



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 sp^3 hybridized 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.

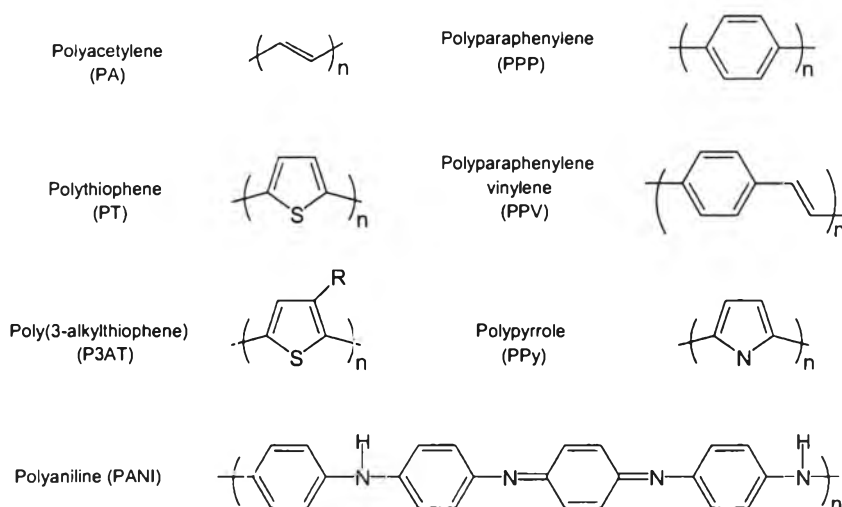


Figure 1.1 Molecular structures of some conjugated polymers: note the bond-alternated structures.

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 *et al* [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 sub levels 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.

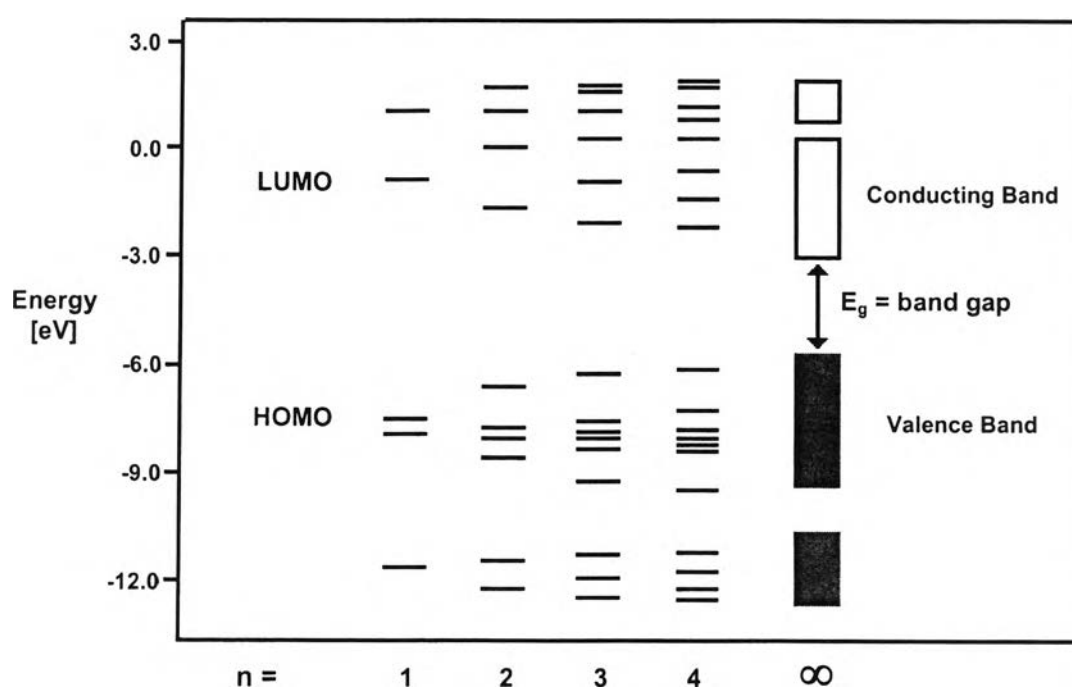


Figure 1.2 Calculated (frontier) energy levels of oligothiophenes with $n = 1-4$ and of polythiophene ($E_g =$ band gap energy)

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**).

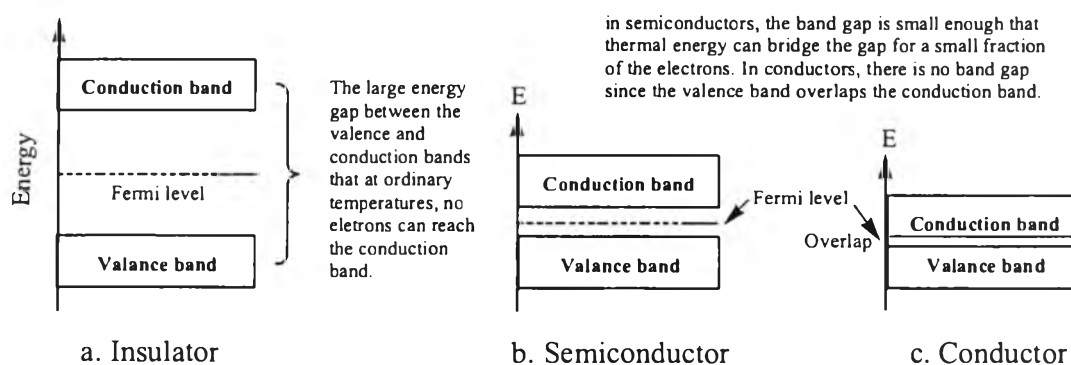


Figure 1.3 Simple band picture explaining the difference between an insulator, a semiconductor, and a metal.

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.

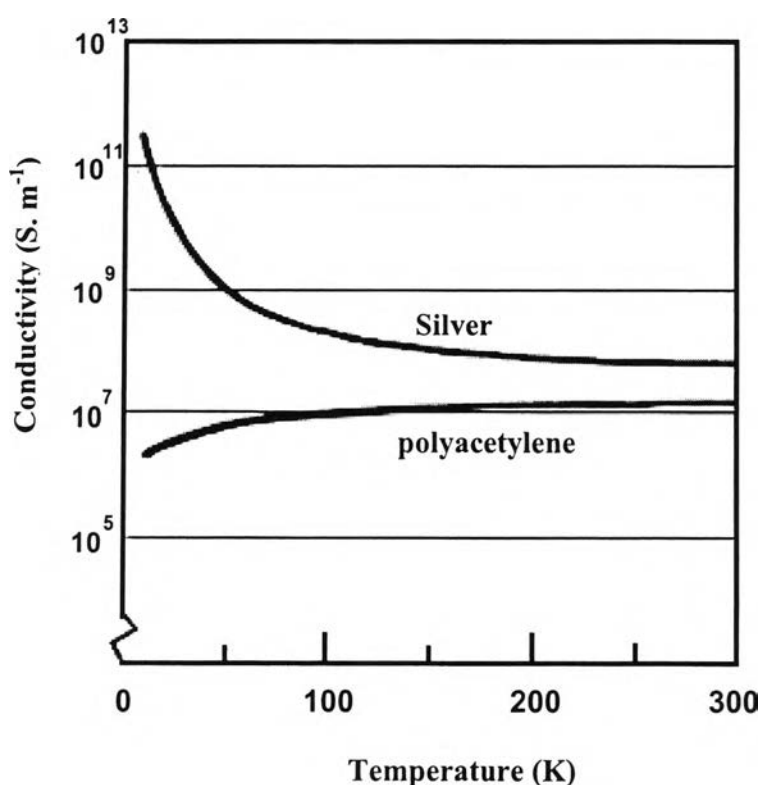


Figure 1.4 The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals.

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 Regioregular Polymers [6,10]

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:

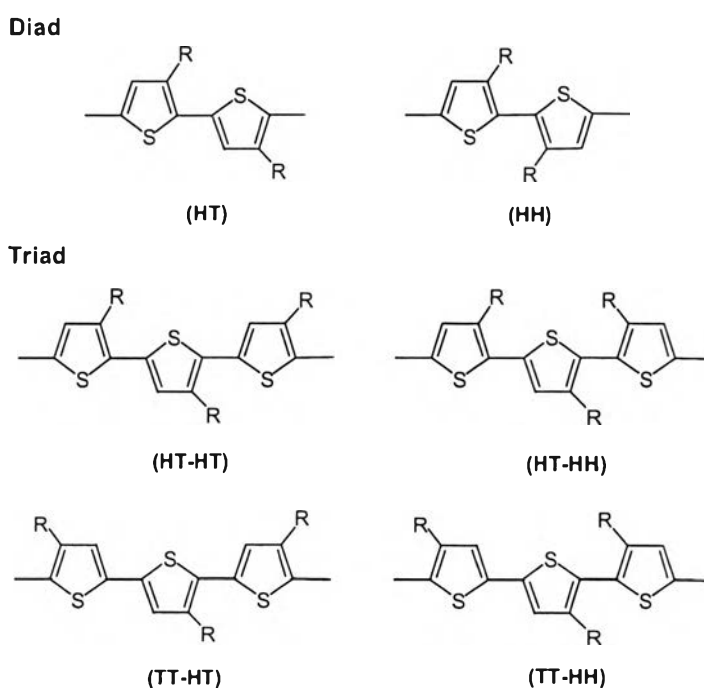


Figure 1.5 regioisomers of the poly(3-alkylthiophene)

1.2.1 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 1.6**). 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 1.7**).

1.2.2 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 1.6**).

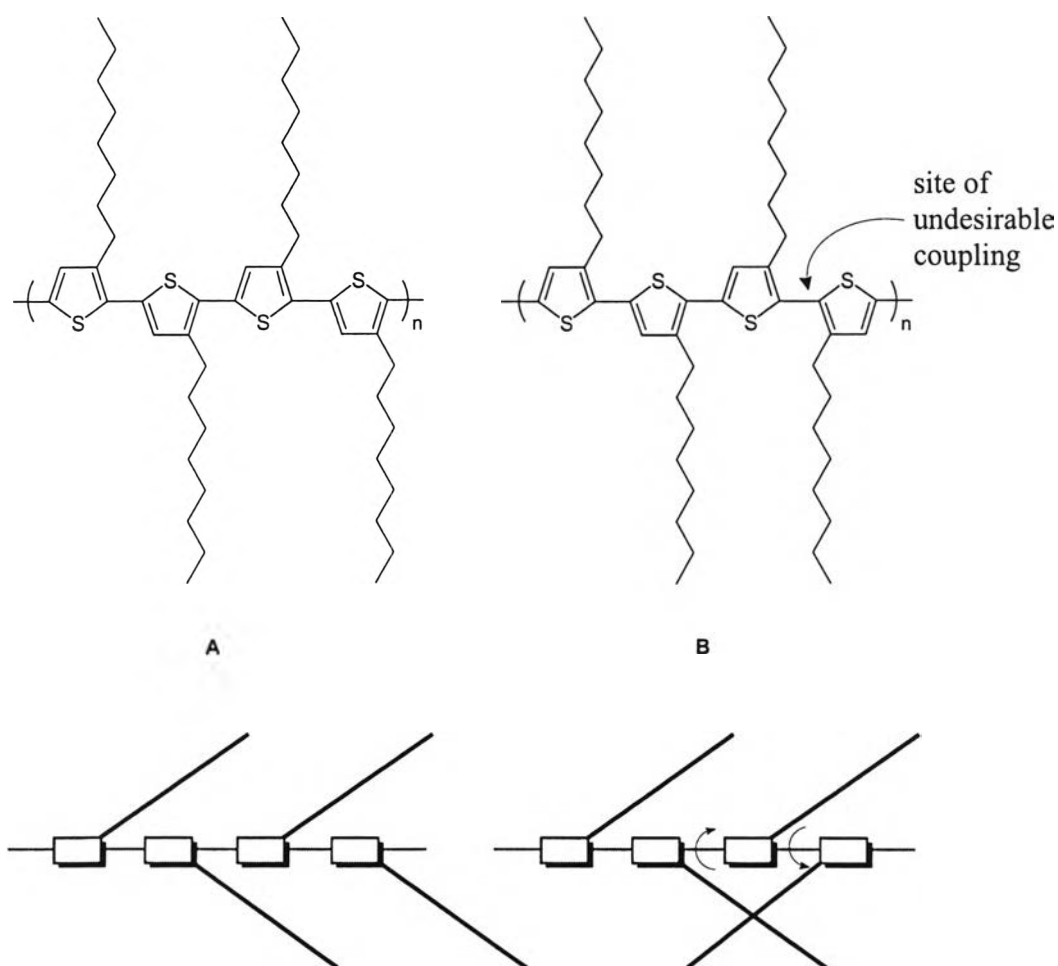


Figure 1.6 Effect of HH couplings on thiophene ring coplanarity (A regioregular P3AT, and B regiorandom P3AT).

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].

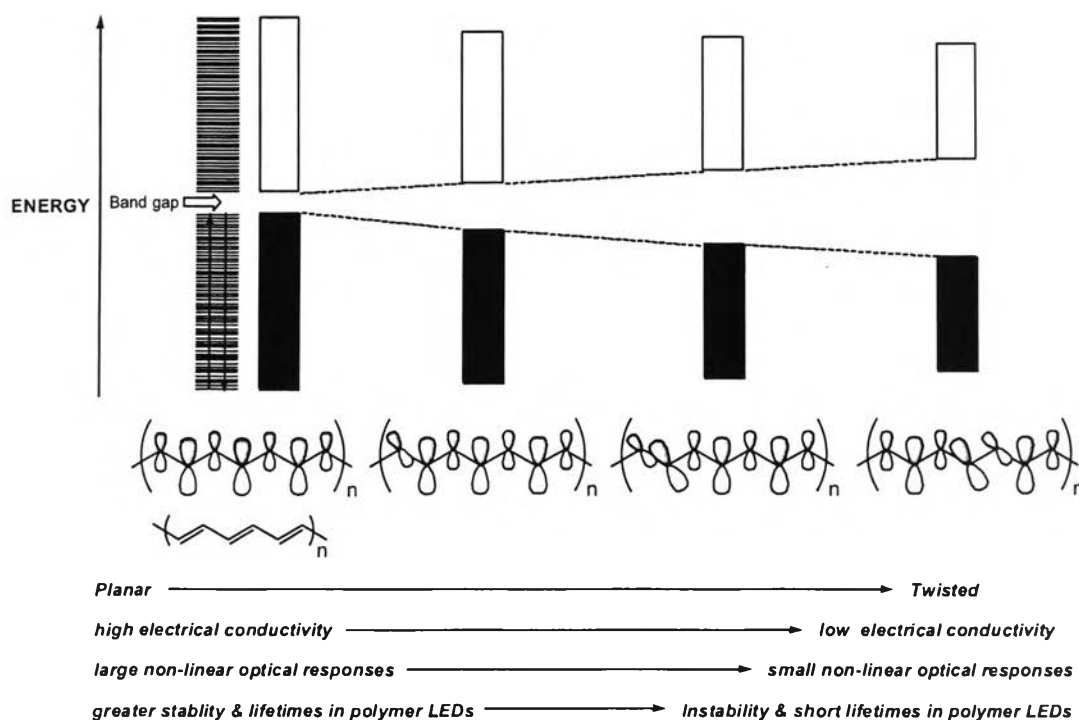


Figure 1.7 Band gaps and electrical and optical properties vary with coplanarity.

1.2.3 NMR spectroscopy

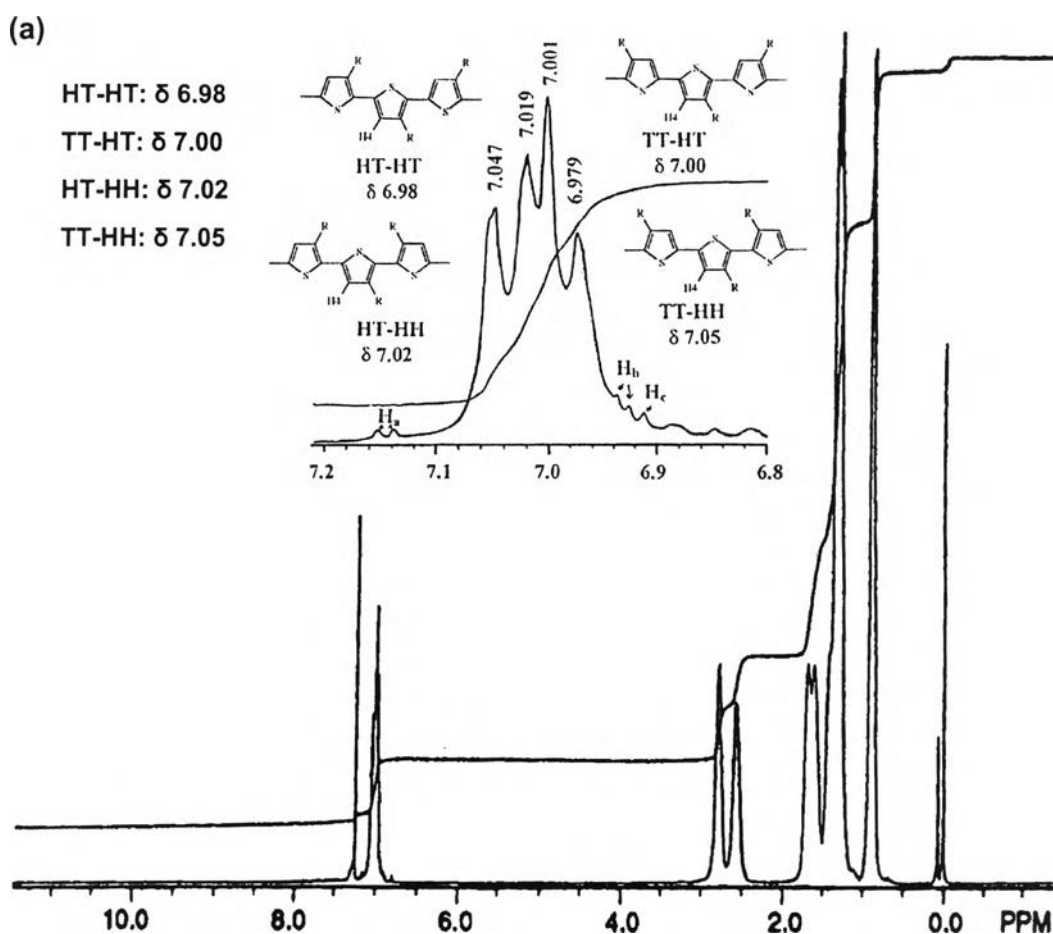
^1H and ^{13}C NMR serve as useful probes for the regioregularities of these polymers. In particular, useful information pertaining regioregularity can be deduced from the aromatic region of the respective spectra. The poly(3-hexylthiophene) shows a dominant signal at 6.98 ppm and three weaker well defined signals at 7.05, 7.03, and 7.00 ppm (**Figure 1.8**) [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.



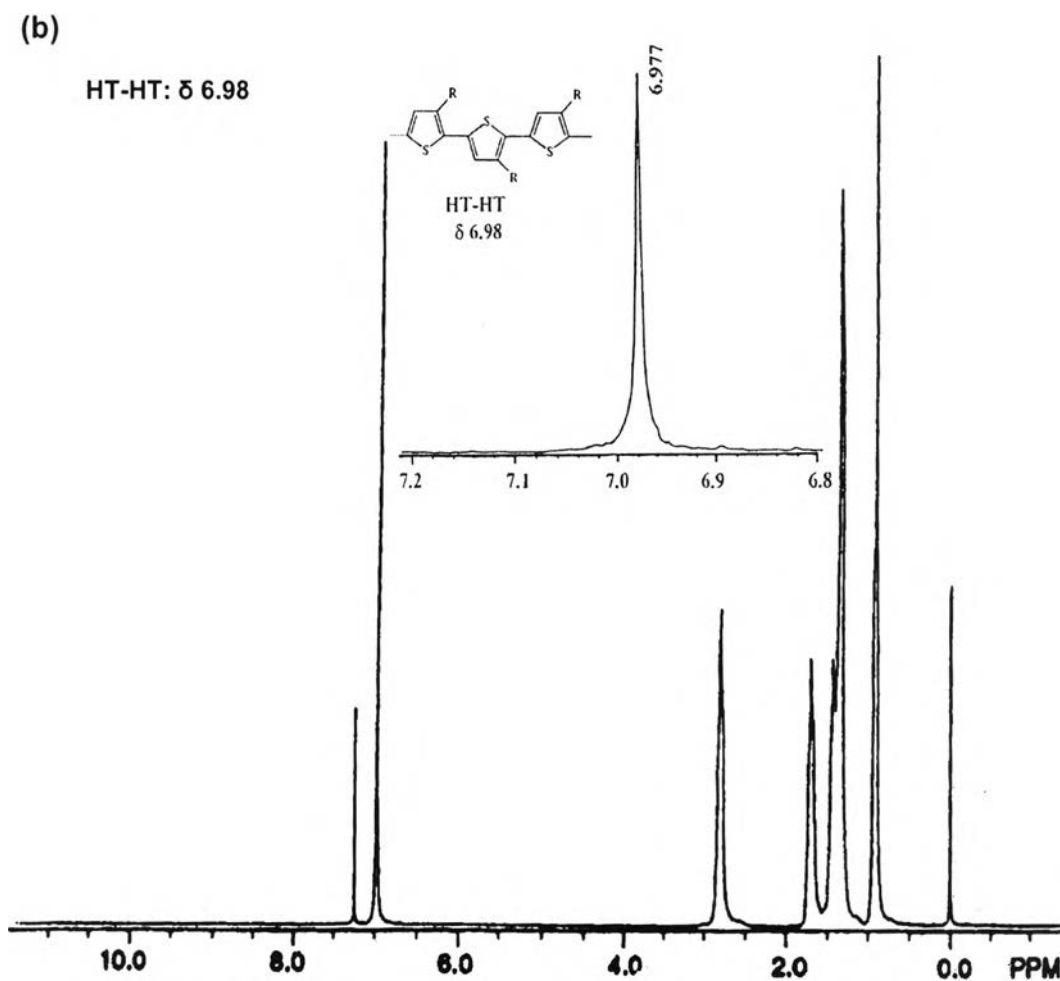


Figure 1.8 ^1H NMR spectra of (a) regiorandom (1:1:1:1, HT-HT: HT-HH : TT HT : TT-HH) P3HT and (b) regioregular (98.5%) of HT linkage P3HT [11,12].

Corroborating evidence for regioregularity is provided from solution ^{13}C NMR. For regiorandom poly(3-hexylthiophene), there are a total of 16 sets of ^{13}C resonances between $\delta = 125$ to 144 ppm (**Figure 1.9a**) [11,12] in the aromatic region corresponding to the ring carbons of the four possible triad arrangements. In contrast, poly(3-hexylthiophene) prepared by oxidative polymerization with FeCl_3 shows four intense absorptions at 128.6, 130.5, 133.7, and 139.9 ppm along with 12 other weak but well defined absorptions which correspond to the HT-HT triads with minor amounts for the other triads, whilst regioregular HT-coupled poly(3-hexylthiophene), is characterized by only four resonances (**Figure 1.9b**) [11,12].

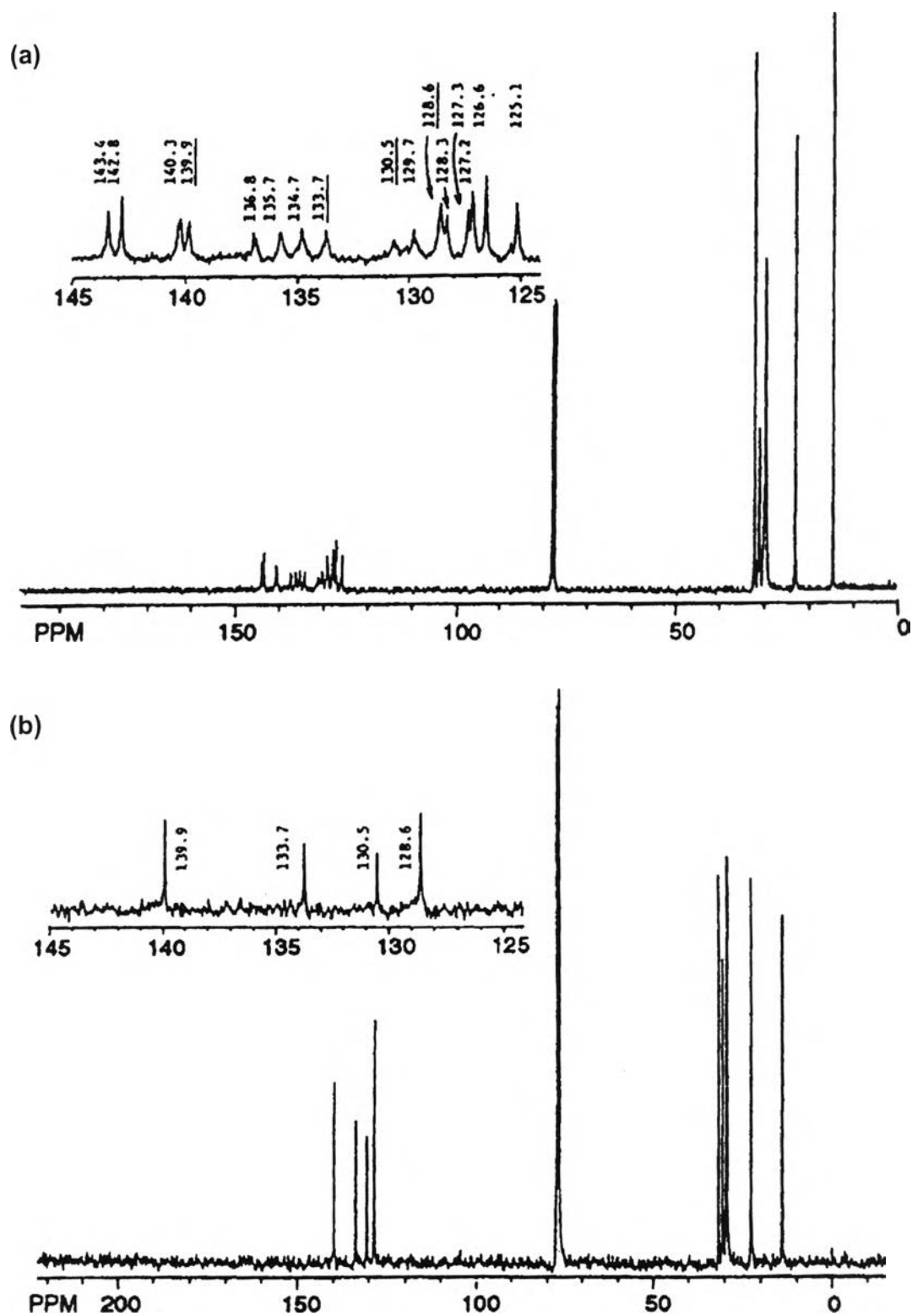


Figure 1.9 ^{13}C NMR spectra of (a) regiorandom (1:1:1:1, HT-HT: HT-HH: TT-HT: TT-HH) P3HT and (b) regioregular (98.5%) of HT linkage P3HT.

1.3 Synthesis of poly(3-alkylthiophene) [6,7]

Over the past few years, it has become clear that structure of polymer plays a critical role in determining the physical properties of conducting polymers. The most striking conclusion is that the control of the regularity and order in the polymeric structure leads to remarkable enhancements in the electronic and photonic properties of these novel materials. This discovery leads to the exciting prospect that the properties of conducting polymers can be selectively engineered through synthesis and assembly.

Research on the generation of regioregular polymers have attracted considerable attention over the past 13 years. In particular, attention has been focused on the controlling of the polymerization process to afford HT regiospecific polymers which have been shown to possess enhanced electrical conductivities, optical nonlinearities and improved magnetic properties over nonregioregular polymers. In the latter, the more sterically encumbered HH linkages can cause defects in the conjugated polymer chain, thus reducing the desired physical properties of the materials.

Polythiophene has been 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.

1.3.1 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 1.10**), 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.

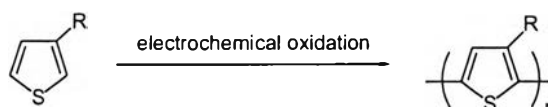


Figure 1.10 The electrochemical method for the synthesis of P3ATs (R = H, Me, Ph).

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.

1.3.2 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 1.11**). 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.

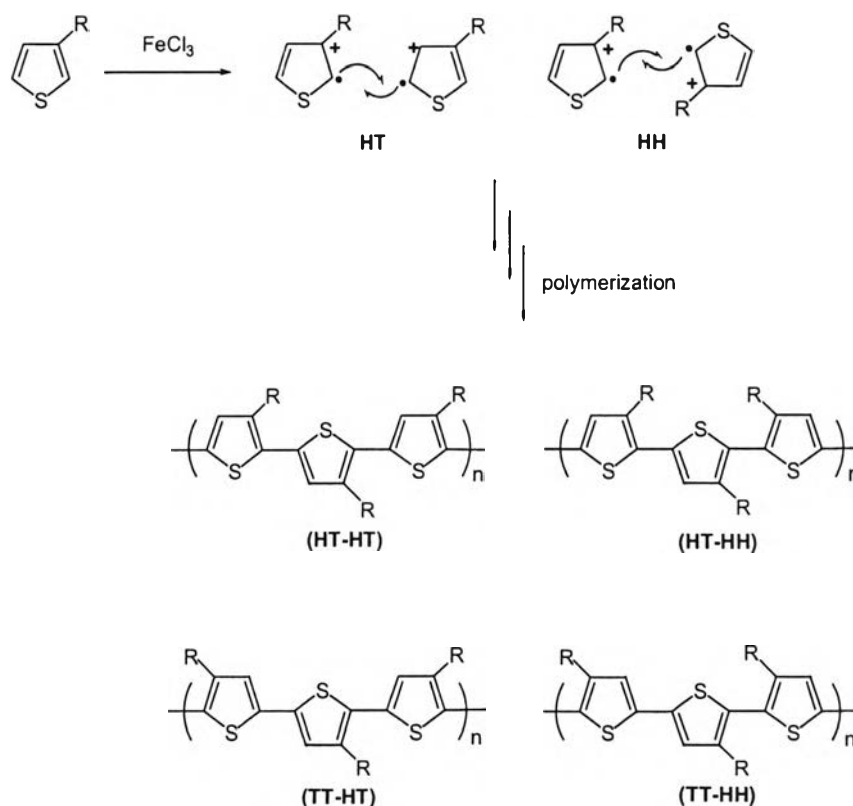


Figure 1.11 The oxidative coupling reaction of 3-alkylthiophene by FeCl_3

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.

1.3.3 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. Transmetallation 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.

Numerous organometallic species (including organomagnesium, organozinc, organoboron, organoaluminum, and organotin) have been demonstrated to be used in cross-coupling reactions with organic halides. Some of the particularly effective methods are;

- Rieke method

The synthetic approach to poly(3-alkylthiophene) was subsequently described by Rieke and coworkers [11,20-22]. This related cross-coupling approach differs primarily in the synthesis of the asymmetric organometallic intermediate (Figure 1.12).

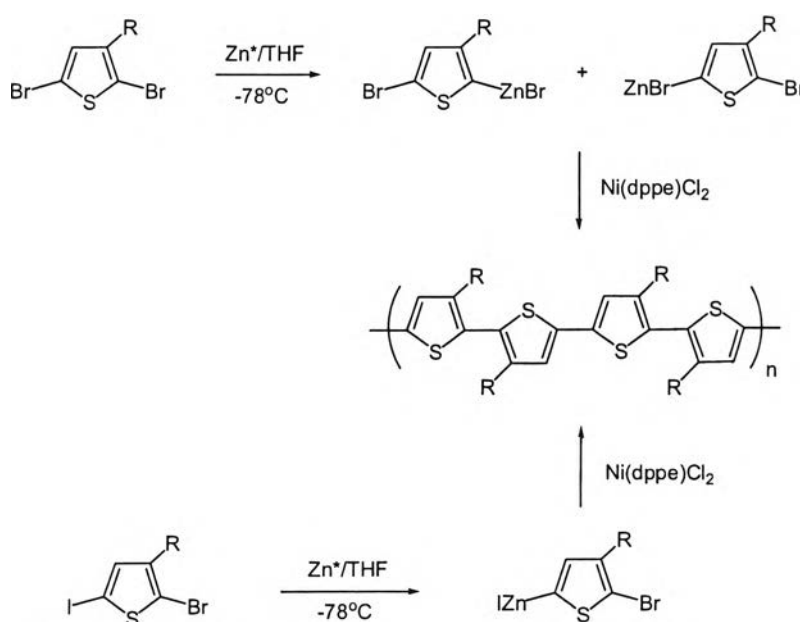


Figure 1.12 The Rieke method for the preparation of P3AT.

In the Rieke method, a 2,5-dibromo-3-alkylthiophene is added to a solution of highly reactive “Rieke zinc” (Zn^*). This metal reacts quantitatively to form a mixture of the isomers 2-bromo-3-alkyl-5-(bromozincio)thiophene (**3**) and 2-(bromozincio)-3-alkyl-5-bromothiophene (**2**). The ratio between these two isomers is dependent on the reaction temperature and, to a much lesser extent, the steric influence of the alkyl substituents. Although there is no risk of metal-halogen exchange, cryogenic conditions must still be employed because the ratio of isomers **3** and **2** production is affected by the temperature. The addition of a Ni cross-coupling catalyst, $Ni(dppe)Cl_2$, leads to the formation of a regioregular HT-P3AT, whereas addition of a Pd cross-coupling catalyst, $Pd(PPh_3)_4$, will result in the formation of a completely regiorandom P3AT. As an alternative approach, a 2-bromo-3-alkyl-5-iodothiophene (**4**) reacts with Rieke zinc to form only 2-bromo-3-alkyl-5-(iodozincio)thiophene (**3**). This species will then react in an identical fashion to form either a regioregular HT-P3AT or the regiorandom equivalent, depending on what catalyst was used for the polymerization [11]. After precipitation and soxhlet extraction, the yield for these reactions is reported to be $\approx 75\%$. Molecular weights for polymers prepared by this method are $M_n = (24-34) \times 10^3$ (with PDI = 1.4). One advantage of the Rieke method is that highly reactive Rieke zinc affords a functional group tolerant synthesis.

- McCullough method

The first synthesis of regioregular HT-P3AT was reported by McCullough and coworkers [23] in early 1992 (**Figure 1.13**). This new synthetic method [24-28] regiospecifically generates 2-bromo-5-(bromomagnesio)-3-alkylthiophene (**9**, **Figure 1.14**), which is polymerized with catalytic amounts of $Ni(dppp)Cl_2$ 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 $(20-40) \times 10^3$ (PDI ≈ 1.4). A recently prepared sample of HT-poly(dodecylthiophene) had $M_n = 130,000$ (PDI = 2.1).

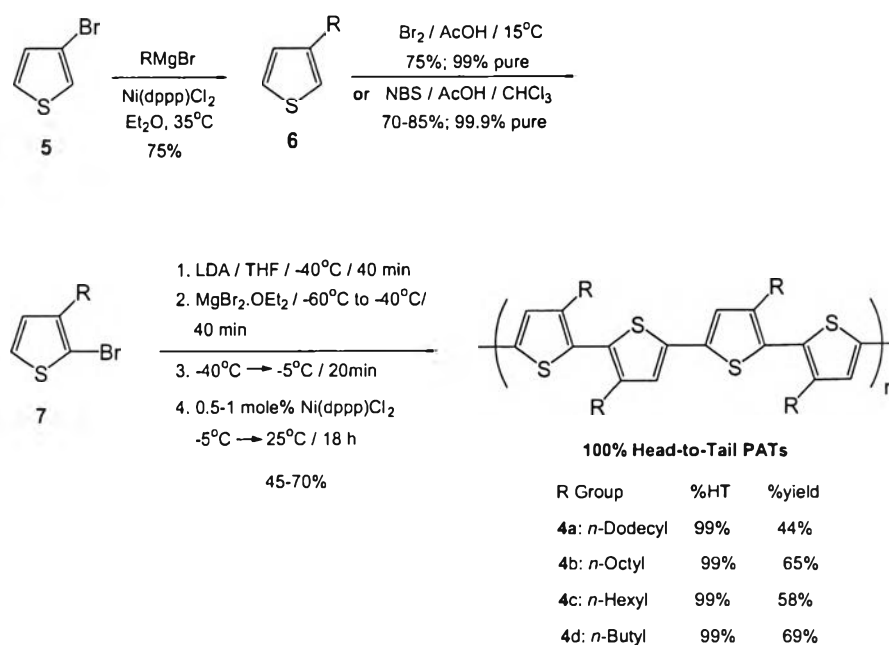


Figure 1.13 The McCullough method for the regiospecific synthesis of poly(3-alkylthiophene)s with 100% HT couplings.

Some key features of this synthesis are the selective metallation of **7** with LDA to generate **8** (Figure 1.14). The organolithium intermediate **8** is stable at -78°C and does not undergo metal-halogen exchange *via* any processes, including the halogen dance mechanism [29]. In addition, thienyllithiums are relatively poor organolithium reagents and therefore are unlikely to undergo metal-halogen exchange reaction with 2-bromo-3-alkylthiophenes.

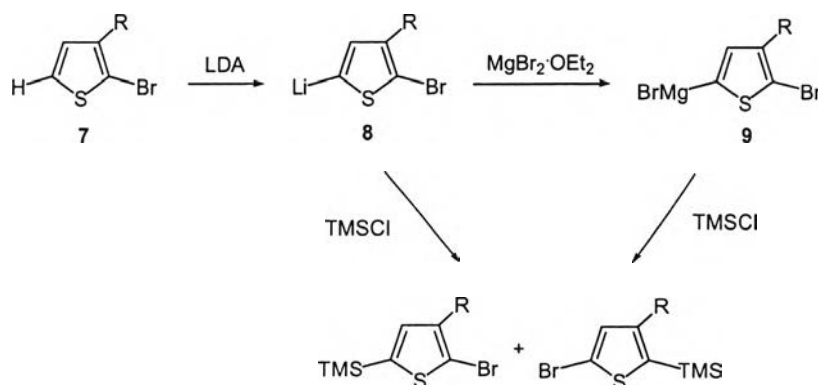


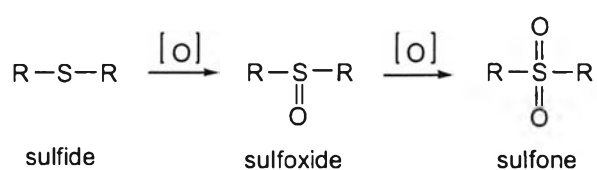
Figure 1.14 Trapping of organometallic intermediates.

The intermediate **8** reacted with $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ and resulted in the formation of **9**, which did not rearrange at higher temperatures. Quenching studies performed on the intermediates **8** and **9** indicated 98-99% of the desired monomer and less than 1-2% of the 2,5-exchange product [25] (**Figure 1.14**). The subsequent cross-coupling polymerization also occurred without any scrambling. The resulting HT-P3AT was precipitated in MeOH, washed (fractionated) with sequential MeOH and hexane Soxhlet extractions, and then recovered by Soxhlet extraction with chloroform [30]. The method is very straightforward and has been used by a number of research groups to prepare regioregular HT derivatives of polythiophene.

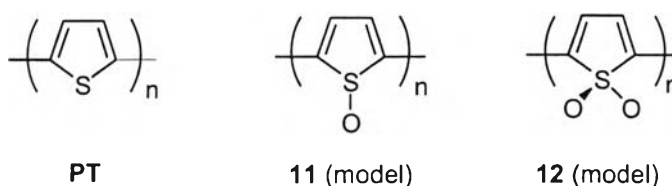
1.4 Synthesis of polythiophene with thienyl *S,S*-dioxide units

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.

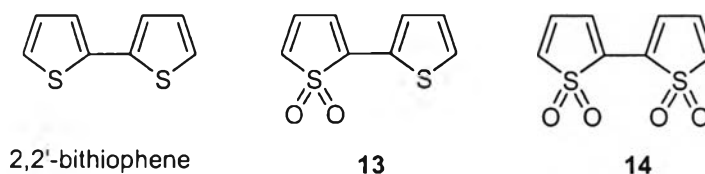
The oxidation of sulfide to sulfones has been studied extensively [31], and applied to oxidation of thiophene derivatives [32].



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 1.5**) [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)

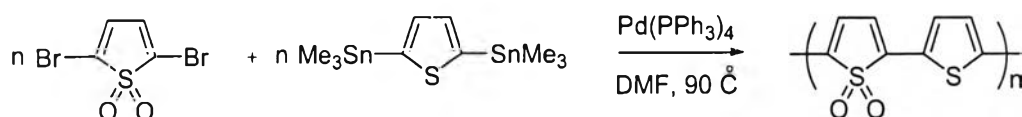


Figure 1.15 Copolymer of thiophene *S,S*-dioxide prepared by a Pd-catalyzed reaction.

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
14		NA	NA
15		NA	NA

^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.

1.5 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:

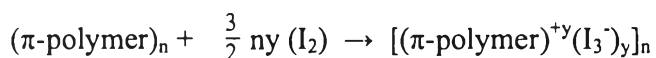
1. Doping introduces carriers into the electronic structure. Since every repeating unit is a potential redox site, conjugated polymers can be doped *n*-type (reduced) or *p*-type (oxidized) to a relatively high density of charge carriers.
2. The attraction of an electron in one unit to the nuclei in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

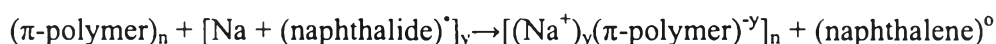
1.5.1 Chemical doping by charge transfer

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

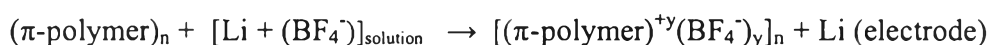


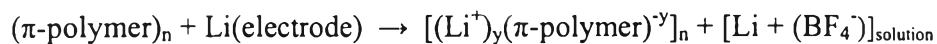
When the doping level is sufficiently high, the electronic structure evolves toward that of a metal.

1.5.2 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 1.16**).

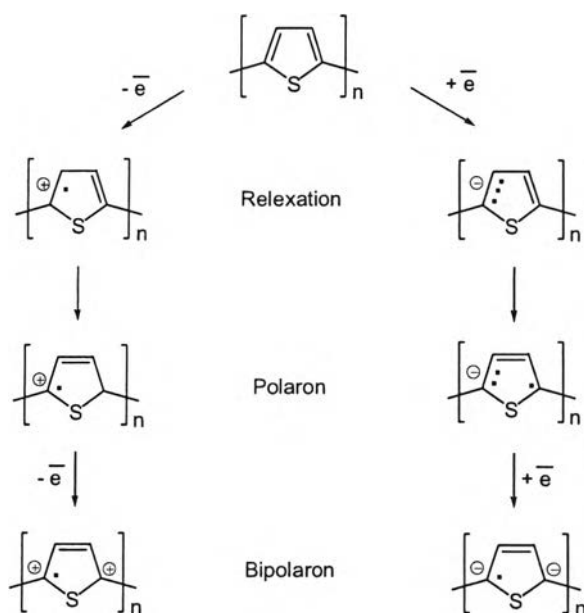


Figure 1.16 Schematic representation of polythiophene in the undoped, singly, and doubly oxidized (left), and singly and doubly reduced (right) states.

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 1.17**.

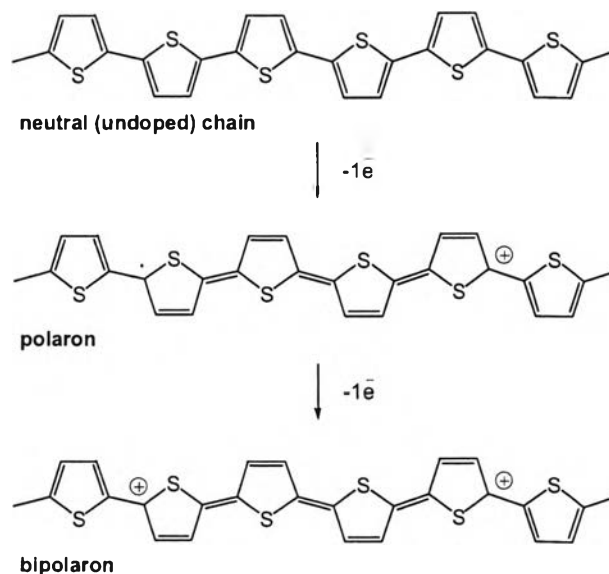


Figure 1.17 Polaron and bipolaron of Polythiophene.

In **Figure 1.18** 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 [41]. 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.

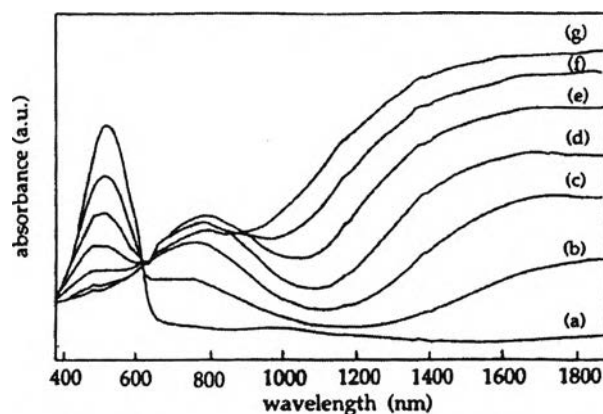


Figure 1.18 UV-vis-nir spectroelectrochemical curves recorded for regioregular poly(3-octylthiophene) in 0.1 M Bu_4NBF_4 solution in acetonitrile: (a) $E = 0$ mV; (b) $E = 500$ mV; (c) $E = 800$ mV; (d) $E = 900$ mV; (e) $E = 1000$ mV; (f) $E = 1200$ mV; (g) $E = 1400$ mV. (E measured vs Ag/AgCl reference electrode).

Further doping yields a dramatic reduction in this spacing. For iodine-doped samples, this substitution allows for dramatic and apparently continuous structural evolution in which there is a crossover from a packing configuration that strongly suppresses alkyl interdigitation into one in which interdigitation is quite pronounced. Among the various *p*-type dopants, iodine is often selected for its chemical simplicity and its straightforward doping procedures (**Figure 1.19**).

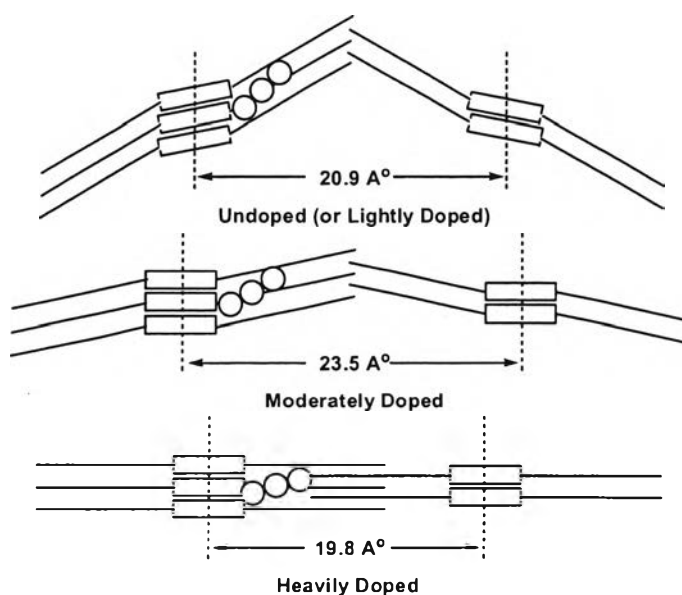


Figure 1.19 Projected equatorial structure of P3OT at various doping levels.

The stability of AuCl₃-doped poly(3-hexylthiophene) thin films was studied at elevated temperatures by means of optical spectroscopy [42]. At room temperature the stability is substantially enhanced relative to that of the FeCl₃-doped system. At elevated temperatures even AuCl₃ is a thermally unstable dopant, although still more stable than FeCl₃. The thermal stability of different doping agent in P3ATs is probably connected to the size of the dopants. Where the stability decreases with the size of the dopant. The sizes of the two dopants compared do not differ much in this case. Thus, the relative thermal stabilities should depend on other factors.

It appears that nitrosyl compounds [43] have considerable potential as chemical dopants for P3AT because of their previous utilization in lithography, nitrosonium tetrafluoroborate, NOBF₄. However, the counterions, such as BF₄⁻ and PF₆⁻, for example, cannot be used with great reliability in microelectronics technology, because boron and phosphorus can act as undesirable dopants of silicon and thus contaminate the silicon substrate. There have been studies on research into other nitrosyl derivatives with the general formula XNO, where X is an organic counterion. The use of a fluorinated anion with a high degree of dissociation, such as bis(trifluoromethanesulfonyl)imide (TFSI), appears to be effective. High conductivities are obtained, even for low doping levels (nearly five times lower than the levels required when using conventional dopants). Moreover, the TFSI anion generates a stable doping process spanning a wide range of conductivities. The order of doping stability for P3OT thin films at ambient atmosphere according to the nature of the doping agent was thus



The majority of potential applications of conducting polymers requires the formation of thin films. The neutral, soluble polymer is first cast as a thin film and then subsequently doped with a solution of the oxidizing agent to impart conductivity. This method can lead to considerable strain in the film, resulting in poor film morphology and cracking since the charge-balancing counterions are required to imbibe into a dense partially crystalline film. Holdcroft and coworkers [44] developed the new chemistry in which conducting polymers can be made soluble, and the film of conducting polymers are spin-cast and formed in a single step. This is, the doping agent can be switched between non-oxidizing and oxidizing by the presence or

absence of a coordinating ligand. Removal of the coordinating ligand during thin-film processing enables the oxidizing agent to dope the polymer. Silver (I) salt is employed to dope poly(3-alkylthiophenes) (P3ATs) and other conjugated polymers. Solutions containing silver (I) salts and P3ATs, which usually undergo spontaneous reaction, doping, and precipitation, were stabilized using coordinating ligands that modify the reduction potential of the Ag(I) species. Upon removal of the coordinating ligand, spontaneous oxidative doping of the polymer occurred. Uniform electronically conducting films were thus obtained by simultaneous evaporation of both solvent and Ag(I)-coordinating ligands, a process termed “solvato-controlled doping”.

There are only few investigations on the influence of dopants on the geometric structure and in particular on the exact position of the counter-ions in the doped materials. Most of these investigations are of a theoretical nature with all known uncertainties.

1.6 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 1.20**. 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.

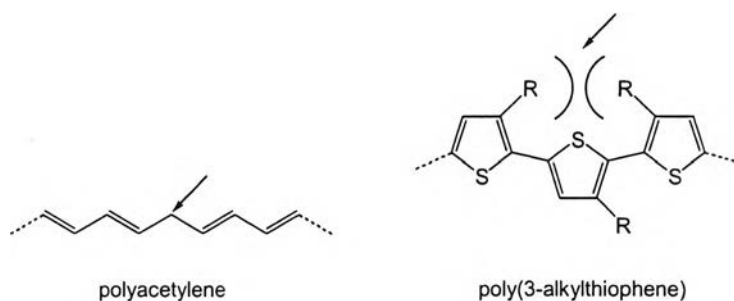


Figure 1.20 A defect in polyacetylene and steric induced structural twisting in poly(3-alkylthiophene)

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 1.21**). Twisting of polymer chain would also cause the reduction of conjugation in the polymer.

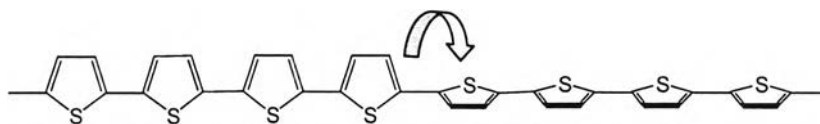


Figure 1.21 Twisting of polythiophene

The effect of the polymer chain length on optical and conductive properties of regioregular poly(alkylthiophenes) which was prepared using a modification of the method of McCullough and coworker [44] has been studied. These compounds has been fractionated into five fractions differing significantly in their molecular weights (**Figure 1.22** and **Table 1.3**) [45,46].

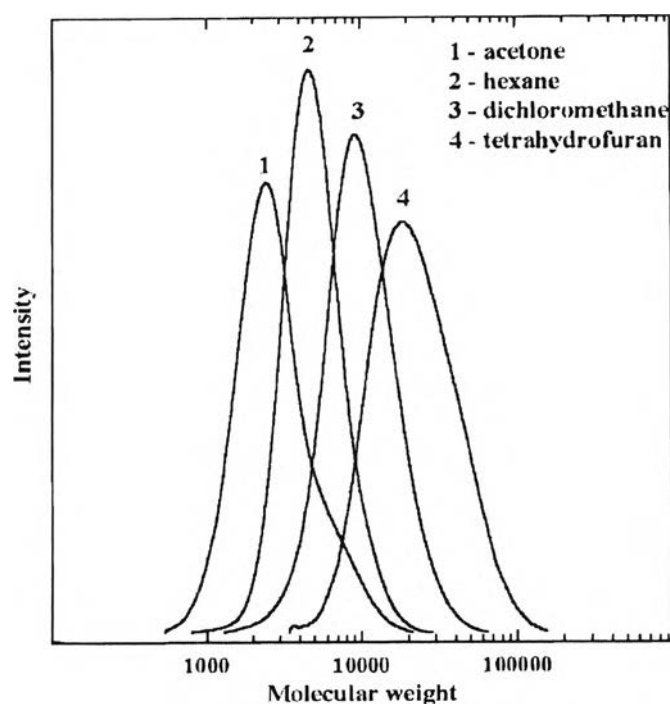


Figure 1.22 Elution Curves of regioregular poly(3-hexylthiophene) fractions obtained by selective extraction.

Table 1.3 Macromolecular parameters of regioregular-P3HT fractions obtained by selective extraction

fraction	wt %	M_n	M_w	P_i	D_n
P3HT/acetone	6.5	2,280	3,150	1.38	14
P3HT/hexane	9.7	4,380	5,340	1.22	26
P3HT/CH ₂ Cl ₂	33.1	8,370	11,100	1.35	50
P3HT/CHCl ₃	1.6	10,800	21,300	1.97	65
P3HT/THF	49.2	17,700	25,700	1.45	106

The separated fractions of neutral P3HT were then subjected to UV-vis spectroscopy measurement (**Figure 1.23** and **Figure 1.24**) [46]. Both the solution spectra and the solid-state ones observed bathochromic shifts of λ_{\max} which increase with the increase of the average molecular weight of the fraction. This effect is, however, much more pronounced in the case of the solid films. In other words, the

solvatochromic effect usually observed for poly(3-alkylthiophene) is amplified from 25 nm for the acetone fraction to 113 nm for the THF one.

The behavior of the acetone fraction closely resembles that of poly(alkylthiophene) with a low value of the average conjugation length. In such cases either no solvatochromic shift is observed or its value is very low. The hexane fraction gives in turn, UV-vis spectra similar to those recorded for nonregioregular poly(3-alkylthiophene) obtained by oxidative polymerization whose polymerization degree (D_n) is roughly 8 times higher. This means that, despite large differences in the molecular weight, the *effective conjugation length* (ECL) is comparable in both cases.

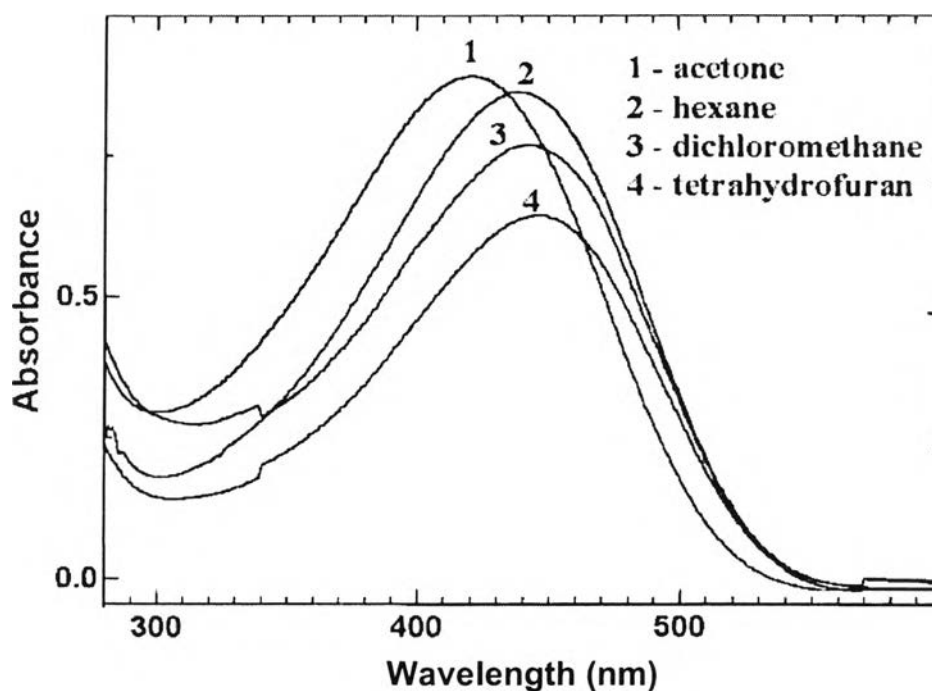


Figure 1.23 THF solution UV-vis spectra recorded for the fractions of regioregular poly(3-hexylthiophene) differing in their average molecular weight, which is an indication of higher conjugation length.



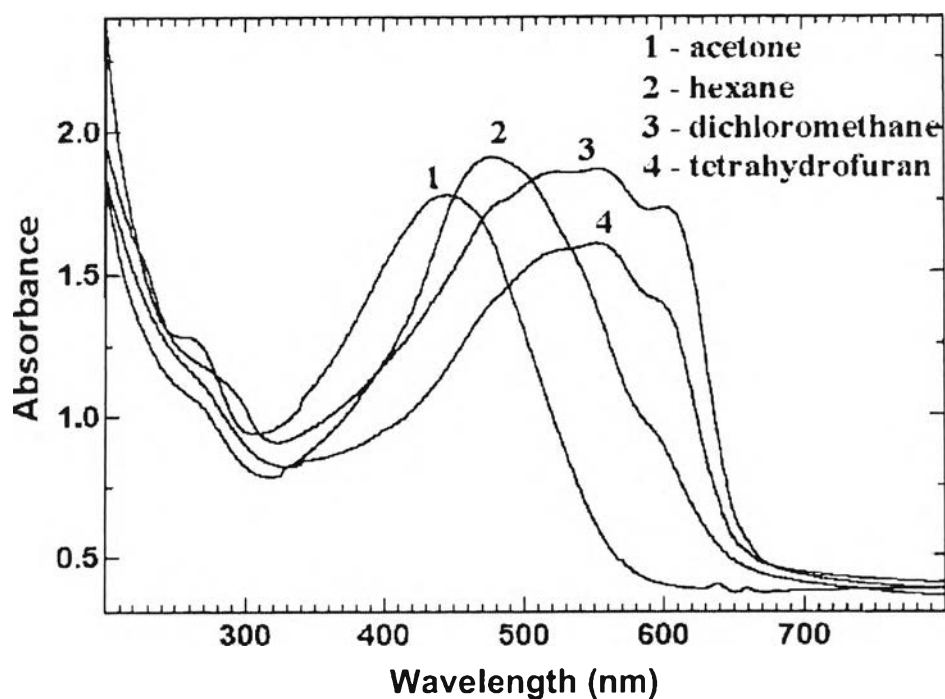


Figure 1.24 THF solution UV-vis spectra recorded for the fractions of regioregular poly(3-hexylthiophene). Note that the bathochromic shift observed for higher molecular weight fractions is much more pronounced than in the case of solution spectra.

1.7 Objectives

1. To study the effects of doping agents on the optical and conductive properties of poly(3-hexylthiophene) in the form of both solution and film.

1.8 Scope of the investigation

The sequential investigation was carried out as follows.

1. Literature survey on related research .
2. Preparation of P3HT by oxidative coupling using FeCl_3 method.
3. Study on acidic doping of Poly(3-hexylthiophene) (P3HT) with organic acids including: trifluoroacetic acid (TFA), chloroacetic acid (CA), dichloroacetic acid (DCA), trichloroacetic acid (TCA), acetic acid, methanesulfonic acid (MSA) and toluene-4-sulfonic acid (TsOH).

Optimize the amount of doping reagent and doping time by monitoring the absorbance of P3HT with UV-visible spectroscopy.

4. Study on the oxidative doping of P3HT with oxidizing agent including: $\text{H}_2\text{O}_2/\text{TFA}$ and UHP/TFA. Optimize the doping conditions similarly to the acidic doping study.
5. Determination of the AC-index values from the data of UV-visible spectroscopy and evaluate them against other parameters.
6. Preparation of P3HT film and doped by appropriate additives and measure the conductivity with 4-point probe technique.
7. Data analysis.