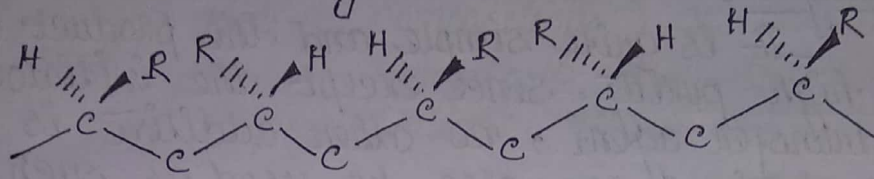


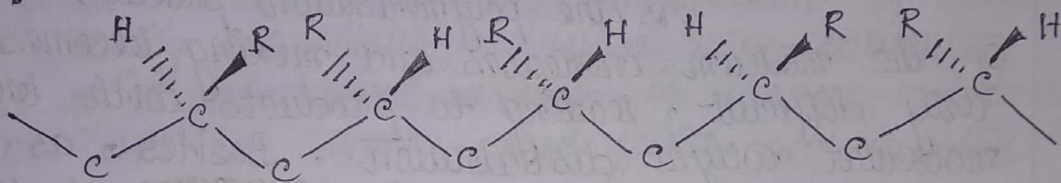
### ⑥ Syndiotactic polymer :

In a configuration, if the R groups regularly alternate from one side of the plane to the other with respect to the extended-chain backbone, the polymer is termed syndiotactic.



### ⑦ Atactic polymer :

In a configuration, if the R groups have no preferred placement w.r.t. the plane of the chain-extended-chain backbone, the polymer is termed atactic.



In general, tactic polymers (i.e. isotactic or syndiotactic) are partially crystalline, while atactic polymers are amorphous indicating the absence of all crystalline order. Thermal and mechanical behavior can also be significantly affected by tacticity of the polymer. Formation of tactic polymer depends on specific conditions such as temperature and solvents.

### ▶ Polymersisation - Fine Technique :

Factors such as nature of monomer, the type of polymerisation mechanism chosen, the required physical form of the polymer & the viability of the process for industrial productions are the conditions under which polymerisation is carried out.

⑧ Bulk polymerisation : The monomer is taken in liquid state. Initiator and chain transfer agents are dissolved in the monomer. The whole system is in a homogeneous phase and is heated or exposed to a radiation source for initiation. The system is kept under agitation

for proper mass and heat transfers.

Example: Polymethyl methacrylate, polystyrene, PVC, polyethylene.

### ▶ Advantages:

It is quite simple and the product obtained has a high purity. Since except the initiator and chain transfer agent, no other additive is used. The polymer obtained can also be used as such since no isolation is involved. It is also used for casting into final product form (i.e. cast polymerization). It has high yield per reactor volume.

### ▶ Disadvantages:

As the polymerisation proceeds, the viscosity of the medium increases and mixing becomes progressively difficult, leading to products with broad molecular weight distribution. Besides, as the medium gets viscous, the diffusibility of the growing polymer chains becomes restricted, the probability of chain collision becomes less, termination becomes difficult, active radical site accumulated and the rate of polymerisation increases enormously. The whole phenomenon is called 'autoacceleration' or 'Trommsdorff' or 'Gel effect'. Sometimes, the uncontrolled exothermic reaction can lead to an explosion.

### ⑥ Solution Polymerisation:

The monomer is dissolved in a suitable inert solvent along with the chain transfer agent, if required. The free radical initiator is also dissolved in the solvent. The ionic or co-ordination catalysts, can either be dissolved or suspended.

Example — Polyisobutylene, Block-co-polymers, Polystyrene, Polybutadiene

### ▶ Advantages :

The presence of inert solvent-medium helps to control the viscosity increase and promote a proper heat transfer. It can be used where the polymer chain is used in its solution form (e.g. adhesives & coating compositions) or in the system where the polymer formed is insoluble in the solvent and precipitation carried out as slurry.

### ▶ Disadvantages :

Although the solvent is inert, chain transfer to the solvent cannot be completely ruled out and, hence, it is difficult to get very high M.W. products. It involves isolation of the polymer formed either by evaporation of the solvent or by precipitation in a non-solvent. Removal of their final traces is always extremely difficult. So, it has a small yield per reactor volume.

### © Suspension Polymerisation :

Only water-insoluble monomers can be polymerized. The monomer is suspended in water in the form of fine droplets & are stabilized by using suitable water soluble protective colloids, surface-active agents. The initiators added are monomer soluble. Each monomer droplet is isolated serves as an independent bulk-polymerisation nucleus. As the products are obtained as spherical beads or pearls, the technique is known as bead or pearl polymerisation.

Examples — Polystyrene beads, Polyvinylacetate beads.

▶ Advantages : The continuous aqueous phase separating monomer droplets acts as an efficient heat transfer medium, hence exothermicity is well controlled. The process is economical as water is used as solvent.

Because of tiny droplets, control on kinetic chain length is good, resulting in a narrow molecular weight distribution. The reaction proceeds to 100% conversion & product isolation is easy by filtration.

### ▶ Disadvantages :

Polymer purity is low due to the presence of stabilizing & suspending additives. Reaction capital costs higher than for solution polymerisation.

### ① Emulsion Polymerisation :

Like suspension polymerisation, emulsion polymerisation is also involved dispersion of monomer in the aqueous phase not as discrete ~~droplets~~ droplets, but as a uniform emulsion. The emulsion is stabilized by surface active agents (surfactants), protective colloids & also by certain buffer. The surfactants can be cationic, anionic or non-ionic and serve the purpose of lowering the surface tension at the monomer-water interface & facilitate emulsification of the monomer.

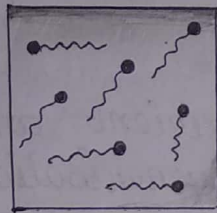
Because of low solubility, surfactants get fully dissolved or molecularly dispersed only at low concentrations. Beyond a particular concentration, the excess quantity does not get molecularly dispersed, but forms molecular aggregates known as "micelles". The highest concentration, wherein all the molecules are in dispersed state, or the concentration beyond which only micelle formation is possible is known as "critical micelle concentration" (CMC).

### ▶ Examples of surfactants

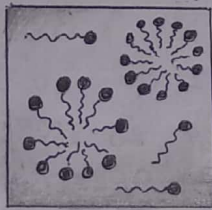
		CMC (g/l)
Anionic	$\text{CH}_3(\text{CH}_2)_6\text{COONa}$	$6.5 \times 10^{-4}$
	$\text{CH}_3(\text{CH}_2)_{10}\text{COONa}$	5.8

Surfactants	CMC (g/L)
Cationic	
$\text{CH}_3(\text{CH}_2)_9\text{-NH}_2\text{HCl}$	8.5
$\text{CH}_3(\text{CH}_2)_7\text{N}(\text{CH}_3)_3\text{Br}$	$7.8 \times 10^{-1}$
Non-ionic	
$\text{CH}_3(\text{CH}_2)_7\text{C}_6\text{H}_{11}\text{O}_6$	7.3

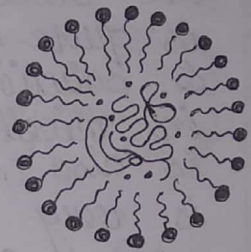
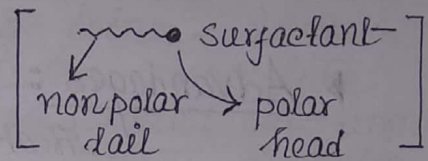
In micelle formation, the emulsion molecule aggregate in such a way that the polar ends align themselves outward & the hydrocarbon ends come close to each other at the interior.



Surfactant molecules completely dissolved



Surfactant molecules dissolved as well as aggregate beyond conc.



The interior of the micelle is hydrophobic where monomers can be stabilized, and therefore undergo polymer.

**N.B**: If the monomer is slightly soluble in water, then the aq. emulsifier sol. phase will also contain a part of the monomer dissolved in it.

Polymerisation starts at the surface layer of the micelle & proceeds inwards. When monomer inside the micelle is condensed, more monomer diffuses into the micelle from the monomer droplets present in the aqueous phase. As the polymer chain concentration increases, they agglomerate (ठोस होना) into fine particles which again absorb the monomer & swell in size. At a particular stage the micelle bursts and form an adsorption layer around the particle.

At the end of the polymerization, the