M.Sc. (Physics)

Study Material for Conducting Polymer

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Conducting Polymers

Polymers

Polymers are materials made of long, repeating chains of molecules composed by structural repeat entities, called Mer. These smallest units for instance are bonded by covalent bonds, repeating successfully along the chain. A monomer molecule composed by one mer is the raw material to produce a polymer. The majority of polymers are insulators, due to unavailability of free electrons to create the conductivity. These materials have unique properties, depending on the type of molecules being bonded and how they are bonded. Some polymers bend and stretch, like rubber and polyester and some are hard and tough, like epoxies and glass. Polymers touch almost every aspect of modern life e.g. water bottles, tires, chairs, wood, rubber, Proteins, Grocery bags, textile fibres, phones, computers, food packaging, auto parts, and toys. The polymer is often used to describe plastics, which are synthetic polymers. However, natural polymers also exist; rubber and wood.

Polymerization and Macro-molecules are two terms related to polymers and need to be understood. Polymerization is the method of creating synthetic polymers by combining smaller molecules, called monomers, into a chain held together by covalent bonds. A single macromolecule can consist of thousands of monomers. The molecules of Polyethylene and Polypropylene may consist of 10,000 to 200,000 monomers. Various chemical reactions caused by heat and pressure alter the chemical bonds and the process causes the molecules to bond in a **linear, branched or network structure**, resulting in creation of polymers. These chains of monomers are also called **Macromolecules**. Most polymer chains have a **string of carbon atoms as a backbone**.

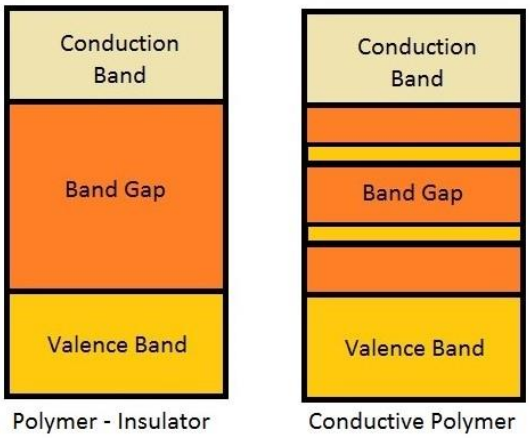
Conducting Polymers

Polymers or plastics are known to have good insulating properties. These polymers are used to coat metal wires to prevent electric shocks. However it has been recognized that there are some polymers which have conducting properties. A Polymer that can conduct electricity is called **Conducting Polymer** or Intrinsic Conducting Polymer or simply synthetic metal.

In the year 2000 the Nobel Prize in chemistry was awarded to three leading researchers Shirakawa, Heeger, and MacDiarmid, for their contribution on conducting polymers. One of such conducting polymer is poly-acetylene whose chemical name is Polyethyne. This is an organic polymer with the repeating unit $(C_2 H_2)_n$ has conjugated double bonds in its molecule, which makes conduction easier.

The cause of conducting current by a polymer is presence of conjugated π electrons in the backbone chain. A conjugated system is a system of connected p orbitals with delocalized electrons in a molecule, which in general lowers the overall energy of the molecule and increases stability. It is conventionally represented as having alternating single and multiple bonds.

In polymers, the conduction takes place by overlapping of orbital of conjugated π electrons in the polymer chain. Due to high coordination number, valence shell electrons are not sufficient for pairing with all surrounding atoms to form covalent bonding. Hence, the lower bands are filled first but the upper band are farthest from the nucleus and they are empty or partially filled due to insufficient electrons.



The lower energy band is called Valence band and the upper energy band is called Conduction band. The band theory explains the position of these mobile electrons and the process of electrical conduction. In polymer, when they occupy a definite positions, the electrons are subjected to a non-uniform electric field. The electrons may now take position in the band. The bands however non-continuous, but are separated by forbidden zones.

The valence band and conduction band are separated by a significant band gap. Thus electrical conduction occurs only after **thermal or photolytic** activation of electrons to give them sufficient energy to jump the gap and reach into lower levels of the conduction band.

Polyacetilene $(C_2H_2)_n$

Polyacetilene is one of the polymers in the study that resulted in the Chemistry Nobel prize in 2000. The polymer is synthetized by the reaction of the etyne, as commercially known as acetylene, with Ziegler-Natta catalyst. The resulting structure is shown in next page.

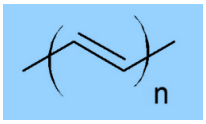


Fig: Chemical Structure of Polyacetylene Molecule designed on *ChemSketch*

Polyaniline $(C_6H_4NH)_n$

Polyaniline is one of the most promising conductive polymers and, therefore, one of the most studied ones. This polymer, in fact, is a family of polymers that is classified by aromatic rings bonded together by nitrogen atoms. Its structure is composed by x units of reduced species alternated with 1-x units of oxidized species as observed in figure.

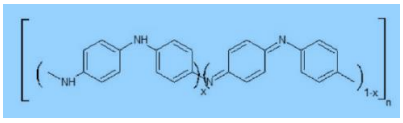
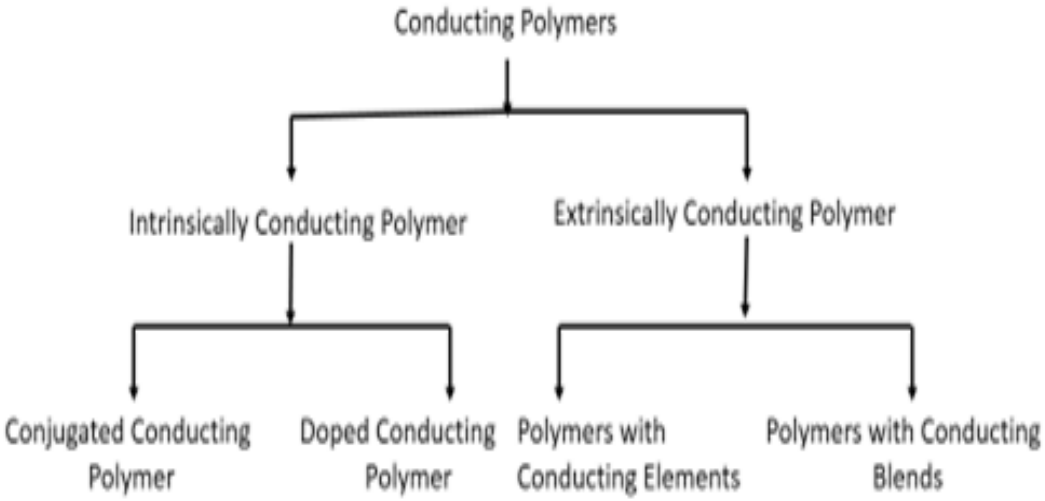


Fig: Chemical Structure of the Polyaniline: Molecule designed on ChemSketch

Important Examples: Polyethyne, Polypyrrole, Polyindole and P**olyaniline** and their co-Polymers are some of important conductive Polymers.

Conducting Polymer are classified in following way:

Classification of Conducting Polymers



Intrinsically Conducting Polymers

A. Conjugated Conducting Polymers:

These have extensive conjugation in the backbone which is responsible for conductance. The process of conductance can be understood by phenomenon of overlapping of conjugated electrons over the entire backbone, which results in the formation of valence bands as well as conduction bands and this extends over the entire polymer molecule. The valence band and conduction band are separated by a significant band gap. Thus electrical conduction occurs only after **thermal or photolytic** activation of electrons to give them sufficient energy to jump the gap and reach into lower levels of the conduction band. But **conductivity** of these polymers having conjugated electrons in the backbone is not sufficient for their use in different electrical applications.

B. Doped Conducting Polymers:

The conductivities of these conducting polymers can be increased by Doping. This doping is done in two ways P-Doping or Oxidative doping and N-doping or Reductive doping.

P doping is oxidation of Intrinsic Conductive Polymer with the Lewis acid **(H^+, K^+, Mg^{2+}, Fe^{3+}, BF_3, CO_2, SO_3, RMgX, $AlCl_3$, Br_2)**. By this oxidation process positive charges on backbone of Conductive polymer are created. These positive charges are current carriers for conduction.

N doping is done by reduction process. N doping involves the treatment of an intrinsic conducting polymer by Lewis bases like Sodium Napthalenide **($Na^+C_{10}H_8^-$)** as doping agent. (**Lewis Bases: OH-, F-, H_2O, ROH, NH_3, SO_4^{2-}, H-, CO, PR_3, C_6 H_6)** to create **Polaron** and **Bipolaron** in two steps. In N- doping, some electrons are introduced to the conjugated π bonds through reduction creating a negative hole or charge inside the polymer. The negative hole or charge can move throughout the polymeric chain and make it conducting polymer.

Extrinsically Conducting Polymers

A. Polymers filled with Conducting Elements: These are Polymers whose conduction power is artificially enhanced by addition of some foreign conducting material or good conductor in powder (carbon dust) form or granule form (metallic fibres). These can be Carbon Black, Metallic Fibre and Metallic Oxides. The role of polymer is to bind the added conducting materials. The minimum con-centration of conducting filler material, which should be added so that polymer starts conducting is known as ‘Percolation Threshold’. At this threshold, a conducting path is formed in polymer. Generally a

special conductive carbon black grade is used which imparts electrical conductivity to polymers at lower critical volume. Conductive carbon black has little influence on mechanical properties of the resulting conducting polymer compound and it is low in cost, light in weight and mechanically durable.

B. **Polymers with Conducting Blends**: These polymers are obtained by blending a conventional polymer with a conducting polymer. The property of resultant conducting polymer during blending becomes important. Normally these blended polymers have better physical, chemical, electrical and mechanical properties in comparison to polymer obtained by filled process. For example a polymer obtained by blending of 40% polypyrrole will be better than a carbon black filled conducting polymer.

Application of Conducting Polymers

Conducting polymers (CPs) are an exciting new class of electronic materials, which have attracted an increasing interest since their discovery in 1977. They have many advantages, as compared to the non-conducting polymers, which is primarily due to their electronic and optic properties. Also, they have been used in **artificial muscles, fabrication of electronic device, solar energy conversion, rechargeable batteries, and sensors**. **Super capacitors, Light emitting diodes (LEDs), Solar cells, Field effect transistor (FET), and Biosensors** also use Conducting polymers. Conducting polymer due to its light weight, low cost than metal semi-Conductor and ease in preparation has following other applications.

A. In wiring in aircrafts and aerospace components.
B. Optical display device
C. Telecommunication system
D. Electronic Toys