small polaron'. However, Duke et.al. [19], have found some failure of this small-polaron hopping model. They

$$\Delta = \left(\left\langle \left(\varepsilon_i - \bar{\varepsilon} \right)^2 \right\rangle AV \right)^{\frac{1}{2}}$$

give the root mean square deviation from the mean

This term is referred to as diagonal disorder whereas to make the nearest neighbor hopping model in organic solid. The schematic comparison of conduction band in the different materials was shown in Figure 2.5.

When $\Delta = 0$, this model describes the traditional energy band (Figure 2.5(a)). If Δ is less than W, where W describes the localization of electronic states at the edges of the band but not the center, states near the edges of bands that would have existed if $\Delta=0$ are localized, whereas those near the center of these bands remain extended. Shade areas in Figure 2.5(c) indicate the localized states. When $\Delta >> W$, it describes the situation in which all electronic states are localized and the concept of energy band has lost its meaning.

Summary, Figure 2.5 indicates how the localized states penetrate into the band and into the forbidden gap with increasing static diagonal disorder Δ until all the states are localized and the gap has completely disappeared when $\Delta >> W$. This disordered semiconductor model is somewhat of simplification of the behavior of electrons in nonperiodic solids, but it permits a systematic interpretation of experiments on molecularly doped conducting polymers.
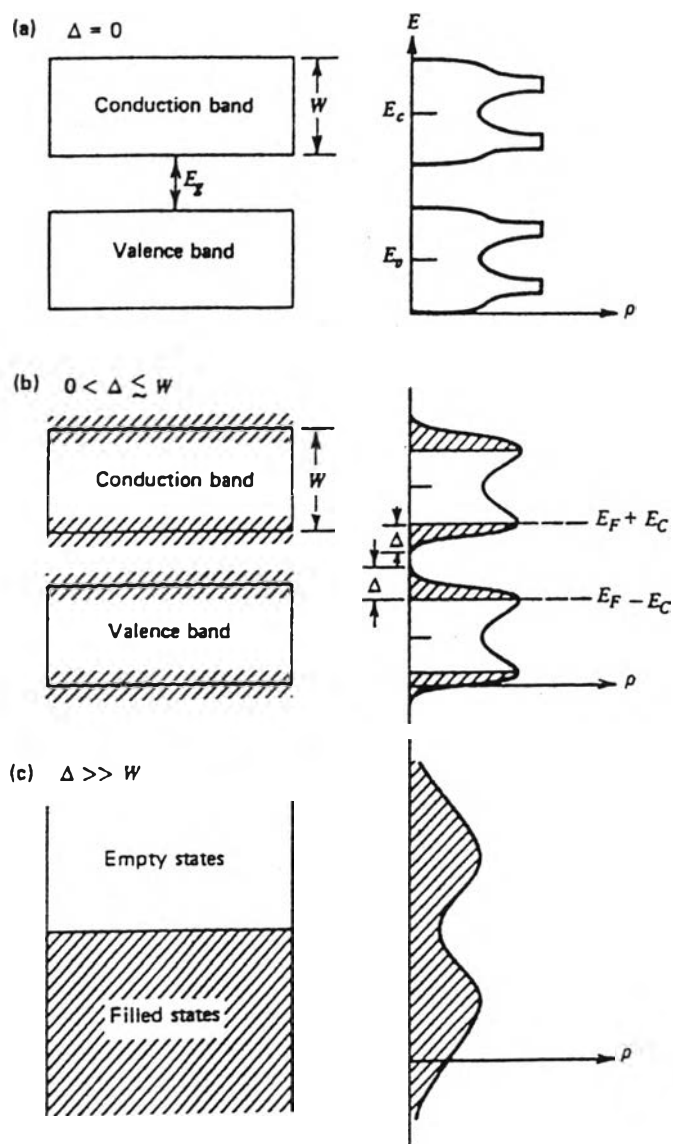
Figure 2.5 Schematic indication of the consequences of static diagonal on the

localization of one-electron states in a nominally three dimensional

undoped polymeric solid

2.2.2 Hopping Conduction [6]

From the previous section, we know that disorder in a lattice affects both the energetic and spatial distribution of electronic states. For a random distribution of atoms the density of electronic energy states tails into what is normally the forbidden zone and the electrons in these tails are localized. For this reason, there is an intermediate range of electronic states in which mobilities are very low. Only when electrons are excited to higher energy states, in which mobilities are higher, can appreciable conduction occur.

Conduction via localized electrons implies discrete jumps across an energy barrier of site 1 next to site 2 (Figure 2.6). An electron may either hop over, or tunnel through, the top of the barrier, the relative importance of these two mechanisms depends on the shape of barrier and the availability of thermal energy
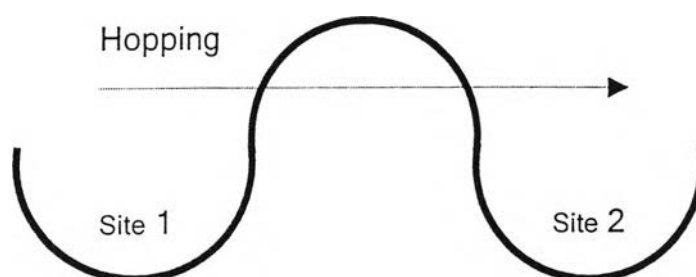
Figure 2.6 Hopping model of electron across an energy barrier

2.2.3 Charge carrier in conducting polymer [2]

In order to shows the behavior of conducting polymer, polyacetylene (PA) is used to investigate. PA is the simplest one-dimensional conjugated system. When π electrons form a π electron cloud due to the overlap of p_z orbitals resulting

from the resonance effect. That explains the stability and identical bond length of a benzene ring. If the resonance effect occurs in a one-dimensional conjugated system in a similar way to a benzene ring, one would expect a one-dimensional metal with a partially filled conduction band and π electrons as charge carriers. However, conjugated polymers without doping (oxidation or reduction) are insulators or semiconductors at best. This indicates that a one-dimensional conjugated chain behaves quite differently from a benzene ring. Since strong interaction between π electrons and the backbone skeletal vibrations occurs. This means that the chain is thermodinamically more stable by lowering its free energy through the transition from the resonance structure of identical bond length to the alternating short and long bonds, which in effect will destroy the electronic delocalization that can take place along the backbond.

Like PA, polypyrrole, PPy have the analogous charge transport behavior. While PA electrical charge is soliton [20] which is a neutral charge in long-chain polyene of PA that have a single unpaired spin localized in the wall, the wall width was assumed to be of order one bond length, leading to a large activation energy for motion and localization of the wall. PPy electrical charges are polaron and bipolaron. Both polarons and bipolarons can move along the conjugated backbond by the rearrangement of the double bonds and single bonds. These are described in later section.

2.3 Polypyrrole and general properties

2.3.1 Synthesis of polypyrrole [21]

Electrical conducting polypyrrole (PPy) can be prepared by electrochemical or chemical oxidative polymerization. In chemical oxidative polymerization, ferric chloride is chosen as an initiator (oxidant). It also acts as the dopant. PPy prepared with this initiator-dopant in the absence of any stabilizer contains about one Cl unit per three-pyrrole units [22]. The reaction stoichiometry is approximated by Figure 2.7.
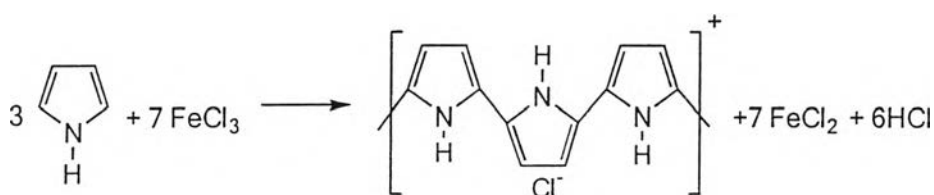

Figure 2.7 Polymerization of pyrrole by using $FeCl_3$ as an oxidant

By this scheme, there are 2.33 moles $FeCl_3$ that is required for the polymerization of one mole of pyrrole. Polymerization in nonaqueous medium requires the use of $FeCl_3$ to pyrrole at mole ratios greater than 2:1 to achieve the highest conductivity. However, in aqueous medium the latter may be obtained using a much lower ratio of $FeCl_3$ to pyrrole, sacrificing the yield, of course.

PPy is insoluble and infusible and hence difficult to process. The color is black. The electrophysical properties of polypyrrole are determined by the variety of factors such as the degree of polymerization, nature of dopants and the heteroatom on the molecule. For PPy, the band gap changes from 2.0 eV to 3.2 eV [23], respectively. Furthermore, PPy have two inequivalent structures. Thus, the

coupling of electronic excitations to chain distortions is lead to polarons and bipolarons as the dominant charged species [24].

2.3.2 Electrical transport of polypyrrole [25]

The electrical transport mechanism in polypyrrole, which has high electrical conductivity, was investigated to understand the band structure on a deformable chain. When polypyrrole was doped by doping oxidant or reductant the polarons and bipolarons are formed. The evolution of the band structure depends on the doping level of dopants. From this, it shows that the formation of polaron and bipolarons are involved the quantity of dopants.

Yakushi and Lauchlan [26] reported the evolution of the optical-absorption spectrum of polypyrrole as a function of doping level. The concentration of perchlorate anions increases from bottom curve in Figure 2.8.

At low levels of oxidation (lowest curve) there is a strong absorption maximum at 3.2 eV, associates with the interband $\pi \rightarrow \pi^*$ 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), 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.
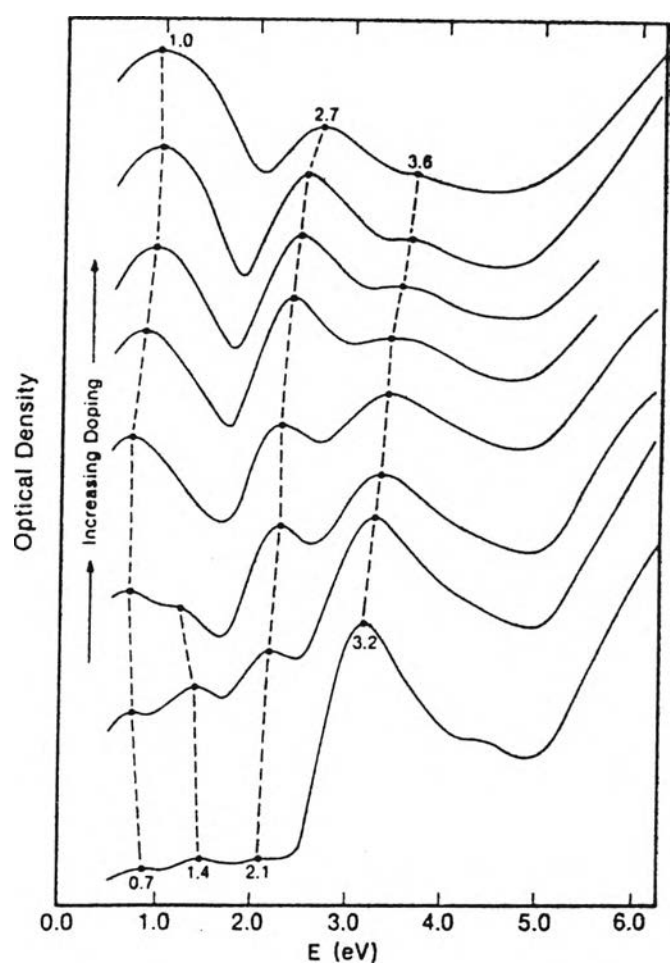
Figure 2.8 Evolution of the optical-absorption spectrum of pyrrole as a function of

doping level from bottom curve (almost neutral polypyrrole) to top curve

(33 mol % doping level)

The calculation of energetics of polaron and bipolaron formation on

PPy chains using tight-binding Huckel theory with s bond compressability and bond-

order-bond length relationships was investigated by Brédas et al. [25] to interprete

the experimental results in Figure 2.8. This study using the technique based on a

quantum chemical version of adiabatic Su-Schrieffer-Heager Hamiltonian.

The polaron is formed with a 0.12 eV binding energy when a single positive charge is introduced on the chain. And then, the presence of a polaron on the chain introduces two localized electronic levels in the gap: a single occupied bonding polaron state 0.49 eV above the valence band (VB) edge an empty antibonding polaron state 0.53 eV below the conduction-band (CB) edge (Figure 2.9 (a)). The polaron states in the gap account for the three transitions observed within the gap in very slightly oxidized PPy (lower curve, Figure 2.8). 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 valence band (VB) to the antibonding polaron state. The peak positions indicate that the location of the antibonding polaron state is further away from the conduction band (CB) edge than the location of the bonding state from the VB edge. This asymmetric location arises because of the different nitrogen orbital contribution to the VB and CB states. The fourth transition, from the bonding polaron state to the CB, should be observed at ~2.5 eV. This energy value unfortunately corresponds to the disorder-broadened edge of the band-gap transition.

As doping level increases, the higher oxidation levels have presented, polaron states start interacting. The two polarons become unstable with respect to the pairing of their spins and the formation of a doubly charged spinless bipolaron in the gap.
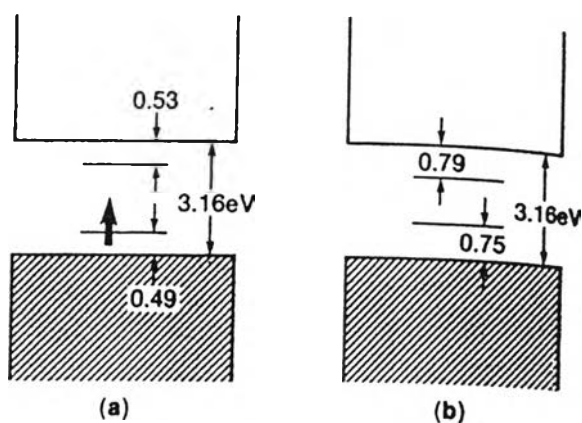
Figure 2.9 Electronic structure diagrams for a polypyrrole chain containing

(a) low doping level, polaron formation

(b) moderate doping level, bipolaron formation

The above picture of polaron recombination to form bipolarons is in full agreement with ESR measurements on PPy chemically doped with oxygen [27] and 0.79 eV below the CB edge (Figure 2.9(b)). Very importantly, the bipolaron bonding state, in contrast to the polaron case, is empty. As a result, only two transitions within the gap are now possible. Thus the emptying of the bonding states in the gap accounts for the loss of the middle 1.4 eV absorption peak when from slightly oxidized PPy.

The band structure of the 33% doping level (highly oxidized)(Figure 2.10) show that the band gap is correctly obtained at 3.56 eV, 0.40 eV larger than in undoped case. The two wide bipolaron bands are present which are calculated to be 0.45 and 0.39 eV, respectively. Furthermore, note that the intensity of lower bipolaron absorption is largest. This is consistent with the oscillator strengths calculated by Fesser, Bishop, and Campbell [28] on the basis of a continuum coupled electron-phonon model adapted for nondegenerate ground-state polymers.
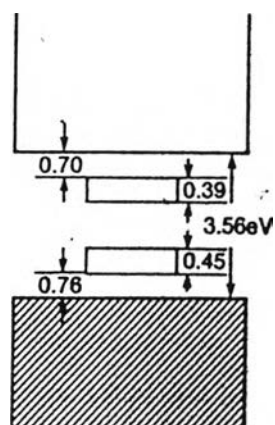
Figure 2.10 Band structure for highly doping level (33 mol %) polypyrrole, showing
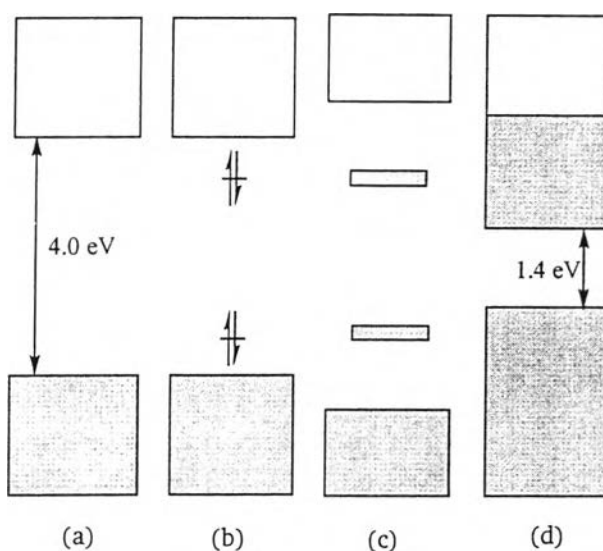
the presence of two broad bipolaron bands in the gap

Figure 2.11 The band structure evolution upon (sodium) doping of polypyrrole

(a) undoped

(b) intermediate doping level: noninteracting bipolarons present in the

chain

(c) per monomer 33 % doping level

(d) per monomer 100 % doping level

The formation of polaron and bipolaron involving the oxidized doping level is rather complicated beyond understand. The band structures of electrical conductivity in polypyrrole at various doping levels were shown in Figure 2.11.

Picture (a) shows that at undoped polypyrrole the band gap is very wide. At (b) picture, low doping levels, it is expected that polarons (singly charged defects corresponding to radical ions and carrying spin) rather are present on the chain. The recombination among polarons leading to bipolaron formation of bipolaron bands in the gap like in Figure 2.9. If still higher doping level could be achieved, bipolaron bands eventually merge with the CB and VB (Figure 2.11(d)). The band gap energy is low.

Summarized again, theoretical studies on polypyrrole demonstrate that

(1)   polarons are formed on the chains at low oxidation level

(2)   at higher oxidation levels, polarons combine to form spinless bipolarons

(3)   wide bipolaron bands are present in the gap in highly conducting regime

2.4 Polypyrrole coating composites

It is well known that pure polypyrrole is insoluble and infusible. To solve this problem, the coating of polypyrrole on the surface of various polymers was investigated. Various insulating polymer have been used to prepare the polypyrrole-coated composite, such as PS latex [29], PP, PE, PVC [30]. Each of insulating polymer may gain the advantage from its character to the prepared composite. Indeed, the preparation of polypyrrole coating composite is rather simply, and similar to the ordinary procedure. The preparation of PPy-coated composite is exhibited in the next section. Furthermore, the important factors that lead to the presence of electrical conduction in polypyrrole coating composite are also described.

2.4.1 Chemical synthesis of polypyrrole coating composites

Conducting polypyrrole (PPy) can be produced by a chemical technique in which the pyrrole monomer is dissolved in a solvent such as methanol, water, etc. with an appropriate chemical oxidant. By adding host polymers (core polymer) into the solution, the composites are formed by the coating of polypyrrole on those polymers. The thickness of polypyrrole layer depends on quantity of pyrrole monomer and concentration of oxidant. The obtained polypyrrole also have the spherical form as their original host polymer features (Figure 2.12)
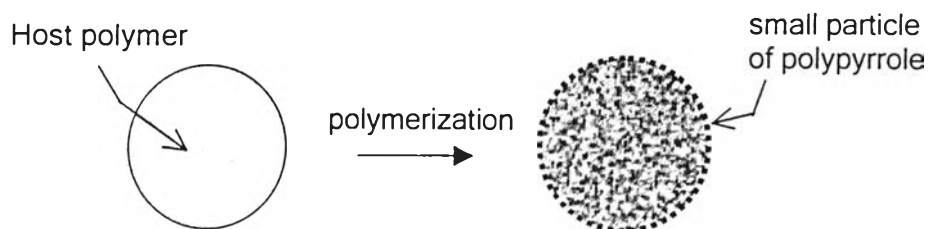
Figure 2.12 The coated-formation of polypyrrole on the host polymer

The polypyrrole products might have the different properties, which unlike pure polypyrrole, i.e. electrical conductivity, physical character, and surface morphology, etc. These properties were influenced by their host characters.

2.4.2 Property of conducting particle system

The art of making a good conducting composite is to be able to use the minimum quantity of conductive component, e.g. polypyrrole, to achieve the required degree of electrical performance. And in this context it is important to know more about the factors that control the formation of conductive networks for a given concentration of PPy. This depends on two main factors:

2.4.2.1 Quality of interparticle contacts

Conductive networks in a 2-phase system depend on the good electrical contact between the particles of the conductive phase. Since a colossal number of interparticle contacts are involved, any changes in contact properties will be highly significant to the conductivity.

2.4.2.2 Shape and size of conductive particles

The Holm's theory [31] expression $\rho\pi/a$ as a contact resistance between two spheres when radius a of the circular area of contact between them is small with respect to the radius of the spheres, ρ being the resistivity of the material of the spheres. Thus, taking into account the way in which compressive forces cause elastic and yielding deformation, thereby altering a, the dependence of the resistivity of the compaction on pressure may be predicted quantitatively. The same theory may be expected to apply also to composites containing high loading of conductive fillers where contacts amongst a certain proportion of particles form the conducting paths through the material. On this basis, where contact resistance dominate, spherical particles will be rather inefficient at imparting conductivity, since most of the material in the spheres is not take part in electrical conduction process (Figure 2.13).
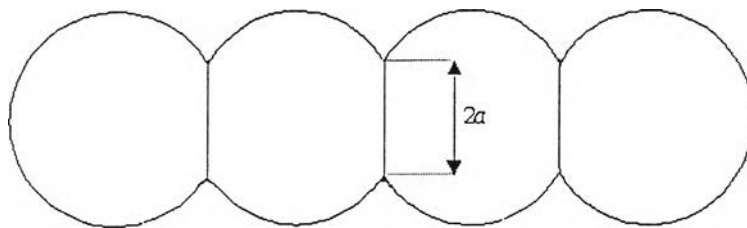

Figure 2.13 Model form of intersphere contacts

2.5 Chemical polymerization of dispersion polypyrrole [32]

Dispersion polypyrrole is prepared from the use of dispersing agent as stabilizer in the chemical polymerization. It is involved with the formation of colloidal dispersions facilitated by the adsorption of stabilizer molecules on the surface of an insoluble phase, i.e. the conducting polypyrrole. It is the protection technique to hinder the agglomeration of PPy particles.

Obviously, the interactions between monomer, polymer, solvent, and stabilizer will be critical to colloid formation and properties. Aldissi and Armes [33] have suggested that the conditions necessary for obtaining well-dispersed colloids depend on the following factors:

1) oxidant/stabilizer compatibility

2) an appropriate number of active sites for adsorption or grafting of the stabilizer, and

3) an appropriate molecular weight of the stabilizer, to provide sufficient coverage of the insoluble core

Both grafted and non-grafted stabilizers have been used for the formation of conductive polypyrrole colloids. Polypyrrole can be stabilized by physical adsorption of stabilizers through their hydrophobic component. This probably involves a hydrogen bonding mechanism with the pyrrole N-H group. Similar mechanisms may also occur in the stabilization of polyaniline. However, it has also been demonstrated that stabilizers may be chemically grafted to the polyaniline by using modified aniline derivatives to form copolymers. This gives greater stability, because the steric desorption of the stabilizers cannot occur.

Stabilizer concentration is also important, because insufficient stabilizer leads to polymer precipitation [34]. Beside, the yield of monomer to colloidal polymer has been found to depend upon the type of stabilizer and oxidant used.

2.6 Literature survey

The use of polypyrrole in composite forms was studied to improve the advantageous properties. Difficulty in preparing thick film, limited shape led to increases the interesting of polypyrrole composite. Therefore, many methods have been proposed to prepare composites that have sufficiently high conductivities, good mechanical strength and allow easy processability.

Tanawadee [5] prepared the pure PPy which had a highly electrical conductivity. The chemical polymerization of pyrrole used anhydrous ferric chloride as an oxidant. The best solvent in this method was methanol. The reaction was accomplished with 2.5 M $FeCl_3$ in methanol at 0 °C for 20 minutes reaction time. Under this condition the synthesized polypyrrole showed high electrical conductivity as about 100 Scm^{-1}. This result introduces the new condition for the synthesis of high conductivity polypyrrole.

Ruckenstein et al. [35,36] synthesized polypyrrole composites by using modified crosslinked porous medium, which is employed as the host for PPy deposition. Crosslinked polystyrene was prepared by the concentrated emulsion polymerization method. They prepared the composite by imbibing the host with a solution of pyrrole and subsequently with an oxidant solution. This method is the improvement of the mechanical properties by inserting PPy particle into porous on PS matrix. The electrical conductivity of the composite and the 'penetration' of PPy

in the host polymer are influenced by the polymerization conditions. However, the best conductivity value, which is about 0.8 Scm^{-1}, is still low.

Omastova et al. [37] studied the polypyrrole composite of PP. Like another particle composite, PPy was coated on the PP particle. $FeCl_3$ was used as the dopant of the water-methanol mixture. All compounds were stirred for a few hours. In this report, the characterization of elemental analysis, infrared spectroscopy, scanning electrical microscopy (SEM) and thermogravimetric analysis were investigated. Additionally, the conductivity of PP/PPy composites was measured to give the ranged value of 10^{-10} to 10^{-2} Scm^{-1}. This value is small compared with that of pure PPy. The report has suggested the applications in antistatic packaging and electromagnetic radiation shielding.

Meng and Chi [38] prepared PPy composites by synthesis of PPy on the surface of PVC particles, which have the average size 0.10 nm. By this method, PVC particle was covered by PPy (Figure 2.14)
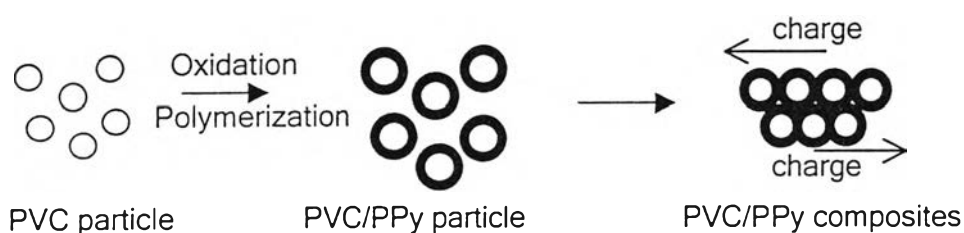

Figure 2.14 Preparation of the compressed PVC/PPy composites

The oxidant solution is $FeCl_3$ in distilled water. The PVC/PPy products was compressed in both hot pressing and cold pressing to give the samples that were measured by conductivity measurement. The PVC/PPy composite samples have

the continuous surface after compression. This raises the conductivity along the surface materials. The optimum electrical conductivity is $\sim 10^{-1}$ Scm^{-1}.

Lascelles and Armes [39,40] synthesized near-monodispersed micrometre-sized, polypyrrole-coated PS latexes with various conducting polymer loadings. PPy was polymerized to cover on PS particles, which have average size 1.6 μm. They show schematic representation of an isolated, micrometre-sized, polypyrrole-coated PS particle (Figure 2.15).
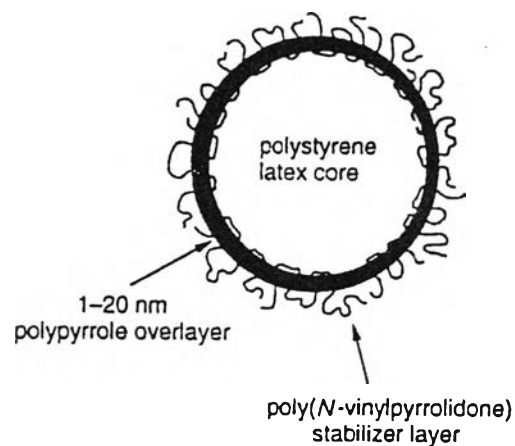

Figure 2.15 Polypyrrole-coated PS paticle using PVP as stabilizer

Poly (N-vinylpyrrolidone) was used as stabilizer, which they suggest that the conducting polymer be formed as a thin layer at surface of the latex particles. This is the 'core-shell' morphology, which was made by dissolving PVP in an aqueous dispersion of the PS latex. The conductivity of this composite is about 1 Scm^{-1}, which is higher than another PPy particle composites. Further, IR spectra of dried polystyrene latex and polypyrrole coated polystyrene were shown. The spectra reveal the enhanced absorption effect with changing the coating polypyrrole percent. Potential applications for these micrometre-sized coated latexes including an

improved stationary phase for electrochromatography and 'novel marker' particles for visual agglutination diagnostic assays.

After the PS/PPy composites were synthesized in the form of thick materials by Ruckenstein and his coordinator, processable conductive PPy/poly(alkyl methacrylate) composites were prepared by an emulsion pathway. In this method, the composite had been prepared using a two-step procedure. First, an emulsion was generated by dispersing a chloroform solution of poly(alkyl methacrylate) and pyrrole in a small amount of an aqueous surfactant solution. The surfactant are sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate. SDS was adsorbed upon the interface between the two phases and ensures, via double-layer repulsion. Second, the pyrrole was polymerized and doped by introducing with stirring an aqueous solution of ferric chloride. The polypyrrole deposited on the host polymer. The electrical conductivity could reach values as high as 1 Scm^{-1}. However, it is still low.

Moreover, for the dispersion polymerization method that is to be studying now, many reaction systems were investigated. Armes and Vincent [41] prepared the conducting PPy particles in dispersion polymerization containing dispersing agents, PVA, PVP, and various cellulose derivatives were used to stabilize the shape of polypyrrole particles. They suggested that using aqueous media of $FeCl_3$ as the initiator could produce the high electrical conductivity to polypyrrole particle. The colloidal polypyrrole particle was the result from stabilizing system in aqueous media, which comprised of ethanol, water, and any dispersing agent.

Cooper and Vincent [42] also proposed the preparation of electrically conductive films by casting aqueous dispersions of mixed polymer lattices on

supporting glass microscope slides. The mixed polymers are the composition of conducting polymer, polypyrrole and polyaniline, and other film forming, a 1:1 co-polymer of polymethyl methacrylate and polybutylacrylate. Conducting polypyrrole were prepared as the dispersion particle form by using poly(vinyl alcohol-co-vinyl acetate) as the dispersing agent. In the same manner with other report, the maximum conductivity is too low, i.e. about 0.1-2 Scm^{-1}.

Digar et al. [43] prepared dispersion PPy at room temperature by oxidative polymerization using $FeCl_3$ oxidant in the presence of poly(vinyl methyl ether) (PVME) as stabilizer, and ethanol or aqueous ethanol as the dispersion. They proposed that, with water as dispersion medium, lower temperatures are required when a solvent property of water towards the PVME stabilizer becomes good enough to affect steric stabilization. PPy prepared in 50% ethanol or in water exhibits specific conductivity, about 10 Scm^{-1}.

The improvement of electrical conductivity and the processability of PPy composites have been studied in many reports. The difficulty to combine high conductivity or processability properties with the other is interesting. In this research, by using our condition, it was believed that the improvement of conductivity into PPy coating composite could be achieved.