CONDUCTING POLYMERS

Polymers, in general are bad conductors of electricity and hence find application in electrical insulations. The poor conductivity is due to non-availability of large no. of free electrons required for conduction. Recently, polymers with conductivities closer to metals have been synthesized.

"A polymer that can conduct electricity is a conducting polymer"

Polymer	conductivity (Siemen cm^{-1})
Teflon (excellent insulator)	10^{-18}
Polyethelene	10^{-22}
Polyacetylene (doped)	1.5×10^{5}
Poly thiophene (doped)	10^{4}
Poly pyrolle	$5 \times 10^{2} - 7.5 \times 10^{3}$
Copper (metal)	6×10^{5}
Silver (metal)	10^{6}

Types of conducting Polymers

1. INTRINSIC CONDUCTING POLYMERS with extended conjugation of π bonds

Polymers having extensive conjugation of π bonds (or electrons) in the polymeric backbone, or ring structure increases their conductivities to a large extent. This is because in such cases π-e's get excited from valence band to conduction band as the band gap decreases from 0.5 - 1eV.

Bandgap for metals is 0 (zero)

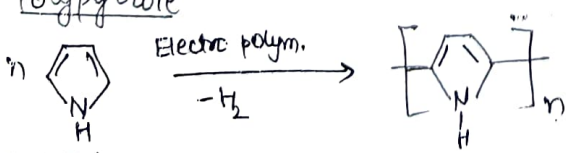
Insulating polymers have band gaps = 1.5 to 4eV.

eg. 1. Trans polyacetylene.

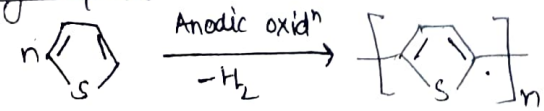
$$n\,CH{\equiv}CH \xrightarrow[-\text{ization}]{\text{Polym}}$$

Trans polyacetylene (double bond in extensive conjugation)

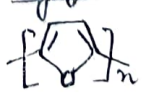
2. Polypyrrole



3. Poly thiophene



4. Polyfuran



(2) Doped Conducting Polymers –

The conduction of polymers, with extensive double bond in conjugation can be increased by doping them with suitable impurities as they can be easily oxidised or reduced due to their low ionisation potentials and high electron affinities. Depending upon the type of dopant used +ive or -ive charge can be created on polymer backbone. It leads to the formation of p-type or n-type polymers analogous to their respective semiconductors. However they differ from semicond -uctors in respect that no atom of polymers is replaced or substituted by doped atom or molecule.

a) p-doping :

Polymer (with extensive conjugation) + A (Lewis acid) {acceptor} $\underset{}{\overset{\text{oxidn}}{\rightleftharpoons}}$ $(\text{Polymer})^{n+}\ A^{n-}$ p-type doped conducting polymer.

A : eg - I_2, Br_2, $FeCl_3$, AsF_5, PF_6, etc.

eg:

$$(C_2H_2)_n + 2FeCl_3 \longrightarrow [(C_2H_2)_n^{+}\ FeCl_4^{-}] + FeCl_2$$

$$2(C_2H_2)_n + 3I_2 \longrightarrow 2[(C_2H_2)_n^{+} + I_3^{-}]$$

b) n-doping –

Polymer (with extensive conjugation) + B (Lewis base e^- donor) $\underset{}{\overset{\text{Redn}}{\rightleftharpoons}}$ $\text{Polymer}^{-n}\ B^{+n}$ (n type doped conducting polymer obtained by redn)

B : eg - Na, Li, Ca, Napthyl amine ($C_{10}H_7NH_2$)

eg: $[CH=CH-CH=CH]$ + $C_{10}H_7\ddot{N}H_2$ $\xrightarrow{\text{Redn}}$ $[CH=CH-\underset{\underset{\oplus}{NH}}{\bar{C}H}=CH]$ + $C_{10}H_8$ napthalene

[NOTE: mechanism of n-doping and p-doping : see on next page.]

Doping leads to formation of new energy bands which in turn overlap with valence and conduction band of the intrinsic polymer. This results in formation of partially filled conduction and valence band apart from the production of high concentration of holes or free electrons at room temp. hence conductivity increases.

3. EXTRINSIC CONDUCTING POLYMERS are those polymers whose conductivity is due to presence of externally added ingredient in them.

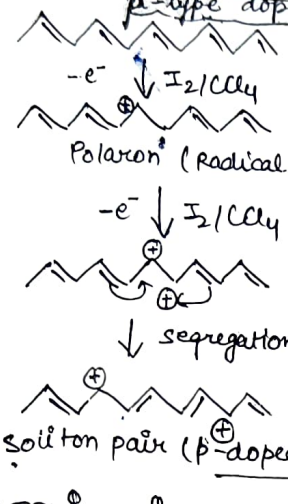
(i) Conductive element filled polymer : It is a resin or polymer filled with conducting elements such as carbon black, metallic fibres, metal oxides etc. Polymer binds the conducting elements together in solid entity. Such polymers are of cheap cost, reasonably high conductivity, light weight, mechanically durable, strong and easily processable to various shapes.

SMART POLYMERS

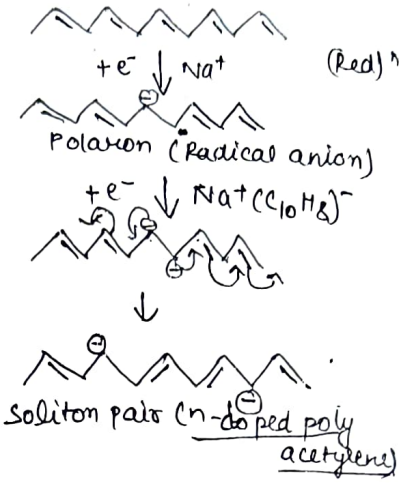
Smart window (Switchable glass/window) - is glass or glazing whose light transmission properties are altered when voltage, light or heat is applied.

b) Blended conducting polymer - It is the product obtained by blending conventional polymer with a conducting polymer physically or chemically. Such polymers are easily processed; have better physical, chemical and mechanical properties

p-type doping mechanism



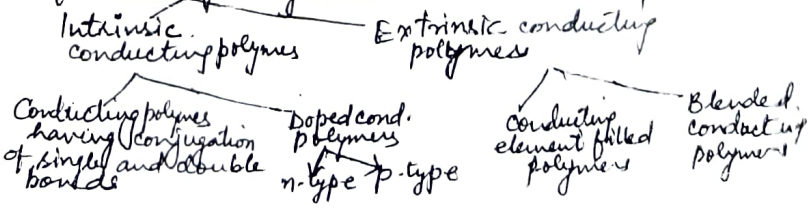
n-type doping mechanism



APPLICATIONS

1) In rechargable batteries : due to light weight, high current density than conventional batteries; Durable and efficient
2) For making ion exchangers
3) In analytical sensors for pH, O_2, SO_2, NO_x, NH_3 & Glucose
4) In electronic devices eg. Diodes and transistors
5) In photovoltaic devices eg Al/polymer/Au photovoltaic cells
6) In wiring in aircrafts and aerospace components
7) Telecommunications
8) solar cells
9) Drug delivery system for human body etc.
10) Smart windows : change colour on change in temp. or amount of sunlight (from yellow green to blue-black)

NOTE: classification of conducting polymers.



BIODEGRADABLE POLYMERS.

Biodegradation is the process by which organic substances are broken down by the enzymes produced by living organisms. Biodegradable polymers are those polymers which get decomposed by the process of biodegradation. Biodegradation can be aerobic (in presence of O_2) or anaerobic (in absence of O_2) -

Aerobic : Polymer + O_2 $\longrightarrow$ CO_2 + H_2O + biomass + residue

Anaerobic: Polymer $\longrightarrow$ CO_2 + CH_4 + H_2O + biomass + residue

Requirements for biodegradation :-

(i) Microorganisms → to synthesize enzymes
(ii) Environment → temperature, pressure, moisture, O_2, light etc.
(iii) Substrate → biodegradable polymer having suitable functional groups, low. mol. wt, hydrophilicity and less crystallinity.

Types of biodegradable polymers (classification)

(1) Natural biodegradable polymers -
- (a) Polysaccharides - e.g. starch, cellulose
- (b) Proteins - e.g. gelatin, casein, silk, wool
- (c) Polyesters - e.g. polyhydroalkanoales
- (d) Others - e.g. lignin, natural rubber, poly (gamma-glutamic acid) etc.

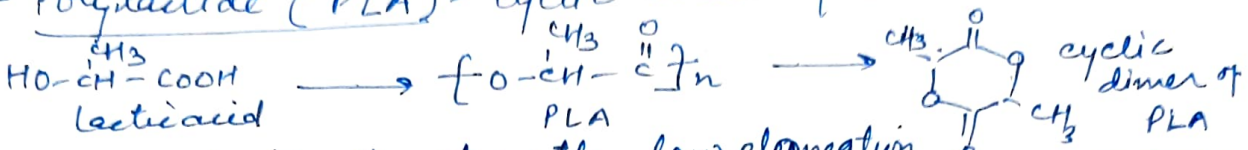
(2) Synthetic biodegradable polymers — e.g. Polyvinyl alcohol (PVOH), Poly-(3 hydroxybutyrate-CO-3-hydroxyvalerate) or PHBV, (PHB (Polyhydroxy butyrate)) Polyvinyl alcohols, Polyanhydrides, Polyvinyl esters etc. Poly lactic acid (PLA)

Need for biodegradable polymers :- Conventional polymers such as polyethene, polypyrrole etc. persist for many years after disposal, thus, creating solid waste problems particularly with regard to decreasing availability of land fills, litter problems and hazardous nature to aquatic life. They create pollution everywhere.
Biodegradable polymers need not to be land filled, they re-enter normal geochemical cycles over time and many of them are derived from renewable resources.

Examples of Biodegradable polymers

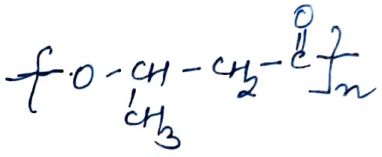
1- Polyhydroxyalkanoates (PHA) - used to make shampoo bottles.

2- Polylactide (PLA) - cyclic dimer of lactic acid

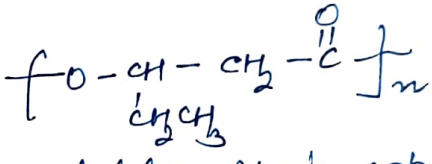


Have high tensile strength, low elongation, high modulus which makes it more suitable for load bearing applications such as orthopedic fixation and sutures. PLA is also used for agricultural applications such as timed-release coatings for fertilizers & pesticides.

2- Polyhydroxybutyrate (PHB) - It is an example of polyhydroxy alkanoate. used to make shampoo bottles.

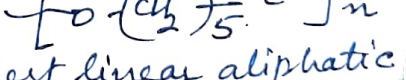


3- Polyhydroxyvalerate (PHV)

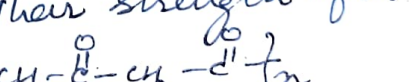


PHB & PHV are used in medical devices. They are low cost biodegradables. Their copolymers HB-HV are suitable as matrices for controlled release of drugs.

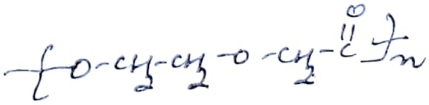
4- Poly(ε-caprolactone) - (PCL) - is thermoplastic biodegradable polyester. It is tissue compatible, hence used as a biodegradable suture in Europe.



5- Poly(glycolactide) (PGA) - Simplest linear aliphatic polyesters sutures of PGA lose about 50% of their strength after 2-weeks and 100% after 4-weeks



6- Poly(dioxanone) - a polyether-ester It provides an advantage over other for slow healing of wounds.



9- Polyvinyl acetate (PVA) -

It is a low mol. wt polymer $\left[CH_2-\underset{\underset{OCOCH_3}{|}}{CH}\right]_n$ and become gum-like when masticated and hence used for making chewing gums. It is harmless when taken orally.

Also used for making water based emulsion paints for finishing textile and other fabrics etc.

Limitations of Biodegradable polymers -

- Not easily available
- Very expensive
- Anaerobic conditions of land fills decrease the rate of biodegradation.