CHAPTER I

INTRODUCTION

Conjugated polymers have been the focus of intense research for more than twenty years. Potential applications for conjugated polymers are widely varied and include smart windows, chemical sensors, batteries, electromagnetic shielding materials, artificial noses, polymer modified electrodes, electronic interconnects, and polymer based transistors. The potential of super-conductivity in these "ultimate poly(ene)s", and their optical properties, were some of the driving forces behind early investigations into the properties of these molecules. Samples of pristine conjugated polymers, however, exhibited electrical conductivities of similar magnitude as the more conventional electrically insulating polymers like polyethylene, nylon, and poly(vinylchloride). In 1977, a shift in focus occurred when Chiang and coworkers [1] discovered that oxidation of polyacetylene with lewis acids resulted in an increase in electrical conductivity by twelve orders of magnitude. This discovery led to a renewed effort in the synthesis and characterization of many more conjugated polymers possessing both aromatic and heteroaromatic repeat units. Some of the more well-known conjugated polymers which have been rendered electrically conductive by oxidation techniques include polyacetylene, polythiophene, poly(paraphenylene), polyaniline, polypyrrole and poly(phenylenevinylene). Their chemical structures are shown in **Figure 1.1**.
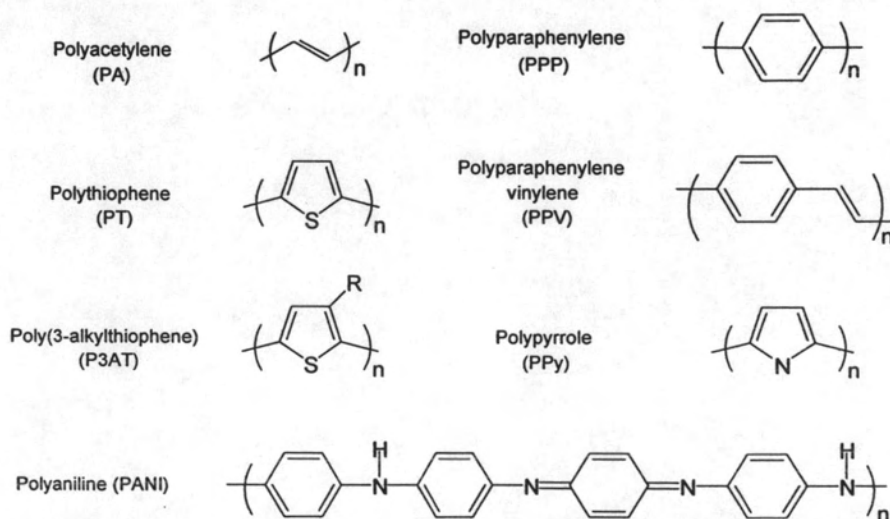

Figure 1.1 Molecular structures of some conjugated polymers

1.1 Conjugated polymers: organic semiconductors

Conjugated polymers [2,3] 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.
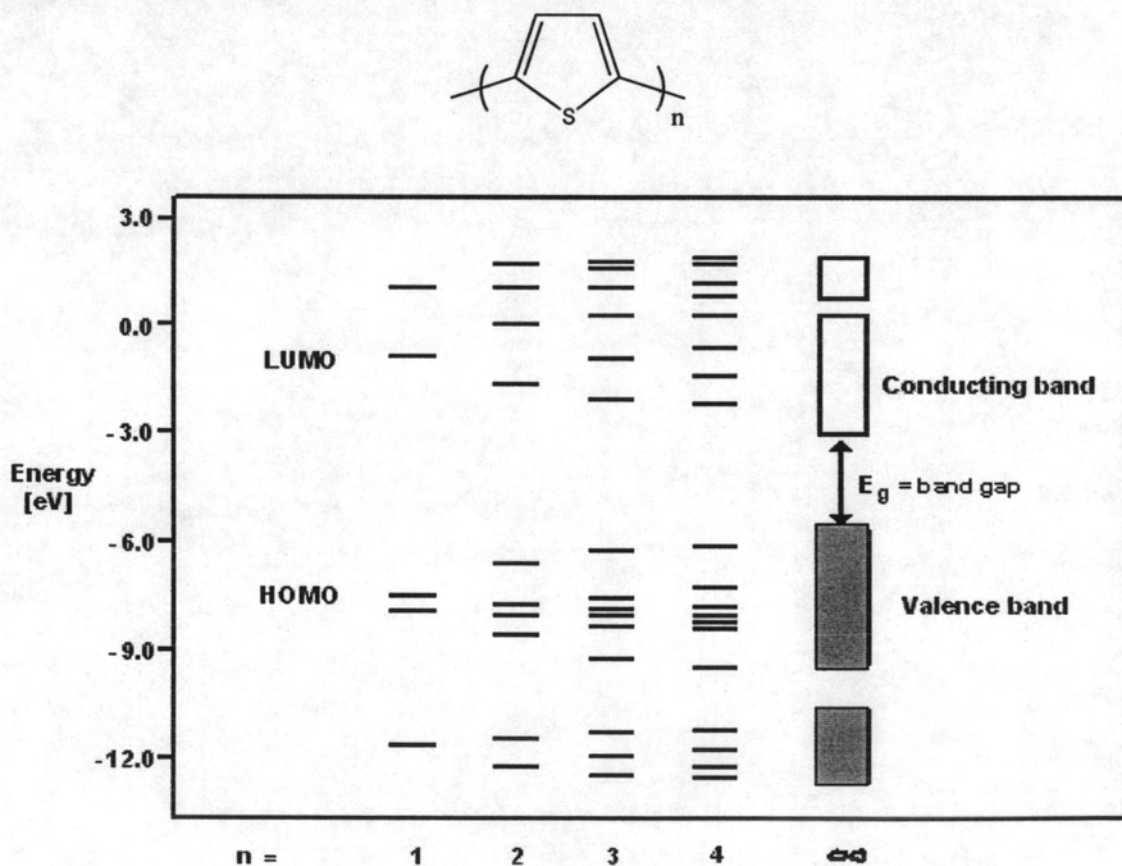

Figure 1.2 Calculated (frontier) energy levels of oligothiophenes with n = 1–4 and of polythiophene (E_g = band gap energy)

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**).
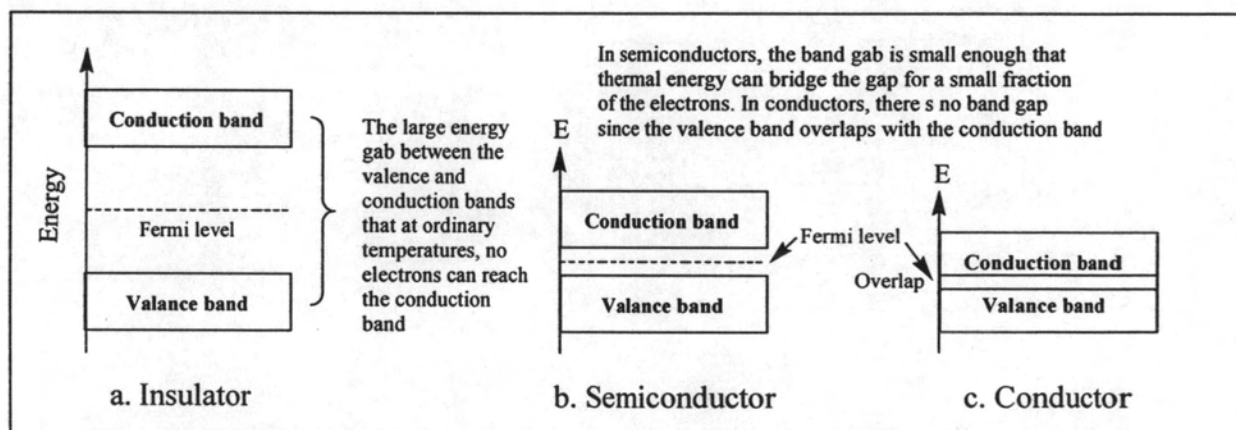

Figure 1.3 Simple band picture explaining the difference between an insulator, a semiconductor, and a metal.

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.
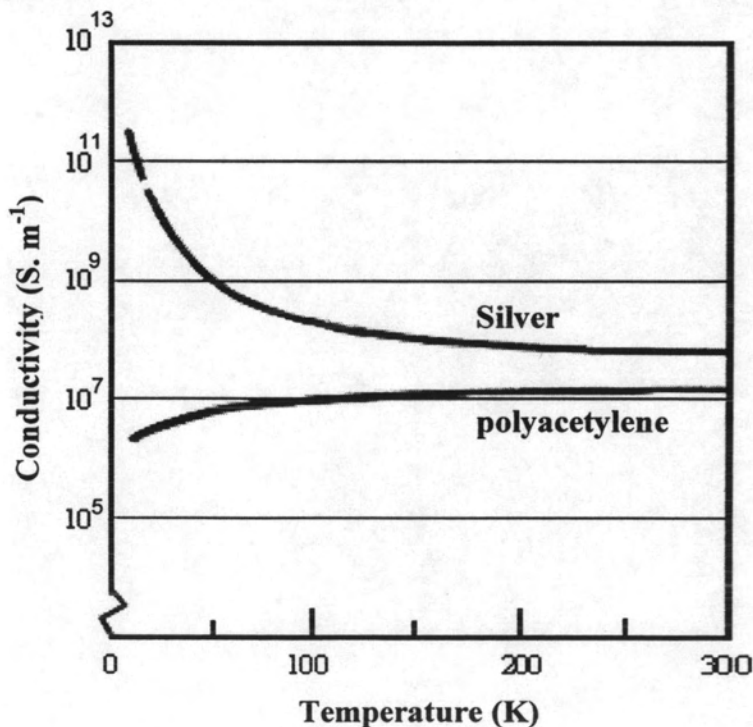

Figure 1.4 The conductivity of conducting polymers decreases with falling temperature in contrast to that of metals.

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 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 Poly(3-alkylthiophene)

Polythiophene is an intractable solid irrespective of the synthetic route, limiting analysis to solid state techniques. From a technological viewpoint, lack of processibility is one reason why these materials are presently of little commercial value.

Since the first synthesis in 1986, poly(3-alkylthiophene) (PATs) have attracted increasing interest [4], owing to the significant improvement of solubility and fusibility resulting from the grafting of flexible hydrocarbon chains on the conjugated polythiophene backbone. Thus poly(3-alkylthiophene) with alkyl groups equal or greater than butyl have been reported to be readily soluble at room temperature in tetrahydrofuran, dichloromethane, chloroform, benzene, toluene, xylene, nitrobenzene and tetrahydronaphthalene. These soluble polymers can subsequently be processed into film from their solutions.

1.3 Regioregular Polymers

Poly(3-alkylthiophene) represent a class of polymers where regioregular of poly(3-alkylthiophene) has dramatically improved the properties of polythiophenes and has ushered in these polymers as materials in new devices.

Since 3-alkylthiophene monomer are asymmetric, polymerization may occur in a nonregiospecific fashion forming three types of diads structures (head-to-head (HH), head-to-tail (HT) and tail-to-tail (TT)) and four types of spectroscopically distinct triad structures (**Figure 1.5**). It has been shown that head-to-head couplings are unfavorable because of the steric repulsion between both alkyl chains with the lone pairs of adjacent sulfur atoms.

Polythiophenes that contain significant amounts of the head-to-head couplings (which implies significant amounts of tail-to-tail couplings must also be present) are referred to as regioirregular, while polymers that contain only head-to-tail couplings are referred to as regioregular.

Regioregular polymers cannot readily adopt planar conformations, and irregular placement of the solubilizing alkyl substituents prevents efficient solid-state packing and limits the materials physical properties. Conversely, regioregular head-to-tail coupled poly(3-alkylthiophene) (HT-P3ATs) can undergo self-assembly, both in solution and in the solid state, resulting in highly ordered two- and three-dimensional polymer architectures. These materials have superior electronic and photonic properties when compared to regioirregular analogues.
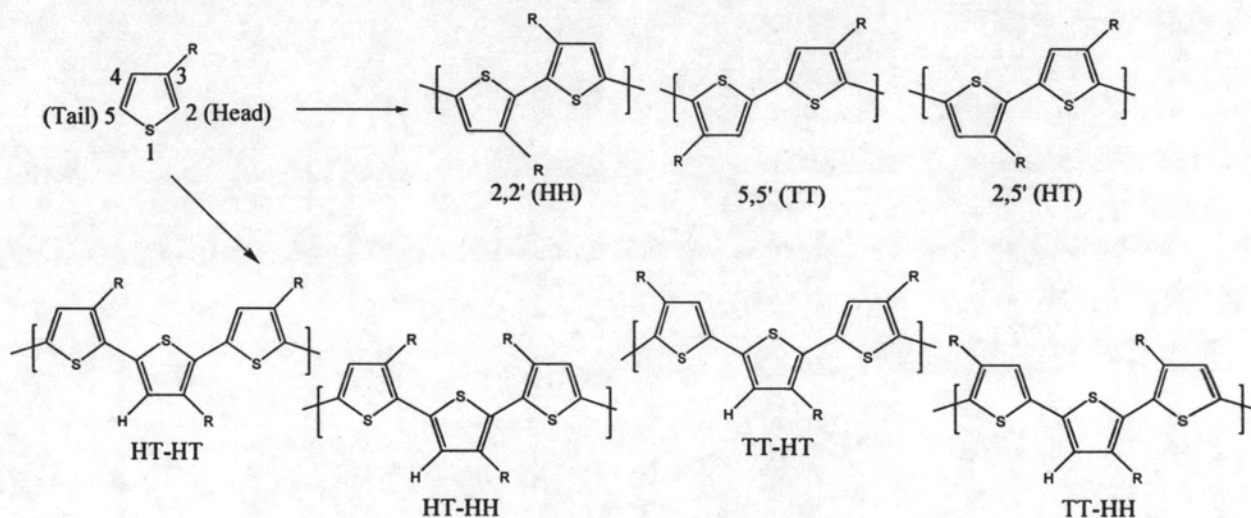

Figure 1.5 Regioisomers of poly(3-alkylthiophene)

1.3.1 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 increased band gap but any deviations from coplanarity also result in an increase in interchain distances arising from poorer π-stracking of polymer chains, thereby reducing the probability of interchain charge carrier hopping with a consequent reduction in electrical conductivity.
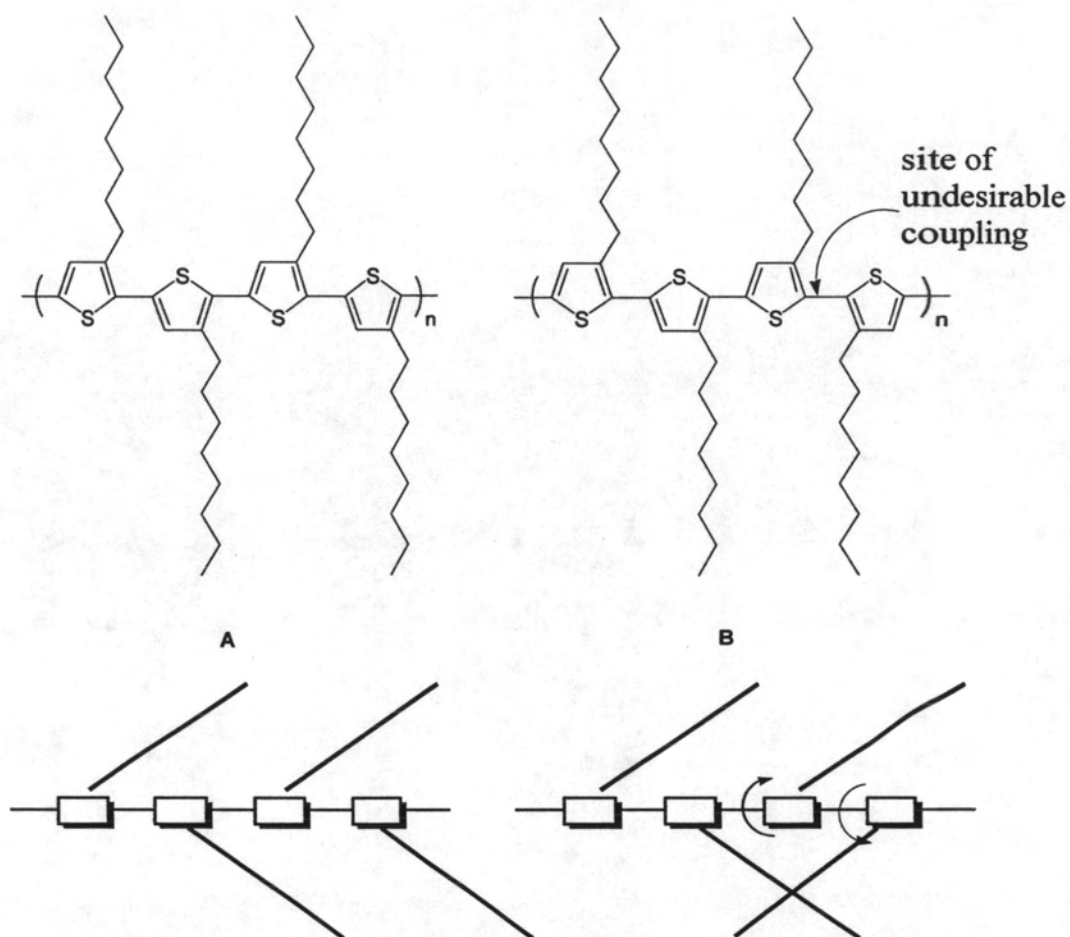

site of undesirable coupling

A

B

Figure 1.6 Effect of HH couplings on thiophene ring coplanarity (**A**= regioregular

P3AT, **B**= regiorandom)

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 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 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} S.cm^{-1}) reported to date [5]. 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**).
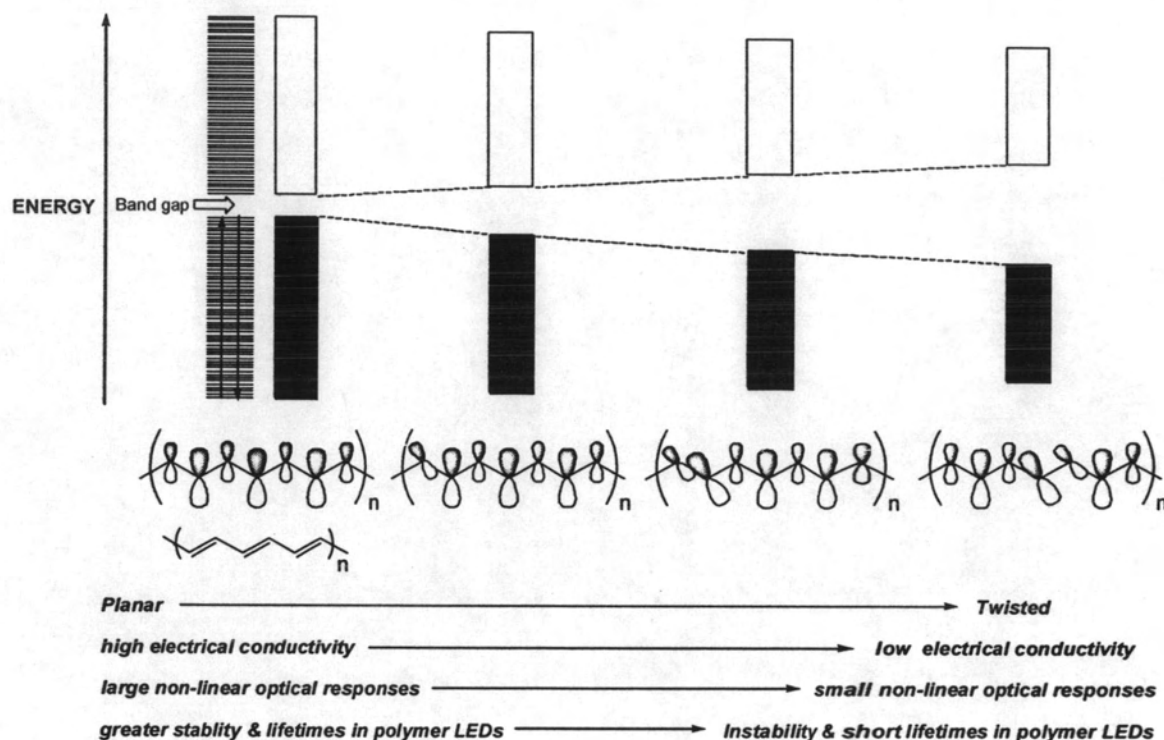

Figure 1.7 Band gaps and electrical and optical properties vary with coplanarity.

1.3.2 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**).

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 [5]. 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) [5].

1.3.3 NMR spectroscopy

^{1}H 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**) [5,6]. 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.
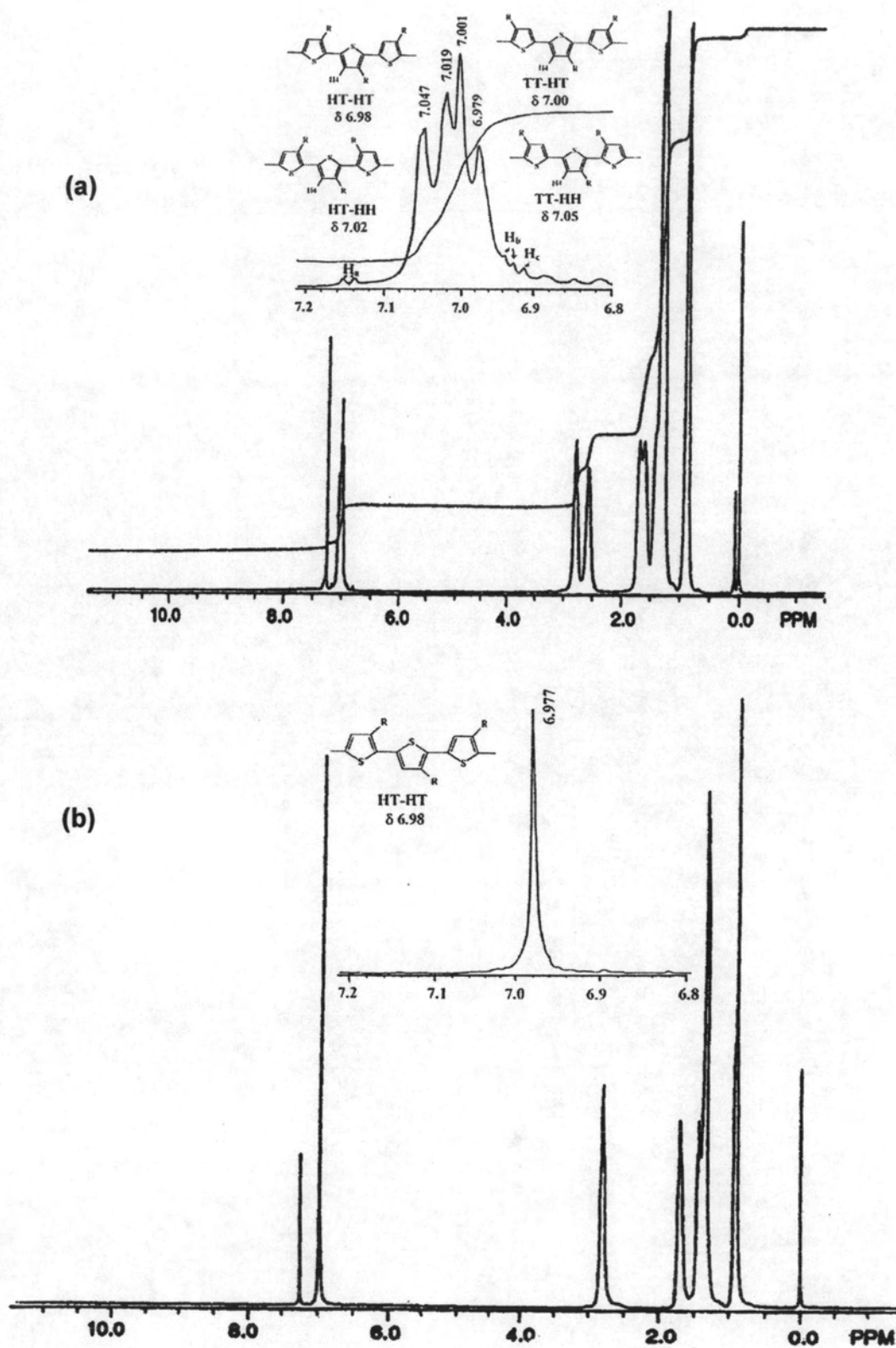
Figure 1.8 ^{1}H NMR spectra of (a) regiorandom (1:1:1:1, HT-HT: HT-HH : TT-HT : TT-HH) P3HT and (b) regioregular (98.5%) of HT linkage P3HT.
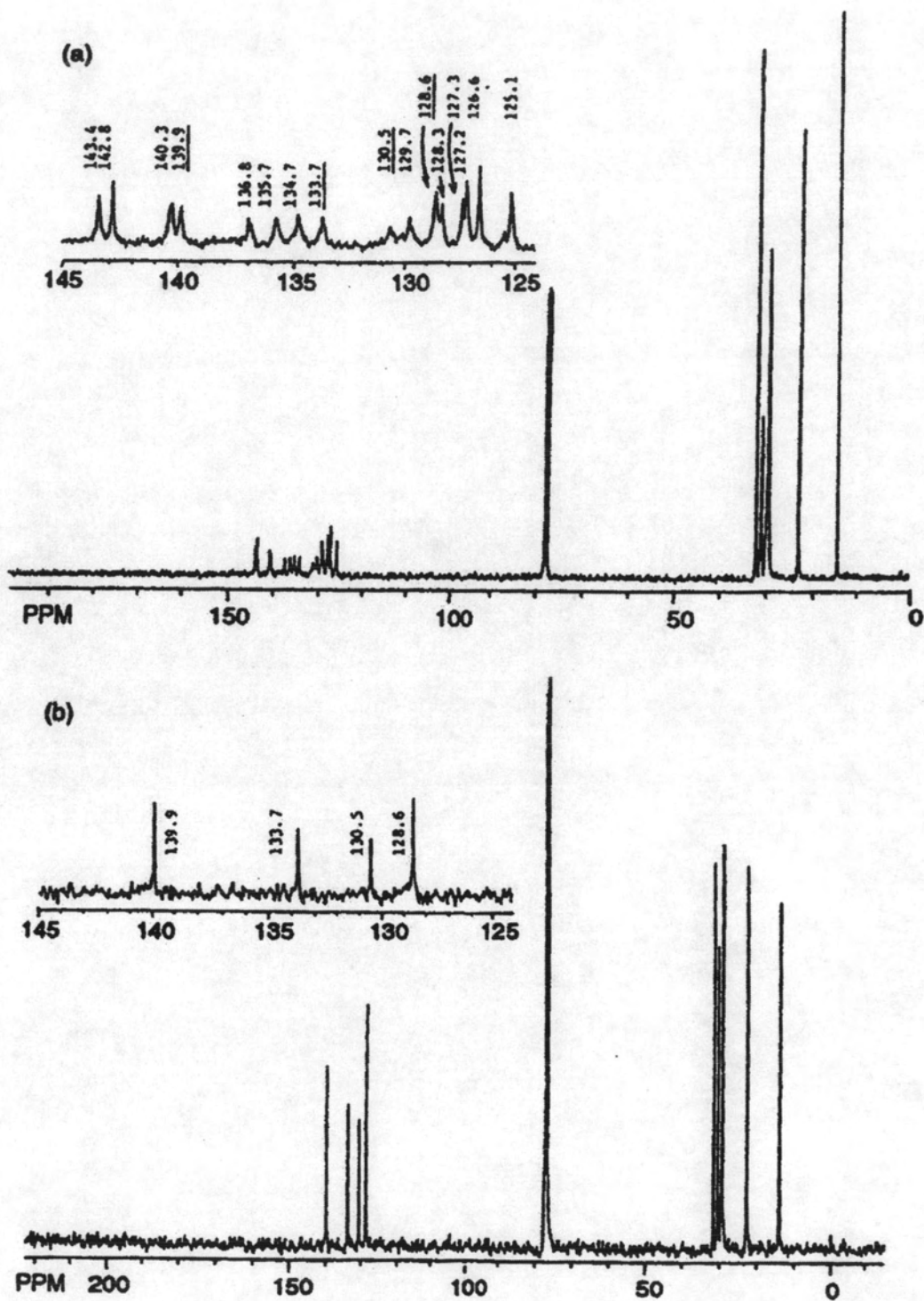
Figure 1.9 ^{13}C NMR spectra of (a) regiorandom (1:1:1:1, HT-HT: HT–HH: TT-HT: TT-HH) P3HT and (b) regioregular (98.5%) of HT linkage P3HT.

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 centered at *ca.* 2.8 and 2.6 ppm ascribable to α-CH$_2$ groups for the configurational HT and HH diads.

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 δ = 125 to 144 ppm (**Figure 1.9a**) [5,6] 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**) [5,6].

1.4 Synthesis of poly(3-alkylthiophene)

Polythiophene has been prepared first by electrochemical polymerization [7]. 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 great deal to the advancement 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

1.4.1 Electrochemical Polymerization

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.
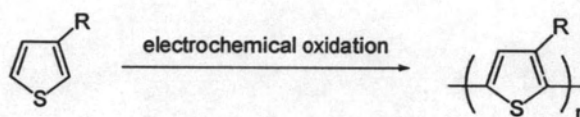

Figure 1.10 The electrochemical method for the synthesis of P3ATs (R = H, Me, Ph).

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.

The electrochemical polymerization of five-membered heterocycles involves many experimental variables such as the solvent, concentration of reagents, temperatures, electrochemical cell geometry, nature and shape of the electrodes and applied electrical conditions. As a consequence of the electrochemical polymerization pathways, electrosynthesis conditions determine to a large extent the structure and properties of the resulting polymer. However, due to the interdependence of many of the experimental variables, the analysis of the effects of an individual parameter and hence the optimization of electrosynthesis conditions constitute a complex problem.

1.4.2 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 alkylthiophenes are commercially available.

Sugimoto and coworkers [4] 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.

Amou [8] studied the polymerization mechanism and polymerization conditions and reported that a lower temperature and a lower concentration were effective for increasing the %HT. Niemi [9] 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.
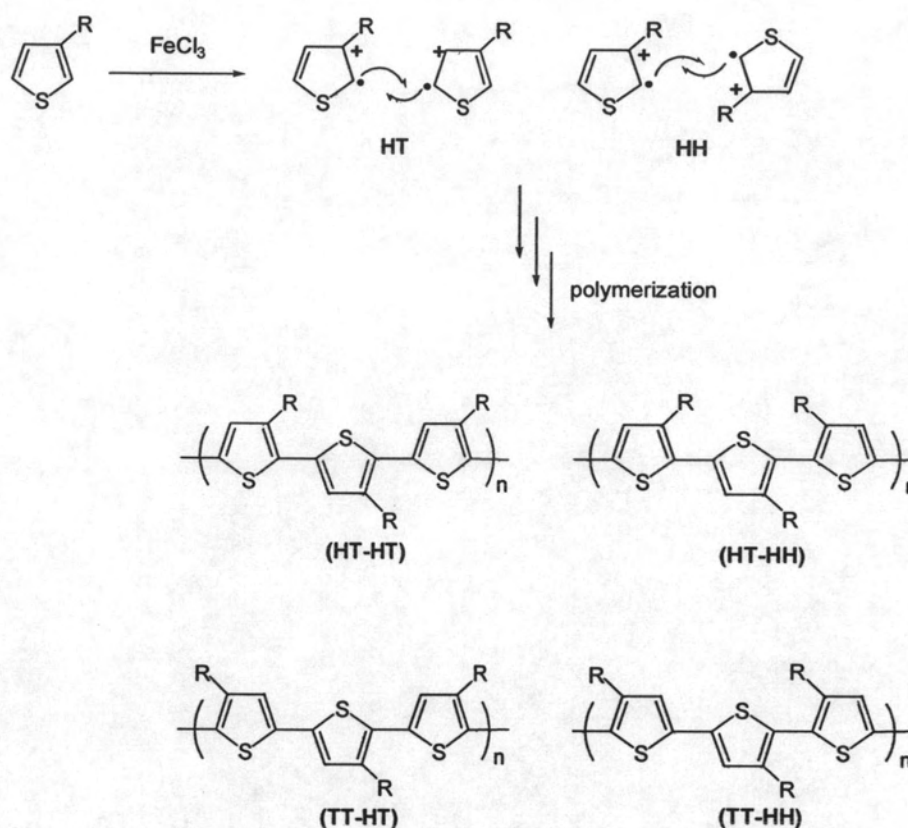
Figure 1.11 The oxidative coupling reaction of 3-alkylthiophene by $FeCl_3$

1.4.3 Grignard coupling and other chemical polymerizations

The polymerizations using a metal-catalyzed cross-coupling technique has been investigated extensively [10,11]. 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 [12-14]. This cross-coupling related approach differs primarily in the synthesis of the asymmetric organometallic intermediate (**Figure 1.12**).
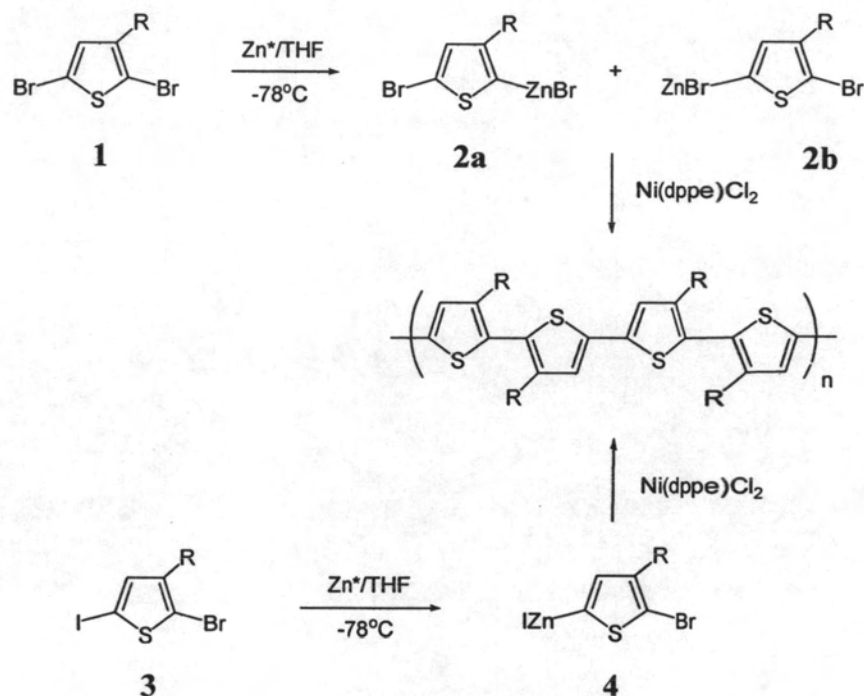

Figure 1.12 The Rieke method for the preparation of P3AT.

In the Rieke method, a 2,5-dibromo-3-alkylthiophene (1) is added to a solution of highly reactive "Rieke zinc" (Zn*). This metal reacts quantitatively to form a mixture of the isomers 2-(bromozincio)-3-alkyl-5-bromothiophene (**2a**) and 2-bromo-3-alkyl-5-(bromozincio)thiophene (**2b**). 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 **2a** and **2b** 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) (3) reacts with Rieke zinc to form only 2-bromo-3-alkyl-5-(iodozincio)thiophene (4). 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 ≈ 75%. Molecular weights for polymers prepared by this method are M_n = (24-34) × 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 [15] in early 1992 (**Figure 1.13**). This new synthetic method [16-20] 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 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)×10^3 (PDI ≈ 1.4). A recently prepared sample of HT-poly(dodecylthiophene) had M_n = 130,000 (PDI = 2.1).

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 [21]. In addition, thienyllithiums are relatively poor organolithium reagents and therefore are unlikely to undergo metal-halogen exchange reaction with 2-bromo-3-alkylthiophenes.

The intermediate **8** reacted with MgBr$_2$·Et$_2$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 [10] (**Figure 1.14**).
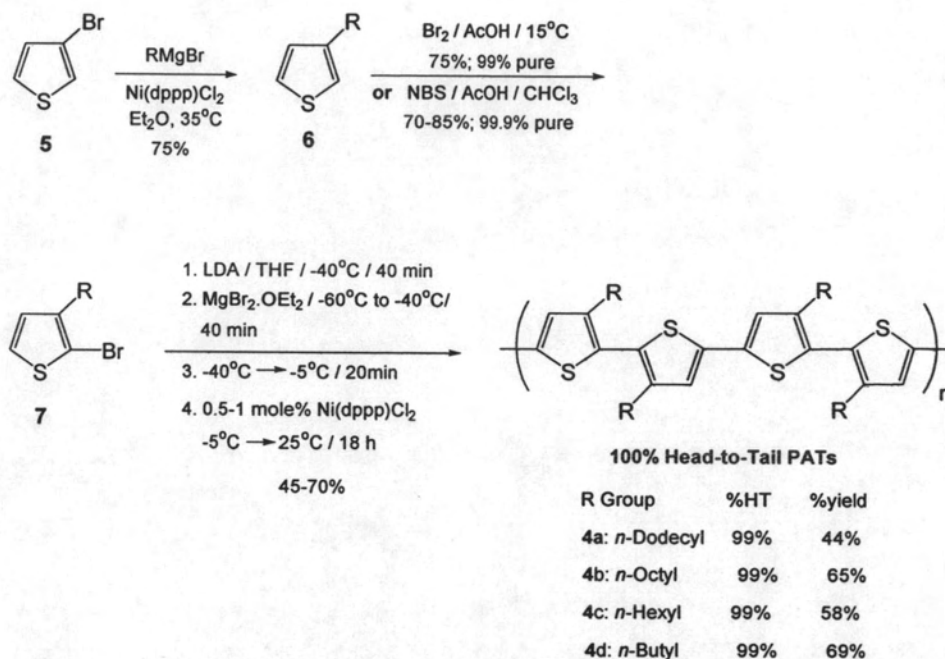
Figure 1.13 The McCullough method for the regiospecific synthesis of poly (3-alkylthiophene)s with 100% HT couplings.
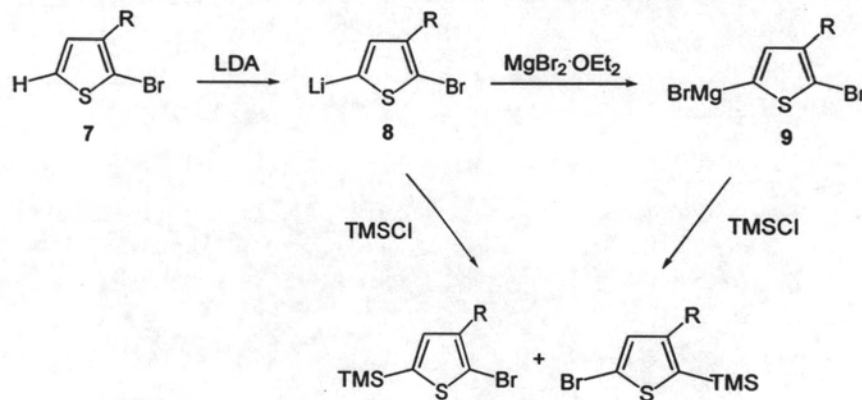

Figure 1.14 Trapping of organometallic intermediates.

The subsequent cross-coupling polymerization also occured 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 [22]. The method is very straightforward and has been

used by a number of research groups to prepare regioregular HT derivatives of polythiophene.

1.5 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 two reasons above are shown in **Figure 1.15**. 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.
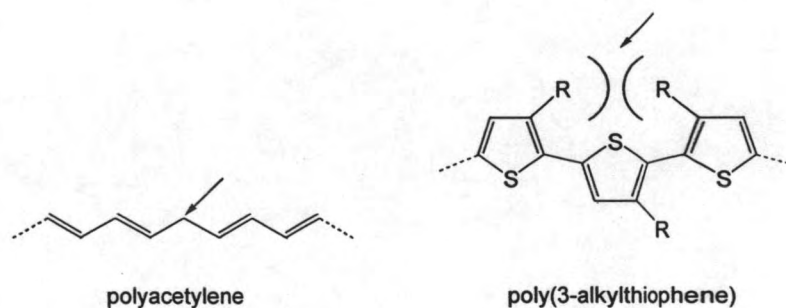

polyacetylene   poly(3-alkylthiophene)

Figure 1.15   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 1.16**). Twisting of polymer chain would also cause the reduction of conjugation in the polymer.
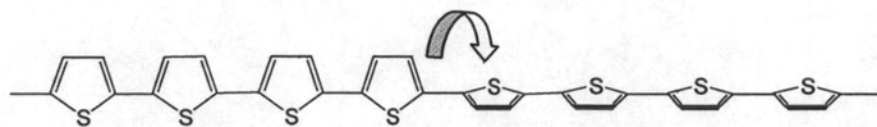
Figure 1.16 Twisting of polythiophene

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 [23] has been studied. These compounds had been fractionated into five fractions differing significantly in their molecular weights (**Figure 1.17** and **Table 1.1**) [24].
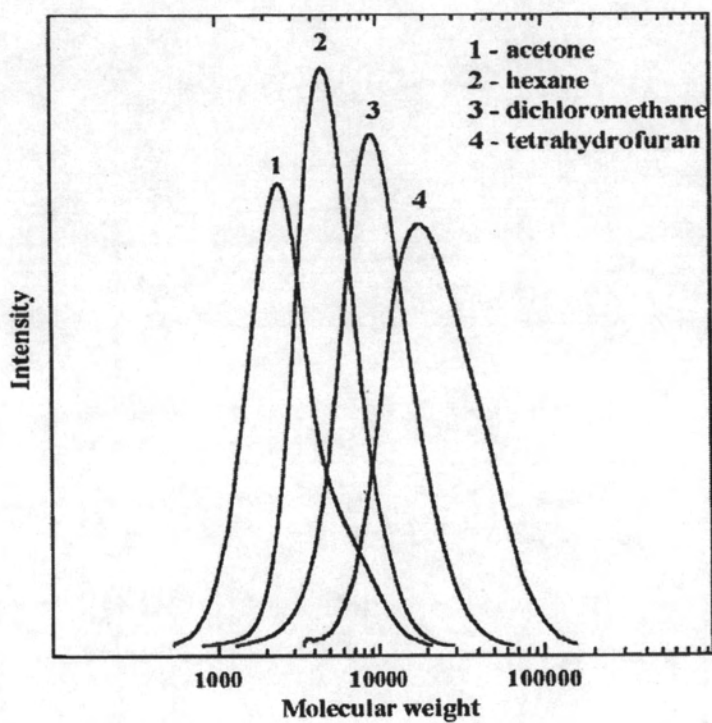

Figure 1.17 Elution curves of regioregular poly(3-hexylthiophene) fractions

obtained by selective extraction.

Table 1.1 Macromolecular parameters of regioregular-P3HT fractions obtained by selective extraction

P3HTfraction	wt %	M_n	M_w	P_i	D_n
acetone	6.5	2,280	3,150	1.38	14
hexane	9.7	4,380	5,340	1.22	26
CH_2Cl_2	33.1	8,370	11,100	1.35	50
$CHCl_3$	1.6	10,800	21,300	1.97	65
THF	49.2	17,700	25,700	1.45	106

The separated fractions of neutral P3HT were then subjected to UV-vis spectroscopic measurement (**Figure 1.18** and **Figure 1.19**) [24]. Both the solution spectra and the solid-state ones observed bathochromic shifts of λ_{max} which increased 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.
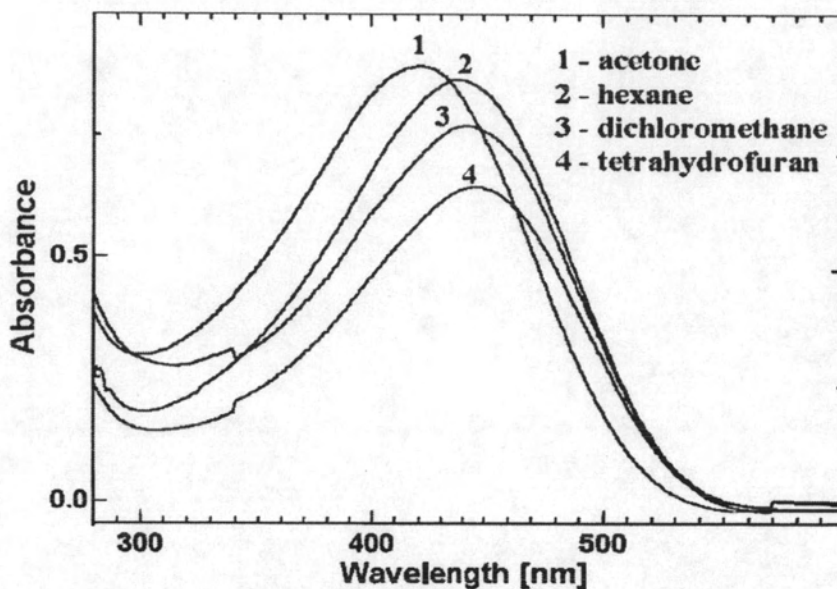
Figure 1.18 THF solution UV-vis spectra recorded for the fractions of regioregular poly(3-hexylthiophene) differing in their average molecular weight, which is an indication of higher conjugation length.

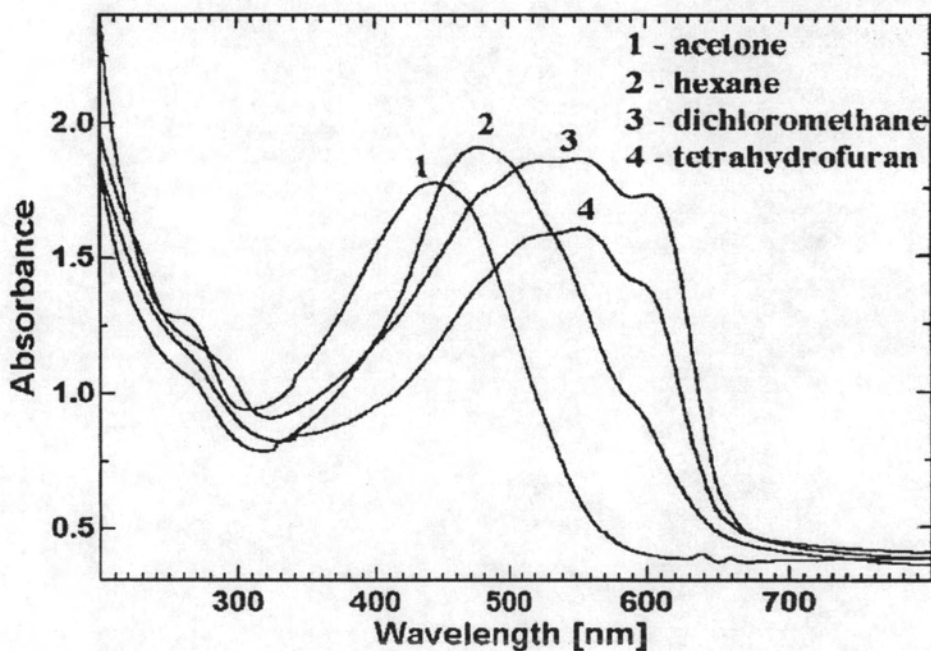

Figure 1.19 Solid UV-vis spectra recorded for the fractions of regioregular poly(3-hexylthiophene). Note that the bathochromic shift observed for higher molecular weight fractions is much more pronounced than in the case of solution spectra.

1.6 Effect of doping [25]

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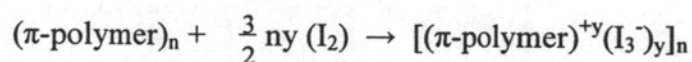
1. Doping introduces carriers into the electronic structure. Since every repeating unit is a potential redox site, conjugated polymers can be doped n-type (reduced) or p-type (oxidized) to a relatively high density of charge carriers.

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 :
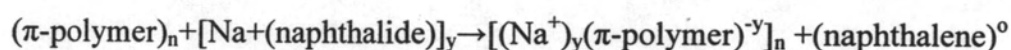
1.6.1 Chemical doping by charge transfer

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:
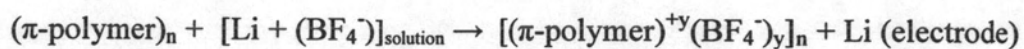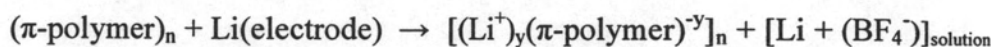
1. *p*-type

$$(\pi\text{-polymer})_n + \frac{3}{2} ny\,(I_2) \rightarrow [(\pi\text{-polymer})^{+y}(I_3^-)_y]_n$$

2. *n*-type

$$(\pi\text{-polymer})_n + [\text{Na+}(\text{naphthalide})]_y \rightarrow [(\text{Na}^+)_y(\pi\text{-polymer})^{-y}]_n + (\text{naphthalene})^0$$

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

$$(\pi\text{-polymer})_n + [\text{Li} + (\text{BF}_4^-)]_{\text{solution}} \rightarrow [(\pi\text{-polymer})^{+y}(\text{BF}_4^-)_y]_n + \text{Li (electrode)}$$

2. *n*-type

$$(\pi\text{-polymer})_n + \text{Li(electrode)} \rightarrow [(\text{Li}^+)_y(\pi\text{-polymer})^{-y}]_n + [\text{Li} + (\text{BF}_4^-)]_{\text{solution}}$$

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 1.20**).
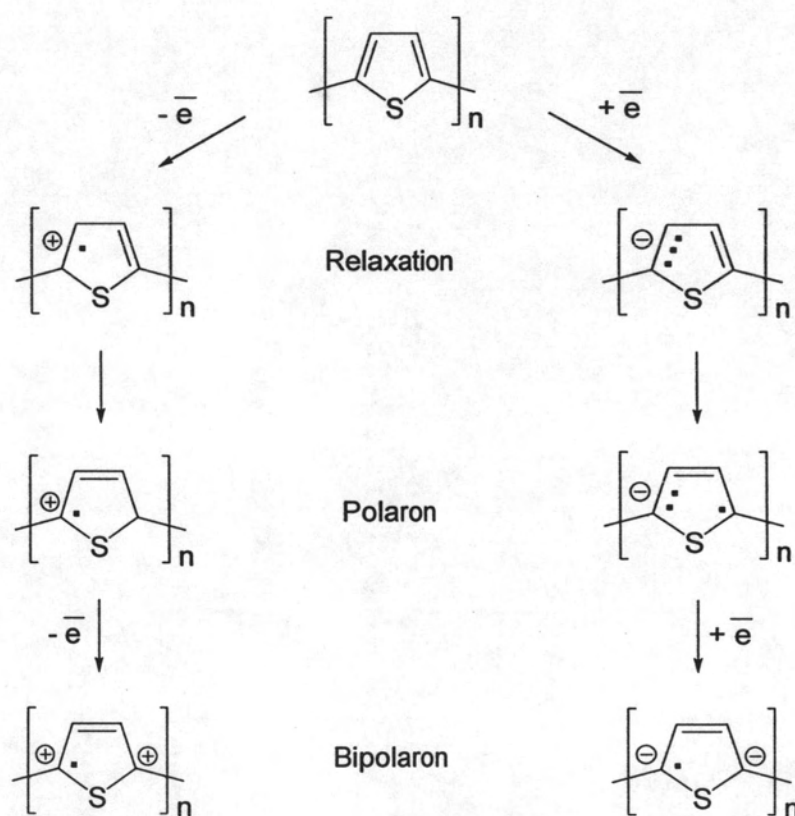

Figure 1.20 Schematic representation of polythiophene in the undoped (center), singly, and doubly oxidized (left), and singly and doubly reduced (right) states.

The polythiophene and derivatives were often doped by oxidative doping because they are electron-rich and favor to lose electron as indicated in **Figure 1.21**.
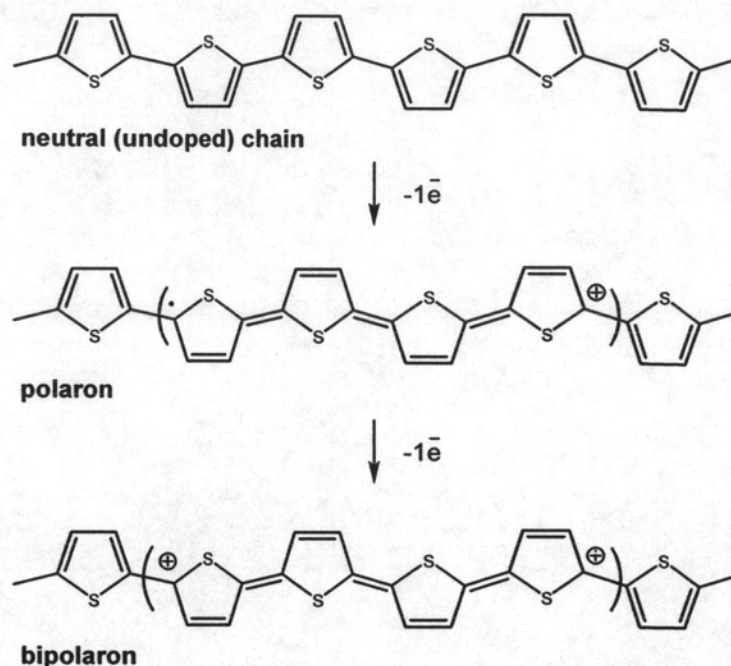
neutral (undoped) chain

-1e̅

polaron

-1e̅

bipolaron

Figure 1.21 Polaron and bipolaron of Polythiophene.

In **Figure 1.22** 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 [20]. 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 [26].

Poly(3-alkylthiophenes) are found to undergo continuous structural transformations upon doping with iodine vapor [27]. 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.
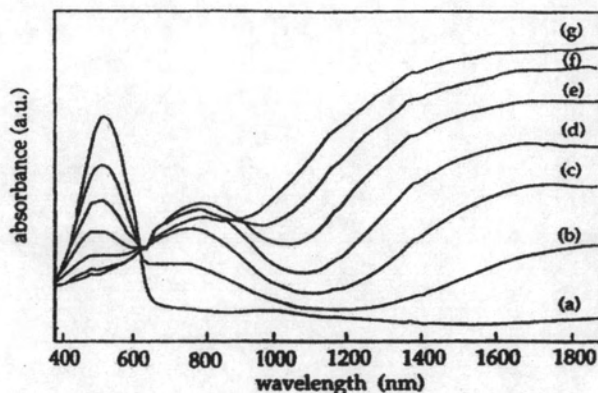

Figure 1.22 UV-vis-nir spectroelectrochemical curves recorded for regioregular poly (3-octylthiophene) in 0.1 M Bu_4NBF_4 solution in acetonitrile: (a) E = 0 mV; (b) E = 500 mV; (c) E = 800 mV; (d) E = 900 mV; (e) E = 1000 mV; (f) E = 1200 mV; (g) E = 1400 mV. (E measured vs Ag/AgCl reference electrode).

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 (**Figure 1.23**). Among the various *p*-type dopants, iodine is often selected for its chemical simplicity and its straightforward doping procedures.

The stability of $AuCl_3$-doped poly(3-hexylthiophene) thin films was studied at elevated temperatures by means of optical spectroscopy [28]. At room temperature the stability is substantially enhanced relative to that of the $FeCl_3$-doped system. At elevated temperatures even $AuCl_3$ is a thermally unstable dopant, although still more stable than $FeCl_3$. 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.
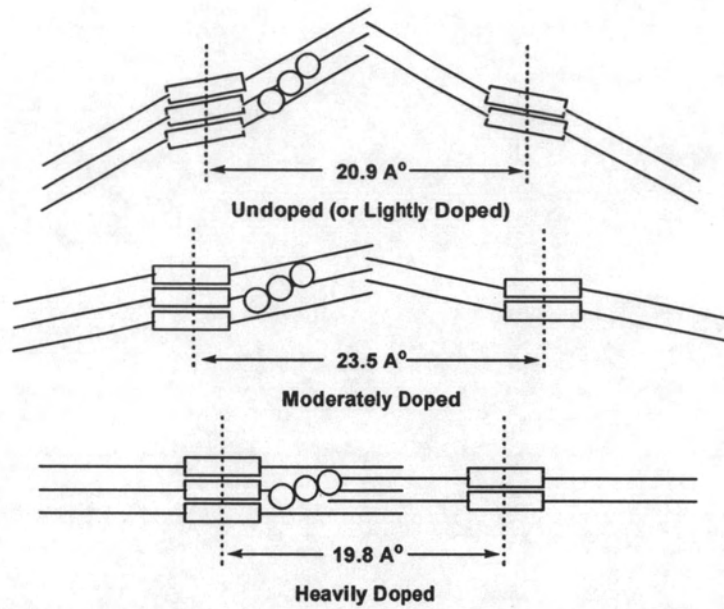
Figure 1.23 Projected equatorial structure of P3OT at various doping levels.

It appears that nitrosyl compounds [29] have considerable potential as chemical dopants for P3AT because of their previous utilization in lithography, nitrosonium tetrafluoroborate, $NOBF_4$. However, the counterions, such as BF_4^- and PF_6^-, 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

$$NOTFSI > AuCl_3 > NOSO_3CF_3 > FeCl_3 > NOBF_4$$

1.7 Solvato-controlled doping

Because conjugated polymer films are generally oxidized via an additional step after film casting or sample preparation. Unfortunately, this technique poses several disadvantages since:

i) immersion of thick polymer films (and subsequent doping) often results in swelling and cracking of the sample,

ii) the doping level (ratio of dopant to monomer units) can not be predicted *a prion,*

iii) the concentration of dopant through a thick sample may not be uniform when lightly doped samples are desired,

iv) the solvent for the dopant solution, or the doping agent, itself, may be incompatible with other components on the substrate, and

v) for solution doping, there is a large amount of wasted reagent since practical use exposes the dopant solutions to air and moisture, resulting in quenching of the active species. Many of these factors would be ameliorated by a technique that provides both simultaneous film casting and polymer oxidation (doping). Additionally, it would be useful to control the conductivity of the product polymer by controlling the doping level, that is, by setting the ratio of injected anions to monomer units a *prion.* Both of these goals have been achieved for several conjugated polymers by a technique which is termed *solvato-controlled doping* [30]. A single-step casting and doping process requires incorporation of both the oxidizing agent, and the charge-balancing counter ions into the polymer solution. However, an effective oxidizing agent is a chemical species which has a reduction potential more positive than that of the polymer. Therefore, upon mixing of the oxidant with the polymer, the dissolved polymer chains become oxidized, they assume a more planar conformation (due to the enhanced interannular double bond character) and they precipitate from solution.

Clearly, the polymer and oxidant must be shielded from each other if an intimate mixture is to be obtained while keeping the polymer both neutral and soluble, postulated that the oxidant could be shielded from the polymer by the presence of coordinating ligands. Silver (I) was chosen as the oxidant as Holdcroft and coworkers found it to be an effective oxidizing agent for P3HT films, and it is known to

coordinate to numerous organic compounds. The counter-ion chosen was trifluoromethanesulfonate (or triflate) ($CF_3SO_3^-$, OTf$^-$) since the silver (I) salt was commercially available, and the anion has a low nucleophilicity.

The reduction potential for silver (I) was found to shift to less positive values upon complexation with pyridine. This shift was sufficient to prevent silver (I)-induced oxidation of poly(3-hexylthiophene) (P3HT). Thus, the oxidant (silver triflate) and the polymer could be mixed in solution, and no chemical reaction was observed. The pyridine was later readily removed by evaporation. The resulting P3HT films had initial electrical conductivities of 2 S/cm and exhibited half-lifetimes that were 17 times greater than P3HT films oxidized by ferric chloride. Thick electrically conductive polymer films were readily produced, and they showed no sign of the cracking and peeling normally evident when similar films were oxidized by immersion into an oxidizing solution. P3HT films were oxidized by silver triflate and ferric chloride. The silver doped films exhibited open-circuit potentials that were lower than those of the ferric chloride doped films. The effect of the open-circuit potential on stability was investigated by electrochemically oxidizing polymer films (in the presence of the triflate anion) to a range of potentials and observing their resultant stability. Only a small dependence was observed. Other P3HT films were doped chemically and electrochemically with the triflate anion. Both techniques resulted in conductive films that were much less stable than the silver triflate doped films.

1.8 Absorption-Conjugation index value (AC-index)

Absorption Conjugation index value (AC-index) [2] has been proposed as a "weighted integrative" absorption at a range of wavelengths. The higher λ values were "weighted" to be more important than that of lower values because of their presumed correspondence to the more conjugated systems. The sum of these weighted absorbances normalized over the sum of the unweighted ones are the AC-index value: high AC-index value would reflect the high effective conjugation length within the polymer chain which could, in turn, correlate to high conductive properties. The equation for the calculation of AC-index value is shown below (An example for the AC-index value calculation was shown in Appendix B):

$$\text{AC-index (from } \lambda_1 \text{ to } \lambda_{n+1}) \quad = \quad \frac{\Sigma\lambda_i A_i}{\Sigma A_i}$$

when λ = wavelength (nm)

               A_i = absorbance at λ_i

               i = 1, 2, 3, ..., n +1

1.9 Copolymer

Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the two or more types of monomer units in the copolymer product.

A prime example of the versatility of the copolymerization process is the case of polystyrene, most polystyrene products are not homopolystyrene since the latter is relatively brittle with low impact and solvent resistance. Various combinations of copolymerization and blending are used to improve the properties of polystyrene.

Copolymerization of styrene with 1,3-butadiene imparts sufficient flexibility to yield elastomeric products [styrene-1,3-butadiene rubbers (SBR)]. SBR is similar to natural rubber in tensile strength, has somewhat better ozone resistance and weather ability but has poorer resilience and greater heat buildup. SBR is also blended with other polymers to combine properties. The major use for SBR is in tries. Other uses include belting, hose, molded and extruded goods, flooring, shoe soles, coated fabrics and electrical insulation.

Neher and coworkers [31] have shown that a statistical polythiophene copolymer, regioregular poly[(3-hexylthiophene)]-co-(3-octylthiophene)] (P3HTOT), is a highly soluble semiconductor with good electrical properties. Transistors made from as-prepared layers of P3HTOT exhibit a mobility of $7.2 \times 10^{-3}\,\text{cmV}^{-1}\text{s}^{-1}$, which is comparable to the performance of transistors made from as-prepared P3HT and almost 6 times larger than the mobility of transistors prepared with P3OT. Moreover, compared to a physical blend of poly(3-hexylthiophene) and poly(3-octylthiophene), the mobility of P3HTOT devices is almost twice as large and the performance does not degrade upon annealing at elevated temperatures. Certainly, other types of

monomers could also be copolymerized or blended to achieve even better ion mobility, especially the monomer of the well known high conducting poly(3,4-ethylenedioxythiophene) or PEDOT [32,33].

1.10 Objectives

1. To optimize the condition of synthesis of poly(3-hexylthiophene) by the oxidative coupling of 3-hexylthiophene monomer with anhydrous ferric chloride in organic solvents.

2. To study the various conditions of doping of poly(3-hexylthiophene) with doping agents, including protonic acids and Lewis acids either through direct mixing or solvato-controlled conditions.

3. To study the possibility of improving the conjugation of poly (3-hexylthiophene) by copolymerizing with EDOT

1.11 Scope of the investigation

The sequential investigation was carried out as follows.

1. Literature survey on related research .

2. Study on the several factors that could enhance the selectivity of such favourable arrangements include appropriate amount of the anhydrous ferric chloride reagent, the reaction temperature, solvents and some additives

3. Study on doping of poly(3-hexylthiophene) (P3HT) with organic acids including: trifluoroacetic acid (TFA), trichloroacetic acid (TCA). Optimize the amount of doping reagent by monitoring the absorption of P3HT with UV-visible spectroscopy.

4. Study on Lewis acid doping of poly(3-hexylthiophene) (P3HT) including: $FeCl_3$, $AlCl_3$, $ZnCl_2$ and $TiCl_4$ by monitoring the absorption of P3HT with UV-visible spectroscopy.

5. Study on solvato-controlled doping of poly(3-hexylthiophene) (P3HT) with thiophene and MSA. Optimize the amount of doping reagent and ligand by monitoring the absorption of P3HT with UV-visible spectroscopy.

6. Study on solvato-controlled doping of poly(3-hexylthiophene) (P3HT) with various pairs of acids (FeCl$_3$, AlCl$_3$, ZnCl$_2$, TiCl$_4$, MSA) and ligands or bases (thiophene, pyridine, pyrrole, dimethylformamide).

7. Study on copolymerization of 3-hexylthiophene and EDOT at various ratios of monomers.