

Research Paper On “Conducting Polymers: Synthesis, Properties and Applications”

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Abstract- Polymers are long chains of repeating chemical units called monomers. They share several characteristics including macro and micro properties, electrical transport properties, semiconducting properties and optical properties. Polymers can be synthesized by chemical and electrochemical polymerization. Polymers prepared through these methods can also be characterized by their electrical, optical, mechanical and electrochemical means.

Conducting polymers (CPs) have drawn significant interest of researchers for more than 30 years because of their economical importance, superior stability, lighter weight, better workability, resistance to corrosion and satisfactory electrical conductivity. Some of the applications of CPs include: rechargeable batteries, electrochromic display devices, light reflecting or light transmitting appliances for optical information, sensors and storage for glare reduction systems and smart windows in automobiles and buildings, polymeric light emitting diodes (PLEDs), photovoltaic devices, transistors, electromagnetic shielding against electromagnetic interferences (EMI) and printed electronic circuits.

During the past two decades, both fundamental and applied research in conducting polymers like polyaniline, polyacetylene polythiophene and polypyrrole has grown enormously. Conducting polymers are unique due to its ease of synthesis, environmental stability and simple doping/dedoping chemistry. polyaniline is one of the most studied conducting polymers of the past 50 years. The most common chemical synthesis of polyaniline is by oxidative polymerization with ammonium per sulfate as an oxidant. Conducting polymers owing to its ease of synthesis, remarkable environmental stability and high conductivity in the doped form has remained thoroughly studied due to their varied applications in fields like biological activity, drug release systems, rechargeable batteries and sensors.

Keywords- CPs, EMI shielding, Properties, Applications, Polyaniline, sensors. Doping, Effect on conductivity, conducting polymers, applications

I. INTRODUCTION

1.1 Introduction of Conducting polymers

Conducting polymers are conjugated polymers possessing an extended π - system and highly delocalized electronic states. This extended electron conjugation is what gives rise to their conductivity. However, unlike inorganic semiconductors (atomic solids), conducting polymers are typically amorphous polymeric materials and therefore charge transport in conducting polymers can be quite different from conventional semiconductors. The polymers themselves are not new; many of them such as polypyrrole are well known in their non conducting form before their conductivity was discovered. Indeed, it may be said that the discovery of conducting polymers is not the discovery of the polymer rather of its unique properties [2, 3].

Conducting polymer share several characteristics; including macro molecular character and electrical transport properties. All the case with poly acetylene is the simplest conducting polymer, in which the electrical transport characteristics are obtaining by placing the alternative carbon double bond structure direction on the back bone of polymer. [4].

Common conducting polymers are; Poly acethlyne, poly pyrrole, polythiophene and Poly3hexythio phone poly (3-hlinr dioxino phne).

Polymers are special class of organic compounds possessing high molecular weights. A polymer is built up of a large number of small molecules called monomers. A monomer is the low molecular weight substance which when redacted under suitable conditions links together to produce high molecular weight polymer. The some unit of two or three different units are repeated a number of times in a polymers. Conventionally polymers have been related with non-conducting properties and are applied as insulators of metallic conductors until the discovery of polyacetylene (PA) in 1977, which resulted in initiated projects in the field of conducting polymers [1].

1.2 OBJECTIVE

General objective

The main objective of this review is to study the synthesis and characterizing of conducting polymers.

Specific objective

To attain the main aim of the study the specific objectives like; realizing synthesis of conducting polymers, identify the origin of semi conducting behavior, understanding the application of conducting polymers and the characterization of conducting polymer.

1.3 The Origin Of Semi Conducting Polymers

Polymers have semi conducting properties due to their unique structural behavior such as formation alternating single and double bonds between the adjacent back bone carbon atoms. The semi conducting polymers have attracted considerable attention due to wide application. Since carbon atom is the main building block of most polymers the type of bond that their valence electrons make with other carbon atom or other element determines the overall electronic properties of the respective polymer. In general they can be categorized as saturated and unsaturated based on the number of the type of the carbon valence electron involved in the chemical bonding between consecutive carbon atoms along the main chain of polymer. Saturated polymers are insulator since all the four valence electron of carbon atom are used up in covalent bonds, whereas most conductive polymers have unsaturated conjugated structure. The fundamental single source of semi conducting property of conjugated polymer originates from the overlap of molecular orbital's formed by the valence electrons chemically bonded carbon atoms [3, 4].

1.4 Doping in conducting polymer

Since the discovery of much of new exciting chemistry and physics in the field of conducting polymers, it is possible to control the electrical conductivity of polymer over the range from insulating to highly conducting (metallic) state. This process is often referred to as "doping" the insulating natural polymer is converted in to an ionic complex consisting of polymeric cation, or anion and a counter ion which is the reduced form of oxidization agent. The oxidation or reduction of polymer can be achieved electro chemically by substituting the neutral polymer to the appropriating oxidizing or reducing voltage in an electro chemical cell [5, 6].

The research priorities at plastics research laboratory postulating new structural properties of polymers made by oxidative coupling copper chloride and aluminum chloride were used to make alko benzene from benzene. The reaction intended to include other aromatic compounds and hetero cycles. These reactive products were characterized in terms of thermo electric power [7].

1.5 Synthesis of Conducting Polymers

There are number of techniques used on conventional small molecules that are related to the conjugation bond of conducting polymer. The key requirement in the synthesis of conducting polymers is that conjugated nature of monomers is conserved in the synthesis process. Furthermore, the

development of novel monomers must be also target the appropriate functionality for polymerization. Polymerization can occur chemically or electrochemically [8].

1.6 Chemical Polymerization

The principle of oxidative polymerization does not mandate the use of electro chemical technique. For example poly 3-hexythiophene is well known and often studied conducting polymer that is almost universally synthesized chemically. When designing for chemical polymerization the key requirement is solubility. Successful polymerization to high molecular weight polymer be reactive and soluble to polymerization [8].

1.7 Electro chemical polymerization

Electro chemical polymerization offers at once a wide variety of parameters and complexities to the conducting polymer. The monomers solved and electrolyte is placed in to three electrodes cell the working electrode is controlled electrode and from surface for polymerization. The reference electrode offers potential by which measures the voltage at the working electrode. The counter or auxiliary electrode balance the circuit and enables the current to flow the electrolyte. Generally, the basic components of electro chemical polymerization are; [4].

1.8 Electrochemical Cell Set Up

Electro chemical process is normally carried out in single compartment electro chemical cell by adopting standard three electrodes configuration, typically electro chemical both consists of monomer and supporting electrolyte dissolved in appropriate solvent. Electro chemical process can be carried out either potentiostatically (constant voltage conditions) recommend obtaining thin films or galvanostatically (constant current condition) which are recommended to obtain thick films. A general set up for electro chemical cell is given below [9].

1.9 Characterization of Conducting Polymer

Conducting polymers can be characterized by electrical, mechanical and electrochemical characterization. Electrical conductivity in polymer is the focus of numerous books. Conductivity polymers are more favorable due relatively low densities thus, for a given current carrying application conducting polymers offer low cost weight solution. The mechanical characterization behavior of conducting polymer does not differ significantly from most polymers. Through the apparent cross linking that complicated traditional characterization methods also confound the observation of mechanical compounds properties. Electro chemical characterization of conductivity of conducting polymers consists of wide battery test applied to conducting polymer. Cyclic voltammeter is often used to assess the basic transport array of time constants to much process including electrochemical behavior [14].

1.10 Application

Conducting polymers (CPs) have been used for many applications due to their chemical, mechanical, optical and electrical properties. Their semiconductor properties allow conjugated polymers to be used particularly in large area, such as electrochromic devices (EDCs), rechargeable batteries, light emitting diodes (LED's), field effect transistors (FET's), photovoltaic cells and chemical Sensors [15]. Conjugated polymers are highly susceptible to the chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state. There are two main groups of Application for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes the electro activity they are shown below [16]. The susceptibility of π -electrons of the conjugated polymers to oxidation or reduction alters the electrical, optical and electro optical properties of the polymers, since mostly the redox processes in the conjugated polymers are reversible. Therefore, the electrical and optical properties can be tuned systematically, with appreciable degree of precision by suitably controlling both the chemical or electrochemical oxidation and reduction. It is even possible to switch from a conducting to an insulating state and vice versa. Conducting polymers are thought to replace metals in future because they have superior Properties, such as ease of preparation, light weight and low-cost fabrication, to metals which are also toxic and hazardous to the environment [17].

II. LITERATURE REVIEW

2.1 Literature Review

In doped polymers, the doping of conjugated polymers generates high conductivities by increasing the carrier concentration n . This is 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, 2015).

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 state. This return to neutrality is referred as compensation. Exposure of oxidatively 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 2016). 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 analogous 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 does not increase 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 (hopping transport) 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.

Conducting polymers (CPs) are a special class of polymeric materials with electronic and ionic conductivity. They can be used in the dry or wet state (Xu *et al.* 2005) owing to their electronic conductivity, their porous structure or because of their processibility in microstructuring processes (Schultze & Karabulut 2005). The structures of the widely used CPs are depicted in figure 1. A range of biomedical applications for CPs are currently being considered, including the development of artificial muscles (Otero & Sansinena 1998), controlled drug release (Abidian *et al.* 2006; Abidian & Martin 2009), neural recording (Abidian *et al.* 2009) and the stimulation of nerve regeneration (Schmidt *et al.* 1997). Moreover, electrically active tissues including the brain, heart and skeletal muscle provide opportunities to couple electronic devices and computers with human or animal tissues to create therapeutic body-machine interfaces (Warren *et al.* 1989). The conductive and semiconducting properties of the CPs make them an important class of materials for a wide range of applications. The important properties of various CPs and their potential applications are discussed in table 1. The origin

of electrical conduction in CPs has been ascribed to the formation of nonlinear defects such as solitons, polarons or bipolarons formed during either doping or polymerization of a monomer (Saxena & Malhotra 2002; Tschmelak *et al.* 2005). Conductivity in CPs arises from the presence of conjugated double bonds along the backbone of an otherwise insulated structure. In conjugation, the bonds between the carbon atoms are alternatively single and double. Every bond in the backbone contains a localized 'sigma' (σ) bond, which forms a strong chemical bond and every double bond also contains a less strongly localized 'pi' (π) bond (Wise *et al.* 1998; Heeger *et al.* 2000). Conductivity is imparted to these polymers through the use of a dopant ion, which must be introduced to the structure to carry charge in the form of extra electrons. The dopant neutralizes the unstable backbone when the polymer is in the oxidized form. On application of a potential across the film, a flux of ions either in or out of the film, dependent on dopant charge and motility, disrupts the stable backbone, resulting in the passage of charge through the polymer film. Conducting oligomers of pyrrole and thiophene connected by ester linkages have been considered for the creation of temporary scaffolds for cell attachment and proliferation for tissue engineering applications. In addition, these scaffolds are biodegradable (Rivers *et al.* 2002). The possibility of growing cells on CPs has proven the biocompatibility of these polymers (Schmidt *et al.* 1997; Garner *et al.* 1999a,b). Further, recently the biocompatibility of PPy and PEDOT films and PPy and PEDOT nanotubes was evaluated using a dorsal root ganglion model (Abidian *et al.* 2010). The implantation of CPs *in vivo* for several weeks has led to only minimal inflammation, again pointing to low toxicities and good tissue compatibility (Schmidt *et al.* 1997; Garner *et al.* 1999a,b; Rivers *et al.* 2002). Moreover, Abidian *et al.* (2009) successfully demonstrated that PEDOT nanotubes could record neuronal spikes about 30 per cent more than control sites with a high signal-to-noise ratio (SNR) for seven weeks post-implantation *in vivo*. Although there have been a number of reviews on CPs with regard to biomedical applications (Rivers *et al.* 2002; Zelikin *et al.* 2002; Gizdavic-Nikolaidis *et al.* 2004a,b; Schultze & Karabulut 2005; Abidian *et al.* 2006; Ahuja *et al.* 2007; Guimard *et al.* 2007a,b), this review focuses solely on the

various tissue engineering and drug-delivery applications. Moreover, this review accentuates the various surface functionalization techniques that can be used in order to modify the physico-chemical, electrical and mechanical properties of the CPs so as to improve their potential biomedical applications.

III. RESULT AND DISCUSSION

3.1 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, σ , is proportional to carrier concentration, n , and the carrier mobility, μ , i. e.

$$\sigma = e n \mu$$

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.

3.2 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 π 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).

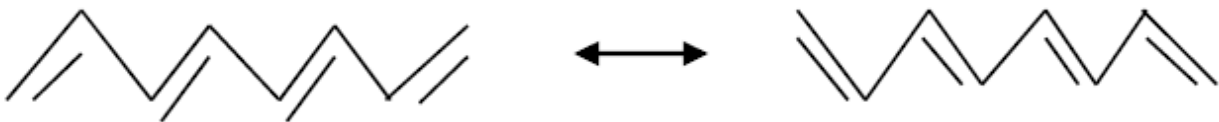


Fig.1: Polyacetylene (degenerate ground stat)

Polythiophene, polypyrrole and heterocycle polymer processes a nondegenerate ground states Kroschwitz J. I, 1988 Fig 3.1.

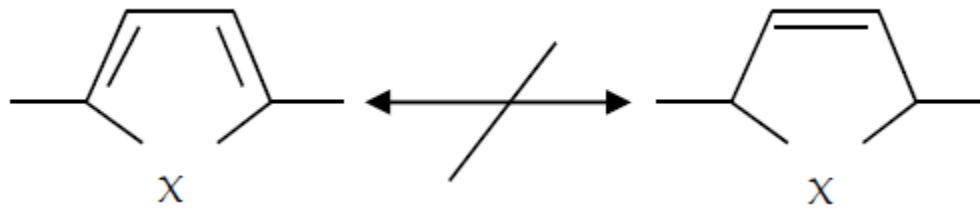


Fig.2: Heterocyclic polymer $x=S, O, NH$ (nondegenerate ground stats).

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 formation of polarons (Single charge parameter state) and bipolarons. (Kareema 1997)

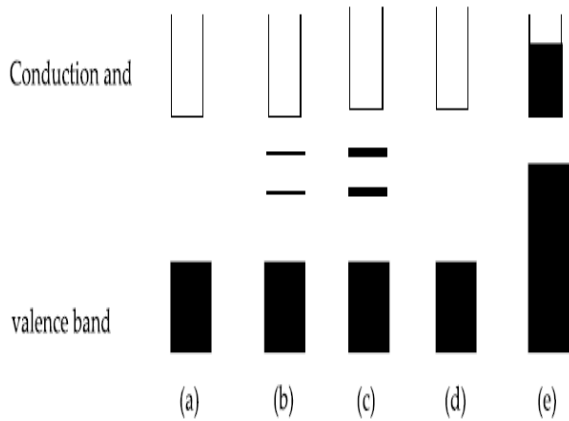


Fig.3: Schematic variation of band gap as a function of doping concentration \ (a) undoped (b) very small doping (polaron) (c) small doping (bipolaron) (d) high doping bipolaronic band (e) 100% doping (theoretically speaking).

Fig. (3.3-a) shows the neutral undoped heterocyclic polymer of band gap tabulated in table (1- 1). Fig. (3.3-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. (3.3-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. (3.3-d) expresses when the doping levels reach (25 – 50) mol. % the bipolarons states overlap and form the bands in the gap. Fig. (3.3-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).

3.3 Chemiresistors

The most widespread group of sensors is those that use Conducting Polymers. They are cheaply and quite easily made-up. In addition they utilize of the main property of Conducting Polymers (their conductivity). See figure. 6 shows a schematic diagram of a chemiresistor.

At its basic, a Chemiresistor is simply formed by two electrodes as contact points with the conducting polymer (CP) put onto an insulate substrate. When applying a constant current, the probable difference occurs on the electrodes represents the response output signal. Although. The easiness of the sensing concept and its recognition does not come without a price. Since it is rarely to know what is occurring between the two electrodes. There will be a number of spots whereby the chemical change of a signal might initiate (Fig 5.8) (Janata, 2002). For the measurements that use a constant current the capacitors used with equivalent resistors could be ignored. However, these capacitors have very significant role if an alternating current is used to excite those chemiresistors as well as if transient signals are involved.

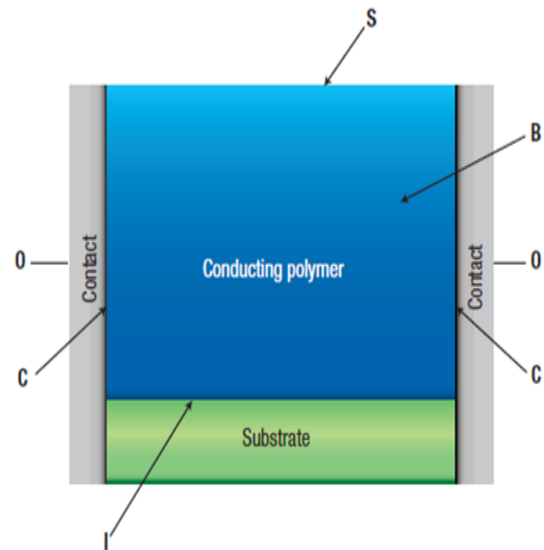


Fig.4: “Chemiresistor; B: bulk of the CP, S: surface, I: interface with the insulating substrate. C: interface with the contacts”.

3.4 Field-Effect Transistor (FET) sensors

The interaction among the neutral gases and organic semi-conductors has been utilized as the principle of transduction in Field-Effect Transistor (FET) sensors from the late 1980s (Josowicz & Janata, 1986), while it has been almost uncared for within non-sensing applications.

The category of sensors that are based on work function modulation contains three kinds of Micro Fabricated Devices which are; "Chemically sensitive Diodes, chemically sensitive capacitors, and chemically sensitive FET's (CHEMFETs) " Several systems of CHEMFETs are found for both applications of liquid and gas species (Josowicz. & Janata, 1988). It is really key point to differentiate whether the current runs throughout the silicon or throughout the conducting polymer CP. In this case they could be divided in more detailed categories as follows; (a) thin film transistors (TFT) (Covington et al., 2001) as seen in figure 7 and (b) insulated gate Field-Effect Transistors (IGFET) (Janata, 1989) as shown in figure 3.5

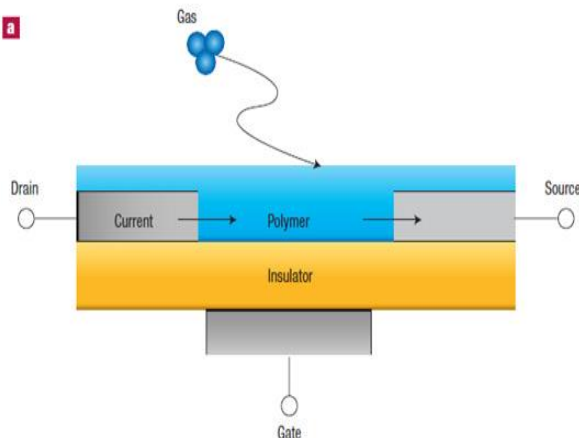


Fig.5: Shows C P'S in field-effect transistors, thin film transistor

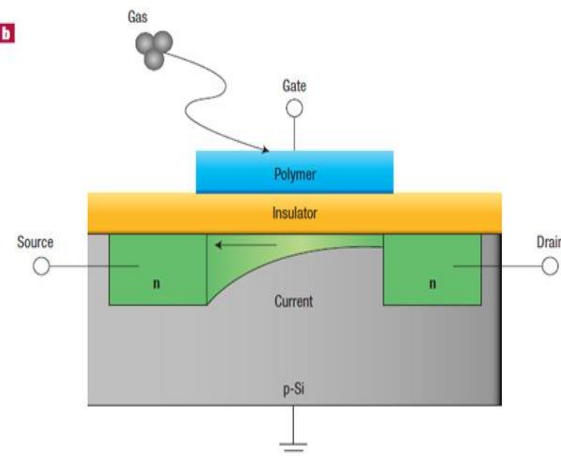


Fig.6: Shows CP's in field-effect transistors, insulated gate

For the TFT the current flows throughout a conducting polymer (CP) that its conductivity produced from the reaction with the analytes and/or by the electric fields. So, it can be said that the response signal depends on two things; the work function and the conductivity of the Conducting Polymer. Therefore, the analysis of the TFTs chemical response will be complex due to the same reasons for the chemiresistors, specifically, the division of different types of conductivity modulation, and of various forms of work function. The work function values can be affected by the interpreted energy states but the conductivity of the Conducting Polymer (CP) cannot be (Polk et al., 2002).

IV. CONCLUSION AND RECOMMENDATION

4.1 Conclusion

From this review it can be concluded that, polymers are applicable in different ways for example solar energy cell sensors and corrosions in heritors and also polymers can be synthesized by differ techniques that is chemical and electro chemical polymerization and can be characterized by different techniques electrical, mechanical and elector chemical characterization and also polymer are doping with other field for example physics, due to this polymers it is more applicable. Since conjugated polymers are highly susceptible to the chemical or electrochemical oxidation or reduction, it is possible to precisely control electrical and optical properties. It is even possible to switch from a conducting state to an insulating state.

4.2 Recommendation

From this point of view it is recommended to deal with these new chemical species through scientific research investigations because of their superior Properties, such as ease of preparation, light weight and low-cost fabrication, to metals which are also toxic and hazardous to the environment. This will signify to have cost effective and green source of electrical energy and to create hazardous free green environment for the future.

V. FUTURE SCOPE OF CONDUCTING POLYMERS

The main concerns for humans in the future will be energy & resources, food, health, mobility & infrastructure and communication. There is no doubt that polymers will play a key role in finding successful ways in handling these challenges. Polymers will be the material of the new millennium and the production of polymeric parts i.e. green, sustainable, energy-efficient, high quality, low-priced, etc. will assure the accessibility of the finest solutions round the globe. Synthetic polymers have since a long time played a relatively important role in present-day medicinal practice. Many devices in medicine and even some artificial organs are constructed with success from synthetic polymers. It is possible that synthetic polymers may play an important role in

future pharmacy, too. Polymer science can be applied to save energy and improve renewable energy technologies.

Biopolymers could especially increment as more solid adaptations are produced, and the cost to fabricate these bio-plastics keeps ongoing fall. Bio-plastics can supplant routine plastics in the field of their applications likewise and can be utilized as a part of various areas, for example, sustenance bundling, plastic plates, mugs, cutlery, plastic stockpiling packs and in this way can help in making environment economical.

In areas of applications of plastics materials, a well-known long standing example is electrical industries have led to increasing acceptance of plastics for plugs, sockets, wire and cable insulations and for housing electrical and electronic equipment. The major polymer targeting industries of the present day life includes Ceramic industries, in stem cell biology and Regenerative Medicine, packaging industries, in retorting method used for food processing industries in automotive industries, in aerospace industries and in electrical and electronic industries.

- Polymers in Stem Cell Biology
- Self-Healing and Reprocess-able Polymer Systems
- Smart Polymers
- Green Synthesis of Functional Materials
- In Gene Delivery Systems
- Ceramic Industry
- Biopolymers in Drug Delivery
- Market growth of Polymers

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