



CHEM3020: POLYMER CHEMISTRY

Polymerization techniques

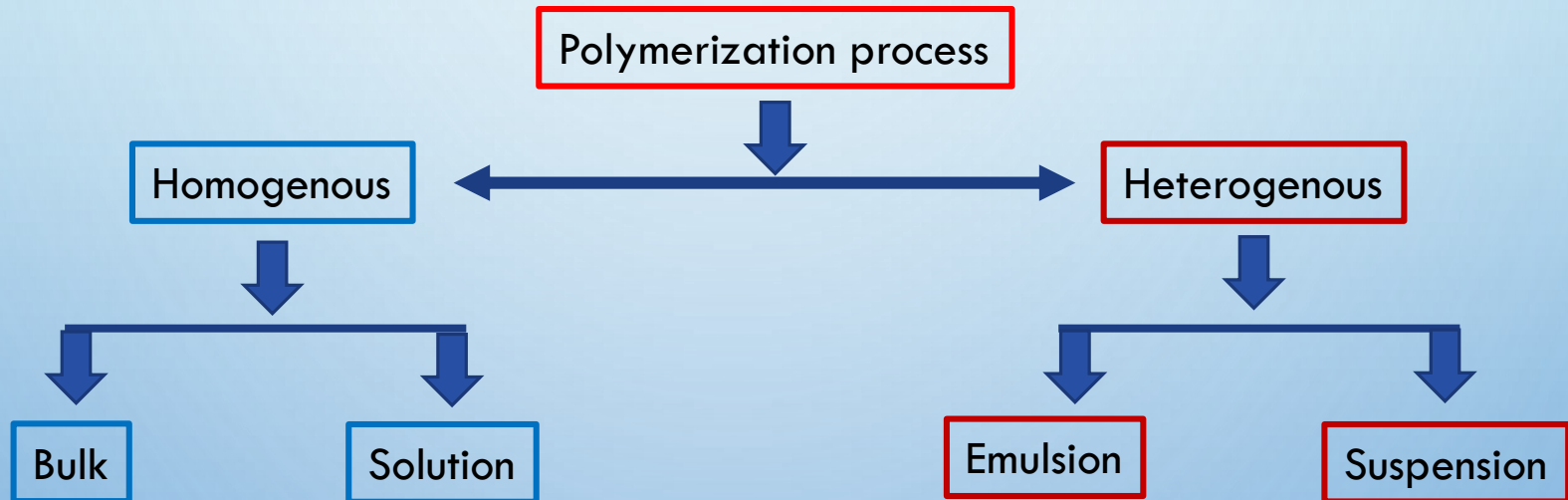
Prof. Rafique Ul Islam
Department of Chemistry, MGCU, Motihari

Polymerization techniques

UNIT-1



Polymerization techniques: Polymerization reactions are exothermic and the main concern during polymerization is to effectively dissipate the heat from the reaction mixture to avoid explosion and also for running heat sensitive polymer products. The main polymer processes are-



Homogenous polymerization process: In this process, the polymerization occurs in one phase, may be in a solvents or in a reaction vessel containing only monomer. So there two main methods, solution and bulk polymerization respectively.



Polymerization techniques

i .Bulk Polymerization : This method involves only the monomer molecule, an initiator and a chain transfer agent (if necessary). The monomer is taken in the liquid state and the initiators is dissolved in the monomer. The chain transfer agents whenever used to control the molecular weight, is also dissolved in the monomer. Therefore the whole system is therefore in a homogenous phase. The reaction mass is heated or exposed to light source for initiating the polymerization and kept under agitation for proper mass and heat transfer. As the polymerization proceeds, the viscosity of the medium increases and mixing become progressively difficult, leading to a broad molecular weight distribution.

The product of polymerization obtained from this type of process is the purest form of polymer, and the greatest yield of polymer per unit volume. The main disadvantage of this method is that as the medium gets viscous, the diffusion of the growing polymer chain become restricted, collisions becomes less and thereby termination becomes difficult. Due to active radical sites accumulation, the rate of polymerization increases enormously and sometimes, the uncontrolled exothermic reactions can leads to an explosion. The whole phenomenon is called “auto acceleration”.

Examples: The free radical polymerization of styrene or methyl methacrylates to get transparent moulding powder and cast sheets and also of vinyl chloride to get PVC resins.



Polymerization techniques

ii .Solution Polymerization : In this process, the monomer is dissolved in a suitable inert solvent along with the chain transfer agents wherever used. The free radical initiator is also dissolved in the solvent medium whereas for ionic and coordination catalyst, can be dissolved or suspended. The solvent enhances the heat capacity, thereby reducing the viscosity and promotes proper heat transfer.

Solution polymerization techniques can advantageously be used where the polymer is used in solution form (as adhesive and coating compositions).

Chain transfer to the solvent used can not be ruled out, hence it is difficult to obtain very high molecular weight products.

The polymer formed will also have to be isolated from the solution either by evaporation or precipitation in a non-solvent and removal of their final traces is always extremely difficult.

Examples: production of Polyacrylonitrile by free radical polymerization, polyisobutylene by cationic polymerization, poly(vinyl acetate) to be converted to poly(vinyl alcohol).



Polymerization techniques

Solution and bulk polymerization

Homogenous	Advantages	Disadvantages
Bulk (Batch type)	Minimum contamination, Simple equipment	heat control important; broad molecular weight distribution
Bulk (Continuous)	Better heat control; narrower molecular weight distribution	Requires reactant agitation, material transfer, separation and recycling
Solution	Easy agitation; may allow longer chains to be formed; easy heat control	Requires some agitation; complete solvent removal is very difficult for polymer recovery; solvent chain transfer may be possible but undesired,



Polymerization techniques

Homogenous polymerization process

i. Suspension Polymerization : In order to control the enormous amount of heat release in bulk polymerization, suspension Polymerization method was developed. Only water insoluble monomer can be polymerized by this technique. The monomer is suspended in water in the form of fine droplets, which are stabilized and prevented from coalescing by using suitable water soluble protective colloids, surface active agents and by stirring. Agitators are used along with suspending agents in the aqueous phase in order to maintain a specific droplet size and dispersion. The size of the droplets formed depends on the monomer-water ratio, the type and concentration of stabilizing agents and also on the type and speed of the agitation employed. Since each monomer droplets are isolated and independent of other droplets, each of these droplets act as tiny bulk reactors. Heat transfer occurs from the droplets to the water having large heat capacity and low viscosity.

As the entire bulk of the monomer is divided into innumerable tiny droplets, control of the kinetic chain length of the polymer is also quite good, so the product has a narrow molecular weight distribution. The polymerization proceeds to 100% conversion and the product is obtained as a spherical beads or pearls. So, the technique is also known as Bead or Pearl polymerization.



Polymerization techniques

Homogenous polymerization process

i. Suspension Polymerization (continued) : Isolation of the polymer becomes easy as this involves only the filtration of the bead and removal of the surface active agents and protective colloids by just washing with water.

The water washed and dried product can be used as such for molding purposes or can be dissolved in a suitable solvent medium for use as an adhesive and coating agents.

Examples: Expandable polystyrene beads (from which polystyrene foams are made), styrene-divinyl benzene copolymer beads(ion exchange) by free radical initiators.

Typical stabilizer used: Gelatin, methyl cellulose, poly(vinyl alcohol), sodium polyacrylate.

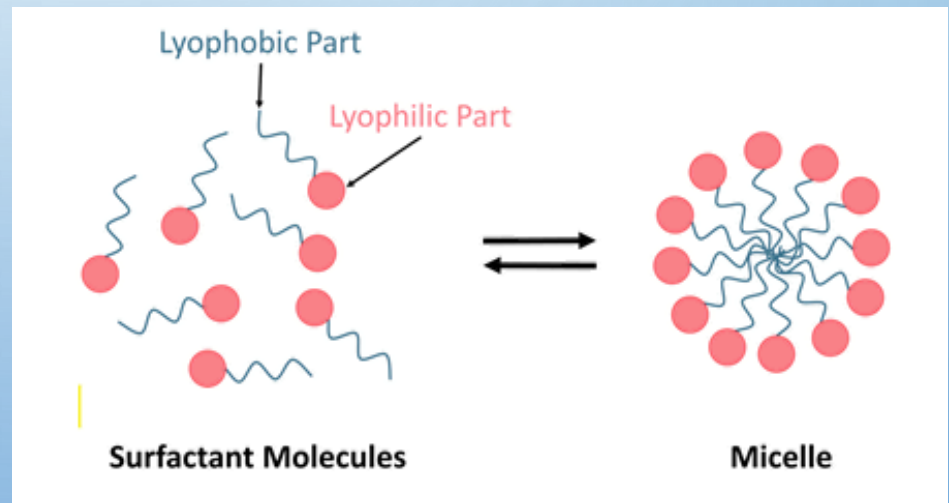
ii. Emulsion Polymerization : This is the most widely used method of polymerization. In emulsion polymerization, the monomer is dispersed in an aqueous phase as fine droplets which are then stabilized (emulsified) by surface active agents (surfactants- soaps or detergents), protective colloids and also by certain buffers. The surfactants can be cationic (alkali salts of fatty acids and of aryl and alkyl sulfonic acids), or non-ionic (alkyl glycosides). An water soluble initiators are used (persulfates).



Polymerization techniques

ii .Emulsion Polymerization (continued): Surfactants serves the purpose of lowering the surface tension at the monomer water interface and facilitate emulsification of the monomer in water. The surfactant will form micelles when their concentration exceeds critical micelle concentration (CMC), that are dispersed throughout the solution. In micelle formation, the emulsifier molecule aggregates in such a way that the polar end of the molecule align themselves outward and the hydrocarbon end come close to each other at the interior. Due to the close proximity of the hydrocarbon ends of all emulsifier molecule, the interior of the micelle acts a hydrocarbon phase where the monomer can be stabilized.

Critical Micelle Concentration (CMC): The highest concentration wherein all the molecules are in the dispersed state or the concentration beyond which only the micelle formation is possible is known as CMC.

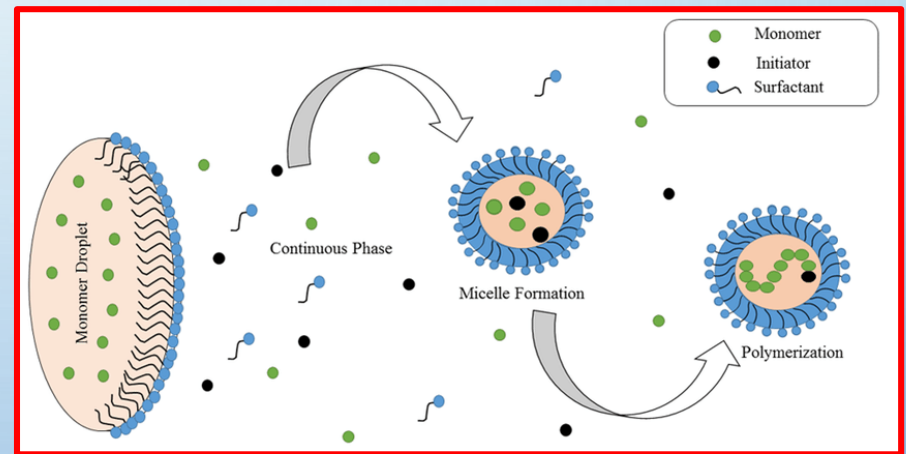




Polymerization techniques

ii. Emulsion Polymerization (continued): Now when the monomer is added and agitated, emulsification take place. The resultant emulsion is a complex system: A molecular solution of the emulsifier in water is the continuous phase wherein the monomer droplets and micelle (having solubilized monomer at their interior) are uniformly dispersed.

Emulsion systems generally utilize a water soluble initiators as persulfate or hydrogen peroxide. With the more and more polymer formation, the polymer aggregate into fine particles and get surrounded and then stabilized by the emulsifier layer of the micelle.



At the end of the polymerization, the fine particles of the polymer stabilized by the emulsifier and dispersed uniformly in the aqueous layer. This milky white dispersion is called Latex. The latex either can be used for making adhesives, water soluble emulsion paints etc. or the polymer can be isolated from the latex by destabilizing the emulsion (using electrolyte) by spray drying or freezing.



Polymerization techniques

ii. Emulsion Polymerization (continued): Emulsion polymerization is the most widely used industrial technique(polymerization of monomer such as vinyl chloride, butadiene, chloroprene, vinyl acetate, acrylates, methacrylate etc.)

Polystyrene: Monomer (styrene), Initiator (Potassium Persulfate), Buffer (Disodium Hydrogen phosphate), water, and emulsifier(Sodium Lauryl sulfate)

Styrene-butadiene copolymer: Monomer: styrene and butadiene (1:3), Initiator(Potassium Persulfate), and emulsifier(Sodium Lauryl sulfate), Lorol mercaptan (chain transfer agent)

Heterogenous	Advantages	Disadvantages
Emulsion	Easy heat control; Easy agitation; latex may be directly usable; high molecular weight and narrow distribution	Polymer may require additional cleanup and purification; difficult to eliminate entrenched coagulants, emulsifiers, surfactants
Suspension	Easy agitation; higher purity product when compared to emulsion, granular polymer directly usable.	Sensitive to agitation; contamination by stabilizer possible, washing, drying and compacting may be required



Polymers

CLASSIFICATION ACCORDING TO PHYSICAL PROPERTIES

Polymers can also be classified according to physical properties as – i. Thermoplastic ;
ii. Thermosetting ; iii. Elastomers ;iv. Fibers

i. Thermoplastic: The polymers in this category are composed of monomers which are linear or have moderate branching. They can be melted repeatedly and casted into various shapes and structures. They are soluble in solvents, but do not have appreciable thermal resistance properties. Vinyls, cellulose derivatives, polyethene and polypropylene are the examples of thermoplastic polymers.

ii. Thermosetting: There are some polymers which, when heated, decompose, and hence, cannot be reshaped. Such polymers have a complex 3-D network (cross-linked or branched) and are called Thermosetting Polymers. They are generally insoluble in solvents and have good heat resistance quality. Thermosetting polymers include phenol-formaldehyde, urea-aldehyde, silicones.

iii. Elastomers: These are resistant solids which have considerable flexibility. They are composed of polymers with glass transition temperature below room temperature.

One major difference between elastomers and plastics is that the elastomer is in a liquid state, while plastics are in the glassy state. Examples of elastomers are Butadiene, Butadiene co – polymers and their derivatives, silicones

iv. Fibers: These are solids which can form thread – like structures and have high tensile strength. Examples of fibers are Polyamides, Polyesters, Polyurethanes, Protein derivatives.



References and suggestions for further reading:

1. Textbook of Polymer Science by Fred W. Billmeyer, Wiley

2. Polymer Chemistry by Charles E Carraher, Jr., Marcel Dekker, Inc.

3. Principle of Polymerization by George Odian, Wiley



THANK YOU