SYNTHESIS AND CHARACTERIZATION OF CONDUCTIVE POLYANILINE USING 24 HOURS CHEMICAL OXIDATIVE PROCESS FOR ORGANIC SOLAR CELLS

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2017

SYNTHESIS AND CHARACTERIZATION OF CONDUCTIVE POLYANILINE USING 24 HOURS CHEMICAL OXIDATIVE PROCESS FOR ORGANIC SOLAR CELLS

by

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Thesis Submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy

July 2017

Acknowledgement

Completion of this doctoral dissertation was possible with the support of several people. I would like to express my sincere gratitude to all of them.

Firstly, I would like to express my sincere gratitude to my advisor Prof. Dr. Kamarulazizi Ibrahim, for the continuous support of my Ph.D. study and related research, for his patience, motivation, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis. I could not have imagined having a better advisor and mentor for my Ph.D.

My sincere thanks also goes to co-supervisor Dr. Naser M. Ahmed, and Dr. Karema Z, who provided me an opportunity to join their team as intern, and who gave access to the research facilities. Without they precious support it would not be possible to conduct this research.

I thank my fellow lab mates in for the stimulating discussions, and for all the fun we have had in the last three years. Also I thank my friends in the following institution of Nano-Optoelectronic Research (INOR).

Last but not the least, I owe a lot to my parents and all my family for their supporting me prayers and supplication throughout writing this thesis and my life in general, and all who encouraged and helped me at every stage of my academic life, and they longed to see this achievement come true.

Above all, I owe it all to Almighty God for granting me the wisdom, health and strength to undertake this research task and enabling me to its completion.

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LIST OF SYMBOLS

α	Absorption coefficient
λ	Wavelength
σ_{DC}	Conductivity of direct current
η	Power conversion efficiency
A'	Absorptions
A''	Absorptions Correction
A_a	Acceptor atoms
D	Grain size
d	Spacing between crystalline plane
e	Electron charge
E_g	Optical energy band gap
E_a	Activation energy
FF	Fill factor
I	Total Current
I_e	electron current
I_{eo}	Small electron current
I_{ho}	Equilibrium hole current
I_{max}	Maximize Current
I_{sc}	Short circuit current
J	Current density
ℓ	Number of fingers
P_{in}	Input power
P_{max}	Maximize Power
P_{out}	output power
P_{light}	Power of the incident light
R	Reflecting
R_s	Series resistance
R_{sh}	Shunt resistance
t	Thickness of spinning speed
T'	Transmittance
V	Voltage
V_{max}	Maximize Voltage
V_{oc}	Open circuit voltage
W	Width distance fingers
W_f	Work function

LIST OF ABBREVIATIONS

$(NH_4)_4S_4O_8$	Ammonium Persulphate structure
C_2H_5OH	Ethanol structure
$CHCl_3$	Chloroform structure
EB	Emeraldine base state of pure polymer PANI
ES	Emeraldine salt state of doped polymer PANI
FESEM	Field emission scanning electron microscope
FT-IR	Fourier Transform Infrared
FWHM	Full width at half maximum
HR-XRD	High resolution x-ray diffraction
HF	Hydrofluoric acid structure
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
IDE	Interdigitated electrodes
J-V	Current-Voltage
PANI	Polyaniline
PANI-HCl	Polyaniline doped with Hydrochloric acid
PANI-H_2SO_4	Polyaniline doped with Sulphuric acid
PV	Photovoltaic cell

SINTISIS DAN PENCIRIAN POLIANILIN KONDUKTIF MENGGUNAKAN PROSES OKSIDATIF KIMIA 24 JAM BAGI SEL SURIA ORGANIK

ABSTRAK

Projek ini menyarankan satu kaedah alternatif untuk sintesis kimia polianilin mengikut kaedah polimerisasi oksidatif dengan persulfat amonium sebagai agen oksida, pada kemolaran sama di antara nisbah anilin ke oksida asid hidroklorik dan sulfurik. Kajian menunjukkan bahawa polimer asli boleh disediakan dengan cara merendamkannya dalam larutan amonia hidroksida untuk masa yang tertentu. Larutan polimer dituang ke atas slaid kaca dan lapisan silikon melalui teknik penyaduran berpusing (*spin-coating*) menggunakan tiga kelajuan pusingan yang berlainan; ketebalan filem yang difabrikasi ialah 949 nm, 285 nm, dan 45 nm untuk mengkaji ciri-ciri elektrik dan optik begitu juga dengan aplikasi elektronik dalam fabrikasi solar sel p-n persimpangan berdasarkan menjalankan polimer PANI-Si serta belajar yang umum ciri-ciri. Persediaan filem nipis polimer dicirikan oleh beberapa teknik. Pola XRD telah direkodkan dalam julat ($2\theta = 20^o$-60^o) menggunakan radiasi CuKα1 ($\lambda = 1.5406$ A^o) menunjukkan bahawa polimer mempunyai struktur separa-kristal; pola XRD PANI menunjukkan satu puncak yang lebar pada $2\theta = 31.94^o$ dan 22^o, 25^o, untuk tulen polimer dan dope, tidak kira apa jenis bahan dop, efek asid bahan dop menyebabkan pertambahan kristal dalam polimer polianilin. Untuk mengenalpasti struktur dan morfologi polimer yang disediakan, sampel teknik FESEM menunjukkan saiz partikel polimer dalam mikro-skala dalam kewujudan asid bahan dop. Spektroskop FT-IR yang dikaji telah digunakan untuk menentukan satu kumpulan aktif sebatian kimia, dan ia mempamerkan satu struktur polimer dalaman melalui kewujudan asid protonasi walaupun kedudukan sebatian tidak berubah. Ciri-

ciri optik persediaan lapisan nipis polimer dikaji termasuk serapan spektroskopi untuk gelombang 200-1000 nm. Satu kajian telah dijalankan untuk menentukan koefisien serapan untuk transmisi secara langsung, dan jurang tenaga yang dianggarkan E_g untuk polimer ialah 4.10eV dan 4.13eV untuk polianilin yang didop dengan asid hidroklorik dan sulfurik. Konduktiviti elektrik telah dikaji dan didapati bahawa lapisan nipis dikatian dengan perilaku ohm polimer yang didop. Kajian menunjukkan bahawa konduktiviti elektrik meningkat dengan peningkatan suhu dari 293°-383° K iaitu salah satu ciri bahan separa-konduktif. Kesan pengedopan ke atas konduktiviti elektrik telah dikaji, dan didapati nilai tertinggi kondutiviti elektrik $\sigma_{DC} = 2.98 \times 10^{-4}$ $S.cm^{-1}$ untuk pengedopan polimer dengan asid sulfurik berbanding dengan polianilin tidak ber-dop 1.4×10^{-7} $S.cm^{-1}$. Tenaga yang diaktifkan Ea yang ditentukan untuk polimer, dan ia mempamerkan tenaga keaktifan yang lebih besar polianilin yang didop dengan asid hidroklorik 0.124eV dari polianilin yang didop dengan asid sulfurik 0.112eV. Sebagai hasil daripada garam yang terkumpul dalam polianilin, asid sulfurik lebih ketara dari asid hidroklorik polianilin. Untuk aplikasi elektronik sampel polianilin konduktif, fabrikasi dibuat daripada pelbagai jenis sel solar. Ciri-ciri elektrik sel solar telah dikaji pada iluminasi 100 $mW.cm^{-2}$. Nilai tertinggi efisiensi yang diperolehi ialah 0.34% untuk polianilin yang didop dengan asid sulfurik.

SYNTHESIS AND CHARACTERIZATION OF CONDUCTIVE POLYANILINE USING 24 HOURS CHEMICAL OXIDATIVE PROCESS FOR ORGANIC SOLAR CELLS

ABSTRACT

The project proposed an alternative way for chemical synthesis of polyaniline following the oxidative polymerization method with ammonium persulphate as oxidant agent, at equal molar of aniline to oxidant ratio of hydrochloric and sulphuric acid. The study revealed that it is possible to prepare pure polymer by dipping it in Ammonia hydroxide solution for specific time. The polymer solution deposited on glass slides and silicon wafers by the spin coating technique using three different speeds of rotation; thickness of the fabricated films was 949 nm, 285 nm, and 45 nm in order to study electric and optical properties as well as electronic applications in the fabrication of p-n junction organic solar cells based of the conducting polymer PANI-Si as well as study of the photovoltaic characteristics. The polymer thin films preparation was characterized by several techniques. The XRD patterns were recorded in the 2θ range of 20°-60° using CuKα1 radiation (λ= 1.5406A°) showing the polymer has semi-crystalline structure; the XRD patterns of PANI shows a broad peaks at 2θ= 31.94° for pure polymer and 22°, 25° for doped, irrespective what type of dopant, the effects of acid dopant caused an increase in the crystallinity of polyaniline polymer. To identify the structure and morphology of the prepared polymer, samples by FESEM technique showed the particle size of polymer in the micro-scale in the existence of dopant acid. Analysed FT-IR spectroscopes were used to determine an active group of the chemical bonds, and exhibited an internal polymer structure by the existence of protonation acid though the position of bonds did not change. Optical

properties of thin films preparation of polymer were studied including the absorption spectroscopy for wavelength of 200-1000 nm. An investigation was carried out to determine the absorption coefficients for the transmissions directly, and the estimated energy band gap E_g of polymers were 4.10eV and 4.12eV for polyaniline doped with hydrochloric and sulphuric acid respectively. The electric conductivity was studied and it was found that the thin films correlate with the ohmic behaviour for the polymers doped. The study showed that the electric conductivity enhances with temperature increased from 293°-383°K which is one of the characteristics of semi-conductive material. The effect of doping on electric conductivity was studied, and found the highest value of electric conductivity $\sigma_{DC} = 2.98 \times 10^{-4}$ S.cm^{-1} for polymer doping with sulphuric acid compared with undoping polyaniline 1.4×10^{-7} S.cm^{-1}. The activation energy E_a determined for the polymers, and exhibited greater activation energy of polyaniline doped with hydrochloric acid 0.124eV than that of polyaniline doped with sulphuric acid 0.112eV. As a result of the localized salt in polyaniline sulphuric acid was more prominent than that of polyaniline hydrochloric acid. As for the electronic application of conductive polyaniline samples, the fabrication was made of different types of solar cells. The electric properties of the solar cells were studied at illumination intensity 100 mW.cm^{-2}. The highest value of efficiency obtained was 0.34% for the polyaniline doped with sulphuric acid.

CHAPTER 1
INTRODUCTION

1.1 Historical Overview

Polymer materials have long been considered to be good insulators because their predominant covalent bonds exhibit low electrical conductivity. Polymers with conjugated π-electron (i. e. system have C=C conjugated bonds) backbones display unusual electronic properties such as low energy, optical transition, low ionization potentials, and high electron affinities. The result is a class of polymers that can be oxidized or reduced more easily and more reversibly than conventional polymers. The effect of this oxidation or reduction on polymer is called doping, i. e. convert an insulating polymer to conducting). Conducting polymers (CPs) such as polypyrrole, polythiophene and polyaniline are complex dynamic structures that captivate the imagination of those involved in intelligent materials research [1]. However, at first it was found that when the linear polymers and hetero-aromatic polymers were doped by chemical or electrochemical methods, their electrical conductivity increased dramatically. Since then, studies on conductive or semi-conductive polymers have attracted considerable attention from chemists, physicists, and material scientists. This interest arises from both the high conductivity obtained, and the polymer materials' special advantages of low cost, light weight, and non-toxicity. Figure 1.1 illustrates the extremely broad range of electrical conductivity behaviour of polymers and different materials. It can be seen from Figure 1.1, [2] that the electrical conductivity of conductive polymers spans a range of from 10^{-10} S.cm^{-1} to around 10^{1} S.cm^{-1} after doping. Doping, as described by MacDiarmid and Epstein [3]. Doping state is a

phenomenological concept. It does not imply the involvement of any specific mechanism or process. In the conducting polymers field a chemical dopant is a substance, a relatively small quantity of which drastically changes the electronic, optical and structural properties of the polymer, and is accompanied by a large increase in conductivity. According to this, a process of increasing the conductivity of materials by a dopant is called doping. There are two common forms of doping which are presently well established in the conducting polymers field, and they involve basically different processes which were also described by MacDiarmid and Epstein [2]:

- Redox doping whereby oxidizing or reducing agents remove or add, respectively electrons from or to the polymer backbone e.g. p- or n- doping of (CH) x.
- Acid/base, protonic acid doping whereby the number of electrons associated with the polymer chain remain unchanged.

The dopants for the first kind of doping can be electron donors (n-type) materials such as Sodium, Sodium naphthalene, and electron acceptors (p-type) materials such as Iodine, arsenic pent-fluoride [3]. In the protonic acid doping process, the dopants usually used are inorganic acids such as Hydrochloric, Sulphuric acid, or organic acids such as toluene sulfonic acid. The application of electrical stimuli can result in drastic changes in the chemical, electrical and mechanical properties of conducting polymers. These complex properties can be controlled only if we understand, first, the nature of the processes that regulate them during the synthesis of the conducting polymers, and second, the extent to which these properties are changed by the application of an

electrical stimulus. Polyaniline and its derivative is one of important conducting polymer, it has many application such as organic light emitting diodes, organic solar cells and corrosion [4-7].

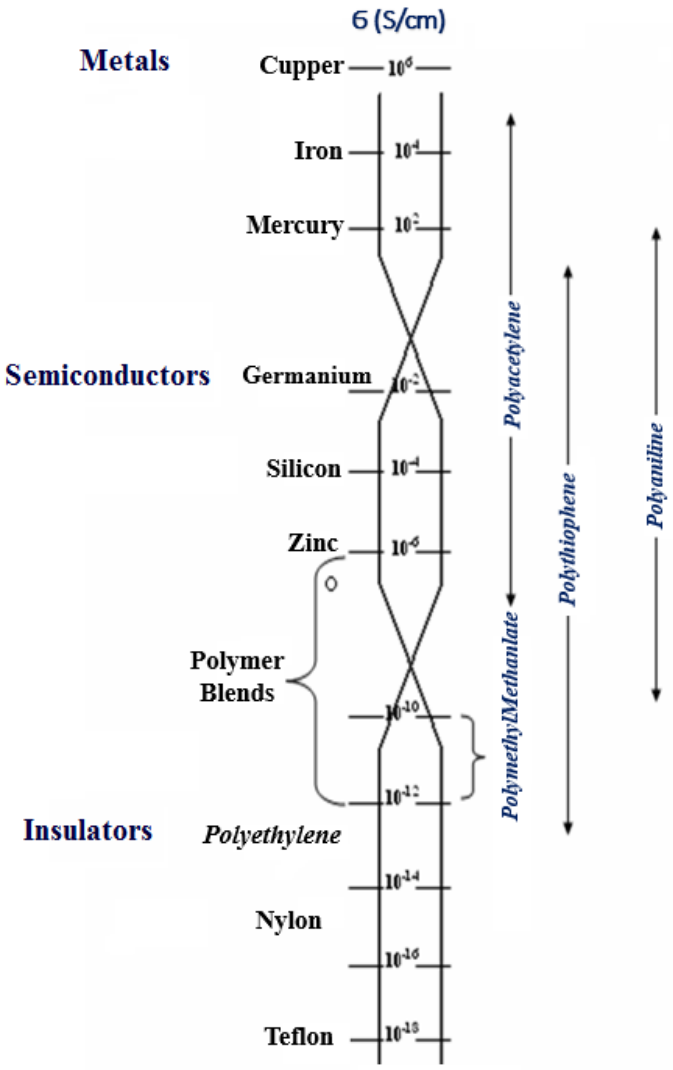

Figure 1.1: Electrical conductivity of Polymers and related Materials [8].

Because of their special features and significantly enhanced conductivity following doping, conductive polymers have been suggested for use as polymeric electrodes in lightweight batteries, sensors, electro-chromic displays, conductive wires, and nonlinear

optical materials [9]. Overall, the number of studies on the conductive polymer materials is increasing rapidly, and some investigators believe that such polymer materials will be in commercial production in the near future. However, many fundamental aspects such as a theoretical understanding of conductive polymers or the required structures of these polymers are not well established. There are two generally proposed hypotheses. Based on a major breakthrough in conductive polymers achieved in 1977, Shirakawa [9] reported that polyacetylene could be turned into a highly conductive polymer by conversion to a salt. By reacting it with Iodine, the conductivity of the doped polymer was increased by 10^{10} $S.cm^{-1}$. Based on this success, other conjugated polymers such as linear polymers were targeted in subsequent research efforts. It was supposed, that polymers with long conjugated chains basically to achieve high levels of electrical conductivity. This scenario depends on the contribution to conductivity from the delocalization of charge carriers along the chain. Later, another view was proposed. In that instance, naphthalene and other simple aromatics could be partially oxidized electrochemically to form monomeric radical cation salts Ar^{+x} which have conductivity 10^{2} $S.cm^{-1}$. These organic materials display crystal structures which suggest that the aromatic parts form stacks. So a concept was proposed that the charges and the electrons are presumably delocalized along the stacks. Delocalization tends to emphasize the contribution of the intermolecular charges and electrons. This hypothesis opens a second potential approach to the production of conductive polymers which is to use non-conjugated polymers containing aromatic parts. Therefore, aromatic structures have received increased interest due to their improved process ability, mechanical properties, oxidative stability, and the large varieties of derivatives. For example,

polyaniline PANI has multiple structural forms, accepts special doping mechanisms to produce high conductivity, and yet retains good environmental stability in air. Moreover, it can be easily synthesized by either chemical or electrochemical oxidation of aniline, and then processed into powder, films fibres and various composites. Again, PANI is also amenable to special doping mechanisms so the electronic properties can be modified through either redox doping (variation of the number of electrons) or protonic acid doping (variation of the number of protons). In summation, PANI exhibits a high potential for several technological applications. According to several reports from MacDiarmid, Epstein [10], Stejskal and Kratochvíl [11] PANI exists in three different stable insulating oxidation forms as different colour powders: (1) Leucoemeraldine base (LEB), violet colour; (2) Emeraldine (EB), dark copper colour; and (3) Pemigraniline base (PNB), colourless. The general form of the repeat unit for these polyaniline is shown in Figure 1.2.

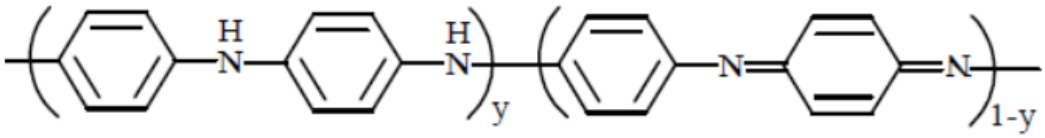

Figure 1.2: The general formula of Polyaniline [2].

On this basis, when y = l/2, the EB form predominates; when y=1, the polymer assumes the (LEB) form; and when y=0, it is said to be oxidized to the (PNB) form. Since the EB form has more solution process ability than the other two forms, and it can be easily converted to a salt form ES which exhibits a much high conductivity from protonic acid doping, the EB form is considered to be the most interesting.

1.2 Problem Statement

Conductive polymer as polyaniline has been the many researches in the field of conducting polymers for many years. It is a more flexible polymer with characteristics similar to most of the semiconductor materials, for this polymer like low cost, easy preparation, and its stable conductive form. However, we have to focus more on a disadvantages, which include low conductivity, insolubility in the most of solvents, and low adhesion on different substrates [12]. The main aim of this work was to prepared polyaniline and to enhance the electric conductivity of polymer at end of the process. A proper blend was prepared by mixing polyaniline powder, with Hydrofluoric acid HF, as solvent used to enhance an adhesive and an electrical properties. Thereafter, the blend was vigorously stirring on a magnetic stirrer for 3h. Polyaniline powder product is a type of conductive polymer form which not melting well in most of the solvents; therefore, it is not adhesive on different substrates used except few of organic solvents like Hydrofluoric acid HF and Dimethylformamide DMF. For achieving sample stable structures on the substrate is needed to thermal treatment by annealing at 80 ^{o}C; we observed a gradual enhancement in adhesion and an increase in the conductivity of polyaniline samples; it was important that the polymer should settle uniformly within all other solvents in order to produce a conductive polyaniline [13].

1.3 Research Objectives

1. To synthesize a conductive polyaniline using chemical oxidative polymerization method, as time fabrication using 24 hour as short time different from other polymerization methods.
2. To enhance the conductivity of polymer films using doping method with protonic acid of Hydrochloric and Sulphuric acid, then follow by thermal treatment annealing at 80^{o}C.
3. To fabricate organic solar cells device using (PANI) as a conductive polymer, and investigate the efficiency of device.

1.4 Originality of the Research Work

1. In this work, fabrication of a conductive polymer PANI depends on chemical oxidative polymerization technique which has an advantage over the other polymerization methods as time preparation 24h only, unlike of other fabricated methods require longer time as 48h and 72h [14].
2. Enhance the electrical conduction of polymer by doping state using inorganic acid such as Hydrochloric and Sulphuric acid.
3. Improve an efficiency of organic solar cells fabrication using different of chemical solvents such as Hydrofluoric acid HF and Dimethylformamide DMF.

1.5 Outlines of the Thesis

The content of the current thesis is divided into five chapters which are organized as; Chapter one includes a historical overview on conductive polymers according to their electrical and chemical properties. Chapter Two includes a review of the related literature survey and review on conducting polymers and doping methods of conductive polymers. Chapter three includes the research methodology and an equipment's used for synthesis of polyaniline by the chemical oxidative polymerization method. The general instruments that were used in this work are also summarized. The measurement of current-voltage characteristics and fabrication different type of devices of organic solar cells are presented too. Chapter four covers the results obtained from the synthesis which explains and investigates the polymer films morphology and structure study by FE-SEM, and HR-XRD techniques. An optical and electrical properties of the polymers prepared in the study. The type of electronic transitions from valence band to the conductive band is determined depending on the absorption coefficient. The electrical conductivity is calculated at different temperatures. Additionally, the doping state is added to improve the conductivity of polymer. Also includes the application on the organic solar cells p-n junction fabrication of the conducting polymer as well as the study of their photovoltaic properties. Chapter five involves the conclusion of the present study and some of suggestions for future works.

CHAPTER 2

LITERATURE SURVEY AND REVIEW

2.1 Introduction

In this chapter relevant literature, general principles and theories of subjects involved in this work are discussed. In particular it presents an overview of conducting polymers, doping methods of polymers materials, conductive polymer of polyaniline PANI, structure and morphology of polyaniline, polymerization mechanism and properties of polyaniline. Apart from that, studies of characterization of conducting polymers as well as optical and electrical properties of these materials are discussed. Subsequently, the fabrication and characterization of various devices of heterojunction solar cells is analysed.

2.2 Overview of Conducting Polymers

Scientific and technological interest in electronic conducting polymers is not required to be demonstrated anymore. The importance of this field of research has been clearly recognized by awarding the chemistry Nobel Prize in 2000 to A.J. Heeger, A.G. MacDiarmid and H. Shirakawa [15]. The ability of conjugated polymer to carry delocalized electronic charges is used in many applications in which metallic, semi-conducting or electrically tunable medium is involved [16]. From here, it is easy to imagine that we are dealing with a field in which the scientific interdisciplinary is privileged especially between chemists and physicists but more recently also with electronics and optics engineers and biologists. Conducting polymers offer a unique combination of properties that make them attractive alternatives to conventional

materials currently used in electronic devices like transistors, photovoltaic cells, light emitting diodes, biochemical sensors, gas and liquid separation membranes, corrosion protection of metals, electrostatic discharge protection and many other potential applications. The conductivity of these polymers can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by degree of doping, and blending with conventional polymers. In addition, they offer light weight, and flexibility. Recent developments in materials sciences and molecular engineering give an excellent possibility for coupling unique electronic properties of conducting polymers with good mechanical properties, stability and low production costs commonly attributed to conventional polymers. Conducting polymers have some similarities to conventional polymers, but the extensive main-chain π-conjugation which radically increases the chain stiffness strongly determines its physical properties [17]. They are usually insoluble and difficult to process. As a consequence, conducting polymers form less ordered structures with many defects and distortions. It is convenient to describe the conducting polymers by considering several groups exhibiting different structural characteristics which depend on the internal chain architecture [18]. The first basic of group consists of linear unsubstituted conducting polymers with a stiff (rigid) chain like polyacetylene or semi flexible chains like Polyaniline [19]. The investigations carried out to develop new materials with better properties for new applications resulted in next group with a range of structural forms. This group of compounds is based on flexible side group substitution to the conducting polymers backbone [20]. Specific examples of these polymers are shown in Figure 2.1.

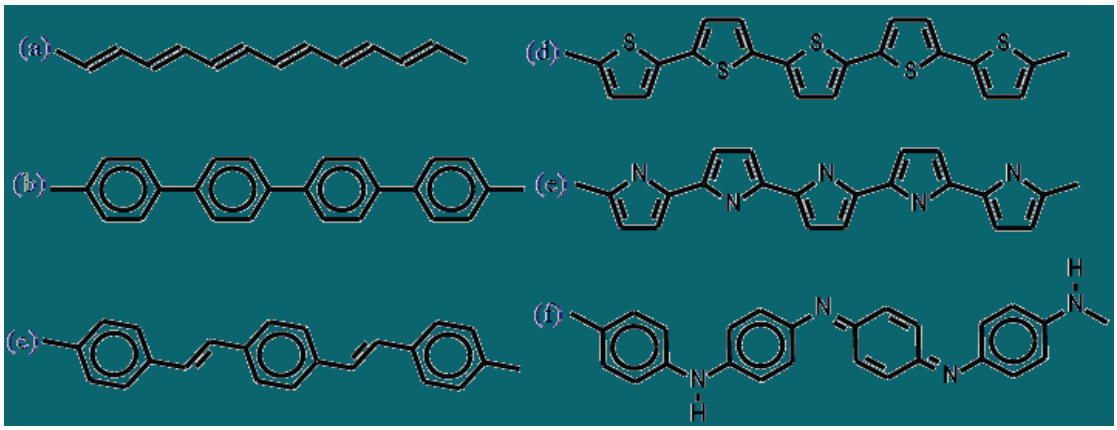

Figure. 2.1: The common family of linear conducting polymers: (a) Trans Polyacetylene, (b) Polyphenylene, (c) Polyphenylene vinylene, (d) Polythiophene, (e) Polypyrrole, (f) Polyaniline [20].

2.3 Mechanism of charges Transport in Conducting Polymers

It is significant to understand that polymers with conjugate bond structure going through the whole molecules are ordinarily electrically conducting. The electrical properties of conducting polymers rely on the electronic bond structure. When the bond conduction is filled or emptied, no conduction happens. If the band gap energy is small compared to thermal excitation energies, electrons are excited to the conduction band along with the conductivity increments [21]. Precisely as the band gap is too wide, thermal excitation is weak to energize electrons to the conduction band and the material is an insulator as shown in Figure 2.2, the conductive polymers transport current without having incompletely vacant or in fractional filled bands. The most essential qualities, in any case, are that when the polymers are exceedingly oxidized, the charge transporters are deficient. To the explication of the conduction state, it is suggested that when an electron is expelled from the highest of the valence band by oxidation, an opening (gap or radical

cation) is made; however, it doesn't delocalize totally. Fragmentary delocalization happens more than a little monomer unit, and the units deform generally. The energy level connected with the radical cation presents a destabilized bonding orbital, and, thus, has a higher energy than that of the valence band. A radical cation that is partially delocalized over some polymer segments is known as a 'polarons'. Now, a "bi-polarons" has double charges: the lower oxidation levels yield polarons and higher oxidation levels yield the bipolarons. Both polarons and bipolarons are compact and can be portable along the polymer chain by the reorganization of the double and single bonds in the conjugated system that happens in an electric field. Conduction by polarons and bi-polarons is an essential way of charge transport in polymers for degenerated ground states. There are a few models for electrical conduction. The most utilized is the one electron band model [21]. This depends on enlarging the essential model of bond among two molecules over entire crystalline solid.

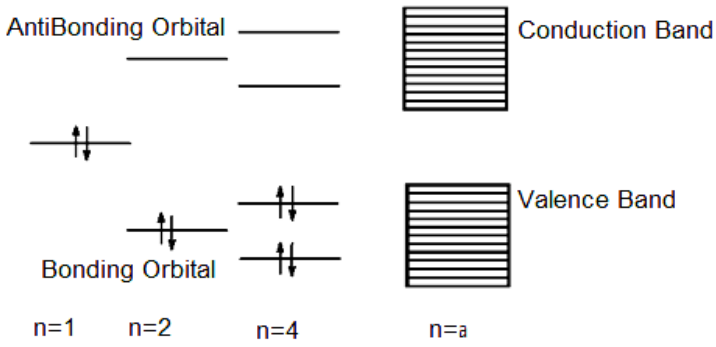

Figure. 2.2 One electron band model for electrical conduction.

As stated, when two compatible atoms, each one having a half filled orbital, are sufficiently united for their orbital to overlap, the two orbitals interact to produce two new orbitals, one of lower energy and one of higher energy. The extent of this energy

variation is known by the level of orbital overlap. The two electrons go into the lowest energy orbital. The lowest energy orbital (full) is a bonding orbital, and the highest energy (unoccupied) orbital is an anti-bonding orbital. The measure of the conductivity is controlled by the concentration of charge transporters which move to consider an effect of temperature on the electrical conductivity of three sorts of materials (metals, semiconductors and insulators). It is necessary to consider its effect on both charge carriers' concentration and mobility. In a metal material, each one of the electrons is available for conduction so the conductivity is determined by the mobility. As the temperature of a crystal lattice is expanded, the atoms vibrate and interact with the electrons to disperse them. As a result, the conductivity decreases when temperature increases. In a semiconductor, the charge carrier concentration increases due to the rise in the temperature. So the charge transporter concentration is significantly, to a greater extent, temperature dependent than the mobility [21]. In an insulator, the band gap is so large that it is extraordinarily difficult to place thermally excitation electrons over it to give charge carriers; along these ways the conductivity stays very low. Conducting polymers are amorphous structures. Hence, it has been suggested that electrical conduction occurs by charge hopping method between polymeric chains. The electrical conductivity in homogeneous system can be well explained by semi particles, polarons, bipolarons and solitons. For this situation, transport process leads to high electrical conductivity. In heterogeneous system the charge transport along the polymer chains takes place by hopping method.

2.4 Doping of Conductive Polymers

Conductive polymers for the most part show poor electrical conductivity $\sigma \leq 10^{-12}$ $S.cm^{-1}$ in the undoped state and exhibit as insulators. These pure polymers should be treated with an appropriate oxidization or reduction operators to astoundingly update their conductivities to the metallic region. This process has been named as "Doping". Doping process results in exciting changes in the electrical, optical, and structural characteristic of the polymer. Doping of polymeric semiconductors is not precisely the same as that in inorganic semiconductors. Inorganic semiconductors have three dimensional crystal lattice and an embodiment of specific dopant, n-type or p-type. The dopant is dispersed along the particular crystal locales on a repetitive basis.

Doping of conducting polymer contains sporadic dissipating or aggregation of dopants in molar concentrations in the disarranged structure of interlaced chains and fibrils [21, 22]. In a likely manner, incorporation of dopant molecules in the one dimensional polymer structure broadly confounds the chain request exciting to rearrangement of the polymer. Doping methodize is reversible, and it makes the polymer with no distortion of the system. Both doping and undoping forms, including dopant counter particles which settle the doped case, might be done chemically, synthetically, or electrochemically. Doping in inorganic semiconductors makes either holes in the valence band or electrons in the conduction band. On the other hand, doping of polymer offers an increase in the arrangement of conjugation deformations, in other words, solitons, polarons or bipolarons in the polymer chain. A great conductivity in semiconductors polymeric relies on upon different segments, viz. nature and concentration of dopants, crystallinity and morphology of polymers.

By controlling the doping concentration, conductivity wherever between that of non-doped (insulating or semiconducting) and that of completely doped (conducting) type of the polymer structure can be easily obtained. The variation oxidation procedures of polyaniline are followed in various doping methods. Generally, in conducting polymers, p-type doping is conducted with an electron acceptor such as p-type and n-type doping is conducted with donor class, for example, Lithium. In the doped state, the base of a conducting polymer includes a delocalized structure. In the undoped state, the polymer may have a conjugated chain, e.g., in trans (-CH) x which is held in a changed structure after doping, or it might have no conjugated chain as in PANI (leucoemeraldine structure), which turns out being really conjugated essentially after p-doping, or a no conjugated structure as in the emeraldine base sort of polyaniline which gets the chance to be conjugated just after protonation acid doping [22].

2.5 Concept of doping polymers Process

The role of the doping is to either remove or add electrons to the polymers. This doping acts as charge transfer agents. The electrical conductivity can be increased by doping i.e. p-type doping (oxidation) or n-type doping (reduction) increases the electrical conductivity to a great extent. This explanation is no over-simplification as the conductivity in polymers is associated with charge carriers that do not have free spins rather than the expected unpaired electrons detected in metals; so a modified model must be developed. Dopants may be classified as ionic dopants, organic dopants, and polymeric dopants. Ionic dopants are oxidized or reduced by an electron transfer with the polymer and the counter ion remains with the polymer to make the

system neutral. Organic dopants are anionic dopants generally incorporated into polymers from aqueous electrolytes during anodic deposition of the polymer [23].

2.6 Conductive Polymer Polyaniline (PANI)

The continuously growing interest in the study of PANI over the years is mainly because of its diverse, but unique properties allowing its potential applications in various fields. Among all the conducting polymers, polyaniline is known for its ease of synthesis, environmental stability and effortless doping by protonation acids. Polyaniline is well-known as an environmentally stable and highly tunable conducting polymer which can be produced as bulk powder, cast films, or fibres. This, in conjunction with the advantages of low-cost and large-scale of production makes it an ideal candidate for various applications. The term polyaniline corresponds to a class of polymers having up to 1000 repeat units also called mers [24]. Much of the structural characterization of polyaniline has taken place in the last 20 years or so, and is fairly well established. However, the large number of papers published in the last five years would indicate that polyaniline is still under much scrutiny. Polyaniline is a typical phenylene rings based polymer having a chemically flexible –NH– group in a polymer chain flanked either side by a phenylene rings. It can also be defined as the simple 1, 4- coupling product of monomeric aniline molecule. The protonating, deprotonating and various other physic-chemical properties of polyaniline are due to the presence of the –NH– group. Polyaniline is the oxidative polymeric product of aniline under acidic conditions and has been known as aniline black. There are several reports of polyaniline found in the literature over the decades about the structure and constitutional aspects of aniline

polymerization [25]. Surville et al reported the proton exchange and redox properties with the influence of water on the conductivity of polyaniline [26].

2.6.1 Structure and Morphology of Polyaniline

There are many levels of polymer structure and one can categorize the levels loosely using terms used to describe protein structure. The primary structure describes the connectivity of the atoms. The secondary structure describes the three dimensional shape due to short range non-bonded interactions such as backbone twisting. The tertiary structure describes the shape, also called conformation, of the polymer chains due to long-range non-bonded interactions which may be inter chain. The terms of quaternary structure could be used loosely to describe the polymer in relation to degree of order for example crystalline, semi-crystalline, or amorphous. Morphology is defined as the study of the form. However, when applied to polymers, morphology generally describes the three-dimensional chain conformation and the relationship between chains as well as the aggregates. Furthermore, morphology includes the physical appearance of polymer particles such as rice grains, spheres, tubules, and fibrils [27]. Polyaniline oxidation of aniline hydrochloric with ammonium persulphate yields polyaniline (Emeraldine) hydrochloric as shown in Figure 2.3.

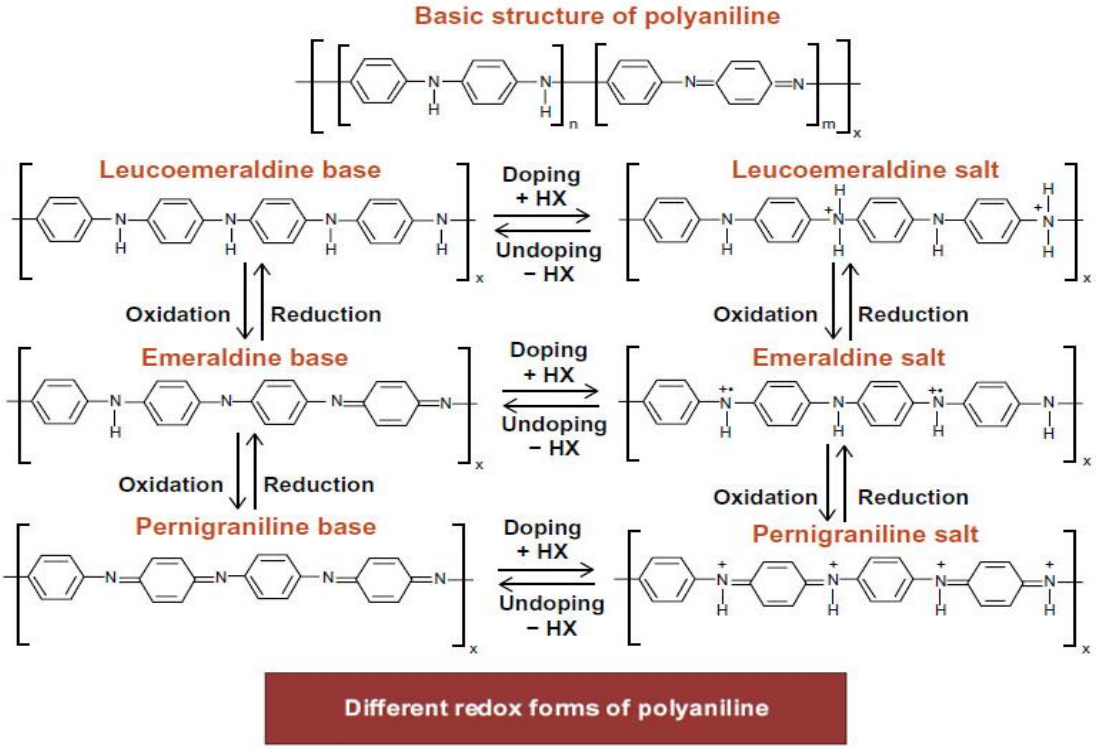

Figure. 2.3: Schematic of polyaniline in different oxidation states [27].

2.6.2 Properties of Polyaniline (PANI)

Polymer PANI can occur in various diverse oxidation methods [28], and each has its own particular name as initially ascribed by Green and Woodhead [29] illustrated in Figure 2.3. The distinctive states range from the completely reduced leucoemeraldine by means of protoemeraldine, emeraldine to the completely oxidized Pernigraniline. On the other hand, in other poly-aromatics, it is the completely oxidized state in the polyaniline not truly conducting anything compared to what was just mentioned about portrayed oxidation states' conducting. Polyaniline gets to be conducting when the somewhat oxidized states, specifically the emeraldine base, are protonated and charge carriers are produced this procedure is, by and large, called "protonation chemical acid doping" [30]

which makes PANI distinctive as no electrons must be included or expelled from the insulating material to make it conducting. The distinctive oxidation conditions of PANI can likewise be created by doping with oxidants, e.g., iodine; however, subsequent conductivity is lower than that acquired by means of protonic acid doping. The conduction system is accepted to include polaronic transporters i.e. the protonated emeraldine which comprises of a delocalized poly (semi-quinine radical cation). The conductivity is influenced by the water content in PANI as totally dry specimens are five times less conductive than specimens containing some water [31]. The emeraldine base is dissolvable in N-methyl-pyrrolidone [32]. However, protonated PANI is insoluble in organic solvents, and just dissolvable in fluid acids [33]. Substitution of aniline monomer with alkyl rings enhances the dissolvability in organic solvents though it affects the conductivity [32-35]. The position of the substituent likewise has an effect on the polymerization procedure. The meta-isomers give the same polymer though the reactivity of the meta-isomer is mainly lower resulting into a lower polymer yield. Self-doped PANI containing Sulphuric acid substituent has been prepared by Sulphuric of the emeraldine base [36, 37]. In spite of no information being available concerning the health dangers of PANI, the conceivable presence of benzene ring moieties is surely understood to be cancer-causing agent. Thus, careful handling of both the aniline and its polymers is required.

2.6.3 Methods of Synthesis Polyaniline (PANI)

Polyaniline can be chemically or electrochemically synthesized by the oxidative polymerization of aniline monomer in the presence of an aqueous acid such as 1M HCl or H_2SO_4 solution [38]. The formed polymer is called an emeraldine salt. For chemical synthesis, there are many different oxidizing agents including ammonium persulphate (APS) [38, 39], hydrogen peroxide [40], ferric chloride [41] and ceric nitrate [42-44]. Typically the ratio of oxidizing species to aniline has been reported to be oxidant/aniline ~1.25 [45]. A typical chemical synthesis of polyaniline is carried out in an aqueous 1M HCl at temperatures between ~0^{o}C and ~-4^{o}C [38]. It has also been shown that higher molecular weight polyaniline Mw>100,000 can be synthesized when the polymerization is carried out at temperatures below -20^{o}C [46-49]. The neutral form of polyaniline, emeraldine base (EB) can be converted from the fully protonated emeraldine salt by non-protonation of the polymer with an aqueous ammonium hydroxide. Polyaniline can also be synthesized electrochemically by the oxidation of aniline on an inactive metallic (e.g., Pt) [50-52] electrode or on a piece of conducting Indium Tin Oxide (ITO) glass [53]. Electrochemical polymerization method of aniline can be carried out in acidic media by constant potential, constant current, and by repeatedly cycling the applied voltage between two selected potentials. These polymerization methods offer the possibility of conveniently investigating various chemical and physical properties of polyaniline in optical spectroscopic techniques and electrical properties.