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 monomers.

(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.

Advantages :-

(i) It is quite simple technique

(ii) Product obtained has no contaminates agent

(iii) Straight forward recovery of the polymer.

(IV) The polymer obtained can also be used as such since no isolation from the others 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

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
$TiCl_4 . Al(C_2H_5)_3Cl$

Advantages :-

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

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

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 solution method often requires handling of flemable 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

Diffusive
CCl_4 Solvent

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