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PROPERTIES OF ORGANIC CONDUCTING POLYMERS

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INTRODUCTION

The discovering of organic conducting polymers with relative ease synthesis by chemical and electrochemical polymerization of monomers, with diverse and interesting optical, physical, electrical and mechanical properties, added to practical application in processes, devices preparation and novel uses, makes this area of practical and commercial interest [1-5]. These materials include conjugated and redox organic conducting polymers, copolymers and olygomers association forming organic conducting compounds. This type of materials can be prepared with specific characteristics, flexible or rigid, amorphous or crystalline, with different shapes, geometry and many others. Conducting polymers [6] offer a unique combination of properties that make them attractive alternatives for certain materials currently used in microelectronics. These polymers are made conductor (doped) by reacting the conjugated polymer with an oxidizing or a reducing agent, or a protonic acid. The conductivity of these materials can be tuned by chemical manipulation of the polymer backbone, by the nature of the dopant, by the degree of doping, and by blending with other polymers. Polymeric materials are lightweight, easily processed, flexible, have potential applications at all levels of microelectronics, in the area of lithography, metallization, as corrosion-protecting coatings for metals and surfaces, as electro static dispersive protector for packages and housings of electronic equipment and with possible use in interconnection technology and as novel organic materials in electronic devices [7]. Conducting polymers are promising transducers for chemsensors and biosensors owing to their unique electrical, electrochemical and optical properties that can be used to convert chemical information or biointeractions into electrical or optical signals [8, 9].

PREPARATION AND ORDERING IN ORGANIC CONDUCTING POLYMERS

The synthetic system used to produce a conducting polymer and ordering in the resulting material has to do with the nature of starting material, the particular electrochemical method used for polymerization, the electrolytic potential and the nature of dopant. According to C. Robinson [10], the first step in designing a polymer to be prepared is to ask what kind of properties one wants: For instance, what type of polymer do you want, which structure, what kind of solubility, which properties (mechanical, electrical, optical, and physical) are you expecting. New interfaces are created by superimposing layers of metals, inorganic oxides, and polymers, or by creating interpenetrating polymer networks. Polymers are being developed that use dyes to increase light collection efficiency. Polymerization methods are being developed that increase the structural order, producing more efficient charge transport properties. Conducting polymers is a class of new materials that combine solubility, processability, and flexibility of plastics with electrical and optical properties of metals and semiconductors. Many conducting polymers have well defined electrochemical activity, stability in air, and in aggressive media. These materials can be used as components of electrochemical, electronic and photonic devices; some of them show excellent anticorrosion properties and some of them have application as components of field effect transistors and polymer light.

CONJUGATED POLYMERS

Conjugated conducting polymers present extended delocalized bonds which form a

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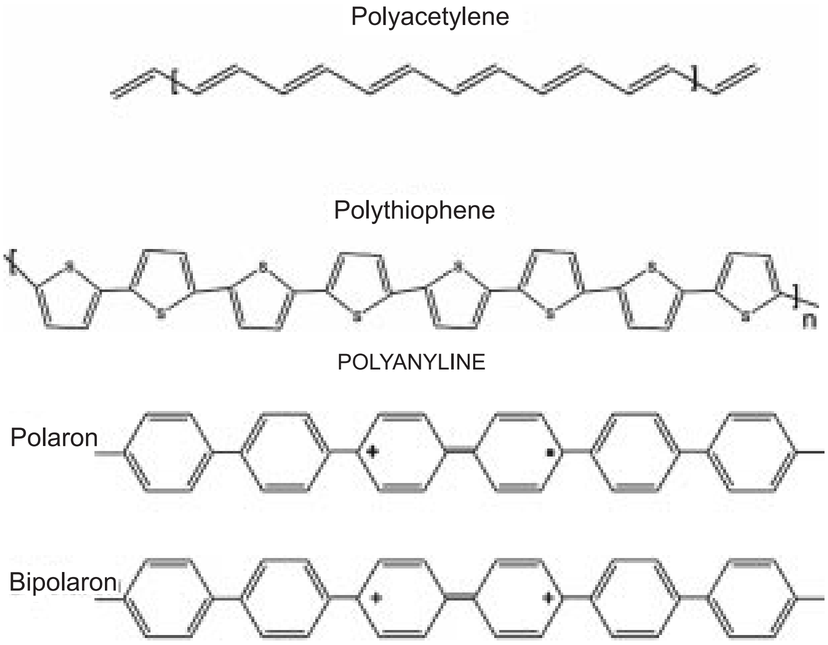
conduction band structure; introduction of charge transporters rapidly increase conductivity. Conjugated polymers are insulators in their neutral state; a polymer can be made conductive by oxidation (p-doping) and/or, less frequently, reduction (n-doping) of the polymer either by chemical or electrochemical means. By this way, organic semiconductors and in some cases organic metals can be prepared. The removing of an electron from the valence band (p-doping) or addition to the conduction band (n-doping) considerable increase conductivity and these charge transporters move in presence of an electrical field. In general, these compounds are of relative low weight, easy processability and manipulation, so that, their use is rapidly increasing [11-13]. These compounds have many important properties as electrical conductivity, non linear optical behaviour, high tensile stress, resistance to ambient aggresivity, charge accumulation, electrochromism, electromagnetic shield, energy dissipation and so [14,15]. In the scheme I are examples of conjugated polymers.

Electronically conducting materials based on conjugated polymers have been applied in diverse items such as sensors, biomaterials, light-emitting diodes, polymer actuators, and corrosion protection agents. Conjugated polymers can exhibit electron–hole conduction similar to conventional semiconductors, an effect that is enhanced by chemical doping. Electrical currents are produced by separating the electron–hole pairs. This is done by forming interfaces between materials having different ionization potentials and electron affinities. The difference in energy between the two levels produces the band gap that determines the optical properties of the material. In a conducting polymer, however, the electron and hole that are generated by the incident photon are bound into an exciton. There are two electrochemical methods of doping a conductive polymer, both through an oxidation-reduction (redox) process. The first method, chemical doping, involves exposing the polymer (typically a thin film), to an oxidant (typically iodine or bromine) or reductant (far less common, but typically involves alkali metals). The second is electrochemical doping in which a polymer coated working electrode is suspended in an electrolyte solution in which the polymer is insoluble along with



Scheme I : Conjugated conducting polymers

separate counter and reference electrodes [16]. A potential difference is created between the electrodes which causes charge (and the appropriate counter ion from the electrolyte) to enter the polymer in the form of electron addition (n doping) or removal (p doping).

REDOX POLYMERS

These polymers are characterized by the presence of specific spatially and electrostatically isolated electrochemically active sites. Typically, a redox polymer consists of a system where a redox active transition metal based pendant group is covalently bound to a polymer backbone which may or may not be electroactive. They have applicability in the area of chemically modified electrodes and the development of new materials with catalytic properties [17, 18]. The bulk of the work has been with systems where the polymer itself is inert and serves only as a support for the electrocatalytic metal sites. On these modified electrodes, electrochemical reactions occur selectively at a modest potential and with a better control. Unlike the electronically conducting polymers, redox polymers characteristically exhibit conductivity only over a very narrow potential range, with maximum conductivity occurring when the concentrations of the oxidized and reduced forms are equal in the film. The redox conduction in these polymers occurs by the electron hopping process, where the electron transfer proceeds as a process of sequential self-exchange steps between adjacent redox groups [19-22]. Model for conduction is shown in figure 1 [22].

CONJUGATED REDOX POLYMERS. HYBRID MATERIALS

In hybrid organic-inorganic materials based on conductive polymers, the electroactivity of molecular doping species or other inorganic components is added to that of the polymers themselves, leading to a whole new spectrum of hybrid materials that allow for the harnessing and control of the electrochemical properties of molecular species and put them to work in the development of all sorts of functional materials and devices, from sensors or catalysts to rechargeable lithium batteries, supercapacitors or photoelectrochemical devices. Redox polymers have a slow rate of electron transport by self-exchange through a potential gradient, and electronically conducting polymers exhibit rapid electron transport through a delocalized electronic structure; a hybrid polymer combines these properties. Materials that possess strong electronic interactions between metal atoms are being examined for use in advanced applications such as energy storage and molecular electronics

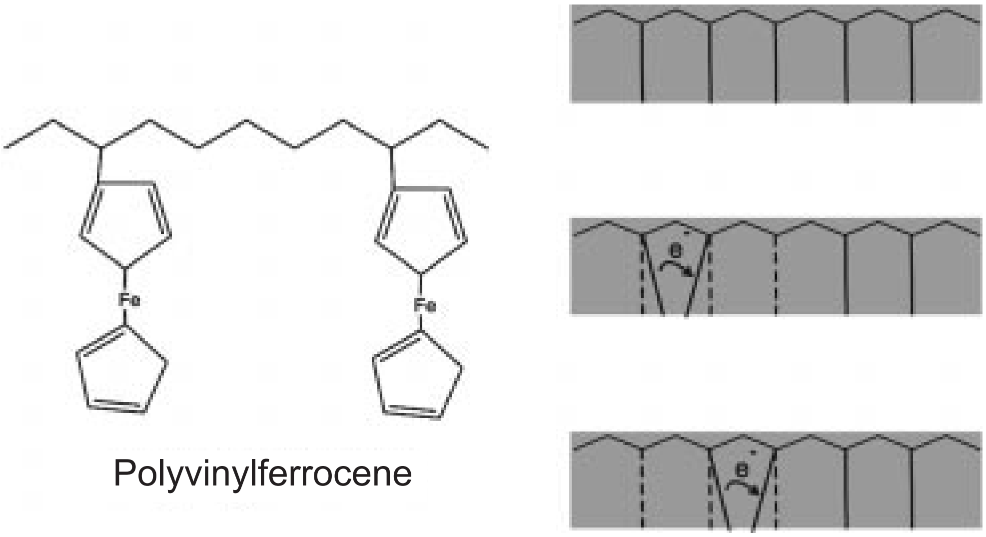


Figure 1 : Electron hopping between adjacent redox groups

[23]. A redox polymer film was prepared; it utilizes an anion exchange polymer, protonated poly (4-vinylpyridine), into which hexacyanoferrate anions have been introduced. The redox polymer film on steel seems to act as a composite three-dimensional bilayer-type coating in which hexacyanoferrate(III,II) anions (that are capable of effective charge storage) exist in the outer portions of the film, whereas the inner polymer layer improves the system's overall adherence and stability [24]. In a series of binuclear Ru (II) complexes bridged with benzimidazole- and benzothiazole-based ligands two pathways are considered [25] (figure 2), in the hole-type superexchange pathway, an electron is promoted from the bridging ligand (BL) HOMO to the M(III) site, giving the symmetric transition state with both metals in the reduced form. The missing electron from the BL HOMO is subsequently replaced by an electron from the other metal atom, resulting in a system where the valences have been swapped. Conversely, electron-type superexchange involves the transition of an electron from the M (II) state metal to the BL LUMO, leaving a symmetric-symmetric transition state with the metals in the oxidized form. Exchange is completed by the electron's transfer to the opposing M (III) atom. The preferred pathway and the ease with which it is taken depend on the relative energies of the metal orbitals and the BL π or π* orbitals; metal-d and BL-π orbital mixing leads to hole superexchange and metal-d and BL-π* orbital mixing leads to electron superexchange. In either route the valences are interchanged, enhancing stability of the mixed valence system.

$$[\mathrm{M{-}{-}L{-}{-}M}]^{(n-1)+} + [\mathrm{M{-}{-}L{-}{-}M}]^{(n+1)+} \Leftrightarrow 2[\mathrm{M{-}{-}L{-}{-}M}]^{n+}$$

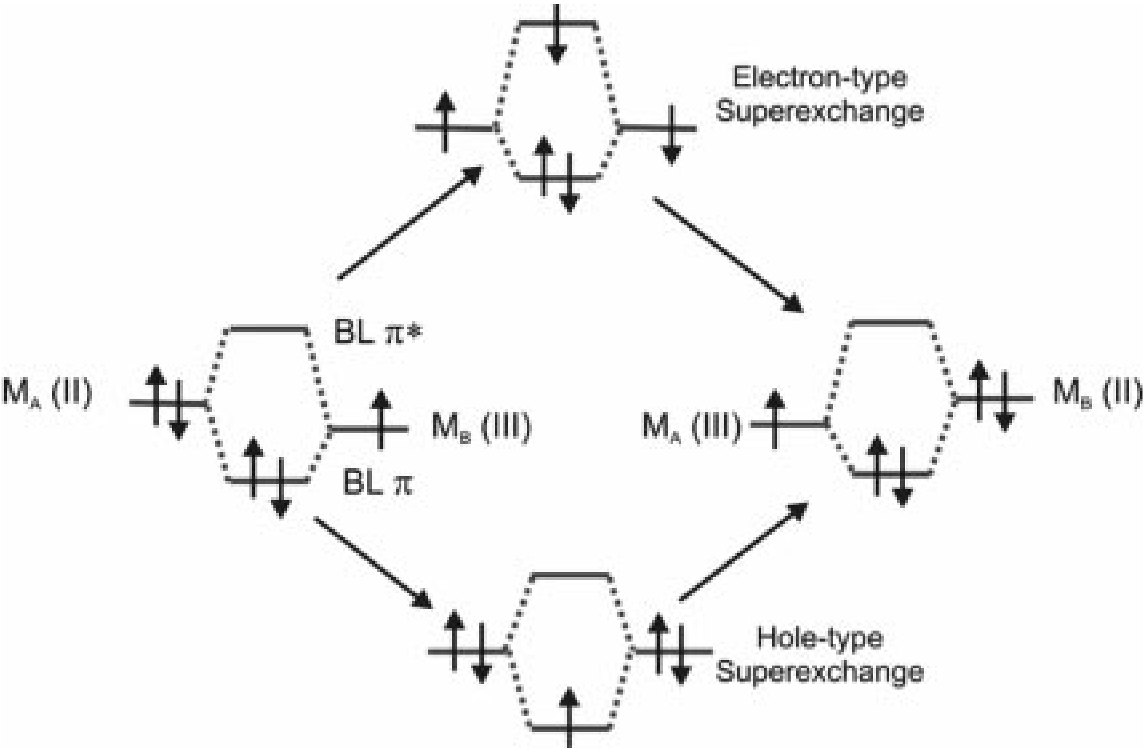


Figure 2 : Super exchange mechanisms. BL=bridging ligand (ref: 25)

COLUMNAR CONDUCTING STRUCTURES

In these materials, the molecular units (olygomers) self-organized into columnar stacks providing a favourable face to face orientation of the aromatic cores; this leads to a large π-overlap between the adjacent molecular units [26]. The charge-carrier transport process occurs preferentially along the columnar axes. It has been shown that one-dimensional electrical conductivity can be achieved by doping these intrinsically insulating discotic liquid crystalline systems with electron acceptors [27, 28]. The applicability of such columnar materials goes to xerography, organic transistors and light emitting diodes.

Polymers prepared from dimethoxybenzenes form a bilayer structure on the electrode surface and are insoluble, stable, adherent, inert and good conductors of electricity [5]. Are coloured and show electrochromic properties and some of them are sensitive to temperature, pressure, light radiation and sound frequency. They can modify electrodes and can be modified by metallic particles [29]. Some of these modified materials have been used as electrodes for the reduction process of carbon dioxide and electrolytic oxygen evolution; preparation of these polymers in different media, modified morphology and properties of the material. Some other properties, for instance of veratrole are paramagnetism, photoconductivity [30] and sensitivity to electrical potential [31].

Polyveratrole is an association of veratrole trimers with supporting electrolyte counter ion (32,33), figure 3. The material is semiconductor and conductivity change with pressure and temperature. Conductivity increases to a maximum when a sample is illuminated and decays in time when illumination ceases. Is also photoconductor and it increases with radiation density and is much higher in vaccum. Radiation absorption is higher in the visible region of the spectrum. Variation in conductivity with pressure, temperature and radiation are associated to structural changes, perhaps in the relative position of trimers in laminar and columnar structures. Photoconductivity is explained by apparition of charge transporters electron-hole. A band gap value of 2.4 eV was found (30) which makes interesting its consideration in solar batteries.

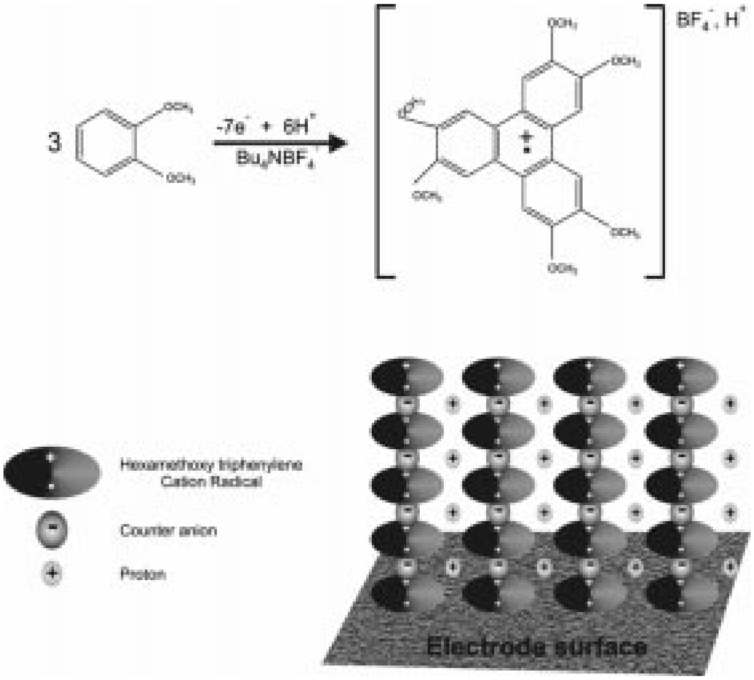


Figure 3 : Poliveratrole fibres formation.

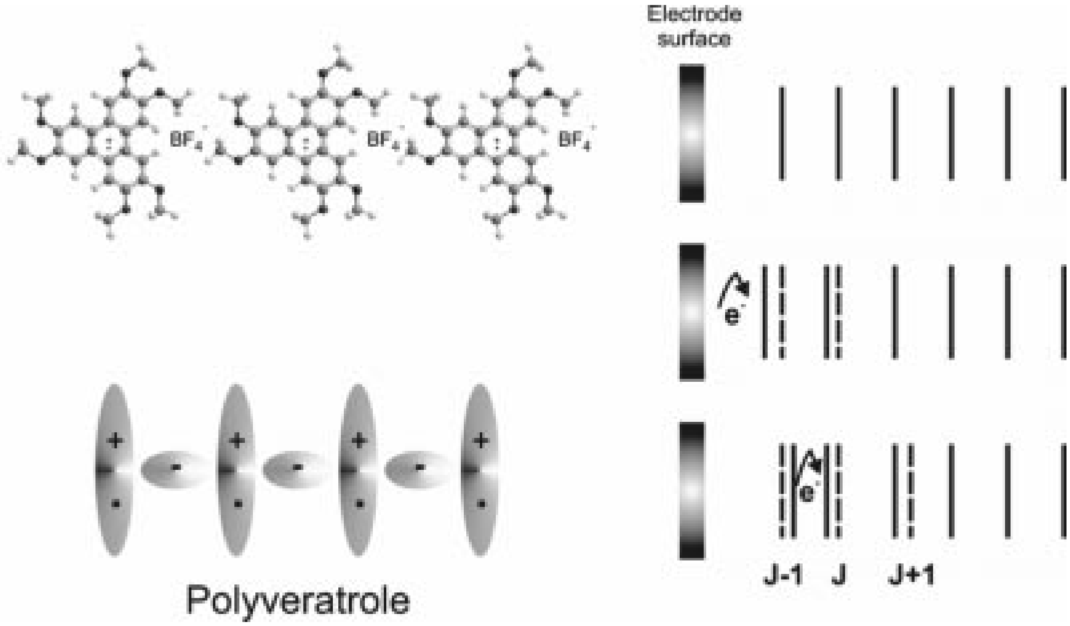
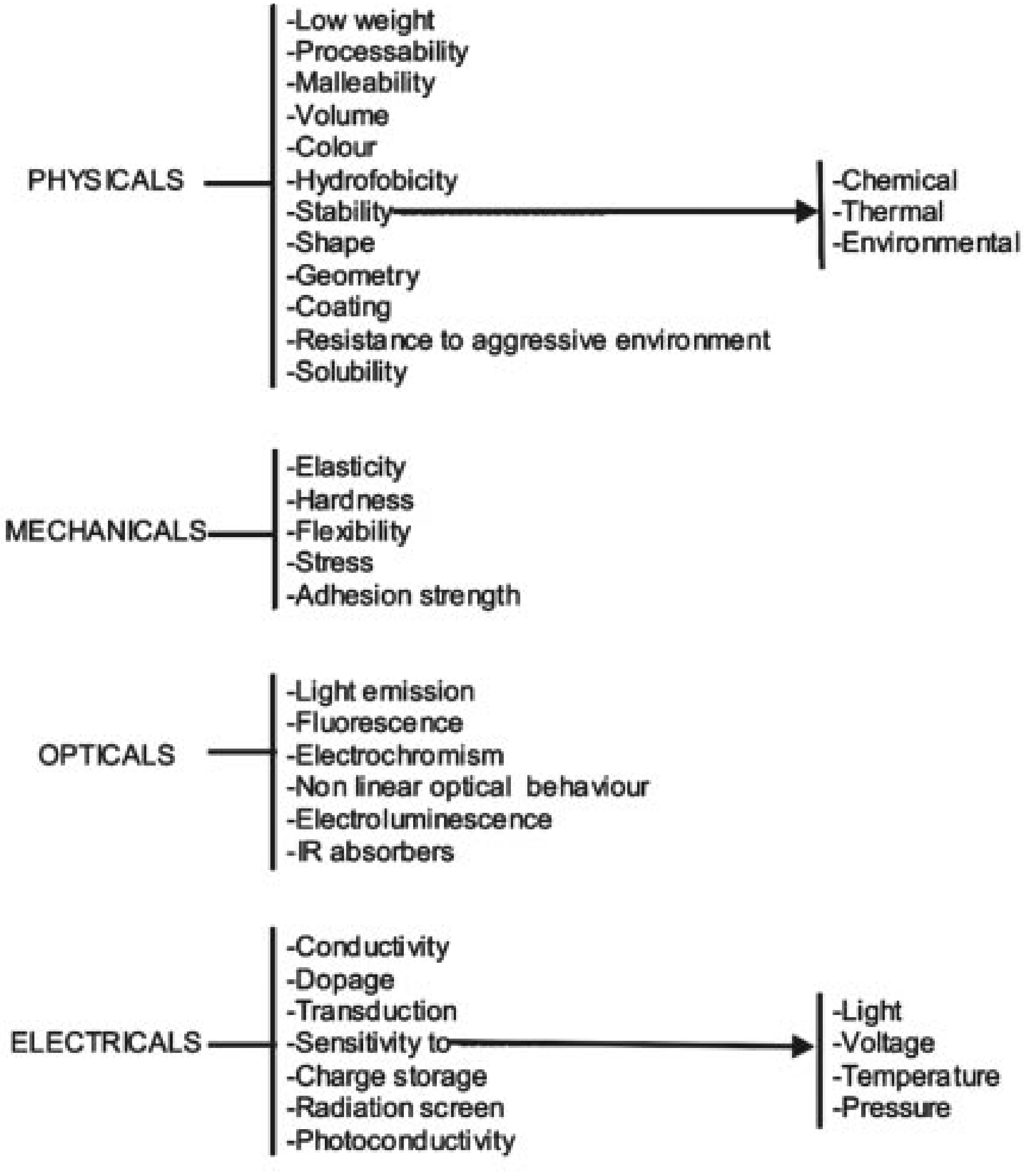


Figure 4 : One-dimensional electron hopping between discotic units (34)

Conducting polymers and organic materials with electrochemical, electrical and optical activity can be used as components of antistatic additives, electromagnetic screens, anticorrosion coatings, organic light emitting diodes, electromechanical actuators, electrochromic mirrors, and ultracapacitors. A list of many of their properties is incorporated below (table I). Among the conjugated conducting polymers, polyaniline (PANI) and polypyrrole (PPy) have attracted much interest because of their high environmental, thermal and chemical stability and their high conductivities. The electrical conductivity of these polymers is between 10^{-5} S/cm and 10^{2} S/cm while being doped. With a simple protonation process in PANI and PPy [35, 36], both solubility in common organic solvents and compatibility with various matrix polymers on the nanometer scale can be improved. These conducting blends or composites have been developed with a wide range of exciting properties for applications in film, fibres, and coatings. Oligo- and polythiophenes are some of the most promising materials among organic conjugated polymers for many applications, including field effect transistors, photovoltaics, light-emitting diodes, antistatic coatings, sensor films, recording materials, rechargeable batteries, and capacitors [37-39]. The intense interest in oligo- and polythiophenes for these applications is due to their high conductivity in the doped and undoped form as well as their high stability with respect to atmospheric exposure. Since the synthesis of first-generation polythiophene, a wide variety of polythiophenes have been synthesized and their physical and chemical properties established. The electron conjugation length of polythiophene increases with chain length, typically leading to red shifts in the photoluminescence and UV/ Vis absorption spectra. This relationship of optical properties, charge mobility, and conductivity to chain length and film structure has driven the development of novel polythiophene films, especially for applications in light-emitting films, photovoltaics, and thin film transistors.



PHYSICALS
- -Low weight
- -Processability
- -Malleability
- -Volume
- -Colour
- -Hydrofobicity
- -Stability
  - -Chemical
  - -Thermal
  - -Environmental
- -Shape
- -Geometry
- -Coating
- -Resistance to aggressive environment
- -Solubility

MECHANICALS
- -Elasticity
- -Hardness
- -Flexibility
- -Stress
- -Adhesion strength

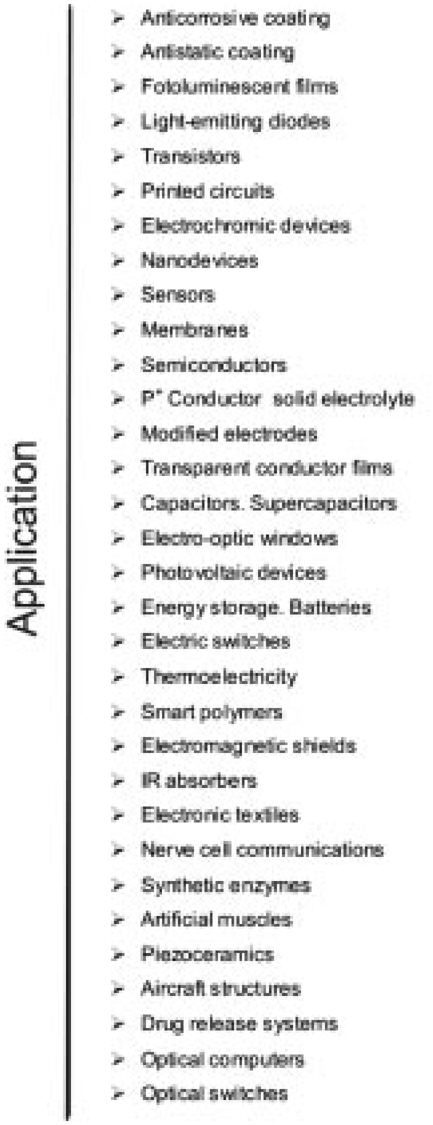
OPTICALS
- -Light emission
- -Fluorescence
- -Electrochromism
- -Non linear optical behaviour
- -Electroluminescence
- -IR absorbers

ELECTRICALS
- -Conductivity
- -Dopage
- -Transduction
- -Sensitivity to
  - -Light
  - -Voltage
  - -Temperature
  - -Pressure
- -Charge storage
- -Radiation screen
- -Photoconductivity

Table I : Properties of organic conducting polymers

A nanolithography technique for patterning conducting polymer nanostructures on semiconducting and insulating surfaces could help facilitate the fabrication of polymer nanodevices for use in the electronics, defence, pharmaceutical, and biotechnology industries. A direct-writing technique known as electrochemical dip-pen nanolithography was developed [40] to prepare well-defined polythiophene lines with widths of less than 100 nm on oxidized silicon wafer surfaces.

Depending on the conducting polymer chosen, the doped and undoped states can be either colourless or intensely coloured. The colour of this state can be altered by using dopant ions that absorb in visible light. Because conducting polymers are intensely coloured, only a very thin layer is required for devices with a high contrast and large viewing angle [41]. Such a variety of properties of conducting polymers give origin to a variety of applications, devices preparation and advances in science and society. A list of many of these applications is presented below.



Application

- Anticorrosive coating
- Antistatic coating
- Fotoluminescent films
- Light-emitting diodes
- Transistors
- Printed circuits
- Electrochromic devices
- Nanodevices
- Sensors
- Membranes
- Semiconductors
- P^+ Conductor solid electrolyte
- Modified electrodes
- Transparent conductor films
- Capacitors. Supercapacitors
- Electro-optic windows
- Photovoltaic devices
- Energy storage. Batteries
- Electric switches
- Thermoelectricity
- Smart polymers
- Electromagnetic shields
- IR absorbers
- Electronic textiles
- Nerve cell communications
- Synthetic enzymes
- Artificial muscles
- Piezoceramics
- Aircraft structures
- Drug release systems
- Optical computers
- Optical switches

Table II : Applications of organic conducting polymers

By coating an insulator with a very thin layer of conducting polymer it is possible to prevent the build-up of static electricity. Such a discharge can be dangerous in an environment with flammable gasses and liquids and also in the explosives industry. In the computer industry the sudden discharge of static electricity can damage microcircuits [42].

By placing monomer between two conducting surfaces and allowing it to polymerize it is possible to stick them together. This is a conductive adhesive and is used to stick conducting objects together and allow an electric current to pass through them [43].

Many electrical devices, particularly computers, generate electromagnetic radiation, often radio and microwave frequencies. This may cause malfunctions in nearby electrical devices. The plastic casing used in many of these devices is transparent to such radiation. By coating the inside of the plastic casing with a conductive surface this radiation can be absorbed. This can best be achieved by using conducting plastics [44].

Many electrical appliances use printed circuit boards. These are copper coated epoxy-resins. This process is being replaced by the polymerization of a conducting plastic [45].

Due to the biocompatibility of some conducting polymers they may be used to transport small electrical signals through the body, i.e. act as artificial nerves. Modifications to the brain might eventually be contemplated [46].

Weight is fundamental for aircraft and spacecraft. Modern planes are often made with light weight composites, this makes them vulnerable to damage from lightnings. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft [47].

The chemical properties of conducting polymers make them useful in the field of sensors. This utilizes the ability of such materials to change their electrical properties during reaction with various redox agents (dopants) or via their instability to moisture and heat [48].

Promising applications are light weight rechargeable batteries. The polymer battery, such as a polypyrrole-lithium cell operates by the oxidation and reduction of the polymer backbone [49].

Conducting polymers can be used to directly convert electrical energy into mechanical energy. What is required are the anodic strip and the cathodic strip changing size at different rates during charging and discharging. The applications of this include micro tweezers, micro valves, micro positioners for microscopic optical elements, and actuators for micromechanical sorting [50].

One of the most futuristic applications for conducting polymers is ‘smart’ structures. Applications of smart structures include active suspension systems on cars, trucks and train; traffic control in tunnels and on roads and bridges; damage assessment on boats; automatic damping of buildings and programmable floors for robotics [51].

Conductive polymers are present in most mammal tissues where electrical conduction or transduction from light or sound are necessary, including the skin, eye, inner ear, and brain. Its electronic conductivity seems to be the underlying mechanism for absorption of light, and electron-phonon interactions are exploited in hearing.

Conducting polymers may therefore find applications in electromagnetic interference (EMI) shielding, transparent packaging of electronic components, solar batteries, nonlinear optical display devices, ‘smart’ fabrics and recording, and so on. Recently, electroluminescence from conjugated polymers was observed at Cambridge Display Technologies (CDT), and this extraordinary feature could open up potential markets for organic light-emitting diodes (OLED) [52, 53]. This light-emitting polymer (LEP) technology is expected to provide an opportunity for the fabrication of flexible, full-colour displays with high luminescence, small power consumption and low-cost technology.

The development of a new generation of membranes based on conducting polymers involves a field of work wherein the excellent advantages presented by electro-dialysis conventional membranes (continuous separation, low energy consumption, ease of combination with other separation processes, absence of additives) are combined with other, highly promising, properties shown by conducting polymer membranes (great selectivity, low electric resistance to minimize specific energy consumption and low electro-osmotic flow). This field is of interest for automotive, chemical, agroindustrial, textile, printing, machine parts, pharmaceutical and others.

Initial results on a novel energy conversion device that uses both semiconducting polymers and organic small molecules as photoactive layers are presented by Breeze et al [54]; polymer/perylene bilayer devices show substantial improvement versus photovoltaics made from pthalocyanine/perylene. Conversion efficiencies of 1.4% have been achieved for simple planar bilayer organic devices.

Schottky devices have been made from conjugated polymers [55]. In general, ITO-coated glass is coated with the polymer, which in turn is coated with aluminium or another low work function metal such as magnesium or calcium. Heterojunction and p–n-junction devices can be configured; the polymer layer now consists of bilayers of a p-type polymer and a n-type polymer [56]. In addition, p–n junctions can be formed between n-type silicon and p-type conjugated polymers [57]. Photoelectrochemical cells have been made from conducting polymers. The polymer is coated onto the ITO-coated glass, and solid polymer electrolyte (SPE) is sandwiched between this polymer-coated electrode and a platinized ITO-coated glass counter- electrode. A liquid electrolyte can be used instead of the SPE (Fig 5) [58].

Development of artificial muscles, controlled drug release, and the stimulation of nerve regeneration is occurring in medicine. Recent studies suggest that the uncontrolled oxidation of lipids, proteins and DNA in biological systems is important in the progression of various diseases, cancer and aging. Low cytotoxicity and good biocompatibility are evident from the growth of cells on conducting polymers and from the low degree of inflammation seen in test animals over a period of several weeks. Given that conducting polymers are redox-active, and can shuttle between reduced and oxidized forms, potential interactions of the polymers with biological media need to be carefully considered for thermoplastics due to their useful electronic, optical and redox properties, and the antioxidant activity of conducting polymer.

Intelligent nanostructures that report on their environment by changing colour from blue to fluorescent red under mechanical, chemical, or thermal stress have been created by researchers at Sandia National Laboratories and the University of New Mexico [59]. When the environmental disturbance is removed, the structures change back

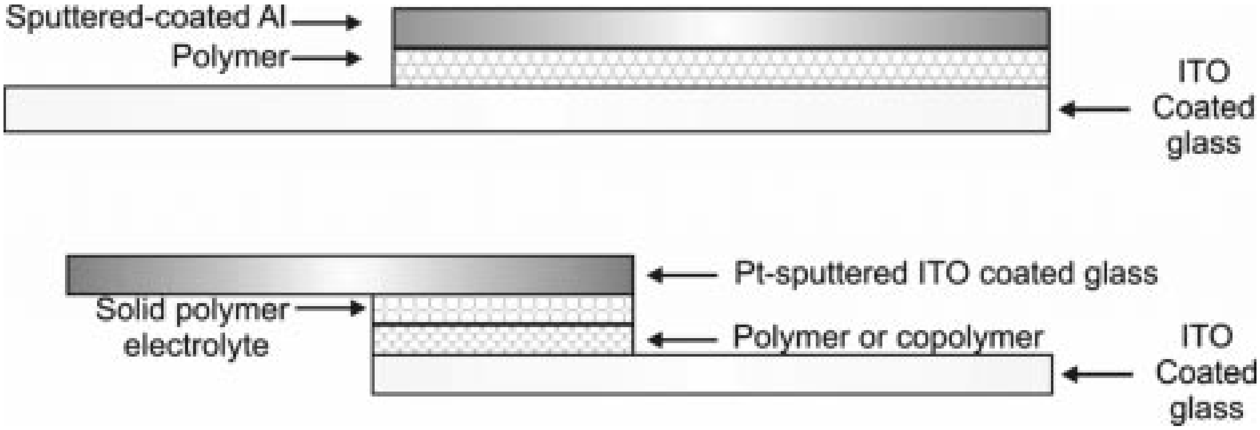


Figure 5 : Schottky device (top) and photoelectrochemical device (bottom). (Taken from Ref. 58)

to their original colour in some cases, making them potentially reusable. Another possible use for the orderly arrangements is to form nanoscopic "wires" of organic polymers. From Sandia too, a process for film preparation has produced a seashell-like layering at once very strong and nonbrittle, nanoscopic spheres that can hold catalysts or medicine, intelligent ink that assembles during ink-jet printing, and self-assembled nanostructures with pore sizes alterable by light to a fineness of 0.2 angstroms.

Natural muscles [60] show large strain, moderate stress, high efficiency and stability, fast response time, high power/weight ratio, long lifetime, etc. Conducting polymers can be used to prepare devices with similar performance to natural muscles. These macromolecules most present characteristics as conductivity, sensitivity to electric pulses, volume variation with conformational changes, reversible processes of oxidation and reduction, large strains, durability, high force density, fast response time and high power/weight ratio. In 1992, T. F. Otero [61] reported for the first time an artificial muscle (polypyrrole actuator). The first actuator based on conducting polymers was made combining a PPy film with a non volume changing layer into a bilayer structure. This was a bilayer: PPy doped with ClO^{-4} / adherent tape. The linear actuation principle is based on longitudinal expansion and contraction of the polymer due to the insertion and remotion of ions. Smela et al. prepared PPy/Au hinges to be able to lift plates of silicon and polysilicon [62]. They were capable to lift 40 000 times their own weight with a good reproducibility. The thickness of PPy influences the performance of the actuator, but the Au layer thickness did not affect the performance appreciably (figure 6). Otero and Sansiñena reported a triple layer actuator based on PPy (ClO^{4-}). This actuator is formed by an adherent polymer layer sandwiched between two PPy (ClO^{4-}) films. During electrodeposition the two faces of the working electrode were covered by PPy (ClO^{4-}). A double-sided tape was used to peel off a film of PPy (ClO^{4}) covering an electrode face. With the other side of the tape the other PPy (ClO^{4-}) film was peeled off. So, a triple layer PPy (ClO^{4-})/adherent tape/ PPy (ClO^{4-}) was formed. In this same year, Otero and Cortés reported the motion characterization of the triple layer (PPy (ClO^{4-})/adherent polymer / PPy (ClO^{4-}) in $LiClO^{4}$ aqueous solution [63]. The testing showed that this actuator presents electrochemopositioning properties; that means, that there is a perfect control of the motion by the magnitude and the sense of the current flow. Until now scientists have been making conducting polymers by doping the materials with ions that expand the volume of the polymer given them strength but additionally it makes them heavy and slow. Shining light of a particular frequency on a conducting polymer can activate a soliton [64]. The polymer could bend and flex quickly and that rapid motion give rise to the high speed actuation to activate a device (The effect of light (hí frequency) is to create positive charges (red) in a localized area. The positive charges enhance the chemical bonding between the polymer's units and straighten out the curved chain in that area). Conjugated polymer can actuate on commands if charges can be send to specific locations in the polymer chain in form of solitons.

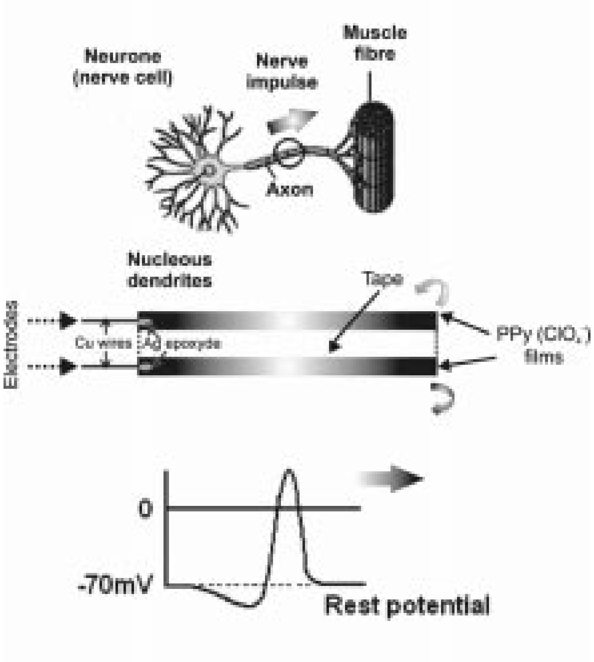


Figure 6 : Electrical stimulus – Response of device

Conducting polymers studies has expanded over the last few years to include a number of different applications. A key step in the continuing efforts to develop more processible materials has been the addition of solubilizing side chains[65]. It has helped create a wealth of new polymers. Electroactive polymers now emphasize molecular level engineering (i.e., creation of tailored molecular structures) in order to achieve specialized behavior [66]. Specific functional groups may also be introduced for a variety of purposes. A centrally important step for developing and exploiting new device technologies is simply learning the key structure/property relationships that exist at molecular length scales. What we can finally conclude is that the field of organic conducting polymers is in expansion and many new materials with many new properties and applications are still to come.

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