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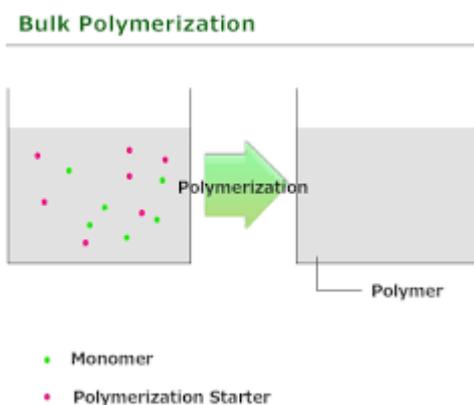
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3 POLYMERIZATION/ POLYMERS

High molecules weight compound which are formed by repetitive joining of small molecules weight components called monomers are called polymers and this process of formation is polymerization

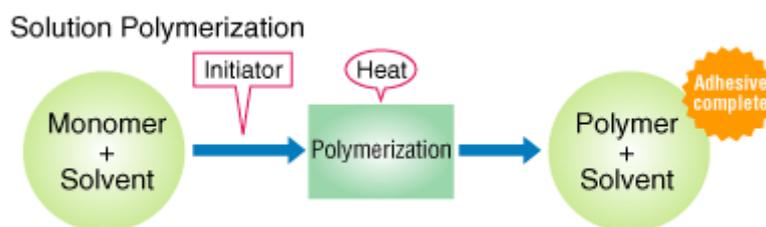
TECHNIQUES OF POLYMERISATION:

- (1) Bulk polymerization
 - (2) Solution polymerization
 - (3) Suspension polymerization
 - (4) Emulsion polymerization
- (1) Bulk polymerization**



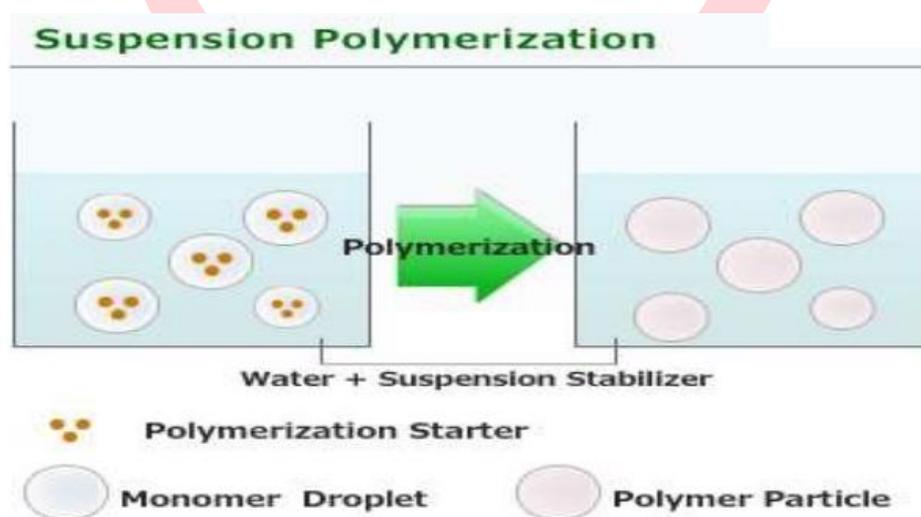
- Monomers are taken in liquid state along with initiator and chain transfer agent, so all system is in homogenous phase.
- Temperature kept high as the reaction progresses molecular weight increases and hence viscosity increases so difficulty arises in proper heat transfer within the tank and heat removal from the tank and motion of chain terminating agents.
- This mode of polymerization may be employed to obtain pure form of polymers.
- The main disadvantage of this process is to control the heat and viscosity because of its exothermic nature and some time, when the conditions are not control run- away reaction may occur

(2) Solution Polymerization



- an inert solvent is added to the reacting component in the reaction vessel
- The solvent enhances the heat capacity of the system and provide heat transfer
- Some of the solvent may be refluxed to remove heat from reacting vessel
- The main disadvantage of this process is that the final product may not be pure and contain some traces of inert solvent; therefore a separation system is required
- Low molecules weight product due to chain transfer to solvent is formed (Disadvantage)
- Low degree of polymerization may be there

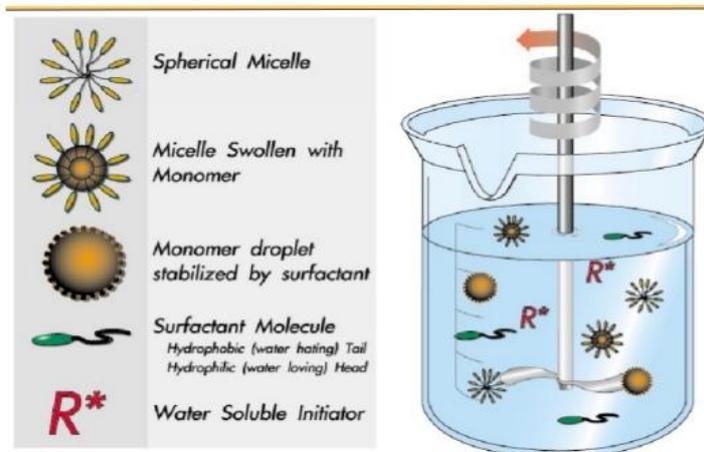
3) Suspension polymerization



- suspension polymerization: in order to control very large amount of heat in bulk, and solution polymerization in a better way, Suspension and emulsion methods are developed
- In suspension , the reaction mass is dispersed as fine droplets of size 0.1 to 1 mm in diameter
- each of these droplets (monomer droplets) act as small bulk reactor, heat transfer occurs from droplets to water having large heat capacity
- suspending agents are used to stabilize the system and also agitators are provided to keep the droplets suspended and specific size
- it produces small uniform spheres as final product
- These small uniform spheres can be used directly or may be molded in any shape.

(4) Emulsion polymerization

Emulsion Polymerization



(1) No need of agitator

(2) Surfactant keeps the micelles in above layer

- In emulsion polymerization, the dispersed particles are smaller in size i.e. less than 0.1micrometer and mass of particles is so small that they do not settle down by gravity.
- Monomers are dispersed in aqueous phase, not as droplets but as a uniform emulsion (micelles), here the formation of micelles takes place & inside that polymerization occurs
- Most used method of polymerization is emulsion polymerization
- It overcomes the difficulties of bulk polymerization, (heat control) and solution polymerization (Lower degrees of polymerization)
- It gives high degree of polymerization because micelles surface to volume fraction is high, hence high molecules weight.

TYPE OF POLYMERISATION



Addition or chain	Linear	Homopolymer	Thermoplastic
Condensation	Branched	co-polymer	Thermosetting
	cross-linked	Block polymers	Elastomer
		Graft polymers	Fines

(A) Addition polymerization or chain polymerization

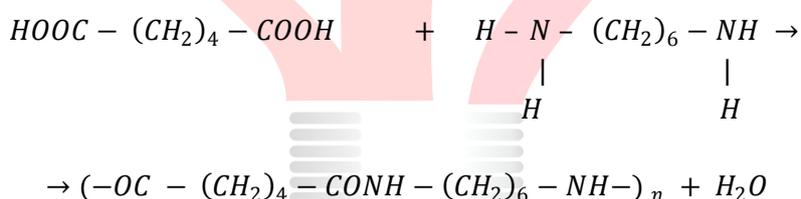
- Monomers is a single unit, it contains double bonds (unsaturated)
- When the monomer combines, there is no elimination of small molecules like water, NH₃ etc
- Example, polyethylene or polyethene from ethylene from ethylene or ethane.
- $n(\text{CH}_2 = \text{CH}_2) \xrightarrow[\text{polymeriatis}]{\text{addition}} (-\text{CH}_2 - \text{CH}-)_n$

(B) Condensation polymerization or step polymerization

- There are two or more than two monomers, here the monomer contains functional group
- When these monomers combine there is elimination of small group like ammonia, water, etc
- Example nylon 66 – (Adipic acid and Hexamethylene diamine)
- Adipic acid = 6 carbon atoms
- Hexamethylene diamine = 6 carbon atom , Nylon 6-6 name is given

->(Adipic acid)

(Hexamethylene – daimio)



1) Homo polymers -> -MMMM-

2) Copolymers -> -NMNMMNM-

3) Block polymer -> -MMM NN MMM NN MMM -

4) Graft Polymer -> -MMM MM

M = 1st Monomer

N = 2nd Monomer

1) Thermoplastic polymer:

- these are those polymer which can be reshaped by the action as heat and pressure.
- They are generally linear molecules having very little branching so that, they can easily be reshape.

Types

(1) Polyethene (2) Polypropylene (3) Polystyrene

(4) Polyvinylchloride (5) Polycarbonate.

a) Polyethene/ Polyethylene

Raw material = ethane / ethylene

The cheap source of ethylene is naphtha cracking and because of availability it is most used thermoplastic. It can be made up of three processes

High pressure process	Intermediate process	Low pressure process
(1) P= 1000 -2500 atm	P = 30 -100 atm	P = 6 – 10 atm
(2) chemical used initiators peroxide, hyper-peroxide and oxygen	(CrO ₃ &MoO ₃ Chromium oxide molybdenum oxide	Zeigler – Natta catalyst aluminum triactivated with heavy metal derivative
(3) LDPE (Low density polythene)	HDPE (High density poly-ethylene) High tensile strength and hardness than LDPE	HPDE

Uses of polyethylene

(1) Generally used as packing material

a) Difference between LDPE, HDPE &LLDPE? ? ?

On the basis as

Density, Uses, Branching, Production, properties

b) Polypropylene

Raw material: propylene

It is made by low pressure Zeigler – Natta process

Used as packing material (more rigid)

Classification of type – 4

Thermoplastic	Thermosetting	Elastomers	Fibers
1) Polyethene/polyethylene	1) Phenol-formaldehyde resins	1) styrene butadiene rubber (SBR)	1) poly-amide Nylon – 66 nylon -6
2) Polypropylene	2) urea – formaldehyde Polymer	2) Poly butadiene	2) polyester 2.1 terylen 2.2 Dacron
3) Polystyrene	3) Melamine formaldehyde resins	3) Polyisoprene	3) Acrylic fiber
4) PVC (poly vinyl chloride)	4) epoxy – formaldehyde	4) Polychloroprene	3.1 orden 3.2 Dyne
5) Poly carbonate Teflon		5) Butyl rubber	4) cellulosic Fiber
		6) Chloral butyl rubber	4.1 viscous rayon
		7) nitrilrubber	4.2 acetate rayon
		8) silicon rubber	4.3 cupramonium rayon
		9) polyutherene rubber	
		10) hypo penal	

(c) Polystyrene:

Raw material = styrene

-> used in electron wires & cables & shoe seal

Because of its ease of fabrication, thermal stabile and low cost

(d) PVC:

Raw material = vinyl chloride

It is 2nd most used thermoplastic and also most versatile as all

it contains about 56.8% chlorine and balanced hydrocarbon

A major portion of chlorine produced in world is used in manufacture of PVC

uses

1) As rigid PVC/Pipes and fittings

2) Flexible PVC/ wires insulation

-> Plasticizer are used to make PVC flexible because actually PVC is rigid in nature

(e) Poly carbonate

It is used as engineering Plastic because of its high optical clarity, impact strength, heat resistance and flame resistance

Polyethene, poly propylene, polystyrene, PVC= addition polymerization

(f) Teflon/ Polytetrafluoroethylene

It is made by emulsion polymerization, linear polymer with no branches because of strong C-F bond linkage

It is used in valves and pipes, non-lubricated bearings

2) Thermosetting polymers

These are those polymers that cannot be reshaped by the action of heat and pressure. Once they form, they are formed because of the presence of cross-linking between layers

eg: - phenol-formaldehyde resin, urea-formaldehyde resin, melamine-formaldehyde resin, epoxy-formaldehyde

(1) Phenol formaldehyde resin:

Raw material phenol & formaldehyde

it is oldest thermoset

(a) it can be acid catalyzed or base catalyzed process and accordingly it is known as novolac / Bakelite and resol

Resins are liquid which become hard with time and cannot be deformed by heat

(b) phenol-formaldehyde resins

if excess of formaldehyde is taken, then a cross-linked 3D polymer will be formed after heating and are called novolac or Bakelite resins

if equal quantity of both, phenol & formaldehyde are taken then it is resol which has limited half life

if quantity as formaldehyde is less or small then only linear molecules will be form

used as adhesives switches

(2) Urea formaldehyde polymer

Raw material: urea & formaldehyde

-> Uses: use as adhesives

(3) Melamine formaldehyde resins

-> (Molten urea) $\xrightarrow[360-700^{\circ}\text{C}]{\Delta\text{-heat}}$ Isocynaic acid + NH_3 -> Melamine (used in kitchen)

molten urea is heated at temperature of 360 to 700⁰C in presence as quartz (SiO_2), which gives isocynaic acid, this isocynaic acid when passed with alumina catalyst will get melamine

-> Uses: in kitchen ware for making crockery items

(4) Epoxy – formaldehyde

Epoxy can be formed by the reaction between phenol and epil chlorohydryl.

Uses: as a coating adhesives (paint industry)

(Glassy stage): it refer to a stage at which material is hard and brittle

Rubbery state: the state at which material is flexible and elastic

GTT (glass transition temperature):

The temperature at which material changes its behavior from glassy state to rubbery state

Elastomers:

they are the solids which have considerable flexibility because their GTT is less than room temperature

eg: SBR, Polybutadiene, polyisoperene, polychloroprene, Butyl rubber, chlorobutyl rubber, nitril rubber, silicon rubber, polyuthene rubber and hypoponal

1) Styere butudyl rubber (SBR)/(BUNA-S)

Raw material: styrene & butadiene

it is used in tier, tier related products, and non-tier application (Soal of shoes)

Most widely used elastomeric in the world

Emulsion polymerization is used in SBR manufacturing process

2) Polybutadiene

Raw material = butadiene

This used in blending agent with other elastomers

It is used with SBR as a blending agent with other elastomers. It is used with SBR as a blending agent to increase the crack resistance.

3) Polyisobutylene

This rubber is gas impermeable, thus used for making balloons, used in tube, tyre inner lining due to low permeability to air

it is also used as adhesive & sealant

Raw material = isobutylene

4) Nitrile rubber

Raw materials are acrylonitrile and butadiene

it is also known as acrylonitrile butadiene rubber

it is used in making seals and gaskets

5) Polyisoprene (Natural rubber /syn rubber)

Raw material = isoprene

it is well known natural elastomer derived from SAP of heavier tree, however synthetic polyisoprene is made by polymerization of isoprene.

6) Neoprene rubber (polychloroprene)

This can be made by dimerization of acetylene to mono vinyl acetylene followed by reaction with HCL

uses: mainly used in transportation industry

7) Chlorobutyl rubber

Raw material is isobutylene, isoprene, and chlorine

It is mainly used tubeless tier

8) Silicon-rubber – (Poly Siloxane)

Also known as polysiloxane and made from monomer having silicon oxide linkage

They have exceptional mechanical and electrical property under extreme T & P conditions
Therefore used in aero space industries & electrical appliances, etc.

9) Polyurethane rubber

It is made by reacting polyisocyanate and polyhydroxyl.

-> They find application in industrial trucks (Heavy truck)

10) Hypalon

They are chloral sulphonated polyethylene, These coms are used in conveyor belt

FIBERS

(1) Poly amide

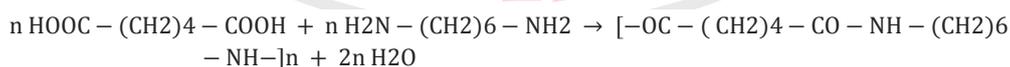
(2) Poly esters

(3) Acrylic fiber

(4) Cellulosic fibers (rayon)

(1) Polyamides: A polyamide is a macromolecule with repeating units linked by amide bonds. Polyamides occur both naturally and artificially. Examples of naturally occurring polyamides are proteins, such as wool and silk. Artificially made polyamides can be made through step-growth polymerization or solid-phase synthesis yielding materials such as nylons, aramids, and sodium poly(aspartate)

Nylon 66 (C₁₂H₂₂N₂O₂)_n: Nylon 66 is synthesized by polycondensation of hexamethylenediamine and adipic acid.



Raw material: Adipic acid Hexamethylenediamine (these both can be made by cyclohexane)

Nylon 6 (C₆H₁₁NO)_n

Raw material: Caprolactum (which can be made by cyclohexane)

Nylon 6 is synthesized by ring-opening polymerization of caprolactam. Caprolactam has 6 carbons, hence 'Nylon 6'. When caprolactam is heated at about 533 K in an inert atmosphere of nitrogen for about 4-5 hours, the ring breaks and under goes polymerization. Then the molten mass is passed through spinnerets to form fibers of Nylon 6.

Nylon 6 fibers are tough, possessing high tensile strength, as well as elasticity and lustre. They are wrinkle proof and highly resistant to abrasion and chemicals such as acids and alkalis. The fibers can absorb up to 2.4% of water, although this lowers tensile strength. The glass transition temperature of Nylon 6 is 47 °C.

(2) Polyesters: Polyester is a category of polymers that contain the ester functional group in their main chain. As a specific material, it most commonly refers to a type called polyethylene terephthalate (PET). Polyesters include naturally occurring chemicals, such as in the cutin of plant cuticles, as well as synthetics through step-growth polymerization such as polybutyrate.

(a) Tereylene c(Polyethylene triphalate)

->Raw material = ethylene glycol and PTA

(b) Dacron (Polyethylene Terephthalate)

Raw material = ethylene glycol and dimethyl terephthalate

3) Acrylic fibers

1) Orlon

Raw material: Acrolonitrile

2) Dyne (modified acrylic fiber)

Raw material = (acrolonitrile) + (vinyl chloride)

4) Cellulosic fiber (Rayon)

4.1) viscous rayon

Raw material are = cellulore, NaOH, CS₂

4.2) Acetate rayon

Raw material are = wood pulp, acetic anhydride and H₂ SO₄

4.3) Cupramonium rayon

Raw material are = copper salt, cellulose and NH_3

