CLASSIFICATION OF POLYMERS

1. Origin	Natural, synthetic and semi synthetic
2. Polymeric Structure	Linear, Branched, Cross-linked, Globular
3. Chemical Structure	Organic & Inorganic
4. Types of monomers	Homopolymers and Copolymers
5. Mode of Polymerization	Addition & Condensation
6. Physical State	Amorphous & Crystalline
7. Tacticity	Atactic, Isotactic, Syndiotactic
8. Molecular Forces	Elastomers, Plastics, Fibres
9. Thermal Behaviour	Thermoplastic & Thermosetting plastics
10. Conductance	Conducting & Non-conducting Polymers
11. Degradation	Biodegradable & Non-biodegradable

Amorphous & Crystalline Polymers
&
Tacticity

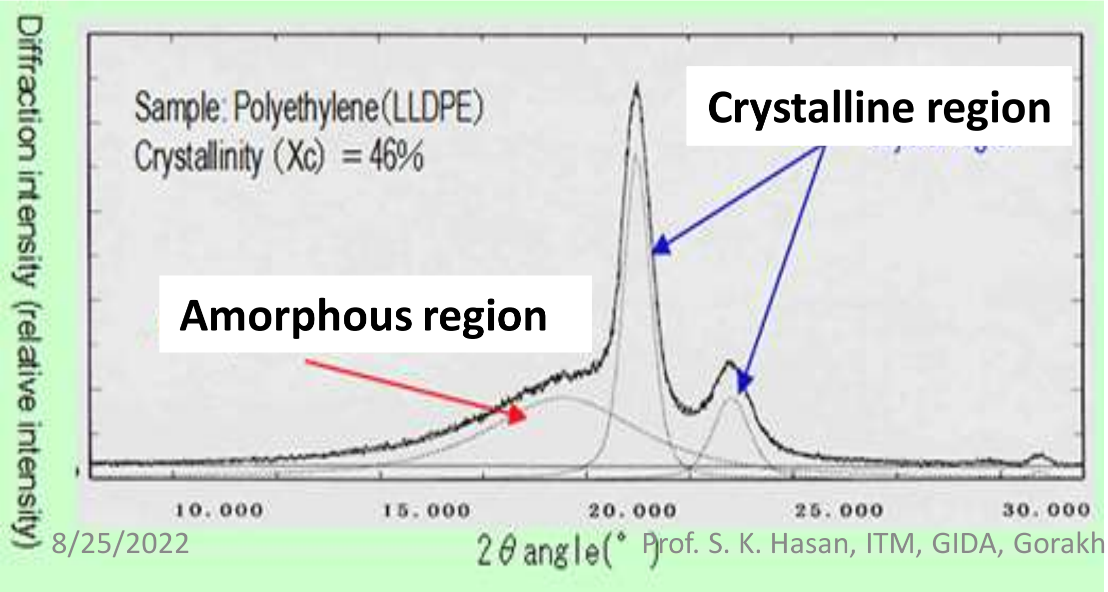
On the basis of Physical State

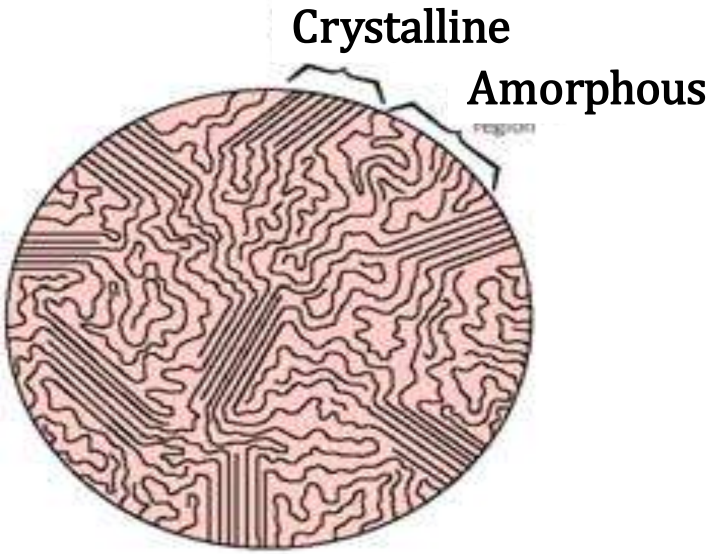
Crystalline

1. Crystalline structures are generally very ordered,
2. Ordered arrangement gives them strength and rigidity.
3. X-ray Diffraction gives Sharp peaks
4. Stereoregular isotactic and syndiotactic

Amorphous

1. The polymer chains for amorphous plastics are more disorganized.
2. Amorphous polymers have flexibility and elasticity.
3. The X-ray Diffraction gives Broad Peaks
4. Amorphous and flexible are Atactic polymers





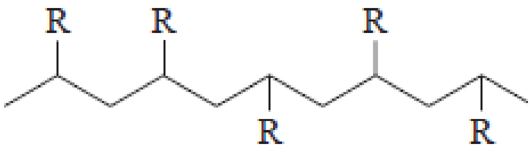
Tacticity

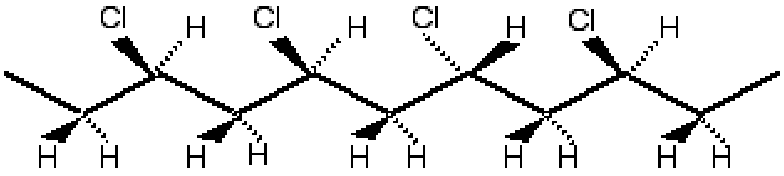
The Tacticity defined as the geometric arrangement of functional groups or side chain of monomer unit with respect to the main polymeric chain (backbone) of the polymers. On the basis of structure, polymer may be classified into three groups,

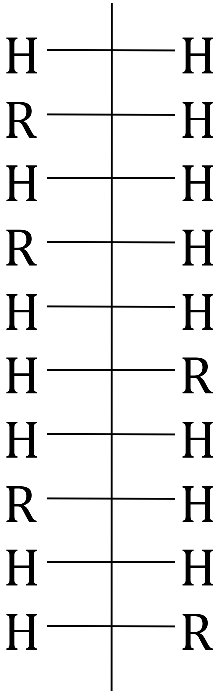
1. Atactic 2. Isotactic 3. Synduotactic

Atactic Polymer

A polymer is said to be atactic, if the functional group or side chain is arranged in irregular fashion (i. e. in random manner) around the main chain.



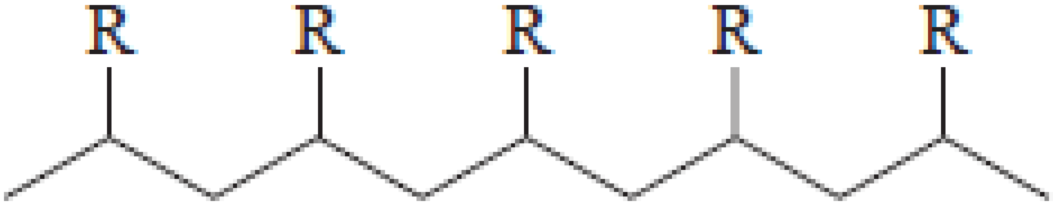


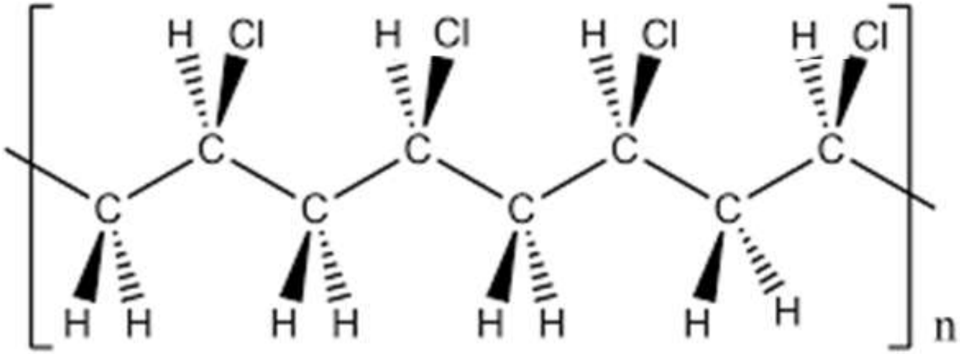


$R = CH_3$	Polypropylene
$= C_6H_5$	Polystyrene
$= Cl$	PolyvinylChloride (PVC)
$= CN$	Polyacrylonitrile (PAN)
$= OH$	Polyvinylalcohol
$= OOCCH_3$	Polyvinylacetate

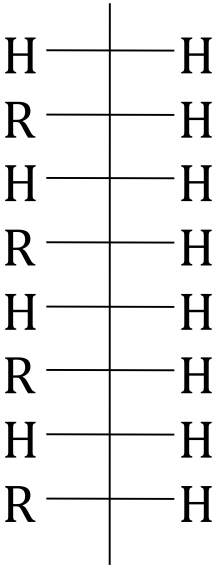
Isotactic polymer

Isotactic polymer are those in which the functional groups or side chains are arranged on the same side of the main chain.



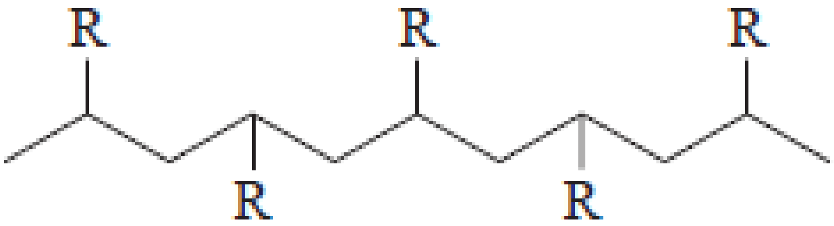


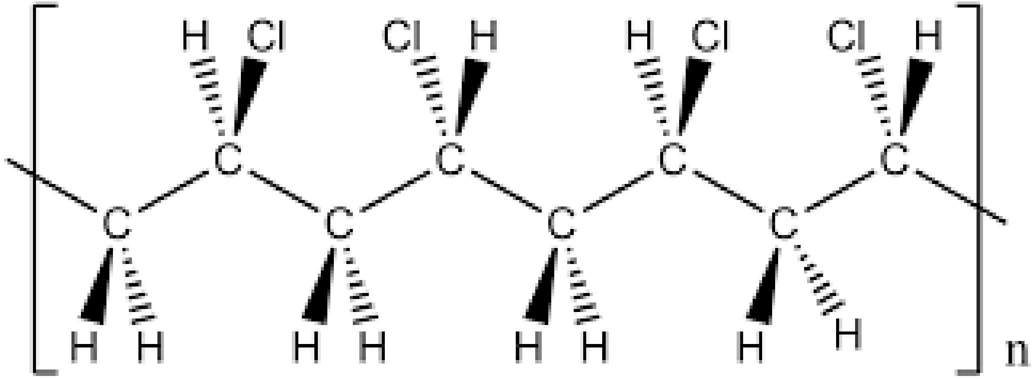
Isotactic



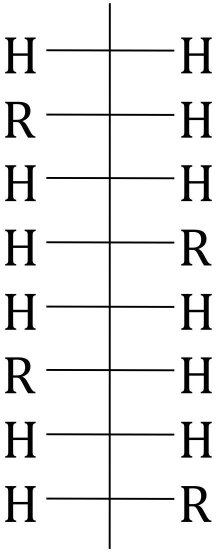
Syndiotactic polymer

A polymer is said to be syndiotactic if the side groups or side chains are arranged in an alternate fashion to back bone chain.



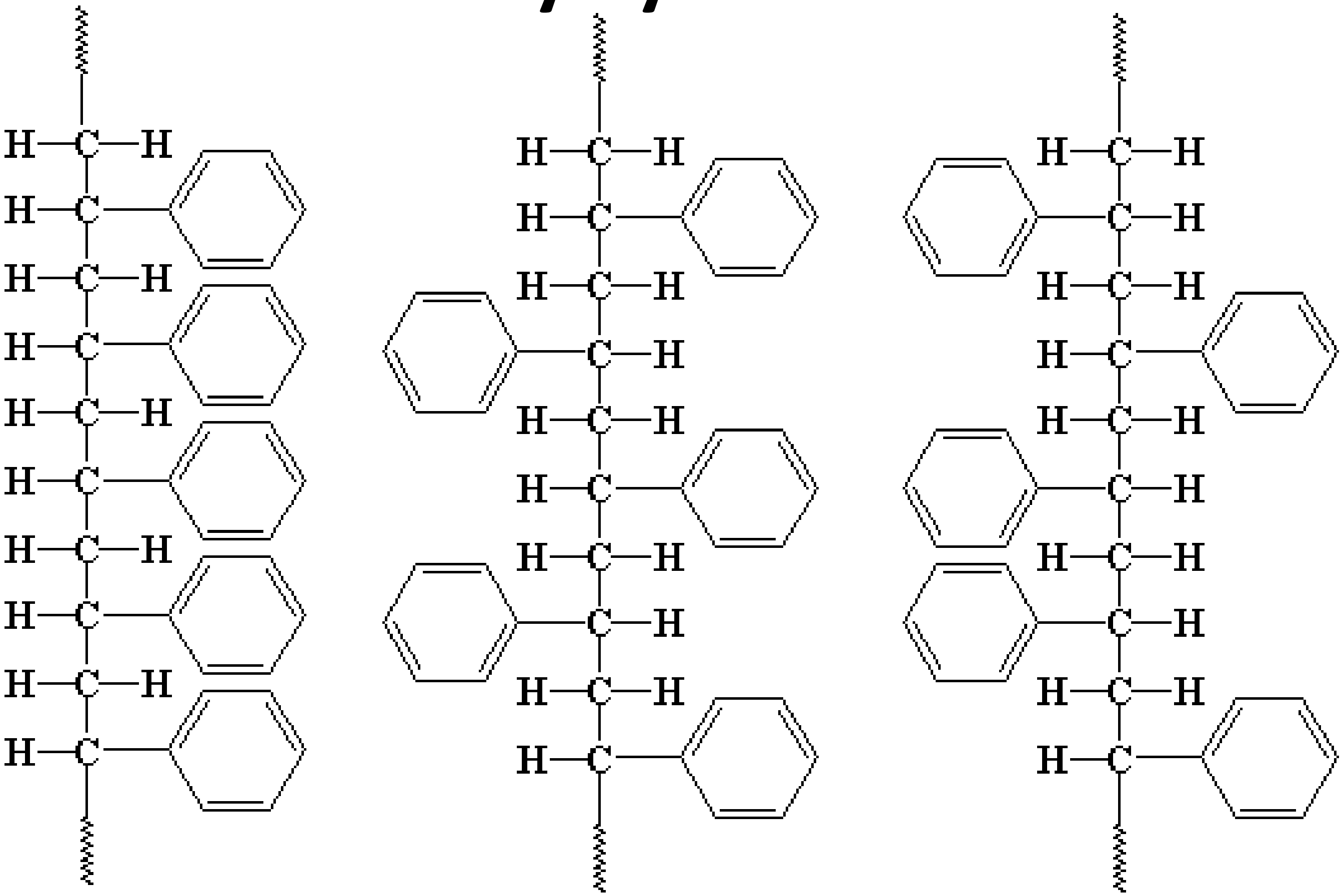


syndiotactic



- Isotactic and Syndiotactic polymers are known as stereo regular and they are rigid and hard.
- Atactic polmers has irregular arrange ment so they are flexible and soft.

Polystyrene



Isotactic Syndiotactic Atactic

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Elastomers, Plastics & Fibres

8. On the Basis of Molecular Forces

a. Elastomers **b. Plastics** **c. Fibres**

a. Rubber (Elastomers)

Rubber is a high molecular weight polymer with long flexible chains and **weak intermolecular forces.** They have elastic property. It can be stretched to 4-10 times of its original length. Its polymeric chain is found in the form of a coil so it can be stretched.

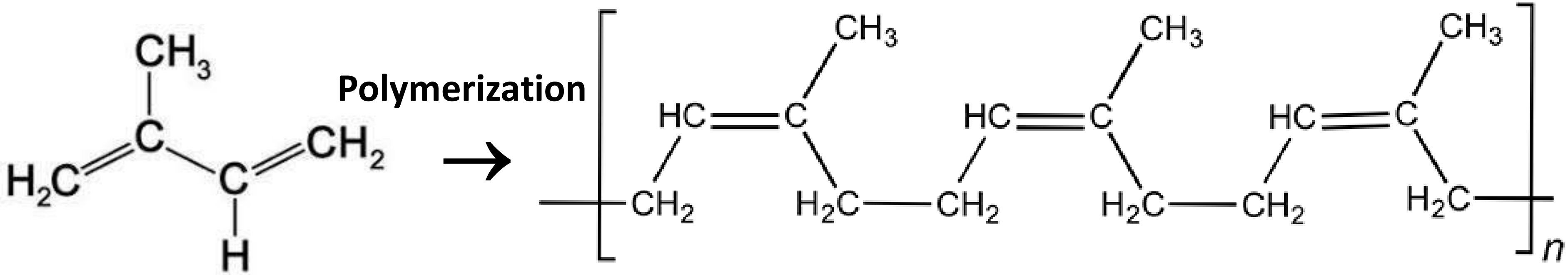
Examples:

Natural & Synthetic Rubber and Vulcanized Rubber

SBR (Buna-S), NBR (Buna-N)

Natural rubber

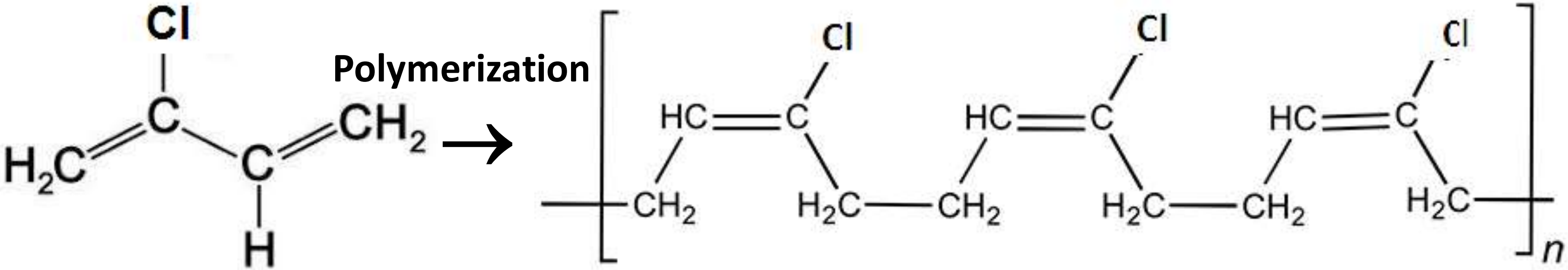
Natural rubber is harvested mainly in the form of the latex from the rubber tree or others. The latex is a sticky, milky colloid. Latex is the polymer cis-polyisoprene



Isoprene
2-methyl-1,3-butadiene

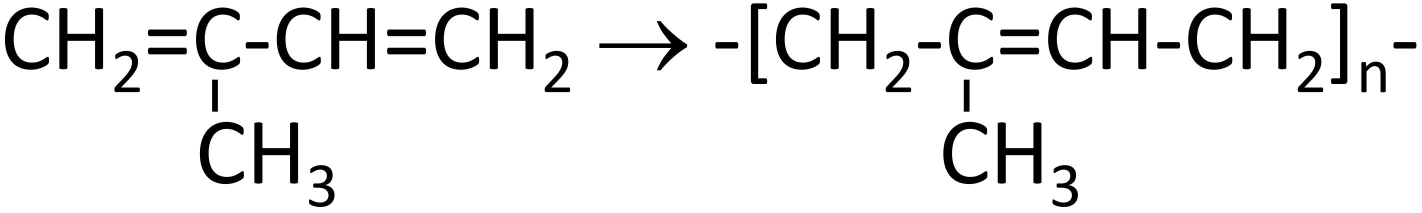
Cis-Polyisoprene
Natural Rubber

Synthetic rubber (Neoprene): Polychloroprene

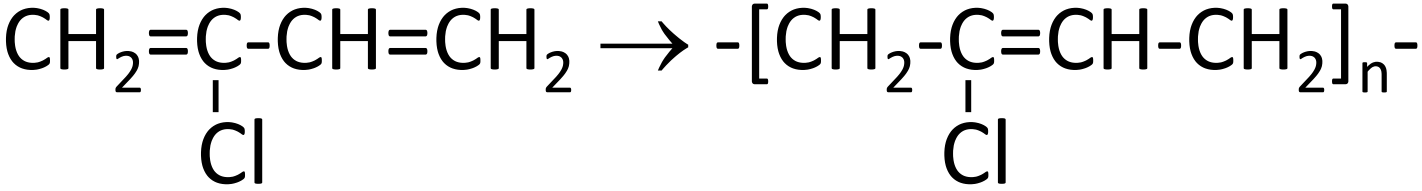


Chloroprene
2-chloro-1,3-butadiene

Polychloroprene
Synthetic Rubber



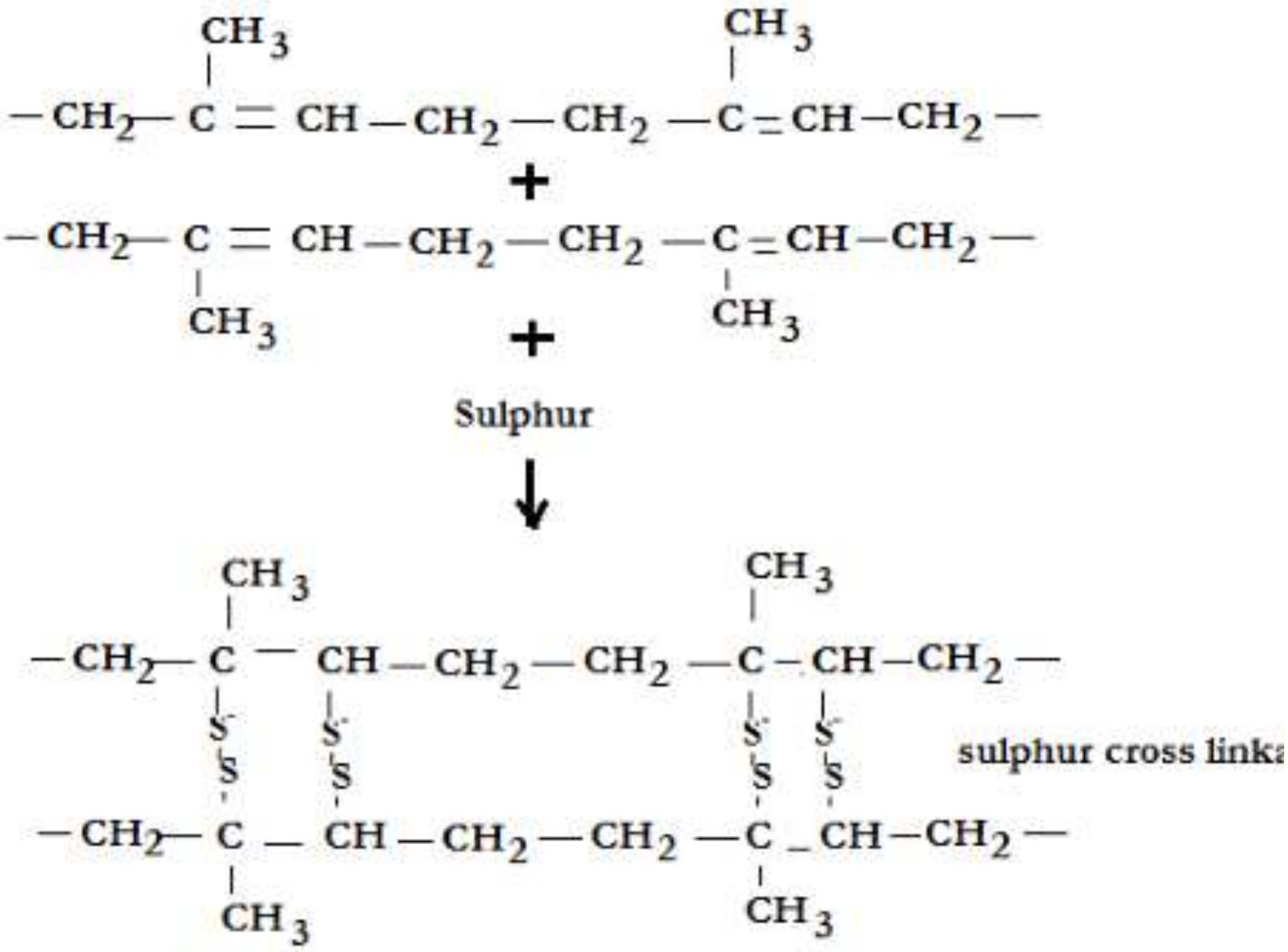
$$CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}CH{=}CH_2 \rightarrow -[CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH{-}CH_2]_n-$$



$$CH_2{=}\underset{Cl}{\underset{|}{C}}{-}CH{=}CH_2 \rightarrow -[CH_2{-}\underset{Cl}{\underset{|}{C}}{=}CH{-}CH_2]_n-$$

Vulcanization and Vulcanized Rubber

Vulcanization is the process of making natural rubber hard by cross linking of polyisoprene chain through Sulphur atom. The hard rubber thus formed is called as Vulcanized Rubber



Vulcanized Rubber

b. Plastics

Plastics are relatively tough substances with high molecular weight that can be molded in various shapes. These are usually much stronger than rubbers due to stronger intermolecular forces.

The examples of plastics are,

Polyethylene, Polypropylene, PVC, Polystyrene, etc.

Types of Plastics

1. Thermoplastic
2. Thermosetting Plastic

c. Fibers

Fibers are long- chain polymers characterized by highly crystalline regions resulting mainly from secondary forces like hydrogen bonding. The intermolecular forces are very strong. They have a much lower elasticity than plastics and elastomers.

Nylon, Dacron, Silk etc

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Thermoplastic
&
Thermosetting plastics

On the basis of Thermal Response

polymers can be classified into two groups

A. **Thermoplastic polymers:-**
B. **Thermosetting polymers:-**

Thermoplastic polymers:-

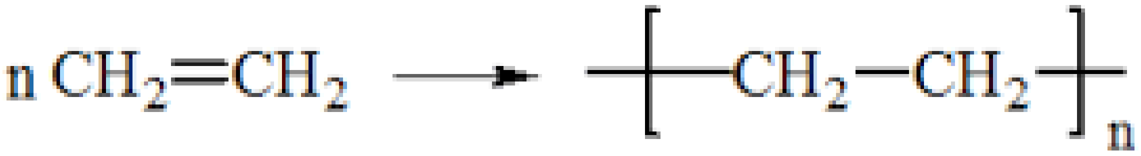
They can be softened or plasticized repeatedly on application of thermal energy. Thermoplastic can be synthesized by addition polymerization. They can be moulded to any shapes by heating and cooling. Thermoplastic can be recycled. Thermoplastics have low melting points and low tensile strength. Thermoplastic is lower in molecular weight, compared to thermosetting plastic.

Example of such polymers are

Polythene, polypropylene, PVC, Nylons, Linear Polyesters and etc.

Uses: Moulded articles like toys, table-chair, bottles, sheets etc.

Polythene

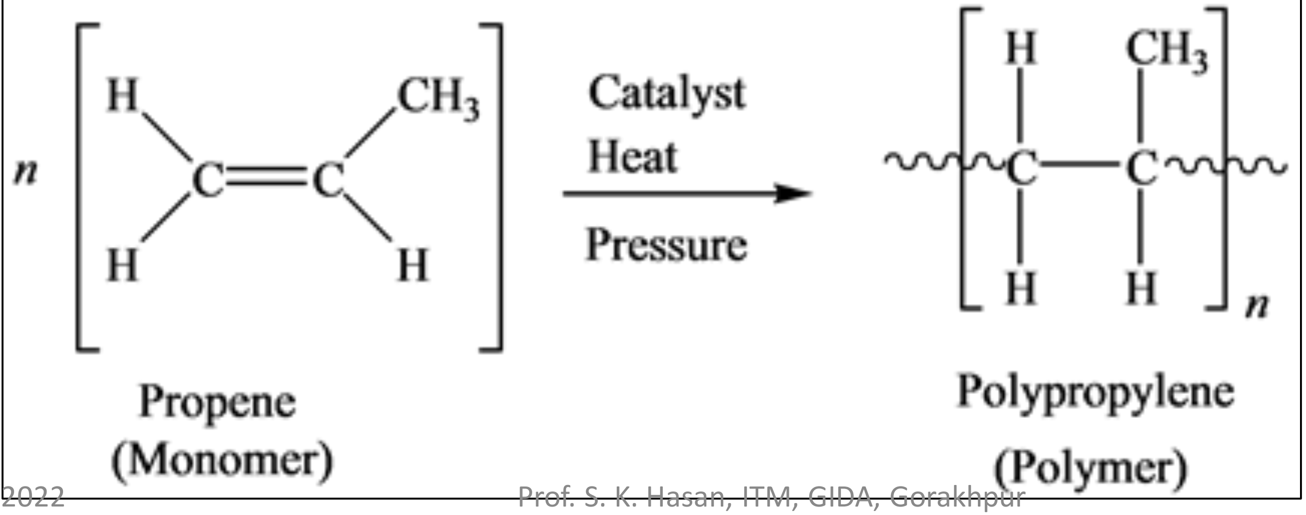


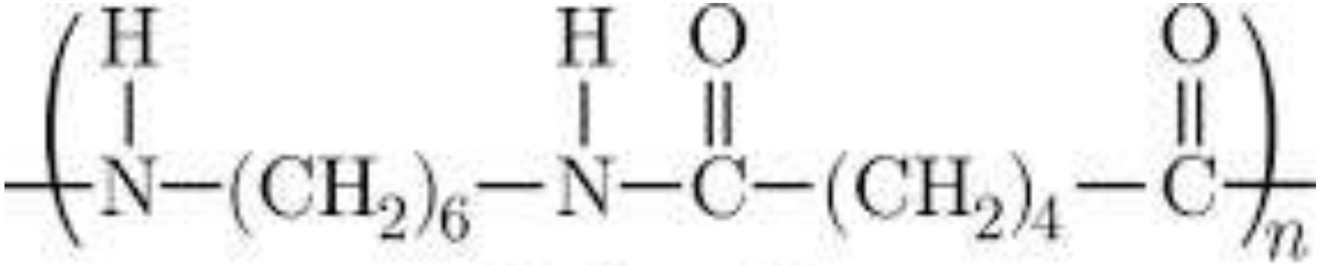
$$n\,CH_2{=}CH_2 \longrightarrow \left[CH_2{-}CH_2 \right]_n$$

Ethene

Polythene

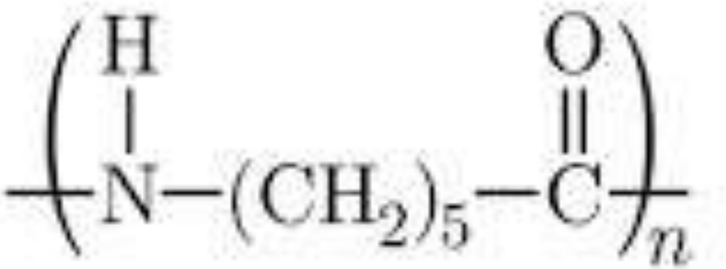
Polymer of Propylene is Polypropylene





$$\left(\overset{\mathrm{H}}{\underset{|}{\mathrm{N}}} - (\mathrm{CH_2})_6 - \overset{\mathrm{H}}{\underset{|}{\mathrm{N}}} - \overset{\mathrm{O}}{\underset{\|}{\mathrm{C}}} - (\mathrm{CH_2})_4 - \overset{\mathrm{O}}{\underset{\|}{\mathrm{C}}} \right)_n$$

Nylon 66



$$\left(\overset{\mathrm{H}}{\underset{|}{\mathrm{N}}} - (\mathrm{CH_2})_5 - \overset{\mathrm{O}}{\underset{\|}{\mathrm{C}}} \right)_n$$

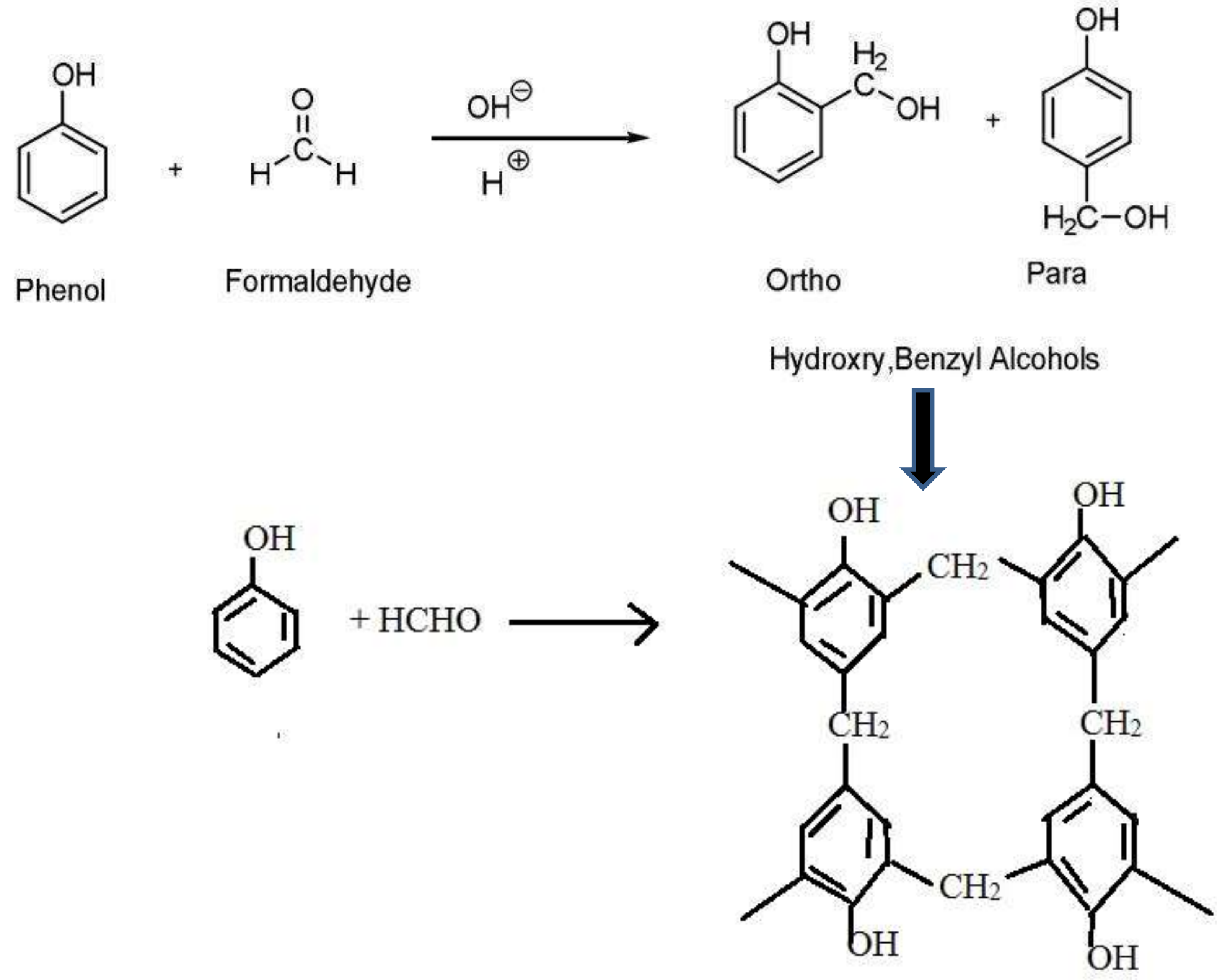
Nylon 6

B. Thermosetting polymers:-

Thermosetting polymers are those which undergo cross linking during chemical process and become rigid and hard under certain condition of temperature and concentration. They can not be further moulded or recycled after getting a fixed shape. They are formed by condensation polymerization

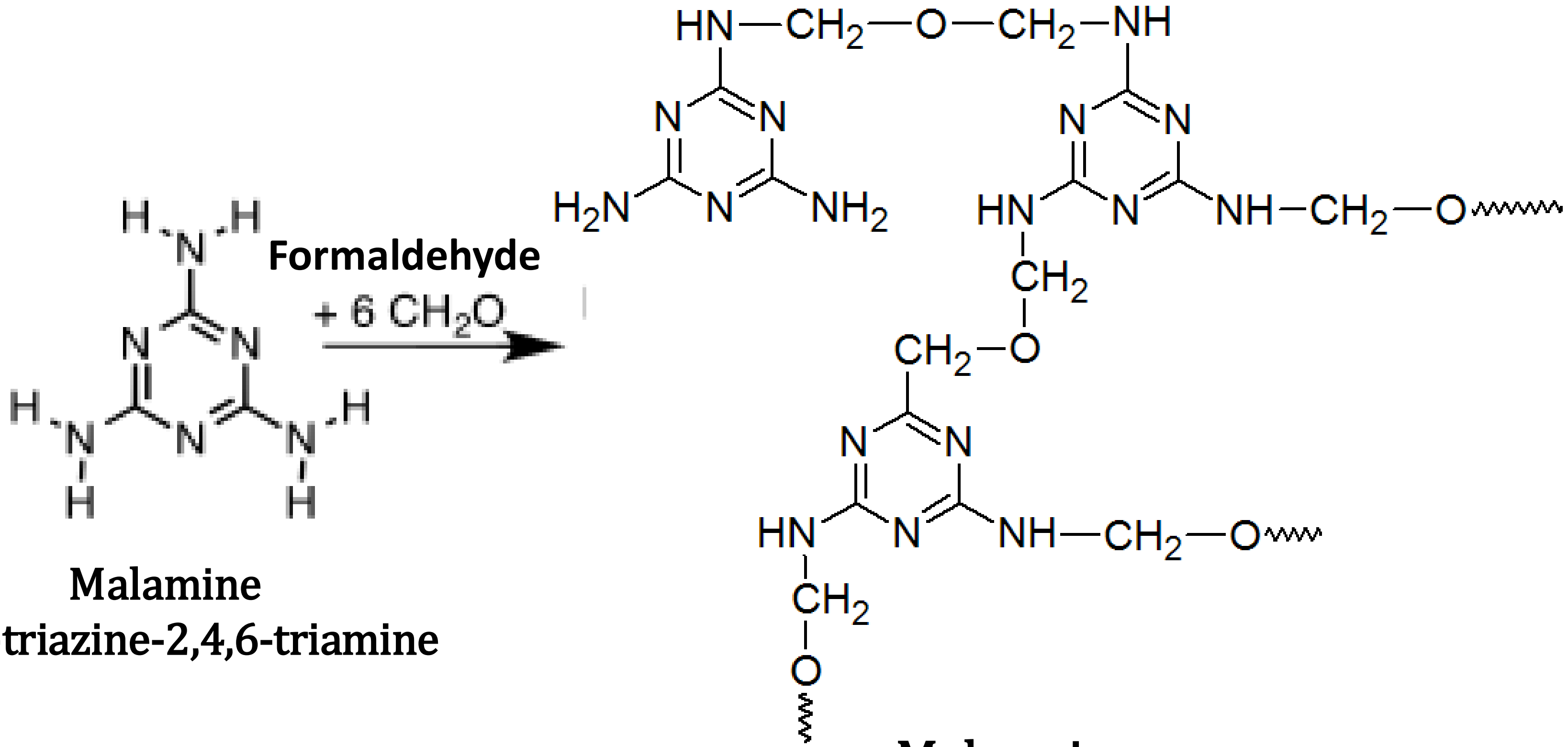
For example:
Bakelite, Urea-Formaldehyde Resin, Epoxy resins, Malamine etc.

Uses:
Electrical switches, non-breakable kitchenware, handles of cooker etc.


OH
+
O
H
C
H
OH⊖
H⊕
Phenol
Formaldehyde
OH
H2
C
OH
+
OH
H2C−OH
Ortho
Para
Hydroxry,Benzyl Alcohols
OH
+ HCHO
OH
CH2
OH
CH2
CH2
CH2
OH
OH

Bakelite

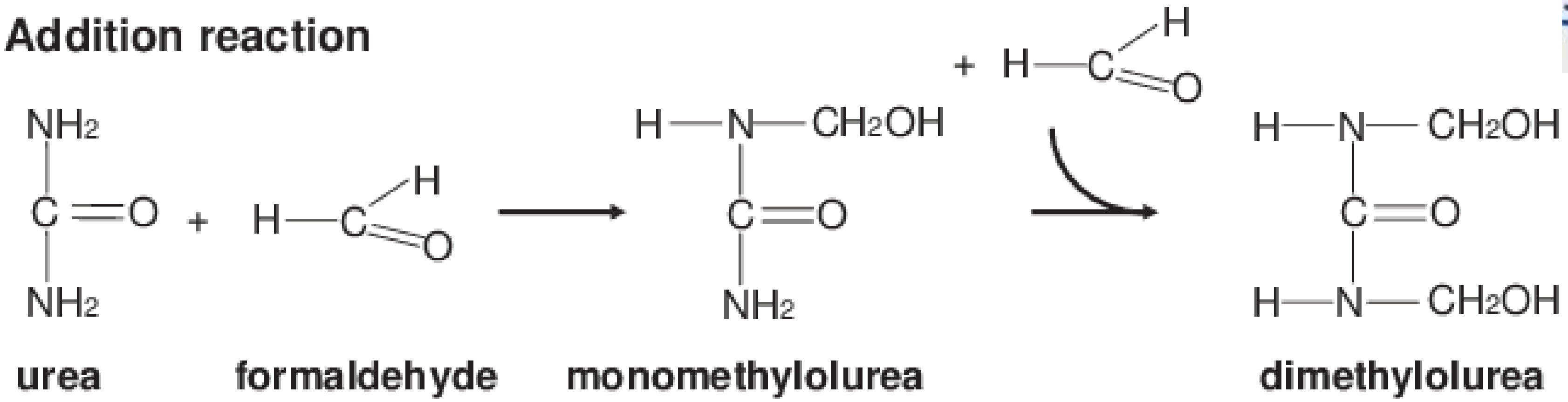
Malamine-Formaldehyde Resin



Malamine
1,3,5-triazine-2,4,6-triamine

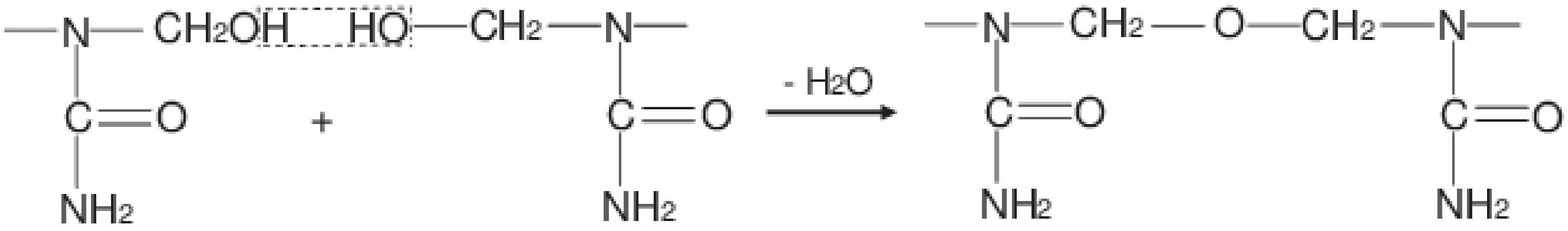
Malamaine

Addition reaction

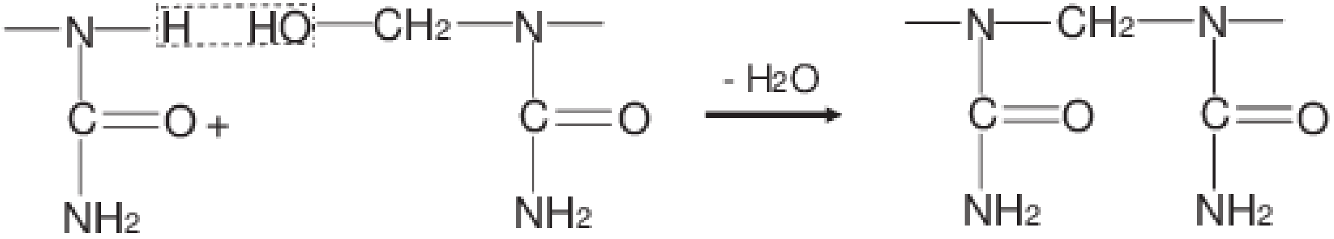


Polycondensation reaction

- by ether links



- by methylene links



Urea-Formaldehyde Resin

	Difference Between Thermoplastic and Thermosetting Plastic	
	Thermoplastic	**Thermosetting Plastic**
1	Thermoplastic can be synthesized by addition polymerization.	They are synthesized by condensation polymerization.
2	They can be molded to any shapes by heating and cooling.	They can not be changed to any other shape after hardening.
3	Thermoplastic can be recycled.	Thermosetting Plastic can not be recycled.
4	Thermoplastics have secondary bonds between molecular chains.	Thermosetting plastics held together by strong cross-links.
5	Thermoplastics have low melting points and low tensile strength.	Thermosetting plastics have high melting points and tensile strength.
6	Thermoplastic is lower in molecular weight, compared to thermosetting plastic.	Thermosetting Plastic is high in molecular weight.
7	Examples: Polythene, polypropylene, PVC, Nylons, Linear Polyesters etc.	Examples: Bakelite, urea formaldehyde, epoxy resins, malamine etc.

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Conducting Polymers

Conducting Polymers

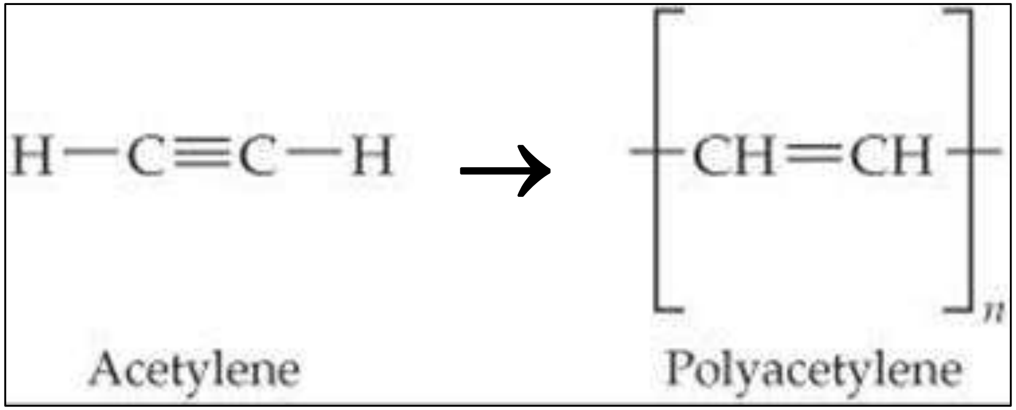
Most of the polymers are insulators

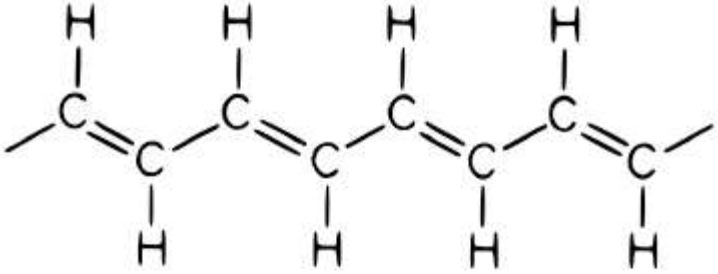
A polymer which can conduct electricity is termed as 'Conducting Polymer'

Conductivity in long chain polymers may be introduce by

1. Due to presence of conjugated double bonds in polymeric chain or in the structure
2. Doping negative or positive charge
3. Blending with conducting materials

Examples of Conducting Polymers

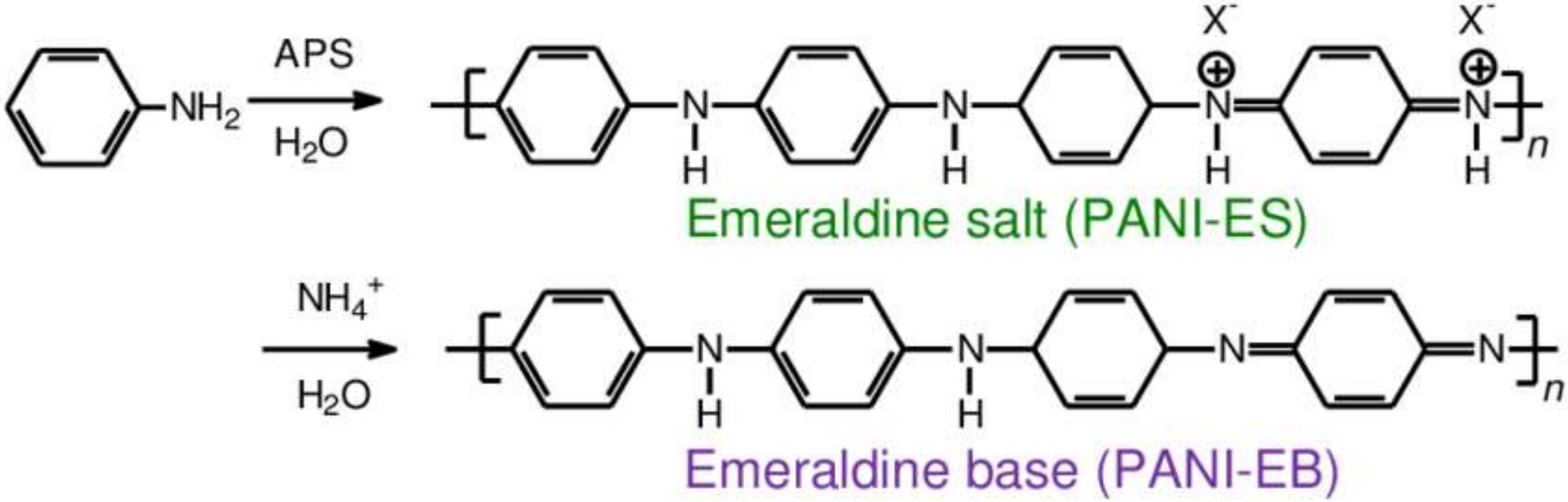


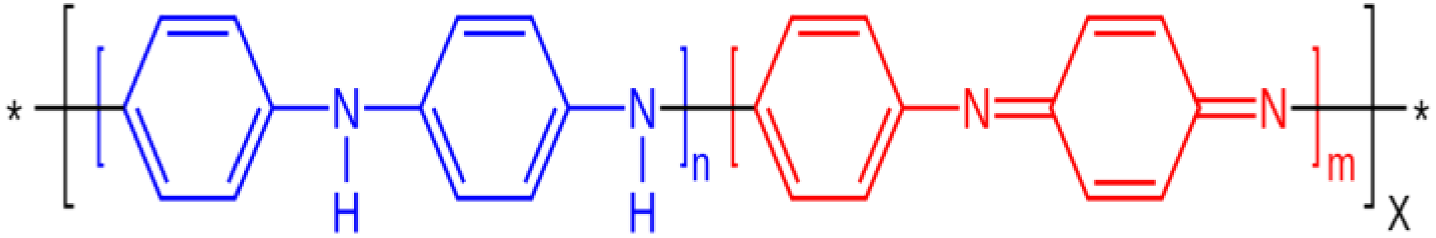


$$----CH_2=CH_2-CH_2=CH_2-CH_2=CH_2----$$

Polyacetylene

Polyaniline PANI

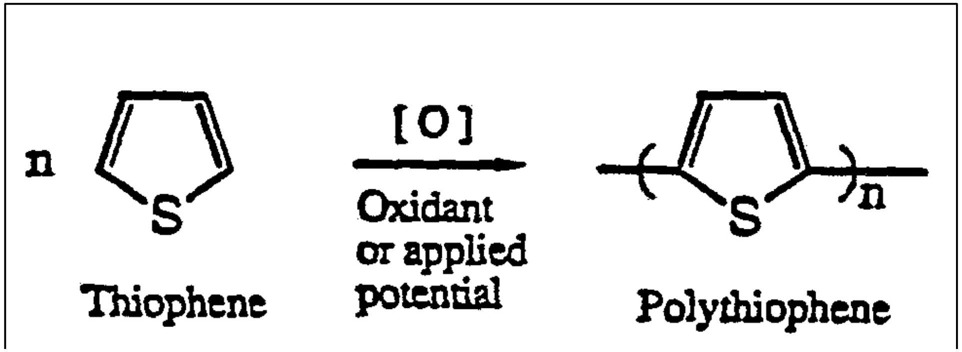


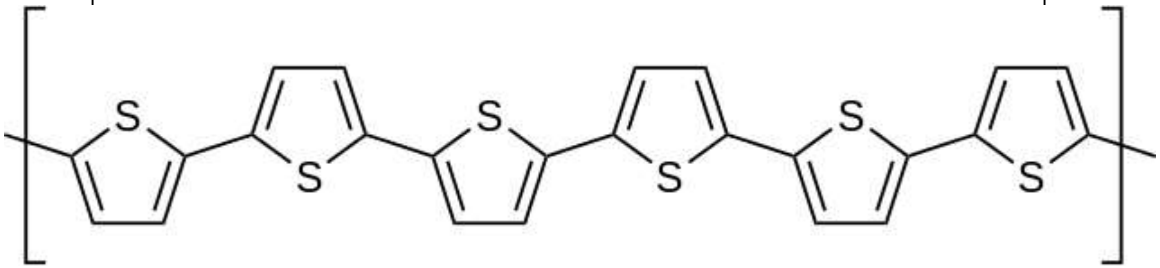


Polyaniline PANI

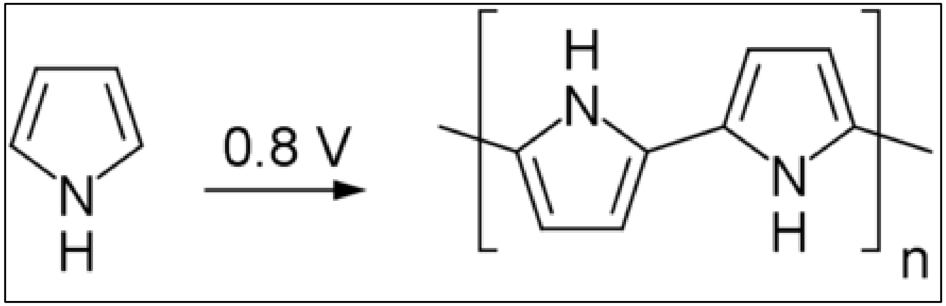
*an oxidant ammonium peroxy disulfate, APS).

Polythiophene

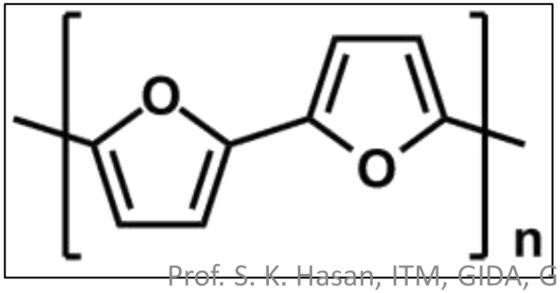




Polypyrrole



Polyfuran



Classification of Conducting Polymers

1. Intrinsically Conducting Polymers
   a. Conducting Polymer having conjugated π –electrons in the backbone
   b. Doped Conducting Polymers

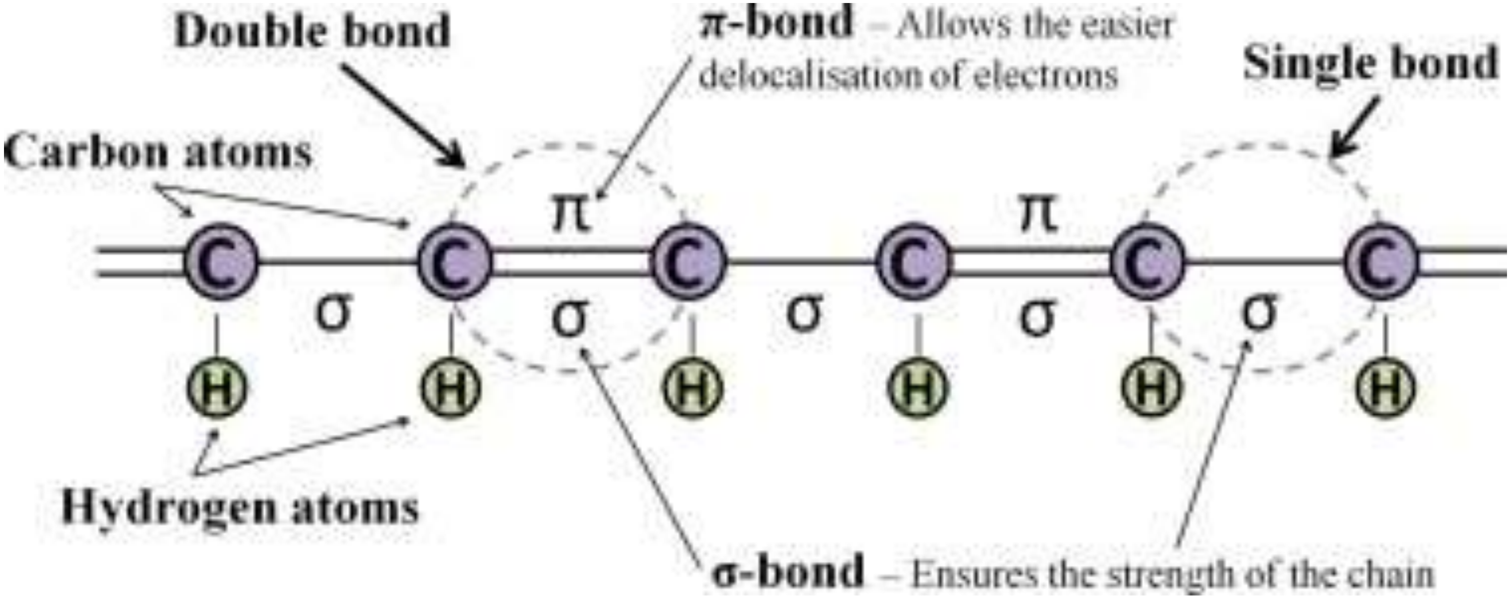
2. Extrinsically Conducting Polymers
   a. Filled with Conductive Element
   b. Blended conducting polymers.

Intrinsically Conducting Polymers

a. **Conducting Polymer having conjugated π-electrons in the backbone**

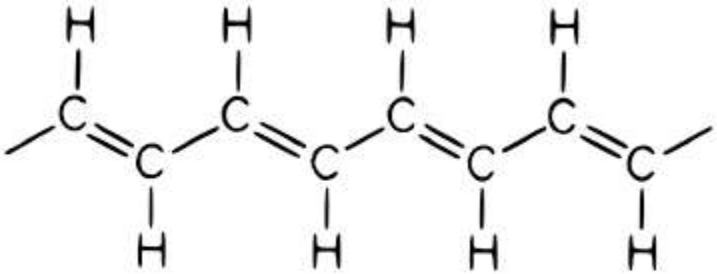
Such polymers contain double bond in conjugation.

i. e. conjugated π–electrons over the entire backbone.

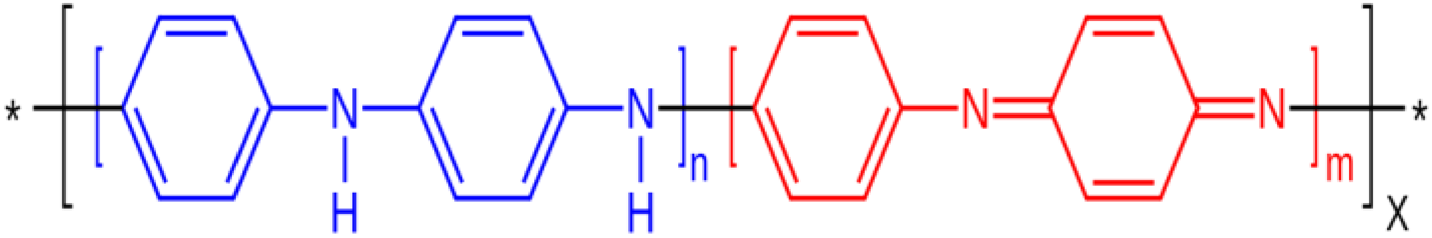


Other Examples

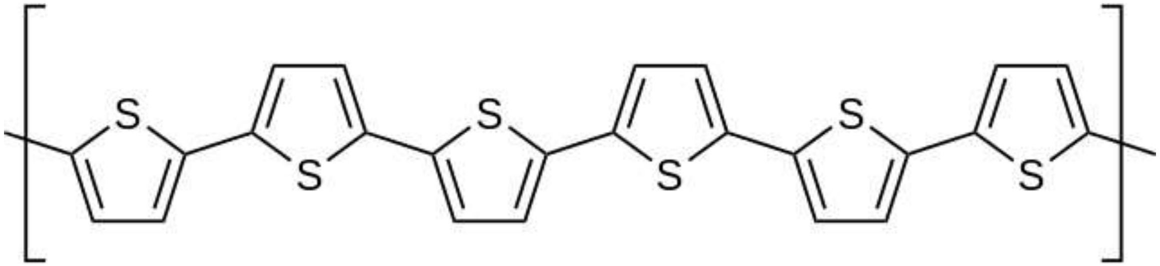
Polyacetylene



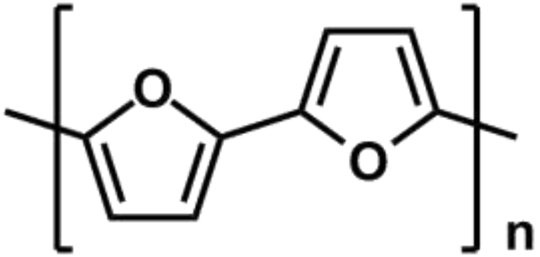
Polyaniline PANI



Polythiophene



Polyfuran



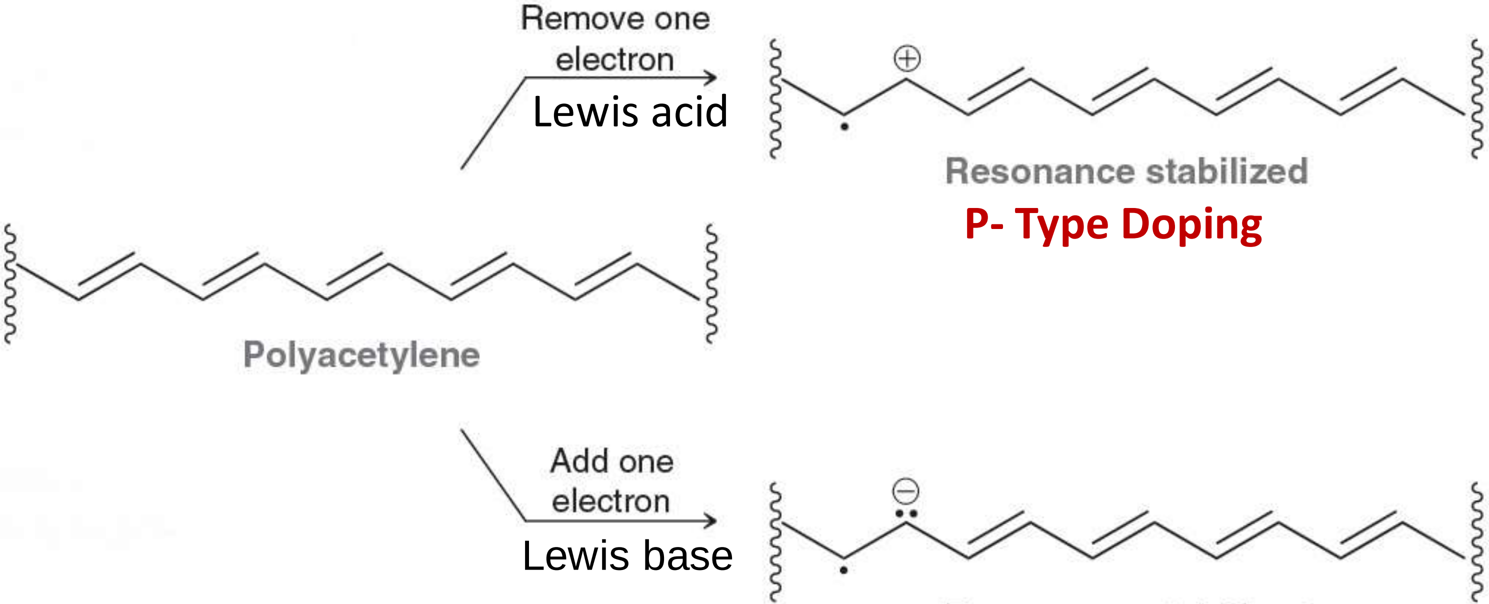
b. Doped Conducting Polymers:

It is of two types

(i) P–doping (oxidative doping).
(ii) N–doping (reductive doping).

P–doping

It is done by oxidation process.
(i.e., removal of e^- from the polymer pi – back bone).
This formation is known as polaron. The doping with a Lewis acid which is electron deficient causes P- type doping.



P- Type Doping

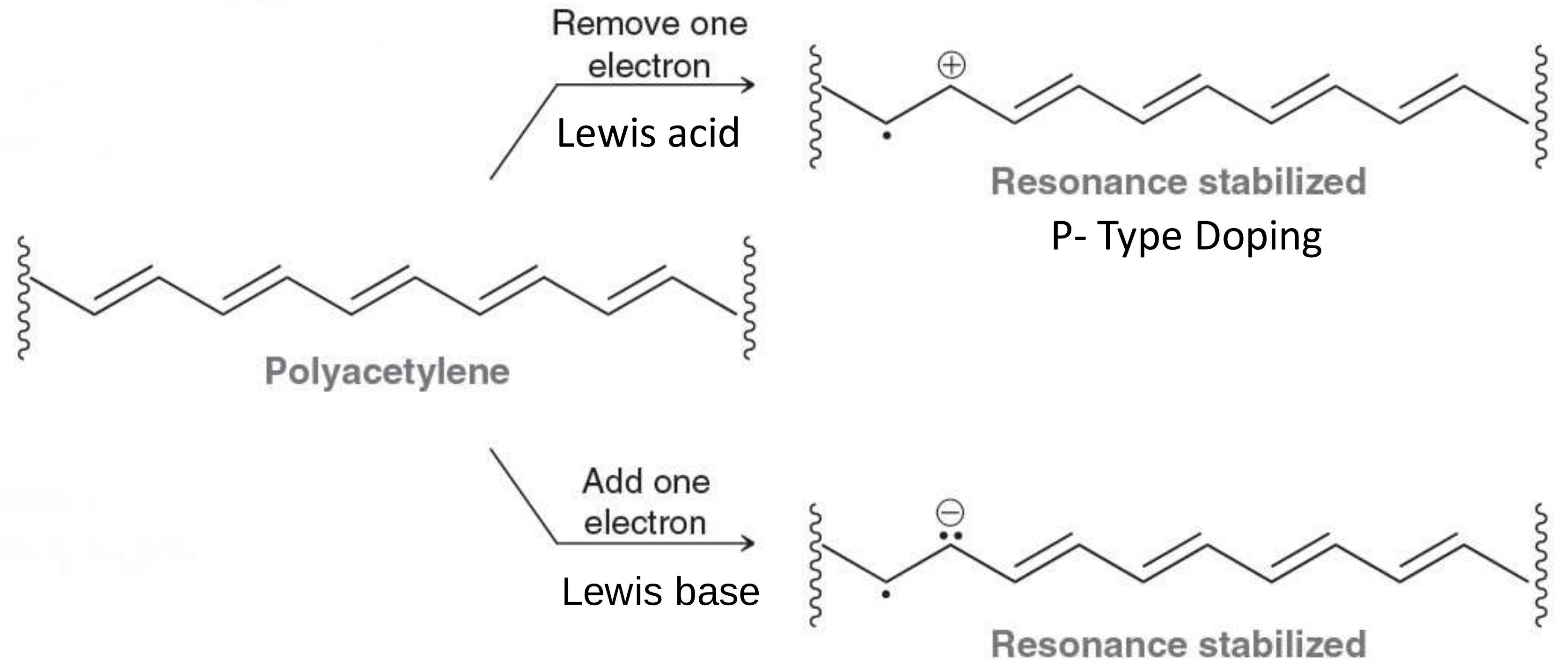
N- Type Doping

N–doping

It is done by reduction process.

i. e. addition of an e⁻ to the polymer.

This also forms polaron. The doping with a Lewis base which is electron rich species causes N-type doping.



Lewis acid

P- Type Doping

Lewis base

N- Type Doping

2. Extrinsically Conducting Polymers

It is of two types

(a) Conductive Element filled polymers.
(b) Blended conducting polymers.

(a) Conductive Element Filled Polymer

The polymers act as the binder to hold the conducting element (such as carbon black, metallic fibers, metallic oxides etc.) together in the solid entity.

Carbon black is very used as filler which has very high surface area and more porosity. It bears good conductive properties and low in cost, light in weight, as well as durable.

(b) Blended Conducting Polymers:

It is obtained by blending (mixing together) a conventional polymer with a conducting polymer.

It shows better physical, chemical, electrical and mechanical properties

Example
polypyrrole with a carbon-black filled compound are used in electromagnetic shielding.

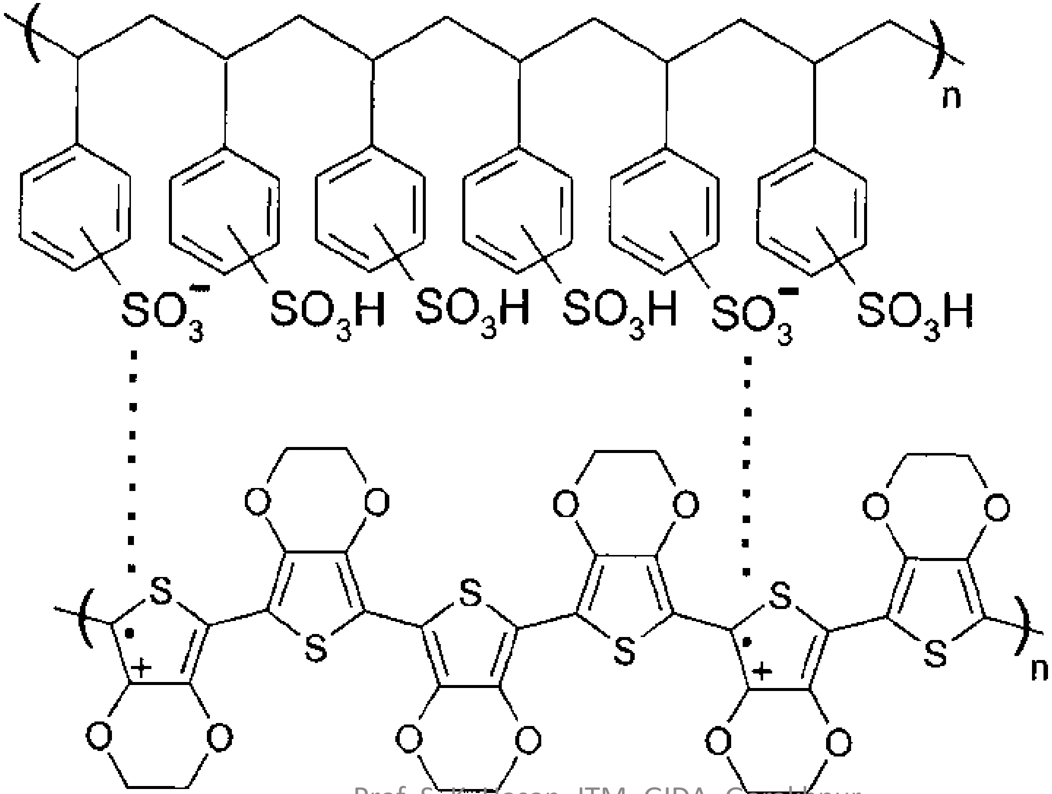
Electrical conductivity of some important polymers is as given below

S. No.	Polymers	Electricalconductivity in Ohm^{-1} m^{-1}
1	Nylon 6, 6	10^{-12}-10^{-13}
2	Polystyrene	$< 10^{-14}$
3	Phenol formaldehyde	$10^{-9} - 10^{-10}$
4	Polyethylene	$10^{-15} - 10^{-17}$
5	Polytetrafluoroethylene	$< 10^{-17}$
6	Poly-methyl methacrylate	$< 10^{-12}$

Applications of Conducting Polymers

PEDOT-PSS, 3,4-polyethylenedioxythiophenepolystyrenesulfonate which is based on Polythiophene. It is marketed under the trade name Baytron.

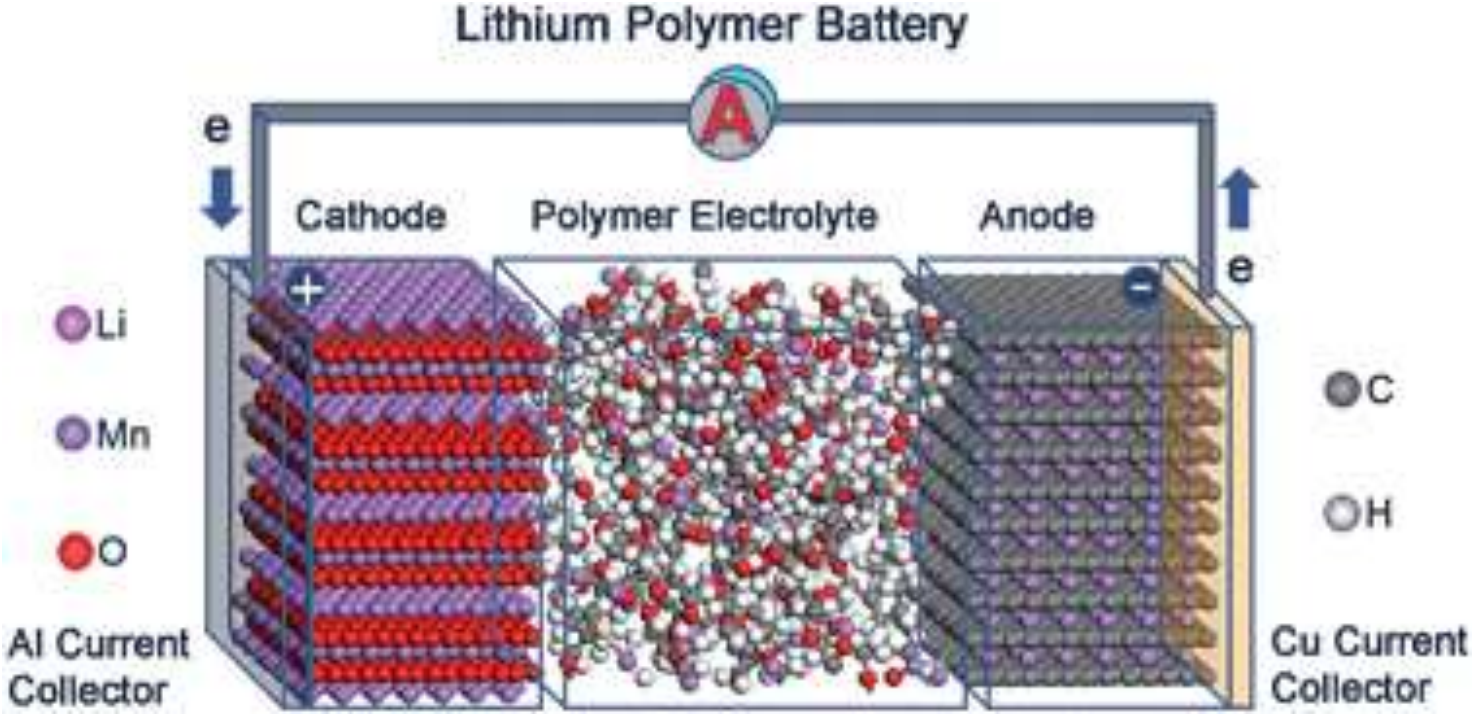
Used in electrodes,
high performances tantalum capacitors
computer and automobile products.



Polymer Electrolyte:

It is prepared by mixing Polyethylene oxide or Polyethylene glycol with Lithium.
Used as electro-chemical accumulators

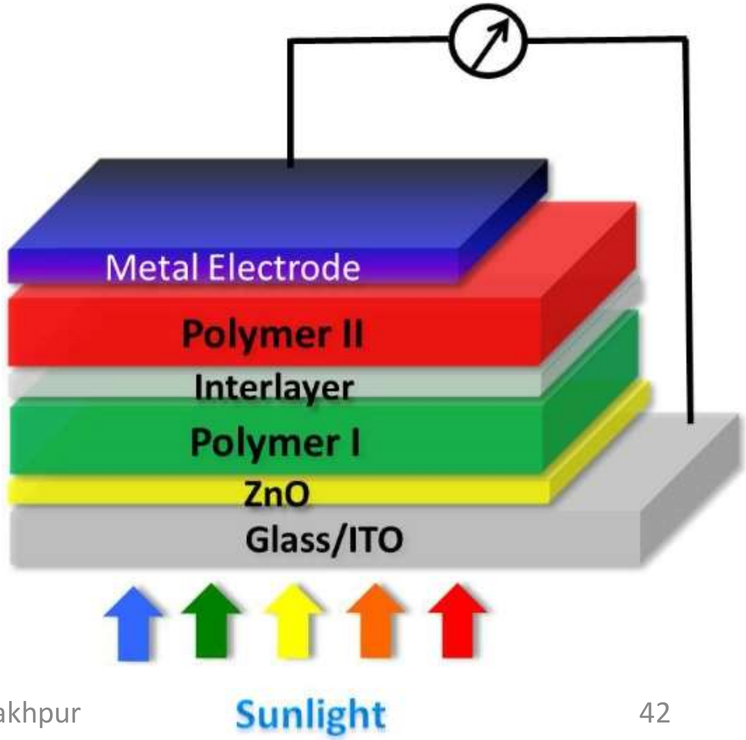
It used in making button type batteries. These batteries are long lasting, recharge-able and can produce current density up to 50 mA/cm^2.



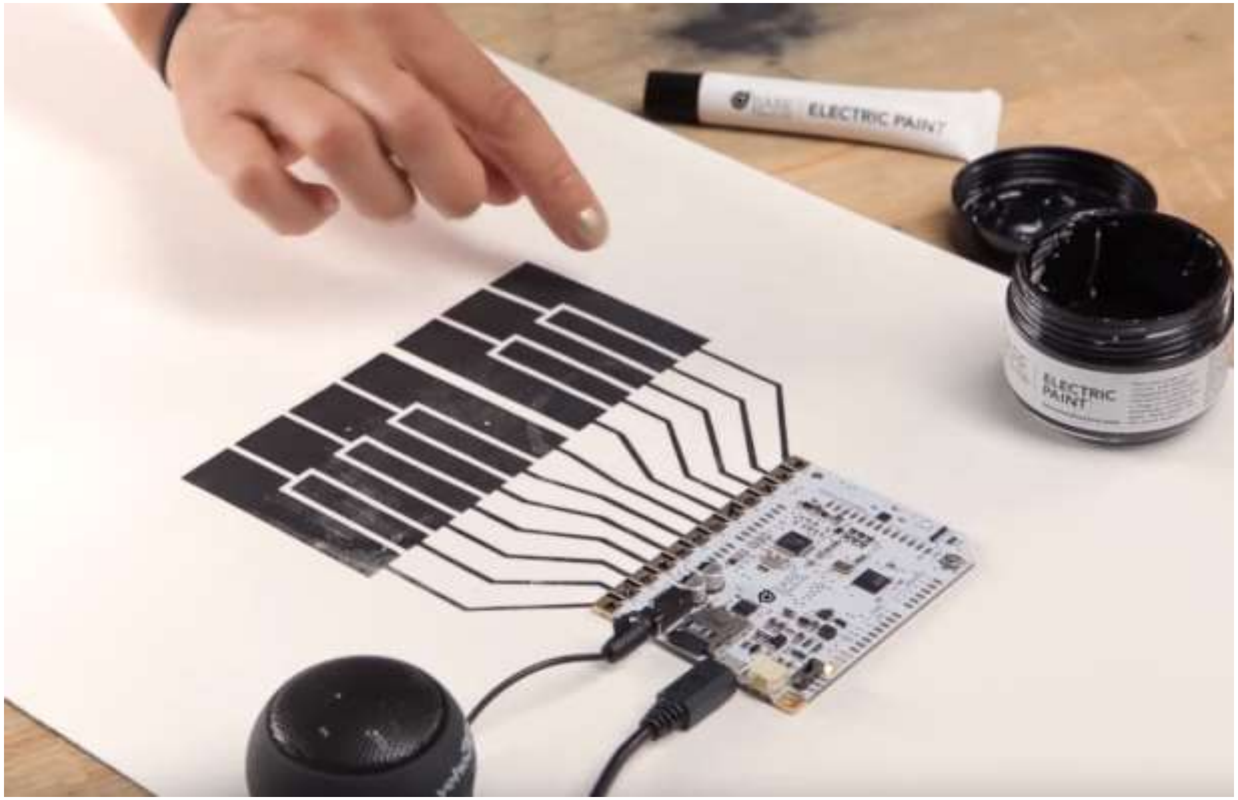
Organic Photovoltaic Cell

In this cell Sunlight is absorbed and converted into electrical current. An organic photovoltaic cell is prepared by using Conjugated polymers. One device used polyacetylene as the organic layer, with Al and graphite. It may be single layer or multilayered.

A double layered cell is shown below.



Used as conductive paints.



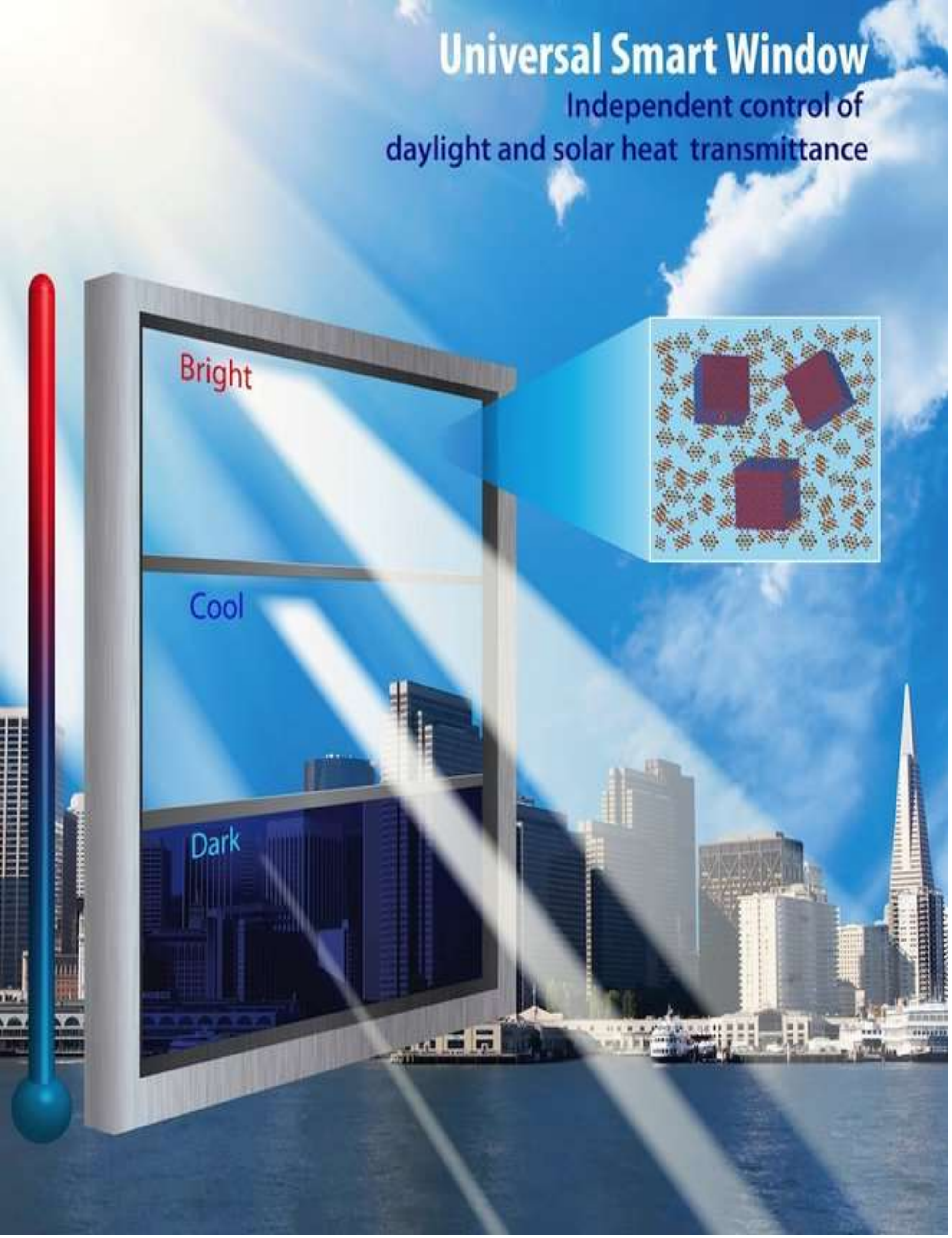
Biosensors and Chemical Sensors,

The conducting polymer which can convert chemical information into measurable electrical response.

Biosensor is an analytical device that converts biological reactions into measurable physiochemical signals.

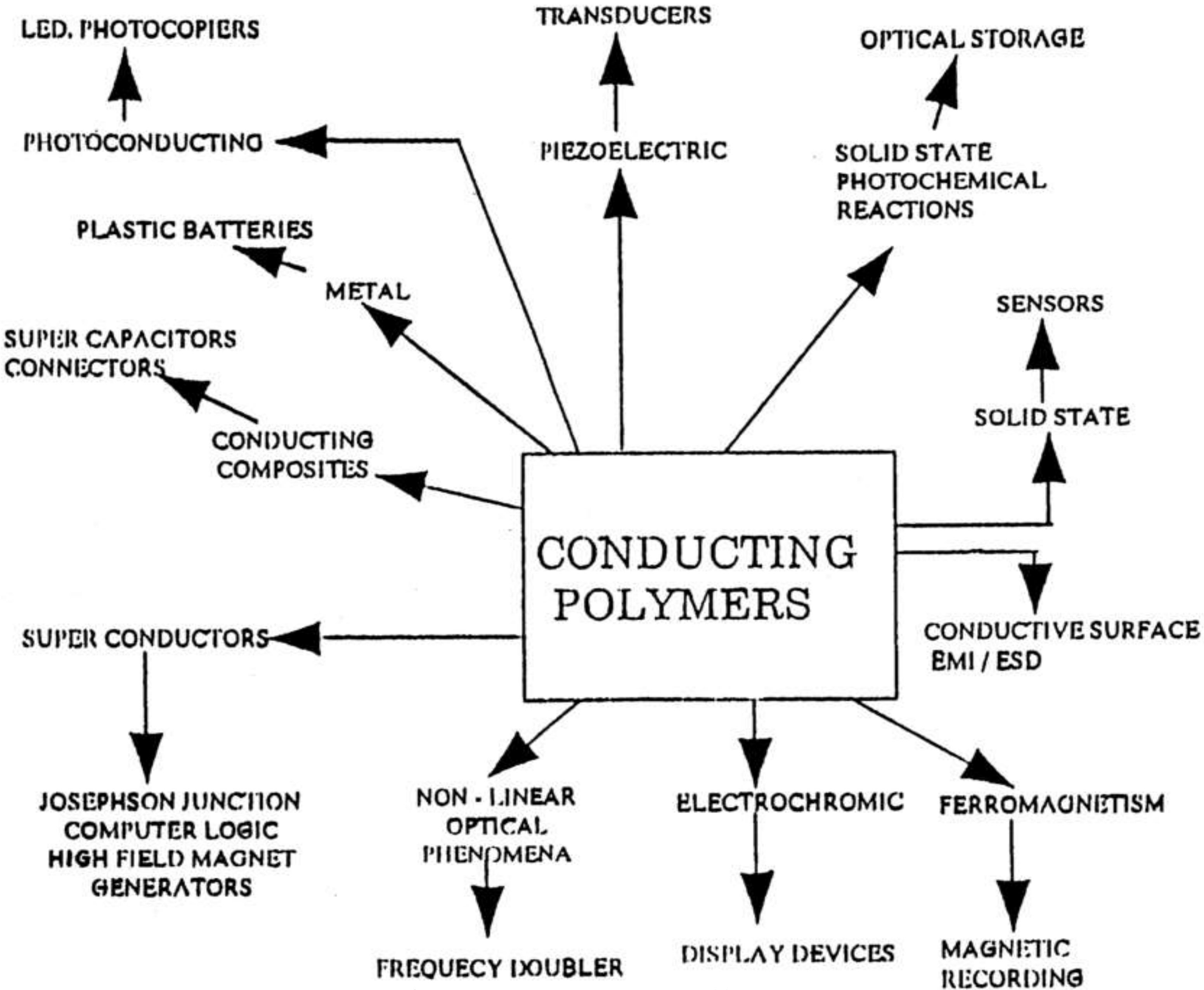
Biosensors can be used for the detection various substances like
metabolites,
pollutants,
microbial load,
control parameters etc.

Smart Window



Conductive polymer poly(3,4ethylenedioxythiophene)-polystyrene sulfonate (PEDOT:PSS) is one of the most attractive materials for transparent conductive electrodes, energy storage and **electrochromic devices for smart window application.**

Used in variable transmission as smart windows etc



CONDUCTING POLYMERS

LED. PHOTOCOPIERS

PHOTOCONDUCTING

TRANSDUCERS

PIEZOELECTRIC

OPTICAL STORAGE

SOLID STATE
PHOTOCHEMICAL
REACTIONS

PLASTIC BATTERIES

METAL

SUPER CAPACITORS
CONNECTORS

CONDUCTING
COMPOSITES

SENSORS

SOLID STATE

CONDUCTIVE SURFACE
EMI / ESD

SUPER CONDUCTORS

JOSEPHSON JUNCTION
COMPUTER LOGIC
HIGH FIELD MAGNET
GENERATORS

NON - LINEAR
OPTICAL
PHENOMENA

FREQUECY DOUBLER

ELECTROCHROMIC

DISPLAY DEVICES

FERROMAGNETISM

MAGNETIC
RECORDING

CLASSIFICATION OF POLYMERS

1. Origin	Natural, synthetic and semi synthetic
2. Polymeric Structure	Linear, Branched, Cross-linked, Globular
3. Chemical Structure	Organic & Inorganic
4. Types of monomers	Homopolymers and Copolymers
5. Mode of Polymerization	Addition & Condensation
6. Physical State	Amorphous & Crystalline
7. Tacticity	Atactic, Isotactic, Syndiotactic
8. Molecular Forces	Elastomers, Plastics, Fibres
9. Thermal Behaviour	Thermoplastic & Thermosetting plastics
10. Conductance	Conducting & Non-conducting Polymers
11. Degradation	Biodegradable & Non-biodegradable

Biodegradable Polymers

Biodegradable Polymers

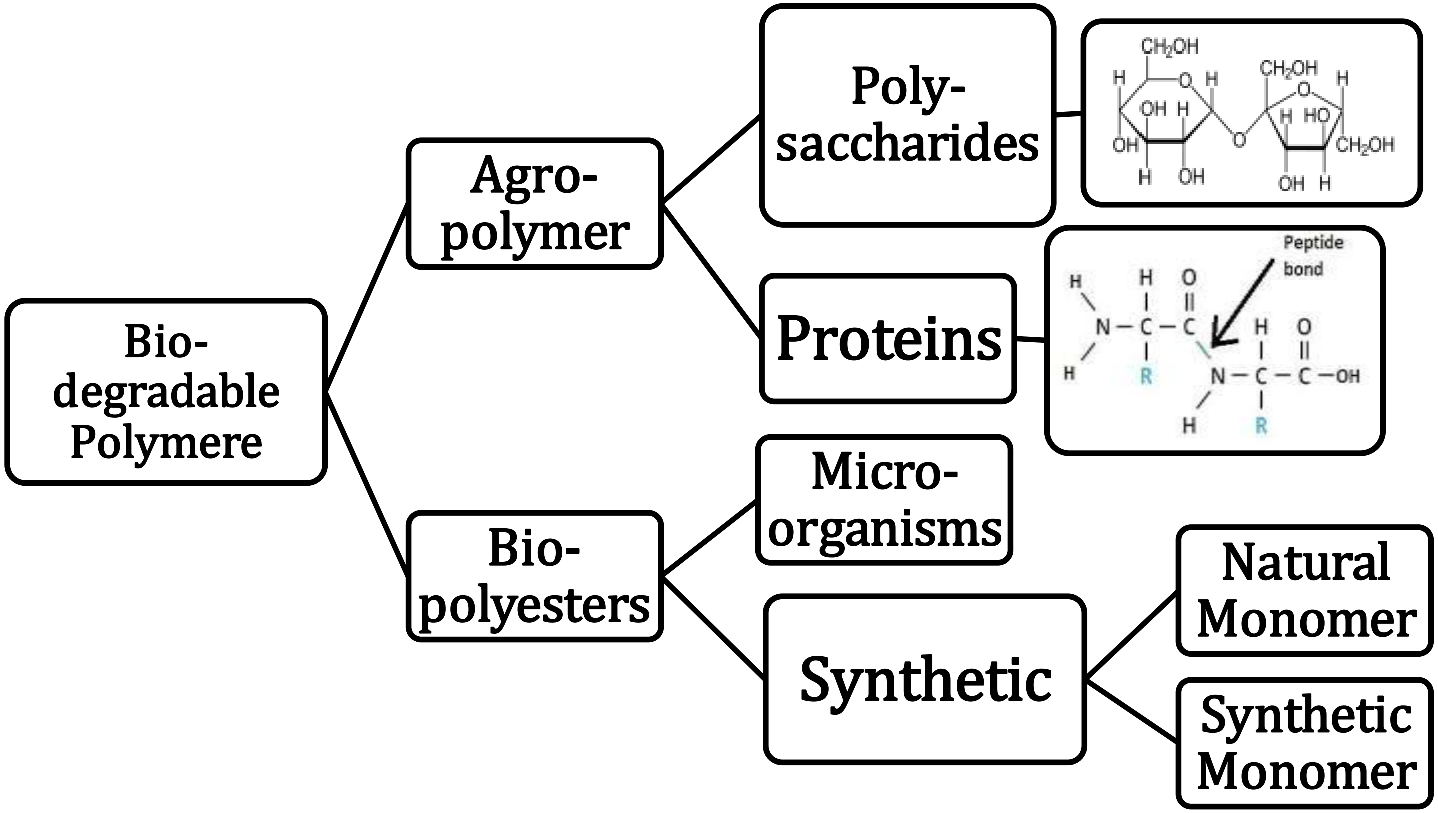
Most of the polymers are non-biodegradable. They remain in the environment for a long time and make the environment polluted.

Biodegradable polymers are those which can decompose by microorganisms naturally.

Characteristics of Biodegradable

- A “biodegradable” product has the ability to break down, safely, reliably, and relatively quickly, by biological means, into raw materials of nature and disappear into nature
- Biodegradable polymers are a special class of polymer that breaks down after some time by bacterial decomposition process to result in natural by products such as gases (CO_2, N_2), water, biomass, and inorganic salts.
- They largely consist of ester, amide and other functional groups.
- These polymers are often synthesized by condensation polymerization

Classification of Biodegradable polymers



- Bio-degradable Polymere
  - Agro-polymer
    - Poly-saccharides
    - Proteins
  - Bio-polyesters
    - Micro-organisms
    - Synthetic
      - Natural Monomer
      - Synthetic Monomer

Rate of degradation of some polymers

Cotton rags	1-5 months
Paper	2-5 months
Wool socks	1 to 5 years
Plastic coated paper milk cartons	5 years
Plastic bags	10 to 20 years
Nylon fabric	30 to 40 years
Plastic bottles	May be never

The basic requirements of the biodegradable polymer

(a) Production of non-toxic products

(b) Capable of maintaining good mechanical integrity until degradation

(c) Controlled rates of degradation

The factors controlling the rate of degradation

(a) Percentage of crystallinity of polymer

(b) Molecular weight of polymer,

(c) Hydrophobicity of polymer and

Classification

1. Naturally occurring biodegradable polymers

There are 4 groups of naturally occurring biodegradable polymers.

1. Polysaccherides-	**Starch and Cellulose**
2. Proteins-	**Gelatin, Casein, Silk, Wool**
3. Polyesters-	**Polyhydroxy alkanoates**
4. Others-	**Lignin, Natural Rubber etc.**

2. Synthetic biodegradable polymers

These polymers are produced from chemicals or biological sources that are biodegradable.

Polyhydroxy alkanoates (PHA):
These are linear polyesters produced by bacterial fermentation of sugars or lipids. These are produced by the bacteria to store carbon and energy.

Such as polylactic acid, polyhydroxybuturic acid, polyglycolic acid etc.

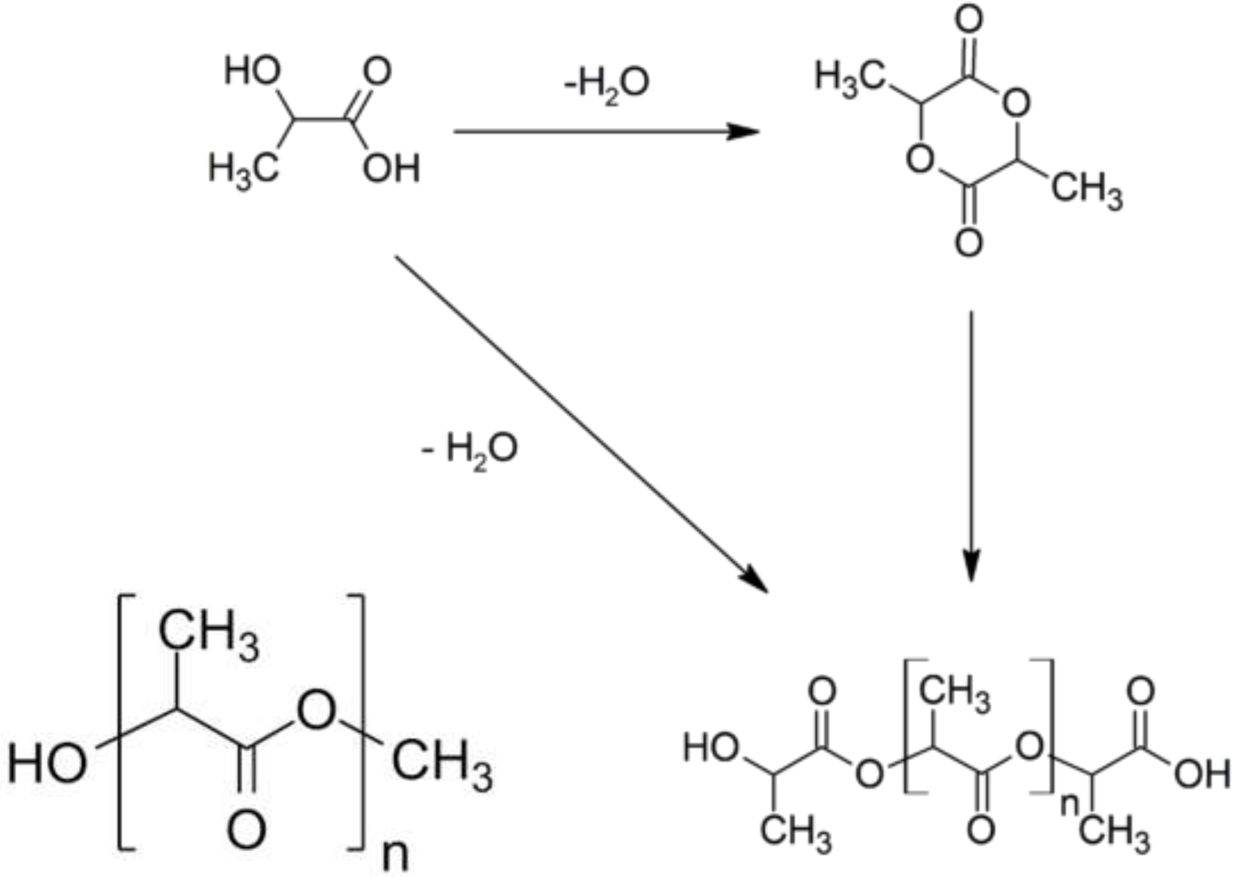
Polylactic acid/ polylactide (PLA):

This is a biodegradable thermoplastic polyester belonging to class of polyhydroxy alkanoates,

Properties:

- They are thermoplastics.
- Stable to UV radiation.
- The crystallinity found up to 70%.
- Good resistance to moisture.
- Good elasticity.
- The glass transition temperature (60-65^{o}C).
- PLA possess melting point 173-178^{o}C

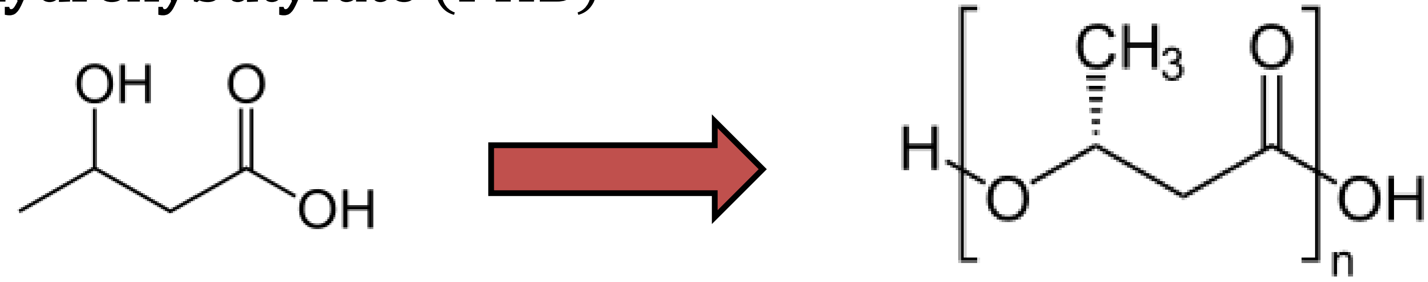
Polymerization of Lactic acid to form Polylactic acid/ polylactide (PLA):



Polylactic Acid

Lactic Acid

Polyhydroxybutyrate (PHB)



3-hydroxybutyratic acid

poly-3-hydroxybutyrate (P3HB)

Polyhydroxybutyrate (PHB) is a polyhydroxyalkanoate(PHA), a polymer belonging to the polyesters family as bio-derived and biodegradable plastics.

The poly-3-hydroxybutyrate (P3HB) form of PHB is probably the most common type of polyhydroxyalkanoate,

other polymers of this class are produced by a variety of organisms:

such as poly-4-hydroxybutyrate (P4HB), polyhydroxyvalerate

Properties of Polyhydroxy butyrate

i. They are water-insoluble.

ii. Relatively resistant to hydrolytic degradation

iii. Good oxygen permeability.

iv. Good ultra-violet resistance.

v. Soluble in chloroform and other chlorinated hydrocarbons.

vi. Biocompatible and hence is suitable for medical applications.

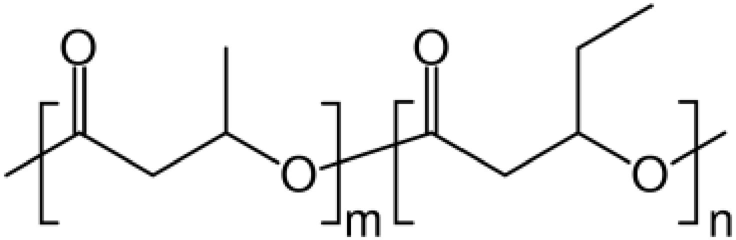
vii. Melting point 175 °C., and glass transition temperature 2 °C.

viii. Anaerobic biodegradation in sediments.

ix. Nontoxic.

x. Less 'sticky' when melted

Poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate),



commonly known as **PHBV**, is a polyhydroxyalkanoate-type polymer.

It is obtained by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

It is a thermoplastic, linear aliphatic polyester.

It is biodegradable, nontoxic, biocompatible plastic produced naturally by bacteria

Applications

✓PHBV is used in specialliy in packaging,

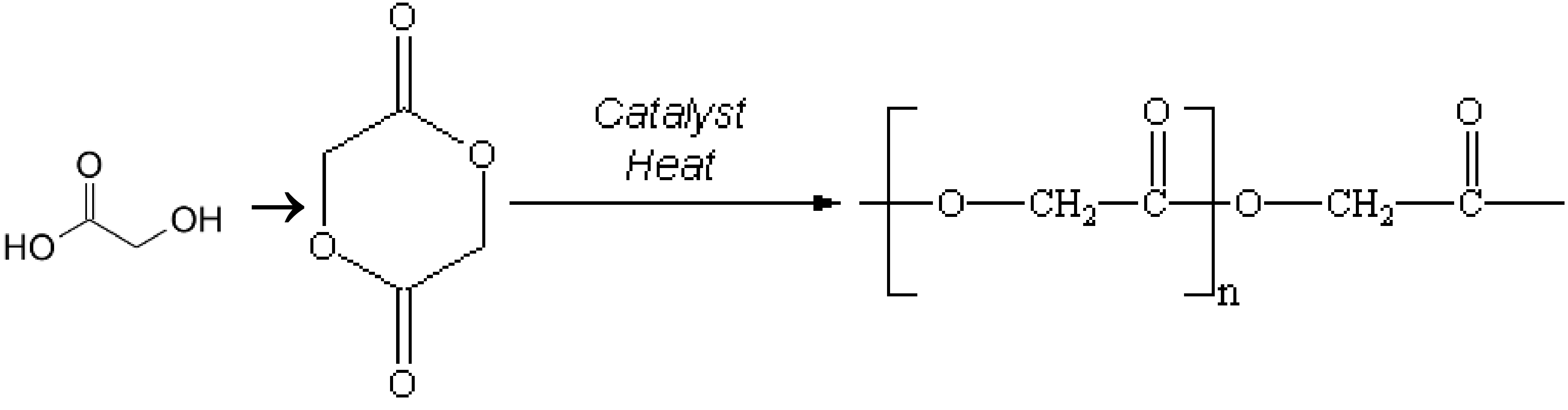
✓orthopedic devices and

✓in controlled release of drugs.

✓PHBV undergoes bacterial degradation in the environment.

Polyglycolide or polyglycolic acid (PGA)

a biodegradable, thermoplastic polymer and the simplest linear, aliphatic polyester.
It can be prepared starting from glycolic acid by means of polycondensation or ring-opening polymerization.



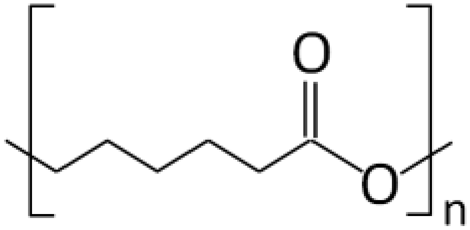
Glycolide

Polyglycolide

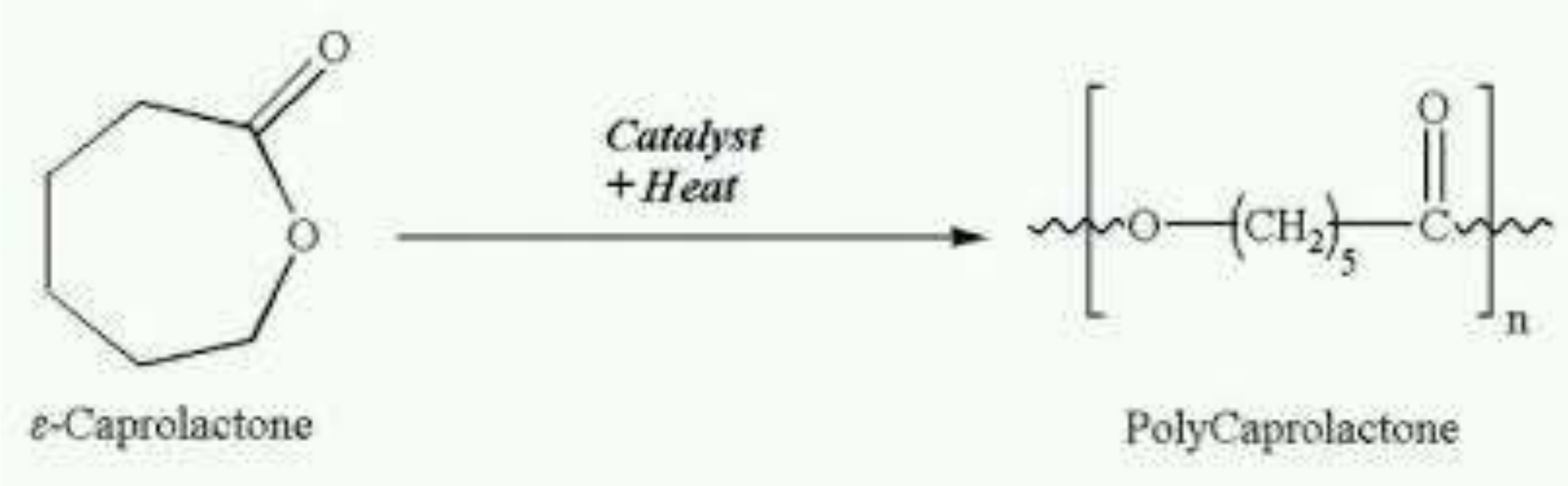
Applications

widely used as a material for the synthesis of absorbable **sutures** in the biomedical applications.
A tough fiber-forming polymer.

Polycaprolactone (PCL)



A biodegradable polyester
with a low melting point of around 60°C and
a glass transition temperature of about −60 °C.

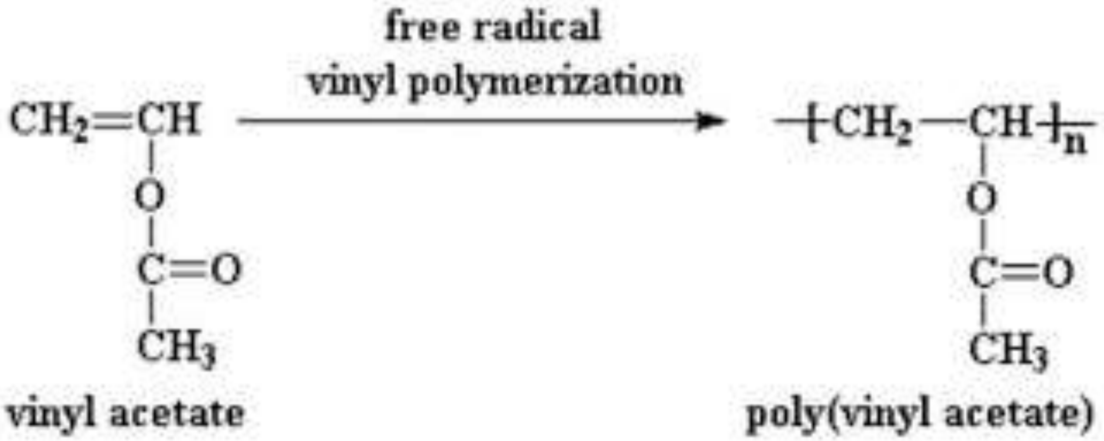


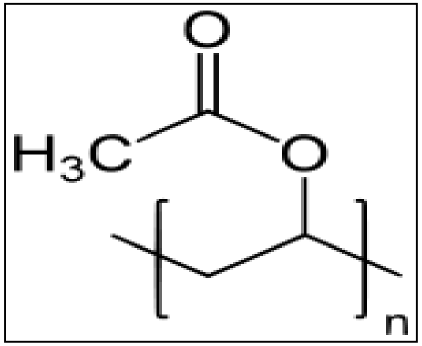
Applications

1. In medical applications such as surgical sutures
2. In agriculture such as seed coatings
3. In food rappers and personal hygiene products

Polyvinyl acetate (PVA):

A biodegradable polymer, possessing excellent mechanical properties



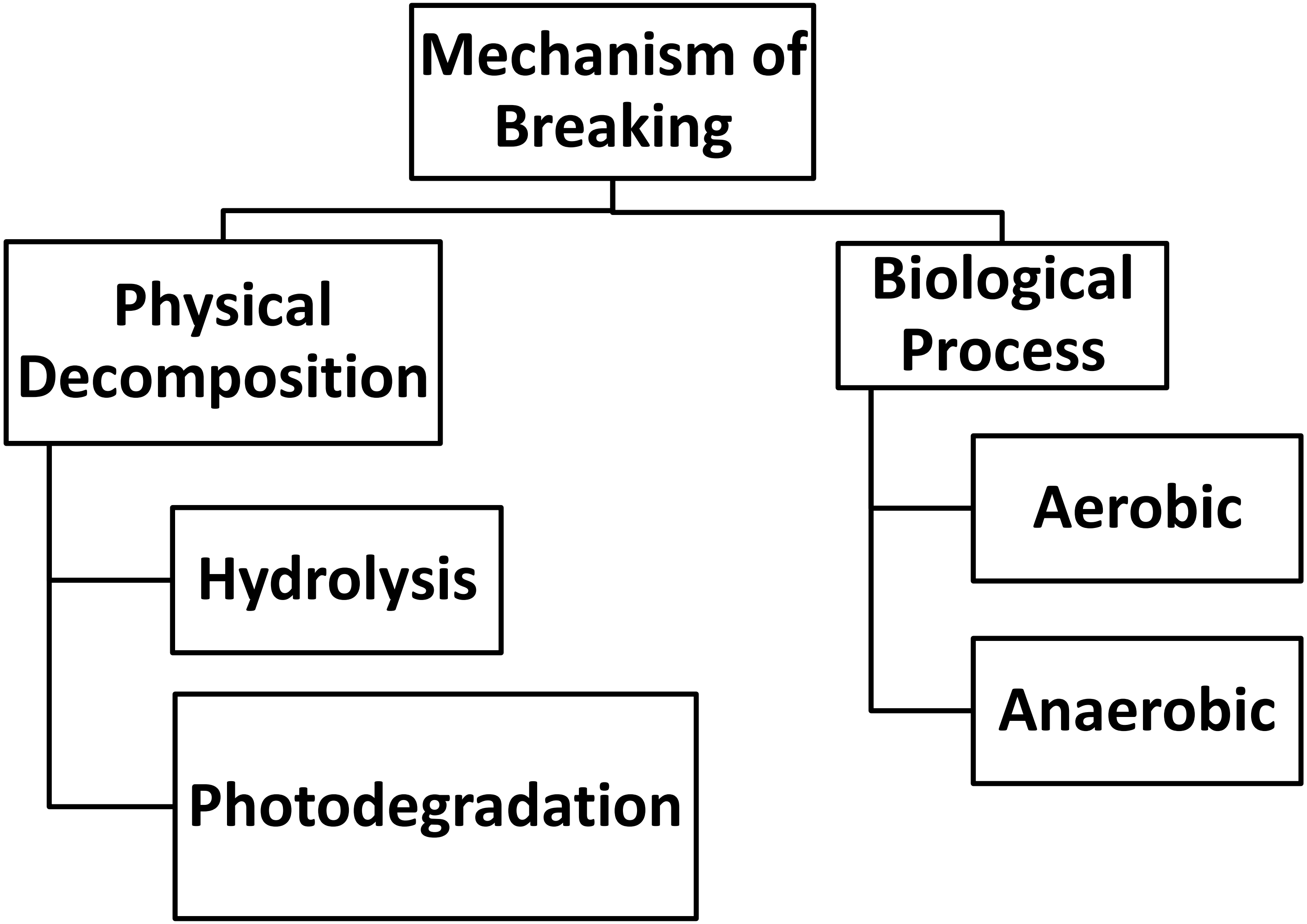


Properties:

1. It belongs to the class of vinyl polymers.
2. It is water soluble
3. Posses excellent mechanical properties
4. It is compatible with starch. i.e starch molecule can be introduced into the backbone for quick biodegradability.

Application:

- in food industry as a packing material, food storage and catering
- Making Adhesives


Mechanism of Breaking

Physical Decomposition
- Hydrolysis
- Photodegradation

Biological Process
- Aerobic
- Anaerobic

Mechanism of breakdown

In general, biodegradable polymers break down to form gases, salts, and **biomass.**

There are two primary mechanisms

1. Aerobic Degradation:
   decomposition through reactions in presence of oxygen.

$$C_{polymer} + O_2 \longrightarrow C_{residue} + C_{biomass} + CO_2 + H_2O$$

2. The second mechanistic route is biological processes which can be further broken down into aerobic and anaerobic processes.

$$C_{polymer} \longrightarrow C_{residue} + C_{biomass} + CO_2 + CH_4 + H_2O$$

Some notable applications of biodegradable polymers

Figure: Biodegradable dishes and packaging

A trash bag made of a poly(lactic acid) blend

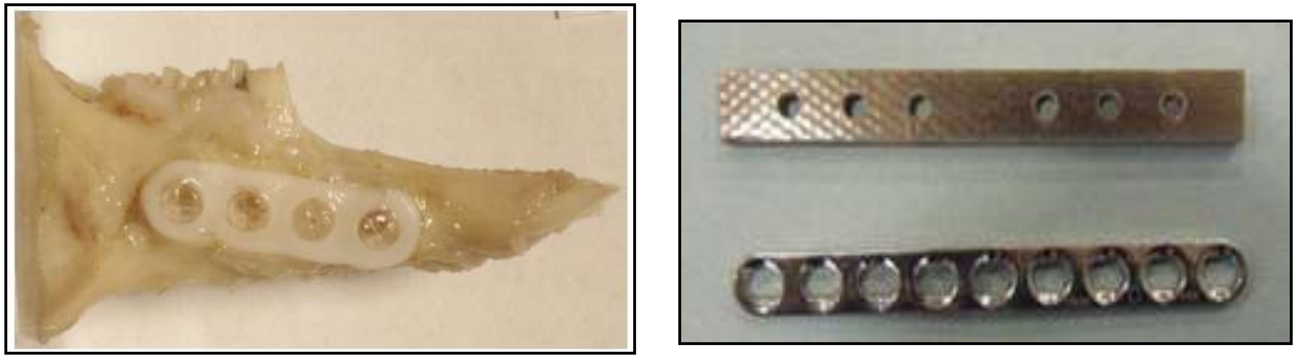


Figure: Biodegradable Bone plates

Biodegradable Fibers

Disposable cutlery of biodegradable plastic

Degree of Polymerization
&
Molecular Weight

Degree of Polymerization (DP)

The term degree of polymerization is defined as the number of repeating units in a polymer molecule.

i. e. the number of monomer units in a polymeric chain. It is usually denoted as '*n*' in the generalized formula $[M]_n$; where *M* is the repeating unit.

$$\underset{\text{Ethene}}{nCH_2{-}CH_2} \rightarrow \underset{\text{Polyethene}}{(-CH_2{-}CH_2-)_{n}}$$

DP

Degree of polymerization (DP) = Mol. Weight of Polymer/Mol. Weight of monomer

$n = M/M_o$

Where, M = Molecular wt. of polymer

M_o = Molecular wt. of monomer

Ex: Calculate the degree of polymerization of a sample of polyethylene $[(CH_2\text{-}CH_2)_n]$, which has a molecular weight of 5600 g/mol.

Solution

The molecular weight of monomer ethene, $M_o = (12 \times 2 + 1 \times 4)$ g/ mol

$= 28$ g/mol

$$DP = M/M_o$$

$$= 5600/28$$

$$= 200$$

Molecular Weight of Polymer

Polymerization is carried out either by chain growth (addition polymerization) or step growth (condensation polymerization). During polymerization a mixture of polymeric chains various lengths is formed. Therefore, it is not possible to determine exact molecular weight of a polymer.

It is expressed as average molecular weight in following manners.

1. Number Average Molecular Weigh ($\overline{M}_n$)
2. Weight Average Molecular Weight ($\overline{M}_w$)
3. Z-Average Molecular Weight (M_z)
4. Viscosity Average Molecular Weight (M_v)

_M_z ≥ _M_w ≥ _M_v > _M_n

1. Number Average Molecular Weight (M_n)

The Number average molecular weight of a polymer containing N molecules of mass M is given by

$$\overline{M}_n = \frac{\Sigma NiMi}{\Sigma Ni} = \frac{N_1M_1 + N_2M_2 + \ldots.}{N_1 + N_2 + \ldots}$$

Where,

Ni = Number of Molecules of molecular weight Mi

N_1 = Number of Molecules of molecular weight M_1

N_2=Number of Molecules of molecular weight M_2

2. Weight Average Molecular Weight (M_w)

The Weight average molecular weight of a polymer containing N molecules of mass M is given by

$$\overline{M_w} = \frac{\Sigma NiMi^2}{\Sigma NiMi} = \frac{N_1M_1{}^2 + N_2M_2{}^2 + \ldots .}{N_1M_1 + N_2M_2 + \ldots}$$

Where,
Ni = Number of Molecules of molecular weight Mi
N_1 = Number of Molecules of molecular weight M_1
N_2=Number of Molecules of molecular weight M_2

3. Z-Average Molecular Weight (M_z)

Z stands for Zentrifuge (German) means centrifuge. The z-average molecular weight of a polymer containing N molecules of Molar mass M is given by

$$\overline{M}_z = \frac{\Sigma NiMi^3}{\Sigma NiMi^2} = \frac{N_1M_1{}^3 + N_2M_2{}^3 + \ldots.}{N_1M_1{}^2 + N_2M_2{}^2 + \ldots}$$

Where,

Ni = Number of Molecules of molecular weight Mi
N_1 = Number of Molecules of molecular weight M_1
N_2=Number of Molecules of molecular weight M_2

4. Viscosity Average Molecular Weight (M_z)

The z-average molecular weight of a polymer containing N molecules of mass M is given by

$$\overline{M}_v = \frac{(NiMi^{1+a})^{1/a}}{NiMi}$$

where the exponent a = ($0.5 \leq a \leq 2.0$) is determined by the polymer, solvent, and temperature.

Where,
Ni = Number of Molecules of molecular weight Mi
N_1 = Number of Molecules of molecular weight M_1
N_2=Number of Molecules of molecular weight M_2

Poly Dispersive Index

The **dispersity index** (**PDI**), or Polydispersive index or heterogeneity index is a measure of the distribution of molecular mass in a given polymer sample.

polydispersity index, is the ratio of the weight-average molecular weight to the number-average molecular weight:

$$\mathbf{PDI} = \frac{\overline{\mathbf{M}_w}}{\overline{\mathbf{Mn}}} \qquad \mathbf{PDI = 1}$$

PDI = 1, Monodispersive (Homogeneous)

PDI > 1, Polydispersive (Heterogeneous)

Q.1. In a sample of Polymer has a mixture of 10 molecules of polymer with molecular weight 1000 and 20 molecules of polymer with molecular weight 2000. Calculate Number average and weight average molecular weight. Calculate PDI also.

$$\overline{M_n} = \frac{\Sigma NiMi}{\Sigma Ni} = \frac{N_1M_1 + N_2M_2 + \ldots.}{N_1 + N_2 + \ldots}$$

$$= \frac{10\times1000 + 20\times2000}{10+20}$$

$$= \frac{10000+40000}{30}$$

$$= \frac{50000}{30}$$

$$= 1666.66$$

$$M_w = \frac{\Sigma NiMi^2}{\Sigma NiMi} = \frac{N_1M_1{}^2 + N_2M_2{}^2 + ...}{N_1M_1 + N_2M_2 + ...}$$

$$= \frac{10\times1000^2 + 20\times2000^2}{10\times1000 + 20\times2000}$$

$$= \frac{10000000 + 80000000}{50000}$$

$$= \frac{90000000}{50000}$$

$$= 1800$$

PDI = Mw/Mn

= 1800/1666.6

= 1.08

Polymer Blends & Composites

Polymer blends and Composites

Polymer blend (PB)

A mixture of at least two polymers or copolymers.

Polymer blend: Polymer + polymer

e.g. Poly Ethylene/Poly Amide

Polymer Composite

Polymer is reinforced with some other material (metal or nonmetal) to enhance its physical and mechanical properties.

Polymer composite:

Polymer + reinforcement or filler

e.g. Epoxy + carbon fiber

Need of Blending and Compositing

It is the process to impart specific properties to the polymers

- To reduce material cost.
- Extended service temperature range
- Light weight
- Increased toughening
- Enhanced ozone resistance
- Improved modulus and hardness
- Improved barrier property and flame retardant property
- Improved impact and environmental stress cracking resistance, etc.

Benefits of Blends

1. Polymer blends comprise 30–40
2. Percent of plastics products,
3. Employed in the design of novel materials.
4. High modulus with toughness,
5. Effective and good mechanical properties,
6. Improved biodegradability and recycling characteristics
7. The low investment costs in new materials design
8. Produce high performance articles from the plastics waste.
9. Blending makes it possible to produce integrated multi-layer structures
10. To get desired properties at lowest cost.
11. Modulus & dimensional stability: more rigid and more heat resistant

Formation of Blend:

The driving force is free energy change
$\Delta G_{mix} < 0$.

Polymer blends can either form **homgenous mixtures** or they can undergo **phase separation.**

The two-phase structure is usually induced by a change in temperature or molecular weight.

The main driving force of blend formation is the free energy change.
Miscibility and solubility of two polymers depends on size, shape and molecular weight..

In general, blends are miscible if the free energy of mixing is negative, $\Delta G_{mix} < 0$.

Types of Polymer Blends

a. On the basis of miscibility

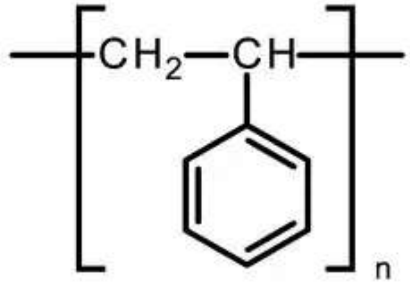
Basically there are three different types of blends depending on the miscibility.

1. **Completely miscible blends**

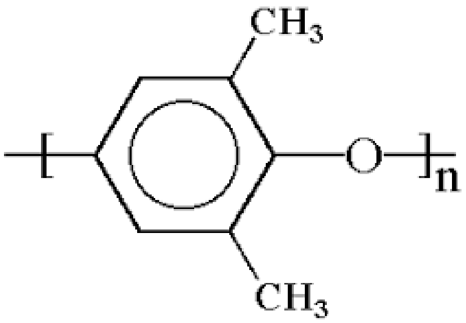
   $\Delta H\ m < 0$ due to specific interactions.

   Homogeneity is observed

Example : which is miscible over a very wide temperature range and in all compositions is Polystyrene-Polyphenylene oxide (PS/PPO)



PS



PPO

2. Partially miscible blends

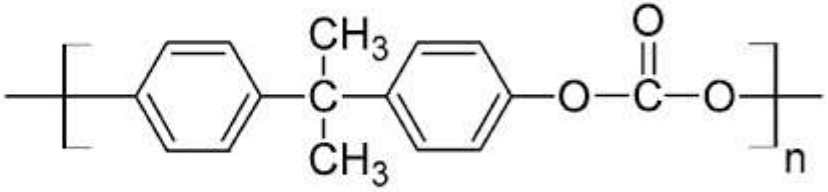
A small part of one of the blend component is dissolved in the other part.

This type of blend, which exhibits

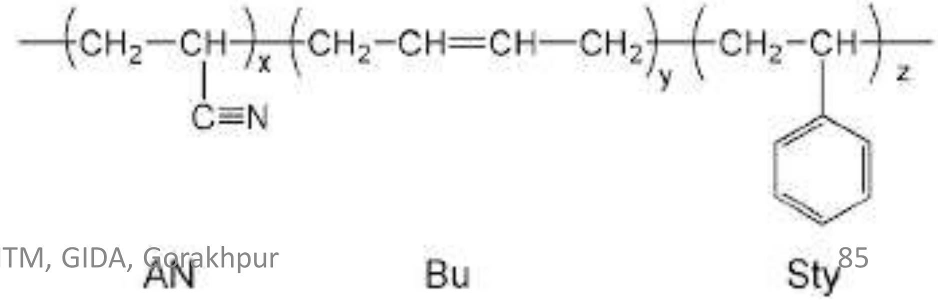
- A fine phase morphology and satisfactory properties, is
- referred to as compatible.

- Both blend phases are homogeneous, and

An example is the Polycarbonate-acrylonitrile-butadiene-styrene (PC/ABS) blends. In these blends, PC and ABS partially dissolve in one another.



PC



3. Fully immiscible blends

Have a coarse morphology,
sharp interface and
poor adhesion between the blend phases.

So these blends are of no use without compatibility.

Examples of fully immiscible blends are

Polyamide (PA)/ABS,
PA/PPO and PA/PP.
For these blends
$\Delta Hm > 0$

b. Homologous polymer blend:

Mixture of two or more fractions of the same polymer each of which has different molecular weight distribution.

c. Isomorphic polymer blend:

Polymer blend of two or more different semi-crystalline polymers are miscible in the crystalline state as well as in the molten state.

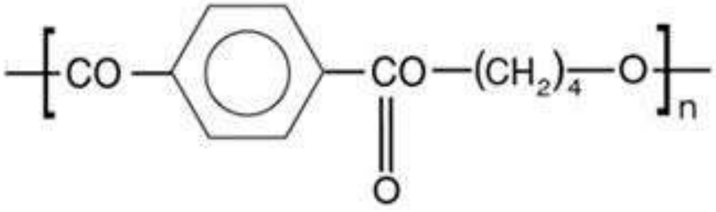
d. Compatible polymer blend:

Blends that is miscible in a certain useful range of composition and temperature, but immiscible in others.

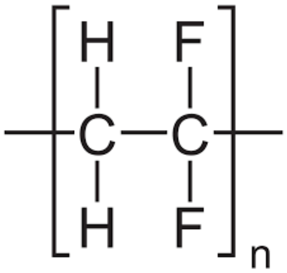
Commercially Important Blends and Composites

Examples of miscible polymer blends:

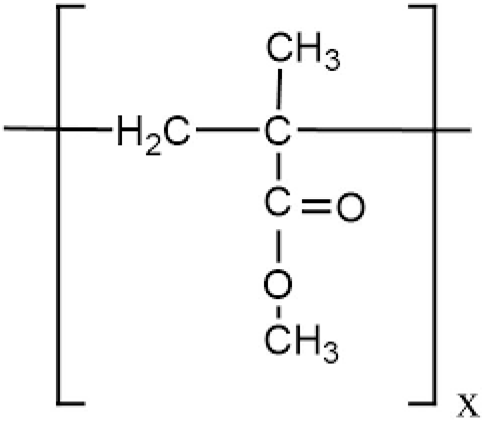
- **Homopolymer–homopolymer:**
    - Polyphenylene Oxide (PPO) – Polystyrene (PS):
    - polyehyleneterephthalate(Dacron)(PET)–polybutyleneterephthalate (PBT)
    - poly(methyl methacrylate) (PMMA) – polyvinylidene fluoride (PVDF)



(PBT)

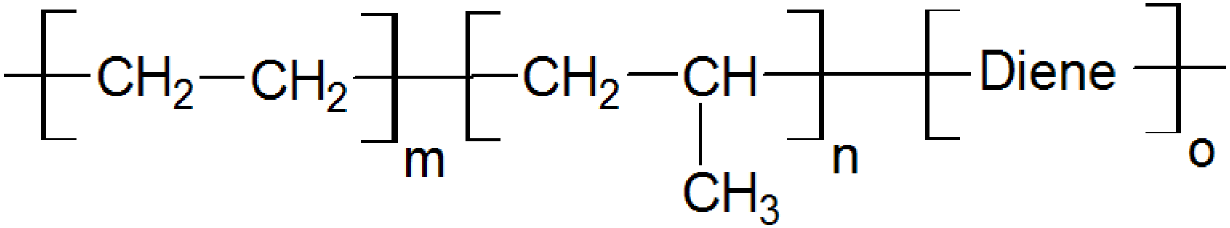


(PVDF)



(PMMA)

- **homopolymer–copolymer:**
    - polypropylene (PP) – Ethylene Propylene Diene Terpolymer (EPDM)
    - polycarbonate (PC) – acrylonitrile butadiene styrene (ABS):



$$-\!\left[CH_2-CH_2\right]_m\!-\!\left[CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}\right]_n\!-\!\left[\text{Diene}\right]_o\!-$$

(EPDM)

Polymer composites

Advantages

- High stiffness and toughness vs. weight
- Chemical stability
- Possibility to orientate the structure
- Shapeability
- Processing of large entities by extrusion, injection molding etc.

Disadvantages

- Poor thermal and electrical conductivity
- Low operating temperature of polymers
- High Price

Characteristics of Composites in structural applications

They generally consist of two or more physically distinct and mechanically separable materials.

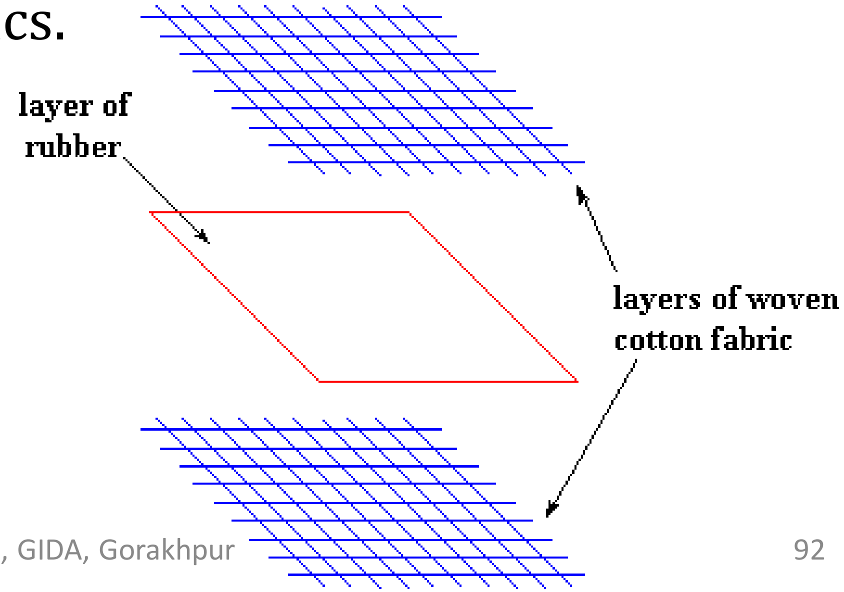
- They are made by mixing the separate materials in such a way as to achieve controlled and uniform dispersion of the constituents.
- They have superior mechanical properties and in some cases uniquely different from the properties of their constituents

polymer matrix composite (PMC)

A **polymer matrix composite** (PMC) is a composite material composed of a variety of short or continuous fibers bound together by an organic polymer matrix. PMCs are designed to transfer loads between fibers through the matrix.

Fibre: The fibers that are commonly found and used withinPMCs include fiberglass, graphite and aramid.

Matrix: The matrix of PMCs consists of resin that is either thermosets or thermoplastics.



Types of PMCs

PMCs are divided into two categories:

1. Reinforced Plastics, And
2. Advanced Composites.

They differ in their level of mechanical properties.

Reinforced plastics typically consists of polyester resins reinforced with low-stiffness glass fibers.

Advanced Composites consist of fiber and matrix combinations that yield superior strength and stiffness.

Overall, the properties of the composite are determined by:

i) The properties of the fibre
ii) The properties of the resin
iii) The ratio of fibre to resin in the composite (Fibre Volume Fraction)
iv) The geometry and orientation of the fibres in the composite

Advantages

High stiffness and toughness vs. weight
- Chemical stability
- Possibility to orientate the structure
- Shapeability
- Processing of large entities (extrusion, injection molding...)

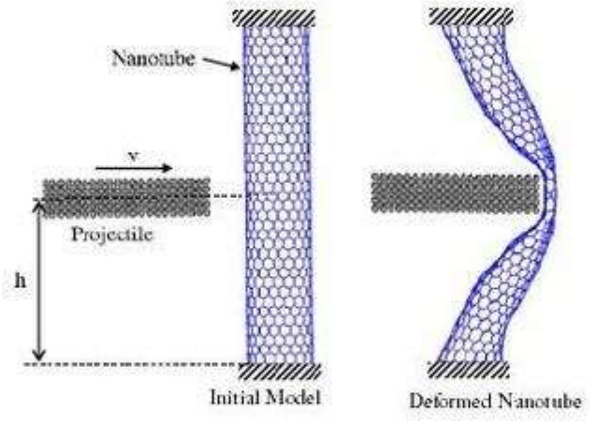
Disadvantages

- Poor thermal and electrical conductivity
- Low operating temperature of polymers
- Serial production not developed widely
- Un-standardized materials
- Sometimes high prizes of the materials

Functionality of polymer composites Materials function together • Stiffness and toughness of the fiber • Flexibility of the matrix • Matrix protect the fibers

Bullet-Proof

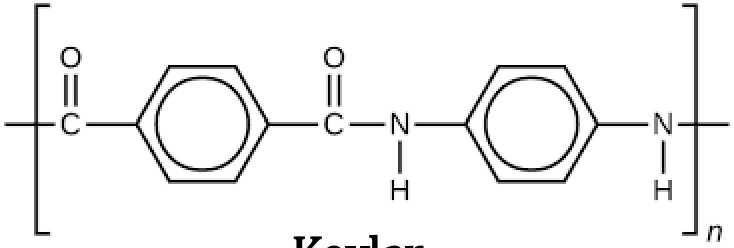
Aramid-based composites are thermosetting plastics, an aromatic polyamide matrix. The most common use for these composites is in Kevlar,



Aerospace & Military Aircraft:

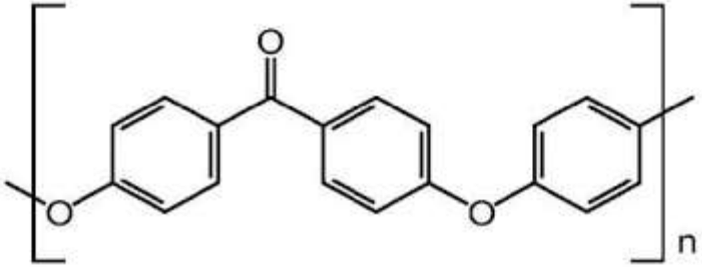
The primary matrix materials used in aerospace applications are epoxies, and the most common reinforcements are carbon/graphite, aramid and high-stiffness glass fibers. High strength Poly ether ether ketone (PEEK) are considered to be for future aerospace applications.

Kevlar an Aramide means aromatic polyamide
A condensation polymer of Terephthalic acid and p-diaminobenzene



Kevlar

Poly Ether Ether Ketone (PEEK) a High Srength Polyme

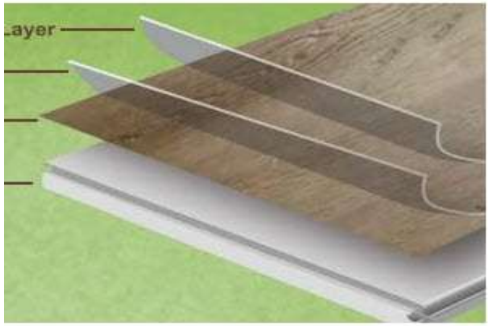


(PEEK)

Automotive Industry:
The next major opportunity for PMCs in automobiles is in structural components.

Naval Applications
The light weight and corrosion resistance of PMCs makes them attractive for a number of naval applications.

Construction
A potentially high-volume market for PMCs lies in construction applications, especially in construction of buildings, bridges, and housing. Additional applications include lampposts, smoke-stacks.



Explore Stone Polymer Composite (SPC) Flooring

Medical Devices

PMC materials are currently being developed for medical prostheses and implants. The impact of PMCs on orthopedic devices is expected to be especially significant.

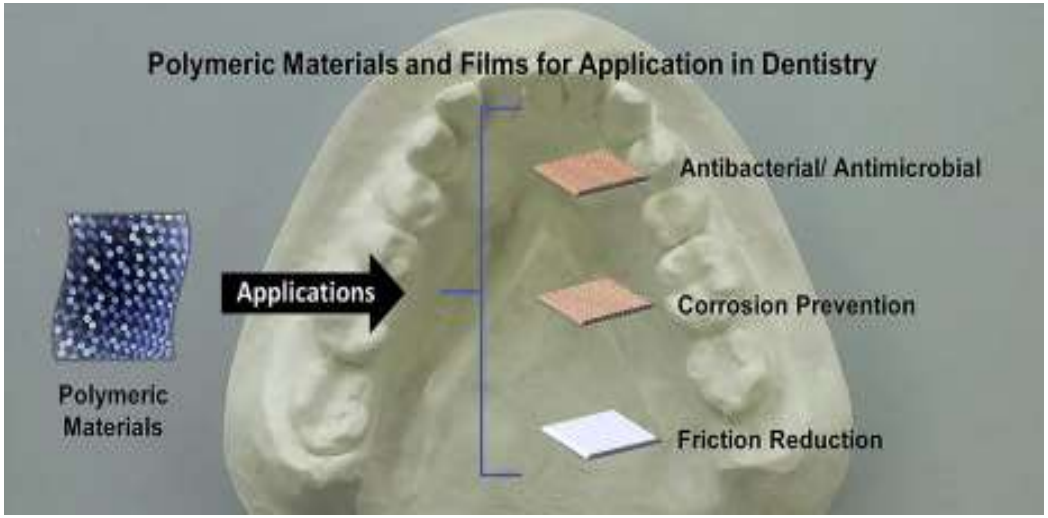


Fig.: PEEK orthopedic implant

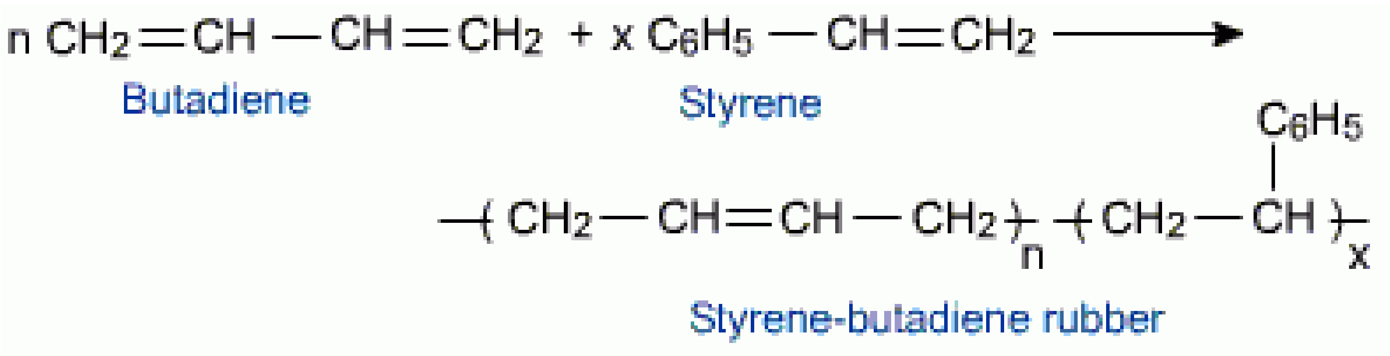
Preparation & Applications
of
Some Industrially Important Polymers

Preparation of Buna-S

Also known as styrene-butadiene Rubber (SBR)
Buna-S name is derived from Bu-butadiene and Na-sodium/natrium and S-styrene

It is derived from two monomers, styrene and butadiene.

It is a random co-polymer formed polymerization of a mixture of 1:3 butadiene and styrene in the presence of peroxide catalyst at 5°C and therefore the product is called as cold rubber The rubber obtained is also called Styrene butadiene rubber (SBR).



$$n\,CH_2{=}CH-CH{=}CH_2 + x\,C_6H_5-CH{=}CH_2 \longrightarrow -\!\left(CH_2-CH{=}CH-CH_2\right)_n\!-\!\left(CH_2-\overset{\overset{\displaystyle C_6H_5}{|}}{CH}\right)_x\!-$$

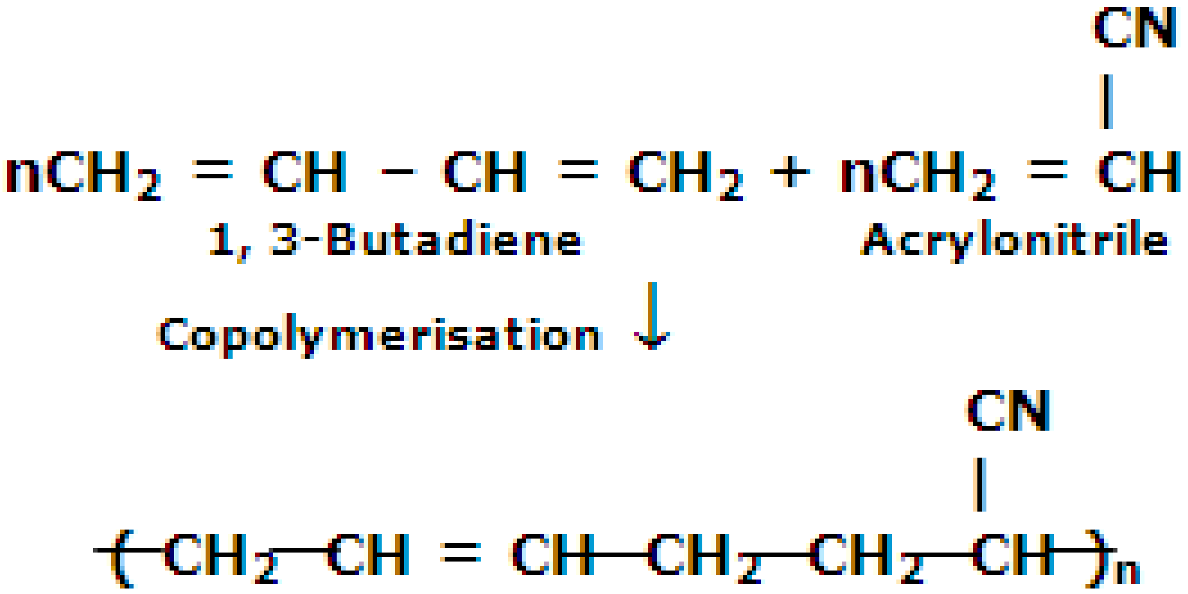
Applications

1) It is used for the manufacture of passenger car tyres and tubes of various vehicles.
2) They are also used for the manufacture of conveyor belts, foot-wares, shoe soles, hoses and electrical insulation.

Preparation of Buna-N

Nitrile Butadiene Rubber (NBR) Buna-N is manufactured by the co-polymerisation of 1, 3-butadiene and acrylonitrile in presence of peroxide or sodium catalyst.

Buna-N, Bu stands for butadiene and na = Na – sodium catalyst, N = nitrile (CN).



$$\underset{\text{1, 3-Butadiene}}{nCH_2 = CH - CH = CH_2} + \underset{\text{Acrylonitrile}}{nCH_2 = \overset{\overset{CN}{|}}{CH}}$$

$$\text{Copolymerisation} \downarrow$$

$$\left(CH_2 - CH = CH - CH_2 - CH_2 - \overset{\overset{CN}{|}}{CH} \right)_n$$

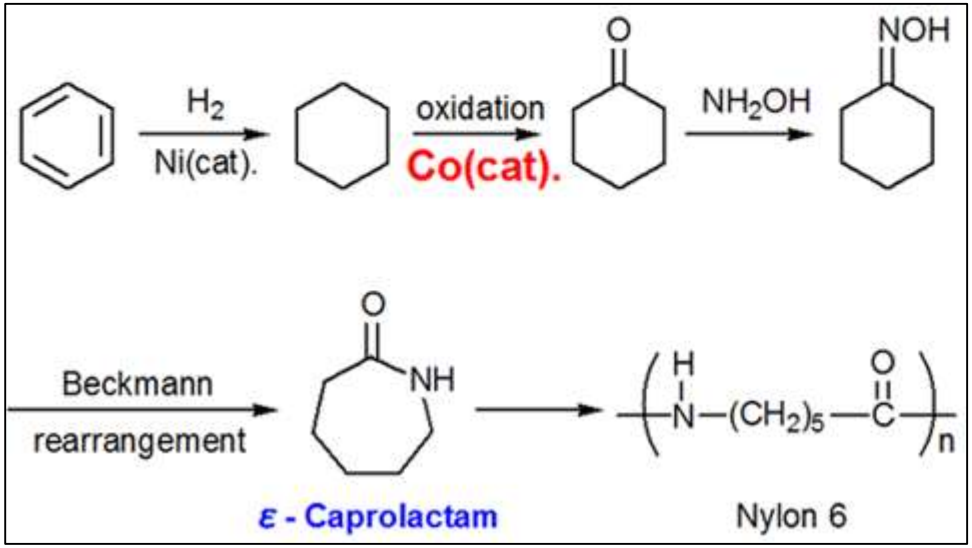
Buna-N

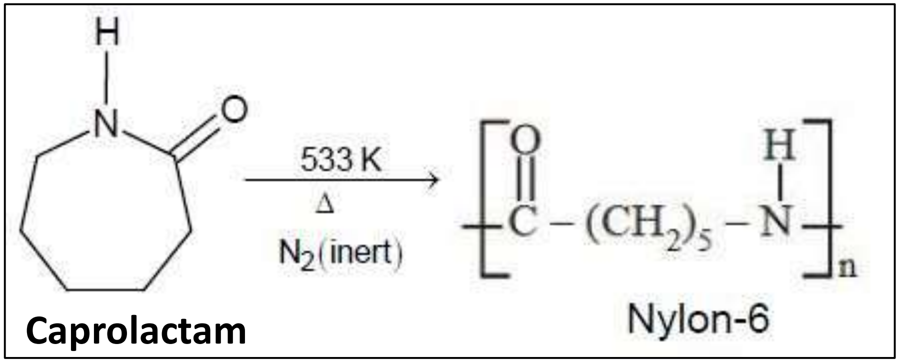
Uses

Buna-N rubber is used in the preparation of adhesives and as a pigment binder. XNBR, an improved version of Buna-N, is used for hoses, rubber belts, sealing parts, special purpose article in **oil** well, reciprocating **oil** seal, rubber seal, gaskets, shoe-soles, varieties molded part for shoe heels etc.

Preparation of Nylon-6

Nylon-6 is a polyamide, synthesized by ring-opening polymerization of caprolactam.
Caprolactam has **6** carbons, hence '**Nylon-6**'.
When caprolactam is heated at about 533K in an inert atmosphere of nitrogen for about 4-5 hours, the ring breaks and undergoes polymerization.



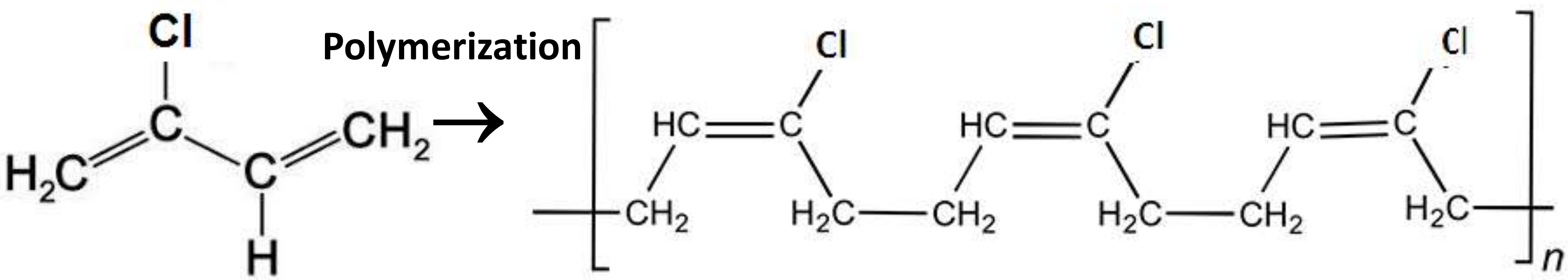


Uses

Nylon 6 is a versatile synthetic material that can be formed into fibers, sheets, filaments or bristles. These are in turn be used in the **production** of fabric, yarn and cordage. For example, fine nylon 6 filaments are used in the manufacture of hosiery, knitted clothing and parachutes.

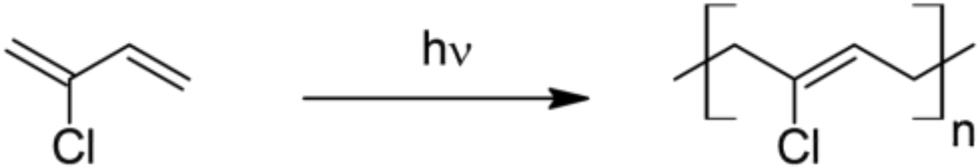
Preparation of (Neoprene): Polychloroprene

Neoprene (also **polychloroprene** or **pc-rubber**) is a family of synthetic rubbers that are produced by polymerization of chloroprene.
Neoprene is produced by free-radical polymerization of chloroprene.
Neoprene exhibits good chemical stability and maintains flexibility over a wide temperature range.



Chloroprene
2-chloro-1,3-butadiene

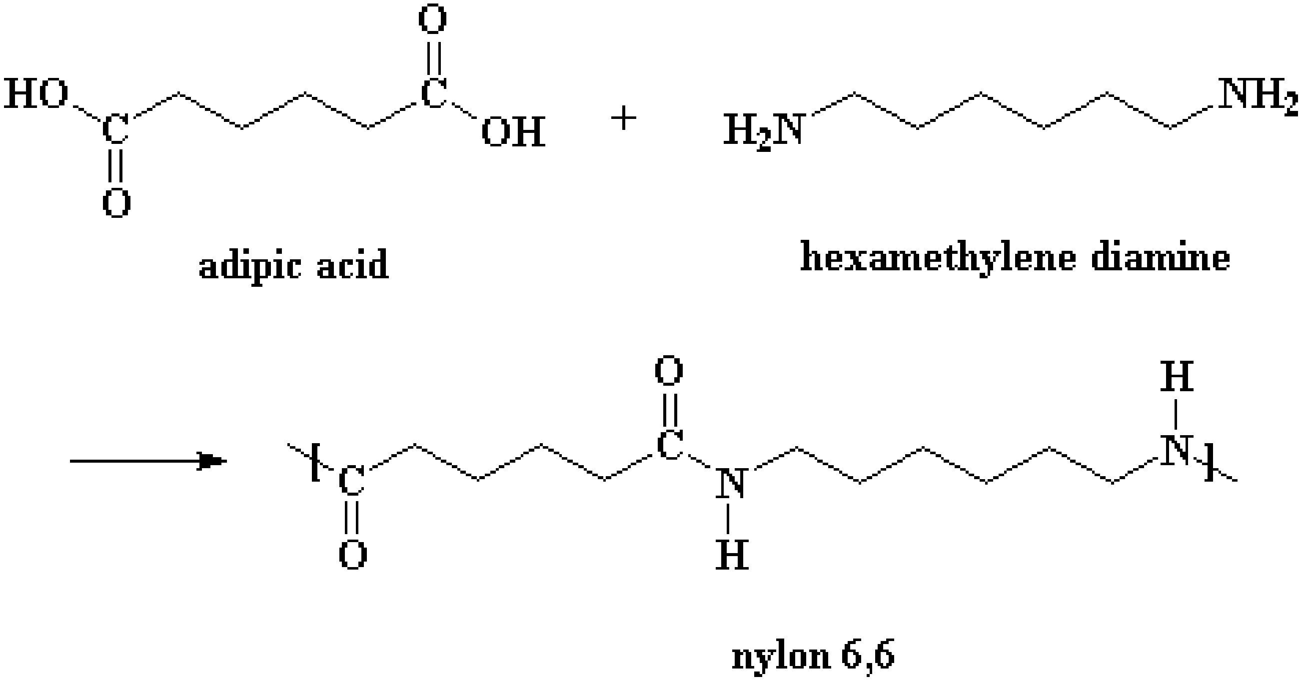
Polychloroprene
Synthetic Rubber



Uses
Neoprene rubber is widely used in manufacturing products such as medical and sports supports. It makes an ideal material for wrist, knee, elbow and other types of supports.

Preparation of Nylon-66

Nylon 66 is synthesized by polycondensation of two monomers each containing 6 carbon atoms hexamethylenediamine and adipic acid, which give its name **nylon-66.**
Equivalent amounts of hexamethylenediamine and adipic acid are combined with water in a reactor.



nylon 6,6

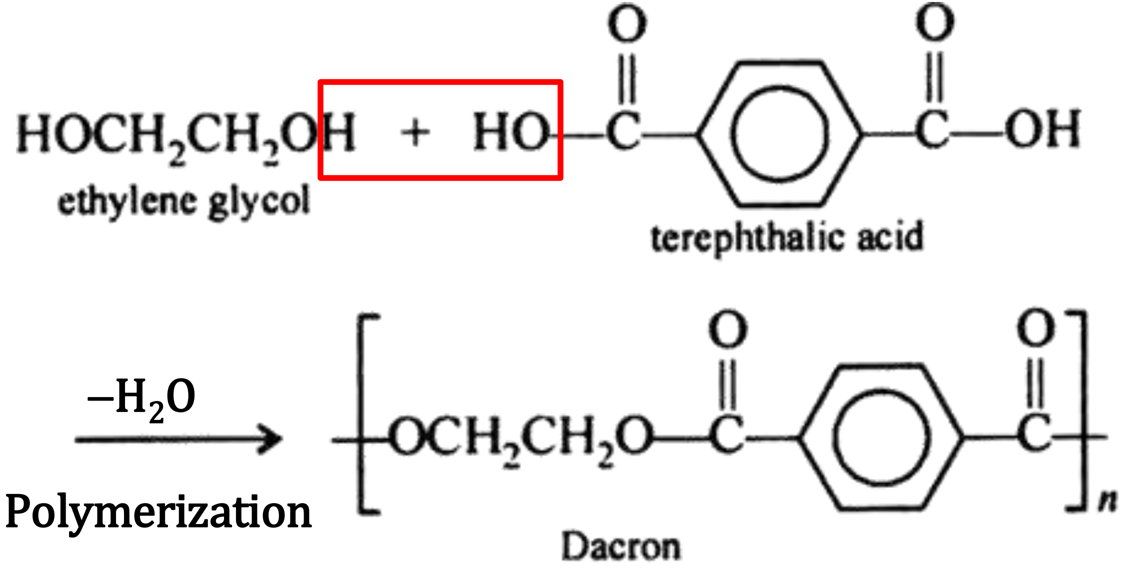
Uses

Nylon 66 is frequently used when high mechanical strength, rigidity, good stability under heat and/or chemical resistance are required. It is used in fibers for textiles and carpets and molded articles, nets, ropes etc.

Preparation of Terylene (Dacron) Polyethylene Terephthalate

Poly(ethyleneterephthalate), commonly abbreviated **PET**, is the most common thermoplastic polymer resin of the polyester family and is used in fibres for clothing, containers for liquids and foods,

Terylene is a synthetic polyester fibre produced by condensation polymerization of ethylene glycol and terephthalic acid with subequent removal of water molecules.



Terylene is mainly used in making plastic bottles and clothing. **Terylene** fiber is used as polyester tericot knit as a fashion garments fabric. Used for the laundry usage as a automatic clothing vacuum packaging machine. It is used to make non woven needle punched carpet.

Thank You

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