

## CHAPTER II

### LITERATURE SURVEY

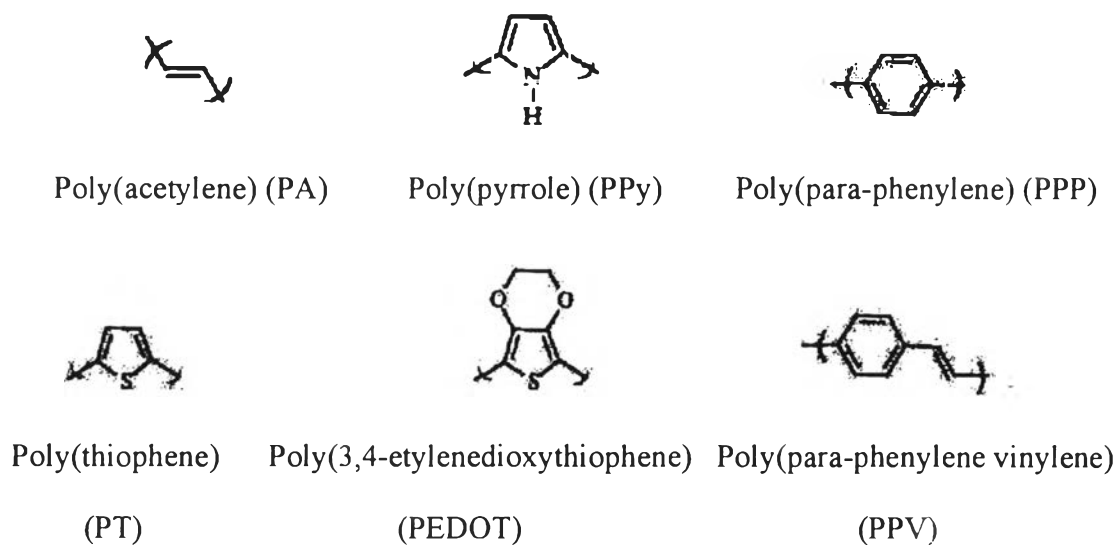
#### 2.1 Conductive Polymers

Conductive polymers are a recently new class of polymers; they are organic materials that are generally comprised of C, H and simple heteroatoms such as N and S and consisting of unique  $\pi$ -conjugation electrons. These materials differ from other typical organic polymers due to their unique  $\pi$ -conjugation electrons properties, which impart higher electrical conductivity at room temperature on oxidation or reduction than ordinary polymers that are usually insulating materials relative to metals such as copper (Chandrasekhar, 1999; Deependra *et al.*, 2004).

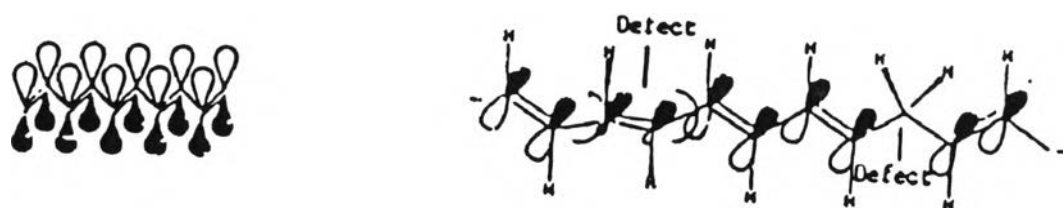
The discovery of conductive polymers began nearly a quarter of a century ago, when Shirikawa and coworkers (Kumar and Sharma, 1998) accidentally discovered and developed an electrically conductive polymer namely polyacetylene which was found to exhibit an increase in electrical conductivity when exposed to iodine vapor. Polyacetylene remains the most crystalline conductive polymer but was not the first conductive polymer to be commercialized due to its ease in oxidation by the oxygen in air and its sensitivity to humidity. Other conductive polymers studied extensively since the early 1980s include polypyrrole, polythiophene (and various polythiophene derivatives), polyphenylenevinylene and polyaniline, as shown in the schematic in Figure 2.1. Polypyrrole and polythiophene differ from polyacetylene in that they may be synthesized directly in the doped form and are very stable in air (Kumar and Sharma, 1998; Chandrasekhar, 1999; Deependra *et al.*, 2004).

The common electronic feature of pristine (undoped) conducting polymers is the  $\pi$ -conjugated system, which is formed by the overlap of carbon  $p_z$  orbitals, with alternating single and double bonds on polymer backbones as shown in the schematic diagram of Figure 2.2. The incorporation of the conjugation along the backbone is important because it provides a pathway for electrons to migrate along a polymer chain and to jump from one chain to another chain (Deependra *et al.*, 2004;

Mark *et al.*, 1996). This process provides conversion from an insulating polymer (conductive range  $10^{-10}$  to  $10^{-5}$  S.cm $^{-1}$ ) to a conductive polymer with near metallic conductivity (conductive range 1 to  $10^4$  S.cm $^{-1}$ ) (Salaneck *et al.*, 1993)



**Figure 2.1** Schematic diagrams of conjugated polymers in their neutral forms.



**Figure 2.2** Schematic diagrams of  $\pi$ -conjugation in the poly(acetylene).

Left: Basic schematic      Right: 3-dimensional, including defect.

Conductive polymers are widely used in a great number of applications because of their several advantages: low density and cost, ease of processing, relative robustness, and lightweight. Applications of conductive polymers which have been developed commercially include gas sensing, light-emitting cells and diodes,

rechargeable batteries, electronic cells, controlled-release applications, actuators, and polymeric electronics such as transistors (Van Vught *et al.*, 2000).

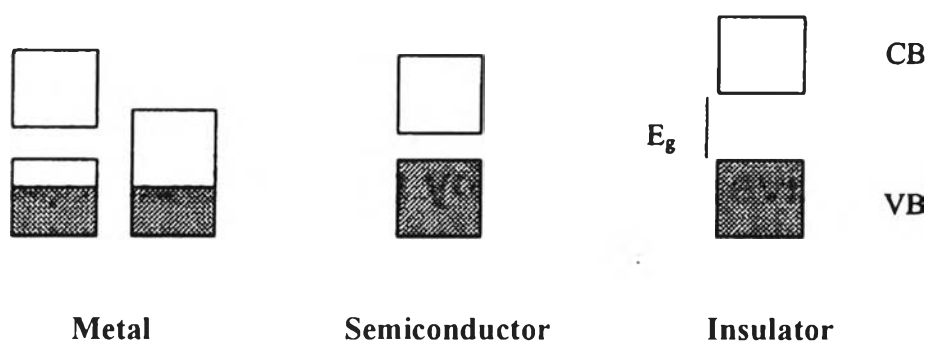
## 2.2 Conduction Mechanism

Materials in the world can be classified into three broad categories according to their room temperature conductivity properties: Insulators, Semiconductors and Conductors (Chandrasekhar, 1999). Conduction is the transport of charge from one point to the other and is governed by charge carriers that move through a specimen. In general, electrical conductivity,  $\sigma$ , [ $\text{S}\cdot\text{cm}^{-1}$ ] is a function of the number of charge carriers,  $n$ , [ $\text{cm}^{-3}$ ], the charge carried by the carrier,  $q$ , [ $\text{A}\cdot\text{s}$ ], and the mobility of the charge carriers,  $\mu$ , [ $\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ] as followed; (Van Vught *et al.*, 2000).

$$\sigma = |q| \cdot n \cdot \mu \quad [\text{S}\cdot\text{cm}^{-1}] \quad (2.1)$$

Conduction in solids can be described with the band model which is shown in the schematic diagram of Figure 2.3. In this model, two molecular orbitals, both with half filled orbitals, are brought close enough to each other until overlapping occurs. The overlapping of individual molecular electronic states in all these materials produces electronic bands; valence electrons overlap to produce a valence band which is a low-energy band, while the electronic levels immediately above these levels also coalesce to produce a conduction band which is a high-energy band. The energy difference between the newly formed bands is called the energy gap. The extent of occupation of the energy bands and the energy gap between them determines the conductivity of a material. If the valence band is only partially filled by available electrons, or if the energy gap vanishes, an overlap between the valence and conduction bands occurs. When electrical potential is applied, some of electrons as charge carriers rise into empty levels where they can possess freedoms of movement ( $\mu = \infty$ ). This leads to the metallic conduction. In semiconductor and insulators, the valence band is completely filled ( $\mu = 0$ ) and the conduction band is

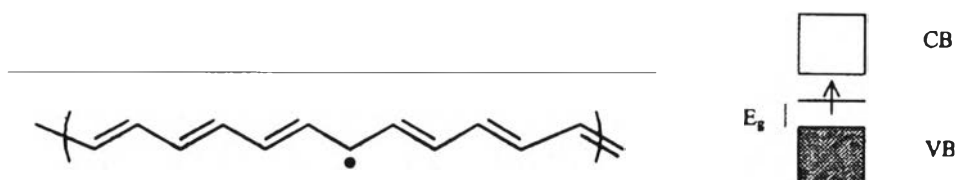
empty ( $n = 0$ ); both bands are separated by an energy gap. Therefore, electrical conduction can only take place when charge carriers are excited from the valence band to the conduction band. For insulators, if the energy gap is too large it is difficult for charge carriers to be excited into the conduction band. If the energy gap for semiconductors becomes smaller charge carriers can be easily excited into the conduction band by means of thermal excitation, vibrational excitation, or excitation by photons (Kumar and Sharma, 1998; Chandrasekhar, 1999; Deependra *et al.*, 2004; Van Vught *et al.*, 2000).



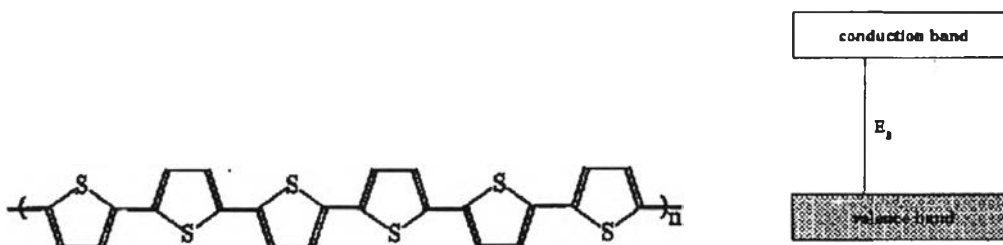
**Figure 2.3** Schematic diagram of the band structure of metals, semiconductors, and insulators ( $E_g$  is the energy gap between the valence band (VB) and the conduction band (CB)).

The band model concepts can be used to describe conductive polymers behaviors. A characteristic of all conductive polymers is the conjugated structure. The conjugation length is an important parameter influencing the conductivity due to the carrier mobility (which is related to conductivity); it increases with increasing conjugation length. The conduction mechanism of all conductive polymers is divided into two paths: charge carriers move along the extent of the  $\pi$ -conjugated system backbone (intrachain conductivity); or they move between the individual molecules (interchain conductivity). The conjugational defects or charge carriers are formed through solitons, polarons or bipolarons in the polymer chain when these conductive polymers are exposed to oxidation/reduction condition as shown in the schematic diagram of Figure 2.4. These defects or the charge carriers generate localized electronic states in the middle of the energy gap between the valence band

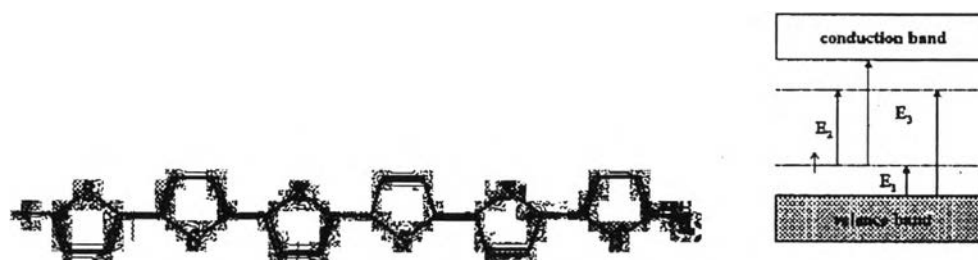
and the conduction band. This effectively reduces the energy gap and the charge carriers can jump into conduction band and electrical conductivity is enhanced (Kumar and Sharma, 1998; Chandrasekhar, 1999; Van Vught *et al.*, 2000).



Soliton in trans-polyacetylene (left) and electronic state induced between the VB and CB by the soliton (right)

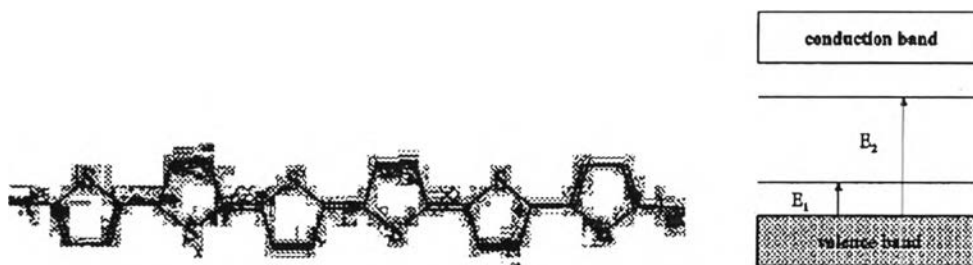


Neutral form of poly(thiophene) (left) and the electronic state of neutral form (right)



The oxidative doping of poly(thiophene) in form polaron (left) and electronic state induced between the VB and CB by the polaron (right)

**Figure 2.4** Schematic diagram of soliton of polyacetylene, and polaron, bipolaron of poly(thiophene).



The oxidative doping of poly(thiophene) in the bipolaron form (left) and the electronic state induced between the VB and CB by the bipolaron (right)

**Figure 2.4(cont.)** Schematic diagram of soliton of polyacetylene, and polaron, bipolaron of poly(thiophene).

### 2.3 Concept of Doping

The naturally  $\pi$ -conjugated electrons systems on conductive polymer backbone are not sufficient to render them highly conductivity; trans-polyacetylene possesses only  $10^{-6}$  S.cm<sup>-1</sup>. The high electrical conductivity is achieved by the process called the “doping process”. This process was firstly discovered by Shirakawa and Ikeda by doping of polyacetylene (PA) with iodine, and conductivity increases by 9-13 orders of magnitude (Kumar and Sharma, 1998).

Doping of pristine (undoped) conductive polymer can be accomplished by the chemical method of a direct exposure of the conjugated polymer to a charge transfer agent (called dopant) in a solution or in vapor phase, or by the electrochemical oxidation or reduction. Dopants are either strongly reducing agents or strongly oxidizing agents. They may be neutral molecules, compounds or inorganic salts, which can easily form ions. Organic dopants are, for example ClO<sub>4</sub><sup>-</sup> or Na<sup>+</sup>. Polymeric dopants are poly(styrene sulfonic acid) or poly(vinyl sulfonic acid), for example. During the doping process, charge carriers can be generated by the oxidation or the reduction of the polymer. The conductivity of either insulator or semiconductor (typically in the range  $10^{-10}$  to  $10^{-5}$  S.cm<sup>-1</sup>) is raised to the metallic conduction (typically in the range 1 to  $10^4$  S.cm<sup>-1</sup>) by controlling addition of doping

level or the extent of oxidation/reduction. Increasing doping level leads to increasing conductivity, via the creation of more mobile charges carriers. The maximum doping levels achievable vary and depend on the conductive polymers and the dopants, as shown in Table 2.1.

**Table 2.1** The dopants and maximum doping levels attainable for specific conductive polymers (Chandrasekhar, 1999)

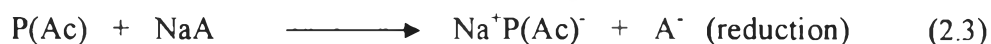
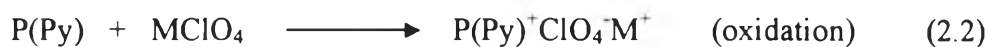
Dopant		Doping level (Typical range)
<b>For Ppy, P(aromatic amines), P(bi/thiophenes)</b> as dopant electrolyte, chemical/electrochemical		
(tetrafluoroborate)	$\text{BF}_4^-$	5% to 33%
(hexafluorophosphate)	$\text{PF}_6^-$	5% to 33%
(perchlorate)	$\text{ClO}_4^-$	4% to 30%
(hydrogen sulfate)	$\text{HSO}_4^-$	2% to 30%
(fluorosulfonate)	$\text{SO}_3\text{F}^-$	5% to 15%
(tri-F-methane sulfonate)	$\text{CF}_3\text{SO}_3^-$	4% to 31%
(benzene sulfonate)	$\text{C}_6\text{H}_5\text{SO}_3^-$	2% to 33%
(Br-benzene sulfonate)	$\text{BrC}_6\text{H}_4\text{SO}_3^-$	2% to 33%
(trifluoroacetate)	$\text{CF}_3\text{COO}^-$	4% to 25%
(sulfate)	$\text{SO}_4^{2-}$	5% to 22%
(chloride)	$\text{Cl}^-$	3% to 42%
(chloroferrate)	$\text{FeCl}_4^-$	3% to 42%
(poly(styrene sulfonate))	$\text{PSS}^{n-}$	3% to 15%
Nafion(DuPont membrane fluoro-polymer)	$\text{Naf}^{n-}$	1% to 15%
Poly(acrylic acid)	$\text{PAA}^{n-}$	2% to 20%

**Table 2.1(cont.)** The dopants and maximum doping levels attainable for specific conductive polymers (Chandrasekhar, 1999)

Dopant	Doping level (Typical range)
<b>For Poly(di/acetylenes), P(Ac), anionic (p-type)</b> from vapor phase : I <sub>3</sub> <sup>-</sup> (iodine), I <sub>2</sub> Cl <sup>-</sup> , Br <sup>-</sup> , I <sub>2</sub> Br <sup>-</sup> (Se, Te, mo, W, U, Re, Os, It, Ru)F <sub>6</sub> <sup>-</sup> , BiF <sub>5</sub> from toluene solution : MoCl <sub>5</sub> , WCl <sub>6</sub> , (Ta, Nb, Zr)Cl <sub>5</sub> In(I, Cl) <sub>3</sub> , (Sn, Ti, Zr)Cl <sub>4</sub> , TiI <sub>4</sub> HSO <sub>4</sub> <sup>-</sup> from NOHSO <sub>4</sub> (Ce, Dy, La, Pr, Sm, Yb)nitrates	2% to 25% 2% to 19% 2% to 7% 0.3% to 7% 1% to 12% 0.9% to 2.2%
<b>For P(Ac), P(phenylene), cationic(n-type)</b> from THF or pentane solution : Na <sup>+</sup> , from NaC <sub>10</sub> H <sub>8</sub> , Na <sub>2</sub> Ph <sub>2</sub> CO Li <sup>+</sup> , from LiPh(CH <sub>2</sub> ) <sub>6</sub> Ph	4% to 28% 6% to 44%

Removal or addition of electrons may also be accomplished through the introduction of a dopant which imparts higher conductivity. If the oxidation in the polymer occurs, it extracts electrons from the valence band (electrons from the polymer to the dopant), creating “holes” in the valence band, which is then known as “p-doping”. It generates a positively charged conductive polymer and an associated anion. When the reduction on the polymer occurs, it adds electrons to the conduction band (electrons from the dopants to the polymer), increasing conducting electrons in this band, which is known as the “n-doping”. This generates a negatively charged conductive polymer with an associated cation. These processes are summarized in the schematic below, where M and A are the cation and the anion, respectively:





In order to maintain charge neutrality, counter-ions (associated ions) are also incorporated. The interaction between counter-ions and the charge carriers on the conjugated polymer can influence the mobility of the charge carriers which is known as pinning effect (Van Vught *et al.*, 2000). This effect becomes less when the size of counter-ions is larger and the degree of charge delocalization is stronger. This means that the stability of the conductivity can be affected by the size of the counter-ions.

Doping of a conductive polymer results in the formation of new, neutral solitons, polarons or bipolarons in conjugated polymers. The doping with n-type dopants, anion conductive polymer is formed which is highly unstable in air and water. So, the conductivity which is generated by n-type dopants e.g. Na, Li is less stable than by p-type dopants e.g. I<sub>2</sub>, AsF<sub>5</sub>, FeCl<sub>3</sub>, HClO<sub>4</sub>. Therefore p-type dopants are more frequently used (Kumar and Sharma, 1998; Chandrasekhar, 1999; Van Vught *et al.*, 2000).

## 2.4 Polythiophene

Polythiophene is a one of the electronic conductive polymers, a heteroaromatic conductive polymer comprising of S atoms and the  $\pi$ -conjugated electron system as shown in the schematic structure of Figure 2.5. This polymer has many advantages: high conductivity (some cases approaching that of metals); large amounts of charge can be stored; high stabilities in aqueous media and air; the polymerization and doping methods are simple and giving high yield; exhibits electrically triggered molecular conformational transition; ease of chemical modification; flexible; lightweight, and ease of fabricating thin films (Kumar and Sharma, 1998; Mu and Park, 1995; Anquetil *et al.*, 2002).



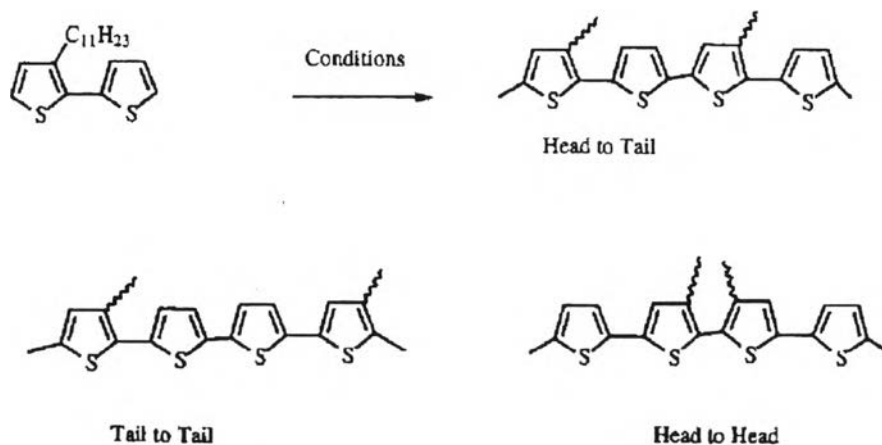
**Figure 2.5** Schematic structure of polythiophene.

There are many applications for polythiophene: e.g., iodine doped polythiophene battery, electro-optical display devices, humidity sensors, radiation detectors, gas sensor and etc. (Kumar and Sharma, 1998; Chandrasekhar, 1999). Although polythiophene is one of the early conductive polymers synthesized and has a lot of advantageous properties, it has some limitations towards these applications: poor solubility in most of common solvents; low thermoplasticity and poor processibility (Kumar and Sharma, 1998). So, the discovery that 3-substitution of the thiophene ring can yield a wide variety of practically very versatile conductive polymers. Illustration of the variation of properties obtainable in 3-substituted polythiophene with different substituents (R group), are shown in Table 2.2 (Chandrasekhar, 1999). For example, poly(3-undecyl thiophene) shows a mechanical flexibility, high processibility, and the isoregic polymer possesses better film properties and higher conductivity by one to two orders of magnitude relative to that of the aregic counterpart as shown in schematic Figure 2.6 (Stenger-Smith, 1998).

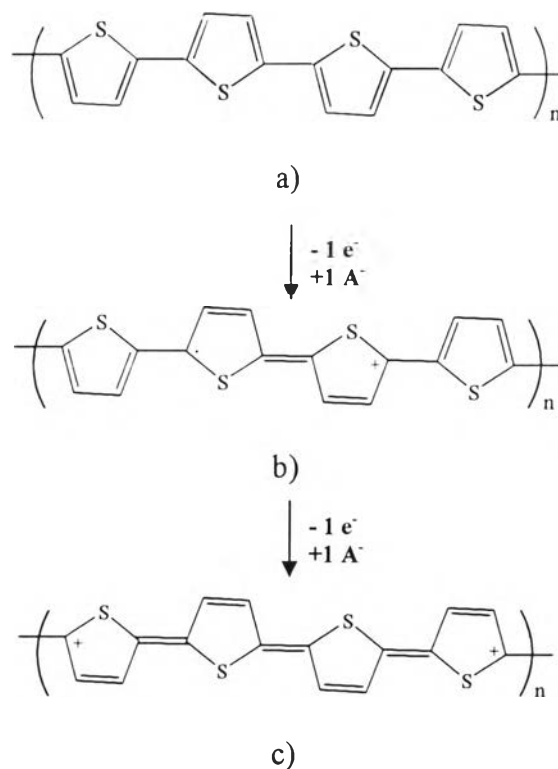
Doping of polythiophene usually employs p-type dopants such as  $I_2$ , triflate doping,  $HClO_4$ ,  $FeCl_3$  as shown in the schematic diagram of Figure 2.7. Consequently, the formation of a radical cation called polaron results.

**Table 2.2** Illustration of the variation of properties obtainable in 3-substituted Polythiophene with different substituents (R group) (Chandrasekhar, 1999)

Substituent, R	Property Imparted
Alkyl, $C_nH_{n+1}$ , $n > 6$	soluble in organic solvents
Alkyl, $n > 10$	distinct m.p., melt processible
$(CH_2)_nY$ , $4 < n < 10$ , Y = halide	useful for further syntheses/processing
$O(CH_2)_n$ , $n > 5$	some solubility in protonic organic solvents, low band gaps
$(CH_2)_nSO_3$ , $2 < n < 5$	water solubility
N-alkyl bipyridyl	redox active group



**Figure 2.6** Regiospecific polymerization of 3-undecylbithiophene.

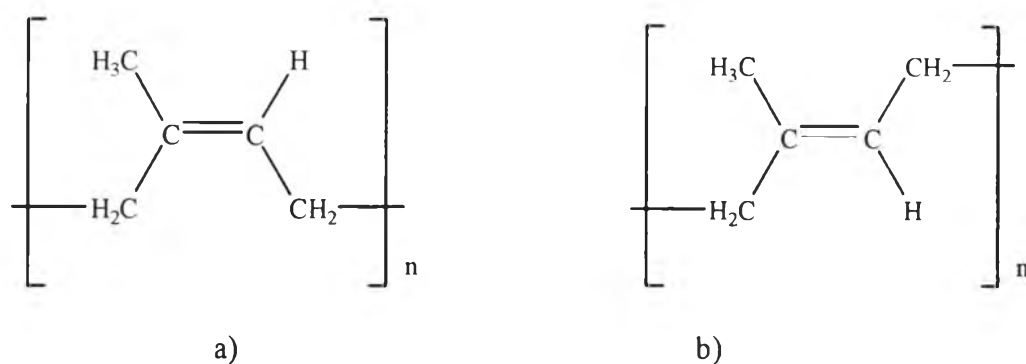


**Figure 2.7** p-Type doping of polythiophene: a) Neutral form; b) Polaron form; c) Bipolaron form.

## 2.5 Polyisoprene (PI)

Polyisoprene or natural rubber or 2-methyl-1,3-butadiene is one of the most well known natural polymers, colorless liquid organic compound. It is a hydrocarbon, and is insoluble in water but soluble in many organic solvents and boils at 34 °C. The isoprene molecule contains two double bonds. Isoprene polymers also occur naturally. The natural rubber is *cis*-1,4-polyisoprene, and *trans*-1,4-polyisoprene is present in the natural rubbers balata and gutta-percha (The *cis* and *trans* polyisoprenes are structural isomers). The chemical structure is shown in the schematic structure of Figure 2.8. It has many advantageous characters; inexpensive due to its natural source, renewable polymer material, flexible polymer, low water swell, high gum tensile strength, good resilience, high hot tensile, and good hysteric. So polyisoprene are being produced in many products, for example; tires, rubber bands, cut thread, baby bottle nipples, footwear, sponge, and sporting goods.

In addition, it is an elastomeric polymer because it can recover its shape after being stretched or deformed and it is an insulating polymer. These characteristics are desirable properties since we want the polymer to attain large actuation strains when subjected to an electrostatic field.



**Figure 2.8** Schematic structure of polyisoprene: a) *cis*-1,4- polyisoprene; b) *trans*-1,4- polyisoprene.

## 2.6 Polythiophene Synthesis and Derivatives

Lee *et al.* (1995) studied the effect of ester substitution and alkyl chain length on the properties of polythiophene. They prepared and characterized the soluble poly(alkyl ester substituted thiophene)s (PAETs) and studied the effect of polar ester group substitution and compared with poly(alkylthiophene)s (PATs). They found that the ester substitution in the side chain of PATs introduced steric hindrance between the neighboring thiophene rings which led to the conformational rotation of main chain and disturbed the ordering in the polymers. The conformational distortions of main chain also led to shortening of conjugating length and the decrease in electrical conductivity of PAET's. The conductivity of PAETs was improved when the alkyl chain length was increased.

Mu and Park (1995) prepared and characterized polythiophene (Pth) in aqueous solution. In this work, they reported the electrochemical polymerization of thiophene in aqueous solution containing monomer, ethyl alcohol and acid. Pth was prepared by repeatedly cycling potentials between  $-0.25$ - $1.75$  V vs. the Ag/AgCl

saturated KCl reference electrode. The Pth film formed on the platinum electrode hindered oxygen evolution, and the film thickness increased with cycles. The polymer films were denser and stable than those prepared in a nonaqueous solution. Polymerization mechanism of thiophene in aqueous solutions and the chain length of the polymer obtained were different from those in an organic media; this led to different electrochemical properties. The film obtained in aqueous solutions could be doped both anodically and cathodically depending on the solution pH and it had a high anodic decomposition potential and a high overpotential to oxygen. The diffusion coefficients were very small due perhaps to the compactness of this film and the impedance values were very sensitive to pH and applied potential.

Davidson and Ponsonby (1996) improved the intrinsic conductivity of electrically conductive polymers that were poly[3-(4-bromophenyl)-2,5-thiophene] (PPTTh) and poly[ $\alpha$ -thiophenediyl(p-bromobenzylidene)] (PTB) by crosslinking them with conjugated linkages (the diboronic acid). The amount of crosslinking was varied between 5-30% and electrical properties of both polymers were examined. They found that an initial increase in the conductivity was followed by a sharp decrease, which in turn led to a further increase at high levels of crosslinking. In the case of PPTTh the decrease in conductivity was related to a loss of interchain planarity and in the case of the PTB there may also be a second reaction taking place, which produced conjugated sequences along the main polymer backbone.

Water soluble salts of 2, 5-poly(thiophene-3-propionic acid) were synthesized by McCullough and Ewbank (1997). They studied the ionochromism of this polymer. They found that this synthesized polymer had head-to-tail couplings, highly ordered, water soluble, tunable bandgap.

Water-soluble poly(3-thiophene acetic acid) (P3TAA) was studied by Kim *et al.* (1999). The solution properties of these water-soluble polythiophene carboxylic acids were studied by potentiometric titration, viscosity measurements, and UV-vis spectroscopy. They found that titration curve showed an inflection of the slope around pH 5-6. The reduced viscosity and electronic spectra ( $\lambda_{\max}$ ) of the P3TAA aqueous solution abruptly changed at this pH region. It showed that these

pH-induced abrupt conformational changes occurred from the aggregated state to the extended state of the polymer main chain.

Kim *et al.* (2000) studied the environmental response of polythiophene hydrogels. They synthesized a chemically cross-linked and a water-swollen poly(3-thiopheneacetic acid) (P3TAA) gel. Its swelling and spectral changes associated with its ionization at certain pH were studied. They found that  $G''$  was much lower than  $G'$  in the measured frequency region, indicating that a P3TAA gel occurred. For the swelling behavior, it was found that the lower crosslinking density, the higher the degree of swelling and the sharper transition. The pH-induced increase in the degree of swelling associated with the electrostatic repulsion among the dissociated carboxylic groups of P3TAA and the increase in  $\lambda_{\max}$  which is the wavelength of UV-visible absorption spectra related to interchain length of molecule were attributed to an enhanced effective electronic conjugation length of the polymer chain. Both cases were due to a backbone conformational transition from the aggregated state to an extended state in the network. But the dissociation of P3TAA gel was strongly suppressed due to the cross-linkage in the low-pH region. The gels prepared in the mixed solvents exhibited a higher  $\lambda_{\max}$  than those prepared in DMSO at any pH, confirming that the increased in the electronic conjugation structure of P3TAA chain. The electrical conductivities of doped water-swollen P3TAA gels with 60 %HClO<sub>4</sub> were higher than undoped water-swollen gel.

Kim *et al.* (2001) studied in titration behaviors and spectral properties of hydrophobically modified water-soluble polythiophenes. The poly(3-thiopheneacetic acid) copolymer with 3-n-methylthiophene or 3-n-octadecylthiophene at 3-position of a thiophene ring and partially hydrolyzed polythiophene (78% hydrolysis) were synthesized. The solution and spectral properties of these modified polythiophene were studied by potentiometric titration and UV-vis spectroscopy. They found that 78% hydrolysis P3TAA showed an enhanced dissociation at low pH but a reduced dissociation at high pH in comparison with completely hydrolyzed P3TAA. The degree of dissociation of copolymers was weaker than P3TAA until the pH reached about 6 when the copolymers became stronger than P3TAA.  $\lambda_{\max}$  of 78% hydrolyzed P3TAA was lower than P3TAA's, due to the low charge density and the enhanced

hydrophobicity that originated from the methyl groups.  $\lambda_{\max}$  of copolymer has a long alkyl side group was much smaller than those of other polymers. They showed that the conformational transition from the aggregate state to the extended state of the modified polythiophene occurred by the change in pH; but this conformational transition was restricted by the introduction of the hydrophobic alkyl or long alkyl side chains.

Khan *et al.* (2003) studied oligosiloxane modified polythiophenes. They synthesized, characterized and observed biocompatibility of these polymers. The homopolymers of 3-oligo(dimethylsiloxane)thiophene macromonomers, V-VIII were prepared by hydrosilylation reaction between  $\omega$ -(Si-H)oligo(dimethylsiloxane), I-IV and 3-propenylthiophene using a platinum-divinyltetramethyldisiloxane complex as the catalyst. The products were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$  NMR, IR, DSC and GPC. They found that only high molecular weights macromonomers (poly[VIII]) could elute through the GPC column. Two distinct glass transition temperatures were observed for poly[VIII]),  $T_g$  at  $-79^\circ\text{C}$  corresponded to the soft oligo(dimethylsiloxane) phase and  $T_g$  at  $190^\circ\text{C}$  corresponded to the hard thiophene backbone. The iodine doped homopolymer of macromonomers (V-VIII) showed low conductivity values but electronic conductivity values increased to  $5 \times 10^{-5}$  S/cm when copolymerization with 3-methylthiophene 50%. The polymers were tractable, soluble in organic solvents and biocompatible.

## 2.7 Doping of Polythiophene

Reedijk *et al.* (1999) studied the charge transport in doped polythiophene (Pth). In this work, the conductive properties of the conjugated polymer, Pth doped with  $\text{FeCl}_3$  and, dissolved in methanol and further diluted in dichloromethane, were studied as a function of frequency, electric field, temperature and dopant concentration. This report contained a study of the inter-chain hopping process as a function of dopant concentration in Pth. Dopant concentration was varied between  $0.02 < c < 0.45$ , where  $c$  is the number of  $\text{FeCl}_3$  dopant molecules per thiophene ring. For low doping levels of  $c \leq 0.22$ , DC conductivity ( $\sigma_{\text{DC}}$ ) followed a power law (e.g.



at room temperature  $\sigma_{DC} \sim c^{1.8 \pm 0.2}$ ) as dictated by the small inter-chain hopping probability, leading to a low mobility  $\mu \sim 10^{-10} \text{ m}^2/\text{Vs}$ . In this regime, the inter-chain hopping was between nearest neighbor chains. The rate of transitions between chains increased due to the presence of interstitial dopants, the inter-chain transport changed to the variable range hopping, with a transition from quasi-one-dimensional (low doping levels) to three dimensional (high doping). The onset frequency increased with doping level ( $\omega_0 \sim c^{0.8}$ ) and the conductivity was related to temperature by the relation  $\sigma_{DC} = \sigma_0 \exp[-(T_0/T)^{1/2}]$ .

Dilute solutions of poly(3-undecyl-2,2'-bithiophenes) (p3UBT) that were doped with solutions of a number of quinone oxidants were studied by Tolbert *et al.* (1999). They found that the doped p3UBT films with dichlorodicyanoquinone (DDQ) produced a highly conducting material, stable conductive materials and exhibited strong bipolaronic absorptions.

## 2.8 Applications of Polythiophene

Kim *et al.* (1995) prepared polythiophene derivatives film by the Langmuir-Blodgett technique and tested the gas sensitive of these films to  $\text{NO}_2$  gas by the quartz crystal microbalance (QCM). They synthesized the ester substituted polythiophene such as poly(octyl thiophene) (POT), poly(propanoate thiophene) (PEPT), and poly(decanoate thiophene) (PEDT) that were mixed with surface active material like ODA at high subphase pH condition for stable films. They tested sensitivity of polythiophene film by exposing to  $\text{NO}_2$  gas of 550 ppm. They found that the POT/ODA (1:1) film had a great  $\text{NO}_2$  sensitivity because the frequency change was the largest. The difference in sensitivity might be the cause because of the ester linkage in side chain. The sensitivity increased linearly with film thickness so they could control the sensitivity by the film thickness.

Poly(3-octyloxythiophene) (PAOT-8) was studied in terms of the electrical and optical properties and its applications as a gas sensor (Kawai *et al.*, 1999). They synthesized PAOT-8 by the chemical polymerization utilizing  $\text{FeCl}_3$ , as a catalytic oxidizing reagent and prepared a thin film PAOT-8. They found that the film

showed about 1.9 eV of the threshold energy of the absorption peak, which corresponded to the band gap energy. The absorbance at photon energy range larger than 1.9 eV decreased and that lower than 1.9 eV increased remarkably. Due to relatively higher energy of valence band top originated from the electro-donating characteristics of the alkoxy group, PAOT-8 exhibited stable state than polythiophene or poly(3-alkylthiophene) and a stronger interaction with electron accepting molecules such as fullerene, which allowed itself to be used as a gas sensor material. The electrical conductivity of PAOT-8 was also increased with C<sub>60</sub> doping. The gas sensing characteristics of PAOT-8 was investigated by measuring the resistance between the gold electrodes covered with PAOT-8 thin film. They found that the change in resistance varied linearly with gas concentration indicating the gas molecules might penetrate into the bulk polymer phase and the weak electron transfer from PAOT-8 to the gas molecule might take place as in the case of C<sub>60</sub> doping resulting in the increase in conductivity.

Holmes *et al.* (2001) synthesized of a new type of supramolecular assembly based on hydrogen bonded complexes between monocarboxylic acids of dithieno[3,2-b;2',3'-d]thiophene or other conjugated thiophenes and a tris(imidazoline) base. They found the complexation with a tris(imidazoline) base indicating that this complex material could be soluble in CHCl<sub>3</sub> and other non-polar solvents. The resulting non-covalent complexes were almost planar and disk shaped and potential applications of these complexes as charge-transporting or light-emitting materials in electroluminescent devices are possible.

Anquetil *et al.* (2002) studied thiophene-based conducting polymer molecular actuators. They synthesized of novel thiophene based conducting polymer molecular actuators that are calixarene and quaterthiophene (QT). These materials exhibited electrically triggered molecular conformational transitions. Molecular actuation mechanisms are the result of conformational rearrangement of the polymer backbone at the molecular level and  $\pi$ - $\pi$  stacking of thiophene oligomers upon oxidation. They also studied synthesized poly(QT)/Sulfated Poly( $\beta$ -HydroxyEther) (S-PHE) composite films. They reported that this composite showed large strains.

S-PHE provided an elastic mechanical support to polymer molecules and has the effect the charge compensation during oxidation or reduction.

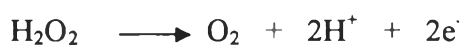
Soluble alkyl- and alkoxy-substituted regiochemically defined polyterthiophenes were prepared and used as active layers in sensing organic thin films transistors (OTFTs) (Torsi *et al.*, 2003). They prepared OTFT sensors based on two different types of active layers comprising of both the same polythiophene backbone but substituted in one case with alkyl side chains that was poly-(3, 3''-didodecyl-2, 2':5', 2''-terthiophene) (Poly DDT), and in the other with alkoxy side chains that was poly-(3, 3''-dipentoxy-2, 2':5', 2''-terthiophene) (Poly DPOT) in order to investigate selectivity to a polymer via side chain. They found that the morphological appearance of both polymer surfaces was that of a polycrystalline material which allowed for good interaction between the organic thin films and the analyses (1-hexanol and ethanol vapors). So, both of the OTFTs exhibited a good degree of reversibility and repeatability and they were also quite fast in their responses. Both the OTFTs were sensitive to 1-hexanol because they had a long linear alkyl chain that could interact with long chain alcohols (1-hexanol). The dipole moment associated with the two OTFTs was quite different. The stronger dipole moment associated to the alkoxy chain of Poly DPOT could allow the detection of shorter, more polar molecules such as ethanol.

## 2.9 Electrically Conductive Polymer Composite

Conducting polyaniline-polyisoprene (PANI-PIP) composite film was synthesized electrochemically (Shen *et al.*, 2001). The film was used to immobilize glucose oxidase (GOD) forming glucose biosensor. When being used for the determination of glucose, the enzyme electrode reaction as followed:



The amount of H<sub>2</sub>O<sub>2</sub> was detected by the amperometric current method during electrode oxidation:



This PANI-PIP/GOD biosensor had good operational stability. The electrochemical activity of this biosensor remained unchanged after 5 months. This biosensor had high permselectivity, which can determine  $H_2O_2$  with high selectivity against the in the electroactive interferent ascorbic acid. When the PIP content in the composite was increased, the selectivity of the biosensor was improved. The PIP content in the composite reached 28.6%, the interference from ascorbic acid was eliminated effectively, which may be due to slow diffusion of the substrate (glucose) and product ( $H_2O_2$ ).

Polydimethylsiloxane (PDMS)/polythiophene (Pth)/carbon fiber (CF) composites was synthesized by the electrochemical polymerization using tetrabutylammoniumtetrafluoroborate (TBAFB) as supporting electrolyte and acetonitrile as solvent was studied by Küçükyavuz *et al.* (2002). Electrical, thermal and mechanical properties of the composites were investigated. They found that conductivities of the composites were in the range of 2-5 S/cm depending on contents of material (PDMS, Pth, carbon fiber). Conductivities of these composites were environmentally stable. From the thermal analysis, these composites still remained more than 50% weight at 900°C. They concluded that the composites were more stable than both PDMS and carbon fiber. In mechanical tests, it was observed that higher percent elongation was obtained by increasing PDMS content whereas tensile strength and modulus of composites increased with increasing carbon fiber content. Knite *et al.* (2004) fabricated electrically conductive polymer composite (ECPC). The composite are acts as large-size flexible pressure and stretch sensors for detecting of dangerous deformations and vibrations of vehicle parts. Reversible change of resistance of electro-conductive polymer nanocomposite depended on stretch and pressure. All the composites were examined; the best results were obtained on samples with 10 mass fractions of carbon nano-particles, which belonged to the region of percolation phase transition. Electrical resistance of the samples is changed by more than four orders upon a 40% stretch and more than three orders upon a 0.30 MPa pressure. The resistance returned to its previous value after the samples were relaxed but in the case of micro-size carbon filler was irreversible. This nanocomposite exhibited a weak semiconductor-like thermal dependence of resistivity. The tenzoresistive and piezo-resistive effects were thermally stable

within the region of 20-70°C. The increase of electrical resistance with uniaxial stretch and pressure can be explained as a result of destruction of the structure of the carbon electro-conductive nano-size channel network. At large deformations, the destruction of the conductive network and decreased of the number of conducting pathways occurred.

Faez *et al.* (2001) prepared the electrically conductive heterogeneous binary polymer blends based on ethylene-propylene-diene-monomer (EPDM) and polyaniline (PAni), doped with dodecylbenzene sulfonic acid (PAni-DBSA). They studied the effect of the doping method on mechanical and electrical properties of these blends. Different doping methods were used: solution (EPDM/PAni-DBSA-S), grinding in a mortar (EPDM/PAni-DBSA-M) and reactive processing (EPDM/PAni-DBSA-R). They observed from the optical micrographies that the EPDM/PAni-DBSA-S blends PAni was homogeneously dispersed into EPDM but the EPDM/PAni-DBSA-M and EPDM/PAni-DBSA-R blends formed non-miscible blends with EPDM. However, the swelling measurements for all blends showed that in the EPDM/PAni-DBSA-R blends the EPDM was partially soluble. This phenomenon observed indicates that entanglements or chemical reaction occurred between the components. Young modulus increased with PAni-DBSA concentration independently of the doping method was related with the reinforcement effect of PAni-DBSA but the less pronounced for EPDM/PAni-DBSA-S due to the low viscosity of these blends. The conductivity values of PAni-DBSA changed with the doping method, being higher for PAni-DBSA doped by the reactive processing and increased linearly with PAni-DBSA concentration, independently of the PAni doping method, until 30%(w/w).

Electrically conductive heterogeneous binary polymer blends based on ethylene-propylene-diene-monomer (EPDM) and polyaniline (PAni) doping with dodecylbenzene sulfonic acid (PAni-DBSA) were prepared (Faez *et al.*, 2002). They studied the effect of the crosslinking method for EPDM rubber on mechanical and electrical properties of this blends. Two difference crosslinking methods, which were phenolic resin and electron beam irradiation, were studied. They found that the electron beam irradiation vulcanization was not precluded by the presence of an acid from doping substance but the phenolic resin vulcanization occurred. The

mechanical properties such as the tension and elongation at break as a function of amount of conducting polymer loading and type of crosslinking method. The tension at break for all blends increased with PANi-DBSA loading increased until 30%(w/w). This indicates that the reinforcement effect of the conducting polymer. Above 30 % (w/w) loading, the tension of blends dropped due to the large PANi-DBSA agglomerated so the absence of phase adhesion between conducting polymer particles and polymer chain matrix occurred. The conductivity increased with PANi-DBSA loading and polymer blends, which were crosslinked by electron beam irradiation, produced high conductivity due to some ionic species that were generated.

## 2.10 Actuators

Zrínyi *et al.* (2000) studied a novel gel actuator containing TiO<sub>2</sub> particles operated under static electric field. They prepared poly(dimethylsiloxane) gels (PDMS gels) and TiO<sub>2</sub> particles were embedded in this gels. The crosslinking reaction occurred in a plastic tube. After the gelation was completed, the gel cylinders were removed from the tubes and were suspended in silicon oil to study the elastic response of the gels to an electric field. The filler-loaded gel cylinders showed significant and rapid bending toward the cathode, when an external electric field was applied. When positive and negative electrodes were changed, this behavior was reversible. The displacement of the free bottom end of the gel cylinders depended on the strength of the electric field. These results showed that in an external electric field the gel accumulated positive charges. The large deflection has been observed due to the interaction of the applied external electric field with the charged gel.