

## CHAPTER I



### INTRODUCTION

#### 1.1 Conducting Polymer as a Growing Class of Electronic Materials

A key property of most polymers, which distinguishes them from metals, is their inability to carry electricity. In fact, the insulating properties of polymers are a significant advantage for many applications of plastics. Electrical wires, for example, are protected from shorting by coating of insulating polymer. It is a general view that plastics and electrical conductivity are mutually exclusive. During the past 15 years, however, a new class of organic polymers has been devised with the remarkable ability to conduct electrical current. Parts of a larger class of materials are called "synthetic metals". An electrically conducting polymer has properties of both conductors and plastics, it may also have other characteristics such as electro-activity and non-linear optical properties. Such a material may avoid problems with metal and inorganic semiconductor and find extensive application in the electronic industries. Some of these conductive plastics are already under development for

practical applications, such as rechargeable batteries, electrolytic capacitors and "smart windows" that absorb sunlight in summer [1].

In the early 1970s, a key discovery in the evolution of conductive polymers was the high conductivity of polysulfurnitride,  $(SN)_x$ , an inorganic explosive polymer, which becomes superconducting at about 0.3 K. This was the first polymeric material that was shown to have metallic properties. These discoveries were of particular importance because they proved the existence of highly conducting polymers and stimulated the enormous amount of work necessary to synthesize other polymeric conductors. In the late 1970s, many researchers directed their interests to organic conductive polymers because they believed these materials probably could be processed using conventional plastic technology.

The term of organic electrical polymers originated with the discovery of polyacetylene. The most important structural feature of polyacetylene is its highly conjugated carbon backbone composed of an array of alternating single and double bonds. However, pristine polyacetylene is an insulating or semiconducting material, but its electrical conductivity increases to the metallic regime simply by electron-acceptor or electron-donor doping. It is the doping reactivity of the  $\pi$ -electron conjugated system which induces

such unique electronic conductivity in polyacetylene. Since the conjugated backbone holds the key to higher conductivity, therefore, based on similar fundamentals, a large number of organic conducting polymers have been generated in the 1980s. Organic polymers which have been looked upon for decades as insulators in the electronic industries have emerged as a new class of electronic material. Some of the important polymers of the conducting family are polyacetylene, polyaniline, polypyrrole, polythiophene, poly(p-phenylene), poly(p-phenylene sulfide), poly(p-phenylene vinylene), heteroaromatic ladder polymer, etc. The electrical conductivity of these conjugated organic polymers can be varied over a very wide range by chemical or electrochemical doping, thus making it possible to consider them for a variety of electronic applications. However, polyacetylene is the most extensively organic polymer, it lacks practical potential due to its instability under ambient condition, in particular polypyrrole and polythiophene are another classes of synthesis and architectural flexibility for appropriate chemical modifications. Further, these polyheterocyclics, polypyrrole and polythiophene, can be switched between conducting (oxidizing) and nonconducting (neutral) state; therefore, it is "straight-forward" and easy to control their electrical and optical properties. The electrical behavior of these polymers is strongly influenced by the presence of counter-anion, solvent etc., in the conducting state [2].

High electrical conductivity and the stability of conducting polymers seem especially important for applications of the material [3]. It has been discovered, however, that most of the reported conducting polymers are unstable in air except those containing nitrogen or sulphur atoms in the polymer backbone, such as doped polypyrrole, polythiophene and polyaniline as well as their substituted analogues. Theoretical study has indicated that the heteroatoms in these polymers could form  $\sigma$  bonds with carbon atoms in the conjugated chain, and the non-bonded electron pairs in p-orbitals of heteroatoms could also interact with  $\pi$  bonds of the conjugated chain. Consequently, heteroatoms such as N or S might be beneficial to the stabilization of doped conjugated polymers. On the other hand, polypyrrole, polythiophene and polyaniline all show some basic behaviour because of the presence of the heteroatoms, and the effective dopants for those polymers were correspondingly lewis acid (electronic acceptors). The doped conducting polymers may actually be regarded as acid-base complexes. Therefore, it appears to be appropriate to choose an electronic donor (or basic) polymer in order to obtain a stable conducting polymer complex. The carriers generated by the doping of polymer result from charge transfer. Charge transfer occurs from polymer to acceptor, with polymer chain acting as a polycation in the presence of  $A^-$  species. For a donor, the polymer chain acts as a polyanion in the presence of  $D^+$  species. The  $A^-$  or  $D^+$  ion called

"counterion" that resides between polymer chains [4-5].

A counterion (in this case an anion,  $A^-$ , typically termed a dopant anion) stabilizes the charge on the polymer but is not very mobile within the dry material. The conductivity of these oxidized organic polymers is p-type, when compared with semiconductors, indicating that the mobile species are positive carriers. Similar processes can occur upon chemical or electrochemical reduction. The anions on the conjugated polymer chain are now mobile, and the polymer is an n-type electrical conductor [6].

## 1.2 Summary of Polymer Properties

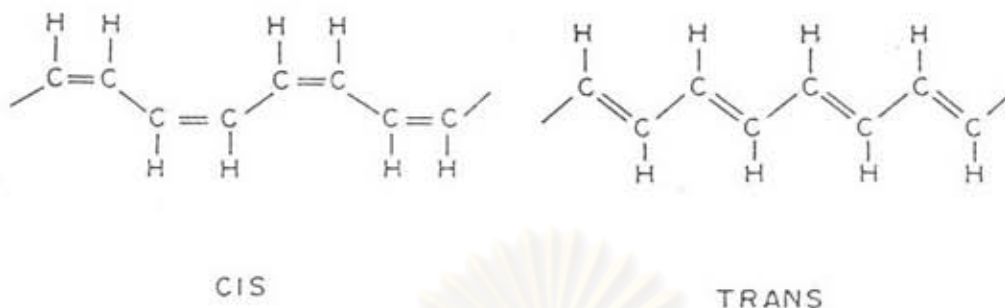
### 1.2.1 Polyacetylene

polyacetylene is the simplest conjugated conducting polymer and is therefore of special fundamental interest in the context of above discussion, although neutral conjugated organic polymers are generally insulating materials or sometimes semiconductor [7]. Electrons cannot move along polymer chain and through materials because of the lack of charged carriers and also the different bond lengths along the polymer chain. The unsaturated bonds which characterize the polymers have an important effect on their electronic structure and the corresponding electronic properties. In a polyene (Scheme 1.1) three of the four



carbon valence electrons are in  $sp^2$  hybridized orbital; two of the  $\sigma$ -type bonds are links in the backbone chain while the third forms a bond with some side group ( e.g. H in Scheme 1.1). The remaining valence electron has symmetry of the  $2p_z$  orbital and forms a bond in which the charge density is perpendicular to the plane of the molecule. In term of an energy-band description , The  $\sigma$  bonds form low-lying completely filled bands, while the  $\pi$  bonds would correspond to a half-filled band. The  $\pi$  bond could be metallic provided there is negligible distortion of the chain , and an independent-particle model proved to be satisfactory.

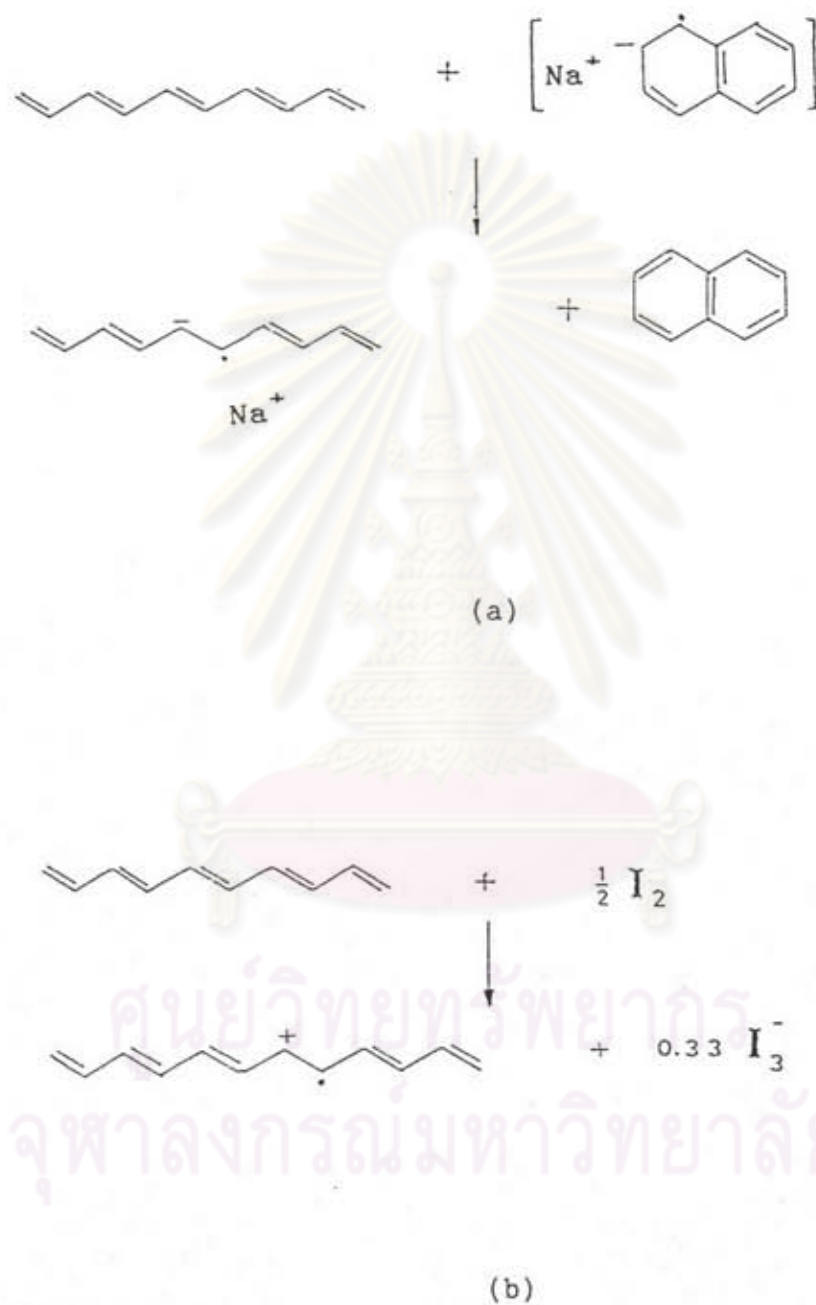
Polyacetylene has two structure forms, trans and cis . The trans type is thermodynamically more stable. When doped, its conductivity is highest along the chain. Any cis : trans ratio can be maintained at low temperature , but complete isomerization from cis-to-trans- $(CH)_x$  can be accomplished after synthesis by heating the film to temperature above  $150^\circ C$  for a few minutes to more extended time periods. It can also be prepared in pure trans form at room temperature [4].



Scheme 1.1 Molecular structure of cis and trans isomers of polyacetylene,  $(CH)_x$

The doping process that transforms polyacetylene from an insulator to a good conductor is ordinary oxidation process, called p-doping. This means that the electrical properties of polyacetylene and other similar polymers can be manipulated by chemistry. Reductive doping called n-doping is also possible by using, for example, alkali metals. But it has been found that the resulting conductive polymers are more sensitive to air and the conductivities decay faster with time [7].

In the doped form, the polymer backbone is either positively or negatively charged, and the small counterion, "dopants", such as  $I_3^-$  or  $Na^+$ , act as simple bystanders that do not directly influence the electrical properties (Scheme 1.2) [1]. The radical ions, on the other hand, are delocalized over a certain portion of the

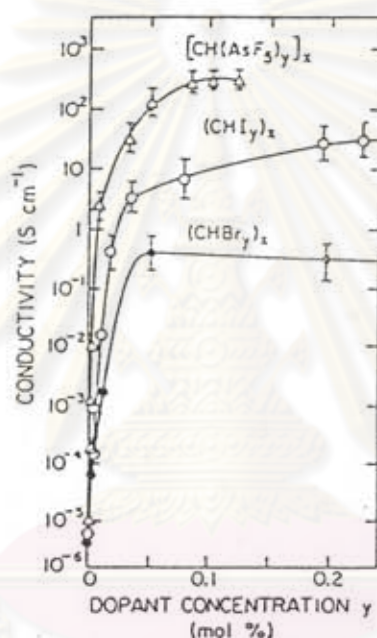


Scheme 1.2 (a) n-doping of polyacetylene with sodium naphthalide

(b) p-doping of polyacetylene with iodene



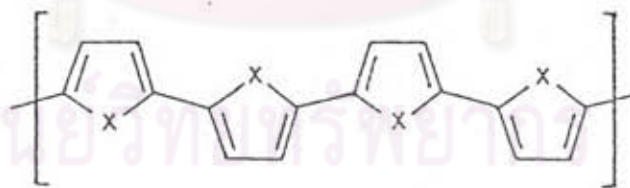
polymer backbones . These radical ions are the charge carriers for the conduction process . The electrical conductivity of polyacetylene can be varied over 15 orders of magnitude through chemical or electrochemical doping [4].



Scheme 1.3 Electrical conductivity of doped trans-(CH)<sub>x</sub> film as a function of dopant concentration

### 1.2.2 Polypyrrole

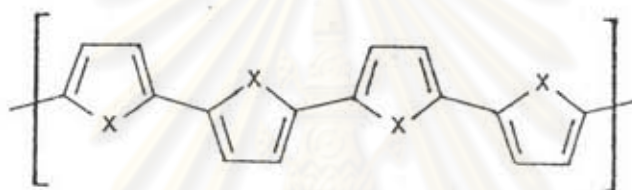
Among the conducting polyheterocyclics, the most intensively studied polymers are polypyrrole [8-9], polythiophene and their derivatives. Polypyrrole was shown to be a conducting polymer in 1968 [4]. It was prepared by oxidation of pyrrole in sulfuric acid. The synthesized polypyrrole was a black powder with room temperature conductivity of  $8 \text{ Scm}^{-1}$ . Polyheterocyclics are another class of electroactive polymer which are thermally and environmentally more stable. The five membered ring heterocycles of pyrrole and thiophene polymerize through  $\alpha, \alpha'$ -coupling (2, 5 - position) and both polymers are structurally similar, their molecular structures are shown in Scheme 1.4.



Scheme 1.4 Polypyrrole ; X = NH and Polythiophene ; X = S

The electrophysical properties of these polyheterocyclics are determined by a variety of factors such as the degree of polymerization, nature of dopants and the heteroatom which incorporated into the  $\pi$ -conjugated

system of carbon atoms. By changing the heteroatom from  $X = S$  (polythiophene) to  $X = NH$  (polypyrrole), the band gap changes from 2.0 eV to 3.2 eV respectively. However, the effect of heteroatom on electrical properties of these polyheterocyclics may not be of that significance because electrical behavior of these highly conjugated polymers was governed by the polymer chain length since defect occur along the  $\pi$ -conjugated system of carbon atoms [10].



(a)



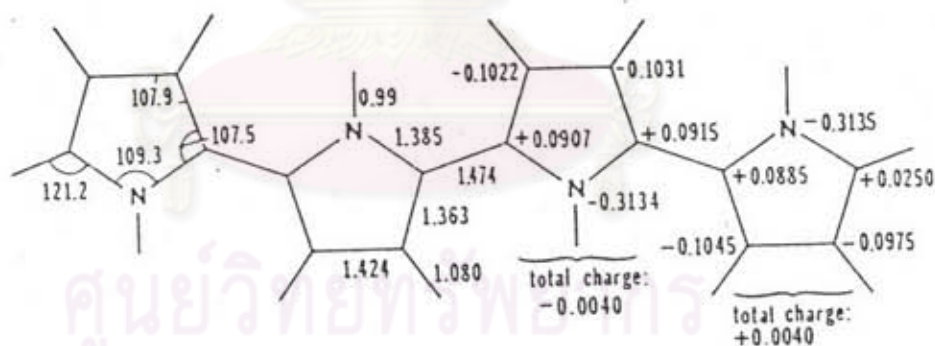
(b)

$X = NH$ , polypyrrole and  $X = S$ , polythiophene

Scheme 1.5 (a) Chemical structure diagram of the polymer  
(b) Two inequivalent structures of the polymer

Polymers such as polypyrrole, polythiophene are of current theoretical interest since the two structures sketched in Scheme 1.5 (b) are not energetically equivalent. Thus, the coupling of electronic excitations to chain distortions (inherent in such linear conjugated polymers) will lead to polarons and bipolarons as the dominant charged species.

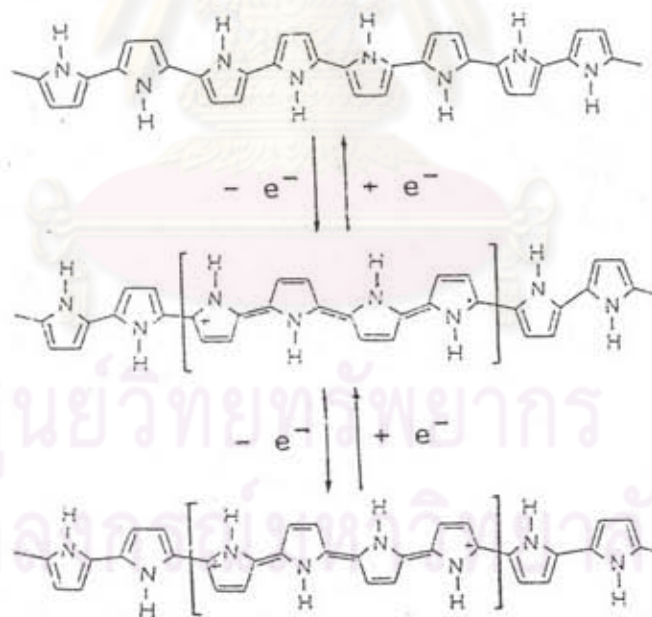
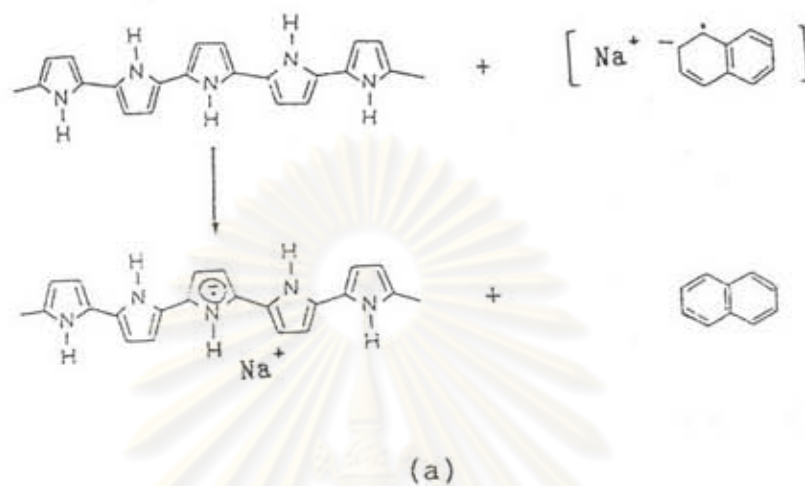
For undoped polypyrrole, the optimized geometry and the charges on C and N atoms are given in Scheme 1.6. The bond connecting rings is larger ( $1.474 \text{ \AA}$ ) than those inside rings, the maximum C-C or C-N bond-length difference is  $0.111 \text{ \AA}$ . Total net charges per ring are negligibly small [11].



Scheme 1.6 The optimized geometry of undoped polypyrrole (bond lengths in  $\text{\AA}$ , bond angles in degree) and carbon, nitrogen atomic charge

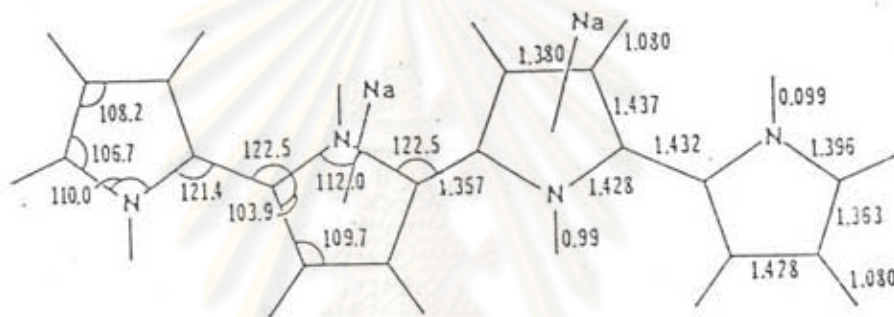
In undoped polypyrrole, electrons cannot move along polymer chain because of the lacking of charged

carriers. We must introduce mobile charge carriers to make these polymers electrically conductive.

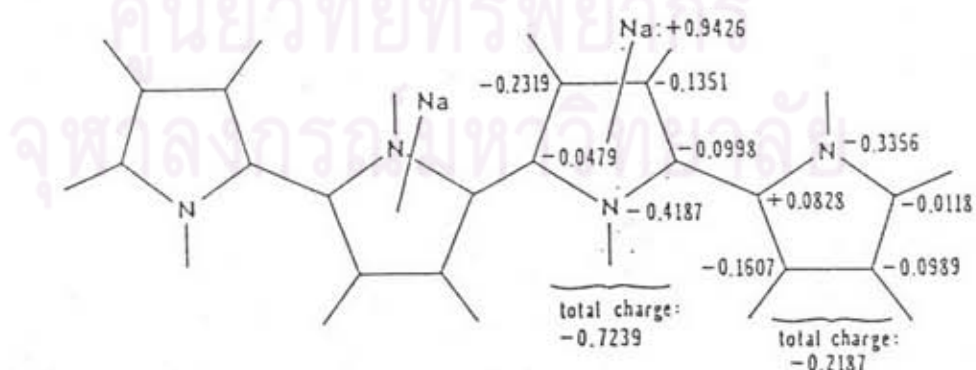


Scheme 1.7 (a) n-doping of polypyrrole with reducing agent  
(b) p-doping of polypyrrole with oxidizing agent

In the n-doping, added sodium atoms to the polypyrrole chain, each sodium atom which located approximately above the middle of inner ring are found 1.98 Å above the plane of an inner rings, at 2.25 Å from the nitrogen and 2.33 Å from the carbons. The charge transfer is predicted to be almost complete, about 0.94 electron per sodium atom (see Scheme 1.8 and 1.9) [8].



Scheme 1.8 The optimized geometry of sodium-doped polypyrrole (bond lengths in Å, bond angles in degree)



Scheme 1.9 Carbon, nitrogen, and sodium atomic charge of Na-doped polypyrrole

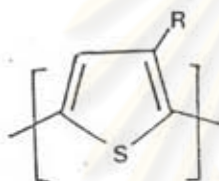
For p-doping the optimized geometry will be described in detail in the section 1.4 .

### 1.2.3 Polythiophene

Polythiophene can be viewed as an  $sp^2p_z$  carbon chain in a structure somewhat analogous to that of  $cis-(CH)_x$ , but stabilized in that structure by the sulfur, which covalently bonds to neighboring carbons to form the heterocycle. The sulfur may also increase the interchain coupling through d-orbital overlap and thereby improve the interchain electron transfer necessary for conductivity. After p-doping , polythiophene is relatively stable in air, due to the resonance effect of the sulfur which acts to stabilize a carbonium ion on the polymer chain. At the present time , polythiophene has been extensively studied and because the thiophene monomer can be 3-substituted , a large family of polythiophene derivatives with remarkable properties has emerged [12].

Derivatives have been synthesized for obtaining a lower energy band gap and possibly intrinsically conducting polymers. However, substitution of long chains in the polymer backbone would seriously affect its conductivity by affecting the planarity of the backbone and interfering with the electron transport between polymer

chains. Indeed, the conductivities of the long chain substituted polythiophene were lower than those of the parent polymer, but the loss in conductivity was not dramatic and it was well compensated by the acquired solubility. Poly(3-methylthiophene) show in Scheme 1.10 obtained by the substitution of long alkyl chains  $n \gg 4$  in the  $\beta$ -position of the polythiophene ring were soluble in common organic solvent [13].



R = butyl

= hexyl

= isosanyl etc.

Scheme 1.10 Organic solvent soluble poly 3-alkylthiophene

### 1.3 Preparation of Conducting Polymers

The field of synmetals remains an active area for fundamental research in experimental and theoretical solid-state physics as well as organic and polymer synthetic chemistry. The variety of new conducting polymeric solids have been continuously discovered. The area of synthesis is extremely fast moving and competitive.



Here, they summarize the major types of synthetic techniques used to prepare polypyrrole [14].

- i) electrochemical polymerization
- ii) chemical vapor deposition (CVD)
- iii) chemical polymerization

### 1.3.1 Electrochemical Polymerization

Electrochemical synthesis of polymer compound has a long history. These polymer compounds are obtained by anode oxidation or cathode reduction of a monomer that is involved in an electrolytic solution together with supporting electrolyte. This technique was for the first time applied to oxidation electrochemical synthesis of conductive polymer, i.e., polypyrrole by Dall'Olio et al. in 1968. This technique was further developed by Diaz et al. in 1979 to obtain polypyrrole of much higher conductivity as high as  $100 \text{ Scm}^{-1}$ . [quoted in 15] Once such a high conductivity polypyrrole is formed on the anode, the surface of the polypyrrole film can operate as an electrode. Thus, polypyrrole can be deposited successively on the anode to form a free-standing film.

After these works , many investigations were carried out to synthesize a variety of conductive polymers electrochemically. In particular, a class of conductive polymers, e.g., polythiophene and its derivatives together with polypyrrole and its derivatives [17-18], which composed of five-membered heterocycles as constituent units have been synthesized through electrochemical polymerization of the corresponding five-membered heterocyclic monomer compound. Since the  $\alpha$ -position (2- and 5-positions) of these five-membered heterocyclic compounds are highly reactive compared with other positions, these compounds are readily oxidized electrochemically and the heterocycles are linked to one another at  $\alpha$ -positions through dehydrogenation on these positions . Finally , polyheterocycles are obtained from successive dehydrogenation condensation. The resulting polymers are highly conducting by in-situ doping with anion species of the supporting electrolyte during the electrochemical synthesis of these polymers.

The electrochemical process gives rise to pure and relatively high molecular weight polymer, but it has the major drawback of having a low yield.

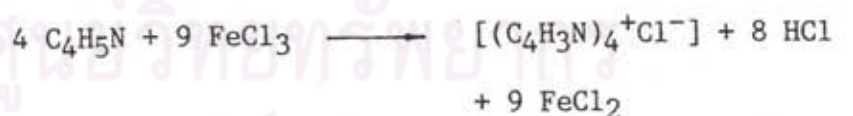
### 1.3.2 Chemical Vapor Deposition [19]

In 1986 , Takeaki Ojio and Seizo Miyata synthesized the conducting composite films of polypyrrole, which can be prepared by exposing polymeric matrix films containing ferric chloride to pyrrole vapor. The composite films are, moreover, highly transparent under the appropriate preparation condition . In that communication , the conductivity and the transparency of polypyrrole composite films by the gas state polymerization was discussed.

Poly(vinyl alcohol) was used as a polymeric matrix.  $\text{FeCl}_3$  was an oxidizing agent for the polymerization. After dissolving PVA and  $\text{FeCl}_3$  in the water, the solution was casted on a poly(ethylene terephthalate) film substrate. The preparation of polypyrrole-PVA composite films was carried out in a desiccator at  $-15\text{ }^\circ\text{C}$  by exposing PVA films containing  $\text{FeCl}_3$  on the PET film to the pyrrole and  $\text{H}_2\text{O}$  vapours which had been deoxygenated sufficiently. The polymerization period was from 30 min to 24 h. The composite films were then dried under vacuum at room temperature. At optimum condition , the composite film shows about  $10\text{ Scm}^{-1}$  conductivity.

### 1.3.3 Chemical Polymerization in Solution

The synthesis of conducting polymer via chemical method is less popular, even though this method allows a simple preparation of large quantities, more convenient and economical. The majority of the chemical synthesis method involves the polymerization and oxidation with oxidative transition metal ions, for example,  $\text{FeCl}_3$ ,  $\text{AgNO}_3$ ,  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{Cu}(\text{NO}_3)_2$  or  $\text{Cu}(\text{NO}_3)_2\text{-AlCl}_3$  over more, the use of other oxidants such as acid, halogens and organic electron acceptors have also reported [20]. Considerable chemical compositions and reaction stoichiometries for polypyrrole complexes were synthesized from  $\text{FeCl}_3$ , based on the observed chemical compositions of the complex, particularly the  $[\text{Cl}]/[\text{N}]$  ratio. At present time two reaction stoichiometries have been proposed.



[21]

and



[14]

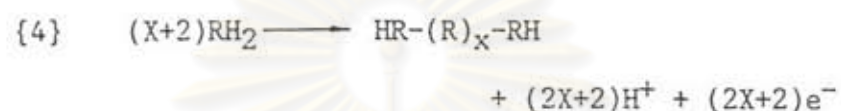
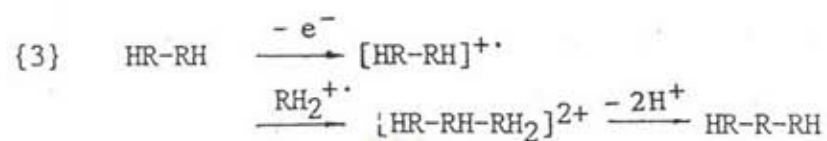
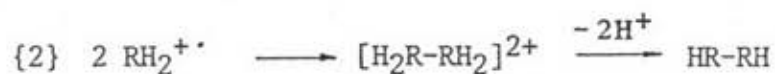
Recently, polypyrrole obtained from chemical polymerization in solution can exhibit very high electrical conductivity when a suitable solvent is selected and the oxidation potential in the solution is controlled.

#### 1.4 The Polymerization Reaction [2,22]

##### 1.4.1 Radical-Cation Coupling

When a molecule (R) is oxidized to its radical cation ( $R^{+\cdot}$ ), these monomeric radical cations can undergo a variety of follow-up reactions depending upon their intrinsic stability. When  $R^{+\cdot}$  is relatively stable, it can react to form a low molecular weight soluble product. If  $R^{+\cdot}$  is very unstable, it can rapidly undergo indiscriminated reactions with either the solvent or anions to form low molecular weight, and thus soluble, products equally well. Between these two stability ranges (which vary depending on the nature of  $R^{+\cdot}$ ),  $R^{+\cdot}$  can undergo dimerization reactions, these reactions are thought to proceed by the coupling of two radical cations. In general, then, the polymerization reaction for a molecule can be summarized by equation {1}-{4}. Equation {1}-{3} describe the step by step polymerization reaction of a monomer,  $RH_2$ , while equation {4} represents the overall polymerization reaction.


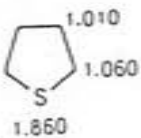
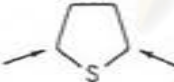
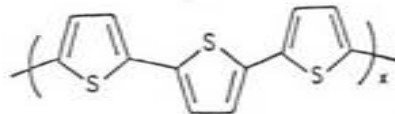
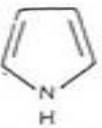
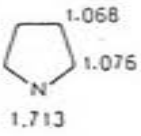
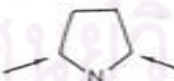
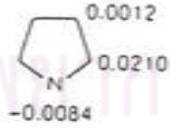
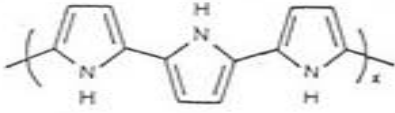


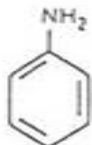
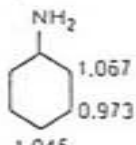
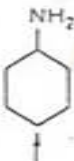
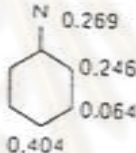
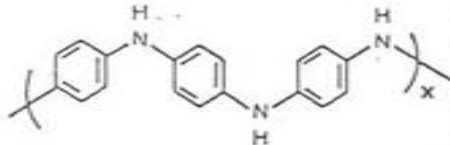
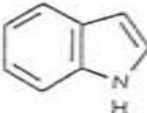
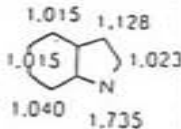
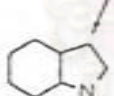
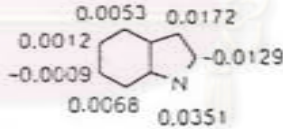
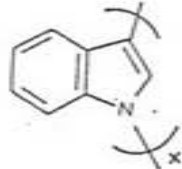

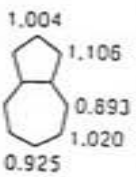
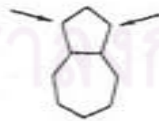
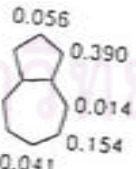
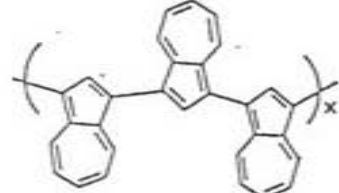


#### 1.4.2 Structure-Reaction Correlation

The oxidation of pyrrole gives rise to polypyrrole which the monomer units are linked primarily via their  $\alpha, \alpha'$ -position, based upon the high selectivity of pyrrole undergoing electrophilic substitution at the  $\alpha$ -positions [2]. The radical coupling of  $\text{R}^{+\cdot}$  to the oligomeric radical cations depends upon the unpaired electron distribution in the oligomer radical cation, which could be different from that of the monomeric  $\text{R}^{+\cdot}$ . Depending upon the unpaired electron distribution, nonregular linkages may occur. Thus, only unpaired electron distribution of monomeric  $\text{R}^{+\cdot}$  would be adequate for consideration which is summarized in Table 1.1. The  $\alpha$ -position of the neutral monomer has the highest  $\pi$ -electron density. Accordingly, it would be the most reactive at these positions. Thus, the primary reactive

Table 1.1 The  $\pi$ -electron density and the unpaired electron density of neutral and cation monomers and idealized polymer structures

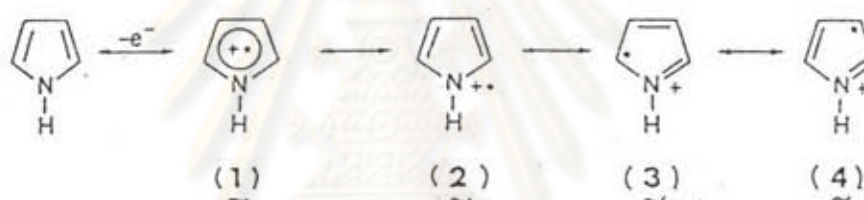
Compound	$\pi$ -Electron Density	Primary Electrophilic Reactive Site(s)	Unpaired Electron Density of Radical Cation	Idealized Polymer Structure
				
				

Compound	$\pi$ -Electron Density	Primary Electrophilic Reactive Site(s)	Unpaired Electron Density of Radical Cation	Idealized Polymer Structure
				
				
				



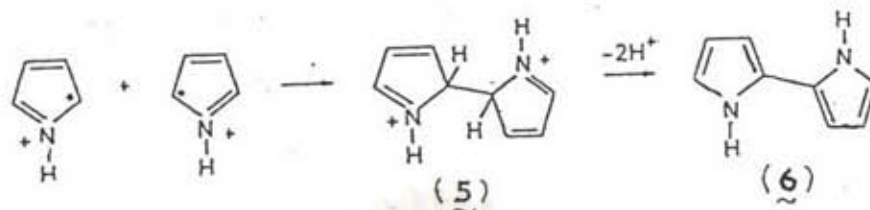
sites are the  $\alpha$ -positions.

From the molecular orbital calculations reveal that, the delocalized pyrrole monomer radical cation (1) has the highest unpaired electron density at its equivalent  $\alpha$ -positions (Scheme 1.13) Thus, among the resonance forms (2)-(4) shown in Scheme 1.11, (3) is the most important. Accordingly, when two monomeric pyrrole radical cations dimerize, radical coupling can be expected

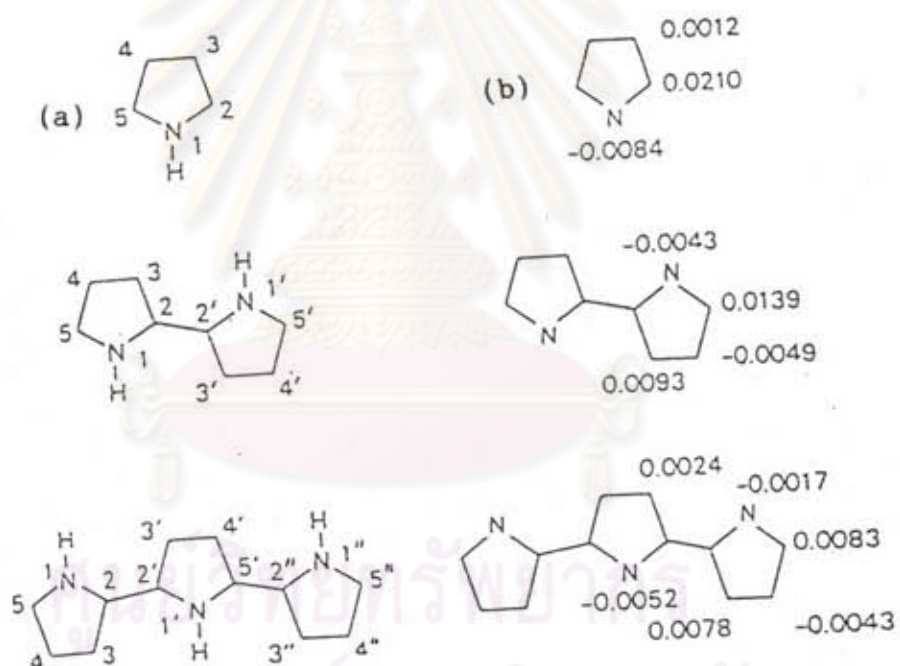


Scheme 1.11 The delocalized pyrrole monomer radical cation

to occur at the  $\alpha$ -positions. Indeed, dimerization to the dihydrodimer di-cation (5) (Scheme 1.12) proceeds with great facility, followed by loss of two protons to yield the neutral 2,2 dimer (6). The driving force for deprotonation among other things is the stabilization by return to aromaticity.



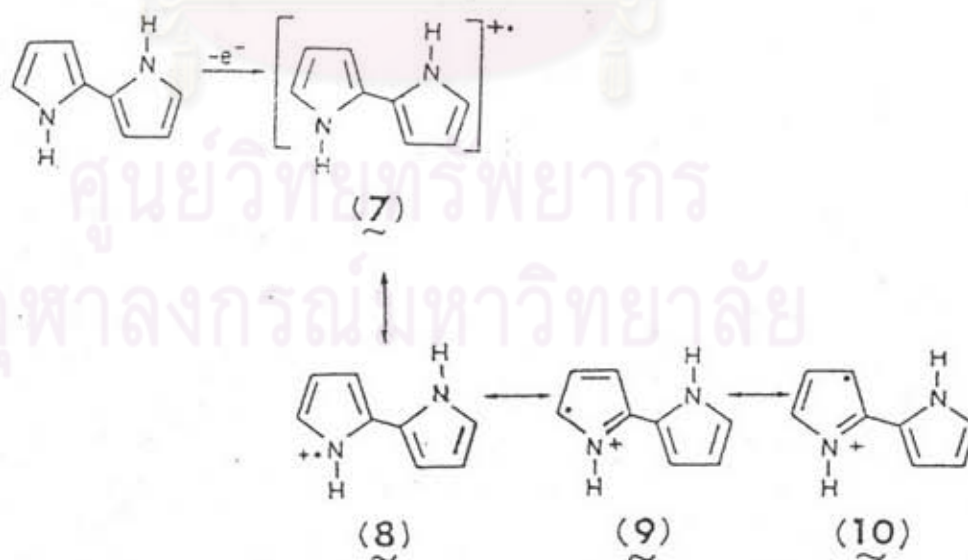
Scheme 1.12 Show radical coupling at the  $\alpha$ -position



Scheme 1.13 (a) The numbering Scheme for pyrrole oligomers.

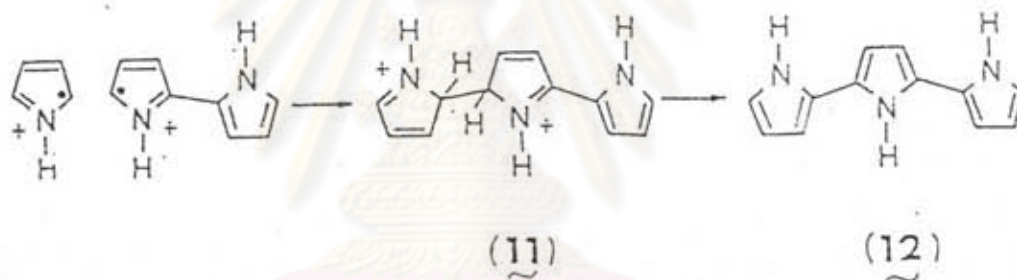
(b) Unpaired electron distribution of pyrrole, coplanar *anti* 2,2 -bipyrrole, and 2,2 :5 ,2- tri-pyrrole radical cation

Since the loss of an electron is now accommodated by two monomer units, the oxidation potential of (6) is lower than that of the monomer. The unpaired electron distribution of the coplanar *anti* form (7) is given in Scheme 1.13. As was the case with the monomer radical cation, the highest unpaired electron density remains at the  $\alpha$ -positions, namely the 5,5'-positions. However, because the unpaired electron is now distributed over two monomer units, delocalization dilutes the unpaired electron density (i.e., reactivity) of the  $\alpha$ -position in the dimer. Conversely, the  $\beta$ -position have acquired more unpaired electron density, indicative of a different type of spin distribution in the dimer radical cation. A resulting consequence is stabilization and thus decreased reactivity of (7) in comparison with (1).



Scheme 1.14 The unpaired electron distribution of the dimer

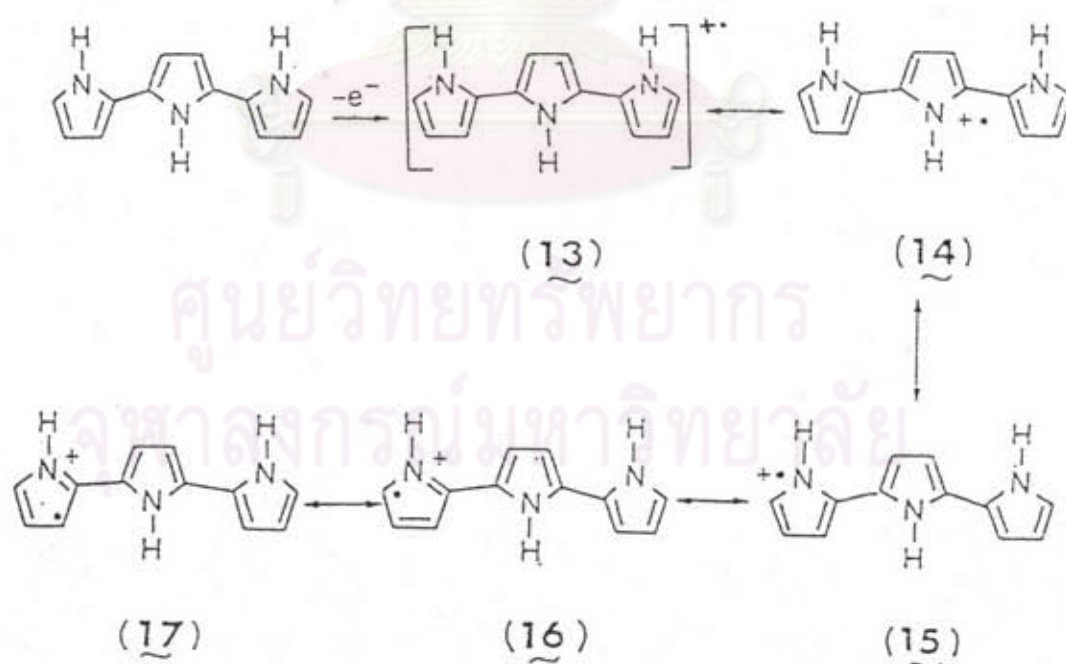
Among the resonance forms shown for the dimer radical cation, (9) is the predominant structure. The dimer radical cation can, therefore, be expected to continue to react primarily via the  $\alpha$ -positions. Thus, at this stage of the polymerization reaction, The surplus of monomer radical cation (3) assures further predominance of  $\alpha, \alpha$ -coupling, to yield the dihydrotrimer di-cation (11), that upon deprotonation, forms neutral trimer, i.e., 2,2 : 5,2''-terpyrrole (12). (see Scheme 1.15)



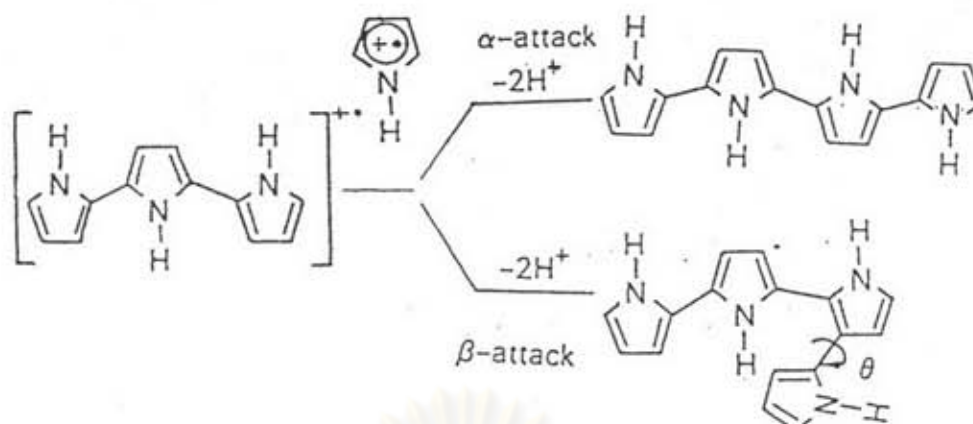
Scheme 1.15  $\alpha, \alpha$ -coupling of tri-pyrrole

The radical cation (13) (see Scheme 1.16) in its coplanar configuration is predicted to be well delocalized, with much the unpaired electron density residing at the 2,5 - , 5,5''- and 3,3''-positions. It is interesting to note that here the  $\alpha$ -positions namely the 5,5''-positions, are no longer the positions with highest unpaired electron density. They are comparable in magnitude of their unpaired electron density to these predicted for the 2,5 - and 3,3''-position. The 2,5 -positions should

sterically inaccessible to monomer radical-cation attack. Conversely, the 5,5''-positions can be easily attacked by the monomer radical cations, thereby propagating  $\alpha,\alpha$ -linkages further. The 3- or 3''-positions, i.e., the  $\beta$ -positions, are somewhat sterically hindered and, therefore, a monomer radical cation would have to couple with the trimer radical cation nonplanar configuration. Thus the monomer radical cations could, in principle, undergo the coupling reactions at either the 5,5''-positions (i.e.,  $\alpha$ -position) or the 3,3''-positions (i.e.,  $\beta$ -position) of these oligomer radical cations. However, because the  $\beta$ -position is somewhat sterically inaccessible coupling, thus  $\alpha,\alpha$ -position couplings is still predominant in the polymerization.



Scheme 1.16 The unpaired electron distribution of the tri-pyrrole



Scheme 1.17 The principal radical cation coupling at  $\alpha$ -position and  $\beta$ -position

### 1.5 Use and Application

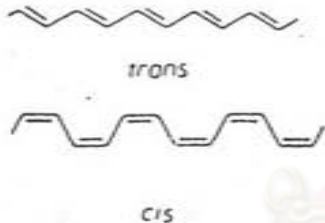
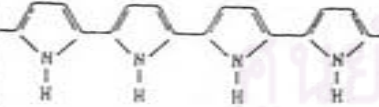
Conducting polymers are not only comparable to inorganic compounds from the point of view of metallic conduction, but in addition, they also impart a blend of interesting optical and mechanical properties. One of the greater advantages of organic polymers over inorganic materials is their architectural flexibility, since they can be chemically modified and easily shaped according to the requirements of a particular device. Their versatility and compatibility coupled with durability, environment stability, ease of fabrication, and light weight make them most fascinating materials for electronic devices. Recently synthetic capabilities as well as the instrumental techniques have developed to such an extent that electronic device based on conducting polymer can be designed and fabricated down to their molecular level; thereby an

evolution of even more sophisticated technology in the field of microelectronics can be foreseen. The electroactive materials cover a broad spectrum of applications from solid-state technology to biotechnology. The first major area of application includes solid-state rechargeable polymer batteries. Because of the versatility of polymeric systems, they can be easily shaped according to the requirement of a device.


The conductivity of the conjugated polymer can easily be maintained in the semiconducting regime by controlling the dopant concentration. In the various fields of industries such as textile, paper technology, photography, printing, etc., an immense danger of electrical shocks, fire, and explosion exist due to the generation of high static electricity. Conducting polymers can easily dissipate electrostatic charges at a much faster rate and can serve as the antielectrostatic agents in these industries.

In some applications, conducting polymers could be used as fillers instead of carbon black, graphite, and metals. These can also replace other materials as conductive adhesives. The electrical conductivities, chemical structures, and possible applications of some of the important conducting polymers which are frequently mentioned in the text are listed in Tabel 1.2.

Table 1.2 Some important conducting polymers and their possible applications [23]

Polymer	Chemical Structure	Possible Applications
Polyacetylene	 <p style="text-align: center;"><i>trans</i></p> <p style="text-align: center;"><i>cis</i></p>	Rechargeable battery, photovoltaics, gas sensors, chemical indicators, radiation detectors, Schottky diode, antielectrostatic, encapsulation, biotechnology, solar cell.
Polypyrrole		Rechargeable battery, condenser, printed circuit boards, gas sensors, potentiometric glucose sensor, electroplating, Schottky diode, electroacoustic device, fillers, adhesive, transparent coating, electromagnetic shielding, electrochemical cells, field-effect transistor, photocatalysts, physiological implantations, conductive textiles.



Polymer	Chemical Structure	Possible Applications
Polythio- phene		Rechargeable battery , display device, field effect transistor, Schottky diode, gas sensor, photocatalysts.

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### 1.6 Objective for this research

1. Synthesis of polypyrrole by chemical polymerization in  $\text{FeCl}_3$  solution, using methanol and chloroform as a solvent. Various chemical conditions must be satisfied to obtain well-defined polymers and, especially, to yield high conductivity samples. The major conditions that influence the quality of the conductive polymers which will be investigated are as follows :

- Reaction temperature
- Concentration of  $\text{FeCl}_3$  solution
- Amount of  $\text{FeCl}_3$  solution
- Reaction time
- Solvent of the solution

The optimum condition for synthesis of polythiophene and poly(3-methylthiophene) were also determined similarly to that of polypyrrole.

2. Study the stability of the conductivity of synthesised polypyrrole conducting polymers in various conditions, such as

- Temperature
- Acid-base solution
- Various atmosphere

It is hoped that the results from these studies will provide some insight as to the potential applications of these conductive polymer and accelerate the use of the conducting polymer as a new function materials.



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