CHEM 4210/5210

Chapter 8

Dispersion and Emulsion Polymerizations

Chain-Growth Methods

- Homogeneous
  - Bulk – monomer only – used for PS, PMMA, PVC
  - Solution – monomer dissolved in organic solvent – used for PE, PVAc, PAN
- Heterogeneous
  - Suspension – monomer droplets dispersed in water – used for PVC, HIPS, ABS
  - Dispersion – monomer is soluble, but polymer product is not
  - Emulsion – reaction in micelles – used for PAN, polyacrylates, PB/PS

Bulk Polymerization

- Suitable for liquid (or liquefiable) monomers
- No solvent used
- Proceed to low conversion, strip and recycle monomer
- Can be carried out in batch or continuous mode
- Low impurity level, suitable for casting, especially clear products (e.g. PMMA sheets)
- Can be inefficient in heat removal, leading to hot spots & autoacceleration (Tromsdorff)

Solution Polymerization

- Uses organic solvent, monomer must be soluble
- Suitable for many solid monomers
- Solvent provides improved thermal control by maintaining low viscosity
- Polymer product is typically precipitated and isolated by filtration
- Removal of residual solvent can be difficult
- Solvent recovery necessary, adds to cost & difficulty
- Chain transfer common, limiting molecular weight

Suspension Polymerization

- Liquid monomer dispersed in water using high speed mixer, droplets ~10 μm-1 cm
- *a.k.a.* pearl or bead polymerization, each droplet acts as micro-bulk reactor
- Utilizes monomer-soluble initiators
- As polymerization proceeds…

monomer droplets ⟹ sticky monomer-swollen particles ⟹ rigid polymer particles

- Water maintains viscosity & thermal control

Suspension Polymerization - 2

- Particle size affected by agitation rate, yields polymer particles ~ 10-1000 nm
- Suspending agent used to prevent coagulation of reacting particles
  - PVA, starch, $BaSO_4$, $Ca_3(PO_4)_2$
- Isolation of polymer particles is simple
- Possible contamination by suspending agent
- Washing, drying, & compacting necessary

Suspension Recipe

Preparation of Poly(vinyl chloride)

Vinyl chloride	100 parts
Water	180 parts
Poly(vinyl alcohol) *(suspending agent)*	0.04 parts
Trichloroethylene *(transfer agent)*	0.2 parts
Lauroyl peroxide *(initiator)*	0.2 parts

Dispersion Polymerization

- *a.k.a.* nonaqueous dispersion (NAD)
- Initial reaction occurs in homogeneous medium of monomer in organic solvent, often the same solvent in which the polymer is used
- As polymer forms it collects into larger insoluble particles, ~ 0.1-15 μm
- Stabilizers, which inhibit excessive coagulation of particles, are present
- Stabilizers are polymeric materials with solvent-friendly groups
  - may be preformed graft or block copolymers or are grafted onto polymer as formed

Dispersion Stabilizers

- For alcohol solvents
  - poly(vinylpyrrolidone), hydroxypropyl cellulose
- For hydrocarbon solvents
  - poly(12-hydroxystearic acid), polyisobutene, poly(dimethylsiloxane)

- Coagulation is hindered by *steric stabilization*
  - Form “shell” of soluble segments around polymer particle, inhibits approach of other particles

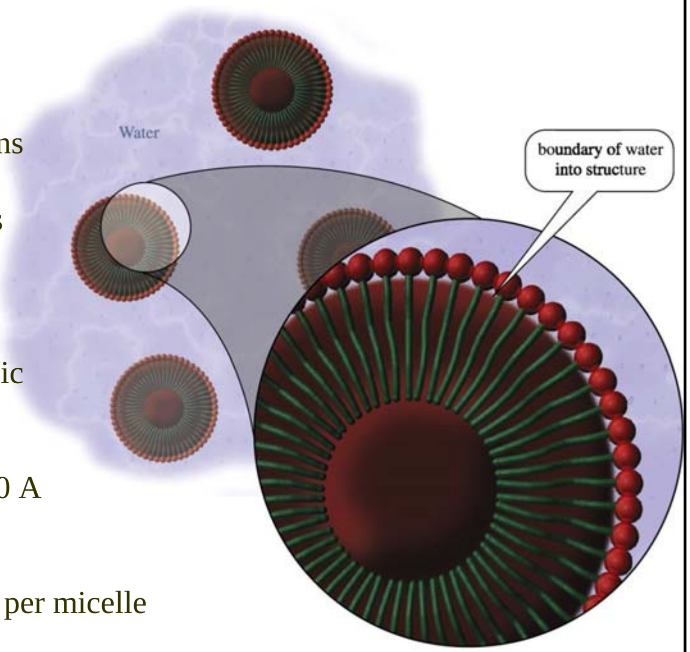
Emulsion Polymerization

- Emulsion – a discontinuous liquid phase, dispersed throughout another liquid phase
  - milk, sap, latex
- Polymerization occurs inside of micelles, one radical per micelle
- Termination reactions are less frequent, yielding higher MW polymer
- Water also acts as a heat sink, providing good thermal control
- Reaction medium maintains low viscosity
- Latex is often directly usable

Micelles

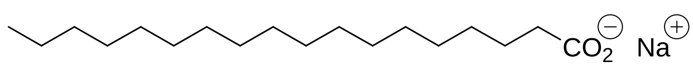
Formed in solutions of surfactants
Hydrophilic heads collect at water boundary
Hydrocarbon tails form hydrophobic interior

Diameter ~ 50-100 A
[Surf] ~ 0.1 M
10^{18} micelles/mL
50-100 molecules per micelle

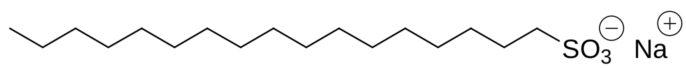


Surfactants
(Surface-Active Agents)

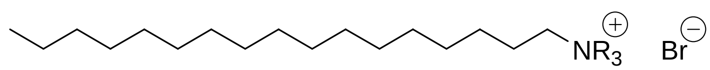
- Soaps – salts of fatty acids



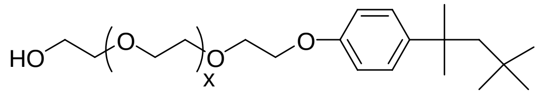
- Detergents – 3 types
  - Anionic – salts of alkane sulfonic acids



  - Cationic – alkyl ammonium salts



  - Nonionic – alkyl polyethers or sugars

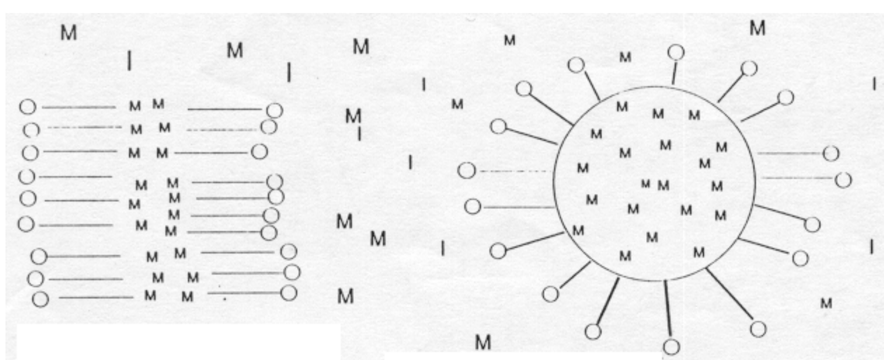


Emulsion Recipe

Preparation of Poly(vinyl chloride)

Vinyl chloride	100 parts
Water	200 parts
Ammonium stearate *(surfactant)*	3 parts
Potassium persulfate *(initiator)*	0.5 parts

Before Reaction



Small amount of monomer is in micelles (~75 A)
Very low [M] in aqueous phase

Most monomer is in surfactant-stabilized droplets (~ 1 μm)

Initiation

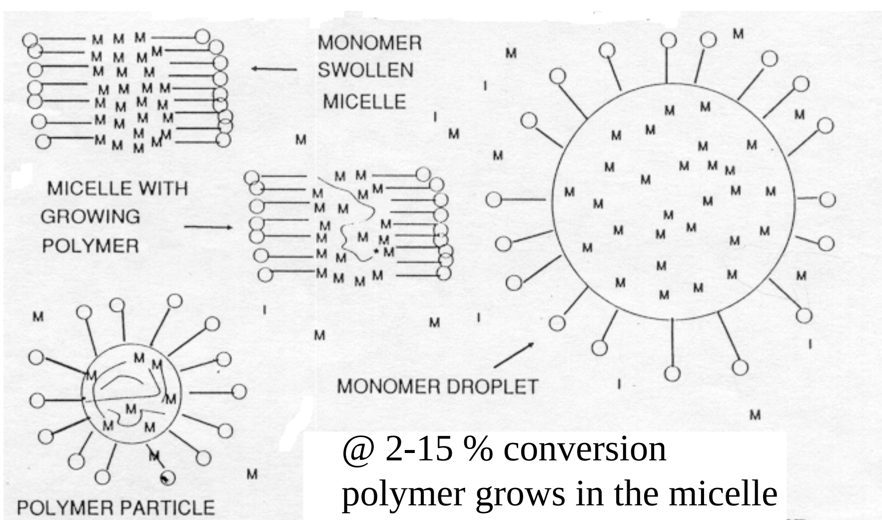
- Use water-soluble inititators, such as $K_2S_2O_8$ or ROOH

$$S_2O_8^{2-} \longrightarrow 2\ {}^{\bullet}OSO_3^{\ominus}$$

$${}^{\bullet}OSO_3^{\ominus} + H_2O \longrightarrow HSO_4^{\ominus} + HO^{\bullet}$$

- Initiator reacts with monomer in aqueous phase
- Activated monomer penetrates into micelle (statistically favored, surface ratio of micelle to monomer = 560 : 1)

Interval I

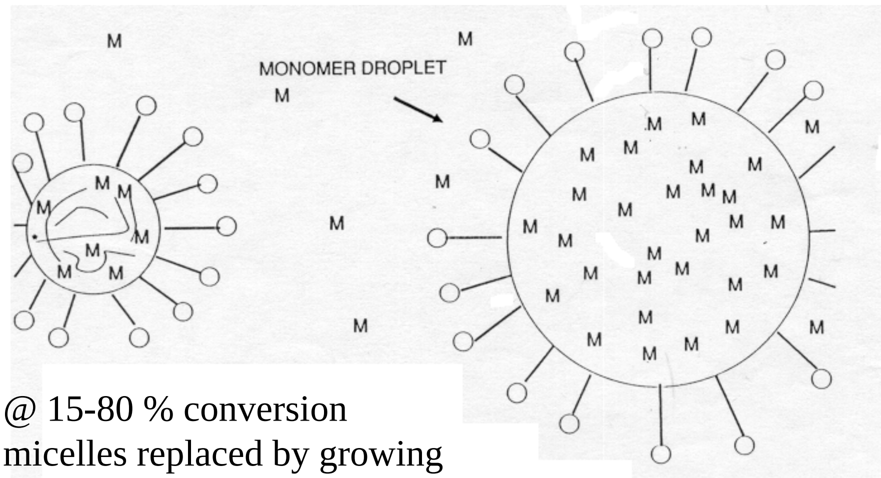


@ 2-15 % conversion
polymer grows in the micelle

monomer equilibrium $M_d \rightleftharpoons M_{aq} \rightleftharpoons M_m \longrightarrow -(-M-)_n-$

droplets begin to shrink as monomer is consumed

Interval II

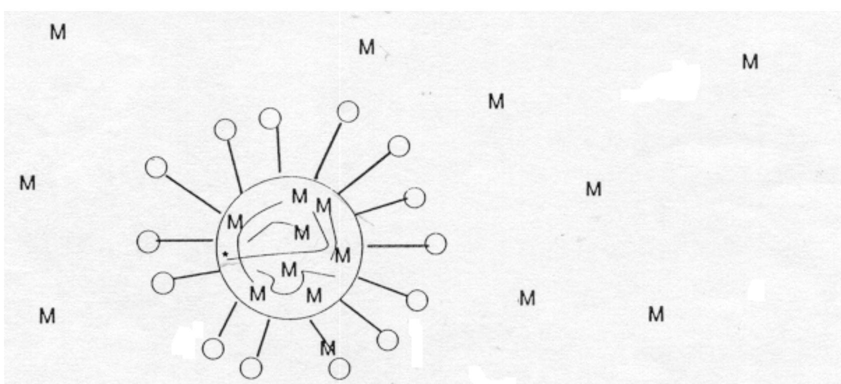


@ 15-80 % conversion
micelles replaced by growing
polymer particles

only 1 radical/particle

@ 30 % droplets begin to disappear

Interval III



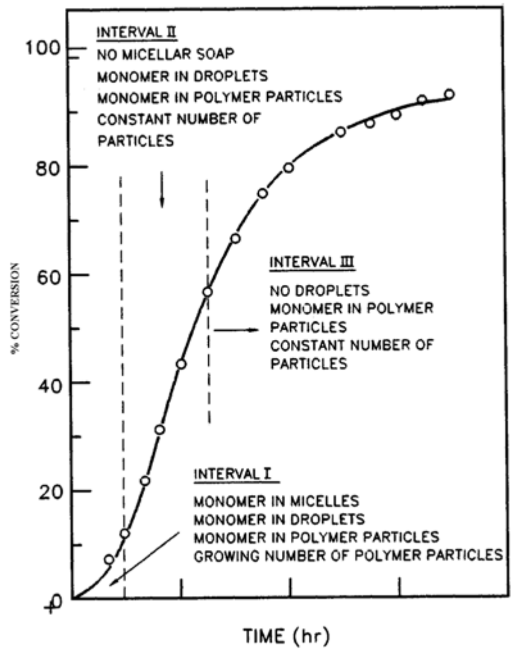
@ 80 % conversion
droplets have totally disappeared, no new monomer
polymerization rate decreases

Harkins-Smith-Ewart Mechanism

Rate of reaction is proportional to:
$[I]^{2/5}$, $S^{3/5}$

Chain length (DP) is proportional to:
$[I]^{-3/5}$, $S^{3/5}$

Number of polymer particles (N) is proportional to:
$S^{3/5}$, $[I]^{2/5}$



Utility of Emulsion Polymerization

- First employed in 40’s for production of styrene-butadiene rubber
- Predominate process for vinyl acetate, chloroprene, acrylates, & ABS
- Also used for vinyl chloride, methyl methacrylate, vinylidene chloride & styrene
- Acrylic latex is used directly for paints and other coatings