

# CHAPTER I

## INTRODUCTION

Over the past several decades since the discovery of metallic conductivity in doped polyacetylene,<sup>1</sup> synthetic organic chemists have showed a growing interest in development of organic conducting molecular and polymeric materials. The superiority of organic conducting materials over their inorganic materials resides in their architectural flexibility, low cost and ease of processing and fabrication. Since then various conducting polymers and their synthetic methods were studied by many researchers. The typical conducting polymers, of which the most works have been done, are summarized in **Table 1.1**.<sup>2,3</sup> Their conductive properties in comparison to those of metals, inorganic, and other organic compounds,<sup>4</sup> are shown in **Figure 1.1**.

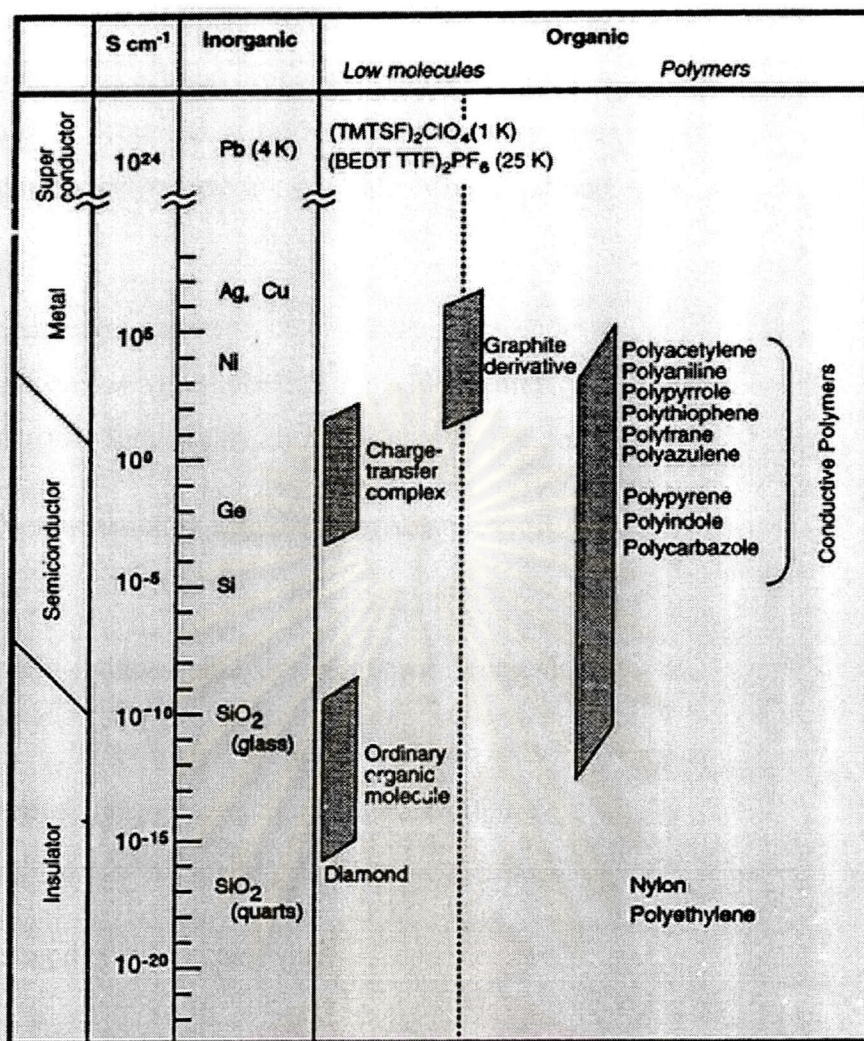
### 1.1 Applications of organic conducting polymers<sup>3-6</sup>

Organic conducting polymer has a unique and practical advantage. Their conductive properties allow the use of electronic tools (computers and interfaces) and other existing and emerging characterization tools to retrieve the information on the behavior of these systems from real *in situ* environments. In addition, their other properties can be manipulated *in situ* using appropriate electronic stimuli. (**Table 1.2**)

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**Table 1.1** Typical conducting polymers

Name	Structure	Name	Structure
<i>trans</i> -Polyacetylene		Poly(phenylene ethynylene)	
<i>cis</i> -Polyacetylene		Polyselenophene	
Polypyrrole		Polyfuran	
Polythiophene		Poly( <i>N</i> -substituted aniline)	
Poly( <i>p</i> -phenylene)		Poly( <i>N</i> -substituted pyrrole)	
Poly(phenylenevinylene)		Poly(diphenylamine)	
Polyaniline		Poly(indole)	
Poly(thienylenevinylene)		Poly(thieno[3,2- <i>b</i> ]pyrrole)	
Poly(furylenevinylene)		Poly(flourene)	
Poly(phenylenesulfide)		Polypyridine	



**Figure 1.1** Conductivity of various organic compounds in comparison to inorganic materials

**Table 1.2** Changes of properties upon electrical stimulation to organic conducting polymers<sup>3</sup>

Property	Typical Change	Potential Application
Conductivity	From $10^{-7}$ to $10^3$ S.cm <sup>-1</sup>	Electronic components, sensors
Volume	3%	Electromechanical actuators
Color	300-nm shift in absorbance band	Displays, smart windows
Mechanical	Ductile-brittle transition	Artificial muscles
Ion permeability	From zero to $10^{-8}$ mol.cm <sup>-2</sup> s <sup>-1</sup> in solution	Membranes

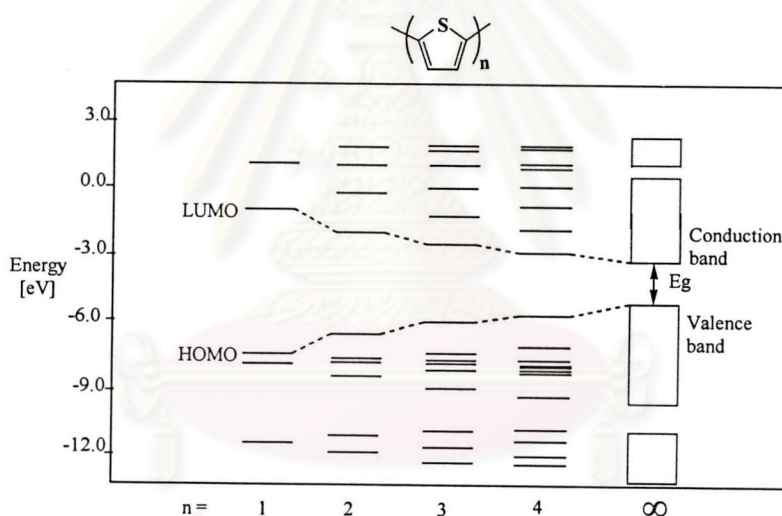


The development of some of these applications to commercial viability began for some time already. The ability to tailor the electrical properties of these systems is one of their most attractive features and, coupled with improved stability and processability relative to the original conducting polymeric systems, new applications are surely on the horizon.

- Applications utilizing the inherent conductivity of polymer: antistatic coating (metals and polymers), microelectronic devices; plastic chip, and “Stealth” materials for providing a minimal radar profile for military aircrafts and naval vessels
- Electrochemical switching, energy storage and conversion: new rechargeable battery, and redox supercapacitors
- Polymer photovoltaics (light-induced charge separation): photovoltaic devices
- Display technologies: electrically stimulated light emission: light emitting diode (LED), and flat panel displays
- Electrochromics: advertising displays, smart windows, and memory storage device
- Electromechanical actuators: artificial muscles, window wipers in spacecrafts, rehabilitation gloves, electronic Braille screen and bionic ears for deaf patients
- Separation technologies; novel smart-membrane, and selective molecular recognition (new chromatographic separation media)
- Cellular communication: growth and control of biological cell cultures
- Controlled release devices: ideal hosts for the controlled release of chemical substances
- Corrosion protection: new-generation corrosion protective coatings
- Remotely readable indicators: electronic noses, biosensors, and biomechanic devices

## 1.2 Conjugated polymer: organic semiconductors

Conjugated polymers are organic semiconductors that with respect to electronic energy levels hardly differ from inorganic semiconductors. Both have their electrons organized in bands rather than in discrete levels and their ground state energy bands either completely filled or completely empty. The band structure of a conjugated polymer originates from the interaction of the  $\pi$ -orbitals of the repeating units throughout the chain. This is exemplified in **Figure 1.2** where the calculated energy levels of oligothiophenes with  $n = 1-4$  and polythiophene are shown as a function of oligomer length. Addition of every new thiophene unit causes hybridization of the energy levels yielding more and more levels until a point is reached at which there are bands rather than discrete levels. Interaction between the  $\pi$ -electrons of neighboring molecules leads to a three-dimensional band structure.

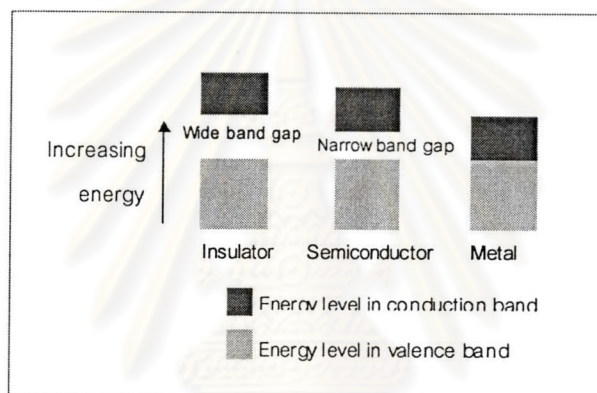


**Figure 1.2** Calculated (frontier) energy levels of oligothiophenes with  $n = 1-4$  and of polythiophene. ( $E_g$  = band gap energy)

Analogous to semiconductors, the highest occupied band (which originates from the HOMO of a single thiophene unit) is called the valence band, while the lowest unoccupied band (originating from the LUMO of a single thiophene unit) is called the conduction band. The difference in energy between these energy band levels is called the band gap energy or simply, band gap. ( $E_g$ )<sup>7</sup> Generally speaking, because conducting polymers possess electrons which are delocalized in  $\pi$ -conjugated system along the whole polymeric chain, its conductivity is much higher than that of

other polymers with no conjugated system.<sup>4</sup> These latter non-conjugated polymers are usually known to be insulators.

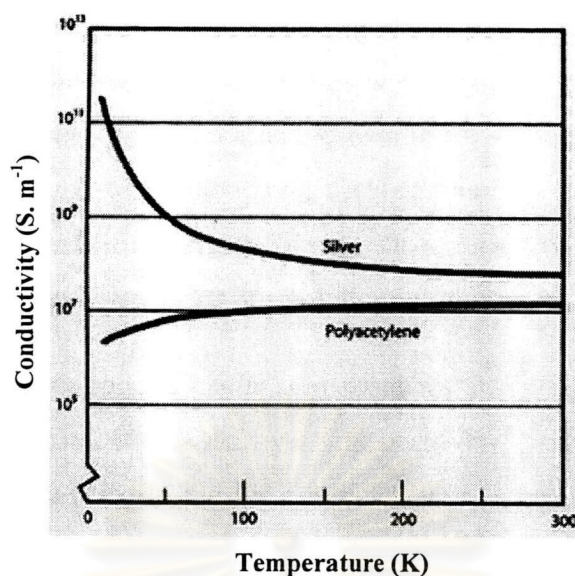
The difference between  $\pi$ -conjugated polymers and a metal is that in a metal the orbitals of the atoms overlap with the equivalent orbitals of their neighboring atoms in all directions to form molecular orbitals similar to those of isolated molecules. With  $N$  numbers of interacting atomic orbitals, there would be  $N$  molecular orbitals. In the metal or any continuous solid-state structures,  $N$  will be a very large number (typically  $10^{22}$  for a  $1\text{ cm}^3$  metal piece). With so many molecular orbitals spaced together in a given range of energies, they form an apparently continuous band of energies. (**Figure 1.3**)



**Figure 1.3** Simple band picture explaining the difference between an insulator, a semiconductor and a metal

The conductivity of the metal is due either to partly-filled valence or conduction band, or to the band gap being near zero, so that with any weak electric field the electrons easily redistribute. Electrons are excited to the higher energy bands and leave unfilled bands or “holes” at lower energy. Metals and conducting polymers exhibit opposite directions of conducting behavior as a function of temperature as shown in **Figure 1.4**. Conductivity generally increases with decreasing temperature for metallic materials, (some of which become superconducting below certain critical temperature,  $T_c$ ) while it generally decreases with lowered temperature for semiconductors and insulators.<sup>8</sup>





**Figure 1.4** The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals.

Since  $\pi$ -conjugated polymers allow virtually endless manipulation of their chemical structures, the control of the band gap of these semiconductors is a research issue of ongoing interest. This “band gap engineering” may give the polymer its desired electrical and optical properties. Reduction of the band gap to approximately zero is expected to afford an intrinsically conductor just like metals.

### 1.3 Polymer doping

A conjugated polymer, a semiconductor with a finite band gap, can be converted into a conductor by introduction of charges onto the polymer chain. This can be accomplished by doping with different species in order to achieve higher conductivities. The term doping means an addition of some specific chemicals called dopants onto either organic or inorganic semiconductor that changes the oxidation state without extensive altering the structure of semiconductor. Thus, polymer doping is a redox process involving charge transfer with subsequent creation of charged species.<sup>7</sup>

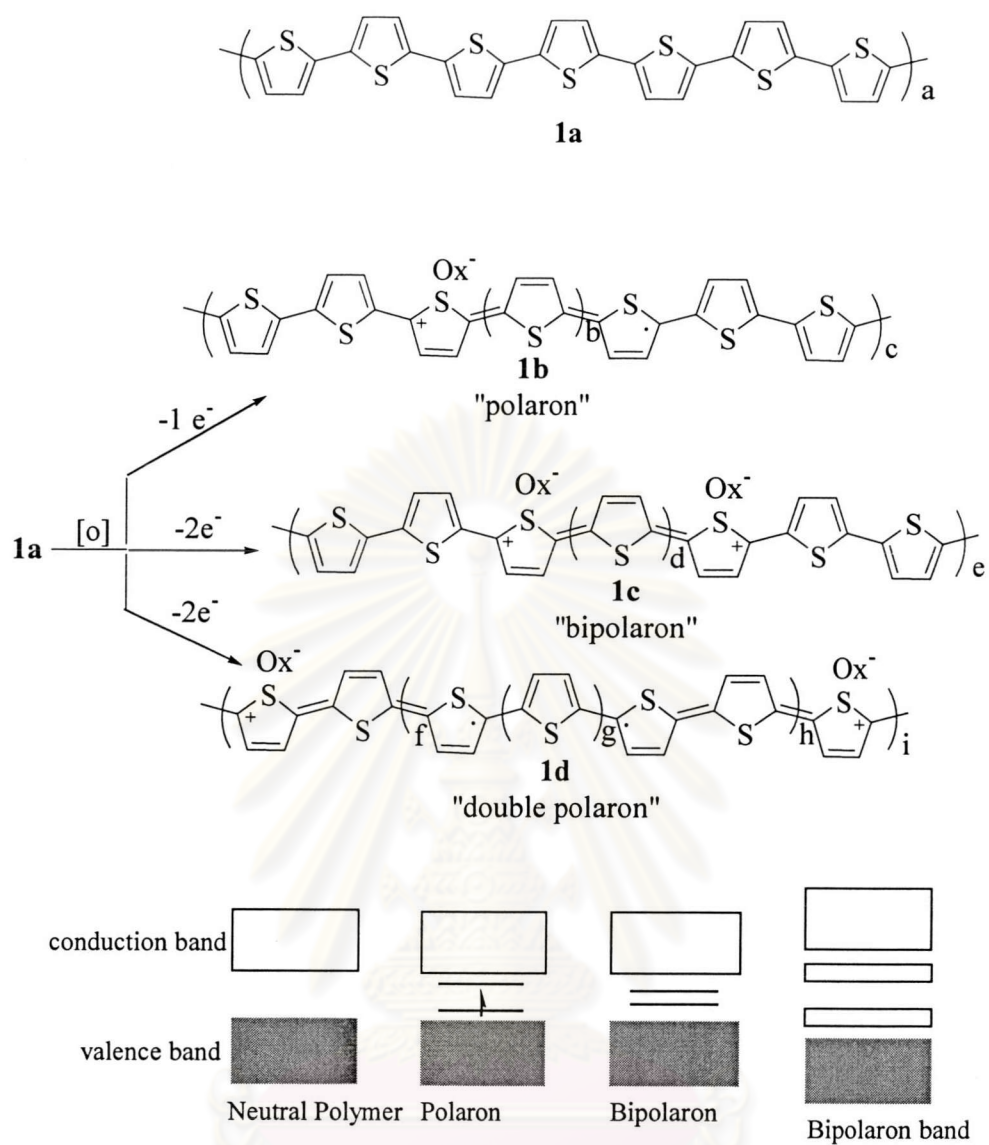
The simple view of doping is that electrons are removed from the valence band (known as oxidation or *p*-doping) or added to the bottom of the conduction band (also called reduction or *n*-doping).<sup>7</sup> Most of the conjugated polymers known today are built up of electron-rich units, making them *p*-type semiconductors. They can be doped with oxidants like I<sub>2</sub> and FeCl<sub>3</sub>. The possible changes that occur in a conjugated polymer upon oxidation are exemplified in **Scheme 1.1** for polythiophene.

The removal of one electron from the polythiophene chain (**1a**) produces a mobile charge in the form of a radical cation (**1b**), also called a *polaron*. The positive charge tends to induce local atomic displacements, leading to the polaronic behavior. This creates new localized electronic states in the gap, with the lower energy states being occupied by a single unpaired electron. Further oxidation can either convert the polaron into a spinless *bipolaron* (**1c**) that is of lower energy than the creation of two distinct polarons, or introduction of another polaron (**1d**). In either case, introduction of each positive charge also creates a negatively charged counterion (Ox<sup>-</sup>). At higher doping levels it becomes possible that two polarons combine to form a bipolaron.<sup>7,9</sup>

For a very heavily doped polymer it is conceivable that the upper and the lower bipolaron bands will merge with the conduction and the valence bands respectively to produce partially filled bands and metal-like conductivity.<sup>9</sup>

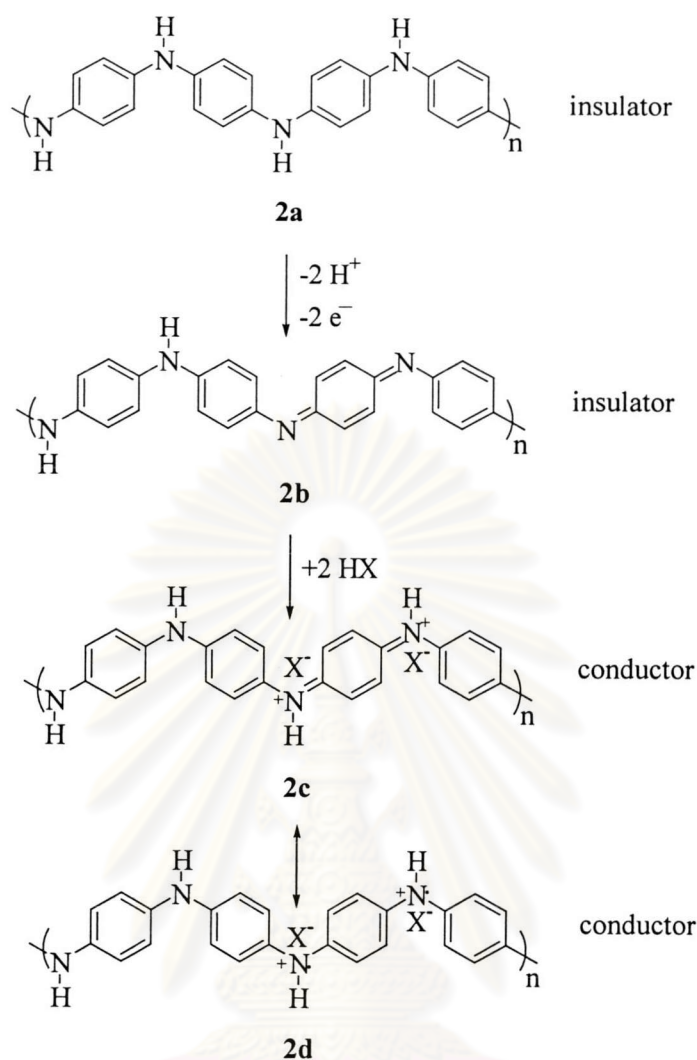
The second method consists of *acid doping* of conjugated polymers having sites that can be protonated, introducing charges in the main chain. The best known example is polyaniline. (**Scheme 1.2**) The neutral leucoemeraldine form **2a** can be oxidized to the emeraldine base **2b** without introduction of counterions. However, the emeraldine base **2b** only becomes conducting after treatment with a sufficiently strong acid (HX) which protonates the imine nitrogens and, at the same time, introduces a counterion. (X<sup>-</sup>) The conducting emeraldine **2c** can also be represented by the mesomeric structure **2d**, in which all phenyl rings are aromatic and radical cations are present on every second nitrogen atom. This degenerate mesomerism is thought to account for a high charge-carrier mobility, and thus high conductivity. However, conformational factors like the crystallinity of polyaniline films also play a crucial role.<sup>7</sup>





**Scheme 1.1** Structural and electronic changes in polythiophene upon oxidative doping.

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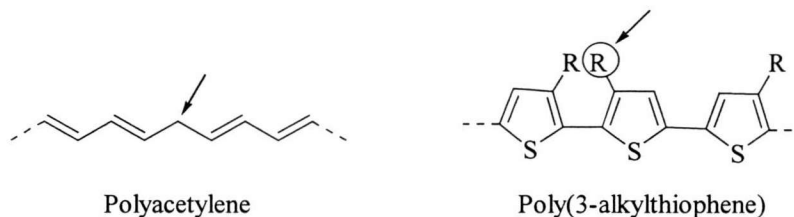
**Scheme 1.2** Acid doping in polyaniline

#### 1.4 Effective Conjugation Length (ECL)

An ideal conducting polymer would have its  $\pi$  electrons in the unsaturated bonds conjugated throughout the whole chain. This requirement usually does not hold due to the following: i) Formation of defects in polymer ii) Twisting of planar structure out of conjugation in the polymer.

Examples of the above 2 reasons are shown in **Figure 1.5**. Formation of a defect in polyacetylene as a saturated  $sp^3$ -hybridized methylene caused the disruptive effect in the flow of electrons on polymer chain. In another case, the steric incumbent between adjacent R groups on H-H thienyl units in irregular poly(3-alkylthiophene) brought about the twisting of the thienyl ring planes out of coplanarity, caused an

increase in the energy needed to allow the flow of electrons through the polymer chain, hence making the polymer chain less conductive.



**Figure 1.5** A defect in polyacetylene and steric induced structural twisting in poly(3-alkylthiophene)

Another possible reason would be the twisting of polymer chain, which occurs randomly at the single bonds and divided the polymer into separated sections with their own coplanarity. (**Figure 1.6**) Twisting of polymer chain would cause the reduction of conjugation in the polymer. The effect of the polymer chain length on optical and conductive properties of soluble oligothiophenes with long alkyl groups has been studied (**Table 1.3**).<sup>10</sup> These compounds (**Figure 1.7**) showed the spectral properties and varied progressively with increasing chain length up to around the 20-mer. The smallest number of monomeric units of a conjugated polymer that shows the highest  $\lambda_{\max}$  for that particular polymer corresponds to *effective conjugation length* (ECL). In the case of the experiment on oligothiophenes, the effective conjugation length value was approximately 20 thienyl units. The conductivity of these iodine-vapor doped oligothiophenes also increased with the chain length, which implied that the extension of the conjugated system to the 27-mer or more may still be advantageous to charge hopping between the adjacent oligomeric chains in the doped state.



**Figure 1.6** Twisting of polythiophene



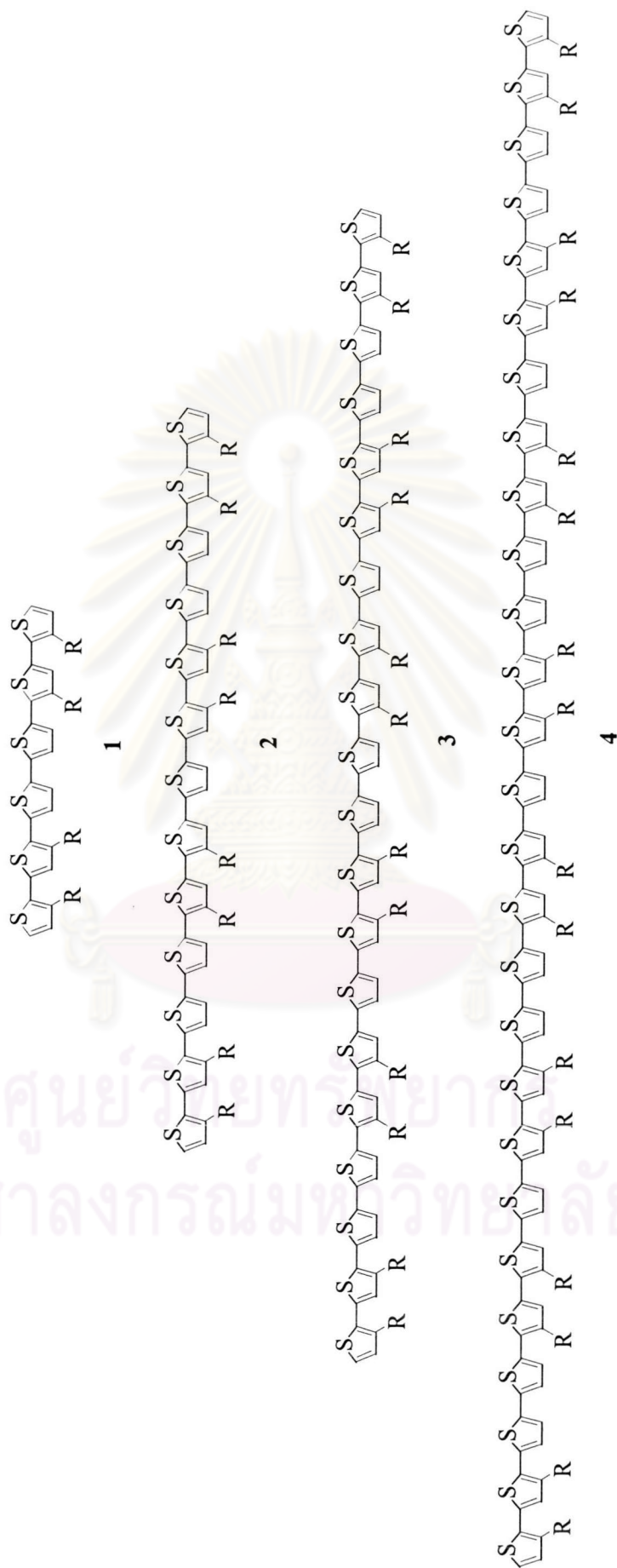


Figure 1.7 Structures of oligothiophene 1-4

**Table 1.3** Electronic absorption and conductivities of doped oligothiophenes

Compound	Number of thienyl units	$\lambda_{\max}$ (nm)	$\sigma$ (S.cm <sup>-1</sup> )
1	6	413	0.041
2	13	453	3.5
3	20	461	7.1
4	27	461	18.5

### 1.5 Polythiophene (PT)<sup>6,11</sup>

Thiophene was found in tar, gas and industrial benzene obtained from coal. Polythiophene is environmentally stable and highly resistant to heat. The development of polythiophene and its derivatives is largely motivated by their multiple potential technological applications. These applications can be divided into three main groups resorted to:

- The electrical properties of the doped conducting state, such as antistatic and EMI shielding, PT-based gas sensors, PT-based radiation detector and corrosion protective films
- The electronic properties of the neutral semiconducting state, such as photovoltaic cells and nonlinear optics
- The electrochemical reversibility of the transition between the doped and the undoped state, such as new rechargeable battery, display devices, electrochemical sensors and modified electrodes.<sup>12</sup>

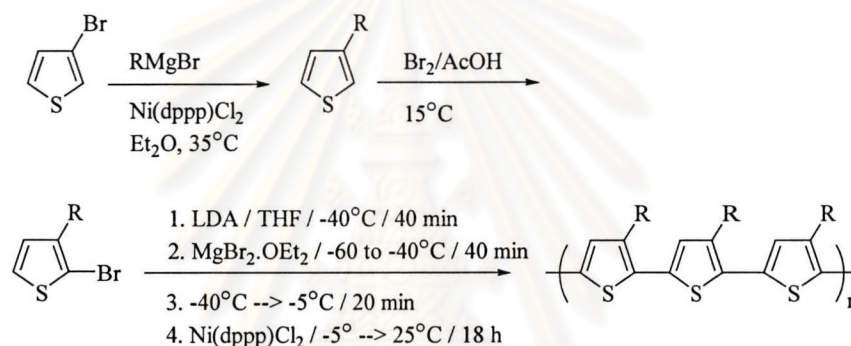
#### 1.5.1 Synthesis of polythiophene

Three general methods were reported for the synthesis of polythiophene:

##### a) Grignard reagent

The soluble poly(3-alkylthiophene) was synthesized in three steps from 3-bromothiophene as shown in **Scheme 1.3**. The polymerization was performed in a one-flask reaction consisting of metalation of 2-bromo-3-alkylthiophene selectively at

the 5-position, followed by trapping the 2-bromo-3-alkyl-5-lithiothiophene with magnesium bromide etherate and treatment with Ni(dppp)Cl<sub>2</sub> leading to regiochemically defined 95-98% head-to-tail-coupled poly(3-alkylthiophene).<sup>13</sup> The electrical conductivity of the regioregular H-T poly(3-alkylthiophene) was very high compared to regiorandom poly(3-alkylthiophene) synthesized from FeCl<sub>3</sub> as shown in **Table 1.4**. While there was a clear trend in the electrical conductivity in HT P3ATs, the conductivity in P3ATs prepared from FeCl<sub>3</sub> decreased in series: poly(3-dodecylthiophene) > poly(3-octylthiophene) > poly(3-hexylthiophene) > poly(3-butylthiophene). Optical data showed that the  $\lambda_{\max}$  was at the highest wavelength for poly(3-dodecylthiophene thin film, with the wavelength decreasing uniformly from poly(3-octylthiophene) to poly(3-hexylthiophene).<sup>14</sup>



**Scheme 1.3** Regioselective synthesis of poly(3-alkylthiophenes)

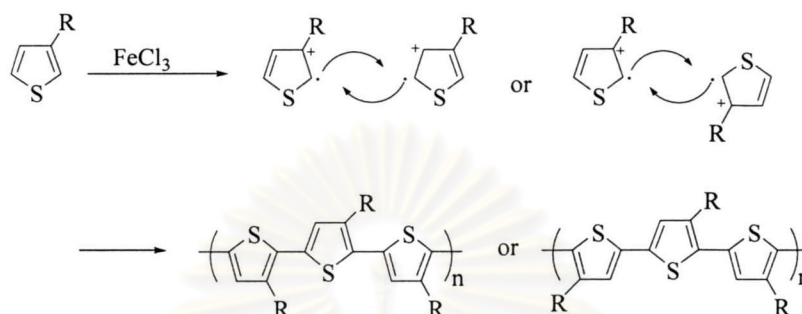
**Table 1.4** Electrical conductivity, electrochemical and optical absorption data on thin films of HT poly(3-alkylthiophenes)

P3AT	Conductivity (S.cm <sup>-1</sup> )	Maximum UV-Visible wavelengths (nm)
Poly(3-hexylthiophene)	1	480
Poly(3-octylthiophene)	1	480
Poly(3-dodecylthiophene)	20	480
HT poly(3-hexylthiophene)	100	613, 562, 505
HT poly(3-octylthiophene)	200	620, 560, 520
HT poly(3-dodecylthiophene)	1000	630, 575, 526



b) Chemical polymerization using  $\text{FeCl}_3$ 

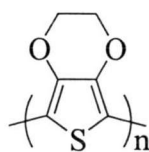
This method is easily accessible to almost all scientists who wish to obtain poly(3-alkylthiophene) and will provide sufficient amount of the polymer for general use. The oxidative coupling reaction of 3-alkylthiophene by  $\text{FeCl}_3$  are shown in **Scheme 1.4**.<sup>15</sup>



**Scheme 1.4** The oxidative coupling reaction of 3-alkylthiophene by  $\text{FeCl}_3$

Normally, the molecular weight of poly(3-alkylthiophene) by coupling 3-alkylthiophene from anhydrous  $\text{FeCl}_3$  were higher than poly(3-alkylthiophene) synthesized by Grignard coupling. Meline et al. used  $\text{FeCl}_3$  to synthesized regiorandom poly(3-octylthiophene)<sup>16</sup> having  $M_w = 100842$  and  $M_n = 35394$ , and regioregular poly(3-octylthiophene) having  $M_w = 31281$  and  $M_n = 9685$ . However, it has been reported that unwanted incorporation of even parts per million of  $\text{FeCl}_3$  into the reaction products (in the form of an octahedral Fe (III) complex) could alter their physical or electronic properties.<sup>17</sup>

There was a study on the relationship between reaction temperature, conductivity of product and %yield of poly(3,4-ethylenedioxythiophene) (PDOT, **5**) synthesized by  $\text{FeCl}_3$ . It was found that after 24 h at room temperature using a stoichiometric amount of  $\text{FeCl}_3$ , the reaction gave only low yields of product. By increasing the reaction temperature, the yield of the PDOT rised, but at the decrease of conductivity.<sup>18</sup>



**5**

### c) Electropolymerization

A polymeric film can be obtained by electropolymerization, a very useful method for preparing insoluble and infusible polymers. When the polymers obtained in the form of powder we cannot process them into a film or other useful forms. Although electrochemically prepared film under certain conditions may be stretch-deformed. Electropolymerization is an easy method for preparing polypyrrole films, but polythiophene films are obtained only under limited electropolymerization condition.<sup>12</sup> The polymers that can be synthesized by this method include PDOT<sup>19</sup> and poly(3-methylthiophene).<sup>20</sup>

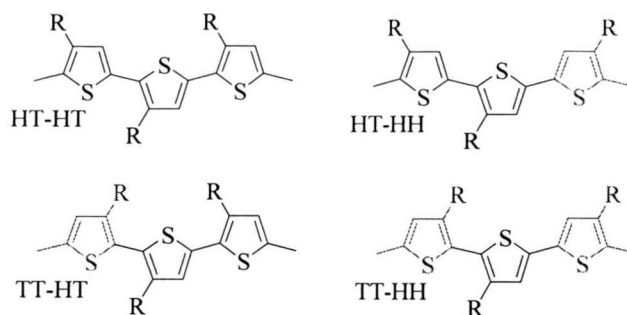
## 1.5.2 Substituted polythiophene

Among the various possible strategies for modification of conducting polymers, the polymerization of monomers modified by the covalent grafting of functional groups represents the most straightforward method to achieve the control at molecular level of the structures, electronic and electrochemical properties of conducting polymers. Consequently, the synthesis of a conducting polymer from a substituted monomer in respect of the above prerequisites implies a detailed comprehension of the structural effects of substitution (inductive, mesomeric and steric) at the various stages of organization of the material.

### 1.5.2.1 Poly(3-substituted thiophene)

The introduction of long-chain alkyl groups at the 3-position of thiophene units in polythiophene converts the polythiophene into a class of identifiable, soluble and processable conducting polymers. The design and synthesis of specially structured poly(3-substituted thiophenes) have become an area of active interest. The variation of 3-substituents on the thiophene rings has a pronounced effect on the physical properties of the polythiophenes.<sup>21</sup>

Elsenbaumer et al. reported the first synthesis of soluble poly(3-alkylthiophene) in 1985, permitting the casting of thin films of the polymers.<sup>22</sup> The nonsymmetrical 3-alkylthiophene monomer unit gives four possible neighboring environments for a given unit in the polymer. Usually these four enchainments are indicated as: HT-HT (head-to-tail head-to-tail) for the regioregular enchainment, TT-HT, HT-HH and TT-HH. (**Figure 1.8**)

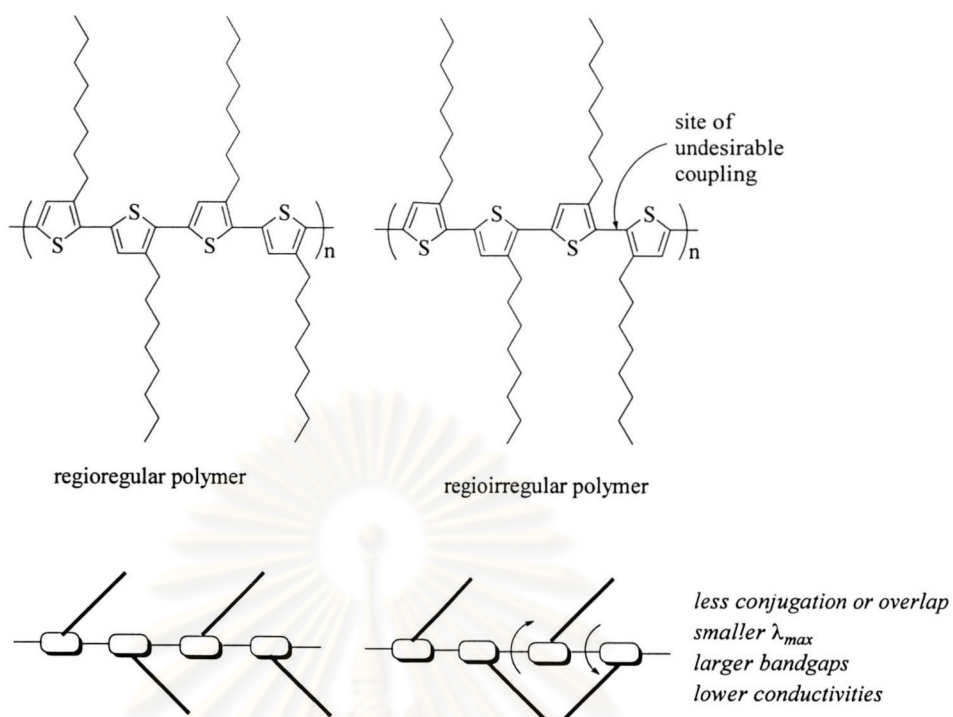


**Figure 1.8** Four possible neighboring environments for a given unit in the poly(3-substituted thiophene)

The relative occurrence of these regioisomeric variations in the enchainment depends on the polymerization method. Grignard synthesis<sup>13,23</sup> usually gives the highest amount of regioregular polymer (70-98%), electrochemical polymerization gives the least (50-60%) while a chemical polymerization with  $\text{FeCl}_3$  as a catalyst occupies a middle position (55-70%).<sup>15,24</sup> From UV-visible spectrum, high regularity poly(3-alkylthiophene) (93-98% HT-HT couplings) shows bathochromic absorption in comparison to regiorandom poly(3-alkylthiophene) that was prepared by oxidative polymerization with  $\text{FeCl}_3$ . These data are an indicative of longer *effective conjugation lengths* of regioregular head-to-tail poly(3-alkylthiophene). The effect of this microstructural irregularity is to create a sterically driven twist of the thiophene rings out of coplanarity and conjugation with one another. This is illustrated by the structural diagram in **Figure 1.9**.

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**Figure 1.9** The effect of microstructural irregularity is to create a sterically driven twist of the thiophene rings.

The larger the torsion angles between thiophene rings, the greater the band gaps will be and hence the lower electrical conductivity.<sup>13,24</sup> The regioregular poly(3-alkylthiophene) exhibits a small band gap, (1.7 eV) which is lower than that of regiorandom poly(3-alkylthiophene) (2.1 eV). The neutral HT poly(3-alkylthiophene)s (pressed pellet) has the range of conductivity between  $10^{-6} - 10^{-7}$  S.cm<sup>-1</sup>, while that of the regiorandom poly(3-alkylthiophene)s is  $10^{-9} - 10^{-10}$  S.cm<sup>-1</sup>.<sup>23</sup> Optical properties and conductivity of poly(3-alkylthiophene)s with different side chains and polymerization method are shown in **Table 1.5**. The poly(3-alkylthiophene)s from electropolymerization method show the gradual decrease of conductivity when the length of the alkyl side chains increase. (Entries 1, 3, 6 and 9) In contrast, regioregular HT-poly(3-alkylthiophene)s from Grignard coupling method show the increase of conductivity with the increase of the length of the alkyl side chains. (Entries 2, 5, 8 and 10)

**Table 1.5** Optical and electrical properties of poly(3-alkylthiophene)

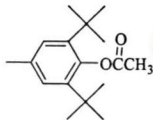
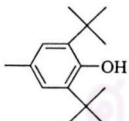
Entry	3-Substituent	Synthetic method <sup>a</sup>	$\lambda_{\max}$ solution (nm)	$\lambda_{\max}$ film (nm)	$\sigma$ (S.cm <sup>-1</sup> )	Reference
1	C <sub>4</sub> H <sub>9</sub>	E	NA	488	150	12
2	C <sub>4</sub> H <sub>9</sub> (93%HT)	GC	438	500	NA	24
3	C <sub>6</sub> H <sub>13</sub>	E	NA	NA	95	12
4	C <sub>6</sub> H <sub>13</sub>	OP	NA	505	NA	12
5	C <sub>6</sub> H <sub>13</sub> (≥99%HT)	GC	442	505	100	24
6	C <sub>8</sub> H <sub>17</sub>	E	440	517	90	12
7	C <sub>8</sub> H <sub>17</sub>	OP	440	NA	30	12
8	C <sub>8</sub> H <sub>17</sub> (≥99%HT)	GC	446	520	200	24
9	C <sub>12</sub> H <sub>25</sub>	E	440	480	4	12
10	C <sub>12</sub> H <sub>25</sub> (≥99%HT)	GC	460	561	1000	24
11	C <sub>12</sub> H <sub>25</sub> (58%HT)	OP	NA	NA	0.1-1	24

<sup>a</sup> E: electrosynthesis, GC: Grignard coupling, OP: oxidative polymerization by FeCl<sub>3</sub>  
NA = Not available

The highest value of the electrical conductivity for a poly(3-alkylthiophene) is 2000 S.cm<sup>-1</sup>, observed in 0.2 μm thin film of poly(3-methylthiophene) (PMT), which has the  $\lambda_{\max}$  of 510 nm. These highly conducting PMT films exhibited thickness-dependent solid-state UV-visible spectra, which correlated with the conjugation lengths and the electrical conductivity. However, PMT is nonprocessable and has the practical problem on the decrease of the stability of the doped state in very thin films when rinsed with acetone.<sup>25</sup>

Other poly(3-substituted thiophene)s such as aryl, alkoxy, alkoxyalkyl, thioalkyl groups and their optical and conductive properties were shown in **Table 1.6**.

**Table 1.6** Optical and electrical properties of poly(3-substituted thiophene)

Entry	3-Substituent	Synthetic method <sup>a</sup>	$\lambda_{\max}$ solution (nm)	$\sigma$ (S.cm <sup>-1</sup> )	Reference
1	Ph	E	560	140	12
2	Ph- <i>p</i> -OCH <sub>3</sub>	E	545	40	12
3	Ph- <i>p</i> -CF <sub>3</sub>	E	535	1.8 x 10 <sup>-3</sup>	12
4	-CH <sub>2</sub> Ph	E	440	13	12
5	-CH <sub>2</sub> CH <sub>2</sub> Ph	E	485	25	12
6	-CH <sub>2</sub> CH <sub>2</sub> OCH <sub>2</sub> Ph	E	510	20	12
7	-(CH <sub>2</sub> ) <sub>6</sub> Br (81%HT)	OP	NA	18	26
8	-(CH <sub>2</sub> ) <sub>12</sub> Br (81%HT)	OP	NA	13	26
9	-CH <sub>2</sub> OCH <sub>2</sub> OCH <sub>2</sub> OCH <sub>3</sub> (≥99%HT)	GC	439	1000 (max.5500)	24
10	-SC <sub>4</sub> H <sub>9</sub> (>90%HT)	GC	497	NA	27
11	-SC <sub>6</sub> H <sub>13</sub> (>90%HT)	GC	503	200-500	27
12	-SC <sub>8</sub> H <sub>17</sub> (>90%HT)	GC	510	400-700	27
13	-SC <sub>10</sub> H <sub>21</sub> (>90%HT)	GC	505	200-600	27
14		OP	NA	5.2 x 10 <sup>-4</sup>	28
15		OP	NA	4.2 x 10 <sup>-4</sup>	28

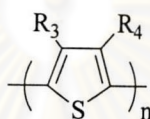
<sup>a</sup> E: electrosynthesis, GC: Grignard coupling, OP: oxidative polymerization by FeCl<sub>3</sub>  
NA = Not available

### 1.5.2.2 Poly(3,4-disubstituted thiophenes)

It has been recognized early that the introduction of a methyl group at the  $\beta$ -position (Figure xx) of the thiophene ring leads to a significant increase of the conjugation and conductivity of its polymer.<sup>20</sup> As a further step, disubstitution at the  $\beta, \beta'$ -positions has appeared as an interesting method to synthesize perfectly by



suppressing the possibility of connection between  $\alpha$  and  $\beta'$  positions. However, this approach is severely limited by the steric interactions between substituents grafted on consecutive monomers that distort the conjugated  $\pi$  system, producing a considerable loss of effective conjugation. As shown in **Table 1.7**, poly(3,4-dialkylthiophene) (Entries 2, 3, and 9) have lower conductivities than their corresponding monosubstituted polymers. (Entries 1 and 4) Although cyclization between the 3 and 4 positions as in dihydrocyclopenta[*c*]thiophene allows a significant reduction of the steric hindrance. (Entry 3) The polythiophenes mono- and disubstituted by alkoxy or thioalkyl groups (Entries 5 - 10) also reveal significant steric hindrance.



**Table 1.7** Optical and electrical properties of poly(3,4-disubstituted thiophenes)

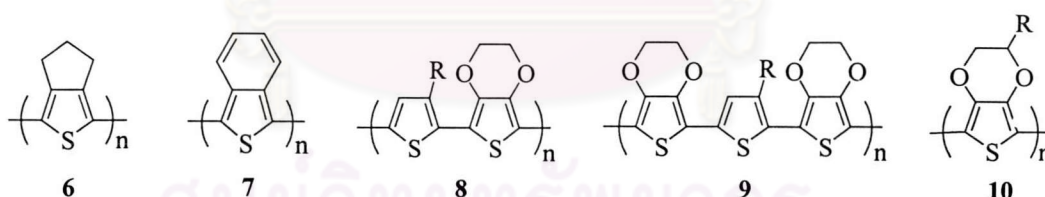
Entry	Polymer		$\lambda_{\max}$ (nm)	$\sigma$ (S.cm <sup>-1</sup> )	Reference
	R3	R4			
1	H	CH <sub>3</sub>	520	500	12
2	CH <sub>3</sub>	CH <sub>3</sub>	350	0.5	12
3	Cyclopenta[ <i>c</i> ]thiophene		510	20	12
4	H	C <sub>2</sub> H <sub>5</sub>	470	180	12
5	CH <sub>3</sub>	OCH <sub>3</sub>	NA	1.8	28
6	CH <sub>3</sub>	OC <sub>2</sub> H <sub>5</sub>	NA	26	28
8	H	OC <sub>4</sub> H <sub>9</sub>	520	$8 \times 10^{-4}$	12
9	OCH <sub>3</sub>	OCH <sub>3</sub>	610	1.5-30	29
10	OC <sub>4</sub> H <sub>9</sub>	OC <sub>4</sub> H <sub>9</sub>	460	$1 \times 10^{-5}$	12
11	CH <sub>3</sub>	OC <sub>4</sub> H <sub>9</sub>	545	2	12

### 1.5.2.3 Fused ring systems

Several types of conducting polymers have been prepared using fused ring systems containing one or more thiophene units as precursors. Polycyclopenta[*c*]thiophene<sup>12</sup> (6) and Poly(isothianaphthene) (PITN)<sup>7</sup> (7) are the examples prepared by either electrochemical or chemical synthesis. In PITN, the

6-membered benzene rings would regain their aromaticity, while there is a small loss of the aromaticity of the thienyl ring. This results in a band gap of roughly 1 eV comparing to polythiophene (2 eV). A conductivity of  $50 \text{ S.cm}^{-1}$  has been reported for the iodine-doped PITN.<sup>12</sup>

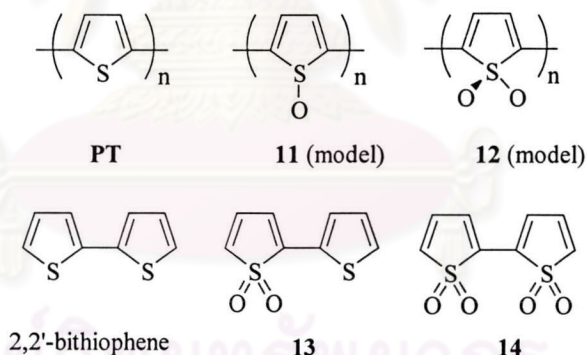
Q. Pei et al. synthesized poly(3,4-ethylenedioxythiophene) (PDOT), (**5**) by electropolymerization. The doped polymer showed a low band gap of 0.5 eV and the conductivity up to  $200 \text{ S.cm}^{-1}$ . However, the lack of processibility as well as the low yield of the monomer synthesis limited the attractiveness of the material.<sup>19</sup> To improve its solubility, copolymers of 3,4-ethylenedioxythiophene and 3-octylthiophene P(EDOT-OT) (**8**) and P(EDOT-OT-EDOT) (**9**) were prepared. The solid state UV-visible spectrum of **8** is very similar to the HT poly(3-alkylthiophene) indicating that there is almost no steric interaction between the two consecutive thienyl units. The polymer **8** shows a small band gap than its homopolymer (PDOT **5**).<sup>30</sup> Another way to improve the conductive properties of PDOT is to add an alkyl group on the fused ring, which becomes alkylated poly(3,4-ethylenedioxythiophene) (**10**). All of the polymers were not soluble in organic solvent, however, an exceptionally high conductivity ( $850 \text{ S.cm}^{-1}$ ) was found for the tetradecyl-substituted polymer.<sup>31</sup>



### 1.5.3 Polythiophene with thienyl S,S-dioxide units

One of the challenges of research in the field of polythiophene is to find a kind of functionalization capable of decreasing the band gap. Apart from adding various substituents on the  $\beta$ -positions, only little attention has been paid to the functionalizations of the sulfur atom. Sulfur is a hypervalent element characterized by several formal oxidation states in which it may be surrounded by more than eight electrons in the valence shell. This allows the functionalization of polythiophene at the thienyl sulfur atom, for example, through the formation of *S,S*-dioxides.

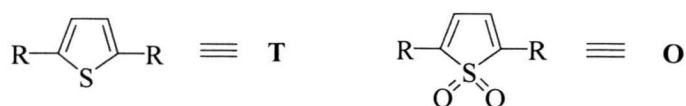
The *ab initio* study of the electronic structure and conductive properties of polythiophene (PT) and its oxy-derivatives **11** and **12** showed a trend for the values of electron affinity and ionization potential to be in the order: **12** > **11** > PT. It means that polymer **12** is expected to have the largest capacity to form highly conducting materials on doping with electron donors (*n*-doping) while PT is expected to be the best candidate for forming p-doped conducting materials. The calculated band gap of PT, **11** and **12** are 2.1, 1.53 and 1.14 eV respectively.<sup>32</sup> The results of *ab initio* calculations on 2,2'-bithiophene and its mono- and bis-*S,S*-dioxide (**13** and **14**) suggested that the contribution to their large  $\lambda_{\max}$  values comes from the more planar conformations of the bithiophene subsystems containing thiophene *S,S*-dioxide moieties and from the smaller inter-ring carbon-carbon distances. The functionalization of the thienyl sulfur to the corresponding *S,S*-dioxide leads to such rigidification of the molecular skeleton. **Table 1.8** shows the UV-Visible maximum wavelength absorption ( $\lambda_{\max}$ ) of oligothiophene *S,S*-dioxide compared to that of the parent oligothiophene. The insertion of the *S,S*-dioxide moieties affects more on the  $\lambda_{\max}$  of the longer oligomers.<sup>33</sup>



Direct oxidations of oligothiophene showed that the thienyl *S,S*-dioxides mainly occurred at the terminal units and the yields of oxidized products decreased with increasing chain length.<sup>34</sup> Therefore, the oligomers and polymers carrying the nonaromatic thienyl *S,S*-dioxide moieties were synthesized from the thiophene *S,S*-dioxide monomer. (**Table 1.9**)<sup>35,36</sup> From UV-visible spectra of the oligothiophene *S,S*-dioxides, (Entries 5-13) bathochromic shifts of the maximum wavelength absorption with respect to that of parent oligothiophenes were observed. The cyclic voltamograms showed that the LUMO of the oligothiophene *S,S*-dioxides lied at lower energy levels than those of the parent oligothiophenes.<sup>37</sup>



**Table 1.8** Maximum wavelength absorption ( $\lambda_{\max}$ ) of *S,S*-dioxide and of the parent oligothiophene;

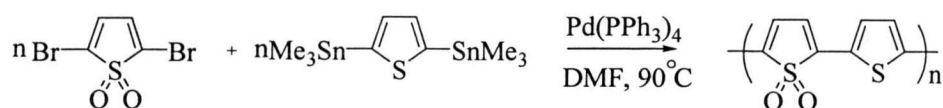


Oligothiophene	$\alpha,\omega$ Substituents (R)		
	-H	-SiMe <sub>2</sub> ( <i>t</i> -Bu)	-C <sub>6</sub> H <sub>13</sub>
<b>T</b>	231	245	254
<b>O</b>	NA	314	300
<b>TT</b>	302	344	340
<b>OT</b>	NA	408	402
<b>OO</b>	352	406	NA
<b>TTT</b>	426	370	380
<b>TOT</b>	NA	440	NA
<b>OTT</b>	NA	460	430

NA = Not available

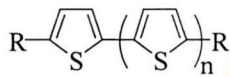

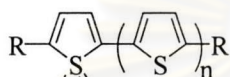

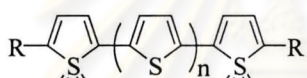
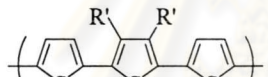
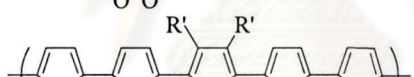

The polymers (Entries 13-15) synthesized by chemical polymerization from oligomer were characterized by good p-doping/undoping cyclability.<sup>35</sup> While Entry 14 made from electropolymerisation showed unsatisfactory cycling stability at the moderate n-doping potentials when compared to poly(bithiophene). Entries 13 and 14 showed lower LUMO energy and unchanged HOMO energy with respect to the parent polythiophene.<sup>38</sup>

In addition to homopolymer mentioned earlier, copolymer of thiophene *S,S*-dioxide and thiophene prepared by a Pd-catalyzed reaction was also reported.<sup>39</sup> (**Scheme 1.5**) The copolymer had limited solubility in DMF. The conductivity of the non-doped and iodine vapor doped copolymer is, however, almost in the range of insulator. ( $6 \times 10^{-5} \text{ S.cm}^{-1}$ )



**Scheme 1.5** Copolymer of thiophene *S,S*-dioxide prepared by a Pd-catalyzed reaction

**Table 1.9** Structures, and maximum wavelength absorptions ( $\lambda_{\max}$ ) of oligothiophenes and polythiophenes with and without thienyl *S,S*-dioxide moieties

Entry	Compound <sup>a</sup>	n	$\lambda_{\max}$ <sup>b</sup> (nm)
1		1	326
2		2	368
3		3	412
4		4	420
5		1	382
6		2	460
7		3	470
8		4	470
9		0	382
10		1	460
11		2	490
12		3	500
13		NA	554
14		NA	NA
15		NA	NA

<sup>a</sup> R = SiMe<sub>2</sub>Bu, R' = hexyl      <sup>b</sup> In CHCl<sub>3</sub>

The synthesis of polythiophene containing thienyl *S,S*-dioxide units so far appeared to be very complicated and difficult to characterize due to the lack of solubility. Here we carried out an attempt to synthesize such polymer by direct oxidation onto the parent polythiophenes by various oxidizing agents and conditions. The subsequent studies on the optical and electrical properties of the resulted products are also reported.

## 1.6 Objectives

1. To synthesize polythiophene and its derivatives containing thienyl *S,S*-dioxide units by direct oxidation onto the polymer chain.
2. To study the optical and electronic properties of the oxidized polythiophene and derivatives compared with their parent polymers.

## 1.7 Scope of investigation

1. Literature survey for related research
2. Prepare the parent PT and P3HT
3. Study the kinetic of oxidation reaction of P3HT in solution
4. Investigate the effect of the thienyl *S,S*-dioxide moieties on the optical and electronic properties
5. Study optical and electrical properties of doped PT and P3HT compared with neutral PT and P3HT

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