Chemical Engineering 160/260
Polymer Science and Engineering

Lecture 13:
Polymerization Techniques - Dispersed Systems

Objectives

- To outline polymerization techniques and describe approaches to reducing viscosity and improving thermal control that involve dispersion of the monomer in water.
- To show how dispersed systems may be stabilized from aggregation by modification of the hydrocarbon/water interface.

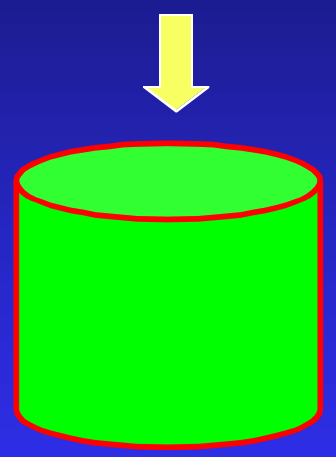
Outline

- Polymerization Techniques
  - Bulk
  - Solution
  - Suspension
  - Emulsion

Bulk (Mass) Polymerization

General Description:

Monomer
Initiator



- Carried out to high conversion
- Free radical kinetics apply
- Used for ethylene, styrene, methyl methacrylate

Advantages:

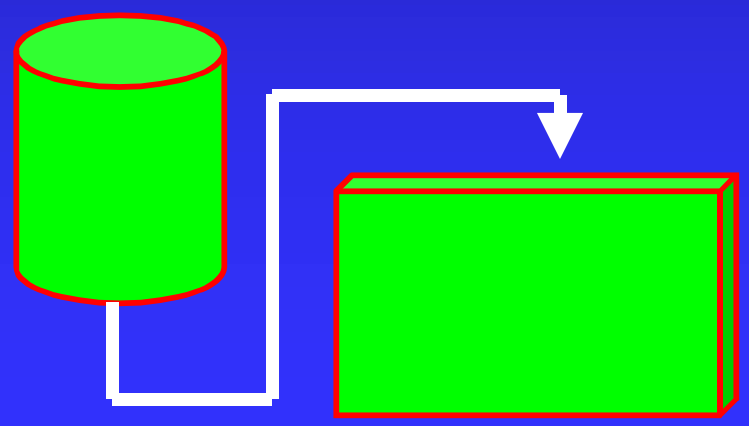
- Minimum contamination of product

Bulk (Mass) Polymerization

Disadvantages:

- R_t decreases at high conversion due to the Trommsdorf effect, making the reaction hard to control.
- R_p and ν increase as conversion increases, broadening the molecular weight distribution.
- Viscosity increases as conversion increases, making heat removal and processing more difficult.

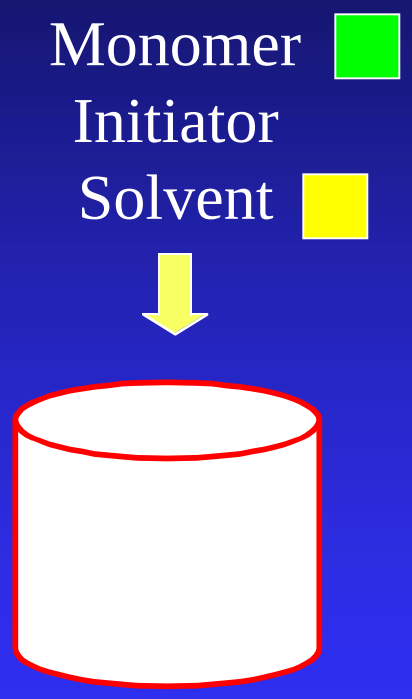
Process schemes:



- Keep to low conversion; separate and recycle unreacted monomer
- Stagewise polymerization; achieve low conversion in large reactor, then prepare slabs or films

Solution Polymerization

General Description:



- Homogeneous, if polymer remains soluble:

  vinyl acetate
  acrylonitrile,
  esters of acrylic acid

- Heterogeneous, if polymer is insoluble, leading to precipitation (powder or granular) polymerization:

  acrylonitrile in water
  vinyl chloride in bulk

- Free radical kinetics apply.

Solution Polymerization

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.

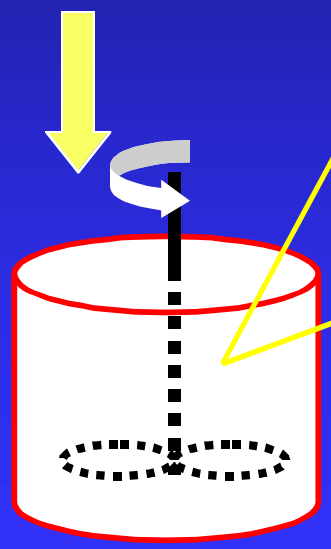
Disadvantages:

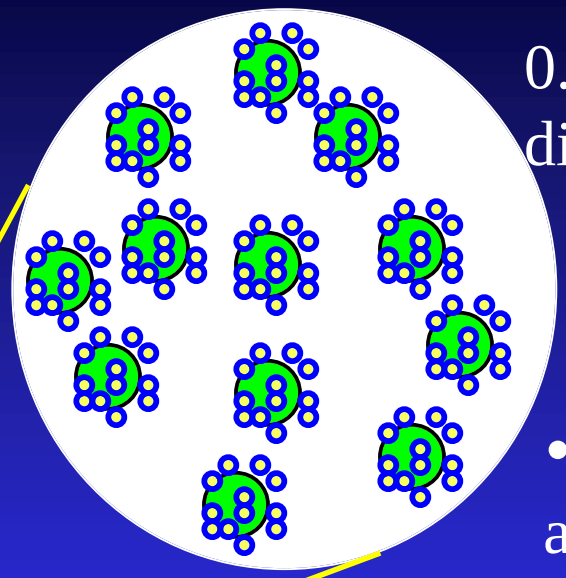
- Chain transfer to solvent occurs, leading to low molecular weights.
- Difficult to remove solvent from final form, causing degradation of bulk properties.
- Environmental pollution due to solvent release.

Suspension (Bead or Pearl) Polymerization

General Description:

Monomer
Inorganic Stabilizer
Oil-soluble Initiator
Water





- Droplets are 0.001-1 cm in diameter.
- Kinetics are the same as in the bulk.
- Must have very low monomer solubility in water or polymer will form in aqueous phase.

- Used for styrene, methyl methacrylate, vinyl chloride, vinyl acetate

Suspension (Bead or Pearl) Polymerization

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.

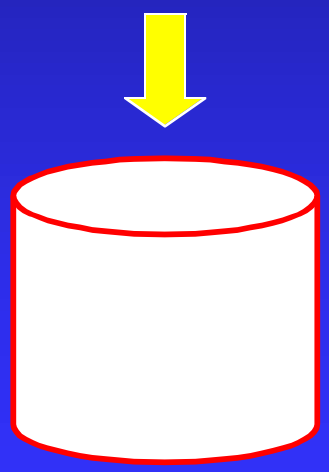
Disadvantages:

- Cannot be used for polymers whose glass transition temperature is less than the polymerization temperature, or else aggregation will occur.
- Must separate and purify polymer, or accept contaminated product.

Emulsion Polymerization: Overview

General Description:

Monomer
Surfactant
Water-soluble Initiator
Water



- Surfactant is aggregated in micelles.
- Monomer is stabilized by surfactant and dispersed in water.
- Predominant process for vinyl acetate, chloroprene, butadiene/styrene/acrylonitrile copolymers, various acrylates.
- Used somewhat for methyl methacrylate, vinyl chloride, vinylidene chloride, styrene.

Typical Emulsion Composition

Component	Parts by weight
Styrene	25
Butadiene	75
Water	180
Emulsifier (surfactant	5
N-Dodecyl mercaptan	0.5
NaOH	0.061
Cumene hydroperoxide	0.17
$FeSO_4$	0.017
$Na_4P_2O_7$-10 H_2O	1.5
Fructose	0.5

Data from G. Odian, Principles of Polymerization, 3rd Ed., 1991, p 336.

Emulsion Polymerization: Advantages

- Thermal and viscosity problems are minimized due to the high heat capacity and ease of stirring of the continuous aqueous phase.
- Molecular weight may be increased without decreasing R_p:

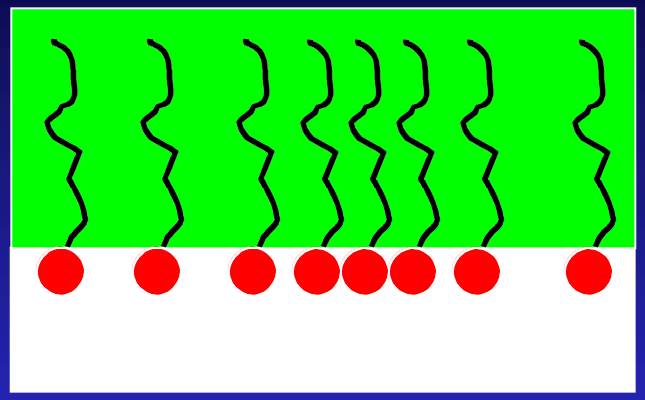
$$R_p \sim [I]^{0.4}[S]^{0.6} \qquad \overline{X_n} \sim [I]^{-0.6}[S]^{0.6}$$

- Recall that in normal free-radical polymerization R_p and X_n are inversely related:

$$R_p \sim [I]^{0.5} \qquad \overline{X_n} \sim [I]^{-0.5}$$

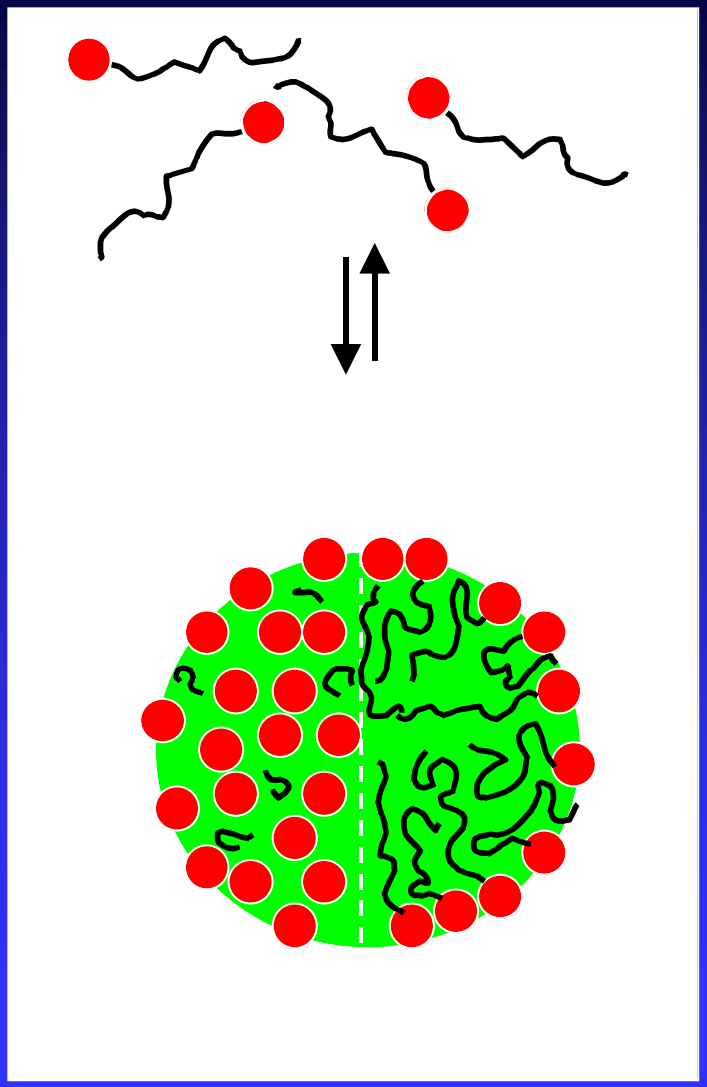
- The latex may be used directly without purification.

Emulsion Components: Surfactant



- Surfactant (emulsifier) molecules have polar or ionic head groups and hydrocarbon tails of 10-20 carbons; dodecyl sulfate ions are typical.
- Surfactants aggregate at the hydrocarbon/water interface and are in equilibrium with free surfactant.

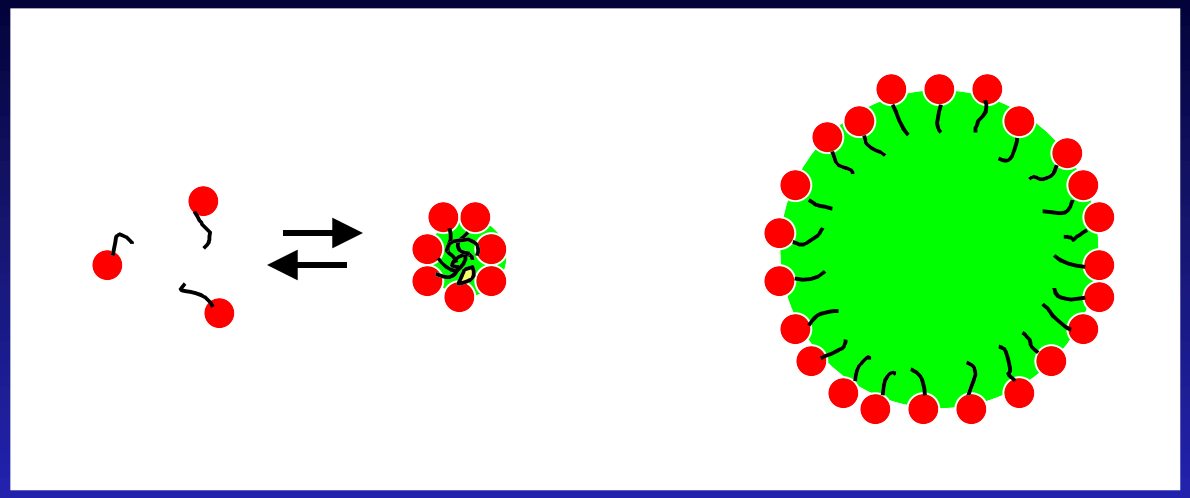
Micelle Formation



- Above the **critical micelle concentration (CMC),** there is an equilibrium involving clusters of surfactants, which are typically spherical (20 to 100 Å in diameter) and which contain 50 to 150 molecules.

- The hydrocarbon core of the micelle will become swollen by monomer molecules.

Emulsion Components: Monomer

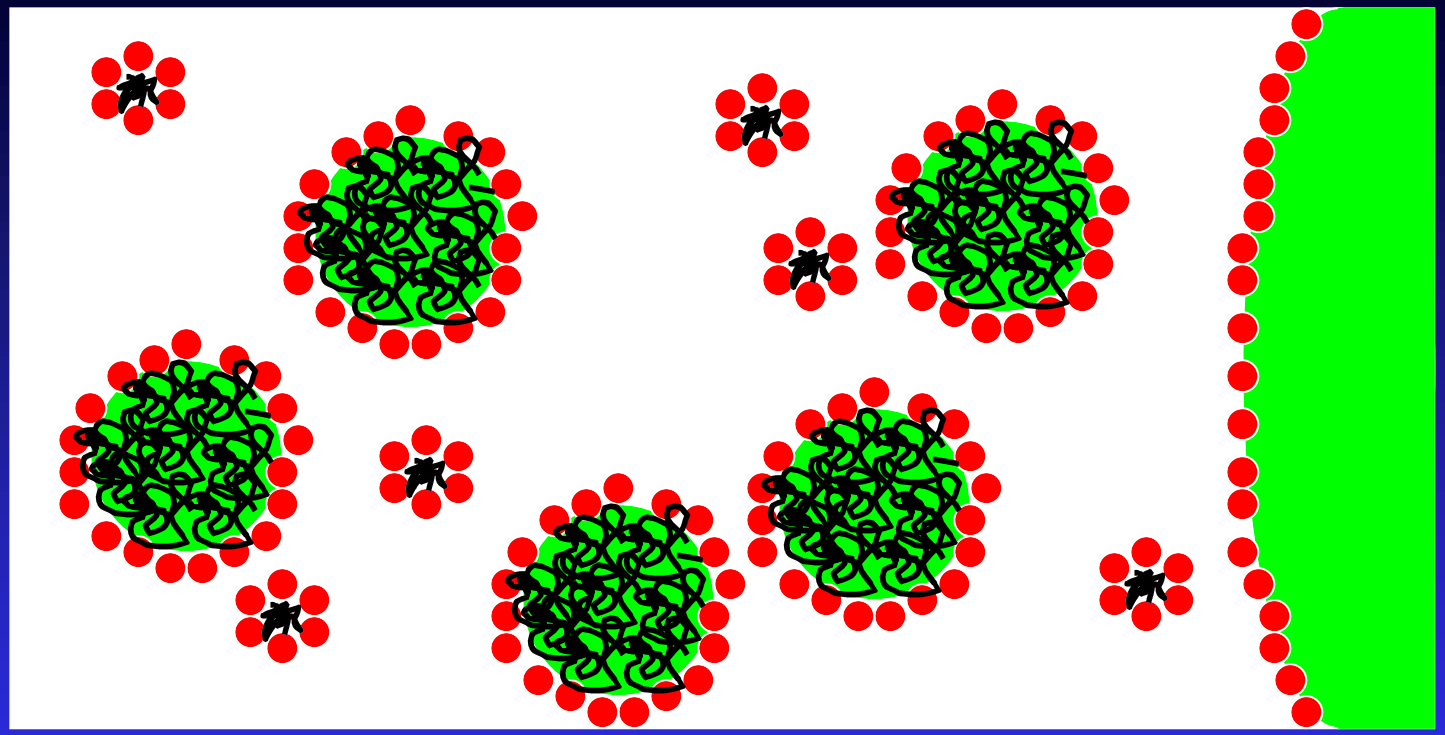


- A small portion of water-insoluble or slightly water-soluble monomer dissolves in solution.
- A larger monomer portion enters the interior of micelles, causing them to increase in size.
- The largest portion is dispersed as surfactant-stabilized monomer droplets having diameters greater than 10,000 Å; there are 10^{10} - 10^{11} monomer droplets/cm^3.

Emulsion Components: Site of Polymerization

- Radicals are produced in the aqueous phase at approximately 10^{13} radicals/cm^3sec.
- Polymerization in the aqueous phase is insignificant due to the low monomer concentration.
- Polymerization mainly occurs in the micelle interiors due to:
    - high monomer concentration
    - high surface/volume ratio
    - presence of interface for organic monomer and water-soluble initiator
- During polymerization, monomer is replenished by diffusion from droplets through the solution to micelles. Surfactant is then redistributed, with more adsorbed on swollen polymer particles and less on monomer droplets

Emulsion Components: Particles



- Three types of particles exist:
  - monomer droplets
  - inactive micelles (no polymerization occurring)
  - active micelles (swollen polymer particles in which polymerization is occurring)

Emulsion Polymerization Intervals

Interval I (0 - 10% conversion):

- Monomer in micelles (diameter ~ 100 Å)
- Monomer in droplets (diameter ~ 100,000 Å)
- Monomer in polymer particles
- Growing number of polymer particles

Interval II (10 - 50% conversion):

- No micellar surfactant
- Monomer in droplets
- Monomer in polymer particles
- Constant number of particles

Interval III (50 - 90% conversion):

- No monomer droplets
- Monomer in polymer particles
- Constant number of particles