

POLYMERS

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Polymer:

- **Definition:**

A polymer is defined as the substance having very high molecular weight and is made by joining of large number of simple molecules.

- The polymer molecules have certain structural unit repeating large no. of times.

e.g. polyethylene

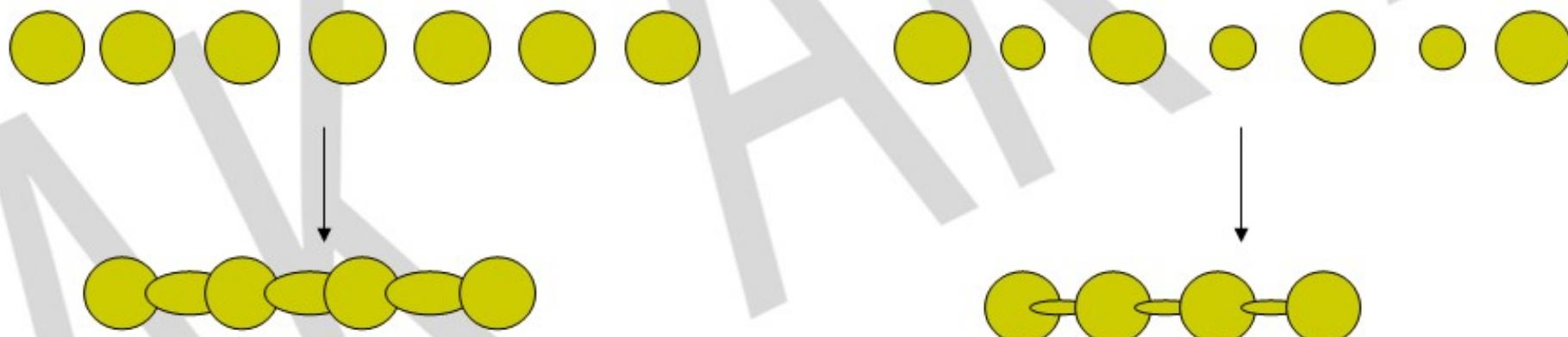


Repeating unit for polyethylene is $\text{-CH}_2\text{-CH}_2\text{-}$

Conceptual Representation of Formation of Polymer

**Rings of same sizes
represents molecules
of same chemicals**

**Rings of different sizes
represents molecules
of different chemicals**



Chains made up of interlinked rings representing polymer molecule

Terms and Definitions

- Monomers
- Polymerization
- Degree of polymerization
- Glass Transition Temperature

Monomers:

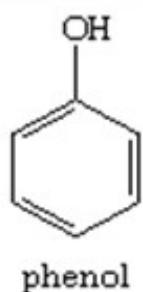
Definition:

- Monomer is the simple chemical substance of low molecular weight which can be converted into a polymer and the molecule of monomer has at least two easily reacting positions.
- Depending upon number of reacting positions there are 3 types of monomers:
 1. Bifunctional Monomers: Monomer molecule contains two easily reacting positions and it forms linear polymer molecule.
e.g. a) HO- CH₂-CH₂- OH Ethylene glycol
 b) CH₂= CH—Cl Vinyl chloride

2. **Trifunctional monomer:** Monomers having three reactive positions or groups and forms highly branched polymer.

e.g. a) HO-CH₂- CH OH-CH₂- OH Glycerol

b)



Phenol

3. **Tetrafunctional Monomer:** Monomers having four reactive positions or groups. It forms 3 dimensional network or crosslinked polymers.

e.g. a) H₂ C = CH -CH = CH₂ Butadiene

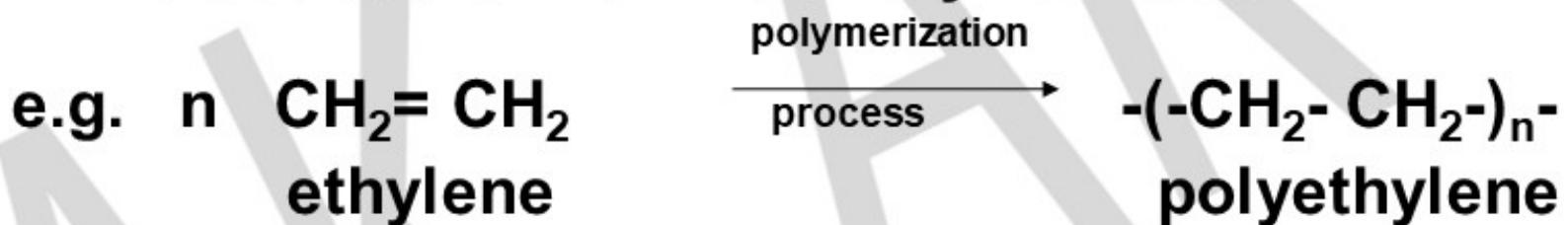
b) H₂ N -CO- N H₂ Urea

Polymerisation:

- The process of synthesis of polymers is called Polymerisation

- Definition:

The chemical process in which a large number of monomer molecules get joined to form the polymer molecules, is known as Polymerization.

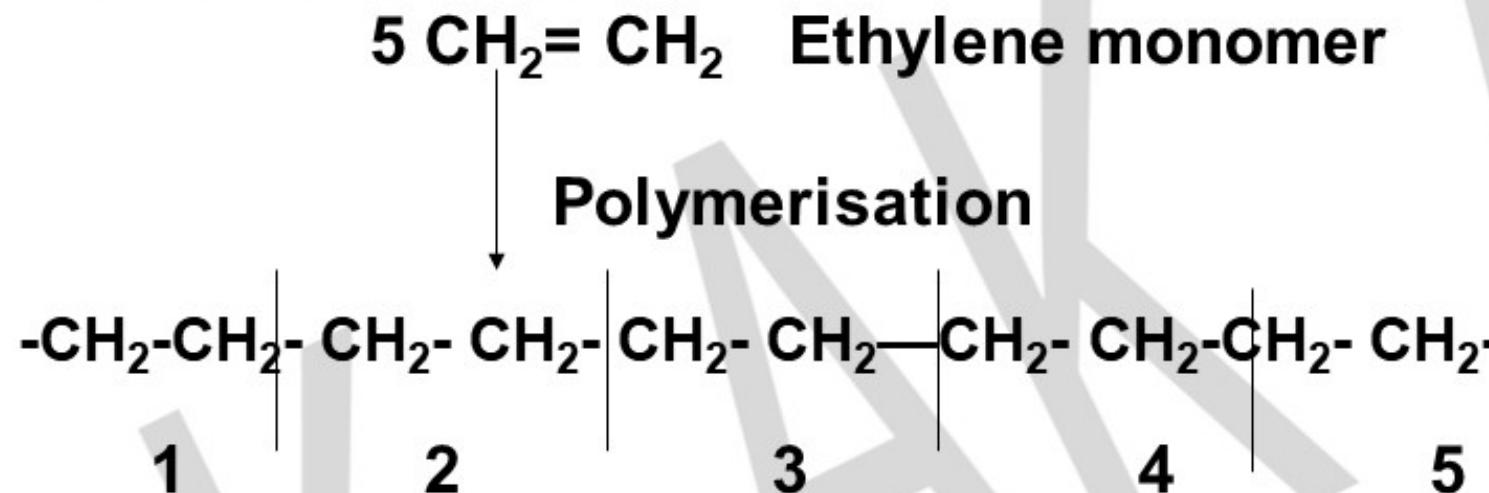


- The number of monomer molecules that get joined to form polymer molecules is generally greater than 100 and may be upto many thousands.

Degree of Polymerisation (DP):

- Definition:

It is the average number of repeating units in the molecules of the polymer.



i.e. $-(-\text{CH}_2-\text{CH}_2-)_5-$ DP = 5

Polyethylene molecule containing 5 repeating units.

- The degree of polymerisation increases with time and the temperature of polymerisation reaction.
- It also depends upon the concentration of monomer and the initiator.

Degree of Polymerisation (DP):

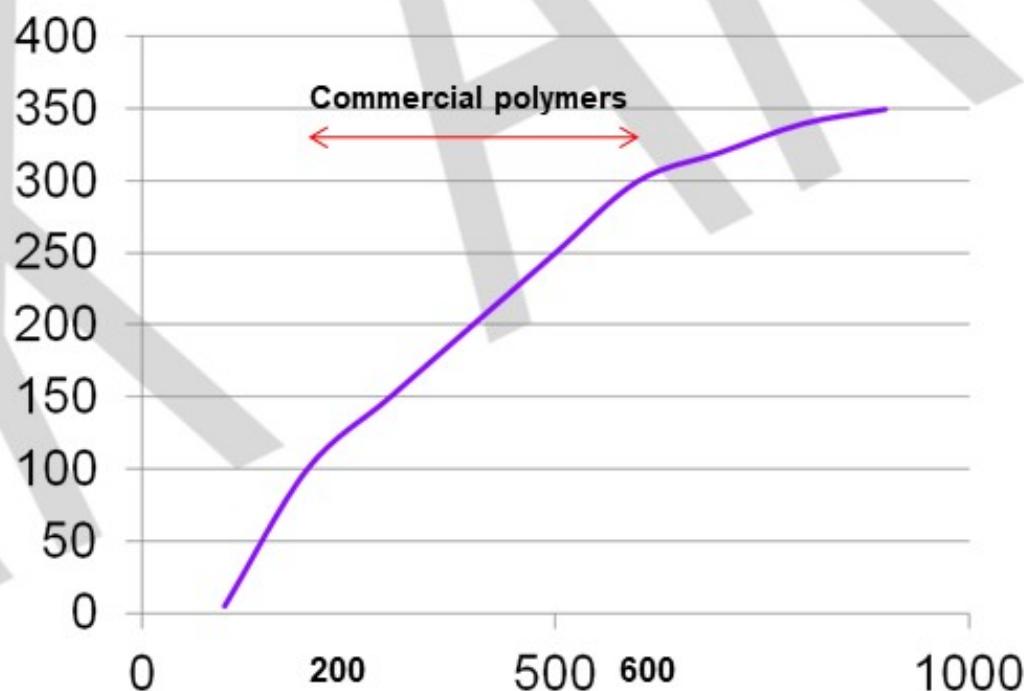
- The degree of polymerisation and molecular weight are related by

$$M = n M_0$$

$n = \text{DP of polymer}$

$M_0 = \text{molar mass of monomer}$

- If DP of polymer is below a limit, then the polymer is either friable powder or liquid.



Glass Transition Temperature (T_g):

- Definition:

The Temperature below which the polymer becomes hard, brittle and glassy and above which it is softer and flexible.

e.g. Polystyrene $T_g = 100^{\circ}\text{C}$

Nylon -6 $T_g = 50^{\circ}\text{C}$

Glassy State
(Brittle plastics)

Rubbery or Viscoelastic state
(Tough plastics & rubbers)

Viscofluid state
(Polymer melts)

T_g Temp.

T_f

Glass Transition Temperature (T_g):

Factors affecting Glass transition temperature

- Higher is the molecular weight, greater is the T_g of polymer
- Presence of bulky side groups on the polymer chain increases T_g .
- Greater is the crosslinking, higher is the T_g .
- Stronger intermolecular forces of attraction increases T_g .
- Addition of polymer decreases T_g .
- Higher the crystallinity of polymer, higher is its T_g . Amorphous polymers have lower T_g .

Importance of T_g :

A polymer should have much lower T_g than the operating temperature. E.g. polymers to be used for refrigerators, air conditioners should have lower T_g , so that they do not break during use.

Classification of polymers

On the basis of :

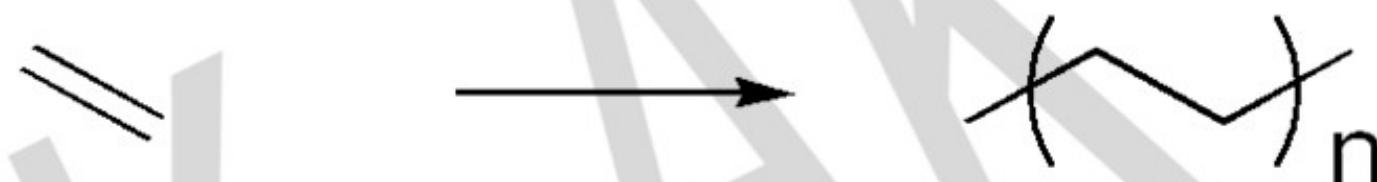
- 1. Polymerization mechanism : step and chain polymers**
- 2. Polymerization reactions: addition and condensation polymers**
- 3. Thermal behavior: Thermosoftening and Thermosetting polymers**
- 4. Types of monomers**

Classification of polymers based on **POLYMERIZATION MECHANISM**

(I) CHAIN POLYMERS

CHAIN MECHANISM : FREE RADICAL MECHANISM

FREE RADICAL : Free radical is a species that has an unpaired e- formed by homolytic fission so that each fragment keeps one electron.



The organic peroxide, $\text{R}-\text{O}-\text{O}-\text{R}'$ used as catalyst.

Generation of free radical :



The oxygen of each free radical contains a septet of electrons. The odd electron is shown by the dot (*) and hence it is very reactive chemically and only exist for a fraction of a second.

Steps involved :

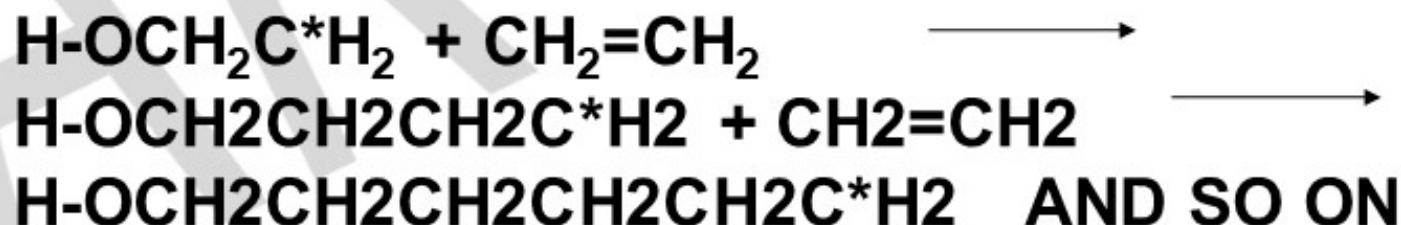
1. Initiation :

Monomer gets attacked by free radical and gets converted into monomer free radical. Free radical joins the ethylene molecule.



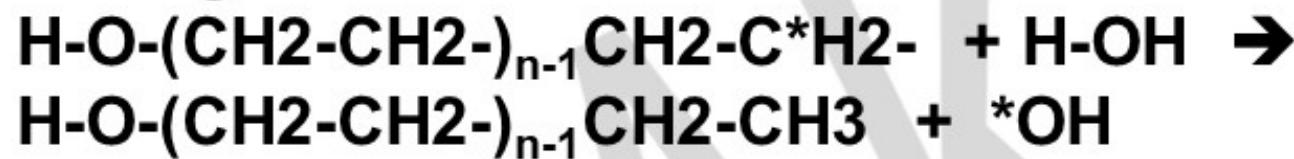
2. Propogation :

Monomer free radical reacts with further monomer giving rise to new monomer free radical and thus reaction proceeds and propogates to form polymer.



3. Termination :

After polymerisation to desired extent taken place, the growing chain ends are made dead by adding a chain terminator like water.

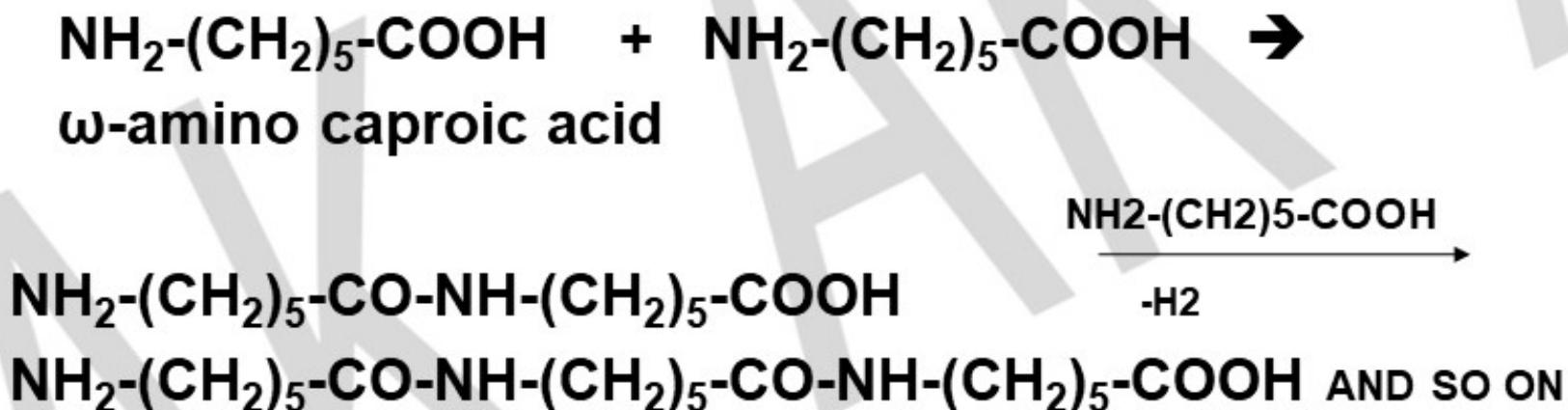


Regeneration of Catalyst :

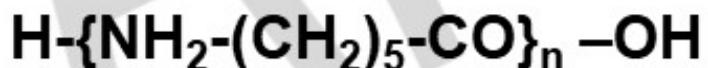


(II) STEP POLYMERS

- Stepwise reaction, byproduct formed, separation necessary.
- Polymer molecule ends are reactive, if monomers are added, polymerization continues.
- E. g. Formation of Nylon 6



The structure of final product of Nylon 6 is



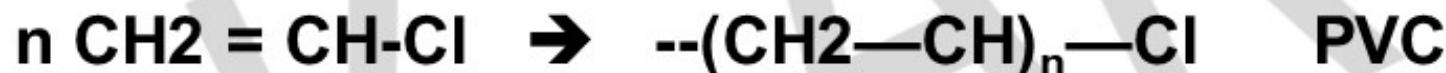
- The two ends of polymer have $-\text{NH}_2$ & $-\text{COOH}$ gr. & hence polymer can grow further if monomer is available.

Classification of polymers based on POLYMERIZATION REACTIONS

1. Addition polymers (formed by chain reactions)
2. Condensation polymers (formed by step reactions)

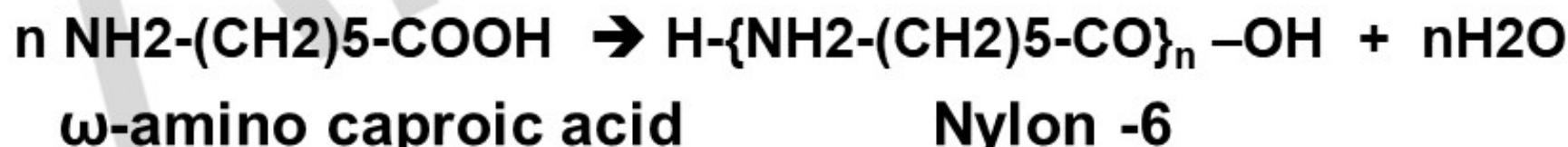
Addition polymers: All vinylic monomers undergo the addition reaction during polymerisation in presence of catalyst/initiator.

Reactions are fast and exothermic.



Condensation polymers: Slow, stepwise progressive reaction between monomers. Byproduct is formed.

Endothermic reaction.



Classification of polymers based on THERMAL BEHAVIOUR

Thermosoftening

- Formed by addn/chain polymerization
- Linear chains
- Bifunctional monomers used
- Soften on heating & harden on cooling
- Low mol. Wt. polymer
- Can be remolded
- Soft, weak, less brittle
- Can be reclaimed from waste
- Soluble in less organic solvents

Thermosetting

- Formed by condensation polymerization
- 3 dimensional due to crosslinks
- Monomers ware with higher functionality are used
- Do not soften on heating & on excessive heating char, decomposse or burn.
- High mol. Wt. polymer.
- Can not be remolded
- Hard, strong and more brittle
- Can not be reclaimed
- Insoluble due to strong bonds & crosslinks.

Classification of polymers based on TYPES OF MONOMERS

(I) Homopolymer : formed by polymerization of only one type of monomer.

e.g. $\text{CH}_2=\text{CH}_2$
 ethylene

--(-- CH_2-CH_2-)_n--
 polyethylene

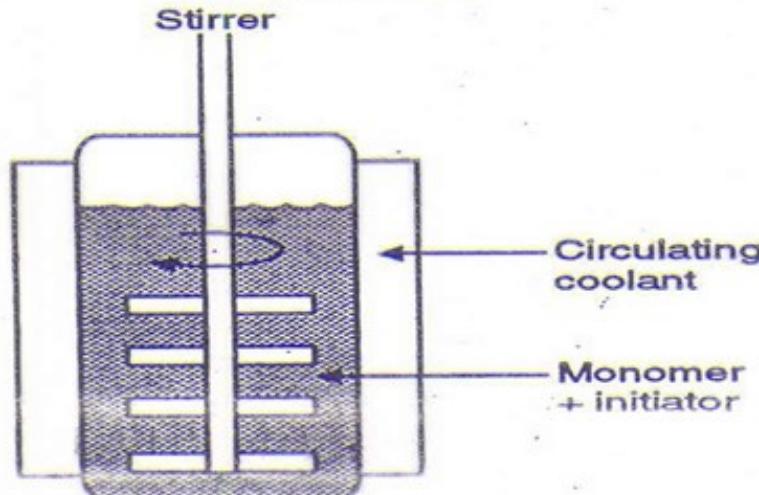
(II) Copolymer/Heteropolymer : obtained by polymerization of two or more monomers.

e.g. --($\text{CH}_2-\text{CHCN-CH}_2-\text{CH=CH-CH}_2-\text{CH}_2-\text{CH-C}_6\text{H}_5-$)—
 formation of Acrylonitrile Butadiene Styrene

Types of Copolymers:

- (a) **Alternating Polymers** : They consist of alternate arrangement of monomers.
e.g. --A—B—A—B—A—B—A—B—A—B—
- (b) **Random Polymers** : They consist of random arrangement of monomers.
e.g. --A—B—B—A—B—A—A—B—A—
- (c) **Block Copolymers** : Consist of different monomers in blocks of individual species.
e.g. --A—A—A—A—B—B—B—B—A—A—A—A—B—B—B—B—
- (d) **Graft polymers** : Consist of blocks of one species of monomer attached to the chain of another species.
e.g. —A—A—A—A—A—A—
 |
 B—B—B—

Bulk Polymerization



(a) Bulk polymerization reactor

Process:

- Monomer used in a liquid form and initiator is added or dissolved in a reactor.
- This homogeneous mixture is heated/exposed to radiation to start polymerization.
- Continuously water is circulating for cooling mixture and control reaction. Duty of stirrer is very important.
- Viscosity of mass inside vessel increases as the reaction proceeds.
- Reaction is exothermic. Heat transfer is very difficult
- If reaction is not controlled, the reactor may explode.

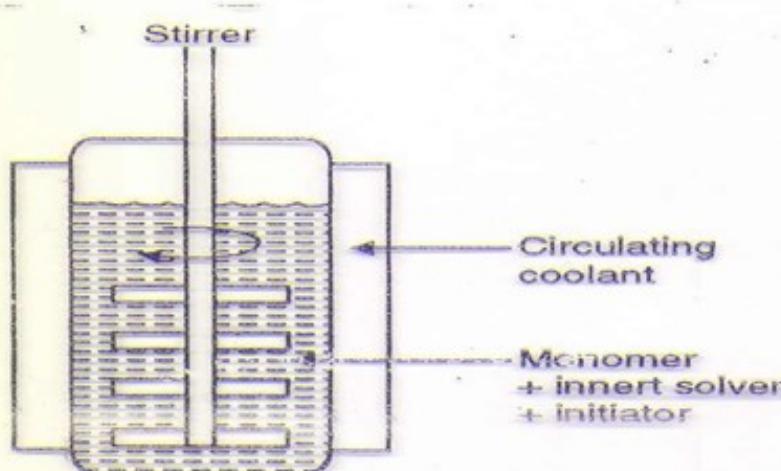
Advantages:

- Product of polymer is pure .
- Technique is very simple.

Disadvantages:

- As the reaction proceeds, mass becomes more and more viscous therefore heat transfer is very difficult.
- Polymer obtained has very broad molecular weight distribution.
- e.g. PE, PVC, PS, PPS.

Solution Polymerization



(b) Solution polymerization reactor

Process:

- Monomer is dissolved in a suitable non-reactive solvent alongwith catalyst and chain transfer agent.
- Heat transfer is easy.
- Solvent helps to control viscosity increase.
- Solvent itself act as chain transfer agent. Therefore polymer of low molecular weight is obtained.
- Polymer can be separated from solution by evaporation of solvent.
- Without separation, it can be used as adhesive or coating material.
- e. g. Polyacrylonitrile, polyisobutylene, block copolymers.

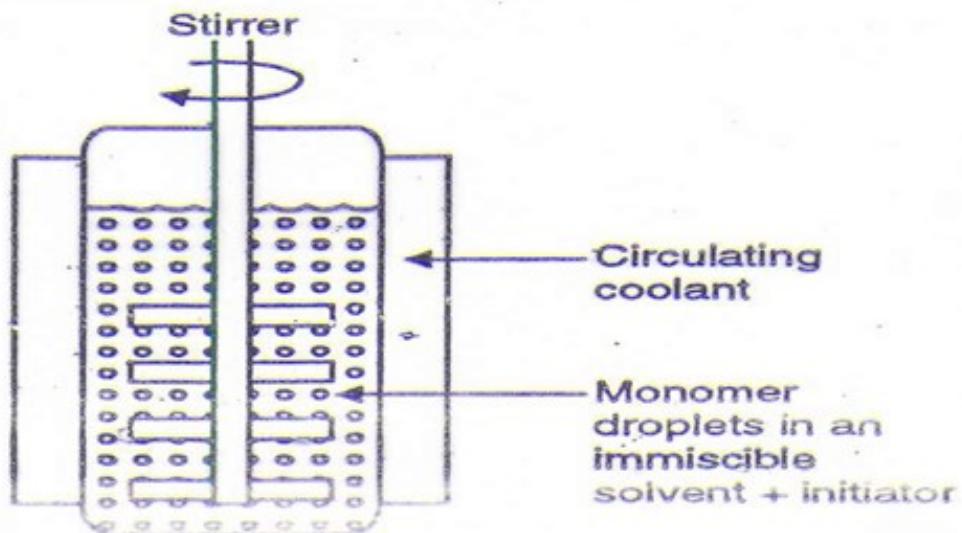
Advantages:

- Heat and mass transfer is easy.
- Polymer solution obtained, can directly used as adhesives or coating material.

Disadvantages:

- Low molecular weight polymers obtained.
- Separation of solvent from polymer is needed.

Suspension Polymerization:



(a) Suspension technique reactor

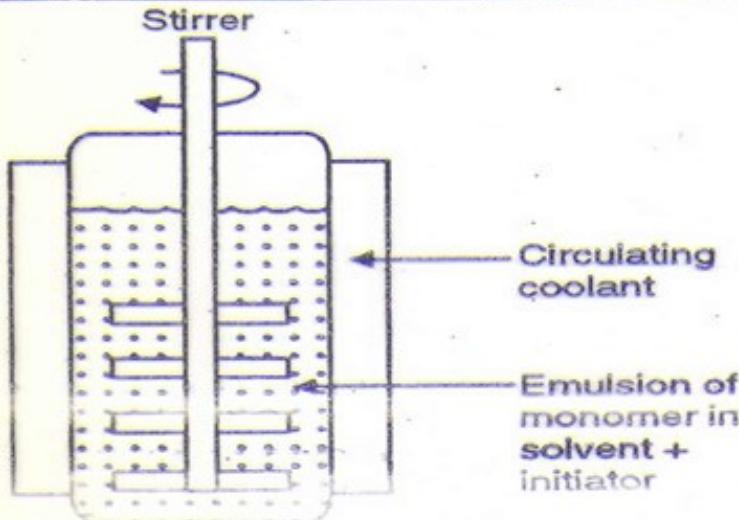
Process:

- Water insoluble monomer liquid is dispersed in water in the form of fine droplets.
- Initiator is added and heat or light is used to start polymerization.
- Polymerization takes place in the droplets of monomer liquid to form beads/pearls.
- Heat and mass transfer are easy.
- Polymer is easy to isolate.
- Molecular weight of polymer is high and of narrow distribution.

Advantages:

- Molecular weight high.
- Narrow molecular weight distribution range.

Emulsion Polymerization:



(b) Emulsion technique reactor

Process:

- Monomer liquid is dispersed in water.
- Emulsifying agent is added to form stable emulsion
- Monomer droplets are colloidal sized.
- Sufficient addition of emulsifier to avoid suspension.
- Initiators like H_2O_2 used.
- Polymerization begins with heat.

Advantages:

- Heat and mass transfer easy.
- Narrow molecular weight distribution range
- Polymer isolation easy.
- Molecular weight high.
- e. g. Vinylic polymers, Polybutadiene, Butadiene copolymers.

Compounding of Plastics

- Polymeric material is mixed with few compounding constituents which have some useful functions or impart useful properties to the final product.
- It can be done with following constituents
 1. Resin: Thermosetting polymer
 2. Plasticizer
 3. Fillers: Saw dust, BaSO_4 , air
 4. Colour or pigments: Organic dyes.
 5. Lubricants: Oils, waxes, vaselines
 6. Stabilisers: Barium salts, lead salts
 7. Accelerators: Benzoyl peroxide

SPECIALITY POLYMERS

- Conducting polymers
- Biodegradable polymers

Conducting Polymer

Structural Requirements:

- If plastics are compounded with metal powder, it becomes conducting polymer
- Polymer shd contain free electrons as in metals.
- Free electrons are there in conjugated systems.

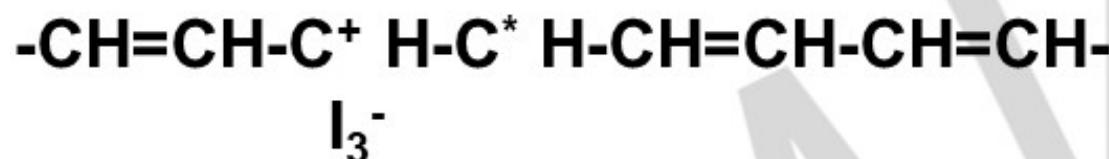
e.g. Polyacetylene



- Sigma e-s localized and Pi e-s delocalized, hence conductivity of polyacetylene is of the semiconductor.
- Shirakawa-Heeger-Mac Diaramid (Nobel prize winners 2000) found that if polymer chain of conjugated system is oxidized or reduced, then conductivity of polymer increases a billion times.
- Oxidation or reduction of chain is called as Doping.

Oxidative/P-Doping

Oxidising reagents like iodine vapours, I_2 /CCl_4 , HBF_4 , Br_2 are used.



Radical ion (polaron)



Biradical ion



The positive charge resonates throughout the polymer chain and can be transferred to neighbouring chains during conduction. Conductivity increases upto 10^5 s/cm

$-e^-$, oxdn, $3/2I_2$

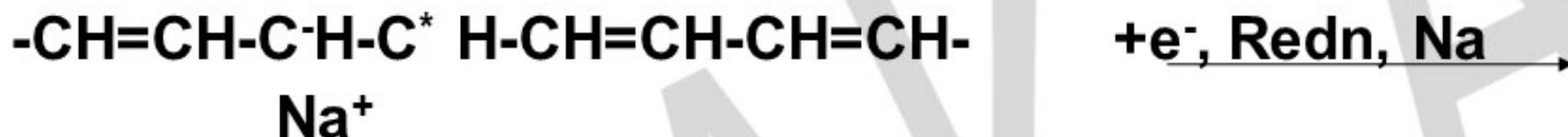
$-e^-$, oxdn, $3/2I_2$

Reductive/N-doping

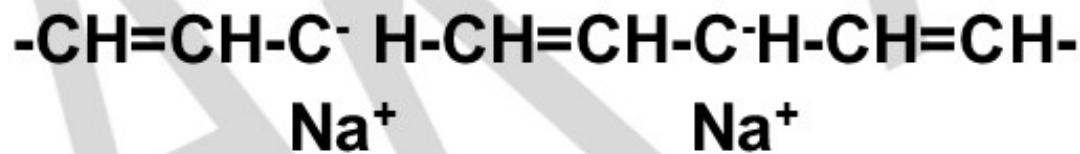
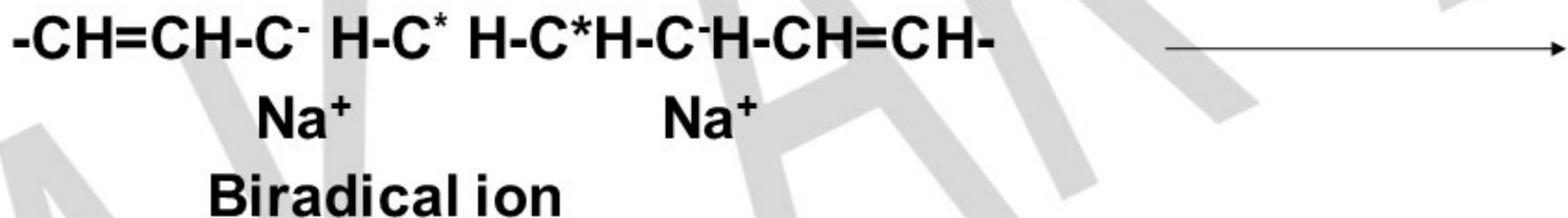
Reducing agents like Na metal, FeCl_2 , Li metal are used.



Polyacetylene



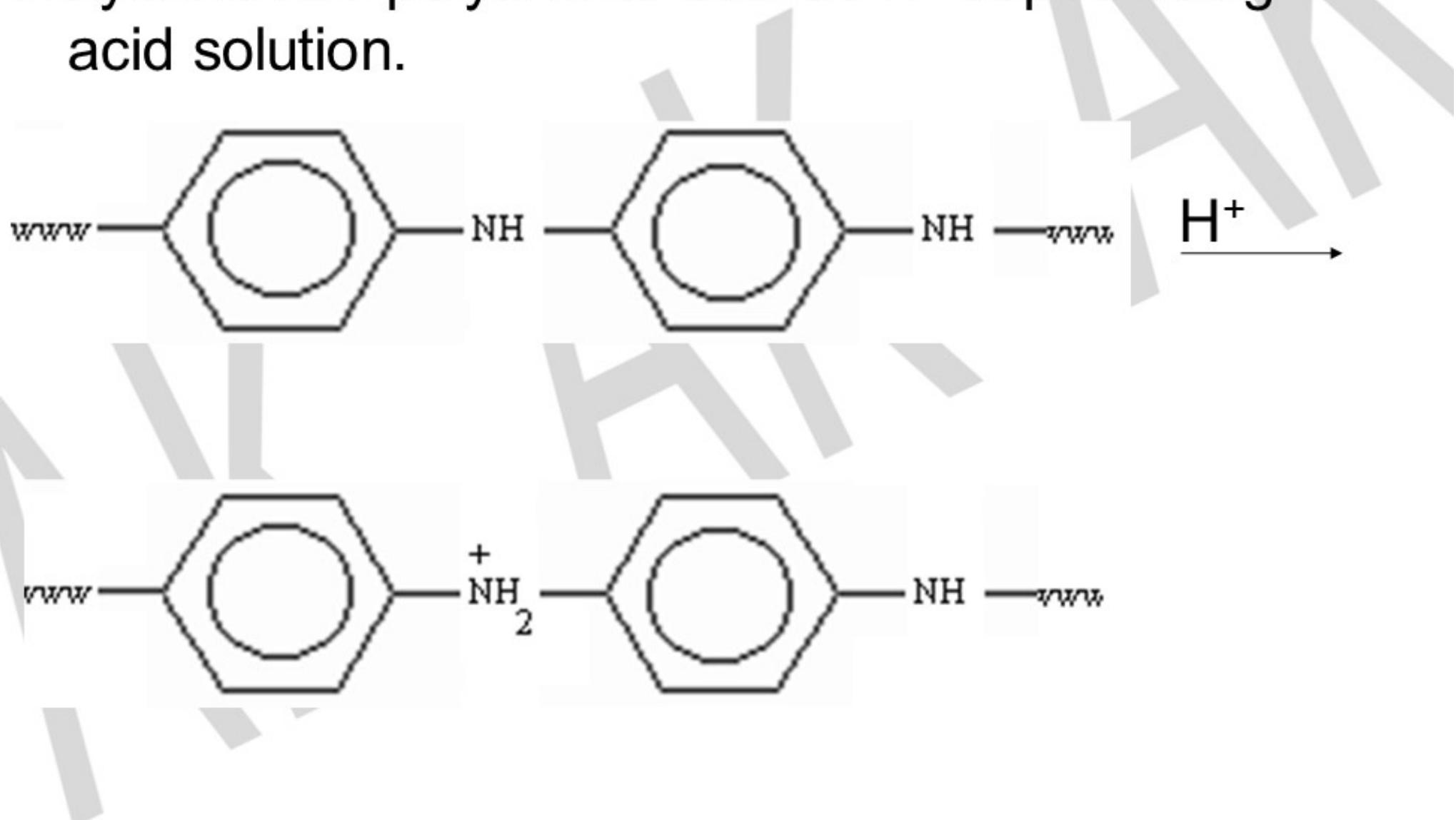
Radical ion (polaron)



Negative charge resonates throughout the chain & transferred to neighbouring chains during conduction.

Protonic Doping

Polymers like polyaniline can be H^+ doped using acid solution.



Applications of Conducting Polymers

- 1) Rechargeable batteries
- 2) Antistatic material
- 3) Electronics: in photodiodes, LEDs
- 4) Photovoltaic cells

Biodegradable polymers

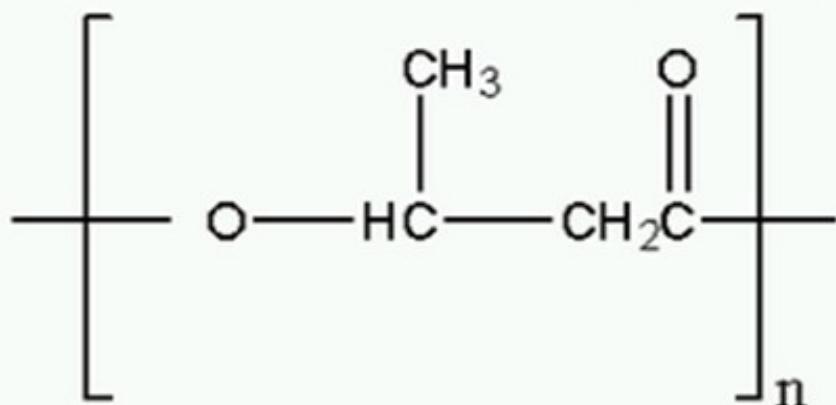
- It is the process of converting polymer chains into harmless simple products, by action of enzymes on micro organisms
- 3 imp elements
 1. Availability of Microorganism like protozoa, fungi
 2. Environment: suitable pH, moisture conditions and availability of salts
 3. Nature of polymer: hydrophilic/phobic

Applications : Biodegradable

- Medical field
- Surgical sutures

Biodegradable polymer

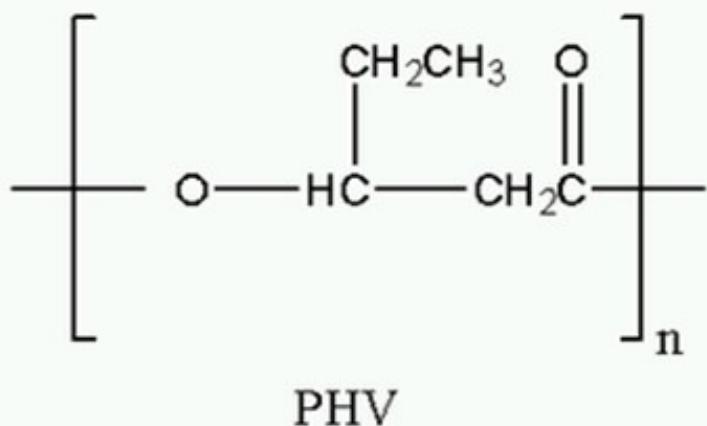
Polyhydroxybutyrate (PHB): obtained by fermentation of sucrose by the bacterium *alcaligenes eutrophus* (A-eutrophous)



PH B

- It is brittle , highly crystalline, water soluble
- non toxic polymer
- High M. P. Tm =200C

Polyhydroxyvalarate (PHB):
obtained by fermentation of sucrose by the
bacterium *alcaligenes eutrophus* (A-eutrophous)
and another bacterium *P. oleovorans*.

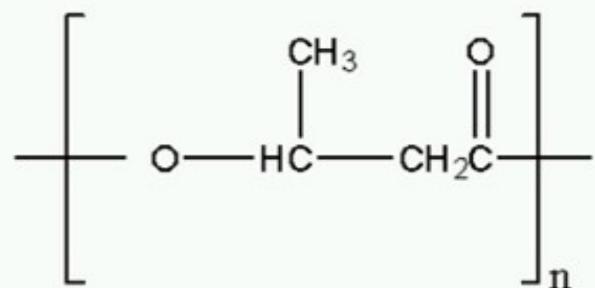


Poly(hydroxybutyrate-hydroxyvalerate) PHB-HV OR PHBV OR HB-HV COPOLYMER i.e. biopol

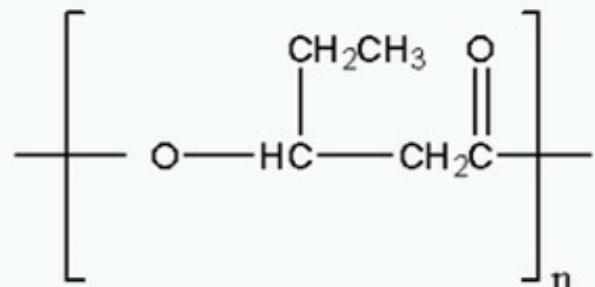
- PHB is a brittle material , it decomposes at 200C
- Addition of HV to polymer leads to several improvements
 - 1. Drop in MP
 - 2. Reduction in average crystallinity
 - 3. Increased flexibility and toughness and strength
 - 4. Improved higher extension at break.
- Produced by *A. eutrophus* when grown in presence of
 - glucose and either Glucose and either propionic acid or valeric acid.

Polyhydroxybutyrate-hydroxyvalerate preparation

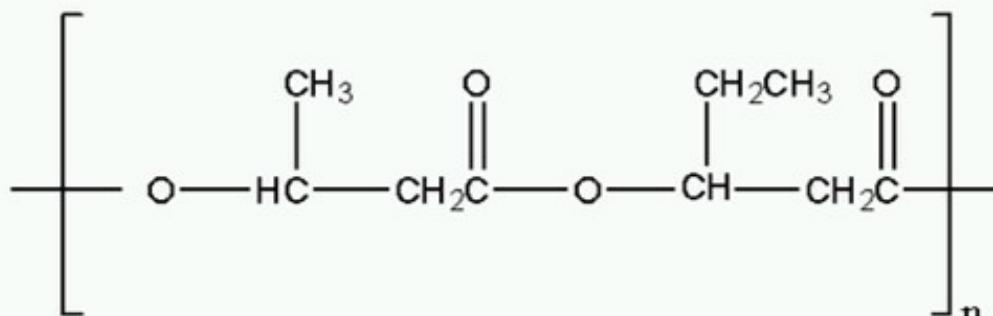
It is a copolymer



PH3B



PHV



PHBV

Poly(hydroxybutyrate-hydroxyvalerate)

Properties

- As HV increases, toughness increases
- Resistant to moisture and impermeable
- Susceptible to hydrolysis above pH 9 and below pH 3
- Resistant to oil
- Is biodegradable in aerobic and anaerobic conditions

applications

- Medical : controlled drug delivery ie. The slowly degrades to smaller fragments thus release drug in controlled manner
- Used as internal suture as non toxic
- Packaging

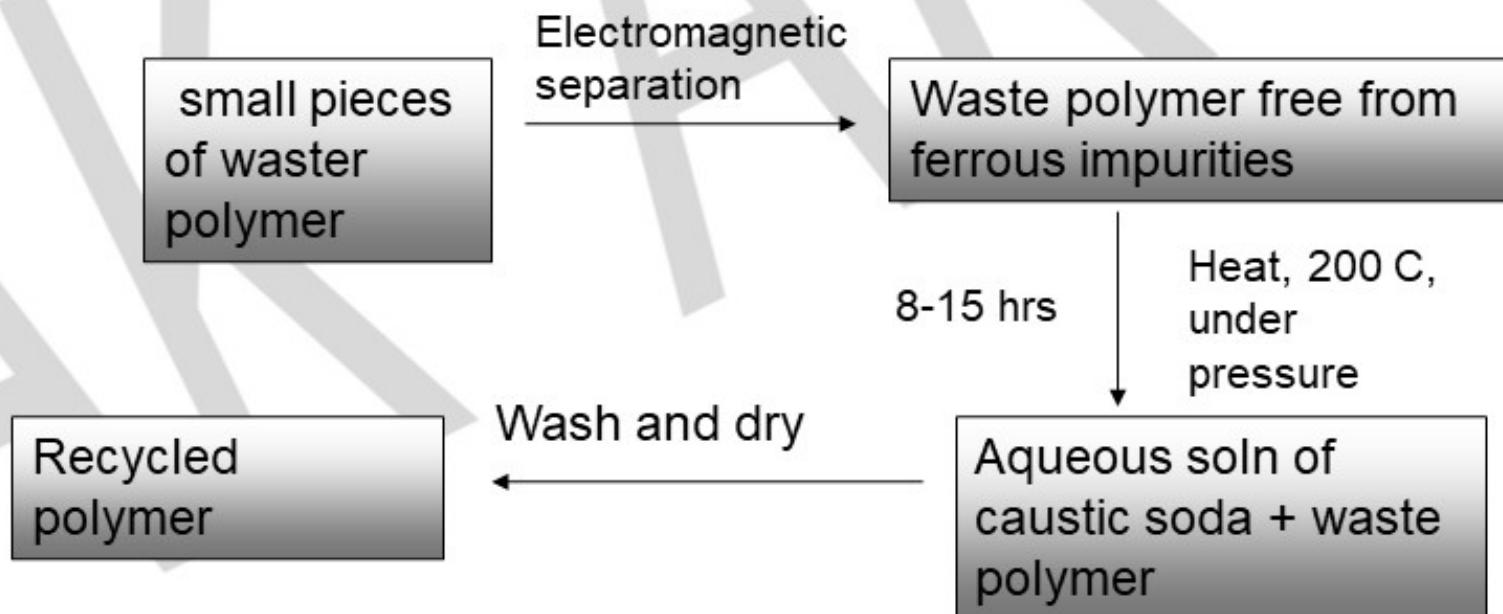
Why to recycle plastic

- Plastic in the ocean is responsible for the deaths of millions of sea animals.
- Plastic never degrades.
- Incinerating plastic contributes to greenhouse gases.
- Plastics contain harmful chemicals.
- Making new plastics requires significant amount of fossil fuels.

Recycling of Polymers/

The process in which new polymers are generated from the waste articles such as waste rubber articles, waste plastic articles etc is called as Recycling of polymers.

Process:



Properties

1. Low tensile strength
2. Low elasticity
3. Less wear resistance
4. Less costly, so economic
5. Uniform in composition
6. Good ageing properties

Uses

1. Automobiles
2. Soles and heels fo footware
3. Battery containers
4. Mechanical goods
5. Making of tyres, tubes and came back
6. Conserving energy
7. Lower emissions
8. Conservation of recourses
9. Reusability
10. Saves landfills space
11. Creates job opportunities