

## **polymerization Methods**

- Bulk Polymerization
- Solution Polymerization
- Emulsion Polymerization
- Suspension Polymerization

### **Bulk polymerization:**

In this method, the monomer is taken in the liquid state and the initiator is dissolved in the monomer. The chain transfer reagent, if required, is also dissolved in the monomer.

The function of chain transfer reagent is to control the molecular weight of the final polymer and result in a homogenous phase.

The resultant mass is heated or exposed to radiations of particular wavelength for the initiation of the polymerization. As the polymerization reaction proceeds, the viscosity of the medium increases and hence the mixing becomes progressively difficult, which is the disadvantage.

Another disadvantage of this process is the restricted diffusibility of the growing polymer chain, because of the higher viscosity of the medium.

the accumulation of active radical sites causes the enormous increase in the polymerization rate, leading to the auto-acceleration mechanism and ultimately to explosion, if not controlled properly.

### ***Advantages of Bulk Polymerization***

- (i) simplicity
- (ii) higher purity of the polymer obtained
- (iii) no requirement of additives other than the initiator and the chain transfer reagent and
- (iv) direct utility of the polymer with no isolation requirement (due to higher purity)

### ***Disadvantages of Bulk Polymerization***

Viscosity increases as conversion increases, making heat removal and processing more difficult.

Bulk polymerization is used in the free radical polymerization of methyl methacrylate ( $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COOCH}_3$ ) or styrene ( $\text{H}_2\text{C}=\text{CHC}_6\text{H}_5$ ) to get transparent powders of PMMA or polystyrene (thermocole) and also the cast sheets of poly vinyl chloride (PVC).

### **Emulsion polymerization:**

In this type the monomer is dispersed in aqueous phase as emulsion. The emulsion is stabilized by the addition of surfactants (surface active agents), protective colloids and some buffers.

Anionic surfactants such as sodium or potassium aryl sulphonates or cationic surfactants such as alkyl amino hydro chlorides or alkyl ammonium halides or non-ionic surfactants such as alkyl glycosides or saccharic esters of higher fatty acids are used.

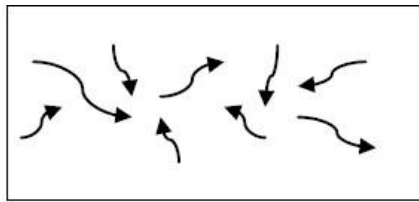
They function by lowering the surface tension at the water-monomer interface and hence facilitate the emulsion of monomer in water. Due to their low solubility, surfactants are molecularly dispersed even at low concentrations.

At a particular concentration, the excess un-dissolved ones form as molecular aggregates, called **micelles** and an equilibrium is established between the dissolved surfactant molecules and the aggregated micelles.

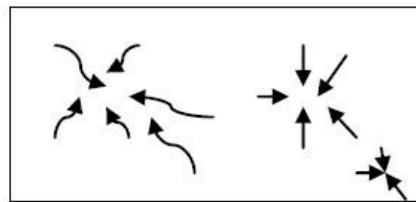
*The highest concentration of surfactants wherein all the molecules are in the dispersed state and the concentration beyond which the micelle formation is possible is termed as critical micelle concentration (CMC).*

The emulsifier molecules are made of two parts – a long, non-polar hydrocarbon (H/C) moiety, to which is attached a polar entity such as  $-\text{COONa}$ ,  $-\text{SO}_3\text{Na}$ ,  $-\text{NH}_2\cdot\text{HCl}$ ,  $-\text{NBr}$  etc.

In micelle formation, the emulsifier molecules aggregate in such a way that the polar ends align outward and the H/C ends come close to each other at the interface.



Randomly aligned but complete  
Distribution at low concentration



Micelles

[— - non-polar H/C chain (tail) ; → polar end (head)

Due to the proximity of the H/C entities of all emulsifier molecules, the interiors of the micelles act as the H/C phases, where the monomers can be made soluble. On further addition of the monomer followed by agitation, emulsification takes place. The resultant emulsion is a complex system.

These micelles possess favourable condition for polymerization to occur. The initiator molecules are available at the surface layers whereas the interior of the monomer is filled with the solubilized monomer.

Hence the polymerization starts at the surface and proceeds inwards. On consumption of the monomer in the micelle, more amount of monomer diffuses from the aqueous phase, into the micelle.

The polymer chain growth continues until another radical species enters and arrests the chain growth. With more and more amount of polymer formed, the polymer chains aggregate into fine particles and get surrounded and stabilized by the emulsifier layer.

At the end of polymerization, the fine particles of the polymer are stabilized by the emulsifier layer and dispersed uniformly in the aqueous phase. The resultant milky white dispersion is termed as **latex**, which can be used as such for applications like adhesives, emulsion paints or the polymer can be isolated from the latex by the destabilization of the emulsified polymer mass using electrolytes or by spray drying or by freezing.

Depending upon the relative solubility of the monomer and initiator in water and the ratios of amounts of monomer / water and emulsifier water, the

polymerization occurs either at the dissolved phase or at the interface or at the surface or inside the monomer droplets.

### **Advantages:**

- Thermal and viscosity problems are minimized due to the high heat capacity and ease of stirring of the continuous aqueous phase.
- The latex may be used directly without purification.

### **Disadvantages:**

- The heat transfer is very difficult with this technique and hence the viscosity build up of the polymer mass is quite low compared to the bulk and solution polymerization techniques.

Emulsion polymerization is the most widely used industrial technique for the polymerization of monomers such as vinyl chloride ( $\text{H}_2\text{C}=\text{CH}.\text{Cl}$ ), buta-diene ( $\text{H}_2\text{C}=\text{CH}.\text{CH}=\text{CH}_2$ ), chloroprene ( $\text{H}_2\text{C}=\text{CCl}.\text{CH}=\text{CH}_2$ ), vinyl alcohol ( $\text{H}_2\text{C}=\text{CH}.\text{OH}$ ), acrylates ( $\text{H}_2\text{C}=\text{CH}.\text{COO}^-$ ) and methacrylates ( $\text{H}_2\text{C}=\text{C}(\text{CH}_3).\text{COO}^-$ ) etc.

### **Solution polymerization:**

In this technique, the monomer and the free radical initiator are dissolved in a suitable solvent, along with the ionic co-ordination catalyst and the chaintransfer reagent, if any.

The selection of some inert solvent enables viscosity control and prevents heat transfer.

The advantage of this method lies in its use when the polymer is used in solution form or when the polymer is insoluble in monomer or any other solvent or precipitates out as slurry and is amenable for easy isolation.

### **Advantages:**

- Solvent acts as a diluent and aids in removal of heat of polymerization.
- Solvent reduces viscosity, making processing easier.
- Thermal control is easier than in the bulk.

**Disadvantages:**

- Chain transfer to solvent occurs, leading to low molecular weights.
- Difficult to remove solvent from final form, causing degradation of bulk properties.
- Environmental pollution due to solvent release.

**Suspension polymerization:**

Water-insoluble monomers are polymerized by this technique.

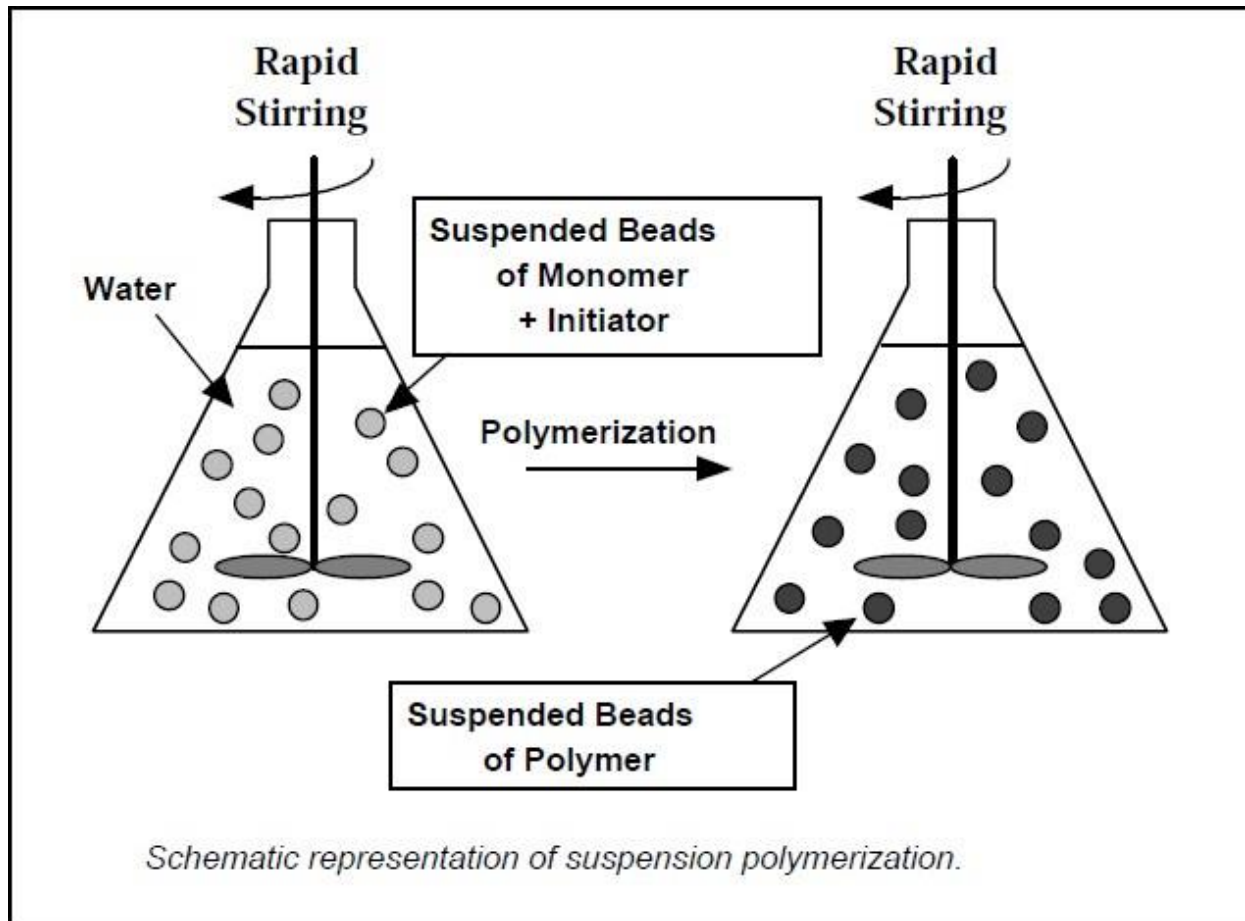
The monomer is suspended in water in the form of fine droplets, which are then stabilized against coalescence, using stabilizers, surfactants, protective colloids and by stirring.

But the initiators are monomer-soluble. Each monomer droplet is isolated and is independent of other droplets and hence acts as an independent bulk polymerization nucleus (where the polymer chain growth starts and proceeds). The continuous aqueous phase separating the monomer droplets, acts as the efficient heat transfer medium and hence the exothermicity is controlled.

The size of the monomer droplets depends upon the monomer/water ratio, type and concentration of stabilizers and the mode and speed of agitation. This technique is more economical compared to solution polymerization technique, since water is used as the heat transfer medium.

As the entire bulk of the monomer is divided into numerous tiny droplets, the control of the kinetic chain length (chain length of living polymer; that in chain propagation stage) of the formed polymer is quite good and results in a fairly narrow molecular weight distribution of the product. Thus the polymerization proceeds to 100% conversion levels and the product is obtained as '*spherical beads or pearls*'. The technique is so termed as *bead or pearl polymerization*.

The isolation of the product is easy as it involves only the filtration of pearls or beads and the removal of surfactants and other additives by mere washing with water. The water-washed and dried polymer sample is as such used formolding purposes or can be dissolved in a suitable medium for use as adhesives / coatings.



Expanded polystyrene beads (for making polystyrene foams), styrene-divinyl benzene copolymers (for the preparation of ion exchange resins) and poly vinyl acetates (for further conversion to poly vinyl alcohol) are produced by suspension polymerization technique.

**Advantages :**

- Low viscosity due to the suspension
- Easy heat removal due to the high heat capacity of water
- Polymerization yields finely divided, stable latexes and dispersions to be used directly in coatings, paints, and adhesives.

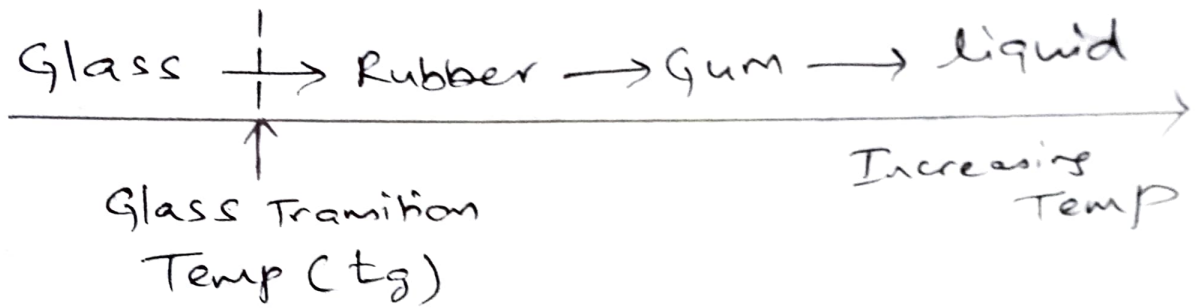
**Disadvantages:**

- Cannot be used for polymers whose glass transition temperature is less than the polymerization temperature or else aggregation will occur.

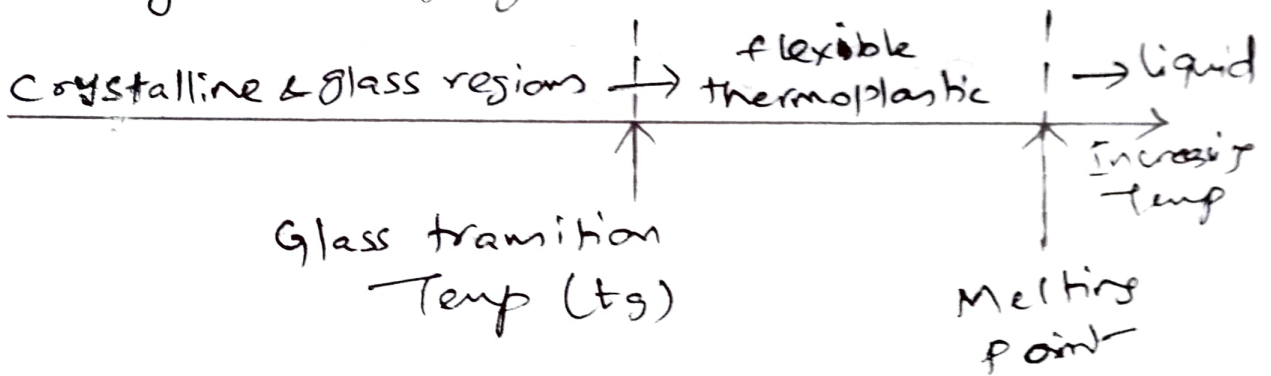
## Unit - IV

### Testing of polymers

(a) Amorphous polymers



(b) Crystalline polymers



(1)  $T_g$ :- The temp at which a hard glassy state of an amorphous material is converted into a rubbery state. This is possible in thermo setting polymers. The glassy state of a thermo setting polymer is very hard & rigid. The rubbery state is very viscous. Only amorphous & semi-crystalline polymers have  $T_g$ .



## factors affecting $T_g$ !

- (1) presence of bulky groups increases amorphous nature thereby it  $\uparrow T_g$
- (2) cross linking  $\rightarrow \uparrow T_g$ . so it affects the chemical structure of the polymer.
- (3)  $T_g \propto$  molecular wt of compound
- (4) plasticizers  $\rightarrow \uparrow$  Amorphous nature  $\rightarrow \uparrow T_g$
- (5) flexibility  $\propto \frac{1}{T_g}$  of the compound

## Applications!

A rigid material with low  $T_g$  is suitable for high Temp applications.

## Melting point!

melting temp is the temp at which a solid material is converted into its liquid form. (a) solid  $\rightarrow$  melt. In this melting point of a substance, the solid phase + the liquid phase exist in equilibrium. (b) phase transition occurs.

(1) The  $T_m$  can also be referred as freezing point. (a) when the temp of a liq gradually decreases, the liq is converted into its solid phase at the same temp. (b)  $\text{solid} \rightleftharpoons \text{liq}$

(2) At this  $T_m$ , entropy of a substance increases since the tightly packed molecules of that solid substances are released.

(3)  $T_m$  is highly dependent on the pressure  
 $\therefore T_m$  is given at a specific pressure  
(a) Standard pressure.

### Factors affecting $T_m$ :-

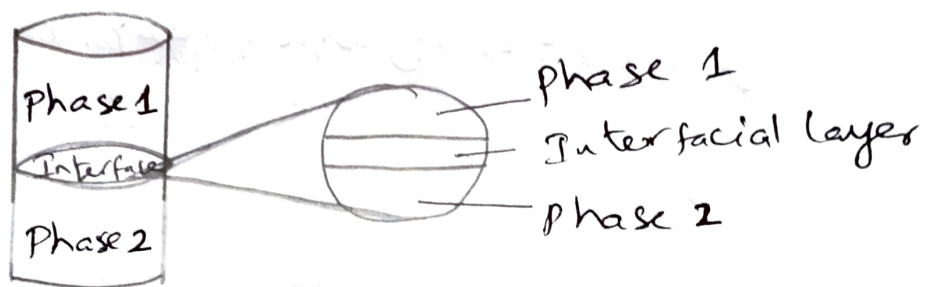
- (1) It depends on pressure (a)  $\uparrow P \rightarrow \uparrow T_m$
- (2) Strong chemical bonds between molecules will have  $\uparrow T_m$
- (3) Size + shape of the molecules affect  $T_m$ . (a) Small molecules melt easily

## Difference between $T_m$ & $T_g$ !

| S.No | $T_g$  | $T_m$   |
|------|--|---|
| 1.   | Temp at which a hard glassy state of an amorphous material is converted into a rubbery state | Temp at which a solid material is converted into its liquid form        |
| 2.   | glass state $\rightarrow$ rubber state   | Solid $\rightarrow$ liquid<br>(Phase transition)                        |
| 3.   | Observed in amorphous & semi-crystalline compounds   | Observed in crystalline substances                                      |
| 4.   | depends on chemical structure of the substance   | depends mainly on the chemical bonding of molecules & external pressure |

## Interfacial polymerization

It is a type of step-growth polymerization in which polymerization occurs at the interface between two immiscible phases (two liqs), resulting in a polymer that is constrained to the interface.



In this both liq phases may contain monomers. So monomers dissolved in both phases & polymerization occurs on both sides.

### Advantages:

- (1) polymerization is rapid & occurs at low temp.
- (2) High conversions are not necessarily required to obtain high molecular weight.

## Disadvantages:

- (1) limited to highly reactive systems
- e) Need appropriate choice of solvents to dissolve reactants.

## examples:

polyaniline, polypyrrole, polythiophene & poly(3,4-ethylenedioxythiophene).

## Polymer melt:

They are solvent free, viscoelastic liquids consisting of entangled macromolecules with a monomer volume fraction comparable with that of simple liquids.

## Polymer solutions:

Solutions containing dissolved polymers (liq solutions or solid solutions). They are used in producing fibers, films, glues, paints, light emitting devices. etc.