UNIVERSITI PUTRA MALAYSIA

EFFECTS OF ZEOLITE AND BISMUTH OXIDE ADDITION ON STRUCTURAL, THERMAL, OPTICAL AND ELECTRICAL BEHAVIOUR OF CONDUCTING POLYMER POLYPYRROLE

EMMA ZIEZIE BT MOHD TARMIZI

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By

EMMA ZIEZIE BT MOHD TARMIZI

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia in Fulfilment of Requirement for the Degree of Doctor of Philosophy

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To them this work is dedicated.

My children Izz Rafique & Izz Zara Adelea who gave me strength and courage throughout the journey. Husband, Papa, Mama, Wandah, Mak, Abah, brothers, sister and best friends who housed, nurtured and praying for my success. Without their understanding and support, I would never have completed this project. Lots of love.

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Chairman : Professor Zainal Abidin Talib, PhD

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Polypyrrole (PPY), Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide powders were successfully synthesized through the chemical oxidation polymerization method containing pyrrole monomer, iron (III) chloride hexahydrate as primary doping agent and Zeolite and Bismuth oxide as secondary doping agents. The Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide conjugated systems prepared at different concentration percentages ranging from 0 % to 20 %. The structural, compositional, morphological, thermal, optical, magnetic and electrical properties of the synthesized compound were characterized by X-ray diffraction (XRD) analysis, Energy Dispersion X-Ray Fluorescence (ED-XRF), Fourier Transform Infrared (FTIR), Field Emission Scanning Elelctron Microscope (FESEM), Thermogravimetry Analysis (TGA), Electron Spin Resonance (ESR), Laser Flash measurement, Diffuse Reflectance Spectroscopy (DRS) and Van Der Pauw (VDP) technique. XRD confirmed the amorphous characteristic peak structure of pristine Polypyrrole at two theta ~25^o. The impregnation of Zeolite and Bismuth oxide resulted in the presence of sharp peak which implies that both Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide has some degree of crystallinity and more ordered arrangement than those pristine of Polypyrrole conjugated system. The elemental analysis confirmed the presence of primary and secondary doping agents in all Polypyrrole conjugated systems and witnessed the increment of every element as it were increased. This is in agreement with FTIR analysis which revealed the successful incorporation of primary and secondary doping agents in Polypyrrole conjugated systems through its nearly identical and positions of IR absorption bands of Polypyrrole, Zeolite and Bismuth oxide to which is available in literature. The FESEM morphology showed the formation of Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide revealing a globular images or cauliflower morphology of Polypyrrole. It also revealed that all the agents of primary and secondary doping have complete miscibility with Pyrrole forming a Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide.

Thermal stability is mainly studied by TGA. It was observed that the impregnation of Zeolite and Bismuth oxide in the conjugated system have shown a remarkable improvement on thermal stability of Polypyrrole conjugated systems which suggested that the structure formed is well orderly structured and strong. The ability of Polypyrrole, Polypyrrole/Zeolite and Polpyrrole/Bismuth oxide conjugated systems to transit heat was measured using Flash technique. Higher molecular weight and higher crystallinity resulted from Zeolite and Bismuth oxide are believed to increase the conjugation length and providing more through-space pathways for electron to migrate and thus increased the thermal diffusivity. Three peaks of absorbance are observed for Polypyrrole, Polyprrole/Zeolite and Polypyrrole/Bismuth oxide at different photon energy which are believed to be associated with transitions from below band edge to bonding and anti-bonding levels of polarons (band gap), bonding to anti-bonding levels of polarons (intraband), and valence band to conduction band (interband). Estimation of energy gap using Kabelka-Munk treatment revealed that the incorporation of secondary doping agents of Zeolite and Bismuth oxide changed the energy gap to a smaller range value.

Presence of polaron in all samples was confirmed by ESR spectroscopy technique. The spin number (N_s) was determined and found to depend on primary and secondary doping agent concentrations level in Polypyrrole conjugated system. ESR linewidth showed temperature dependence and suggests the validity of the Elliot relaxation for Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide conjugated system.

The electrical conductivity studies were investigated using Van Der Pauw technique at temperature range between 20 K until 300 K. From the results, it was observed that the electrical conductivity increased with increasing of primary and secondary doping agents in Polypyrrole conjugated systems. It was found that the electrical conductivity of pristine Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide conjugated systems strongly depends on the applied temperature. There were two regimes of electrical conductivity observed where the first regime is from 20 K to 50 K and the second regime starts from 50 K up to 300 K. Temperature dependence of conductivity of pristine Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide conjugated systems samples between temperatures of 50 K until 300 K suggests a transition from semiconducting nature to metallic nature. In the temperature range from 50 K to 300 K range, the charge carrier mechanism was dominated by 3-D variable range hopping mechanism, VRH transport.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Doktor Falsafah.

KESAN BAGI PENAMBAHAN ZEOLITE DAN BISMUTH OXIDE KE ATAS SIFAT STRUKTUR, TERMA, OPTIK DAN ELEKTRIK BAGI KONDUKSI POLIMER POLYPYRROLE

Oleh

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Februari 2015

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Serbuk Polypyrrole (PPY), Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide telah berjaya disintesis melalui kaedah pempolimeran oksidasi kimia berasaskan monomer Pyrrole, Iron (III) chloride hexahydrate sebagai agen dopan primer dan Zeolite and Bismuth oxide sebagai agen dopan sekunder. Sistem konjugat Polypyrrole, Polypyrrole/Zeolite dan Polypyrrole/Bismuth oxide dihasilkan dari berbeza konsentrasi dan peratus bermula dari 0 % to 20 %. Sifat-sifat struktur, komposisi, morfologi, terma, optik, magnet dan elektrik untuk sebatian yang disintesis telah dilaksanakan oleh analisis pembelauan sinar-X (XRD), tenaga penyerakan floresen sinar-X (ED-XRF), Jelmaan Fourier inframerah (FTIR), mikroskopi medan pancaran pengimbasan elektron (FESEM), analisis permeteran graviti haba (TGA), elektron paramagnetic resonans (ESR), teknik fotokilat, spektroskopi refleksi resapan (DRS) dan kaedah Van Der Pauw (VDP). Teknik XRD mengesahkan puncak lebar iaitu ciri-ciri asli amorfus Polypyrrole dengan kehadirannya pada dua theta ~ 25^o. Impregnasi Zeolite dan Bismuth oksida mendedahkan kewujudan puncak tajam yang mengandaikan bahawa kedua-dua Polypyrrole/Zeolite dan Polypyrrole/Bismuth oksida mempunyai tahap penghabluran yang lebih tinggi mengatasi system konjugat Polypyrrole yang asal. Analisis unsur mengesahkan kewujudan agen dopan primer dan sekunder dalam sistem konjugat Polypyrrole dan menyaksikan kenaikan setiap unsur seperti juga meningkat. Ini adalah bersesuaian dengan analisis FTIR yang mendedahkan kejayaan kobelarasi agen primer dan sekunder di dalam sistem konjugat Polypyrrole melalui kedudukan jalur penyerapan IR yang hampir mirip bagi Polypyrrole, Zeolite dan Bismuth oksida yang terdapat dalam penerbitan penyelidikan. Morfologi FESEM menguatkan pembentukan Polypyrrole, Polypyrrole/Zeolite dan Polypyrrole/Bismuth oksida mendedahkan yang imej globular atau morfologi bunga kobis bagi Polypyrrole. Ini juga mendedahkan bahawa semua agen dopan primer dan sekunder telah bertindakbalas sepenuhnya dengan Pyrrole menghasilkan Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oksida.

Kestabilan terma dikaji sepenuhnya melalui kaedah TGA. Dapat diperhatikan bahawa impregnasi Zeolite dan Bismuth oksida ke dalam sistem konjugat telah menunjukkan peningkatan yang luar biasa pada kestabilan terma sistem konjugat Polypyrrole yang mencadangkan bahawa struktur yang dibentuk adalah juga teratur tersusun dan kuat. Keupayaan pemindahan haba bagi sistem konjugat Polypyrrole, Polypyrrole/Zeolite dan Polpyrrole/Bismuth oksida telah dijalankan menggunakan teknik kilat. Berat molekul dan hasil penghabluran yang lebih tinggi terhasil dari Zeolite dan Bismuth oksida dipercayai menambahkan panjang konjugasi dan menyediakan lebih banyak melalui ruang laluan bagi elektron untuk berpindah dan oleh itu meningkat penyerapan haba. Tiga puncak penyerapan diperolehi bagi semua Polypyrrole, Polyprrole/Zeolite dan Polypyrrole/Bismuth oksida pada tenaga foton yang berbeza yang dikaitkan dengan peralihan daripada bawah pinggir jalur ke ikatan dan tahap anti-ikatan polaron (pita-intra), ikatan ke tahap anti-ikatan polaron (jurang jalur), dan jalur valensi ke jalur konduksi. Anggaran jurang tenaga yang menggunakan rawatan Kabelka-Munk mendedahkan bahawa kehadiran agen dopan primer dan sekunder Zeolite dan Bismuth oksida mengecilkan jurang tenaga kepada julat nilai yang lebih kecil.

Kehadiran polarons telah dipastikan melalui spektra ESR yang diperolehi melalui spektroskopi ESR. Nombor spin telah diperolehi dan didapati bergantung kepada kandungan agen dopan primer dan sekunder sistem konjugat Polypyrrole. Nilai puncak-ke-puncak garislebar ESR menunjukkan kebergantungan terhadap suhu dan relaksasi Elliot dicadangkan bersesuaian bagi sistem konjugat Polypyrrole, Polypyrrole/Zeolite dan Polypyrrole/Bismuth oxide.

Kajian kekonduksian elektrik telah dijalankan menggunakan teknik Van Der Pauw pada lingkungan suhu diantara 20 K until 300 K. Melalui keputusan ini, diperhatikan kekonduksian elektrik meningkat dengan penambahan dopan primer dan sekunder di dalam sistem konjugat Polypyrrole. Dapat diketahui bahawa kekonduksian elektrik bagi sistem konjugat asas Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth oxide sangat bergantung kepada suhu. Diperhatikan terdapat dua bahagian kekonduksian elektrik dimana bahagian pertama adalah dari 20 K sehingga 50 K dan bahagian kedua bermula dari 50 K sehingga ke 300 K. Kebergantungan suhu terhadap kekonduksian elektrik bagi sistem konjugat asas Polypyrrole, Polypyrrole/Bismuth oxide diantara suhu 50 K sehingga 300 K mencadangkan peralihan transisi dari sifat separakekonduksian kepada sifat metalik. Di dalam lingkungan suhu dari 50 K sehingga 300 K, mekanisma cas pembawa telah didominasi oleh pergerakan julat lompatan (VRH).

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I certify that a Thesis Examination Committee has met on 10th February 2015 to conduct the final examination of Emma Ziezie Bt Mohd Tarmizi on her Doctor Philosophy thesis entitled "Effects of Zeolite and Bismuth Oxide Addition on Structural, Thermal, Optical and Electrical Behaviour of Conducting Polymer Polypyrrole" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS/NOTATION/GLOSSARY OF TERMS

A	Absorption
E_g	Energy gap
FTIR	Fourier Transforms Infrared
XRD	X-ray Diffraction
FWHM	Full Width at Half Maximum
ESR	Electron Spin Resonance
ED-XRF	Energy Dispersion X-Ray Fluorescence
eV	Electron volt
PPY	Polypyrrole
VRH	Variable Range Hopping
FESEM	Field Emission Scanning Electron Microscopy
UV-VIS-NIR	Ultraviolet-Visible-Near Infrared
DRS	Diffure Reflectance Spectroscopy
TGA	Thermogravimetric Analysis
MR	Molar Ratio
ΔH_{pp}	Peak-to-Peak Linewidth
Ns	Spin Number
ρ	Resistivity
σ	Conductivity
K	Kelvin
LED	Light Emitting Diode
$FeCl_3$	Iron (III) Chloride
L_g	Particle Size/Mean Crystallite Size
β	Full-Width Half Maximum (FWHM)

θ	Bragg Angle
D_δ	Dislocation Density
M	Molar
E_F	Fermi Energy
E_f	Fermi States
E_C	Mobility Edge
σ_C	Conductivity at the Mobility Edge
T^{-1}	Spin-Lattice Relaxation Rate
A	Numerical constant
λ	Spin-Orbit Coupling Constant
ΔE	Energy Separation
T	Relaxation time of electron momentum
Δg	g-shift
$\rho(T)$	Electrical Resistivity
T_0	Characteristic Temperature
α	Coefficient of Exponential Decay
k_B	Boltzmann’s constant
$N(E_F)$	Density of States
R_{hop}	Hopping Distance
W_{hop}	Hopping Activation Energy
T	Temperature
S	Siemens
%	Percent
cm	Centimeter
s	Second

R^2	Linear Regression
Cps	Conducting Polymers
ΔH_{pp}	Peak-to-Peak Linewidth
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
DMA	Dynamic Mechanical Analysis
XPS	X-Ray Photoelectron Spectroscopy

CHAPTER 1

INTRODUCTION

1.1 Preamble

The development of science which covers every aspect of materials and technology in present time is undeniable. New findings are reported every single day; the excitement, the enjoyment and the successful of every research colors every part and branch of sciences making the world of technology interesting day by day. Whilst there are so many materials in the line of science were being developed for various applications, conducting polymers appear to be one of the unique and interesting material as they possess electronic properties of metals or semi-conductors, with the advantageous processing and mechanical characteristics of polymer. Polymer, which is known long time ago as insulating material has been orchestrated into new form of property which gives new dimension to the new era. Particularly, the conducting polymers, whose discovery almost three decades ago, offer an almost infinite spectrum of technological development for the world as we know it. The uses of polymers have expanded from inactive materials such as housewares and constructions to indispensable materials with useful optical, electronic, energy storage and good mechanical properties. Ever since the discovery of the simplest conducting polymer, polyacetylene (doped with halogen), in 1977 by a physicist, Heeger, inorganic chemist MacDiarmid and polymer chemist, Shirakawa, this material has become one of the most interesting materials for research in science. The level of publications in conducting polymers increase rapidly after 1980s where only a few hundred were published that year and later reaching about 8000 journals published annually towards the end of 2000. This shows that the field becoming extremely exciting from year to year. Figure 1.1 shows the publications base on the main areas of interest in conducting polymers where much of the attentions were on new syntheses or modifications to the existing one followed by electrical conductivity and applications. In the applications of conducting polymers, batteries show the highest interest followed by sensors, membranes, light emitting diode (LED), corrosions, photovoltaics and actuators.

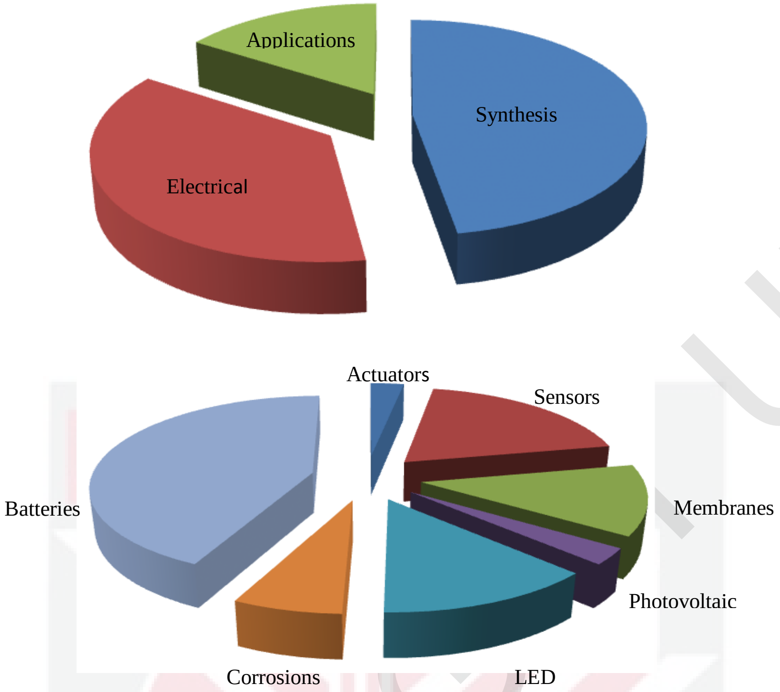

Figure 1.1. Scientific papers published for various topics of conducting polymers from 1990-2000 (Source: Wallace et al., 2009).

Yet still, conducting polymer is not a common material especially to layman as through experiences every time the conducting polymer topic was raised, they will act surprisingly because of the uniqueness. No one would have possibly believed before the discovery, a polymer could conduct electricity as good as copper. Apart from the combinations properties of metals/semi-conductors and polymers, these materials is believed to have potential over a large scale electronic materials production at low temperature. They are light weight, greater processability, and resistance of corrosion and these scenarios were seen as promising low cost in commercialization of electronics.

In the last decade, the interest in the development of conducting polymers such as polypyrrole, polyaniline, polythiophene and polyphenylene in have increased vastly due to their versatility promising applications in sensors (Nicolas *et al.*, 2001; Harris *et al.*, 1997), energy storage (Novak *et al.*, 1997; Mermilliod & Tanguy, 1986), bioelectrochemistry (Palmisano, 1997), organic electrochemistry (MacDiarmid, 2002), optical and electronic devices (Potember *et al.*, 1987), electrochemical devices (Belanger *et al.*, 2000; Gazotti *et al.*, 1999), microsystem technologies (Gardner & Bartlett, 1995), ion-exchange membrane (Wang *et al.*, 2001) and so forth. Conducting polymers can be synthesized by both chemical and electrochemical polymerization (Toshima & Hara, 1995). The chemical polymerization is favorable as it offers mass production at a reasonable cost while electrochemical technique involves construction of conducting polymers with better control of film thickness and morphology.

1.2 What are Conducting Polymers (CPs)?

Polymers are formed of very large molecules (macromolecules) that are built up of smaller units or monomers. They are generally not thermoplastic or thermosoftening which are flexible or moldable at certain temperature and return to a solid state upon cooling but they are a new class material in organic materials family which can offer an electrical conductivity. It is possible to tailor a different type of arrangements of the units, the various types of chains and shapes, results in a class of materials that are characterized by a diverse range of properties. For instance, electrical properties can be manipulated to produce a material with different conductivities or capacitance. Every step of synthesis is very crucial as it plays an important role in producing a material with different chemical, optical, electrical and mechanical properties. All these complex properties are in need of a very deep understanding of the nature of the processes before it can successfully be controlled in various operational environments.

These organic materials which have a very unique intrinsic conductivity is generally comprises of C, H atoms and simple heteroatoms such as N and S along their backbones. Huge properties of the conducting polymer are coming from the intrinsic structure of organic polymer and also π-conjugation. Conjugation system refers to p_z orbitals which overlap another p_z orbitals, connected with delocalized electrons in a compound with alternating single & double bonds across an intervening σ bond (In larger atoms d-orbitals can be involved). This overlapped region bridging the inter-adjacent single bond and allows the delocalization of π electron across all the adjacent aligned p_z orbitals. This system generally may lower overall energy of the molecules while the stability is increased. σ electrons which in concept of binding energy is regarded as localized between two bonded nuclei and are seen as the essential structural glue while n electrons are primarily associated with heteroatoms (O, N, S, P, etc) . This σ electron are not normally considered as important in relation to bonding but is believed to have influence on reactivity. While for π electrons, they are believed to involve in bonding but tend to form weaker and often less-localized bonds than the specifically internuclear σ bond. π electrons are regarded as moving in the field set up by the disposition of the nuclei and the core plus σ and n electrons. They are less tightly bound than σ electrons, and compounds processing π electrons (unsaturated compounds) generally have a more varied and interesting chemistry than those possessing only σ and n electrons. The π-bands are either empty (lowest unoccupied molecular orbital ~ LUMO) or filled with electrons (highest occupied molecular orbital ~ HOMO).

1.3 Types of Conducting Polymer

Each writer may have classified the types of polymer differently depending on how they define and group the polymer and they may or may not agree with others classifications. Brief descriptions of conducting materials have been given here but present study deals with intrinsically conducting polymers and are further discussed as below. Basically there are four types of conducting polymers include intrinsically conducting polymers, conducting polymer composites, redox polymers and ionically conducting polymers.

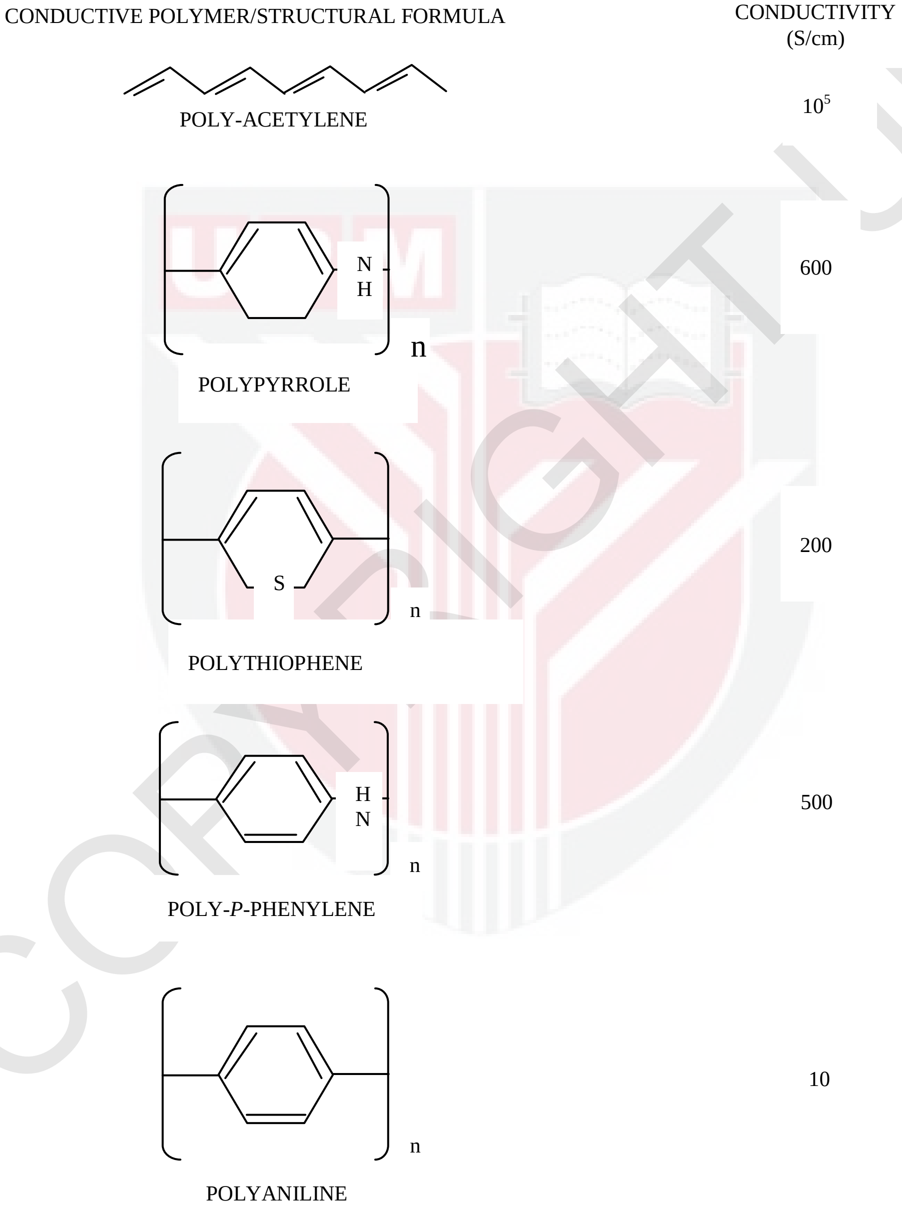

Figure 1.2. Schematic represent conjugated polymers chemical structure and its conductivity.

Intrinsically conducting polymer (ICP) is applied to a type of an organic polymer which possesses the electrical properties of a metal while preserving its mechanical properties and process ability as a polymer. This type of polymer is also known as ‘synthetic metal’ as its conductivity lies beyond the insulator and extend into the region of common metal. These polymers are made conducting by the reaction of conjugated semiconducting polymer with an oxidizing agent, a reducing agent or a protonic acid, resulting in highly delocalized polycations or polyanions (Skotheim, 1986). The general characteristic of most ICP’s is the presence of alternating single and double bonds along the polymer chain, which enable delocalization or mobility of charge along the polymer backbone. Figure 1.2 shows the structure of some conjugated polymers in their neutral insulating form.

In order to make them electronically conductive, it is necessary to introduce mobile carrier into the conjugated system; this is achieved by oxidation or reduction reactions and the insertions of counterions (called ‘doping’) (Freund & Deore, 2007). The conductivity is thus assigned to the delocalization on π-bonded electrons over the polymeric backbone, exhibiting unsual electronic properties, such as low energy optical transitions, low ionization potentials and high electron affinities (Patil *et al.*, 1988). The electrical properties of these materials can be tuned by chemical manipulation of the polymer backbone, introduction of dopant’s type or degree of doping.

1.4 Synthesis

The synthesis of polymer requires selection of appropriate monomer molecules coupling in order to form polymer chain. The capability and functionality of the monomer to incorporate to two (or more) other units is very important as it is a basic requirement to achieve the successes of conducting polymer’s network constructions (functionality of two or higher). With this demand there are multitudes of chemicals reactions and associated monomer types that can be used to hit polymerization.

Some of the researcher categorized and term the syntheses differently from other researchers. Thus, the discussions below might be or might not be familiar to reader. The information below is compiled based on reading through books and journals and rewrite again as a summarizations in order to help ones for better understanding between each technique and their specific technique initial. According to Elementary polymer chemistry or organic chemistry, conducting polymer syntheses can be divided to two categories which are Condensation Polymerization (also sometimes called *Step-Growth Polymerization)* and Addition Polymerization (also sometimes called *Chain-Growth Polymerization)* (Chandrasekhar, 1999). Condensation polymerizations are those which yield polymer with repeated units having fewer atoms than present in the monomers from which they were formed. This usually arises from chemical reactions which involves the elimination of a small molecule (e.g. H_2O, HCl). Addition polymerizations are those which yield polymers with repeat units having identical molecular formulae to those of the monomers from which they are formed (Young & Lovell, 1991).

Another two common classes of that falls below above characterizations syntheses are chemical and electrochemical syntheses where nearly all Electrochemical syntheses are Additions Polymerizations and most of the Chemical syntheses are Condensation Polymerizations (Chandrasekhar, 1999). Wallace Hume Carothers who is also a champion in Polymer Science suggested above classifications which was accepted earlier by other researchers and argued later due to conflict characteristic of the syntheses. Certain condensation polymerization features the characteristic of addition polymerizations and some addition polymerizations pose characteristic of typical condensations polymerizations.

Selection of the monomers is very crucial as the alternate single and double bonds (conjugation) have to appear as a resulting polymer chain. Monomer of polyaromatic classes such polyacetylene, poly(*p*-phenylene), polythiophene, polypyrrole and polyaniline have been extensively studied. Also there are selections of other polymers which also exhibit conducting behavior such as polyazine, polyazulene, polycarbazole, polynaphthalene, polyanthracene, polyfuran and ladder polymers. Ladder polymer is a subclass of polymer that is made of cycles or heterocycles where the structure can be either two polymer chains linked by covalent bond or single chain that is double stranded. Each of these polymers can be tailored according to applications requirement as they can also be blends between each other such as poly(vinyl chlroride), polyasterene or mixed with composites such as metal oxide, silica, etc.

Conductive polymers may be synthesized by any of the following techniques available such as chemical polymerization, electrochemical polymerization, photochemical polymerization, pyrolysis, concentrated emulsion polymerization, inclusion polymerization, solid-state polymerization, plasma polymerization, metathesis polymerization or soluble precursor polymer preparation. Among all the categories, chemical polymerization which method is independently in need of any cell or electrodes has become the most popular and appeared to be useful method for preparing large amounts of conductive polymer. Chemical polymerization (oxidative coupling) is followed by the oxidation of monomers to a cation radical and their coupling to form dications and the repetition of this process generates a polymer.

Chemicals such as potassium dichromate, persulfate and iron chloride are few examples of oxidizing agents that are commonly used in the chemical polimerization. Iron chloride is a common oxidant used particularly for pyrrole and thiophene. According to Patent Article No: US006072027A, the combination of a chlorate salt or chloric acid with a salt of Fe(II) or Fe(III) provides an oxidant that promotes higher yields of conductive polymer than either the chlorate salt or chloric acid, or the salt Fe(II) or Fe(III) alone and hydrated is preferable (Ansari, 2006; Scortichini & Babinec, 2000). As an addition, Cl^- is known to be a very reactive material and is believed can initiates such an active polymer. The counterion usually the anions play a very important role in polymerization as it maintains the neutrality as well in determining the physical properties of the matrix. It is also mentioned in the article where the oxidant material can be hydrate or anhydrous but hydrate is preferable as through some reading it is believed that they are more stable at room temperature, act as structure-makers and they will delocalized through force of penetration to compensate positive charge that are generated along the chain during polymerization. Iron (III) chloride hexahydrate also is cheaper compared to other dopants employed on pyrrole polymerization such as 2,6-napathalene disulfonic acid disodium salt, 2,6-naphthalene disulfonic acid disodium salt, 1-naphthalene sulfonic acid etc (Macasaquit and Binag, 2010). As an addition, the hydrate property can be switched to anhydrous by heating the hydrate to remove the water. Water or acetonitrile are the most preferable reaction medium for conducting polymer polymerization poor nucleophiles (Ansari, 2006; Babinec & Scortichini, 1999).

Major factors such as medium, concentration of oxidant, nature of dopant, duration and temperature at which the reaction is carried out affect directly the final product of the polymerization. Through own experiences and observations there is no success polymerization occurred at a very short of time and 6 hours is the optimum for the best production and the advantage of this synthesis compare to other type of syntheses is the large quantity of polymer will be obtained. Conductivity influence of temperature studies also have been done by Whang and coworkers and they found that the conductivity for the PPy-$FeCl_3$ to be at maximum as a product of synthesis at 0 ^{o}C (Whang *et al.*, 1991). This technique is applicable to synthesize all classes of conjugated polymers. In this work, Pyrrole as monomer have been used together with Iron (III) Chloride Hexahydrate ($FeCl_3.6H_2O$) as oxidizing agent which referred as primary dopant and mixed with two types of secondary dopants that are Zeolite and Bismuth (III) Oxide. All polymerizations were carried for 6 hours using chemical polymerizations technique.

1.5 Doping

Doping in conducting polymers will result in the increasing of conductivity by some degree of magnitude and this shows obvious distinguishing between conducting polymers and other type of polymers. At the beginning, organic polymer whether insulator or semiconductor portrays only a minute conductivity, usually between 10^{-10} to 10^{-5} Scm^{-1} were then converted to a ‘metallic’ phase with conductivity ranging from 1 to 10^{4} Scm^{-1}. To date, the production of iodine doped polyacetylene shows the highest conductivity around > 10^{5} Scm^{-1} with the theoretical limit predicted about 2 x 10^{7} Scm^{-1}. This is higher than copper about one order of magnitude (Chiang *et al.*, 1977). Conductivity of metals, semiconductors and insulators can be referred to Figure 1.3.

In conducting polymer, the introduction of dopants materials in the range of a few degree up to 30 wt %) which is considered large amount if compared to semiconductor material which only a small amount of donor or acceptor that is used. The conductivity of the material can be low or high as it can be controlled by varying the amount of dopant that is introduced into the polymer system.

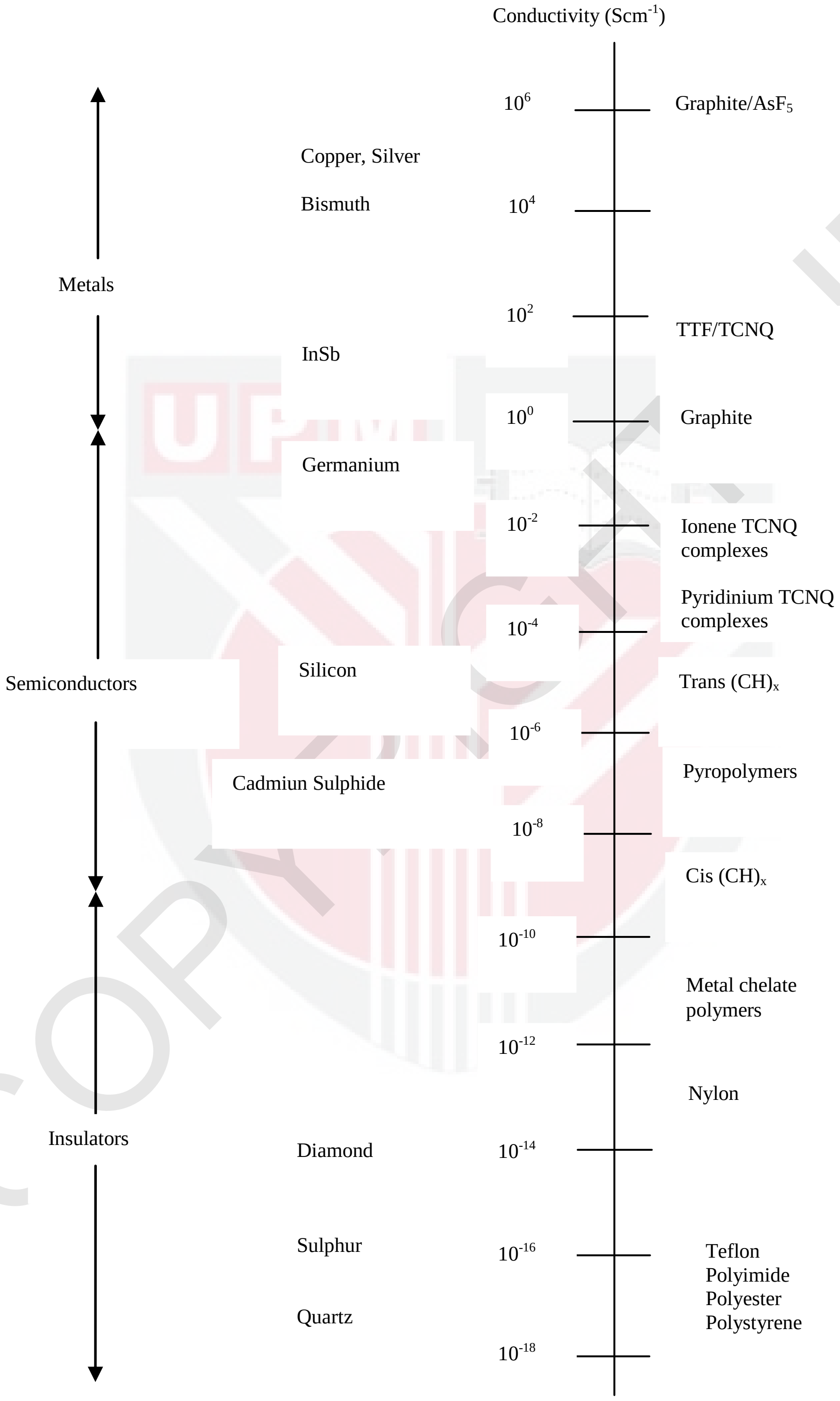

Figure 1.3. The conductivity of materials (Source: Przyluski, 1991).

Doping also is reversible (also known as dedoping), as shown in Figure 1.4.

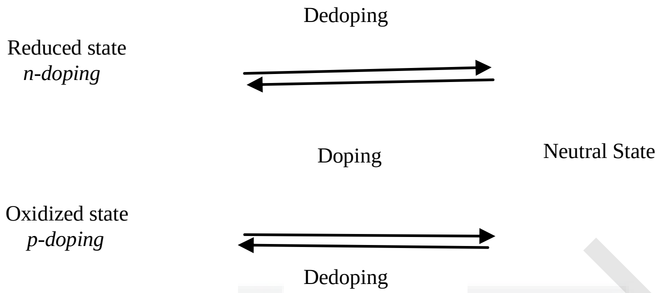

Figure 1.4. Doping/dedoping process in conducting polymers (Source: Macdiarmid, 2001).

During the doping process, carriers is introduces into the electronic structure which involved the presence of oxidation or reduction element to alter the backbone of the polymer. The π-conjugations of the polymers chain offers a system of high energy occupied and low energy unoccupied molecular orbitals which allows reduction or oxidation to happen through chemical or electrochemical polymerization (Diaz *et al.*, 1988). Oxidation is described as 'p-doping' where as a process of removing an electron and producing a positively charged polymer while 'n-doping' refers to electron addition producing negatively charged backbone. Figure 1.5 shows the polymer chain of polypyrrole with a positive charges usually 3-4 monomer units per unit positive charge. A^- is a counter ion incorporated during synthesis.

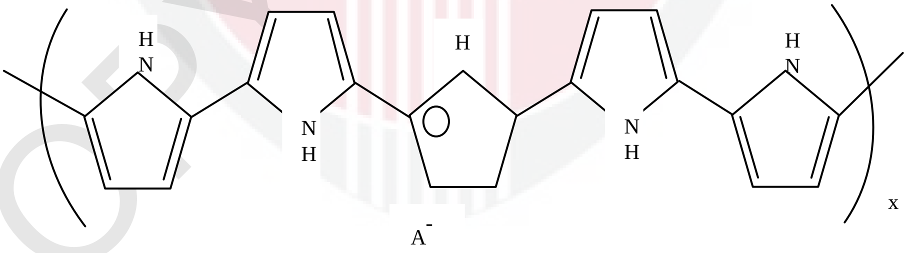

Figure 1.5. Anions (A^-) incorporated interstitially between Polypyrrole chain (Source: Wallace et al., 2009).

There are about seven types of doping but most regularly used are gaseous doping, solution doping and electrochemical doping because of the expediency and cost effective (Kumar & Sharma, 1998). Other available types of dopings are ion-exchange doping , radiation-induced doping, self-doping, and proton doping. In this work the doping process is a combination of a solution & self-doping as all the doping materials is stirred in distilled water before dropped for the oxidation of polpyrrole π-system. Iron (III) chloride hexahydarte, Zeolite and Bismuth (III) Oxide were spread all over the solution in order to get a well interaction with the Pyrrole which is believed a small cation migration to happen compare to ordinary process. The advantage of the method as it doesn't need of a particular current or potential or even a specific circumstances such as vacuum.

1.6 Conduction Mechanism

Band theory has long been used to explain electronic structure of materials. Each material has its own energy band structure and the variation of the band structure reflect their physical properties which help to explain the electrical characteristics, optical absorptions and form of foundations in solid state devices. In solid state physics, band structure describes those range energy that an electron within solid may have (energy bands or bands) and ranges of energy that it may not have (energy gaps, band gaps or forbidden gaps). At the atomic scale, the electron of a single atom forms a discrete set of energy levels. As more atoms are brought together, their orbital splits and forming a molecular orbital which grows larger as more atoms were combined together and this explains the construction of a solid. At this point when atoms as well as all of its energy levels are very closed to each other (depends on the structure), they form energy bands and band gaps is formed as a result to the leftover width with no electron state or energy levels exist between the energy bands. The highest occupied energy level represent valence band while the lowest occupied energy level represent conduction bands. The energy gap generally refers to the energy difference between the valence band and conduction band and is equivalent to free an electron from its outer orbital in order to become mobile charge carrier and able to move freely within the materials. Generally insulators have a large band gaps, smaller band gaps for semiconductors while metal may have a very tiny or may not have at all as the bands overlapped each other.

The electrical properties of conventional materials depend on the electronic band structure and on the distribution of electron and its energy level that form bands. No conduction can be occurred when the bands are fully occupied or empty. With specific amount of energy, electrons are able to hop from valence band to conduction band (differs for different materials) by absorbing either phonon (heat) or photon (light) and if the band gap is narrow enough for the transition. This thermal excitation gives rise to conductivity value. For example, semiconductor behaves as insulator at absolute zero and only allows thermal transition of electron below its melting point while wide band gap in insulator makes the excitation not possible at all at room temperature. The conductivity for metal is high due to a very small energy gap and normally they are overlapped. In general the conductivity for above materials depends on the energy gap as well the temperature.

Conducting polymers are basically quasi one-dimensional as they are soft, results from a covalent bonding within the chains and Van Der Waals interaction between chains. The general property, geometrical nature and structure of conducting organic molecules are depends on the ionic state of the molecules which leads to the birth of unusual charge carrier species (Salaneck *et al.*, 1999). It is believed that nor electron or holes work as carrier but some kinds of quasi-particle, with each consisting of a couple charge lattice deformation creatures. Hence, conducting polymers does not belong exactly to any groups as mentioned above as they conduct current through the unusual ways. For instance, polyacetylene can be multi-behaviour as it can be semiconductor and insulator too and because of the introduction of doping through chemical reactions, it can become a conductor with specific conductivity (Przyluski, 1991). Based on this condition, the theoretical concepts of soliton, polaron and bipolaron have been applied to explain the electronic phenomena in these organic conducting polymers (Roth & Bleier, 1987; Su *et al.*, 1979). Solitons are actually kink- or pulse-like excitations of physical systems. By analogy, solitons are related to harmonic excitations (phonons, Block, waves, magnons) as flood waves to ordinary waves (Roth & Bleier, 1987). In conjugated system, solitons may be neutral, positively or negatively charged according to number electron in the π orbital and therefore not only one solitons is expected to accommodate in the system. A bound state of neutral soliton creates polaron while two polarons create bipolaron. Polarons and bipolaron are generated in conducting polymer with non-degenerate ground state by photoexcitation. Bipolaron is spinless as the two localized electronic states in the gap are either fully occupied (n-type doping) or empty (p-type doping). Some typical properties of solitons, polarons and bipolarons are given in Table 1.1. According to Brazovskii-Kirova (BK) model, only two optical transitions can be obtained for bipolaron. The BK model also predicted that the difference in the optical properties of polarons and bipolarons comes from the occupancies of the localized states (Brazovskii & Kirova, 1981). Spinless conductivity and or electrochromic effect are the signatures of the formation of bipolarons on doping.

Table 1.1 Typical properties of solitons, polarons and bipolarons (Source: Nalwa, 2001).

Defect	Spin	Charge
Soliton	Neutral 1,2	0
Soliton	Charged 0	+e or –e
Polaron	Charged 1,2	+e or –e
Bipolaron	Charged 0	+2e or -2e

It is known that polyacetylene is the only polymer with a degenerate ground state while the other types of conducting polymer such as polypyrrole, polyparaphenylene, polythiophene etc produces higher–energy geometric configuration which is termed as non-degenerate ground state systems. Polypyrole, for instance have two oxidation states as shown in the Figures 1.6 and 1.7 below shows the oxidative formation of polypyrrole. The radical cation is produced due to removal of one electron from the π-conjugated system of polypyrrole (Freund & Deore, 2007). Radical cation that is partially delocalized is called polaron which is stabilized through the polarization of the surrounding medium and has a spin of ½. The radical and cation are coupled to each other via local resonance of the charge and radical. The polaron creates lattice distortion of a high energy where a domain of quinone-type bond sequence is created within Polypyrrole resulting in an aromatic bond sequence. The creation and separation defect limit the number of quinoid-like rings which can link a radical and cation together and is believed that the distortion extends over three to four rings. Both polaron and bipolaron are mobile and can move along the polymeric chain by the rearrangement of alternating double and single bonds of the system in electric field.

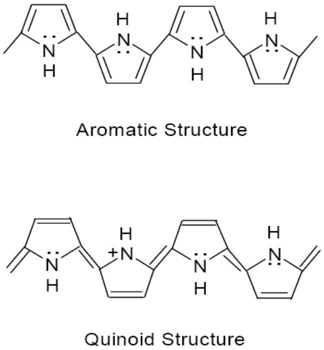

Figure 1.6. Various oxidation states of Polypyrrole (Source: Saville, 2005).

Upon increasing of oxidation, another electron is removed and results in two possibilities: another independent polaron is created as a result of the electron from a different part of polymer chain or from a polaron level, dication or bipolaron is created which will act to separate domain of quinone bonds from the sequence of aromatic-type bonds in the polymer chain (Figure 1.8). Creating a bipolaron is of lower energy than creation of two polarons so at higher doping levels it is more possible two polarons to combine to form a bipolaron (Ofer *et al.*, 1990; Bredas & Street, 1985).

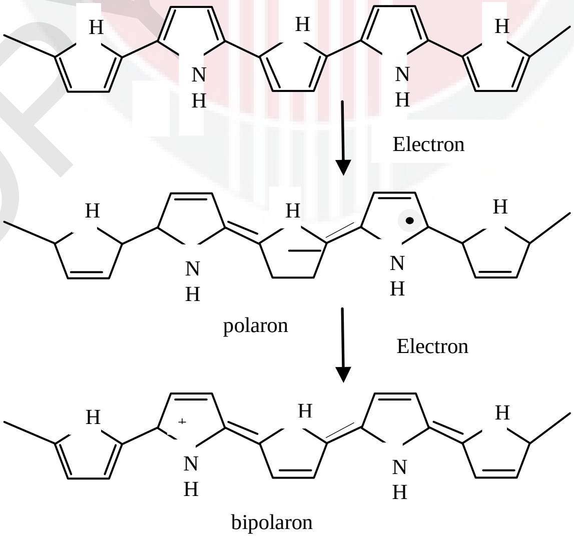

Figure 1.7. Polaron and bipolaron formation on backbone of Polypyrrole.

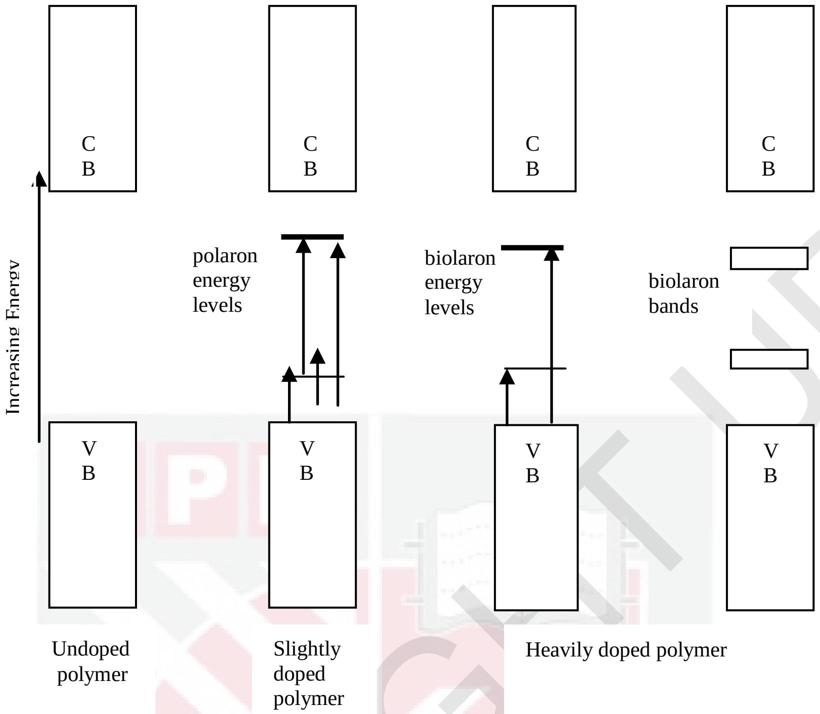

Figure 1.8. Illustration of energy levels and allowed transitions of polarons and bipolarons (Source: Nalwa, 2001).

1.7 Polypyrrole (PPy)

Studies on Polypyrrole have been found increased remarkably since it offers several advantages such as commercially available, environmental stability, interesting redox properties and good electrical conductivity (Ilicheva *et al*., 2012; Rodriguez *et al*., 1997). It is also favorable in commercial applications due to its high conductivity, long term stability of its conductivity and the possibility of forming homopolymers or composites with optimal mechanical properties. On the other hand, the typical Polypyrrole suffers from several drawbacks for instance insoluble and infusible, exhibits poor processability and lacks essential mechanical properties. Abundant of studies on the synthesis of Polypyrrole have been conducted in order to overcome it weaknesses. Among them a significant strategy to approach both high electrical conductivity and desirable mechanical properties is through the use of bulky organic sulfonate dopants (Takeoka *et al*., 1998; Bunting *et al*., 1997; Kiani & Mitchell, 1992; Cheung *et al*., 1990; Buckley *et al*., 1987; Wernet *et al*., 1984).

Polypyrrole can be synthesized by various methods as mentioned earlier such as chemical polymerization, electrochemical polymerization etc. Chemical polymerization is one of the most frequently technique used and was first reported in the year 1916 by Angeli and his group. They synthesized Polypyrrole by the oxidation of Pyrrole with H_2O_2. Polypyrrole powder as obtained was amorphous in nature and known as Pyrrole black. Generally, Pyrrole black have been prepared in presence of various oxidizing agents like H_2O_2, PbO_2, Quinones or O_3. The materials thus obtained by this method are mainly insulating in nature with room temperature conductivity 10^{-10} to 10^{-11} Scm^{-1}, but after subjecting to doping with halogenic electron acceptor, the conductivity rises to 10^{-5} Scm^{-1}. The low conductivity of Polypyrroles prepared from acid or peroxide initiators is associated with the high degree of saturation of the pyrrole rings in the polymer. Commonly used oxidants for Pyrrole polymerization are oxidative transition metal ions. Various metallic salts such as $FeCl_3$, $Fe(NO_3)_3$, $Fe(SO_4)_3$, $K_3Fe(CN)_6$, $CuCl_2$ etc have been employed to polymerize pyrrole with conductivity between 10^{-5} to 200 Scm^{-1}. One of the most oxidizing agent commonly used for the synthesizing of highly conducting Polypyrrole is ferric salts.

1.8 Zeolite and Bismuth (III) Oxide

There are two types of additional dopants that will be used in this study apart from Iron (III) Chloride Hexahydrate which will act as oxidation material and primary dopant for Pyrrole system. Both secondary dopant elements, Zeolite and Bismuth (III) Oxide are believed to serve as addition which can form equilibrate and improve the host system in every ways.

Zeolite are crystalline aluminosilicate minerals with the general formulation $M_x((AlO_2)x(SiO_2)_y.nH_2O$ (Yoon, 2000). Their structure is based on a three-dimensional network of $(AlO_4)^{5-}$ and $(SiO_4)^{4-}$ tetrahedral that are linked to each other via doubly bridging oxygen atoms. Their surfaces are negatively charge-balanced with exchangeable cations (Nakayama *et al*., 2003). The framework structures are build up from a regular arrays of very open void spaces often called cages or channels, depending on the shape of the pores (cavities), which are normally filled with cations or water. Cations are not covalently bound to the Zeolite framework structures; therefore they can readily replaced by variety of other cations via conventional aqueous ion exchange. The cavity-filling water molecules are readily lost and regained reversibly without damaging the framework structure. When dehydrated, other guest molecules can occupy void spaces as long as the interior spaces are large enough and the aperture sizes allow passage of substrates (Yoon, 2000).

Polypyrrole may complex with Zeolite in composites that are characterized by the fast electronic mobility of polypyrrole and the capability of Zeolite to incorporate cations into its structure. This questions that arises in such materials, where electronic and ionic conduction coexist, is how the composition of such mixtures affects their effective electric behavior. In other hand, it is also believed that this kind of encapsulation protects the polymer from degradation, and which oxygen and moisture from the atmospheric air play a leading part, reducing its aging rate (Malkaj *et al*., 2006). Aging, i.e. the irreversible decrease of the electrical conductivity of the conducting polymer with time also have been the subject of studies as it has been the main restriction of their use in technological applications. The isolation of the functional PPy chains into the porous and the improving of their alignment are expected to decelerate aging and to increase their electrical conductivity.

Bismuth Oxide is one of the most industrially important due to its fascinating structures and physical properties such as high ionic conductivity, lower processing temperature of ceramics, high electrical conductivity, chemical stability and good strength, easy to handle, can endure minute moisture and safe (Ding *et al.,* 2010; Kokkinos & Economou, 2008; Singhal & Dokiya, 1999). Bismuth Oxide is known to have low toxicity and widespread use in pharmaceutical as it is environmentally friendly. In addition, Bismuth Oxide also has found to show remarkable applications in environmental and clinical tracing metal analysis with combinations of advanced stripping technique (Naseri *et al.*, 2008). The remarkable features of Bismuth Oxide make it favorable for several applications in photovoltaic cells, coatings, sensors and electronics. Yilmaz *et al.* (2011) found that Bismuth Oxide based electrolytes have a high ionic conductivity and δ-Bi_2O_3 is found to be stable up to its melting points of approximately 825^{o}C.

1.9 Applications of Conducting Polymers

The past decades has witnessed tremendous advanced in the development of organic conductive polymer though a transformation of passive polymer. These new materials known as conducting polymer or synthetic metal (synmet) possess the characteristic of metal while retaining polymer properties such as light weight, resistance to corrosion, low manufacturing cost, flexible, ease of processing and some are biocompatibility. The applications for conducting polymers can be divided into two groups, Group A and Group Band as shown in Figure 1.9.

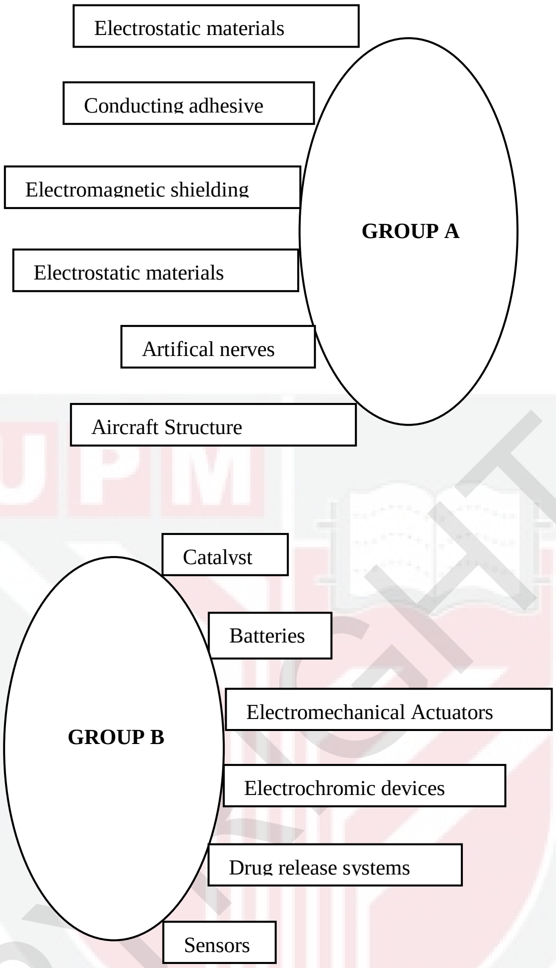

Figure 1.9. Various applications of conducting polymers.

Conductivity of the polymers plays a major role for Group A applications. For instance conducting polymer can be used as electrostatic materials where a thin layer of conducting polymer is coated to an insulator is needed to avoid buildup of static electricity. This is important where such a discharge is undesirable which will cause hazard such explosion if exposed to flammable gasses and liquids. Polythiophene as an example uses as anti-static layer in film products. Conducting polymer also can be used as conducting adhesive between two conducting surfaces. It acts as glue to get the conducting surfaces stick to one another while allowing the flow of current passing through all layers. Most of electrical devices such as computers and television generates electromagnetic of radio and microwave frequencies. Conducting polymer can be act as a shielding by coating inside of the casing and absorbs all the radiations. The other applications of conducting polymers are printed circuit boards, artificial nerves and aircraft structures.

Polymers such as polyacetylene and polyaniline have a wide application in batteries. The use of a polymeric electrolyte was thought to offer a number of potential advantages upon aprotic liquid electrolyte systems. Armand *et al.* (1979) were first discussed the concept of poly(ethyelene oxide)/lithium salt complexes for rechargeable systems utilizing intercalation/insertion cathodes. Up to date, there are a lots of manufacturer who already applied the use of Li-poly cells such in telecommunications radio-controlled aircraft and cars etc. For instance, in telecommunications where size and weight really matter, this type of battery is very promising as it can be shaped as however they please. Also there is rapid growth in the development of organic polymer for sensing/monitoring parameters such as temperature, pressure, position/speed, humidity, flow, chemical species etc. Due to increasing need in modern life for health control, energy conservation and limiting pollution has directed much research activity towards minituarization and health safe approach, silicon technology have been the best approach but due to some disadvantages such as limited temperature range, scientists have been looking for other promising materials as improvement. Organic polymer is listed to be as one of the candidates which capable in fabrication of new low-cost sensors with extra advantages. The other applications for Group B are electrochromic devices, electromechanical actuators, catalyst and drug release system etc which utilize the electroactivity character property of the materials (Adhikari, 2004).

1.10 Problem Statements

The preparation, characterization and application of intrinsically conducting polymeric systems are still at foreground in electrochemistry and physics. Thus, there is still room of improvement that can be done. There are at least a few major reasons of this intense interest. Since the properties of resultant powder depends on a number of parameters such as type of monomer, type of primary doping agent or oxidant material, type of secondary doping agent, mode of synthesis and synthesis temperature, the research on the preparation and characterization of conducting polymers are still continuing. The search of the monomer and primary doping agent is still ongoing by other researcher but in present work Polypyrrole and iron (III) chloride hexahydrate are preferred as they are by far the most extensively studied due to easily oxidized, water soluble and commercially available (Ekramul, 2005). For instance, iron (III) chloride hexahydrate have been one of the promising primary doping agents that successfully introduced in Polypyrrole and give rise in conductivity. Somehow present system capacities are approaching its limits and new paradigm should be created for the development of the next-generation materials. It is believed that there shall be another entity that can be introduced in Polypyrrole so it can further increase the conductivity and improved other properties of Polypyrrole.

In this work, both secondary doping agents are a versatile material which Zeolite which is in microparticle while Bismuth Oxide a macroparticle has been introduced in Polypyrrole. There are at least three motivations for choosing these peculiar environments. First of all, it is believed that when polymerization performed within Zeolite cavities, Polypyrrole polymerization may be viewed as rather facile reactions. Same goes to Bismuth Oxide. Second, one can speculate that the presence of metal and metal oxide clusters (or any other species) randomly distributed in the Zeolite channels may play some role in the properties of the final materials for example conductivity (Larsen *et al*., 1992). Lastly, the acidity surface of Zeolite, its porosity and leafy material properties ensures the good adhesion with the Polypyrrole, protects from degradation and reducing its aging rate (Malkaj *et al*., 2006). Although these materiasl can be considered ordinary, only a few research efforts on mesoporous materials such as Zeolite and most industrially important compound Bismuth Oxide with Polypyrrole have been reported in literature (Rozita, 2006). Only few studies have been highlighted relating to FTIR study, XRD analysis, morphological and electrical but no reports are available on the thermal properties, magnetic and optical properties of the prepared powder of Popypyrrole/Zeolite and Polypyrrole/Bismuth Oxide. Thereafter, the need to understand the behavior of Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth Oxide in particular on the stability and transport mechanisms through the technique explained in methodology, which may or may not have improved current systems properties and benefit any applications in life. It is of great opportunities to be part of organic team network contributing genuine knowledge which may have commercial development and potential in science or technology near future and so research in conjugated polymers remains extremely fruitful with this fundamental work. Even if the realization of the concept may only occur in the future or found to be impractical, all related fundamental knowledge obtained in this work can lead to interesting development to many areas of interest such as, in the area of chemical sensor where this work contributes immensely.

In most applications such as sensor, fuel cell, solar cell etc, it is very crucial to have properties of materials with a large surface area, pore structure and good electrical conductivity. All this may be obtained in this work since Polypyrrole, Zeolite and Bismuth Oxide itself equipped with such properties. In any applications, metal normally suffer from corrosion but with the advantage of polymer characteristic, this problem can be solved. Among other things, the stability of the polymeric system for certain period of time especially long time is still an issue. As an example in application of fuel cell, carbon has been used as electro catalyst, support material for Pt and Pt alloys for fuel oxidation and oxygen reduction. Unfortunately carbon suffers from corrosion in the presence of water (Lee *et al*., 2009). The presence of water not only caused the loss of support material but also results in an increment of pressure due to formation of CO_2. Not just that, the agglomeration of the Pt also caused carbon corrosion become severe with the presence of water. All these cause the degradation in the quality of the catalyst resulting in a weak performance and lifespan of fuel cells which cause a higher cost of the power produced (Jayasree *et al.*, 2012). In the case of solar system, a system should be developed in order to slow down or to have a control over energy wasting rates. This effort is parallel with the purpose in lengthen the lifetime of charge-transferred state to achieve higher efficiency and economic solar energy harvest (Yoon, 2000). Among the conducting polymers, conducting polypyrrole can be considered as promising material with mesoporous properties, which have the potential application as catalyst supports owing to its good conductivity and ease of preparation by chemical and electrochemical processes (Choi *et al*., 2008; Zhang & Manohar, 2004; Qi & Pickup, 1998).

The present research seeks to fill this gap. It emphasizes the Polypyrrole as a host polymer prepared by chemical oxidation polymerization using Iron (III) Chloride Hexahydrate as oxidant materials in primary doping. Two types of secondary doping agents which are Zeolite and Bismuth Oxide have been introduced into the host polymer. Both Zeolite and Bismuth Oxide are three-dimensional structure with large specific area and high surface free energy, which is ideal for sensor applications. With the properties of organic polymers which is covalently linked along the chains, interchain interactions are much weaker and this can cause collective instabilities such as Peierls distortions. Peierls' theorem states that a one-dimensionally equally spaced chain with one electron per ion is unstable (Youngmin Kim, 2005). As the organic polymer is unstable and degrades from time to time, it is believed with the introduction of Zeolite and Bismuth Oxide can help to stablize and improves the performance of polymer system in any applications.

1.11 Research Objectives

The objectives of this research are laid down below:

1.) To prepare intrinsically conducting compound Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth Oxide through chemical oxidative polymerization method with optimum ratio of oxidation/monomer, synthesis duration and polymerization conditions.

2.) To produce Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth Oxide with optimal physical properties such as stability, morphology as well as good thermal, optical and electrical responses.

3.) To study and characterize the effect of primary and secondary doping agents, Iron (III) chloride hexahydrate, Zeolite and Bismuth Oxide at different concentration levels and percentage through various analytical technique which included, Fourier Transform Infrared (FTIR) Spectroscopy, Thermal Gravimetry Analysis (TGA), X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersion X-Ray Flourescence (ED-XRF).

4.) To investigate the temperature, current and applied voltage dependence on the thermal, magnetic and electrical properties of Polypyrrole, Polypyrrole/Zeolite and Polypyrrole/Bismuth Oxide intrinsically conducting polymer using Laser Flash technique, Electron Spin Resonan (ESR) and Van Der Pauw (VDP) method.

1.12 Outline of the Thesis

This thesis is arranged in the following manner: Chapters are divided into sections as well as sub-sections. Chapter 1 gave an overview of conducting polymer, Polypyrrole, Zeolite and Bismuth Oxide. It also rationalized the aim of the research work and underlined several objectives to achieve the address the issues raised in the problem statements. Chapter 2 surveyed the work researcher have done in investigating the polymeric system understudy through different perspectives and approaches. Chapter 3 discussed in detail the materials used and the preparations of the polymeric systems used in the study. Chapter 4 highlighted the important observation of the study and discussed and compared with previous related studies covering eight types of measurements that, all results will be discussed and compared with previous related studies covering eight types of measurements that involves in this study included X-Ray Diffraction (XRD), Energy Dispersion X-Ray Fluorescence (ED-XRF), Fourier Transform Infrared (FTIR), Field Emission Scanning Electron Microscope (FESEM), Thermogravimetry Analysis (TGA), Laser Flash measurement, Diffuse Reflectance Spectroscopy (DRS), Electron Spin Resonance (ESR) and Resisitivity measurement - Van Der Pauw (VDP) technique. Chapter 5 summarized the important findings and gave recommendations for future work.

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