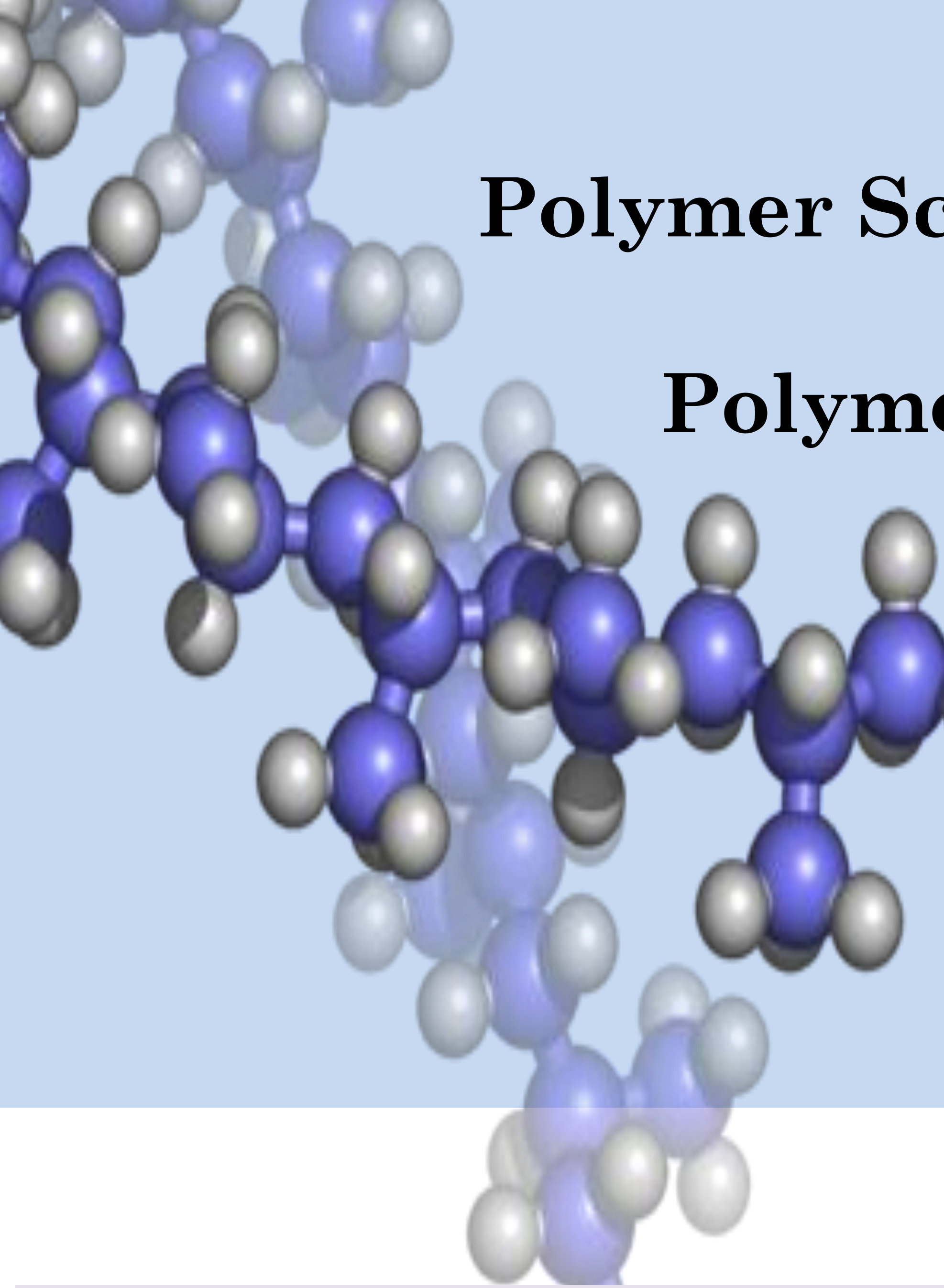

Polymer Science & Engineering

Polymerization Techniques

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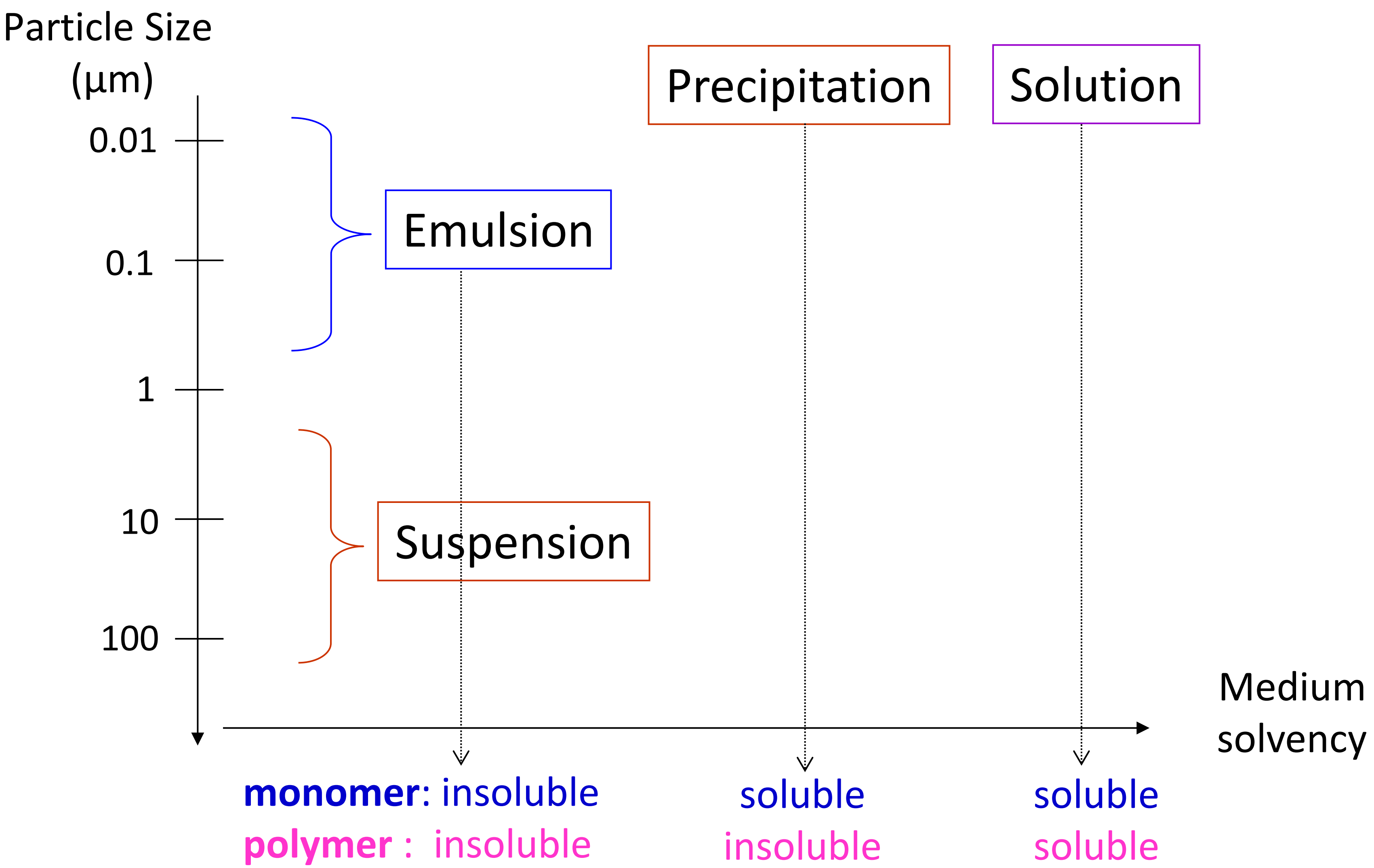
Polymerization Techniques

There are five commonly used methods for free radical polymerization

1. Bulk polymerization
2. Solution polymerization
3. Precipitation polymerization
4. Suspension polymerization
5. Emulsion polymerization

- Distinguished by:
  - Initial state of the polymerization mixture
  - Kinetics of polymerization
  - Mechanism of particle formation
  - Shape and size of the final polymer particles


Particle Size
(µm)
0.01
0.1
1
10
100
Emulsion
Suspension
Precipitation
Solution
Medium
solvency
monomer: insoluble
polymer : insoluble
soluble
insoluble
soluble
soluble

Bulk polymerization

- The simplest method of polymerization where the reaction mixture contains only the monomer and a monomer soluble initiator ,
- Polymerization of pure liquid or gaseous monomer,
- Only monomer, polymer, and initiator are present in the reaction, therefore, pure product is obtained,
- The polymerization is very rapid (high degree of polymerization) and exothermic, thus molecular mobility increases which results in an increasing of reaction rate,
- With ongoing polymerization the monomeric concentration decreases and viscosity increases,
- A highly transparent polymer can be achieved via bulk polymerization, such as PMMA and PS,
- There is a difficulty in removing of heat!

Solution Polymerization

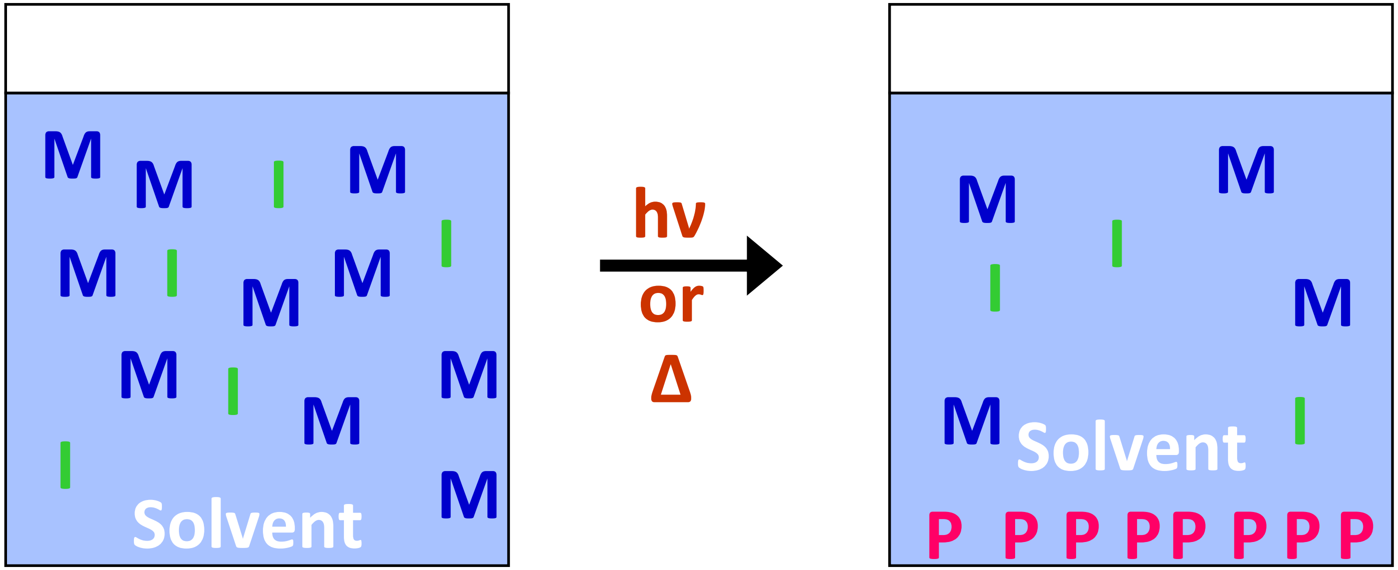
- This method is used to solve the problems associated with the bulk polymerization because the solvent is employed to lower the viscosity of the reaction, thus help in the heat transfer and reduce auto-acceleration.
- During the polymerization, the solvent evaporates and thus removes the heat of polymerization,
- Since the boiling point of solvent is constant , then this ensures constant polymerization temperature,
- Examples: manufacturing of adhesives .

The disadvantage of solvent presence is

1. Reduce monomer concentration which results in decreasing the rate of the reaction and the degree of polymerization,
2. Solvent may cause chain transfer,
3. Clean up the product with a non solvent or evaporation of solvent (some difficulty in removing the remaining of solvent from the polymer after polymerization completion).

Precipitation Polymerization

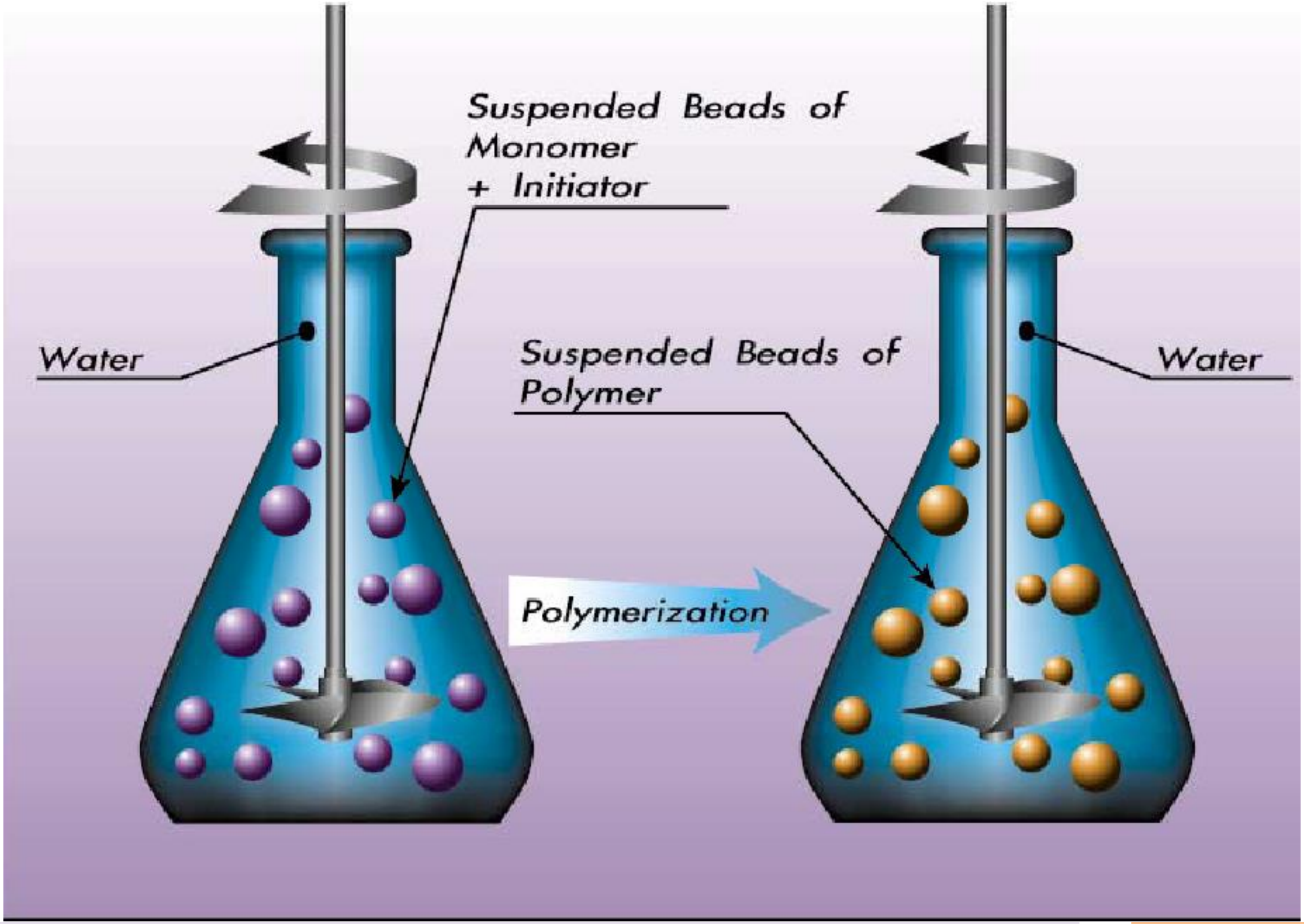
- A special case of bulk polymerization and solution polymerization (soluble monomer in solvent but not soluble polymer),
- The polymer is insoluble in its own monomer, thus it precipitates and then filtered or centrifuged out at the end of polymerization,
- Solvent, monomer & initiator are needed for precipitation polymerization,
- Polymer becomes insoluble in the solvent (dependent on MW, crystallinity, rate of polymerization,
- Viscosity remains relatively low during the polymerization process,
- Polymerization continues after precipitation (?)



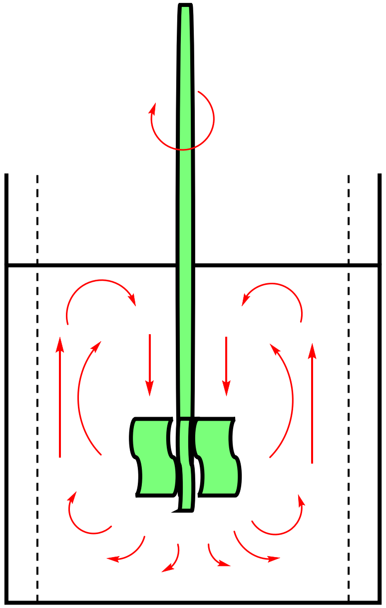
Suspension polymerization

- It is carried out in water or in an aqueous solution in which monomer is dispersed but is not soluble,
- The polymer precipitates in the form of finely distributed spheres with range of 0.01 to 1 mm, thus it is called “Pearl Polymerization”,
- This method is used also to solve the problem of heat transfer.
- It is similar to bulk polymerization where the reaction mixture is suspended as droplets in an inert medium.
- Monomer, initiator and polymer must be insoluble in the suspension media such as water.
- Stabilizers (protective colloids) are added to prevent particles coagulation and to produce uniform size of polymers particles,
- The purity of suspension polymers is not as high as that produced by bulk polymerization,

Suspension polymerization



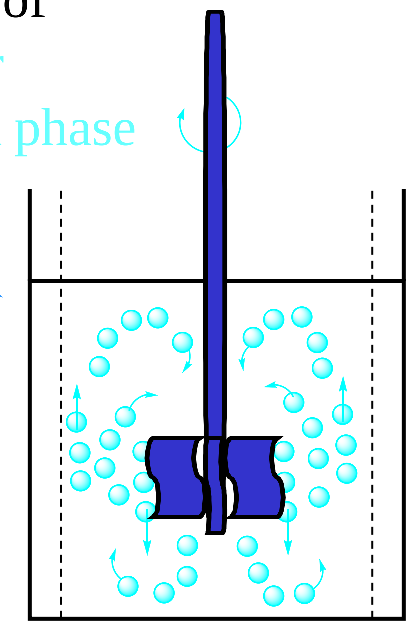
Suspension polymerization



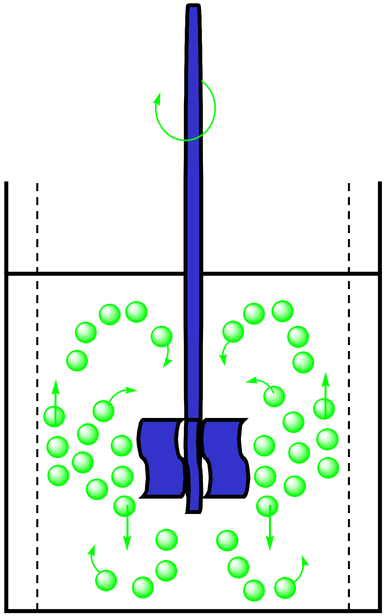
Aqueous Continuous phase

- Vertical flow pattern
- Presence of stabilizers

Addition of
monomer
dispersed phase



Suspension
polymerization in
polymer micro-droplets



- ***Controlled agitation***
- ***Coagulation prevented***
- ***Particle diameter range***
  30µm to 2mm

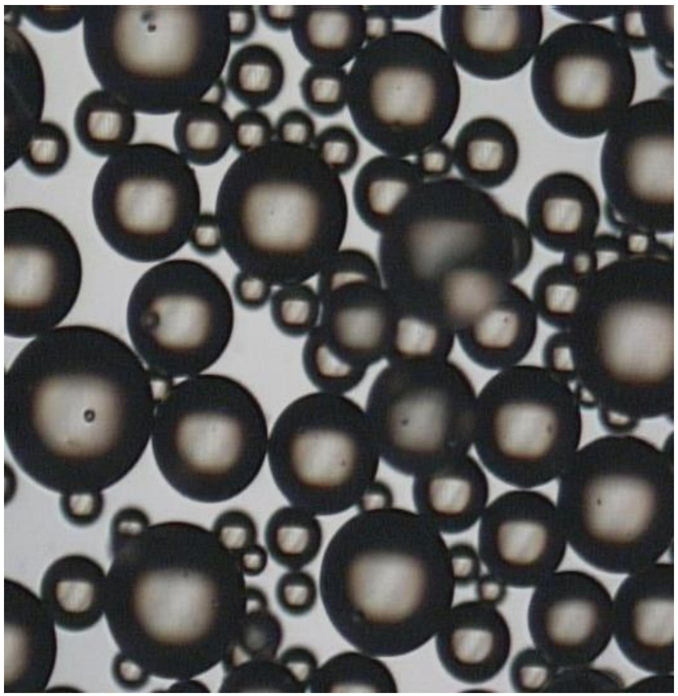
Monomer beads

Polymer beads

Suspension separation

Copolymer particles separated into fractions with US standard sieves using a sieve shaker

Broad size distribution



100mm

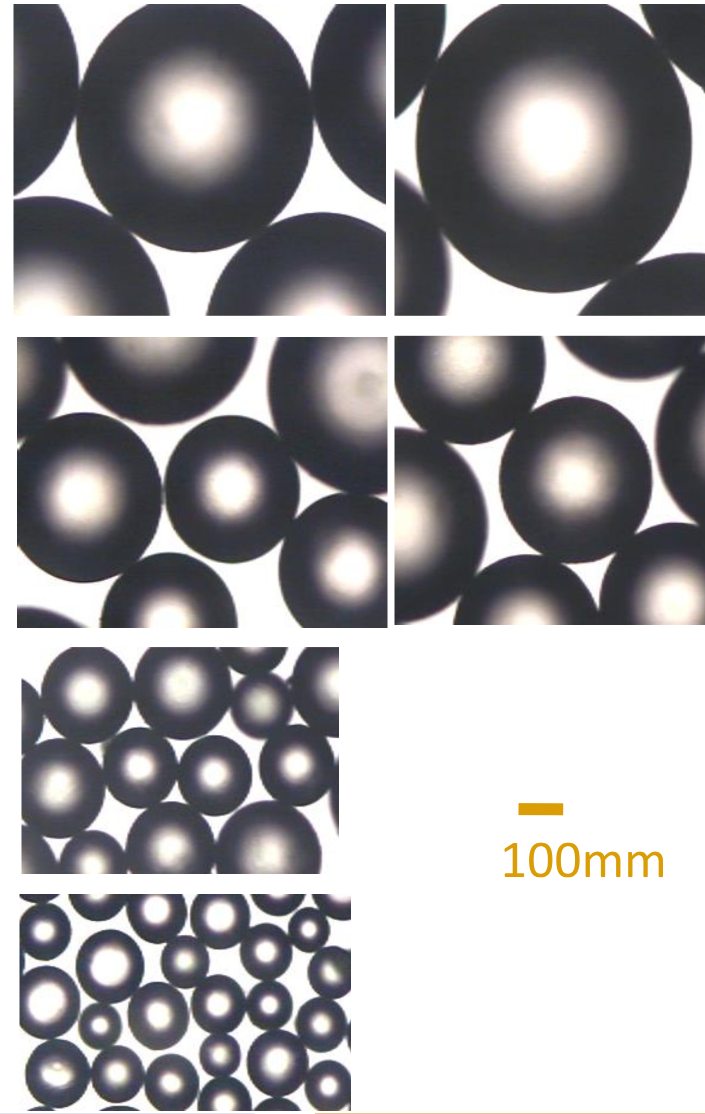
250mm sieve

125mm sieve

75mm sieve

45mm sieve

Particles after sieving

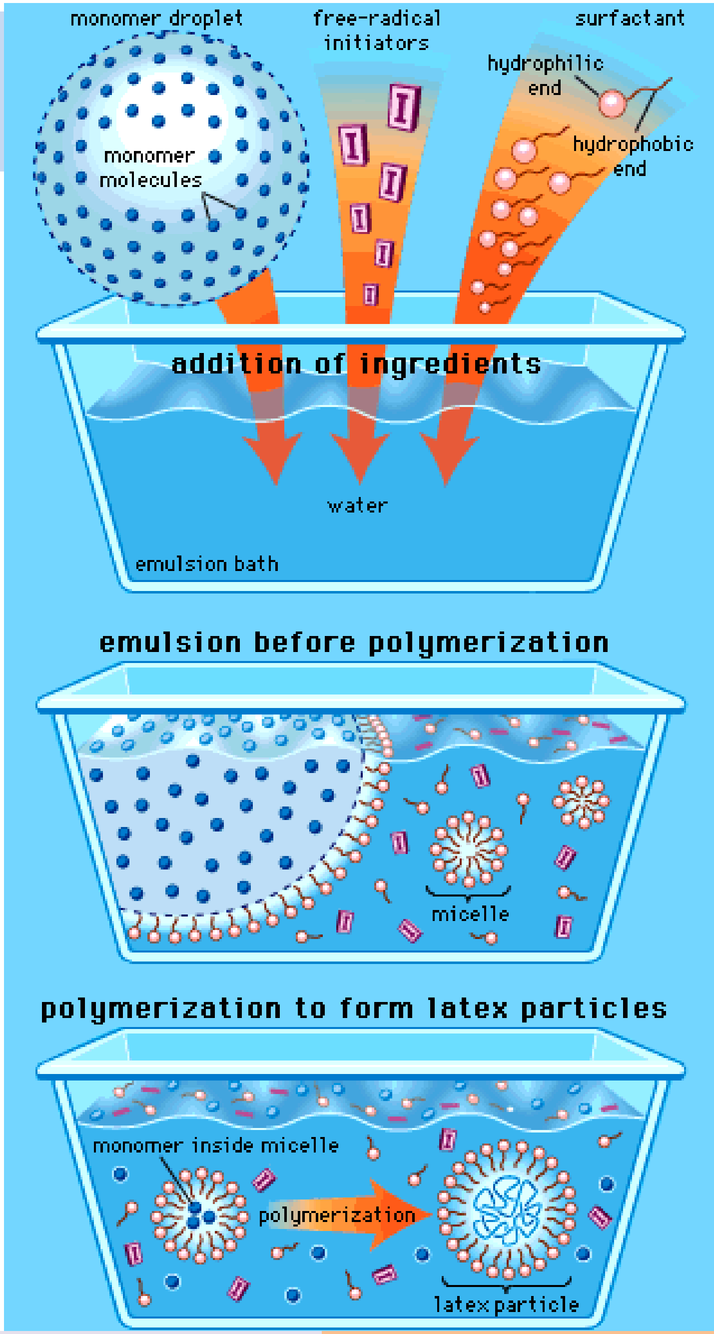


100mm

* All pictures are optical micrographs

Emulsion polymerization

- This is similar to suspension polymerization except that the initiation is soluble in suspension media and insoluble in the monomer.
- The monomer is dispersed in water but in much smaller droplets created with the use of emulsifiers (which form small micelles in water),
- The reaction product is colloidally stable dispersion known as latex.
- The polymer particles have diameter in the range of (0.05 - 1μm) smaller than suspension.
- Coagulants are added and spheres flocculates out and then separated from water ,
- The emulsifiers cannot be totally removed, so the purity is less than that of suspension polymerization,
- Advantage: high MWT @ high rxn rate.



Three stage of emulsion polymerization

- **Interval I** : Particle initiation stage
  - Continuous until micelles have disappeared

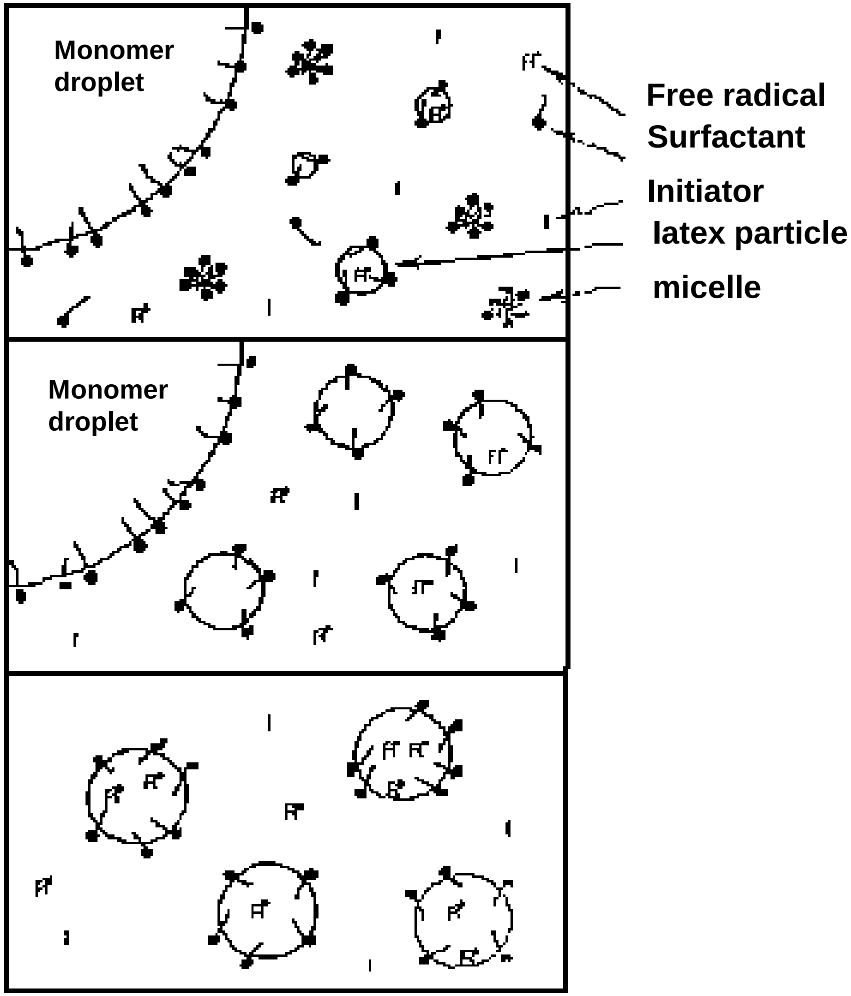
- **Interval II** : Particle growth stage
  - Constant number of particles plus monomer emulsion droplets
  - Particles grow until monomer droplet phase disappears and all monomer is in the particles

- **Interval III** : Particle growth stage
  - Particles grow until monomer is completely polymerized or initiator is exhausted

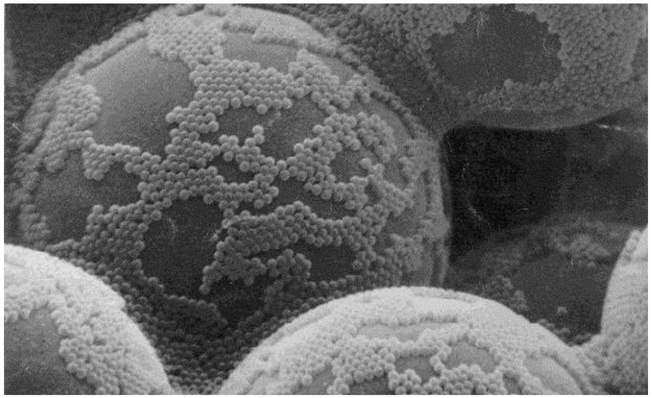
INTERVAL 1

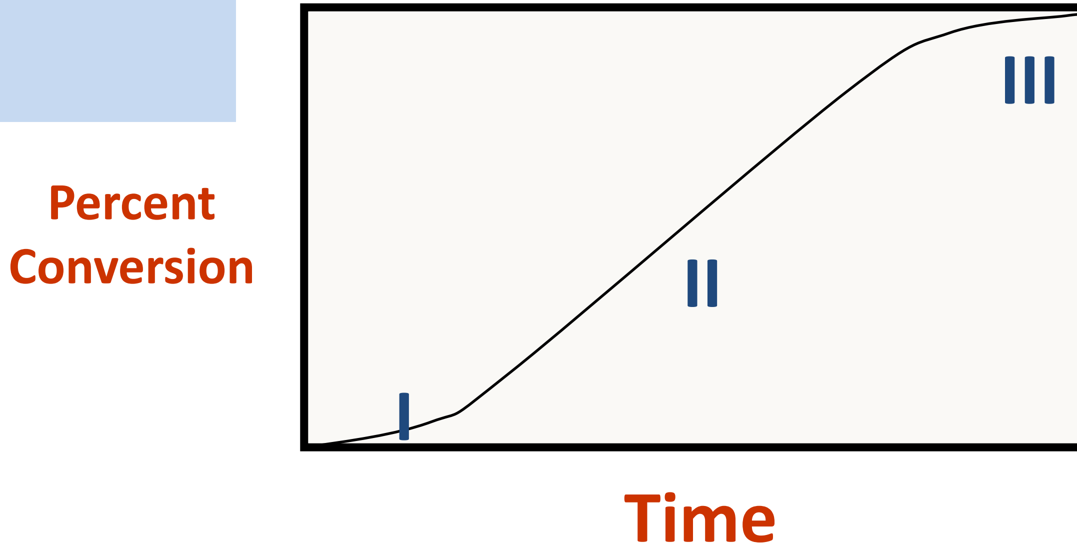
INTERVAL 2

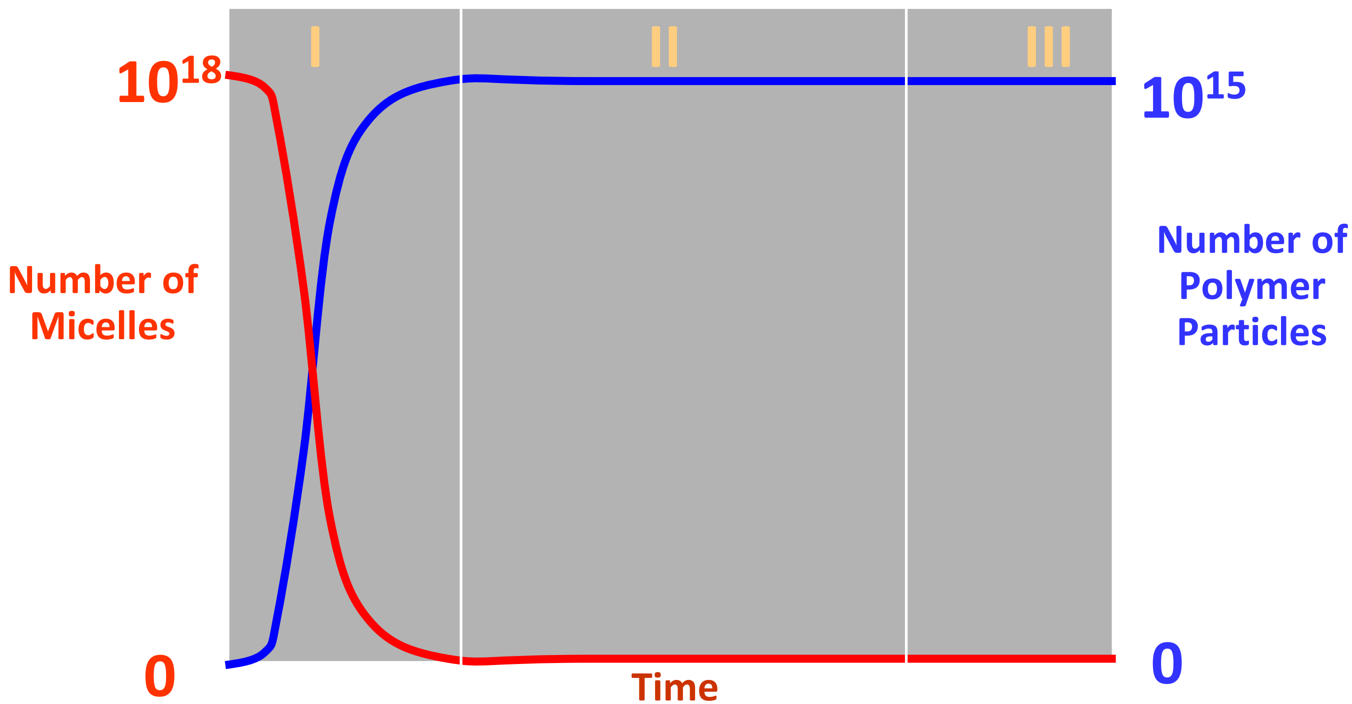
INTERVAL 3



Emulsion polymerization







Emulsion polymerization

	Conversion	Micelles	Monomer Droplets	Particle Number	Particle Size	Comments
I	0 – 15%	present	present	increases	increases	Nucleation period, Increasing Rp
II	15 – 80%	absent	present	constant	increases	Constant # of particles,
III	80 – 100%	absent	absent	constant	roughly constant	Constant # of particles,