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ELECTRONICALLY CONDUCTING POLYMERS: RECENT ADVANCES IN BIOMEDICAL APPLICATIONS

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ABSTRACT

Initially polymers were mainly used in the packaging and insulation. But past few decades has seen new classes of polymer showing properties like electronic and ionic conductivity. These electronically conducting polymers ECP have the response to external stimuli like pH, temperature, solvent, electric field, magnetic field, light etc. These ECP are organic in nature and called conducting polymers. ECP have the special ability to deformation, rapid response, long life, light weight, low density and higher reliance are the unique properties make them useful in various applications likely to be biologically compatible and imitate biological systems. ECP can also be used in biological, pharmacological and electrical field. Therefore, these materials have found numerous biomedical applications such as artificial muscles, neural interfaces, biosensors, actuators, controlled drug release, tissue engineering and stimulation of nerve regeneration. Biomaterials for tissue engineering can mimic the structure and environment of native extracellular matrix without aggravating adverse reaction. This paper outlines biomedical applications of electronically conducting polymers.

Keywords- Conducting polymers, mimic, biosensors.

I. INTRODUCTION

Three decades ago all carbon based polymers were regarded as insulators. But lately plastics have been extensively used by the electronics industry because of its unique conducting property. This unique property converts polymer into a new class of polymer known as electroactive polymers or conducting polymer. In 1958 a conducting polymer was synthesized known as polyacetylene by Natta et al [1]. Again in 1967 conducting polyacetylene synthesized by H. Shirakawa was found to be 1000 times faster than previous one synthesized almost a decade ago. In 1980s polyhetrocycles were first discovered. The origin of electrical conductivity in these polymers is because of delocalization of charge or pi-electrons present as the integral part of polymer chain. The pi-bonds in conjugated polymer are extremely sensitive to electrochemical or chemical oxidation or reduction. These conducting polymers are intrinsic as well as extrinsic in nature. Their properties can be modified with the help of addition of dopant in polymeric back bone. The electrical properties change over several orders magnitude with changing in pH, applied potential or there environments. Physical properties can also be altered by addition of organometallics in to the back bone of polymer.

These electroactive organic conducting polymers are highly selective, specific and stable in nature. The electronically conducting polymers are involved in diversified applications ranging from photovoltaic equipment's, rechargeable cells, molecular electronics, electrochromic CRT's, solar powered cells, ion exchange compatible membranes in fuel cells, Semiconductor diodes, electronic capacitors, field effect transistors, microelectronics, in biomaterials and microsurgical equipment's due to their useful electronic, redox and optical properties.

II. PROPERTIES AND STRUCTURE

Table 1 depicts the conjugated structure of the conducting polymer with alternating single and double bonds or conjugated bond makes the polymer intrinsically conducting. Metals have high conductivity due to the free unrestricted motion of electrons through their structure; in order for.

| | | | |
|-----------------|------------|--------------------------------|---------------------------|
| Cyclic Polymers | Conducting | Hetrocyclic conducting polymer | Acylic conducting polymer |
|-----------------|------------|--------------------------------|---------------------------|

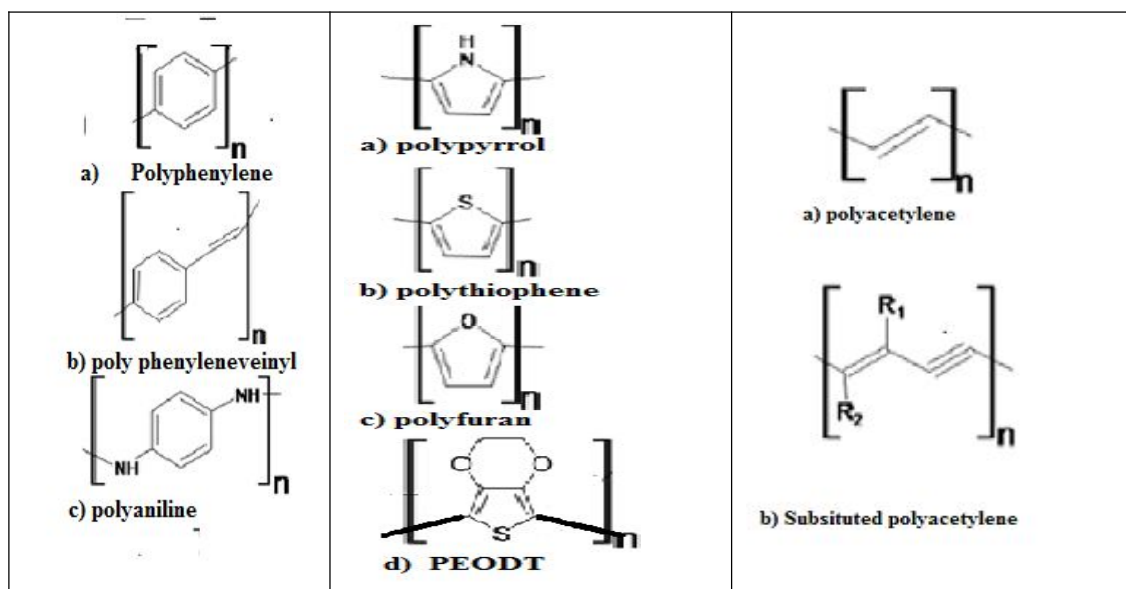


Table 1: Types of Conducting Polymers

polymer backbone. Due to the conjugated molecular structure and remarkable electronic properties, Polyacetylene has been universally studied as a prototype for other electronically conducting polymers. polymers to be electrically conductive they must possess charge carriers in addition to orbital system that allows the charge carriers to move. The conjugated structure meets the second requirement via a continuous overlapping of pi-orbitals inside

Doping

Organic polymers by nature do not possess intrinsic charge carriers therefore requirement of charge carriers is taken care by fractional oxidation (p-doping) of the polymer chain with acceptors electron or by fractional reduction (n-doping) with electron donors (e.g. Na, K). With such a doping process, charged defects (e.g. polaron, bipolaron and soliton) are inherited, which could then be available as the charge carriers. [5]

Chemical Doping

Most of the conjugated polymers, including those listed as in Table 1, will be either fractionally oxidized (p-type redox doping) or fractionally reduced (n-type redox doping) by acceptors or donor electrons. The electrochemical reaction of transpolyacetylene with oxidizing agent like iodine leads to the doping reaction and increase in conductivity of about 10^{-5} to 10^2 S/cm (Table 2). Similarly, almost all other polymers which are conjugated like trans-polyacetylene can be doped with donor electrons (n-doping) in order to gain high conductivities.

Electrochemical Doping

The extensive conjugation of pi-electrons, conjugated polymers can also be fractionally oxidized (p-doping) or fractionally reduced (n-doping) acting as either an electron source or an electron sink.

| S.No. | Polymer | Dopent | Conductivity ($\Omega^{-1} \text{ cm}^{-1}$) |
|-------|----------------------|---|--|
| 1. | Polyacetylene | $\text{I}_2, \text{Br}_2, \text{Li}, \text{Na}, \text{AsF}_6$ | 10000 |
| 2. | Polypyrrole | $\text{BF}_4^-, \text{ClO}_4^-$ | 500-7500 |
| 3. | Polythiophene | $\text{BF}_4^-, \text{ClO}_4^-$ | 1000 |
| 4. | poly phenyleneveinyl | AsF_3 | 100000 |
| 5. | poly phenylene | $\text{AsF}_3, \text{Li}, \text{Na}$ | 1000 |
| 6. | Polyaniline | HCl | 200 |
| 7. | Polyfuran | $\text{BF}_4^-, \text{ClO}_4^-$ | 100 |
| 8. | PEODT | $\text{BF}_4^-, \text{ClO}_4^-$ | 50 |

Table 2: shows the dopant and conductivity of different electronically Conducting Polymer

Photo-doping

The conjugated polymer macromolecule when exposed to radiation with an light energy more than its band gap could promote electrons into the conduction band examples of which can be. trans-polyacetylene. Although the photogenerated charge carriers will vanish as the irradiation ceases, if an appropriate potential difference is applied during irradiation then electrons can be separated from holes, leading to photoconductivity.

III. PROCEDURES FOR SYNTHESIS

There are two methods used for synthesizing of ECP's Electrochemical and Chemical polymerization.

Polymerisation

This process involves intermixing of monomer solution with an oxidizing agent e.g. FeCl₃, ammonium persulphate. After polymerization a powder or a thick film of polymer is formed. This method can be used to create all type of conducting polymer. This method is mostly used in commercial production of conducting polymer.

Electrochemical Synthesis

Electrochemical polymerization [5] done by applying an electrochemical current through an electrode placed into the solution containing the monomer, the solvent and the doping agent. By this method a thin film of polymer is formed with controlled thickness and morphology on the surface of electrode. This method enables the rapid deposition of polymer along with bioactive molecule. Polymerization take place by this method only when the monomer undergoes oxidation on the applied electrical potential. This process can be carried by three techniques

- Galvanostatic method
- Potentiostatic method and
- Potentiodynamic Method

There are some other technique to prepare conducting polymer with desirable properties [6].

Composites

Polymer formed by the polymerization have some drawbacks like rigidity, brittleness, smoothness on surface. Addition of some other material may improve the qualities of both materials called compositing. Composites of PANI and polypropylene used in neurobiological application. Compositing of polypropylene with polyester and PET fabrics increase flexibility of conducting polymer. Nanocomposites of Ppy/PDLLA conducting polymers have good conductivity and antimicrobial activity.

Electrospinning

This process allows the formation of nano and microscale fiber with wide range of polymers. While electro-spinning a Potential difference of large order electrostatic field is used to draw a jet from polymer solution. When this jet moves to the collector electrode the solvent evaporate and polymer fiber is formed. These fibers are excellent substrate for tissue engineering.

| conducting polymer | synthesis technique | Properties | Applications |
|--|--|---|---|
| polypyrrole (PPy) | electrochemical and chemical synthesis | high conductivity (up to 160 S cm ⁻¹) when doped with iodine); opaque, brittle, amorphous material | biosensors, antioxidants, drug delivery, bioactuators, neural prosthetics, cardiovascular application |
| polythiophenes (PT) | electrochemical and chemical synthesis | good electrical conductivity and optical property | biosensors, food industry |
| polyaniline (PANI) | electrochemical and chemical synthesis | belongs to the semiflexible rod polymer family; requires simple doping/dedoping chemistry; exists as bulk films or dispersions; high conductivity up to 100 S cm ⁻¹ | biosensors, antioxidants, drug delivery, bioactuators, food industry, cardiovascular application |
| poly(3,4-ethylenedioxythiophene) (PEDOT) | electrochemical and chemical synthesis | high temperature stability; ability to suppress the so-called 'thermal runaway' of the capacitor; transparent conductor; moderate band gap and low redox potential; conductivity up to 210 S cm ⁻¹ | biosensors, antioxidants, drug delivery, neural prosthetics |

Table 3: Properties and application of the conducting polymer (CP)

Hydrogels

Hydrogels are organic porous structures that are light weight and soft organic materials which are made to conduct electricity by mixing conducting polymers in form of composites forming co-networks. These polymers possess the property of mimicking the biological membrane. [11]

IV. APPLICATIONS

Conducting polymers have different mobilized functional groups that can be used in specific applications involving biological, pharmaceutical or electrical properties. These can be summarized as.

Biosensor

Biosensor [3] is an analytical device, which includes sensing elements such as receptors, enzymes, nucleic acids, antibodies, cells, etc. Enzymatic biosensors employ bio specificity of a chemical reaction, with an electrode that produces potential difference for quantitative analysis. [4]

Polypyrrol with enzyme used to prepare GO_x biosensor as hydrogel PPy/P(HEMA) membrane. It is also helps in for screening of physiological disturbances of ascorbic acid, uric acid and acetaminophen [11].

Electro-active polyaniline forms are extremely helpful in studying the effect of electrical stimulation on tissues and excitable cells for neuronal and cardiac engineering application.

The bio compounds such as cholesterol, glucose, triglycerides, ureaes, and pesticides are compounds of utmost importance because of their adverse effects on health.

Tissue engineering

Conducting polymers are extremely useful materials for tissue engineering applications owing to their electronic conductivity. Materials which are biologically active can work with tissue engineering applications and can mimic the structure and environment of cellular matrix without instigating adverse reactions *in vivo*. Their biocompatibility can be modify and improve by covalent grafting and direct encapsulation of biomolecules Further, specific stimulation can also play an important role in tissue regeneration, like electrical instigation has been shown to improve nerve and muscle cell regeneration , promote wound healing of skin and bone repair. [7]

Bio electrode

Conducting polymers are attractive compounds for neural electrode alteration due to easy synthesis procedure and their inherent electrical conductivity owing to electrochemical polymerization which happens on the surface. Large surface area and porous structure facilitates exchange of ions between tissues around and the electrodes. Conducting polymers can be altered to improve the differentiation and adhesion of nerve cells, like for example; enhanced nerve cell adhesion and spreading were seen on laminin fragment altered polypyrrole. Enhanced nerve cell differentiation was also seen and observed on polymers that were electrically conducting after electrical stimulation [8].

Control Drug release

Current drug-delivery systems are best and effective with controlled input of drugs. The use of Conducting polymers in the areas of bioanalytical sciences is of wide interest since their biocompatibility brings new possibilities of using them in *in vivo* biosensor applications for continuous check of drugs in biological fluids or as initiative of opening up the field to a variety of new analytes. Electrical stimulation of Conducting polymers has been employed to release various therapeutic proteins and drugs like nerve growth factor and heparin. The drug-delivery systems are of immense scientific interest and give new possibilities for the treatment of cancer and also minimum invasive techniques for various neural and cardiovascular applications.

Bioactuators and Artificial muscle

Bioactuators are elements that can be used to recreate mechanical force, which can be used as artificial muscles and in close agreement to mimicking the natural muscle system.

The phenomenon of change in the volume of the conducting polymer scaffold upon electrical input has been utilized in the making of artificial muscle by creating bioactuators. Here a two layers of conducting polymers are placed in a three layer arrangement, here the middle layer comprises of a non-conductive material. When potential difference is applied across the two conducting polymer films, one of them gets oxidized and the other is reduced. The film that was oxidized expands due to the inflow of dopant ions, whereas the reduced film shrinks as it expels the dopant ions. [9]

They can then be monitored and controlled for injecting the target biomolecules at the fixed time and controlled speed. Anti-inflammatory (dexamethasone), anticancer (5-fluorouracil), anticoagulant (heparin) and antirheumatic (2,6-anthraquinone disulphonic acid) drugs have been used successfully and is injected with help of conducting polymers. The redox process causes

a decrease in the volume of the conducting polymer as an outcome of uptake and expulsion of anions or cations as the polymers swell with ion uptake and shrink with ion expulsion. [10]

Micro Pump

Change in the volume of conducting polymer in controlled way can be used to implement a micro pump system capable of moving fluids at a micro flow rate with high accuracy and precision.

Integrated cell sensor

Sensors are being developed based on Cell technology for sensing applications, starting from smell detection to pathogen classification. The structures used for confining the cells are micro-vials which can be open or close the path way using polypyrrole (pPy) bilayer actuators.

Biodegradability

In spite of the fact that many conductive polymers (e.g. PPy and PTh) are not biodegradable by nature, they can be altered to be so. One solution out of the three main answers is to synthesize the conductive polymer as a composite with biodegradable small molecules together to form the biodegradable polymer [13].

V. CONCLUSION

Conducting polymers have found diversified applications in various fields like drug delivery, devices for neurosciences, cardiovascular equipment's, bioactuators, biosensors and the medical industry. The surface modifications that can brought about in conducting polymers should (i) facilitate the movement of charge carriers in between the tissue and implanted device, (ii) facilitate large difference in mechanical modulus, (iii) Reduce impedance to improve the sensitivity of the recording site (electrode), and (iv) Possess biocompatibility and display stability in the physiological environment. Functionality of conducting polymers with various biomolecules / dopants has allowed biomedical engineers to change conducting polymers with biological sensing elements, and to turn on and off various signalling paths needed for different cellular processes. Conducting polymers provide an effective opportunity for implementing and fabricating highly stable, biocompatible, specific, selective, cheap and handy biomedical devices.

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