

CHAPTER I

INTRODUCTION

Polymers have been used as insulating materials. Polymers were being discarded traditional role as electric insulators to take charge as conductors with a range of new applications. Scientists from many disciplines are combining expertise to study organic solid that exhibit remarkable conducting properties. A new class of polymers known as intrinsically conducting polymers or electroactive conjugated polymers has recently emerged. This materials exhibit interesting electrical and optical properties previously found only in inorganic materials. Electronically conducting polymers differ from all the familiar inorganic crystalline semiconductors [1].

The last few decades of the field materials science have been marked by the growing importance take by two classes of materials, organic polymers and inorganic semiconductors. Thus the lightness of weight, processability, and resistance against corrosion of organic polymers had led in many applications to the replacement of metals [2]. Conducting polymers have unique properties that are interesting for new technology. Conducting polymers are good materials to be employed in the fabrication of electronic devices because their properties can be fine-tuned by external parameters during chemical synthesis within a certain band width [3].

1.1 Conducting polymers

In general, polymers are considered good insulator. Conducting polymers are classified as organic semiconductors. Conducting polymers are conjugated polymers consisting of alternating single and double bonds along their backbones. These conjugated sp^2 -hybridized carbons and p-electrons. These p-electrons form a delocalized π -system, which gives rise to semiconducting properties [4]. As is the case with polyacetylene, the simplest conducting polymer structure the electrical transport characteristics are obtain by placing the alternating carbon-carbon double bond structure directly on the backbone of the polymer [5]. The subsequent electrical



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conductivity is mistakenly visualized from resonance structures and the mobility of π electrons as depicted for polyacetylene.

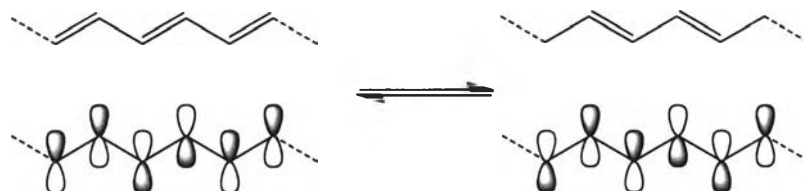


Figure 1.1 The delocalized π system of conjugated polymers

Conducting polymers have received attention towards numerous applications in electronic and optoelectronic devices such as light-emitting diodes (LEDs) [6, 7], photovoltaic cells (OPVs) [8] and chemical and bio-sensors [1, 9].

1.2 Historical background of conducting polymers

A tremendous amount of research has been carried out in the field of conducting polymers. The high levels of conductivity in polymer was observed in 1977 when a polymer chemist Hideki Shirakawa, an inorganic chemist Alan MacDiarmid and a physicist Alan Heeger presented their discovery of the simplest conducting polymer, polyacetylene (doped with halogens). This discovery was award the Nobel Prize in chemistry in 2000 “for the discovery and development of electrically conductive polymer” [10]. This work reinforced the concept of organic materials behaving as metal or semiconductors [11]. An important step in the development of conjugated poly(heterocycles) occurred in 1979 when Diaz and coworker obtain polypyrrole (PPy) as a free standing film by oxidative electropolymerization of pyrrole. The polypyrroles appeared in this field as the first example for conductive poly(heterocycles) [12]. In recent years, there has been growing interest in research on conducting polymer. Since then, an active interest in synthesizing other organic polymers possessing this property has been initiated. As a result, other conducting polymers having π electron conjugated structure such as polyaniline (PANI), polypyrrole (PPy), poly(*p*-phenylene), poly(*p*-phenylene vinylene) and polythiophene (PT) have been synthesized for exploring them. The conductivity of these polymers can be tuned from insulating regime to



superconducting regime, by chemical modification, by the degree and nature of doping. Besides these, polymers offer the advantages of lightweight, flexibility, corrosion-resistivity, high chemical inertness, electrical insulation and the ease of processing [13]. The field of conductive polymers have been in development for a long time, and is more interest in the many applications of plastic electronics ries.

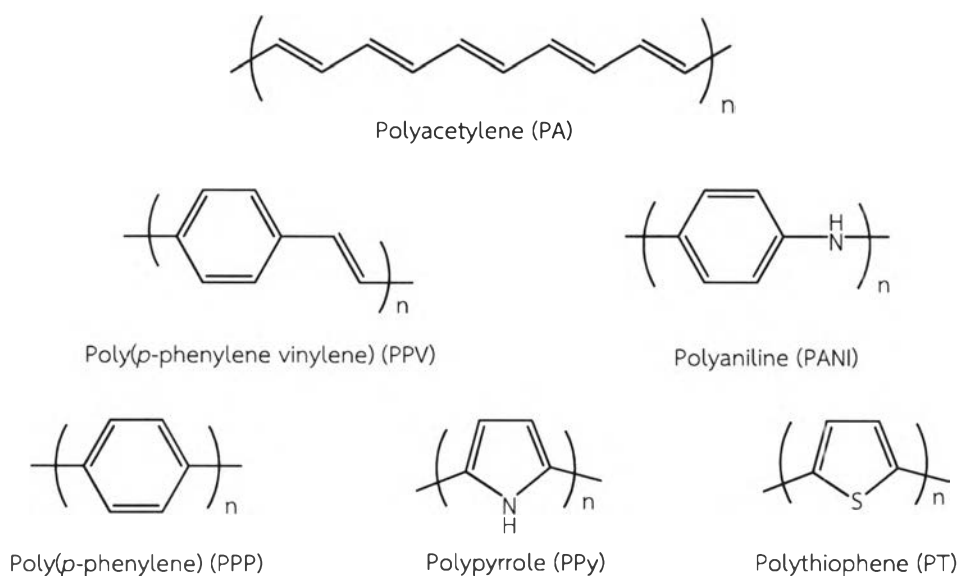


Figure 1.2 Structure of some conjugate polymers

The field of conjugated polymers, polythiophenes and their derivatives have received significant attention for electrical properties, ability to exhibit environmental stabilities, the ease of derivatization and ability to be polymerized by various methods (Table 1.1).



Table 1.1 Stability and processing attributes of some conducting polymers

Polymer	Conductivity (S/cm)	Stability (doped state)	Processing possibility
Polyacetylene	10^3 - 10^5	poor	limited
Poly(<i>p</i> -phenylene)	1000	poor	limited
Poly(<i>p</i> -phenylene vinylene)	1000	poor	limited
Polypyrroles	100	fair	good
Polythiophenes	100	good	excellent
Polyaniline	10	good	good

1.3 Organic versus Inorganic semiconductors

Organic materials offer several major advantages over inorganic materials. Some potential benefits are:

- *Low weight.* The densities polymers are much lower than those of traditional metals (1 - 2 g/cm³ compared to 3 - 10 g/cm³).
- *Low cost.* Inorganic semiconductors are sensitive to impurities and must be produced, handled and assembled in high-tech clean rooms. Organic materials, on the other hand, may be synthesized in relatively unsophisticated laboratories and are much more tolerant to contaminations.
- *Tunability.* The art of organic chemistry offers an infinite amount of chemical modifications of the active materials, which may be fine-tuned to suit each desired application.
- *Flexibility.* Inorganic semiconductors are stiff and therefore useless for flexible devices. Many organic semiconductors are on the other hand quite flexible and useful for flexible devices.
- *Solubility/Processability.* Many molecular materials are soluble in common organic solvents and can be applied onto the substrates by evaporation.



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1.4 Band theory of conjugated polymers

A conducting polymers are an organic base polymer that can act as a semiconductor. They are conjugated. They are have electron delocalization along their polymer backbone. It is giving optical and electrical properties. With respect to electronic energy levels, hardly differ from inorganic semiconductor. Both have their electrons organized in bands rather than in discrete levels and their ground state energy bands are either complete filled or completely empty. The band structure of a conjugated polymers originates from the interaction of π -orbital of repeating units throughout the chain [14].

The energy band results from the bonding orbital of molecule is known as the valence band, while the conduction band is as a results of the anti-bonding orbital of the molecule. The width of individual band across the range of energy levels is called band width. The valance band (VB) represents the highest occupied molecular orbital and the conduction band (CB) represent the lowest unoccupied molecular orbital (LUMO) [15]. The gap between the highest filled energy level and lowest unfilled energy level is called band gap (E_g). This band gap is a range of energies between HOMO and LUMO. The size of the energy band gap will define whether the conducting polymers is metal, semiconductor or insulator [15]. The electronic properties of metals, semiconductors and insulators can be differentiated with reference to energy band gap as shown in **figure 1.3** [16].



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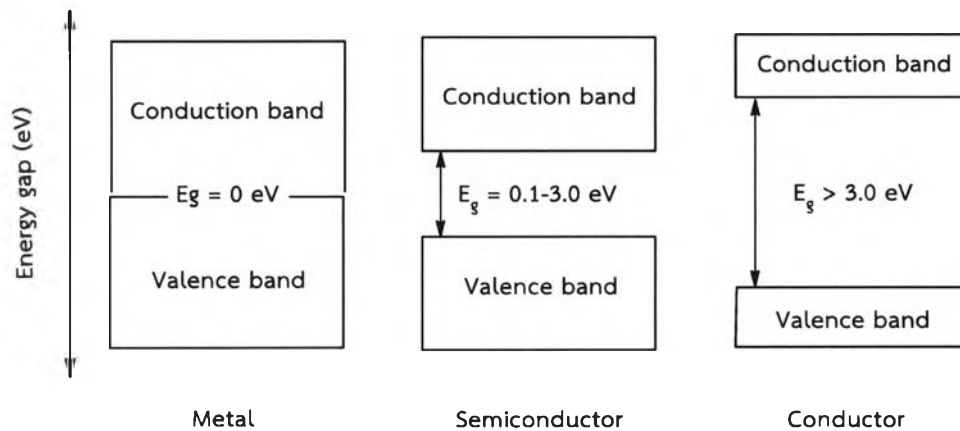


Figure 1.3 Simple band picture explaining the difference between an insulator, a semiconductor and a metal

In metals there is no range of energies which is deemed unavailable to electrons, which simply means that the forbidden gap or band gap in metals is $E_g = 0$ eV. Metals have a partially filled free-electron band because the conduction and valence bands overlap. Insulators have a band gap which is larger than 3 eV, the energy gap between conduction and valence bands is too large. The electron is not able to make that jump to detach from its atom, in order to be promoted to the valence band. Insulators are poor electrical conductors at ambient temperatures. In semiconductors, there is a small enough gap ($E_g = 0.1-3.0$ eV) between the conduction and valence bands, which allows some excitation of charge carriers to conduction bands. Thermal or other excitations can bridge the gap. The electrons can raise their energy and detach from their atom by jumping to a higher energy level in the conduction bands. There are several methods, which can be used to excite electrons into the conduction bands. Another method known as doping is also used to generate the charge carriers (electrons and holes) [14].



1.5 Doping process

Conjugated polymers have a narrow band gaps (**Figure 1.3**). Conjugated polymers are insulator or poor conductivity due to their energy gap, doping can these systems become highly conductive allowing for new optical transition to be seen. The doping process is an addition of a doping agent in to polymer expecting to the conductivity of the polymer. Doping of conducting polymers, with associated control of the electrical conductivity over the full range from insulator to metal. Doping process can be accomplished either by chemical doping or by electrochemical doping [17]. Doping can change band structures by either taking electrons from the valence band (*p*-doping) or adding electrons to conduction band (*n*-doping). Both *n*-type (electron donating) and *p*-type (electron accepting) dopants have been used to induce an insulator-to-conductor transition in electronic polymers. Doped conjugated polymers are good conductors for two reasons:

1. Doping process 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.

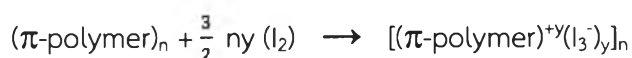
However, limits the carrier mobility and in the metallic state limits the electrical conductivity. Indeed, research directed toward conjugated polymer with improved structural order and hence higher mobility is a focus of current activity in the field. Charge injection onto conjugated, semiconducting 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:



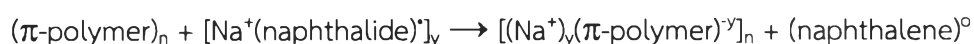
1.5.1 Chemical doping

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

1. *p*-type



2. *n*-type

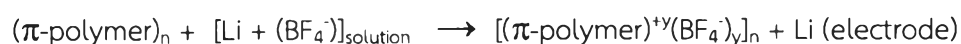


When the doping level is sufficiently high, the electronic structure of conjugated polymers approached to that of a metal.

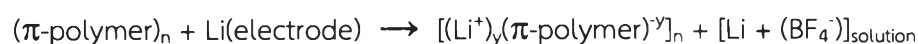
1.5.2 Electrochemical doping

Although chemical doping is an efficient and straightforward process, it is normally 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 originated 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



1.6 Solitons, polarons and bipolarons

Polymer doping leads to the formation of conjugational defects; solitons, polarons and bipolarons in the polymer chain. The presence of localized electronic states of energies less than the band-gap arising from changes in local bond order, including the formation of solitons, polarons and bipolarons have led to the possibility of new types of charge conduction. **Table 1.2** give the charge and spin characteristic of these defects [18].

Table 1.2 Typical properties of solitons, polarons and bipolaron

Defect	Spin	Charge	
Soliton	Neutral	$\frac{1}{2}$	0
Soliton	charged	0	+e or -e
Polaron	charged	$\frac{1}{2}$	+e or -e
Bipolaron	charged	0	+2e or -2e

Solitons are three categories: neutral soliton, positive soliton and negative soliton. An interesting observation at this point is that charged solitons have no spin; while neutral solitons have spin but no charge. Positively charged soliton occurs when an electron is removed from localized state of a neutral soliton by oxidation. Negatively charged soliton is produced when an electron is inserted by reduction [19].

Polarons are obtained as a combination of a neutral and a charged soliton on the same polymer chain. Further oxidation causes more and more polarons to form and eventually the unpaired electron of the polaron is removed, or two lone polarons can combine to form dications or bipolarons [20].

The neutral polymer has full valence and empty conduction bands with a separated band gap. Formation of polaron and bipolaron generates new energy levels located at mid gap.



1.7 Structural design and synthetic methodologies for low band gap materials

Band gap value is extremely important for conjugated polymers since it is directly related with the electron or hole affinities, absorption values and conductivities of polymer. Conjugated polymers were classified as the low band gap materials. Low band gap polymer are expected to have n-doping property which allows their usage in energy storage applications. Therefore, it is important to study the factors which affect the band gap value of conjugated polymers.

In order to functionalize a polymer have desired electrochemical and optical properties. Both the valence and conduction energies can be controlled by the energy gap (the relation of the energy levels to one another) or the position of the energies (oxidation or reduction potentials). Low band gap materials will provide a means for stable n-doped states on the intrinsically conducting polymer systems.

In designing low band gap systems, the variety of methodologies can be used to achieve polymers with band gaps less than 2 eV. There are five basic approaches that have been used to reduce band gap; controlling bond-length alternation, creating highly planar systems, inducing order by interchain effects, resonance effect along the polymer backbone and using donor-acceptor effects.

1.8 Polythiophene

Polythiophene is composed of repeating five-membered heterocyclic monomeric unit. It is also considered one of the promising classes of conducting polymers for technological used. This is attributed to its good environmental stability in neutral form, its structural versatility which allows their electronic and electrochemical properties to be modified by chemical means and its characteristics of having non-degenerate ground state for the two limiting structures of polythiophene aromatic ground state and quinoidal ground state [2, 19]. Polythiophene has an excellent thermal stability (42% weight loss at 900 °C) and good conductivity (3.4×10^{-4} to 1.0×10^{-1} S/cm when doped with iodine). Despite the lack processability,



environmental stability, thermal stability and high-electrical conductivity of the polythiophene films still make it a highly desirable material [4].

The conjugated polymer systems polythiophenes have a poor solubility due to the strong π -stacking interaction between the aromatic rings. The standard procedure of attaching long, flexible chains onto the conjugated backbone of an insoluble polymer can improve the solubility but it has deleterious effects on the electrical conductivity of polymers in their conducting state. A significant discovery demonstrated that polythiophene belongs to one of few cases in which substitution of hydrogen at the β -position by alkyl chain or electron donating group with flexible chain does not affect polymer conductivity of the polymer, whereas it imparts solubility and consequently enhances processability. The flexible substituents solubilized the polythiophene chains by this disruption of their interchain stacking. This in turn facilitated the processability of these polymers [21-23]. In addition, introducing an electron donating substituent into the thiophene ring has decreased polymerization potential and significantly enhanced polymer electroactivity in solution. Oxygen directly attached to the thiophene ring was further substantially stabilized the conducting p-type of polymers by stabilization of the positive charge in the polymer backbone [24].

1.9 Synthesis of polythiophene

Many intensive research efforts, polythiophene is generally prepared by means of two main routes which are the electrochemical and the chemical syntheses.

1.9.1 Electrochemical polymerization

Initially, polythiophene was obtained by electrochemical polymerization of thiophene monomers. The synthesis of polythiophenes by electrochemical oxidation has been widely used. Polythiophene was prepared from the electrochemical polymerization using a potential applied across a solution containing thiophene. Polymer film was produced at the anode surface after electropolymerization. The polymer is deposited in its oxidized conducting form onto the electrode, allowing the polymerization to proceed. The yield of polymers prepared from electrochemical



polymerization is moderate to low yield and their structures are not well-defined [22]. Electrochemical polymerization is proposed the polymerization proceeds via the coupling of two radical cations, formed by the oxidation of monomer as outlined in figure 1.4 [25].

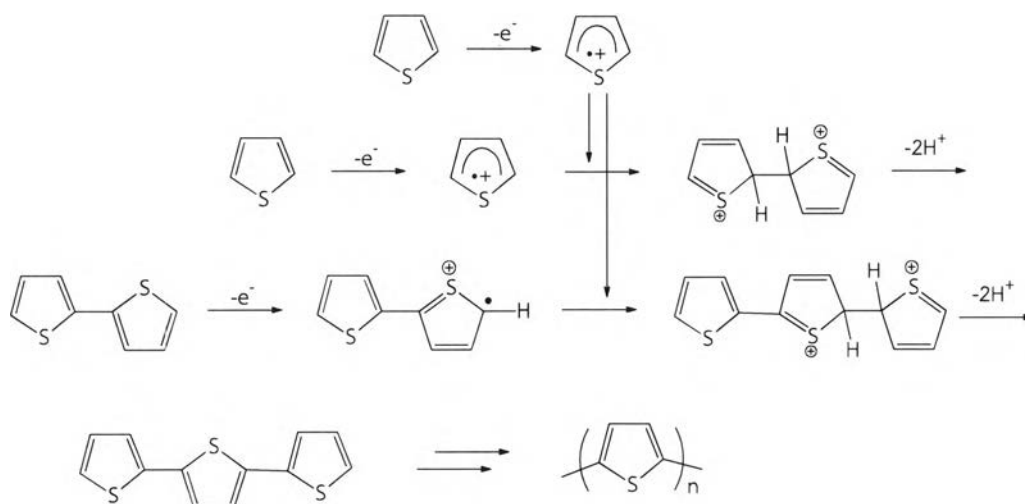


Figure 1.4 Electrochemical polymerization of thiophene

Electrochemical polymerization is very useful method for preparing polymers such as polythiophene, poly(3-methylthiophene), and poly (3-phenylthiophene), which are insoluble and infusible. Polymers are obtained in the form of powder they cannot be processed into a film or other useful forms [23].

1.9.2 Oxidative coupling polymerization

Polythiophene are formed in the oxidation of thiophene monomers with arsenic(V)pentafluoride (AsF_5). Due to the poisonous properties of arsenic(V)pentafluoride this method has not been widely adopted. A more convenient method was developed by Yoshino et al [26] who used iron(III) trichloride (FeCl_3) as the oxidizing agent and chloroform as solvent under anhydrous condition [25]. The yield of polymers prepared from this method is relatively high. The oxidative coupling of thiophenes provides with high molecular weights than the route describe above. Polymer obtained from this method are soluble in common organic solvents and their films can be formed by simply casting its solution on a solid substrate. Many 3-

alkylthiophene was prepared by this method. Sugimoto and coworker [26] elaborated transition metal halides as oxidizing agent for polymerization of 3-hexylthiophene and found that iron (III) chlorides were the effective one (**Figure 1.5**). The films were fabricated by casting a solution of the resulting poly(3-hexylthiophene) on substrate and the results showed similar characteristics to those prepared by the electrochemical method [25].

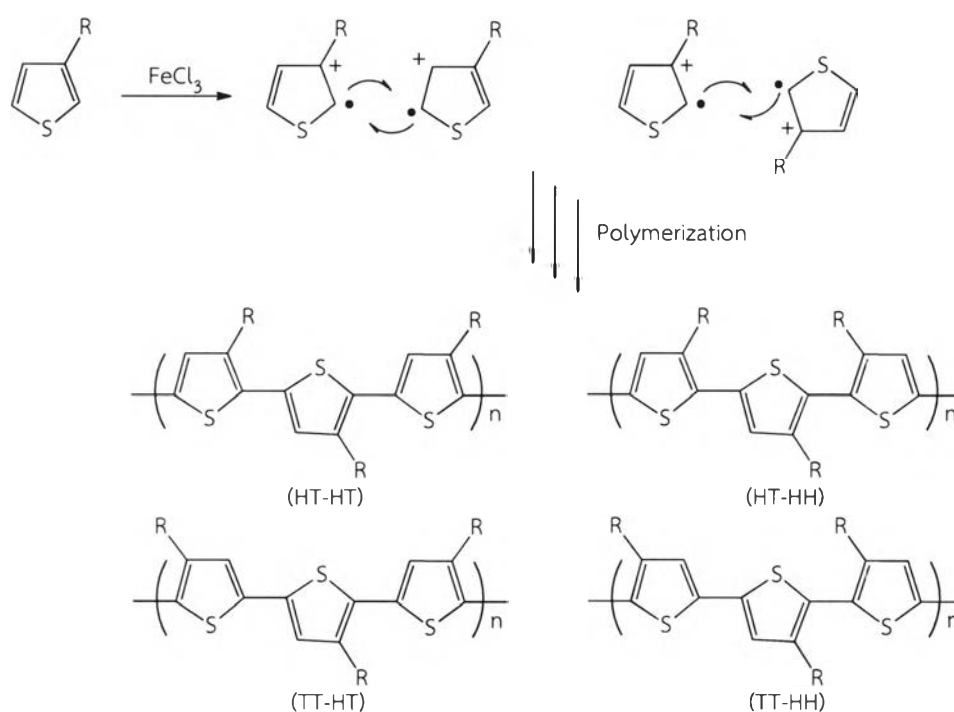


Figure 1.5 The oxidative coupling reaction of 3-alkylthiophene by FeCl_3

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 [27, 28] studied the polymerization mechanism and polymerization conditions, and found that a lower temperature and concentration were effective for increasing the HT coupling.

1.9.3 Grignard coupling and other chemical polymerization

Polymerization using a metal-catalyzed cross-coupling technique has been extensively investigated. The generally accepted mechanism of these reactions is 1) oxidative addition of an organic halide with a metal-phosphine catalyst, 2) transmetallation between catalyst and reactive organometallic reagent (or disproportionation) to generate a diorganometallic complex, and 3) reductive elimination of the coupled product with regeneration of the metal-phosphine catalyst. The synthesis of regioregular HT-P3AT was reported by McCullough and coworkers [29] in early 1992 (**Figure 1.6**). This synthetic method [30-33] regiospecifically generated 2-bromo-5-(bromomagnesio)-3-alkylthiophene which was polymerized with catalytic amounts of Ni(dppp)Cl₂ using Kumada cross-coupling methods to give P3ATs with 98-100% HT-HT couplings.

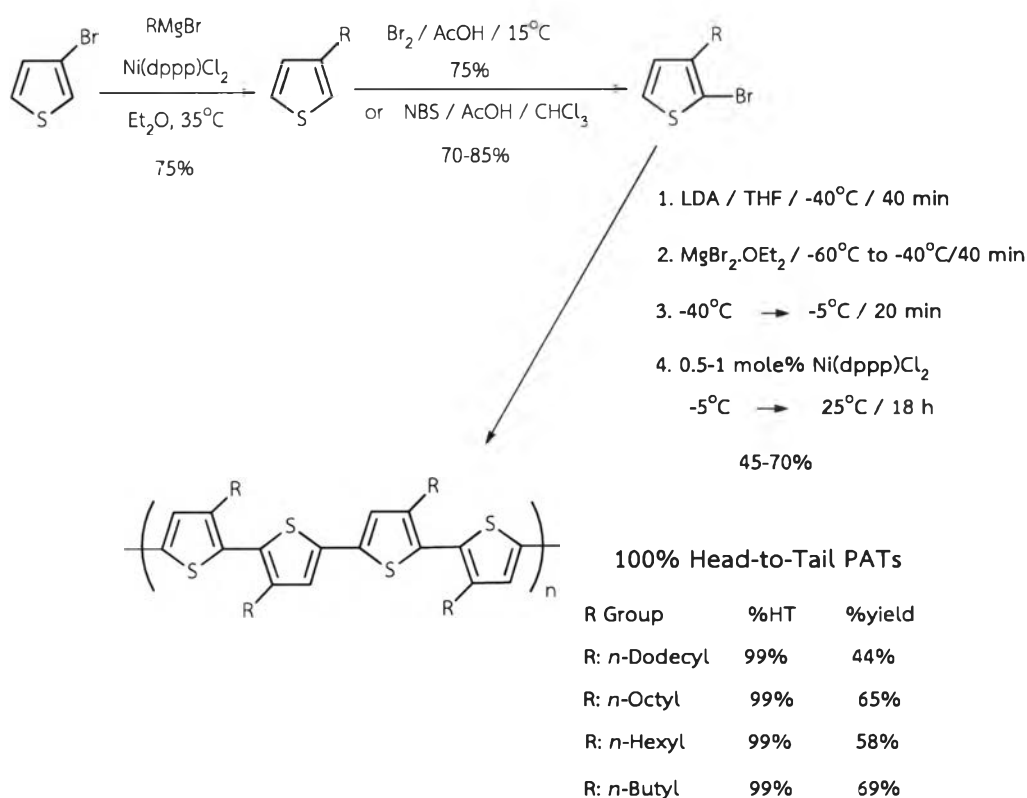


Figure 1.6 The McCullough method for the regiospecific synthesis of poly(3-alkylthiophene)

1.9.4 Solid state polymerization

The poly(3,4-ethylenedioxythiophene) (PEDOT) was prepared by traditional oxidative polymerization. Oxidative polymerization of 3,4-ethylenedioxythiophene (EDOT) with FeCl_3 in organic solvents gives an insoluble blue-black dope polymer powder. The limitations of oxidative polymerization method can be a serious problem for PEDOT applications as well as for in-depth investigation of molecular order in this conducting polymers. It is generally not possible to obtain a well-defined polymer structure. The synthesis of conducting polymers is carried out via pure chemical polymerization routes, without adding any catalysts. A possible solution for this lies in a solid-state polymerization (SSP) of a structurally pre-organized crystalline monomers. The idea of SSP of a suitable monomer in a well-ordered crystalline state was already realized in the 1960s and 1970s with polydiacetylenes and $(\text{SN})_x$. SSP is normally conducted between the glass transition temperature and the melting point [34]. SSP is a catalyst-free cross-coupling reaction without solvent. The SSP has many advantages: low costs, low operating temperature, which less side reaction, simplicity in process and environmental friendliness. At SSP low temperature, rate of reactions are slow compared polymerization in liquid phase because of the reduce mobility of the reacting species and the slow diffusion of the by-product [35].

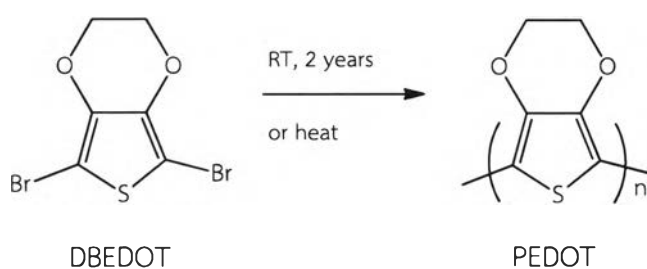


Figure 1.7 Solid-state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT)

Meng and coworkers [35, 36] reported the first solid-state polymerization of 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) to give PEDOT through an unprecedented catalyst-free cross-coupling reaction in solid state. This polymerization was discovered by chance as a result of prolonged storage (2 years) of the monomer

at room temperature or heating (50-80 °C) (**Figure 1.7**). The colorless crystalline DBEDOT transformed into a black material without apparent change of morphology. Surprisingly, the conductivity of this decomposition product appeared to be very high (up to 80 S/cm) for an organic solid. The most likely explanation for the observed transformation was polymerization with formation of bromine-doped PEDOT.

Meng and coworkers have continued to study solid state polymerization (SSP) of other dihalogen-substituted derivatives of 3,4-ethylenedioxythiophene (EDOT) (**Figure 1.8**), whose halogen atoms are Cl, Br or I, respectively. The polymerization results indicated that 2,5-dibromo-3,4-ethylenedioxythiophene (DBEDOT) was the most reactive monomer, and polymerization reaction occurred via radical cationic polymerization which electron donating group (3,4-ethylenedioxy group) enhanced the stability of cation intermediate (**Figure 1.9**) [35].

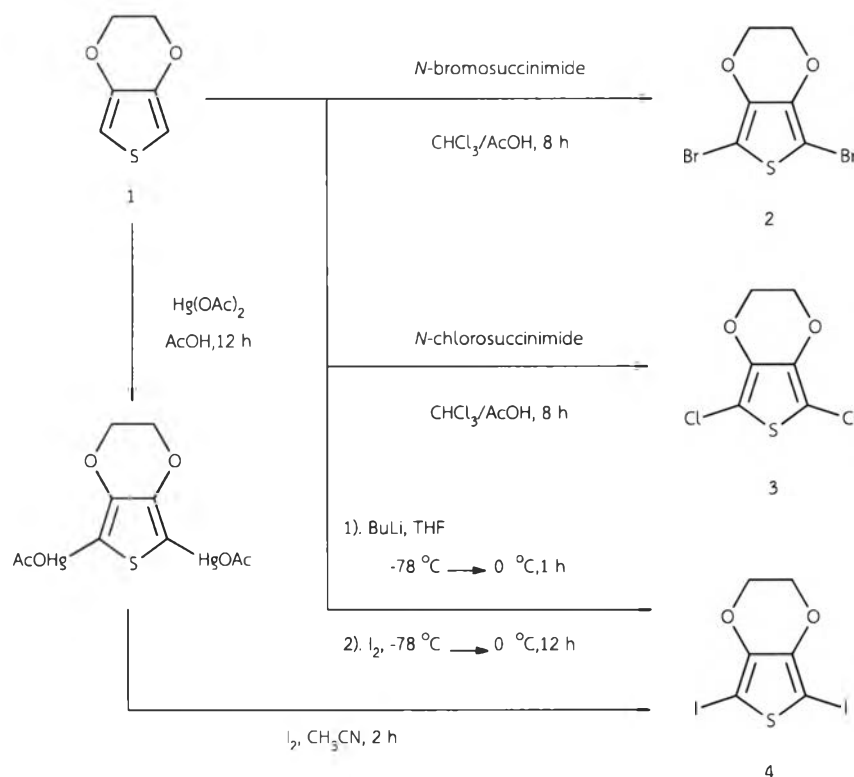


Figure 1.8 Synthesis of dihalo-3,4-ethylenedioxythiophene monomers

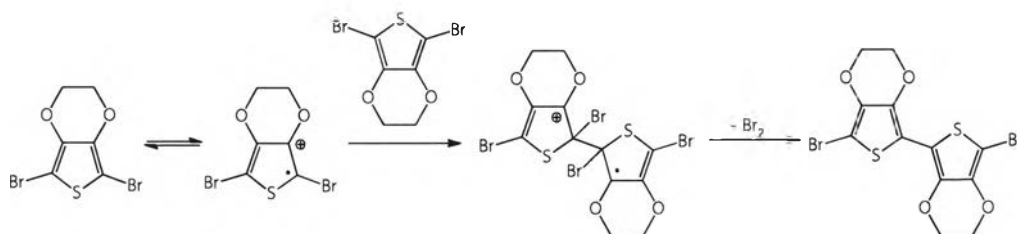


Figure 1.9 Mechanism of the initiation of SSP of DBEDOT

The highest conductivity belongs to the polymer prepared at lowest temperature and longest reaction time, which may reflect achievement of a higher degree of order. Indeed, heating above the monomer's melting point results in dramatically reduced conductivity (0.1 S/cm), which rises up to 5.8 S/cm after doping with iodine, approaching the value of an FeCl₃-synthesized PEDOT (7.6 S/cm). Not very significant, but certain increase in conductivity of SSP-PEDOT (about 2 times) was found on exposing a sample to iodine vapor.

Table 1.3 Conductivity data of SSP-PEDOT

	Conductivity (S/cm)			
Reaction temperature (°C)	20	60	80	120
Reaction time	2 years	24 h	4 h	24 h
Crystals/ fibers	80	33	20	-
Pellets as synthesized	30	18	16	0.1
Pellets after I ₂ -doping	53	30	27	5.8

From the report, they concluded that heating DBEDOT in the solid state gave high conductivity and relatively well ordered bromine-doped PEDOT. Polymerization of DBEDOT above the melting point lead to a lower conductive polymer. The temperature dependence of the conductivity of SSP-PEDOT reveals a semiconducting behavior. Highly conducting thin films of PEDOT can be easily fabricated using this method.

Based on the research as listed above, it seems that the shortage of suitable monomers and difficulty of making uniform conductive film further restricts SSP's wide

applications. Yin and coworkers [37] have found that PEDOT can be obtained by acid-assisted polycondensation from bromo-2,3-dihydro-thieno[3,4-*b*][1,4]dioxine (BEDOT) (Figure 1.9). Under the exposure to ambient atmosphere, the formed PEDOT is in doped state to some extent, showing poor conductivity of 10^{-6} S/cm while improved to 0.3 S/cm along with further iodine doping. Such finding provides another alternative for the synthesis of conjugated polymers through simple acid-assisted-polycondensation.

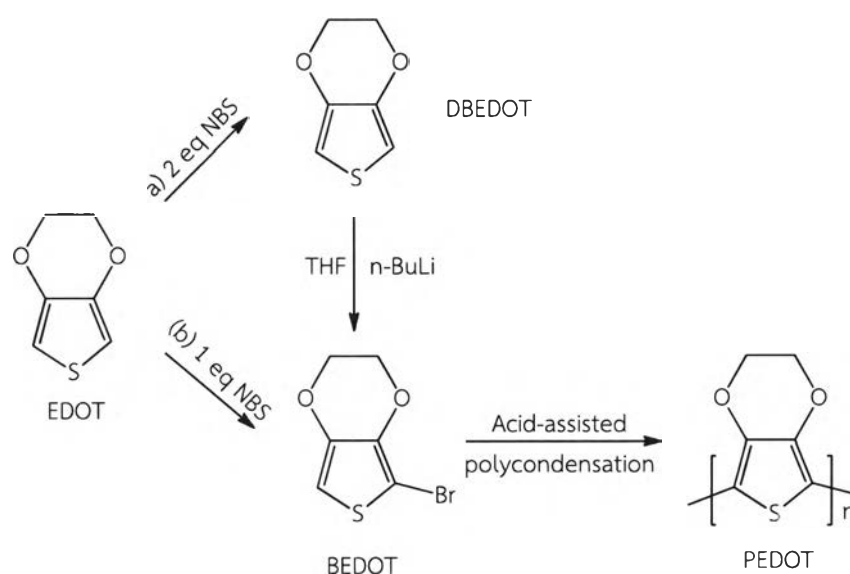


Figure 1.10 Synthesis of the monomer and polymer

Among the derivatives of polythiophene, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most successful conducting polymers because of its low bandgap, excellent environmental stability, high electrical conductivity and excellent optical transparency in the visible region. The ether groups at β, β' -positions of thiophene ring in PEDOT prevented the formation of $\alpha\text{-}\beta'$ linkages defect during polymerization. Substitution of thiophene ring by other substituents at β position could lead to improve solubility and conductive properties.

1.10 Literature reviews

Navarro and coworkers [38] have synthesized a novel hydroxysuccinimidyl ester derivative of EDOT and the bis-EDOT compound. Its co-electropolymerization with oligo(oxyethylene)diEDOT in potentiostatic condition in acetonitrile leads to a stable film. The use of this copolymer film for the immobilization of ferrocene-modified oligonucleotides (ODNs) probes shows a sensitive and selective DNA sensor. These results show great promise for the development of direct DNA hybridization electrochemical sensors.

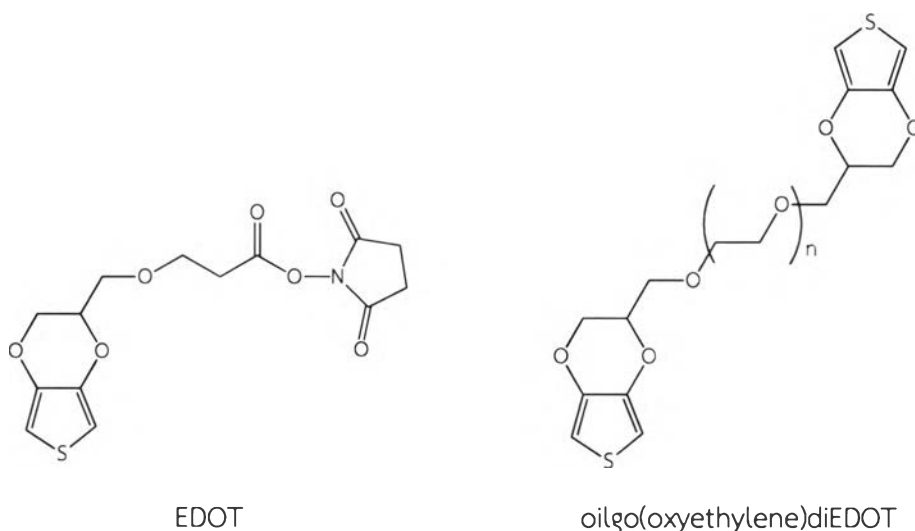


Figure 1.11 Structure of EDOT and oligo(oxyethylene)diEDOT

Leriche and coworkers [39] has been synthesized a 3,4-vinylenedioxythiophene (VDOT) by ring-closing metathesis. Its dimer was prepared using oxidative coupling of the lithiated derivative of VDOT. The X-ray data for dimer revealed a more compact crystal structure than that of BEDOT, consistent with stronger π -intermolecular interaction. This property associated with the higher oxidation potential of the dimer and its polymer, suggesting that VDOT-based extended π -conjugated systems should exhibit a better environmental stability than their EDOT analogs.

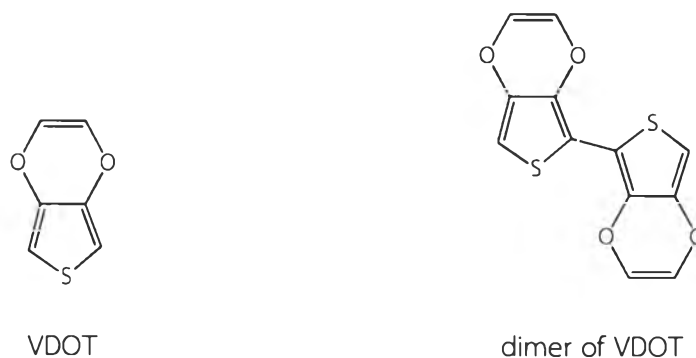


Figure 1.12 Structure of VDOT and dimer of VDOT

Su and coworkers [40] have performed the synthesis and electrochemical polymerization of a new EDOT-based monomer based on 3,4-ethylenedioxythiophene methanol (EDTM). The new monomer, named 3-((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy)propane-1-thiol (EDTMSHA) was developed from the structure of EDTM, in which the functional thiol group is connect to the EDTM hydroxyl group via an alkyl linkage. The new monomer successfully produced a self-assembled monolayer (SAM), which was deposited on a gold dis celectrode and the electrochemically polymerized. The SAM formation of the new conducting polymer films exhibited relatively low oxidation potentials with a well defined reversible and stable electrochemical behavior compared to conventional electropolymerized film.

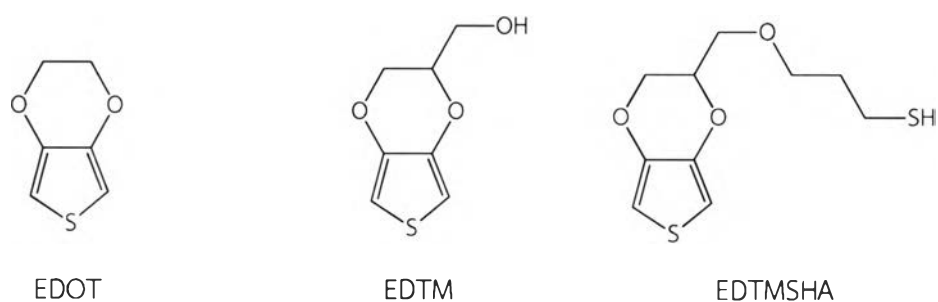


Figure 1.13 Structure of EDOT, EDTM and EDTMSHA

Dey and coworkers [41] reported the synthesis of 1,3-disubstituted 3,4-propylenedioxythiophene (ProDOT) derivatives, which exhibited excellent characteristics for electrochromic applications. Fine tuning of color was possible by simply changing the size of the substituents at the 1,3-position, which is one of the most important aspects of this system. The bulky substituents used were designed to increase the solubility of the polymers.

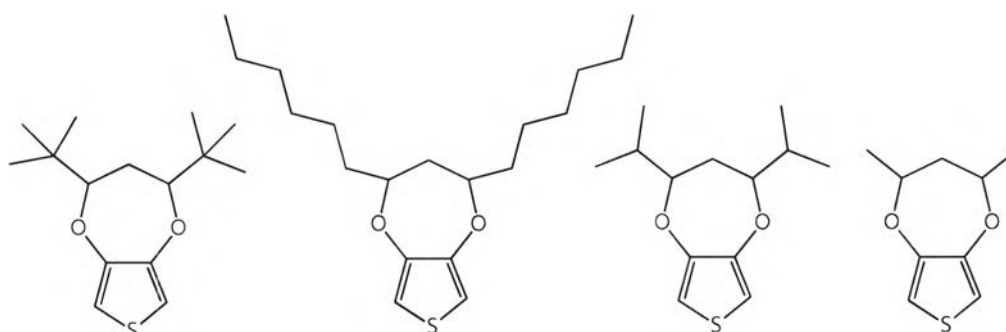


Figure 1.14 Structure of 1,3-disubstituted ProDOT derivatives

Oskan and coworkers [42] have synthesized 3,4-vinylenedithiathiothiophene (VDTTs) and dithieno[2,3-b;2',3'-d]thiophenes (DTTs) derivatives, which were achieved through the reaction of 1,8-diketone with phosphorus decasulfide (P_4S_{10}). The reaction could be shifted between VDTT and DTT by adding base or acid. While acidic conditions favour the formation of the DTT in high yields, use of a basic medium selectively leads to the production of VDTT in moderate yield. Polymers of the VDTTs were prepared using $FeCl_3$. Unfortunately, all attempts for their electropolymerization failed. Considering their good physical properties, solubility and various functional groups, which could be further derivatized. They are useful building blocks for the preparation of new organic materials.

Zhao and coworkers [43] reported a method to synthesize various substituted dioxothiophenes bearing ProDOT and EDOT by C-H arylation polycondensation approach. This approach is step economical because it does not require the preparation of organometallic intermediates. It is also more environmental-friendly due to the reduction of toxic byproduct waste. The resulting materials are promising

for applications including organic electronics and conductive nanobiointerface with cells.

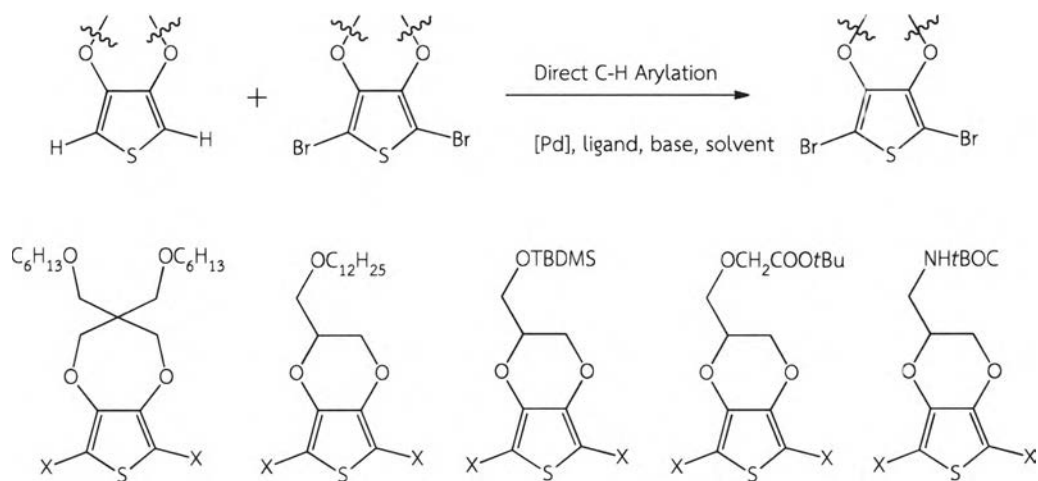


Figure 1.15 Synthesis of polydioxithiophenes by direct C-H arylations

Chen and coworkers [44] have researched on the synthesis, chemical oxidative polymerization of 3,4-ethylenedithiathophene (EDTT) and solid-state polymerization of 2,5-dibromo-3,4-ethylenedithiathophene (DBEDTT) and 2,5-diiodo-3,4-ethylenedithiathophene (DIEDTT) under solventless and oxidant-free conditions. As-formed poly(3,4-ethylenedithiathophene) (PEDTT) synthesized from SSP showed similar electrical conductivity, poorer stability, but better thermoelectric property than oxidative polymerization. Contrastingly, PEDTT synthesized from DIEDTT showed higher electrical conductivity (0.18 S cm^{-1}) than DBEDTT which showed better thermoelectric property with higher power factor value.



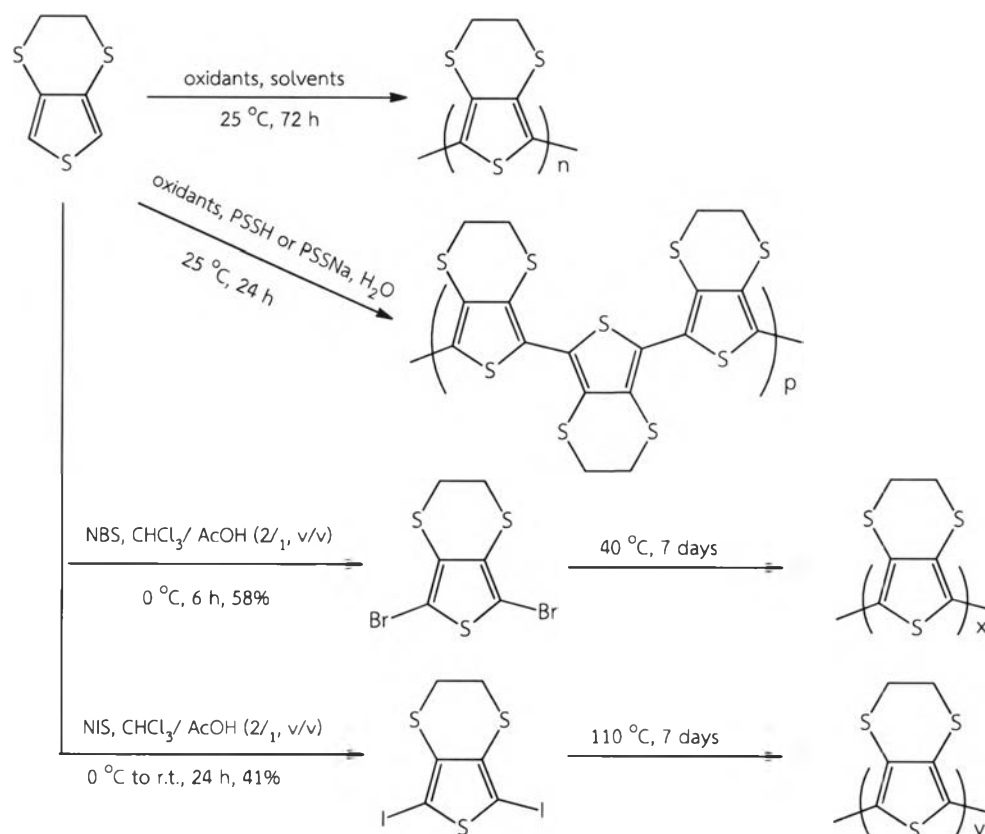


Figure 1.16 Chemical oxidative and solid-state polymerization of EDTT

Yin and coworkers [45] reported the high-performance Pt-free counter electrode (CE) based on PEDOT film for plastic dye-sensitized solar cell (DSCs). PEDOT has been synthesized via a facile solid-state polymerization using DBEDOT as the monomer. The optimal SSP-PEDOT CE-based rigid and plastic DSC presented a power conversion efficiency of 7.04% and 4.65%, respectively, which are comparable with the values obtained from the devices based on a thermally deposited Pt (7.35%) and sputter-deposited Pt CE (5.38%). The superior performance indicates that PEDOT film synthesized a low-temperature SSP is a promising CE material for high-performance Pt-free plastic DSCs.

Poly 3,4-ethylenedioxythiophene (PEDOT) represents a class of conducting polymers. It has become one of the most successful conducting polymers due to a combination of properties such as moderate band gap, low oxidation potential, high conductivity, good optical transparency, ease of derivatization with various functional

groups and exceptional environmental stability. Despite all these advances, there is still a major problem for PEDOT on its insolubility, leading to difficulties in fabrication process. Thus derivatization of thiophene ring by other substituents at the β positions could lead to higher solubility and improved physical and chemical properties. In some attempts to solve this problem, new monomers were synthesized by functionalization of thiophene derivatives carrying other functional groups. An alternate approach to obtain derivatized polymer with high conductivity is the well-ordered polymer synthesis or polymerization of a structurally preorganized crystalline monomer (SSP). This research will aim at functionalization of thiophene derivatives and the synthesis of new polythiophene will be attempted from these monomers through SSP or other polymerizations for improved electronics and processability.

1.11 Objective

The goal of this project emphasizes the synthesis of a new series of 3,4-dialkoxythiophene derivative monomers and study the processes of polymerizations of thiophene derivative monomers through the solid-state polymerization or the traditional oxidative coupling polymerization, expecting extended conjugation length in the resulted polythiophene chain and improved conductivity and optical properties of polythiophene.

