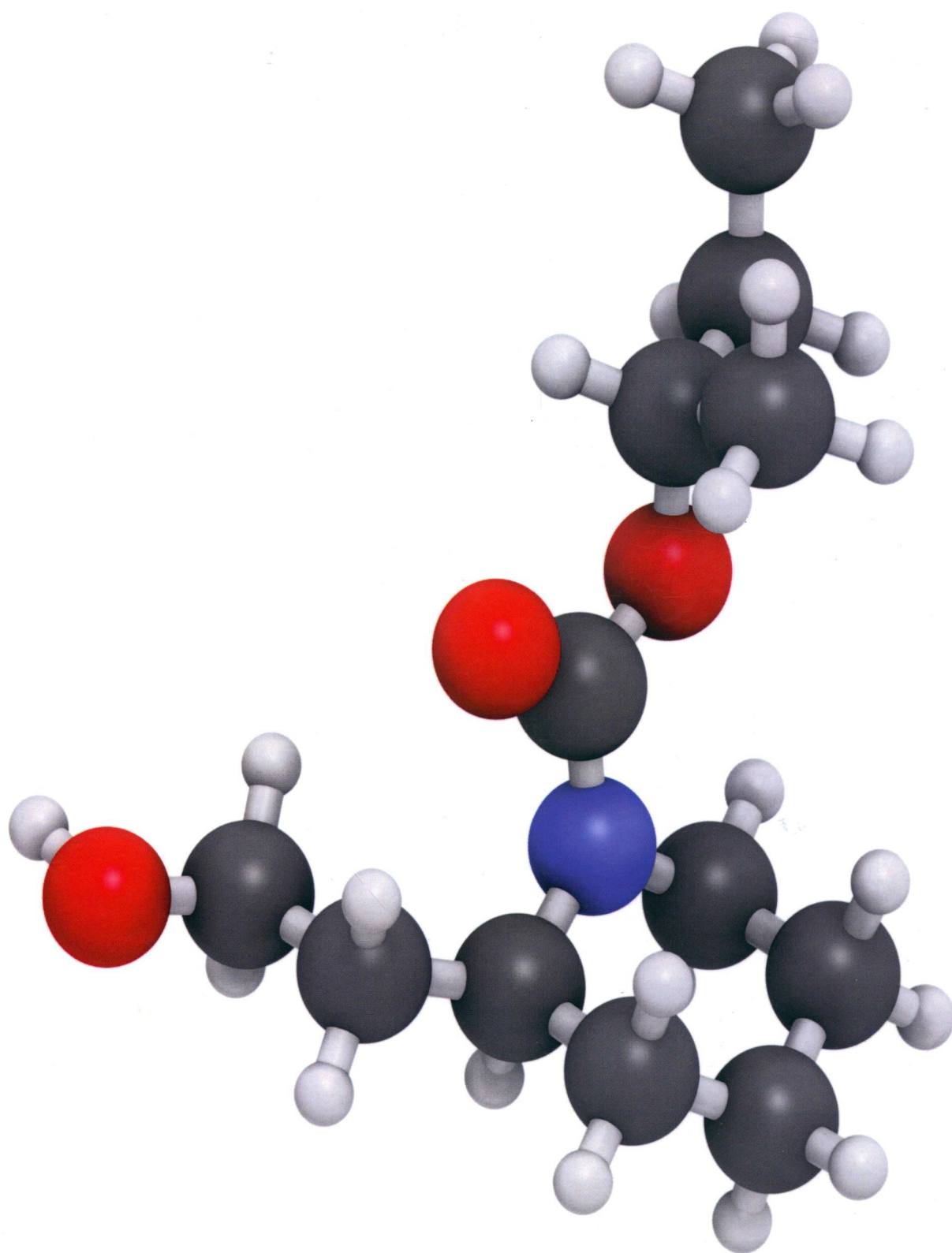


# Application of Conducting Polymers

Contributors: Kareema Majeed Ziadan, et al.



## About the Book

Conducting polymers are an important class of organic materials with electric conductivity and have experienced a rapid development. Intrinsically conducting polymers, also known as "synthetic metals," are polymers with a highly conjugated polymeric chain. They have been studied extensively due to their intriguing electronic and redox properties, along with the resulting numerous potential applications in many fields since their discovery in 1970s. Conducting polymers (CPs) such as polypyrrole, polythiophene and polyanilines are complex dynamic structures that captivate the imagination of those involved in intelligent materials research. The application of electrical stimuli can result in drastic changes in the chemical, electrical and mechanical properties of CPs. 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 (OLEDs), corrosion and solar cells. Conducting polymers (CPs), which combine the electronic characteristic of metals and inorganic semiconductors, possess the attractive advantage of having easy synthesis control over the properties of the polymeric exposed surface such as structure, morphology and thickness. The use of these polymers represents the most important development in the preparation of modified electrodes to make sensors and biosensors. Their synthesis can be achieved by two conventional methods.

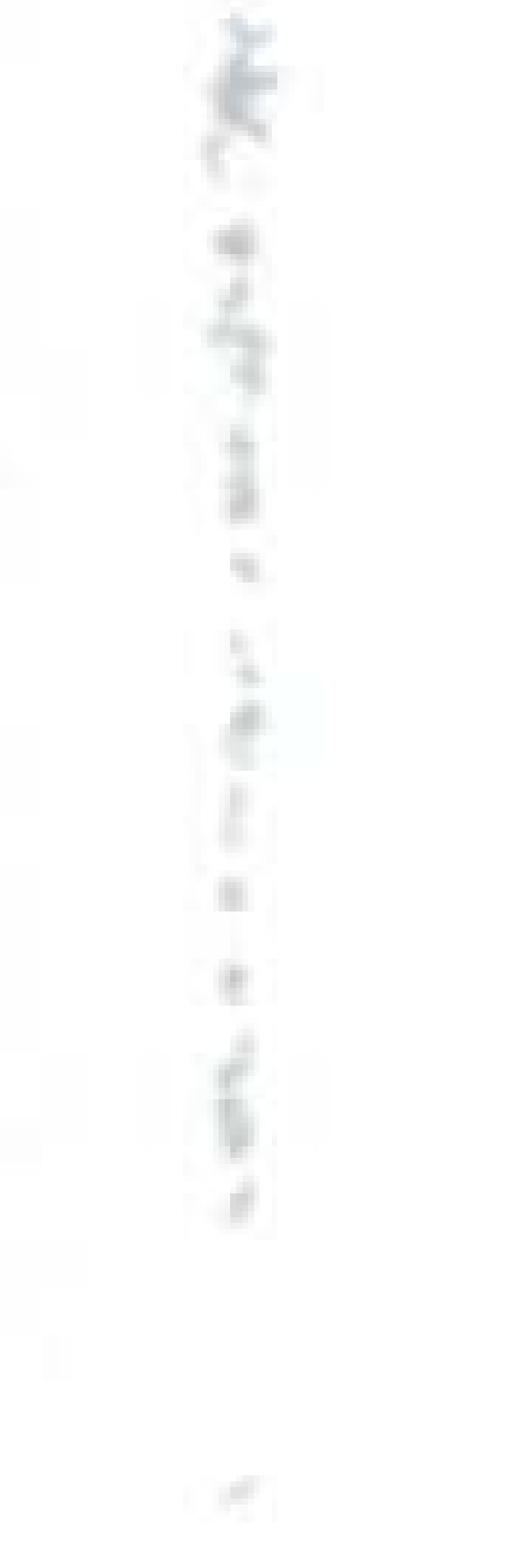
Application of Conducting Polymers focuses on mechanism of conduction and mechanism of charge transport of conducting polymers. The rich literature concerned about different applications of CPs: conducting polymers (CPs) in electronic, electromechanical, and optoelectronic devices, and conducting polymers (CP's) in electronic chemical sensors that are based on the mechanisms of mechanical, electronic, or optical transduction.

Conducting polymers, such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PTh) and their derivatives, have been used as the active layers of gas sensors since early 1980. There are two main types of applications for the Conducting organic polymers in electronics: first one is that a polymer can be used as a material for constructing different devices and as discriminating layers in electronic chemical sensors. In both cases, interacting with surrounding gases is vital. It can possibly determine the performance of the devices that are depending on conducting polymers, while it is helpful and supportive in chemical sensors. Conductivity has been the main property of concern; the aim is of study and to identify the usability of the conducting polymers in the two kinds of electronic applications mentioned above. Electronic Chemical Sensors for gases are thought of to be at the top of gaining the information related to the environment that we live in. The quality of the air that we breathe in our bodies is very important issue and is a real concern of modern society.



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**Ziadan**

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**Application of Conducting Polymers**

ISBN: 978-1-78802-143-2

British Library Cataloguing in Publication Data

A CIP record for this book is available from the British Library

Printed in the United Kingdom

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# Preface

Conducting polymers are an important class of organic materials with electric conductivity and have experienced a rapid development. Intrinsically conducting polymers, also known as “synthetic metals,” are polymers with a highly conjugated polymeric chain. They have been studied extensively due to their intriguing electronic and redox properties, along with the resulting numerous potential applications in many fields since their discovery in 1970s. Conducting polymers (CPs) such as polypyrrole, polythiophene and polyanilines are complex dynamic structures that captivate the imagination of those involved in intelligent materials research. The application of electrical stimuli can result in drastic changes in the chemical, electrical and mechanical properties of CPs. 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 (OLEDs), corrosion and solar cells. Conducting polymers (CPs), which combine the electronic characteristic of metals and inorganic semiconductors, possess the attractive advantage of having easy synthesis control over the properties of the polymeric exposed surface such as structure, morphology and thickness. The use of these polymers represents the most important development in the preparation of modified electrodes to make sensors and biosensors. Their synthesis can be achieved by two conventional methods.

*Application of Conducting Polymers* focuses on mechanism of conduction and mechanism of charge transport of conducting polymers. The rich literature concerned about different applications of CPs: conducting polymers (CPs) in electronic, electromechanical, and optoelectronic devices, and conducting polymers (CP's) in electronic chemical sensors that are based on the mechanisms of mechanical, electronic, or optical transduction.

Conducting polymers, such as polypyrrole (PPy), polyaniline (Pani), polythiophene (PTh) and their derivatives, have been used as the active layers of gas sensors since early 1980. There are two main types of applications for the Conducting organic polymers in electronics: first one is that a polymer can be used as a material for constructing different devices and as discriminating layers in electronic chemical sensors. In both cases, interacting with surrounding gases is vital. It can possibly determine the performance of the devices that are depending on conducting polymers, while it is helpful and supportive in chemical sensors. Conductivity has been the main property of concern; the aim is of study and to identify the usability of the conducting polymers in the two kinds of electronic applications mentioned above. Electronic Chemical Sensors for gases are thought of to be at the top of gaining the information related to the environment that we live in. The quality of the air that we breathe in our bodies is very important issue and is a real concern of modern society.



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# CONDUCTING POLYMERS APPLICATION

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## INTRODUCTION

Organic polymers are normally insulators, it can be presumed that conducting polymers must have an unusual structure. Polymers with conjugated  $\pi$ -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 one) Kroschwitz, 1988).

Conducting polymers (CPs) such as polypyrrole, polythiophene and polyanilines are complex dynamic structures that captivate the imagination of those involved in intelligent materials research. (Spinks, et al., 2000; Riley, & Wallace, 1991). The application of electrical stimuli can result in drastic changes in the chemical, electrical and mechanical properties of CPs. 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 (OLEDs) (Burn et al, field-effect transistors (OFETs) (Nam et al 2011), corrosion (Solange, (2007) and solar cells (Alet, 2006. & McEvoy et al, 1994; Williams, 2005) In this chapter focusing on mechanism of conduction and mechanism of charge transport of organic conducting polymer. Also on application solar cell. Chemical sensor and corrosion.

## THE MECHANISM OF CONDUCTION

The polymer in their pure (undoped) state are describe as electronic insulators. When these polymer are doped the conductivity change from insulators to metals. The conductivity,  $\sigma$ , is proportional to carrier concentration,  $n$ , and the carrier mobility,  $\mu$ , i. e.

$$\sigma = e n \mu \quad (1)$$

For intrinsic conductivity,  $n$  decreases exponentially with increasing band gap, since the conjugated polymers have relatively large band gap, consequently,  $n$  is very low in normal temperature, so that a low value of  $n$  leads to

a low value of conductivity of undoped polymers even-though the polymers have high carrier mobility Kroschwitz J. I, 1988

In doped polymers, the doping of conjugated polymers generates high conductivities by increasing the carrier concentration  $n$ . This accomplished by oxidation or reduction with electron acceptors or donors respectively. The polymer is oxidized by the acceptors (removal of electron), thereby producing a radical cation (hole) on the chain.

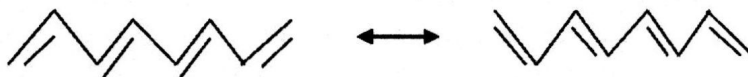
The radical cation with lattice distortion around the charge is called polaron with positive charged hole site. This hole site moves through the polymer and contributes to the conductivity. This polymer is called p-type polymer. For donor doped polymer (n-type) that is obtained by reduction is adding electron to the chain. This process produces polaron with negative charge. The Hall effect measurement in polymer shows positively charged carriers for acceptor doped polymer (p-type) and negatively charged carrier for donor-doped polymer (n-type). The thermo power and junction measurement show the same result as that determined by Hall-effect (Krichelore, 1992).

The doping concentration in polymer is high compared with that in organic semiconductors (in parts per – million). In some case the doping reaches 50% of the final weight of conducting polymer. This can be determined by chemical or spectroscopic analysis or simply by weight up take. The conducting polymer doped can be return to insulating state by neutralization back to the uncharged stat. This return to neutrality is referred as compensation. Exposure of ox datively doped polymers to electron donors or conversely, of reductively doped polymer to electron acceptors effects compensation. This ability to cycle between charged and neutral states forms the base for the application of conducting polymer in rechargeable batteries (Kareema 1997).

The doping process produce number of carriers in polymer, but these carriers must be mobile in order to contribute to conductivity, eq. (1). The carriers transport in doped conjugated polymer are analogies to doped semiconductor. In both cases doping introduces new electronic states within the band gap of material. The difference is that in conductive polymer, the total oscillator strength dose not increased upon doping, and generated polaron density of state is created by shifted the band density of state to band gap. At high doping concentrations these states interact strongly with each other, and as a result, the overlap of their electronic wave functions yield a band of electronic state within the band gap instead of discrete levels. The mechanism of carrier transport in conducting polymer is probably more likely to that in amorphous semiconductors (hoppingtransport) than crystalline semiconductors (band transport). A conclusion may be drawn that the doping creates an active sites (polarons) which enable the carriers (electronic & holes) to move from one site to another. By hopping mechanism through these sites.

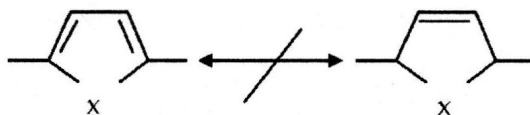
## THE MECHANISM OF CHARGE TRANSPORT

The doping of conducting polymer induces charge transfer along the chains which leads to local relaxation. The equilibrium geometry in ionized states is different from that in ground state, and that the electronic structure is affected by the localized electron states in the gap which modify the  $\pi$  system. In order to understand the mechanism of conduction, we must have information about ground-state geometries and doped state. Polyacetylene has degenerate ground state (two geometric structures having the same total energy). The defect divides the chain of PA into two parts with the same energy. The movement of defect can be described by soliton scheme (1).



**Scheme 1:** Polyacetylene (degenerate ground stat)

Polythiophene, polypyrrole and heterocycle polymer processes a nondegenerate ground stats Kroschwitz J. I, 1988 scheme (2).



**Scheme 2:** Heterocyclic polymer  $x=S, O, NH$  (nondegenerate ground stats).

It has suggested that the stable defect state formed upon doping are polarons and bipolarons and optical data seem to support the evidence of the fommation of polarons (Single charge parameter state) and bipolarons. (Kareema 1997)

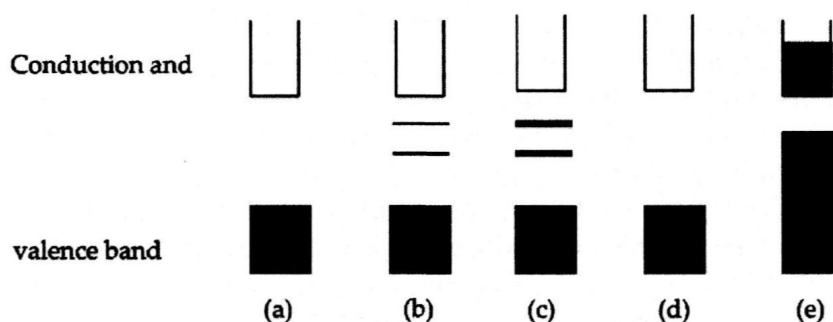


**Figure 1:** Schematic variation of band gap as a function of doping concentration \ (a) undoped (b) very small doping (polaron) (c) small doping (bipolaron) (d) high doping bipolaronic band (e) 100% doping (theoretically speaking).

Fig. (1-a) shows the neutral undoped heterocyclic polymer of band gap tabulated in table (1-1). Fig. (1-b) shows the doping levels of order (0.1-1%) %. The appearance of an ESR signal and of optical bands in the gap is consistent with formation of polarons. Fig. (1-c) indicates the increasing of the doping give rise a few percent (1-5%), leading to drop in spin concentration and the presence, in the optical data, two peaks located respectively below the conduction band and above the valence band indicated that the polarons bind in pairs to form diamagnetic bipolaron state. Fig. (1-d) expresses when the doping levels reach (25 – 50) mol. % the bipolarons states overlap and form the bands in the gap. Fig. (1-e) shows when doping reach to 100% (theoretically speaking) the bipolaronic band may merge with conduction band and valence bands respectively leaving a reduced gap. This is consistent with optical data indicating that the band gap disappear (Skotheim, 1986).

## POLYMER SOLAR CELL

Polymer solar cells have attracted broad research interest because of their advantageous solution processing capability and formation of low-cost, flexible, and large area electronic devices. (Williams, 2005); Vignesh et al, 2006, Schiff, 2002). However, the efficiency of polymer solar cells is still low compared to that of inorganic solar cells. Therefore, it is a challenge to find a polymer that has all the required properties for high efficiency devices, such as strong and broad absorption, high carrier mobility, and appropriate energy levels. One possible solution to avoid the strict material requirements is to stack two or more devices with different spectral responses, which enables more efficient utilization of solar energy.

A typical example of the usability of organic semiconductors is the dye-sensitised solar cell which owes its first demonstration Gratzel and his co-workers (McEvoy et al., (1994); Michael, 2003).

Organic/inorganic hetero structure solar cells have also been studied recently and power conversion efficiency in the region of 2.5% has been achieved by (Hussein, 2010). Solar cells based on conducting polymer/amorphous silicon (a-Si:H) structures have also been reported which demonstrate solar conversion efficiency in the range of 2% (Williams et al., 2005; Alet 2006). Blend heterojunctions consisting of a bulk mixture of poly (3-hexylthiophene) (P3HT) as donor and 6, 6-phenyl C61-butyric acid methyl ester (PCBM) as acceptor are very promising structures Brabec, C. J. (2004). Studies on blend nanoscale morphology Hoppe H. et al (2006) and stability of organic solar cells (Bettignies et al, 2006) are currently subjects of intense research.

In recent years, the development of thin film plastic solar cells, using polymer-fullerene (Gao et al., 1995); Shaheen et al., 2001) or polymer-polymer (Granström et al, 1998) bulk heterojunctions as an absorber (and transport layer at the same time), has made significant progress. Efficiencies between 1% and 2.5% for laboratory cells under AM1.5 illumination conditions have been reported (Gao et al., 1995;. Dyakonov. et al 2001). The typical structure of these devices consists of a composite of two materials with donor and acceptor properties, respectively, sandwiched between two electrodes. One advantage of this type of devices is their ease of processability. The active layer is solution processed by using spin-coating technique. Kareema et al, 2010). study photovoltaic properties of Polyaniline/Si solar cell in the dark and under illumination investigated hybrid and was found to deliver short circuit current density  $J_{sc} = 45 \mu A/cm^2$ , open circuit voltage  $V_{oc} = 400mV$ , and solar cell efficiency  $\eta = 0.3\%$  under AM 1.5 simulated solar light with the intensity of  $100mW/cm^2$ .

In this paragraph investigated some of the photovoltaic properties of organic polymer poly (o-toluidine) (POT) doped with para-toluene sulphonic acid (PTSA) deposited onto n-type silicon substrates (Kareema, 2012) (this study part of thesis done under my supervisor by Hussein, 2010).

Poly (o-toluidine) (POT) doped with para-toluene sulphonic acid (PTSA) were prepared following chemical methods described in the literature (Kulkarni, & Mulik, 2005). Powder of the doped polymer was dissolved in formic

acid (HCOOH) in the concentration of 10 mg. ml<sup>-1</sup>. Single layer heterojunction solar cells were then prepared by spin casting solutions of POT-PTSA onto the silicon substrates using spin speeds in the range 1000-5000 rpm and spinning time of 60 sec. Thin films were then placed on a hotplate with temperature of 90°C for a period of 15 min for drying. Aluminum (Al) contact of about 90 nm in thickness was thermally evaporated onto the back (the unpolished side) of the Si substrate. This was carried out under vacuum of 10<sup>-5</sup> -10<sup>-6</sup> mbar and evaporation rate of 5 nm. sec<sup>-1</sup>. Similar procedure was followed for the deposition of gold (Au) contacts onto the polymer film, with Au film thickness of about 20 nm evaporated through a suitable mask which provides device area of about 3x10<sup>-6</sup> m<sup>2</sup>. For DC electrical measurements of the solar cell devices a Keithley electrometer (Model 6517A) was used to measure current density (J) as a function of applied voltage in range ±1 V and in steps of 0.05V.

The photovoltaic properties of the solar cells were measured under illumination using a Bentham 605 solar simulator fitted with a xenon lamp. The photocurrent was measured for devices of different polymer film thickness and under four different light illuminating intensities between 10-100 mW/cm<sup>2</sup>.

Figure (2) shows the J (V) characteristics of the fabricated POT-PTSA/n-Si solar cell structures, both in dark and under illumination. The polymer film thickness for this particular result is 35nm as determined by spectroscopic ellipsometry measurements and the illumination intensity is of 100 mW/cm<sup>2</sup>. Both J (V) curves clearly possess good diode characteristics which clearly demonstrates the occurrence of a rectifying junction. This junction is expected to exist at the interface between the silicon substrate and the polymer film. This can be further justified by the fact that the silicon substrate used in this work is of n-type while the POT-PTSA films are considered as the hole transporting layer (Mangal et al., 2009). The POT-PTSA films are thin enough to allow the photon flux to reach the n-Si substrate and thus allowing the photocurrent current to saturate. Solar cell parameters, i. e., V<sub>oc</sub>, J<sub>sc</sub>, V<sub>p</sub>, J<sub>p</sub>, P<sub>max</sub>, and FF have been determined and are summarised in Table I. The solar conversion efficiency η is given by the formula:

$$\eta = (FF V_{oc} J_{sc} / P_{in}) \tag{2}$$

where P<sub>in</sub> is the power of the incident light. A typical solar conversion efficiency value value of 2.55% for the studied devices is found to be in line with data found in the literature and are thought to be limited by uncontrolled interface states at the POT-PTSA/n-Si junction (Wang & Schiff, (2007). A closely related structure of the type aluminium / polyaniline / GaAs metal-insulator semiconductor solar cell was found to give efficiencies in the region of 5%. The value of 0.46 V for the short circuit voltage obtained in this work compares well with the value 0.51V obtained for Pani /n-Si solar cell devices (Wang & Schiff 2007). A low values of FF of about 0.43 is associated with a high series resistance and a low shunt resistance with typical values of 37Ω and 465Ω, respectively. High values for RS may originate from a poor absorber morphology limiting the electron hopping transport transport, (Levitsky et al., 2004; Riedel et al., 2004).

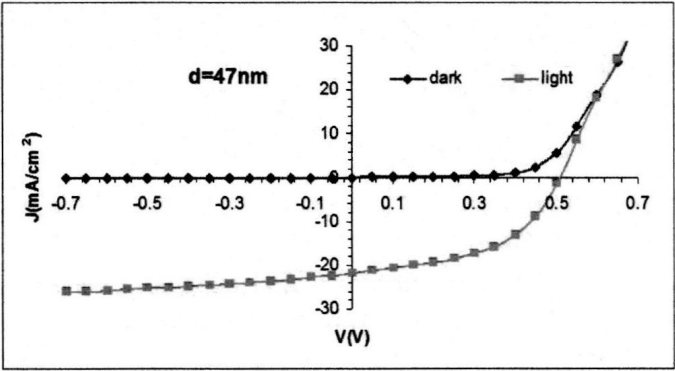


**Figure 2:** Current density as function of voltage for Au/POT-PTSA/n-Si/Al solar cell. The white light illumination intensity is 100mW/cm<sup>2</sup>.

Figure (3) shows the conversion efficiency as a function of film thickness of POT-PTSA spun films in the range 25-73nm. The efficiency is shown to increase sharply with increasing film thickness reaching a maximum value of 2.55% for film thickness of 35nm, and then decreases for slightly larger thickness (43 nm), before it starts to increase again, but more gradually, for higher thicknesses. The organic thin film of POT-PTSA is typically characterized with a lower charge carrier density and charge mobility compared to polyaniline which is subjected to a similar doping treatment (Kulkarni. & Viswais, 2004).

It is expected that for thin films of relatively small thickness (in this case 35nm), the surface texture is more suitable for light trapping compared to smaller or larger film (25nm and 43nm) (Izabela et al., 2008; Haug, et al.,