

CHAPTER I

INTRODUCTION

Intensive research in the area of conducting polymers started in 1977 when it was demonstrated that polyacetylene [1], the simplest conjugated polymer, could be rendered conductive through the so called “doping reaction” which involved partial oxidation (*p*-type doping) or partial reduction (*n*-type doping) of its partially extended π -bonding system. This discovery, although accidental at that time, induced intensive research devoted to the synthesis, doping and spectroscopic characterization of other conjugated polymers such as poly(*p*-phenylene), polypyrrole, polythiophene, poly(*p*-phenylene vinylene), polyaniline and their derivatives. Their structures are summarized in **Figure 1.1** [2]. Some of these compounds were known for decades, however, they attracted little attention since in general they were insoluble and prone to degradation. In fact they were “re-discovered” in the last two decades and enormous progress in their synthesis and spectroscopic characterization has recently been observed.

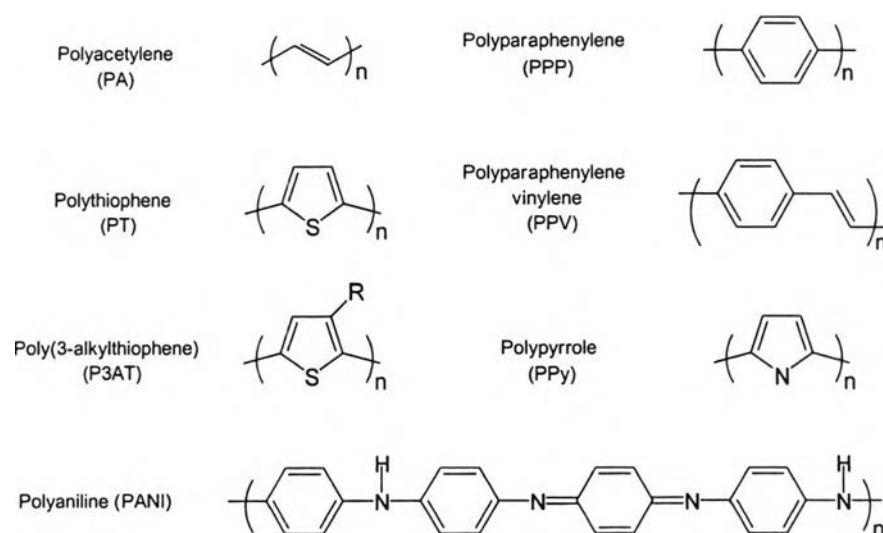


Figure 1.1 Molecular structures of some conjugated polymers: note the bond-alternated structures.

Due to strong interchain interactions, initially synthesized conjugated polymers were insoluble and infusible. These two features are extremely disadvantageous from both the basic research and technological application points of view. For these reasons, from the very beginning of conducting polymer research, chemists have sought to prepare conjugated polymers which are soluble and, at the same time, achieve high electrical conductivity upon doping. In 1986 Elsenbaumer and coworkers [3] reported the synthesis of the first class of soluble conjugated polymers which could be rendered conductive upon chemical or electrochemical doping. These were poly(3-alkylthiophenes) with sufficiently long alkyl substituents.

More recently, polymers soluble in the doped (*i.e.* conducting) state have been prepared by the use of appropriately functionalized dopants. For example, it was demonstrated that acid doping (protonation) of polyemeraldine base with sulphonic acids [4] or phosphoric acid diesters [5] resulted in the fabrication of soluble conducting polyaniline.

Solubilization of conjugated polymers led to enormous progress in the spectroscopic investigations of these compounds. In particular ^1H , ^{13}C NMR, and UV-visible-NIR spectroscopic studies enabled careful control of the chemical and structural homogeneity of individual polymer chain. This resulted in the development of synthetic procedures in which the creation of conjugation-perturbing defects could be efficiently limited. Consequently, modern studies on polythiophene have started in the 1980s [6,7].

Polythiophene is environmentally stable and highly resistant to heat. Usually, conjugated molecules and polymers are labile to degradation by oxygen. β -Carotene and polyacetylene are easily attacked by oxygen and made their conjugated systems to be interrupted by sp^3 hybridized carbon atoms. Polypyrrole is stable in the anion-doped state but unstable in the neutral state, thus is rather difficult to clarify molecular characteristics of polypyrrole. Due to the stability of neutral polythiophene, great progress in the chemistry of polythiophene has been made in the last decade.

1.1 Conjugated polymers: organic semiconductors

Conjugated polymers [8, 9] 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 are either completely filled or completely empty. The band structure of a conjugated polymer originates from the interaction of the π -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 rehybridization of the energy levels yielding more and more sublevels until a point reached at which there are bands rather than discrete levels. Interaction between the π -electrons of neighboring molecules leads to a three-dimensional band structure.

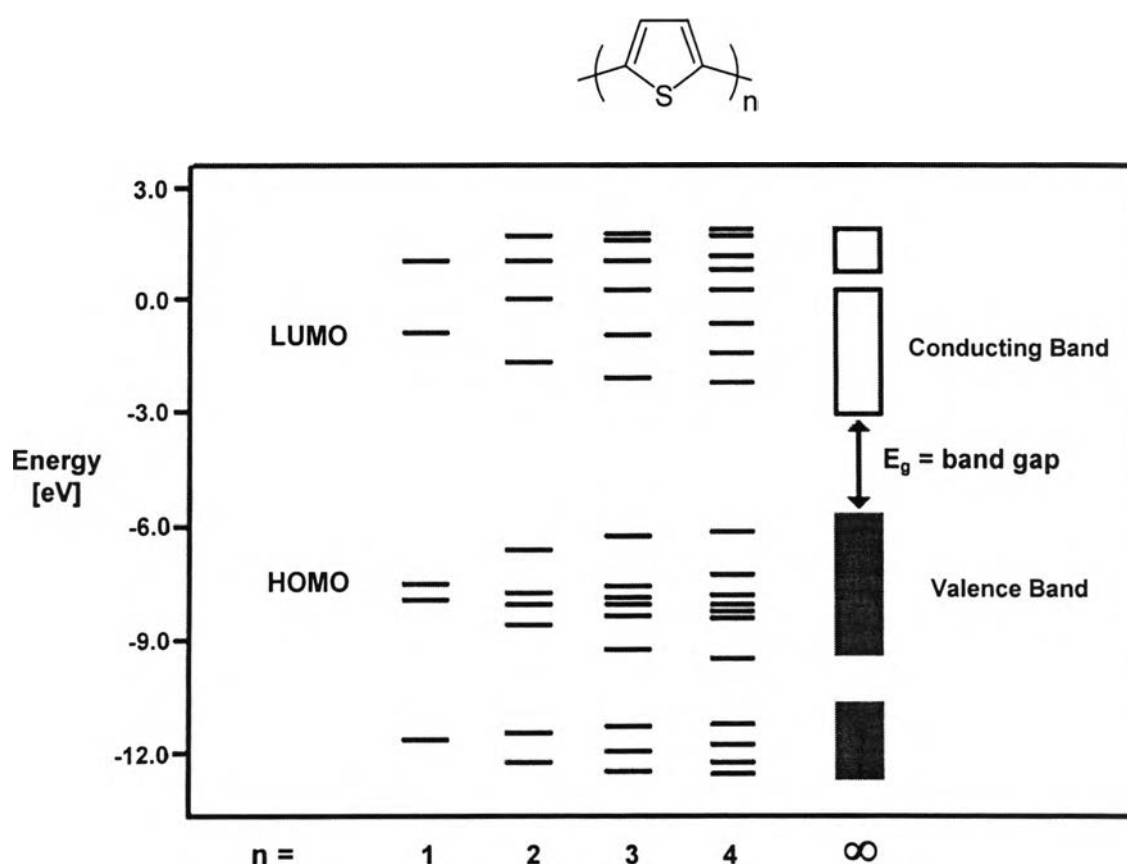


Figure 1.2 Calculated (frontier) energy levels of oligothiophenes with $n = 1-4$ and of polythiophene ($E_g =$ band gap energy).

Analogous to semiconductors, the highest occupied band (originating 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). Generally speaking, because

conducting polymers possess delocalized electrons in π -conjugated system along the whole polymeric chain, their conductivity is much higher than that of other polymers with no conjugated system. These latter non-conjugated polymers are usually known to be insulators.

The difference between π -conjugated polymers and metals is that in metals, 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 metals or any continuous solid-state structures, N will be a very large number (typically 10^{22} for a 1 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).

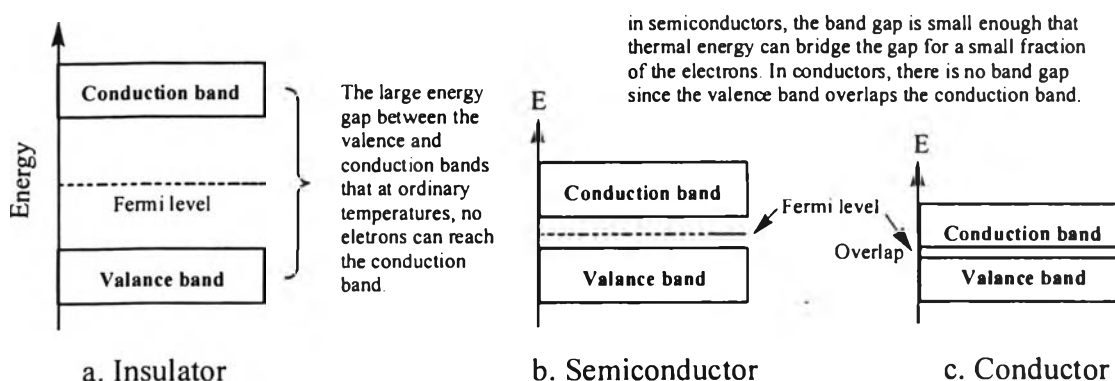


Figure 1.3 Simple band picture explaining the difference between an insulator, a semiconductor, and a metal.

In insulators, the electrons in the valence band are separated by a large gap from the conduction band. However, in conductors like metals, the valence band overlaps with the conduction band. And in semiconductors, there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically.

An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperature. The position of the Fermi level

which relates to the conduction band is a crucial factor in determining electrical properties.

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 polymeric semiconductors and insulators.

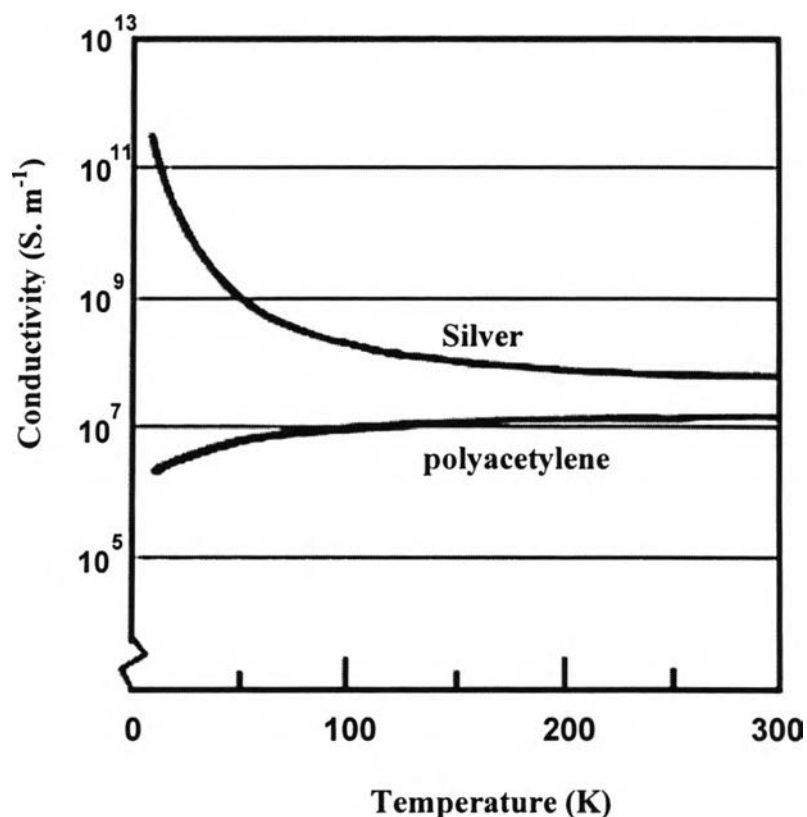


Figure 1.4 The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals.

Since π -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 to its

desired electrical and optical properties. Reduction of the band gap to approximately zero is expected to afford an intrinsic conductor like metals.

1.2 Polythiophenes (PT) [12] and poly(3-alkylthiophene) (P3HT) [6,10]

Polythiophene is a polymer composed of five membered heterocyclic monomeric units. It is environmentally stable and highly resistant to heat. Polythiophene attracted much attention as a conducting polymer due to ease of synthesis, stability, and structural versatility. It has often been considered a model system for the study of charge transport in conducting polymers with a nondegenerate ground state. Polythiophene has been aimed or used in many applications such as:

- 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 natural 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 [7]

Unsubstituted conjugated polymers are generally insoluble, thereby presenting a significant disadvantage for their characterization and possible technological applications. The standard procedure of attaching long, flexible pendant chains to the conjugated backbone can often have deleterious effects on the electrical conductivity of polymers in their oxidized (conducting) states. A significant discovery demonstrated that polythiophene belongs to one of few cases in which substitution of hydrogen at the 3-position by an alkyl chain does not affect the conductivity of the polymer, while impart solubility and consequently enhance processability. The 3-substituent can be incorporated into the polymer chain with two different regioregularities : head-to-tail (HT) and head-to-head (HH) orientations which can in turn result in four triad regioisomers in the polymer chain, *i.e.* HT-HT, HT-HH, TT-HT and TT-HH (**Figure 1.5**). Although HT couplings are generally favored, about 15-

20% of HH couplings are often observed. This is not surprising since the less repulsive HT couplings are expected.

Comparative trends in properties between regioregular and nonregioregular polymers are as follow:

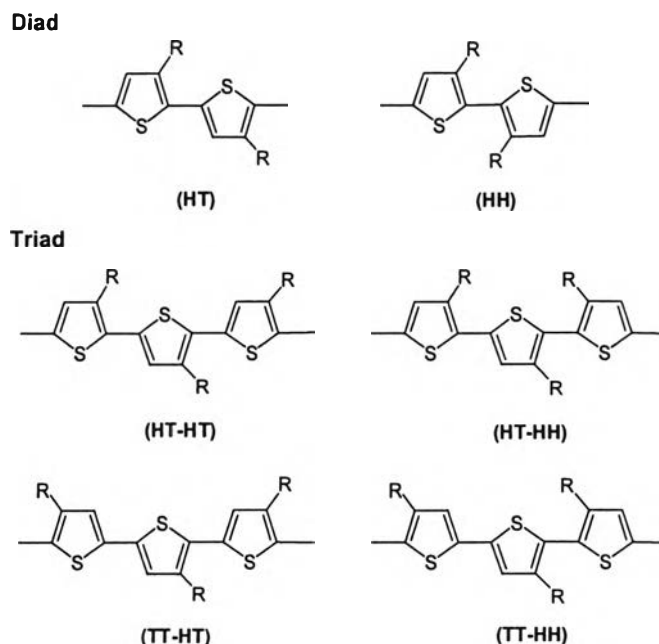


Figure 1.5 Regioisomers of the poly(3-alkylthiophene).

1.2.1 Synthesis of polythiophene

Polythiophene was prepared first by electrochemical polymerization [13]. Since a film is produced on the anode during polymerization, this method is suitable for the preparation of polymers such as polythiophene and poly(3-methylthiophene), which is not processable after polymers are formed. However, in electrochemical polymerization, the yield of polymers is low and the polymers often do not have a well-defined structure. On the other hand, since facile oxidative polymerization with iron (III) chloride produces polythiophene in high yield, this method is suitable for processable polythiophenes such as poly(3-alkylthiophene) because the electrochemical polymerization can give the polymer at only on the electrode surface. The molecular weight of polymer obtained by this method is sufficiently high for a film to be cast. The method has contributed a lot to the advance in the science of polythiophenes. Grignard coupling is also an important route to produce polythiophenes. Polymers created by this method often show lower conductivity than

those obtained by other methods. This technique is still important for the preparation of polymers with a well-defined structure, since no migration of substituents takes place during the coupling reaction.

1.2.1.1 Electrochemical polymerization [14]

A polymeric film can be obtained by electrochemical polymerization. This is a very useful method for preparing polymers such as polythiophene, poly(3-methylthiophene), and poly(3-phenylthiophene) (**Figure 1.5**), which are insoluble and infusible. When these polymers are obtained in the form of powder they cannot be processed into a film or other useful forms.

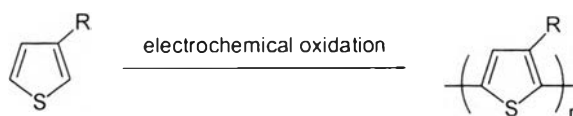


Figure 1.6 The electrochemical method for the synthesis of P3ATs (R = H, Me, Ph).

Polythiophene is not stable at the potentials used for the electrochemical polymerization of thiophene. Thus, polythiophene deposited on the anode at the earlier stages of the polymerization is overoxidized and has deteriorated, while electrochemical polymerization produces new polymer.

1.2.1.2 Oxidative coupling polymerization with iron (III) chloride

This method is easily accessible to almost all scientists who wish to obtain poly(3-alkylthiophene) and will provide sufficient amounts of the polymer for laboratory use. The resulting polymers are soluble in common organic solvents and their film can be formed by simply casting its solution on a substrate. In addition, many 3-alkylthiophenes are commercially available.

Sugimoto and coworkers [15] explored transition metal halides as oxidizing agent for polymerization of 3-hexylthiophene and found that iron (III) chlorides were effective (**Figure 1.7**). The yield was 70%. The films obtained by casting a solution of the resulting poly(3-hexylthiophene) showed similar characteristics to those of the electrochemically prepared one.

Poly(3-alkylthiophene) was undoped from trace of FeCl_3 by extraction with methanol, but this polymer remained in partially doped states. Completely undoped polymer was obtained by reduction with an aqueous solution of hydrazine.

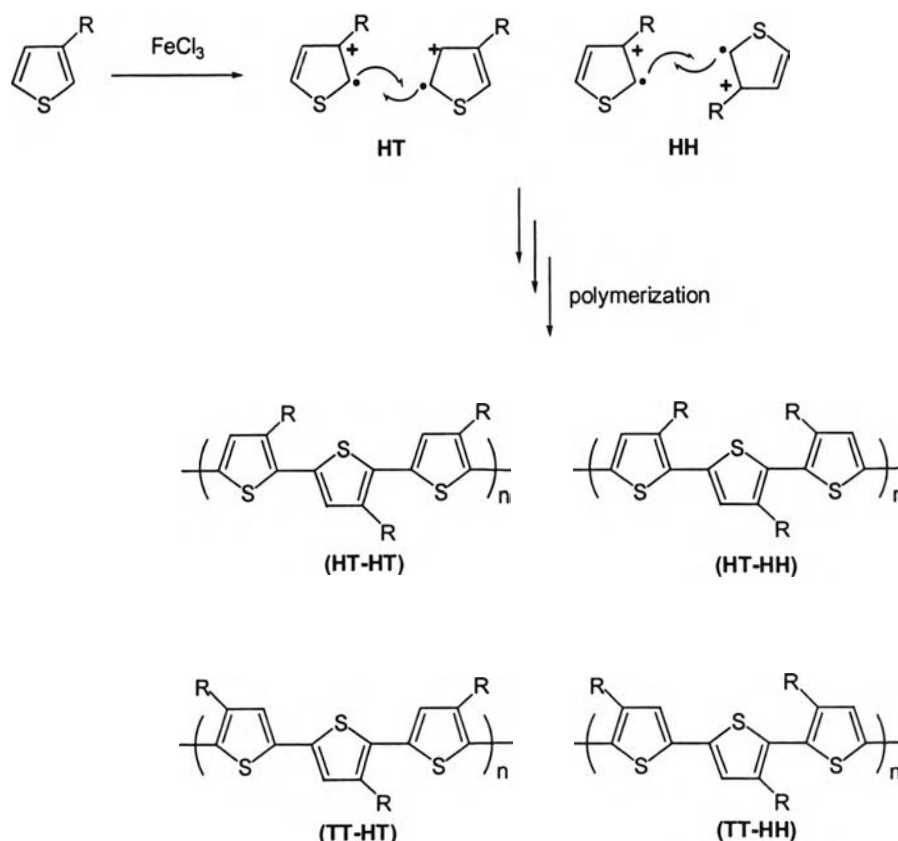


Figure 1.7 The oxidative coupling reaction of 3-alkylthiophene by FeCl_3 .

Amou [16] studied the polymerization mechanism and polymerization conditions, a lower temperature and a lower concentration were effective for increasing the HT. Niemi [17] studied the mechanism of the polymerization of 3-alkylthiophene with iron (III) chloride. Only solid iron (III) chloride was active as an oxidative polymerization agent for 3-alkylthiophene. The soluble part of iron (III) chloride was inert. The solubility of iron (III) chloride in chloroform and the consuming effect of evolved hydrogen chloride gas explained the extra amount of iron (III) chloride that was necessary initially to obtain high conversion in polymerization. A feasible polymerization mechanism for 3-alkylthiophene was developed on the basis of the crystal structure of iron (III) chloride and quantum chemical computations of thiophene derivatives. Polymerization was proposed to proceed through a radical mechanism.

1.2.3 Grignard coupling and other chemical polymerizations

The polymerizations using a metal-catalyzed cross-coupling technique has been investigated extensively [18,19]. The reaction is believed to proceed firstly by an oxidative addition of an organic halide with a metal catalyst. Transmetalation between the catalyst complex and a reactive Grignard or other organometallic reagent (or disproportionation) then generate a diorganometallic complex. The last step involves reductive elimination of the coupled product with regeneration of the metal catalyst. The first synthesis of regioregular HT-P3AT was reported by McCullough and coworkers [23] in early 1992 (**Figure 1.8**). This new synthetic method [24-28] regiospecifically generates 2-bromo-5-(bromomagnesio)-3-alkylthiophene, which is polymerized with catalytic amounts of Ni(dppp)Cl₂ using Kumada cross-coupling methods [20] to give P3ATs with 98-100% HT-HT couplings. In this approach, HT-P3ATs were prepared in yields of 44-69 % in a one-pot, multistep procedure. Molecular weights of HT-P3ATs are typically in the range of (20-40) × 10³ (PDI ≈ 1.4). A recently prepared sample of HT-poly(dodecylthiophene) had $M_n = 130,000$ (PDI = 2.1).

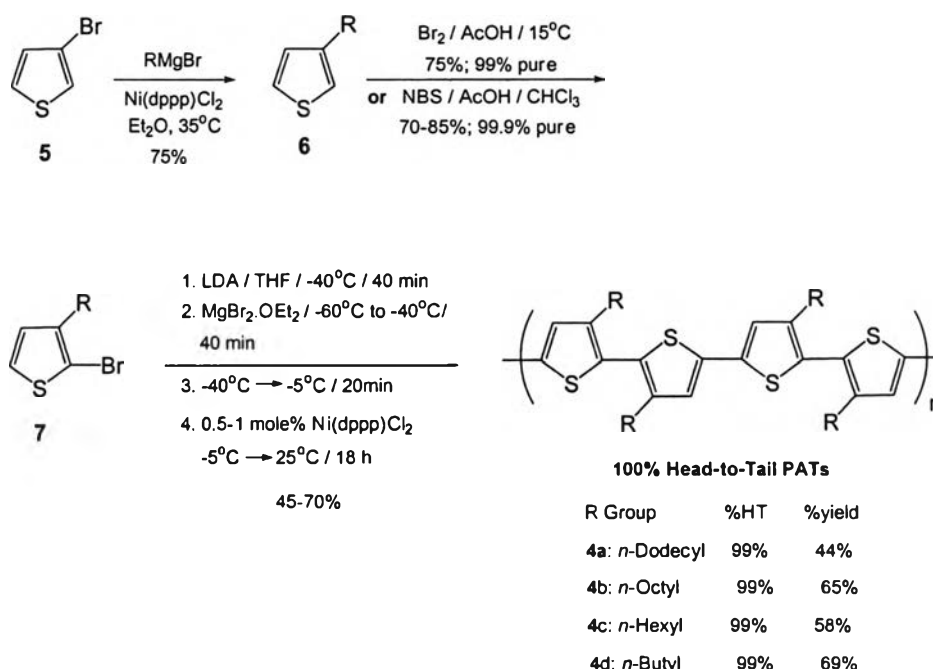


Figure 1.8 The McCullough method for the regiospecific synthesis of poly(3-alkylthiophene)s with 100% HT couplings.

1.2.2 Electrical conductivity

The electrical conductivity of functionalized polythiophenes is dependent to a large extent on both the stereoregularity and regioregularity achieved during polymerization. The regioregularity in 3-substituted thiophenes is determined by the preference for HT vs HH coupling in the polymerization. The presence of HH couplings represents a “defect” that can result in a significant deviation from coplanarity between adjacent rings (**Figure 1.9**). This not only results in a reduced conjugation length and band gap but any deviations from coplanarity also result in an increase in interchain distances arising from poorer π -stacking of polymer chains thereby reducing the probability of interchain charge carrier hopping with a consequent reduction in electrical conductivity.

A clear contrast between regioregular and nonregioregular functionalized polythiophenes is reflected in their conductivities, particularly for the HT-coupled regioregular P3AT polymers. Thus, the highly regioregular 3-substituted P3AT have conductivity in excess of 1000 S.cm^{-1} upon doping for several different substituent types which is in contrast with the usual $< 10 \text{ S.cm}^{-1}$ for other chemically generated P3AT. Interestingly, this series of regioregular P3AT have also the lowest band gap (1.7 eV) and highest intrinsic conductivity ($10^{-6} \text{ S.cm}^{-1}$) reported to date [11]. Clearly the absence of unfavorable HH diads has a positive effect on electrical conductivity and band gap. The conjugated polymer is twisted out of conjugation, therefore, the electrical conductivity, nonlinear optical response, and stability will dramatically decrease (**Figure 1.10**).

1.2.3 UV-visible spectroscopy

Clear difference is an evidence from the electronic absorption spectra of regioregular and nonregioregular P3ATs. As depicted, the thin-film UV absorption maxima, λ_{max} (polymer π - π^* transition), is clearly dependent upon the amount of HH diads in the polymers. Here, unfavorable steric effect from the alkyl pendent substituents on adjacent rings in the HH diads have the effect of creating a sterically driven twist from coplanarity with a consequent reduction in the effective conjugation lengths in the polymer (**Figure 1.9**).

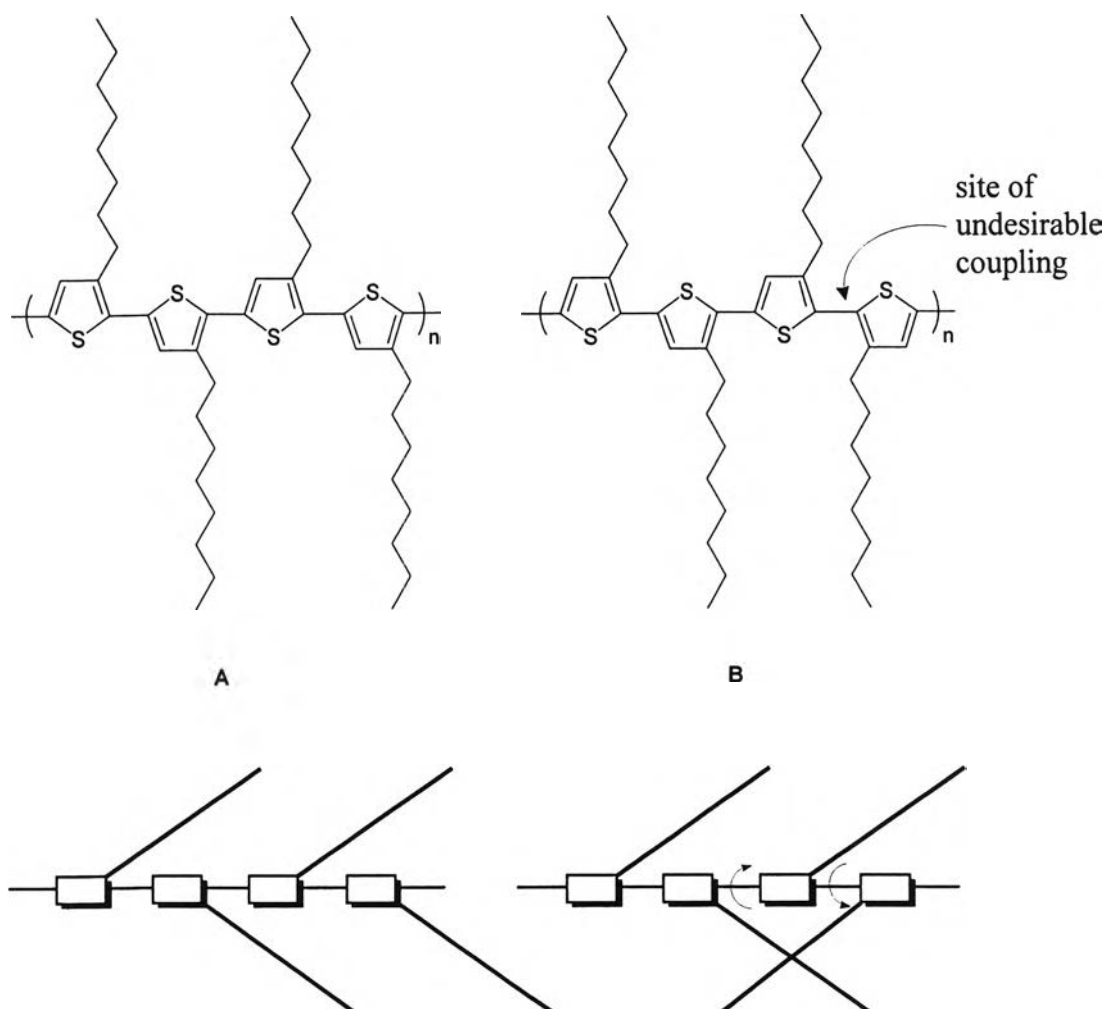


Figure 1.9 Effect of HH couplings on thiophene ring coplanarity (A regioregular P3AT, and B regiorandom P3AT).

For regioregular HT-HT poly(3-hexylthiophene) (P3HT) with < 2% HH diads, the λ_{\max} displayed two almost equally intense λ_{\max} peaks at 560 and 610 nm with a shoulder at 526 nm [11]. The higher intensity of the longer wavelength peaks (560 and 610 nm) suggest a larger proportion of longer conjugation length of the polymer chain, or a longer average conjugation length of the polymer chain. In P3HT with an increasing proportion of HH, the λ_{\max} value is progressively shifted to shorter wavelengths: 451 (70% HT, 30% HH), 446 (35% HH), and 438 (50% HH) [11].

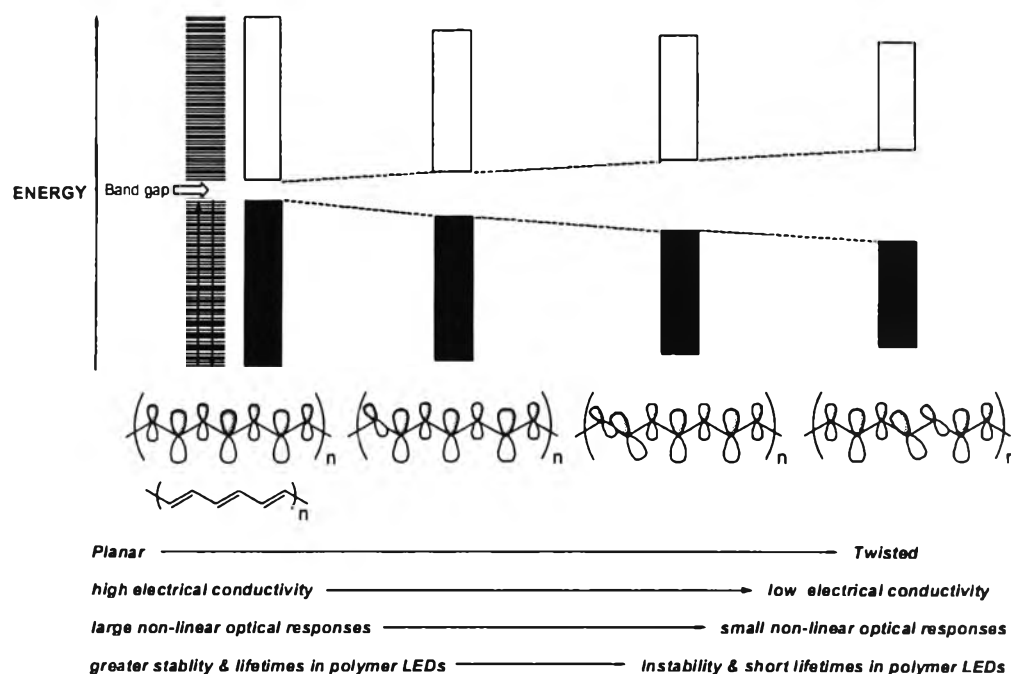


Figure 1.10 Band gaps and electrical and optical properties vary with coplanarity.

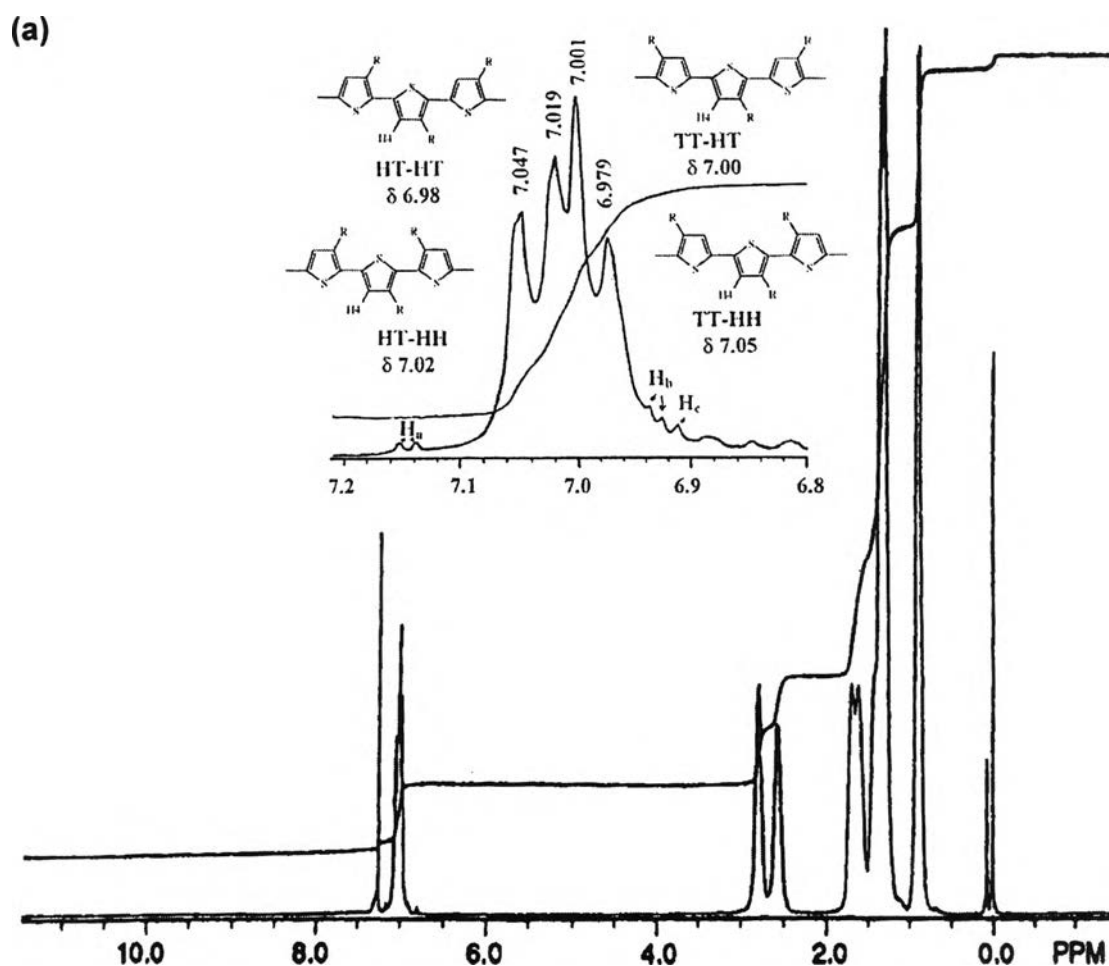
1.2.4 NMR spectroscopy

^1H NMR serve as useful probes for the regioregularities of these polymers. In particular, useful information pertaining regioregularity can be deduced from the aromatic region of the respective spectra. The poly(3-hexylthiophene) shows a dominant signal at 6.98 ppm and three weaker well defined signals at 7.05, 7.03, and 7.00 ppm (**Figure 1.11**) [11,12]. The 6.98 ppm resonance arises from rings involved in the HT–HT linkages whilst that at 7.05 ppm arises from TT–HH linkages and the resonances at 7.00 and 7.02 ppm account for the remaining connectivities. Here these resonances were reasonably assigned based on the following considerations :

- The HT configurations facilitate coplanarity of adjacent thiophene rings with the consequence that β -protons of triads associated with this configuration resonate at higher shields due to enhanced delocalization of electron density associated with the hexyl group of adjacent rings.
- The TT configurations, whilst being able to maintain coplanarity, have a diminished inductive effect of the alkyl moiety arising from a greater distance between the alkyl and the β -proton.

- Steric effects associated with the HH configuration forces adjacent thiophene rings out of coplanarity, thus decreasing conjugation and diminishing the inductive effects of the alkyl groups on adjacent rings.

Based on the above discussion, β -protons of triads with HH configurations experience less shielding than those of HT or TT configurations and appear downfield. From the integration of these peaks, the relative amounts of triads can be evaluated. Additional information can also be abstracted from the intensity ratio of triplets centred at *ca* 2.8 and 2.6 ppm ascribable to α -CH₂ groups for the configurational HT and HH diads.



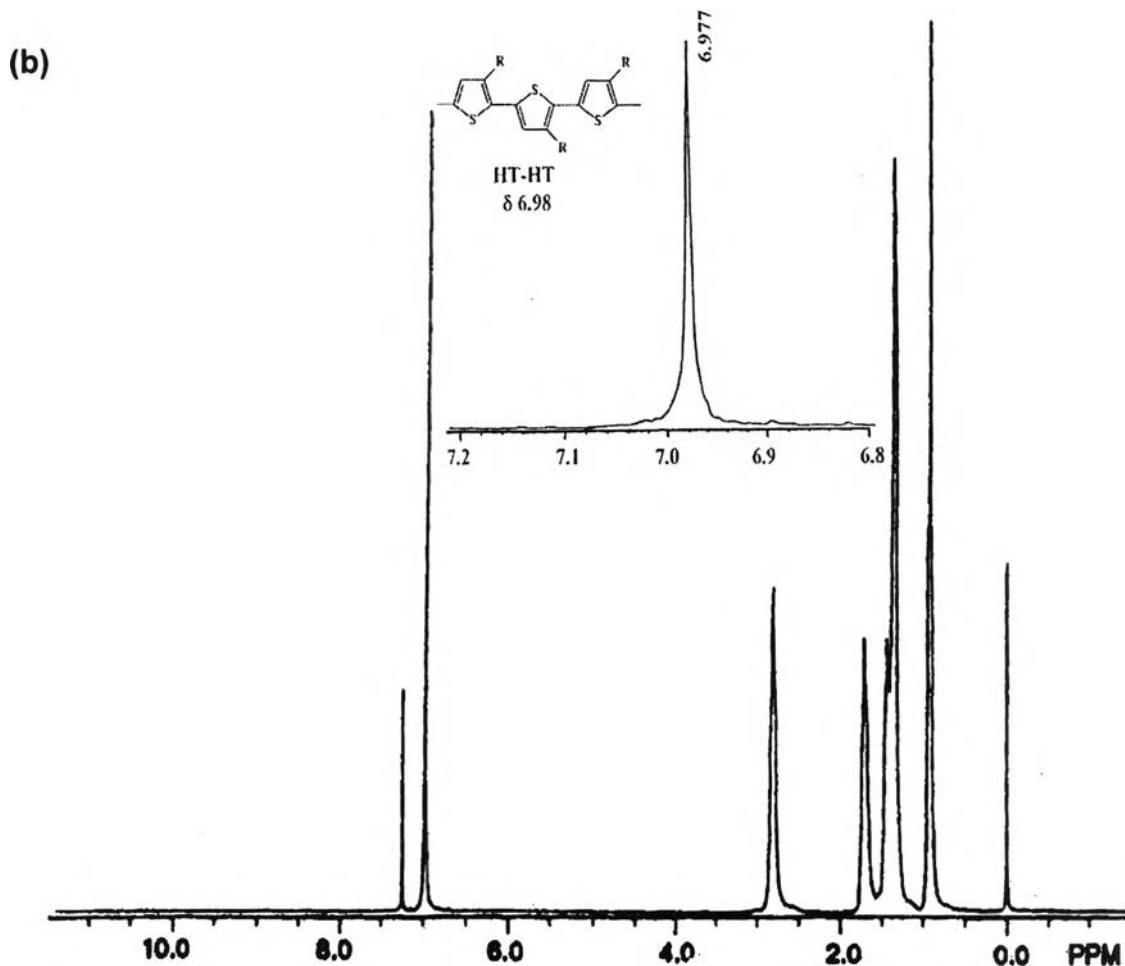
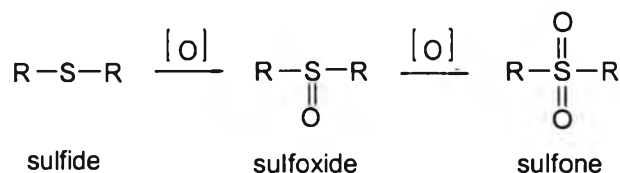


Figure 1.11 ^1H NMR spectra of (a) regiorandom (1:1:1:1, HT-HT: HT-HH : TT HT: TT-HH) P3HT and (b) regioregular (98.5%) of HT linkage P3HT [11,12].

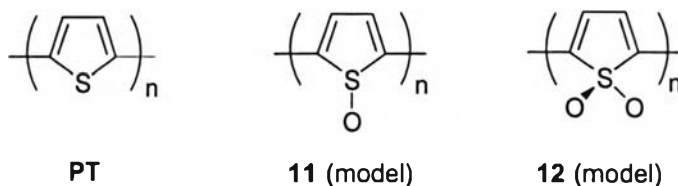
1.3 Synthesis of polythiophene with thienyl *S,S*-dioxide units

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 β -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.

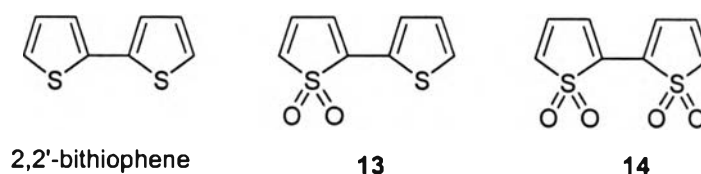
The oxidation of sulfide to sulfones has been studied extensively [31], and applied to oxidation of thiophene derivatives [32].



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 [33]. 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 λ_{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 1.1** shows the UV-Visible maximum wavelength absorption (λ_{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 λ_{max} of the longer oligomers [34].

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 [35], although λ_{max} increased with increasing chain

length [36] or the alkyl group [37]. Therefore, the oligomers and polymers carrying the nonaromatic thienyl *S,S*-dioxide moieties were synthesized from the thiophene *S,S*-dioxide monomer (**Table 1.2**) [38,39]. From the UV 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 [38,39].

Table 1.1 Maximum wavelength absorption (λ_{\max}), nm of oligothiophene containing thienyl *S,S*-dioxide and of the parent oligothiophene.

Oligothiophene	α,ω Substituents		
	-H	-SiMe ₂ (<i>t</i> -Bu)	-C ₆ H ₁₃
T	321	245	254
O	NA	314	300
TT	302	344	340
OT	NA	408	402
OO	NA	406	NA
TTT	352	370	380
TOT	426	440	NA
OTT	NA	460	430
OTO	NA	460	442

NA = Not available

The polymers (entries 13-15, **Table 1.2**) synthesized by chemical polymerization from oligomer were characterized by good *p*-doping/undoping cyclability. Increasing number of aromatic units leads to much better *n*-doping/undoping cyclability [38]. Entry 14 which was made from electropolymerization showed unsatisfactory cycling stability at the moderate *n*-doping potentials when compared to poly(bithiophene). Entry 13 and 14 showed lower LUMO energy and unchanged HOMO energy with respect to the parent polythiophene.

In addition to homopolymer mentioned earlier, copolymer of thiophene *S,S*-dioxide and thiophene prepared by a Pd-catalyzed reaction was also reported (**Figure 1.12**) [40]. The copolymer had limited solubility in DMF. The conductivity of the non-doped and iodine vapor doped copolymer is, however, almost insulator. (6×10^{-5} S.cm⁻¹)

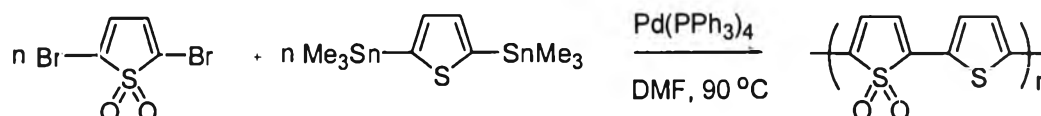


Figure 1.12 Copolymer of thiophene *S,S*-dioxide prepared by a Pd-catalyzed reaction.

Table 1.2 Structures and maximum wavelength absorptions (λ_{\max}) of oligothiophenes and polythiophenes with and without thienyl *S,S*-dioxide moieties.

Entry	Compound ^a	n	λ_{\max}^b (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

^a R = SiMe₂Bu, R' = hexyl. ^b In CHCl₃

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.

1.4 Synthesis of thiophenes and polythiophene with substituents

1.4.1 Synthesis of thiophenes with bromine atoms [41]

Kellog and co-workers have studied the bromination of thiophene and 3-substituted thiophene using *N*-bromosuccinimide in a 50:50 (v/v) mixture of chloroform and glacial acetic acid. The reaction gave products that are brominated at the 2 and 5 position.

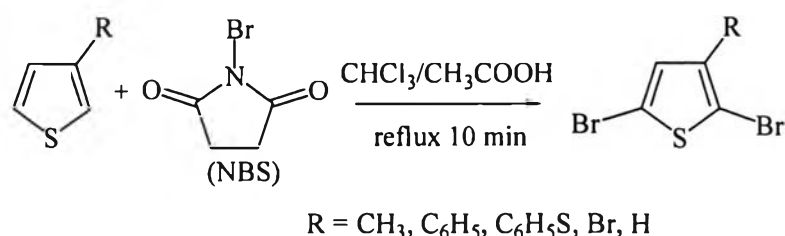


Figure 1.13 The bromination of 3-substituted thiophenes.

Some of 2-substituted thiophenes including 2-alkyl, 2-phenyl, and 2-phenylthiothiophene were also investigated with the result in 5-brominated products.

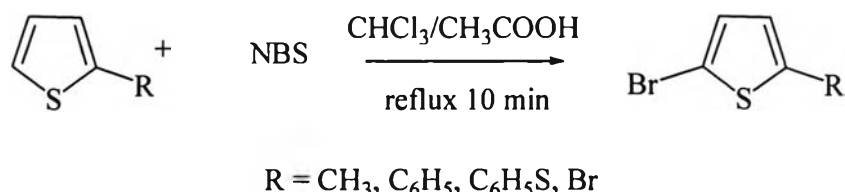


Figure 1.14 The bromination of 2-substituted thiophenes.

1.4.2 Synthesis of P3HT with substituents in the 4-position [42]

The processability, molecular organization, and electronic and optical properties of polythiophene can be controlled through derivatization of the thienyl ring. However, the scientific demand for poly(thiophene)s that possess more complex structural motifs is offset by synthetic limitations. For example, preparation of poly(thiophene)s with functional side chains requires tedious procedures involving the synthesis of monomers. All but a few functional groups are intolerant of the harsh polymerization conditions, with the result that many potential functional poly(thiophene)s simply cannot be prepared. An alternate approach to obtaining derivatized polymers is post-functionalization of precursor polymers.

The post-functionalization of conjugated polymers, e.g., polyacetylene [43], polyaniline [44], polypyrrole [45], and polythiophenes [45, 46], as a method to modify the properties of these polymers has drawn much attention in recent years [47]. The nucleophilic substitution of the overoxidized polythiophenes with Cl, Br, or methoxy groups in the 4-position using an electrochemical method has been investigated to functionalize polythiophenes [46]. On the basis of electronic effects alone, however, the 4-position of the thiophene ring in poly(3-alkylthiophene)s (P3ATs) should be more susceptible to electrophilic substitution due to the high electron density on the backbone that originates from the extended π -system and the electron donating effect of the 3-alkyl side chain. The replacement of the 4-position of P3ATs by functional groups via electrophilic substitution, and further derivatization of the functional groups, should provide a useful strategy to tailor the structure and the band gap of the polymers and therefore control their electrooptical properties.

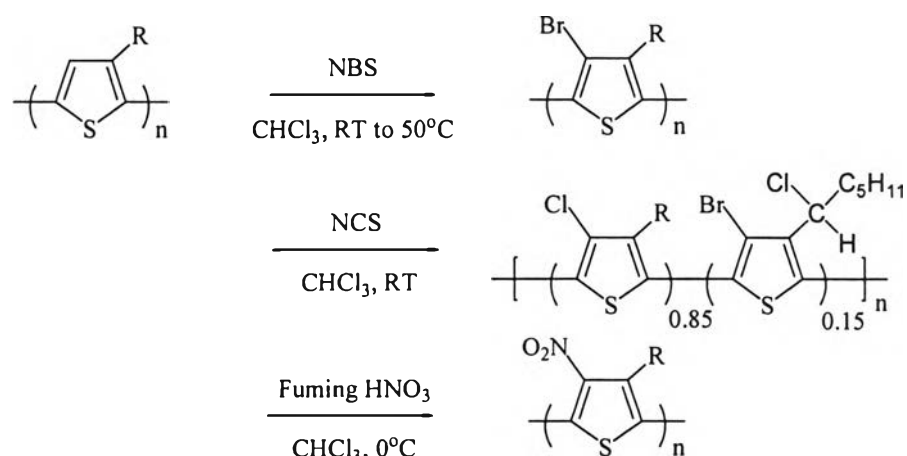
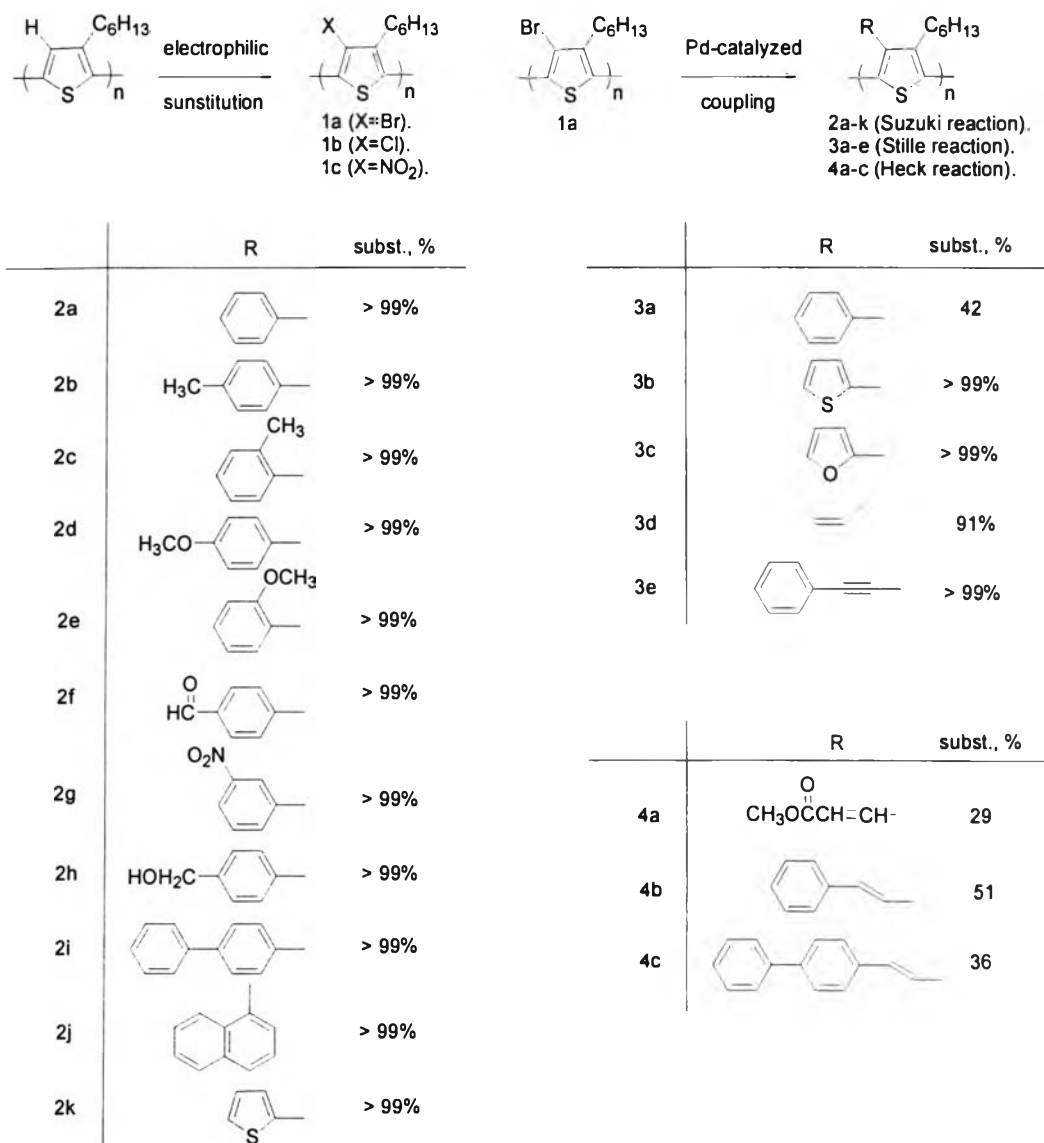


Figure 1.15 The functionalization of poly(3-hexylthiophene).

These 3,4-disubstituted poly(thiophene)s should be capable of further substitution with other functional groups. It was demonstrated that Suzuki, Stille, and Heck coupling chemistry involving poly(3-bromo-4-hexylthiophene) and appropriate reagents can be used to prepare poly(thiophene)s possessing aryl, vinyl, and alkynyl side chain groups.



Scheme 1.1 The post-functionalization of poly(3-hexylthiophene) [58].

Another interesting functional group is acyl groups. When acyl groups attach to thiophene rings in polythiophene, it alkyl chains might help the polymer gain more processibility. The primary acyl group, acetyl, and longer alkyl chain, octanoyl, will be introduced to this reaction. With processable P3HT, acetyl should also investigated if there is any change of properties after the substitution. The acylation followed the Friedel-Crafts acylation and will be subjected to thiophene monomer as well.

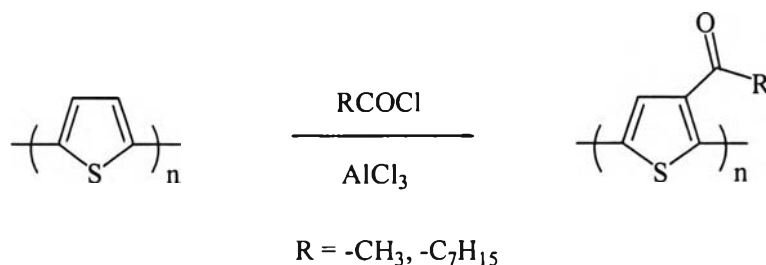


Figure 1.16 The acylation of polythiophene.

1.5 Synthesis of *S*-alkyl and *S*-aryl thiophenium salts

A way to decrease the band gap of polythiophene is the functionalization of polythiophene at the thienyl sulfur atom. There have been studies about formation of *S,S*-dioxides at the sulfur atom of thiophene units. In addition to the formation of *S,S*-dioxides, *S*-alkylation [48] and *S*-arylation [49] have also been studied, however with the monomer only.

Acheson and co-workers have been successfully synthesized *S*-alkylthiophenium salts by treatments the corresponding thiophenes with alkyl halide in the presence of silver tetrafluoroborate or similar reagents. (**Figure 1.17**)

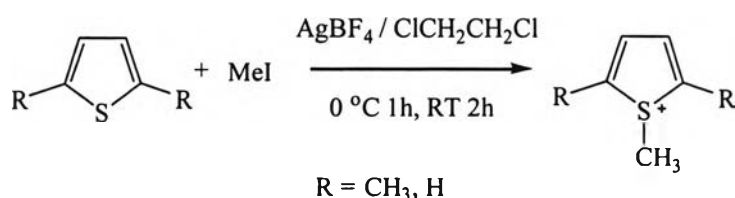


Figure 1.17 The *S*-alkylation of thiophenes.

Nevertheless, because of their instability, the alkylated thiophenes usually undergo dealkylation to return to the original thiophenes in a few weeks. Therefore, a substituent forming a strong bond with sulfur atom is necessary. Generally, a phenyl group strengthens the chemical bond more than an alkyl group does. A Ph-S bond is about 12 kcal mol^{-1} stronger than a Me-S bond [50].

Kitamura and co-workers have prepared 1-phenyl-1-benzothiophenium triflates by a direct *S*-phenylation with diphenyliodonium triflate in the presence of catalytic amount of copper(II) acetate. (**Figure 1.18**)

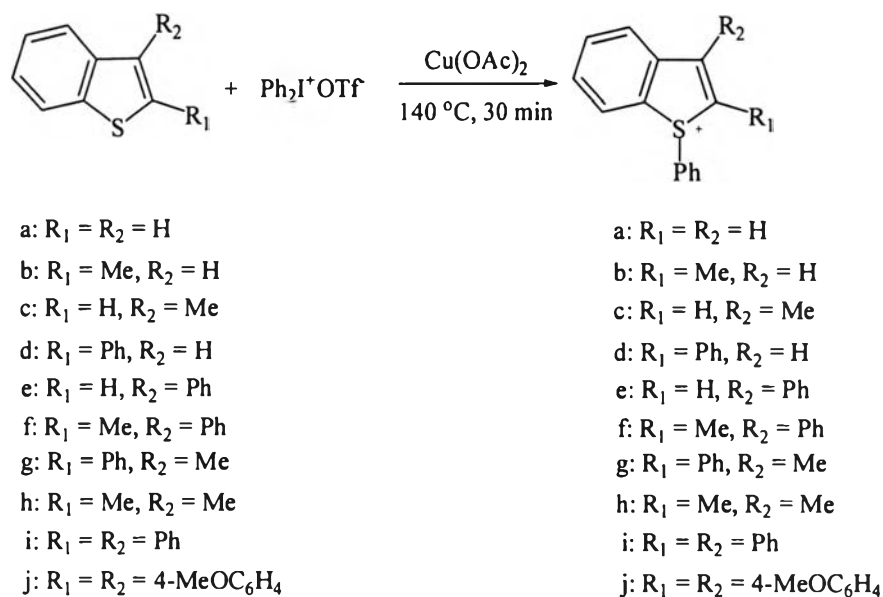
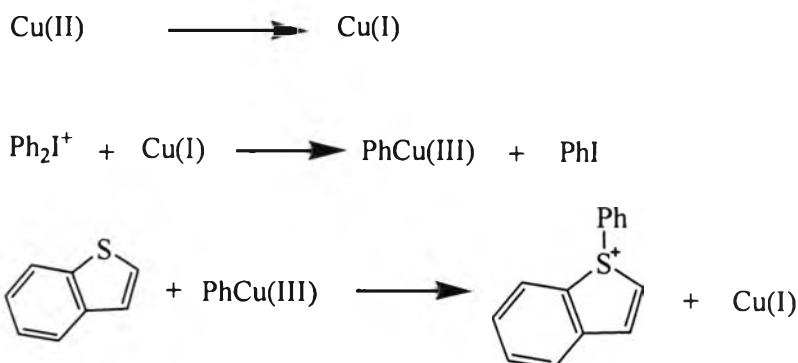
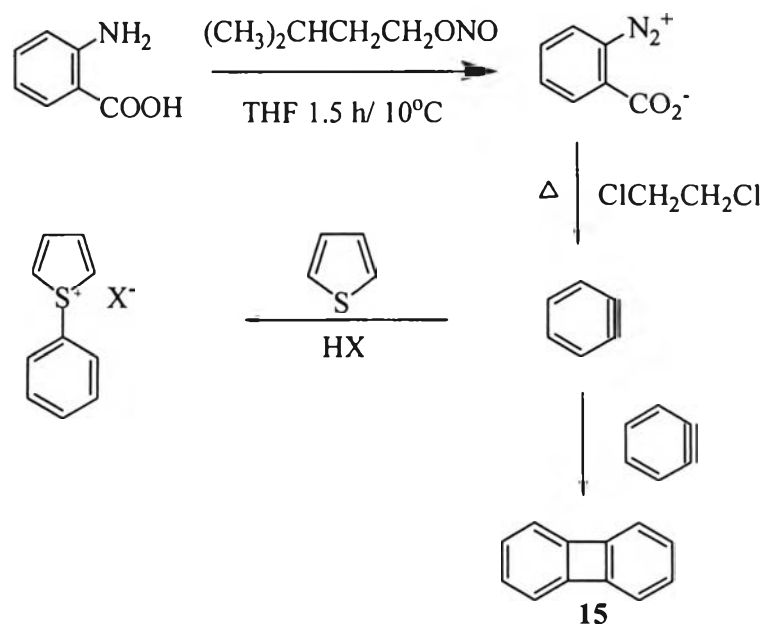


Figure 1.18 The *S*-arylation of 1-benzothiophenes.



Scheme 1.2 The phenylation of 1-phenyl-1-benzothiophene catalyzed by Cu^+ [49].

Another method to synthesize *S*-aryl thiophenium salts relied on the trapping of a benzyne intermediate by thiophene before it was dimerized to biphenylene. Anthranilic acid, one of the well-known precursors, was used to prepare benzyne [56]. By treating anthranilic acid with isoamyl nitrite, diazonium carboxylate was generated. The diazonium carboxylate would decompose to benzyne shortly after heating. Normally, a benzyne molecule would quickly react with another benzyne molecule to form biphenylene. If there was a presence of thiophenes or other trapping agents [57], lone pair electrons of the sulfur atom of thiophene ring might add on the benzyne forming thiophenium salt after a subsequent protonation.



Scheme 1.3 Formation of biphenylene and trapping with thiophene.

1.6 Effect of doping [2]

The doping is an addition of a doping agent into the polymer and expect to improve the conductivity of the polymer. Reversible “doping” of conducting polymers, with associated control of the electrical conductivity over the full range from insulator to metal, can be accomplished either by chemical doping or by electrochemical doping. Concurrent with the doping, the electrochemical potential (the Fermi level) (**Figure 1.3**) is moved either by a redox reaction or an acid-base reaction into a region of energy where there is a high density of electronic states; charge neutrality is maintained by the introduction of counter-ions. Metallic polymers are, therefore, salts. The electrical conductivity results from the existence of charge carriers (through doping) and from the ability of those charge carriers to move along the π -bonded “highway”. Consequently, doped conjugated polymers are good conductors for two reasons:

1. Doping introduces carriers into the electronic structure. Since every repeating unit is a potential redox site, conjugated polymers can be doped *n*-type (reduced) or *p*-type (oxidized) to a relatively high density of charge carriers.

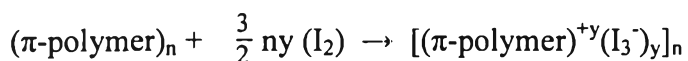
2. The attraction of an electron in one unit to the nuclei in the neighboring units leads to carrier delocalization along the polymer chain and to charge carrier mobility, which is extended into three dimensions through inter-chain electron transfer.

Disorder, however, limits the carrier mobility and, in the metallic state, limits the electrical conductivity. Indeed, research directed toward conjugated polymers with improved structural order and hence higher mobility is a focus of current activity in the field. Charge injection onto conjugated, semiconducting macromolecular chains, or “doping”, leads to the wide variety of interesting and important phenomena which define the field. The doping can be accomplished in a number of ways:

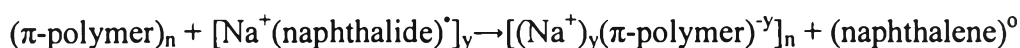
1.6.1 Chemical doping by charge transfer

The initial discovery of the ability to dope conjugated polymers involved charge transfer redox chemistry; oxidation (*p*-type doping) or reduction (*n*-type doping), as illustrated with the following examples:

1. *p*-type



2. *n*-type



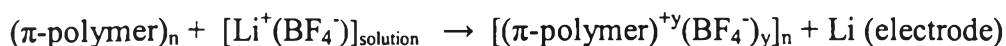
When the doping level is sufficiently high, the electronic structure evolves toward that of a metal.

1.6.2 Electrochemical doping

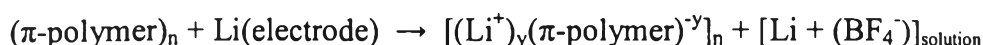
Although chemical (charge transfer) doping is an efficient and straightforward process, it is typically difficult to control. Complete doping to the highest concentrations yields reasonably high quality materials. However, attempts to obtain intermediate doping levels often result in inhomogeneous doping. Electrochemical doping was invented to solve this problem. In electrochemical doping, the electrode supplies the redox charge to the conducting polymer, while ions diffuse into (or out of) the polymer structure from the nearby electrolyte to

compensate the electronic charge. The doping level is determined by the voltage between the conducting polymer and the counter-electrode; at electrochemical equilibrium the doping level can be achieved by setting the electrochemical cell at a fixed applied voltage and simply waiting as long as necessary for the system to come to electrochemical equilibrium as indicated by the current through the cell going to Zero. Electrochemical doping is illustrated by the following examples:

1. *p*-type



2. *n*-type



In conducting polymers with a non-degenerate ground state, the charge introduced upon doping can be stored in a form of polarons and bipolarons. Polythiophene, polaron, and bipolaron can be visualized as follows (**Figure 1.19**).

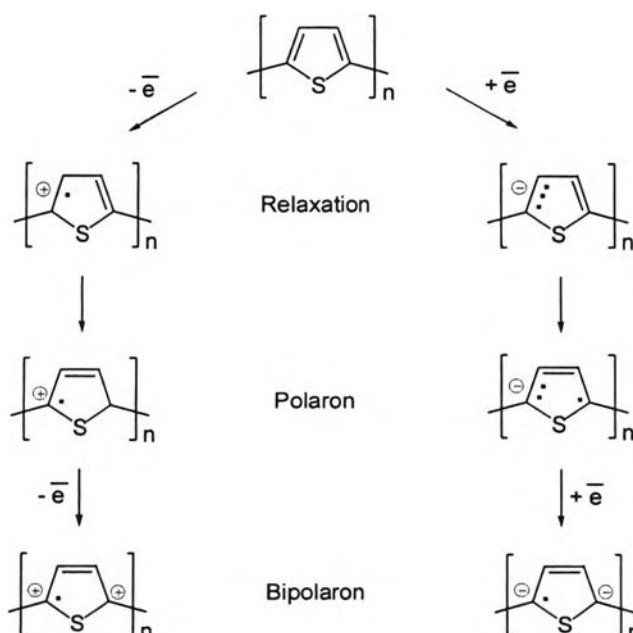


Figure 1.19 Schematic representation of polythiophene in the undoped, singly, and doubly oxidized (left), and singly and doubly reduced (right) states.

The polythiophene and derivatives were often doped by the oxidative doping because they are electron rich and favor to lose electron as indicated in **Figure 1.20**.

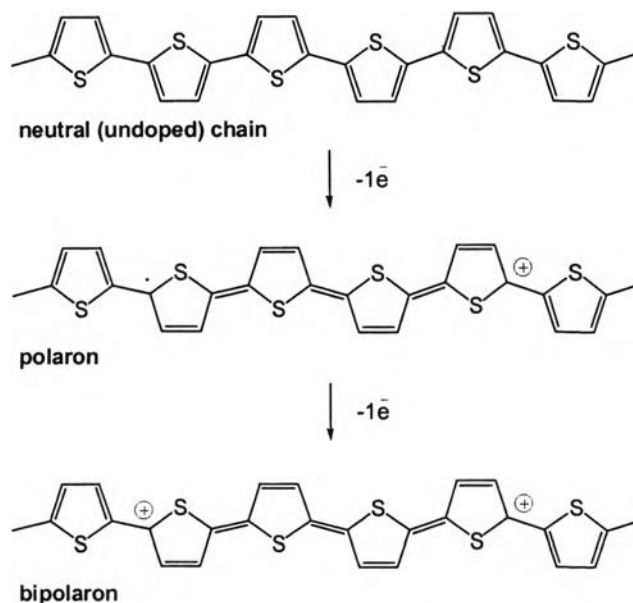


Figure 1.20 Polaron and bipolaron of Polythiophene.

In **Figure 1.21** UV-visible-NIR spectroelectrochemical curves recorded for different electrode potentials are shown for regioregular poly(3-octylthiophene) prepared using the method of McCullough and coworker [12]. Cyclic voltammograms of poly(3-octylthiophene) unambiguously indicate that oxidative doping of this polymer is a two-step phenomenon since two overlapping redox couples are clearly seen. This two-step oxidation is also manifested in UV-vis-nir spectroelectrochemical studies. The spectra recorded for increasing doping levels show gradual bleaching of the π - π^* transition with simultaneous growth of two peaks at 780 nm and 1780 nm, usually ascribed to the formation of bipolaron sub-gap states [6].

Poly(3-alkylthiophenes) are found to undergo continuous structural transformations upon doping with iodine vapor [51]. The X-ray diffraction resulted from oriented iodine-doped poly(3-*n*-octylthiophene) (P3OT) and poly(3-*n*-dodecylthiophene) (P3DT) films, highlighting the general features of this doping process and the presence of striking structural behavior unavailable to unsubstituted systems. It was found that there is extreme sensitivity of the side-group orientations to the presence of the dopant ions. This conformational change, when combined with rotation of the polymeric backbone about its chain axis, results in dramatic variations in the interlayer spacing within semicrystalline regions of the film. Initial doping is marked by a rapid increase in the interlayer repeat.

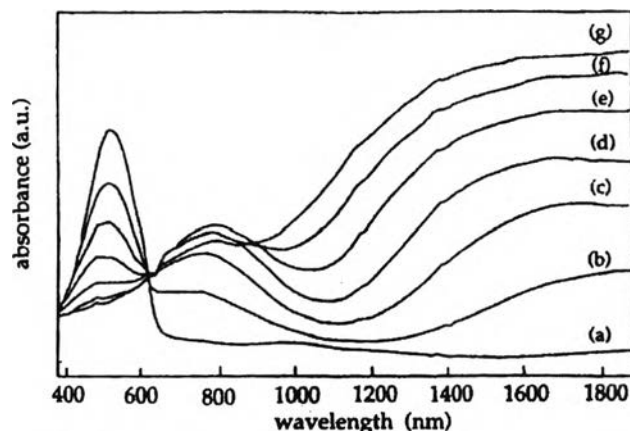


Figure 1.21 UV-vis-nir spectroelectrochemical curves recorded for regioregular poly(3-octylthiophene) in 0.1 M Bu_4NBF_4 solution in acetonitrile: (a) $E = 0$ mV; (b) $E = 500$ mV; (c) $E = 800$ mV; (d) $E = 900$ mV; (e) $E = 1000$ mV; (f) $E = 1200$ mV; (g) $E = 1400$ mV. (E measured vs Ag/AgCl reference electrode).

1.7 Effective Conjugation Length (ECL)

An ideal conducting polymer would have its π 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 two reasons are shown in **Figure 1.22**. 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 HH thienyl units in irregular poly(3-alkylthiophene) brought about the twisting of the thienyl ring planes out of coplanarity, causing an increase in the energy needed to allow the flow of electrons through the polymer chain, hence making the polymer chain less conductive.

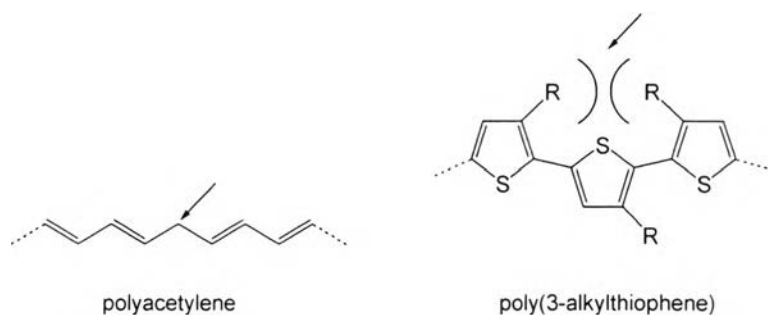


Figure 1.22 A defect in polyacetylene and steric induced structural twisting in poly(3-alkylthiophene)

Another possible reason would be the twisting of polymer chain, which occurs randomly at the single bonds and potentially divides the polymer into separated sections with their own coplanarity (**Figure 1.23**). Twisting of polymer chain would also reduce the conjugation in the polymer.

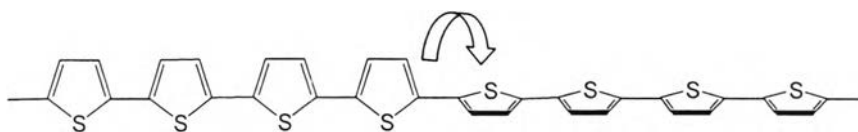


Figure 1.23 Twisting of polythiophene.

1.8 Statement of problems

The processability, electronic and optical properties of polythiophene can be controlled through derivatization of the thienyl ring. However, the scientific demand for poly(thiophene)s that possess more complex structural motifs is offset by synthetic limitations. For example, preparation of poly-(thiophene)s with functional side chains requires tedious procedures involving the synthesis of monomers. All but a few functional groups are intolerant of the harsh polymerization conditions, with the result that many potential functional polythiophenes simply cannot be prepared. An alternate approach to obtaining derivatized polymers is post-functionalization of precursor polymers. Such methodology applied to polythiophenes would considerably simplify the procedures for acquiring complex structures and greatly diversify the functional groups available. The 4-hydrogen of poly(3-hexylthiophene) (**P3HT**) is susceptible to electrophilic substitution and might be quantitatively replaced with bromo or acyl groups. The interesting point of adding bromo and acyl groups onto the thiophene units is that they could be readily converted into many other useful

functional groups. The replacements of the 4-positions of polythiophene by bromo or acyl groups via electrophilic substitutions, and further derivatizations of these groups, should provide a useful strategy to tailor the structure and the band gap of the polymers and therefore control their electrooptical properties. In addition, apart from adding various substituents on the β -positions, only little attention has been paid to the functionalizations of the sulfur atom. There were investigation the oxidation of S-atoms at thiophene units. After the oxidation in particular, thiophenes showed bathochromic shift of maximum wavelength absorption and less band gap, representing more conjugation and perhaps more conductivity. The functionalization at the S-atoms of polythiophenes using aryl or methyl groups expects the same trend of the results as the oxidation at the S-atoms of thiophenes. This research will aim at functionalization of thiophene and polythiophene derivatives using four functional groups: bromo, acyl, aryl, and methyl groups.

1.9 Objective

To synthesize polythiophene and poly(3-hexylthiophene) with bromo or acyl substituents at β -positions and aryl or methyl substituents at S-atoms of thiophene rings.

2.0 Scope of the investigation

The sequential investigation was carried out as follows.

1. Literature survey on related research
2. Preparation of PT and P3HT by oxidative coupling using FeCl_3 method
3. Study on the incorporation of bromo, acetyl, and octanoyl group onto PT or P3HT
4. Study on the oxidize of PT and P3HT by arylation, or methylation onto S-atom of thiophene units in PT and P3HT
5. Data analysis