POLYMERISATION – TECHNIQUES

There are four types.

① BULK – POLYMERISATION ⇒ It is also called mass or Block polymerisation.

Components :-

(i) The monomer is taken in the liquid state and the initiator is dissolved in the moromers.

(ii) The chain transfer agent (whenever used to control the mol. wt.) also dissolved in the monomer itself.

(iii) The whole system is in homogeneous phase.

(iv) The reaction mass is heated or exposed to a radiation source for initiating the polymerisation & is kept under constant mixing (हिलाना मेलगाए रखना).

Advantages :-

(i) It is quite simple technique.

(ii) Product obtained has no contaminates (दूषित) agent.

(iii) Straight forward (सीधा आगे) recovery of the polymer.

(iv) The polymer obtained can also be used as such since no isolation from the other components is involved.

Disadvantages :-

(i) As the polymerisation proceeds the viscosity of medium increases and mixing become difficults.

(ii) Broad mol. wt distribution curve is found.

(iii) As the medium gets viscous, the diffusibility

of the growing polymer chains become restricated so the probability of the chain collision becomes less, Termination becomes difficult, active radical sites accumulates and the rate of polymerisation increases enormously. The whole phenomenon is called auto acceleration / Def

OR

* In this tech the medium become viscous and diffusibility of growing polymer chains becomes restricated. Polymer chain could not collide with each other & chain termination become difficult and ~~rate of~~ reaction increases rapidly.

Sometimes due to this uncontrolled exothermic reaction explosive takes place all phenomenon is called autoacceleration

Uses: ① free radical polymerisation of PMMA, styrene to get transparent moulding powder / cast sheeting

② Polymerisation of vinyl chloride to get polyvinyl chloride, (PVC)

③ PF condensation carried-out in a mold under pressure

Imp. feature

① It is usually a homogeneous system

② for very high conversion, longer duration is required

③ Polymer obtained is highly pure

④ viscosity of the medium rapidly increases and proper mass transfer

n ; Kfr

Diffusive

C.Cl4 Solvent

② SOLUTION POLYMERIZATION ⇒

Procedure ⇒ The monomer and chain transfer agents is dissolved in a suitable inert solvent (CCl_4). Then the free radical initiator is also dissolved in solvent medium while ionic and coordination catalyst can either be dissolved or suspended.

Co-ordination catalyst ⇒ Zeiglar Natta catalyst / Tichy. Al (C_2H_5)$_3$ e.g.

Advantages :-

① In this tech inert solvent medium helps to control viscosity increases and promote a proper heat transfer.

② This tech can be used where the polymer is employed in its soln form, as in the case of certain adhesives and coating compositions.

③ It is also useful in systems where the polymer formed is insoluble in its monomer

Disadvantages ⇒

① In this tech the use of inert solvent the chain transfer to the solvent so it is difficult to get high mole. wt polymer. (major disadvantage)

② The polymer solution method often requires handling of flamable of hazardous solvent and removal or recovery of solvent to isolate the polymer after the polymerisation is over

③ The polymer formed is isolated from soln either by evaporation of solvent or by precipitation in a non solvent. and removal

of their final traces is always extremely difficult.

Advantages: But however it can advantageous where the polymer is used in its soln form by brushing or spraying as in a case of certain adhesive & coating, or In systems where polymer formed is insoluble in its monomers or solvents

USES:

PAN

① Industrial production of poly acrylonitrile by free radical polymerisation.

② Production of poly isobutylene by cationic polymerisation.

~~③ Block co-polymerisation are also made exclusive by this tech.~~

③ Block co-polymers are mostly prepared by this tech.

④ This tech most suitable for making low mole. wt. products.

	Bulk	Solution	Suspension	Emulsion
	Case1	Case2	Case3	Case4
Monomer & solvent	Soluble	soluble	soluble	soluble
Initiator	soluble	insoluble	insoluble	soluble
Polymer	Soluble	Soluble	Insoluble	Insoluble

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(3) SUSPENSION - POLYMERISATION

* It is also known as Bead / pearl polymerisation

Procedure :-

(i) This tech. is used only for water insoluble monomer.

(ii) The monomer is suspended in water in the form of fine droplets.

Water + Monomer ⟶ Droplets formation

(iii) The monomer droplets are stable and can not undergo collision by the use of suitable water soluble protective colloids, surface active agent & by stirring.

(iv) The size of the monomer droplets depends on (a) the monomer-to-water ratio.
(b) The type & the conc^n of the stabilizing agent
(c) The type & speed of agitation

(v) The initiators are monomer soluble

(vi) Since each monomer droplets is isolated & independent of the other droplets.

(vii) In suspension polymerisation oil soluble initiators such as organic peroxide, hydroperoxide or azo-compound are used and thus each tiny droplets behave as a miniature bulk polymerisation system.

(viii) At the end of the process polymer appear in the form of tiny beads or pearl hence the process is also known as pearl polymerisation.

(ix) Monomer extracted by filteration or wash by water.

Polymer

* The polymer are filtered or washed by the water to remove the water soluble stabilizer & then dry.
* The size of the monomer solvent droplets usually range b/w 0.1 to 5 mm diameter and depend on (IV) point

Advantage ⇒

* (1) This tech. is designed to combine the advantages of both bulk & Soln tech.
(2) Each monomer droplet is isolated & independent of other droplets
(3) The continuous aq. phase act as efficient heat transfer medium & hence exothermally is well controlled
(4) Since water is used as heat transfer medium & the process is also economical, available at low cost, non-toxic nature, ease of storage and handling.
(5) Polymerisation proceed to 100% conversion i.e from monomer to polymer.
(6) Isolation of the product become easy by filteration of the beads & removal of the surface active agent and protective colloids by water washing.
(7) water washed and dried product can be used as moulding purpose or can dissolved in suitable medium for use adhesives and coatings.

Disadvantage:

1. Continuous agitation is required
2. Contamination by stabilizer agent
3. Washing and drying may required
4. It require longer duration for very high conversion.

USES →

(i) Expendable polystyrene beads (from which polystyrene foams are made), styrene-divinyl benzene co-polymer beads (for the preparation of ion exchange resins) and polyvinyl acetate beads are produced by the suspension tech, using free-radical initiators.

(ii) Polyvinyl acetate beads convert into polyvinyl alcohol.

EMULSION - POLYMERISATION

Monomer water insoluble but do not form droplets

1. This is tech in which addition polymerisation is carried out in a water soluble medium containing soap (emulsifier) & suitable initiator.
2. The most interesting & useful polymers formed by this method. Exa: Synthetic rubber of Sunatype.
3. In this tech water is used as a medium
4. In this tech reaction takes place within a small hollow sphere composed of a

film of soap molecule is micelle.

⑤ Monomer is dispersed in water not as droplets but as a uniform emlusion. monomer diffused into this micelles

~~⑥ Monomer is dispersed in water not as droplets but as a~~

⑥ Initiator ⇒ Persulphate or hydrogen peroxide are water soluble & monomer is water insoluble

⑦ The emulsion system is added with various types of ingradients to make the polymerisation possible.

Nine basic ingradients are

① Basic phase ⇒ This is usually water freed from all inorganic impurities

Amount 60-80%

② Main monomer ⇒ The principle component of reaction (butadiene or vinyl chloride)

60-80% final polymer

15-30% Emulsion

③ Additional ⇒ The monomer which co-polymerised with the main monomer

Exa: vinyl acetate, Styrene, acrylates, or acrylonitriles 5-15% of the emulsion system.

Note ⇒ By changing the ratio of main & additional monomer we can change the properties of polymer

④ Emulsifying agent ⇒

Required for the production of colloidal dispersion.

Selection of Emulsifying agent depend upon the reaction.

Typical Emulsifying agent are soap & detergents.

Exa: Carboxylic acid & sulphonic acid soaps, resin soaps, sulphonated long-chain alcohols, amines.

The amount usually ranges from 0.2 - 2%

emulsifier molecule or surfactant molecule has two part.

- Head (Polar) water soluble
- Tail (Nonpolar) Long hydrocarbon chain Insoluble.

(V) Emulsion stabilizer ⇒

It is used to protect the colloidal particles from precipitation. Emulsion stabilizer are known as protective colloids.

Exa:- Carboxy methyl cellulose, Polyvinyl alcohol, gelatine, starch.

★ They are used in emulsion polymerisation not to control rates / degree of polymerisation but for the purpose to obtained and to prevent emulsion breakdown with progress of polymerisation.

★ (VI) Surface tension regulator (Surfactants) :-

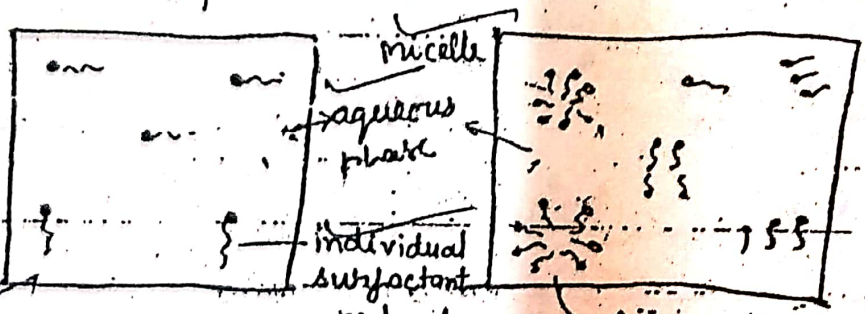
Exa: octanol, roryl alcohol

surfactants reduced the surface tension & gives good emulsion of the monomer in water.

At low conc. surfactants are dissolved in aq phase. But when their Conch is increased they form molecular aggregates known as Micelle

The conch. beyond which micelle formation is possible is known as CMC.

Emulsifier molecule or surfactant molecules are made of two parts a polar group and a long non polar hydrocarbon chain



(a) surfactant molecules dissolved in water at low conc.

(b) surfactant molecules dissolved in water at CMC.

→ In the interior of micelle, monomers are present.

→ Initiators are insoluble in monomer but soluble in water. so they are present in a aqueous phase.

→ The surface layer of micelle formed by the polar ends of the emulsifier

molecules is highly hydrophillic and, hence an appreciable conc of the micelle is filled with the solubilised monomer. Initiator is found at this place.

Polymerisation, therefore, starts at the surface layer of micelle and proceeds inwards. At the micelle however, we have a very favourable condition for the polymerisation to occur.

At the end of polymerisation, we have fine particles of the polymer. This milky white dispersion is often called 'latex'

Use: The latex can either be used as such for making adhesives, water-soluble emulsion paints.

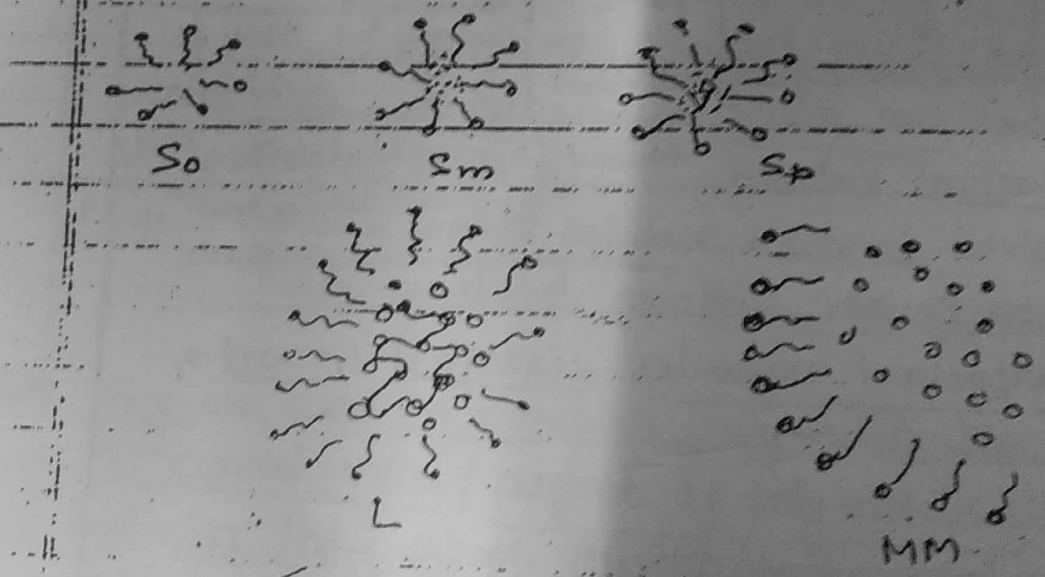


fig: So = the empty micelle
Sm = Monomers filled micelle
Sp = Micelle with growing polymer chain
MM = Monomer droplets
L = latex particle containing monomer as well as growing polymers.

(vii) Catalyst :- Used to accelerate the polymerisation.

(viii) Regulator ⇒ It is added to have a disactive effect on the reaction and perticularly tend to decrease the amount of cross linking or side chain reactions.

Exa: Dodecyl mercaptane

(ix) Buffer :- The pH of the emulsion must be mention for proper stability Exa: phosphate Carbonates, acetates are used for this purpose.

(x) Short stops ⇒ A selected inhibitor known as short stop may be added in small amount into the system in order to stop the reaction

Advantages :-

1. Rapid polymerisation to high mol. wt
2. The homogeneity of the polymer
3. Narrow distribution curve of m.wt.
4. Good heat control
5. Direct usable
6. Viscosity build up of the polymerisation mass is quite low
7. high mol. wt product is achieved by this techniques.

Disadvantages :-

1. Isolation- The polymer can be isolated from the latex by destabilizing the emulsion (using some electrolyte) by spray drying or by freezing.

(3) Leads to poor colours
(4) Washing, drying & combing may be required

USES:
* This tech is extensively for the free radical polymerisation of vinyl monomers containing water soluble initiator
* The monomers like vinyl chloride, butadiene, chloroprene, vinyl acetate, acrylates and methacrylates are polymerised by this tech.

क्रीम मार्क

The conc of the surfactant at which the phenomenon of micellization occurs is called CMC (critical micellar concentration)

Surfactant types

Cationic, Anionic, Nonionic, zwetterion

Suspension	Emulsion
① It have monomers droplets	① It have micelle in which the monomer is solubilized
② The quantity of emulsifier added is less than CMC	② The quantity of emulsifier added is to equal or more than CMC

Bulk polymerisation	Soln polymerisation
① Monomer is polymerized in its own medium only	① Monomer dissolved in a solvent
② Monomer soluble in catalyst is used	Catalyst soluble in monomer water mixture
③ Heat transfer is difficult	Heat transfer is done by solvent
④ No separation and drying of the polymer (for solid)	separation & drying (for some) is tough process (can be used as such)
⑤ Polymer very pure	Polymer contains solvent molecule
⑥ Rate of Polymerisation (R.P) & Degree of polymerisation (DP) is high	D.P is depend on solvent D.P is limited
⑦ Equipments are simple	equipment complex
⑧ Conversion cost high	Conversion cost highest

Emulsion polymerization	Suspension polymerization
Monomer is in emulsified form agitation weaker than suspension.	Monomer is suspended in water stabilizer very rapid agitation
water soluble catalyst is used	Monomer soluble catalyst is useds
Heat transfer is rapid and Emulsion act as a medium	Heat transfer is rapid and takes place to water
Coagulation after processing is costly	Separation & drying process are simple
Purity of polymer is poorest than suspension	Polymer is pure but has lower stability and clearity than in bulk method.
R.P is fastest D.P is also very high	R.P is high. D.P is high.
Rate of polymerization (R.P.) Degree of polymerization (D.P.)	
Simplest	Simplest
Conversion cost lowest	conversion cost higher than emulsion and lower than bulk.