Emulsion Polymerization

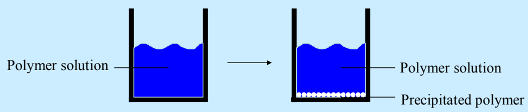
Overview

Phase Separated Polymerizations:

1. Precipitation Polymerization: (1-20 µm) Polymerization starts in the homogeneous solution phase → as polymer chain grows-phase separation occurs with precipitation of the polymer
   - begin homogeneous → convert to heterogeneous
   - bulk or solution
   - polymerization occurs in both solution and solid phases

Components:

1. Monomer
2. Solvent (optional)
3. Initiator-soluble in initial reaction medium



Emulsion Polymerization

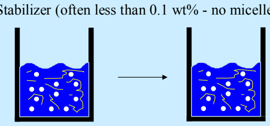
Overview

Phase Separated Polymerizations:

2. Suspension Polymerization: (0.5-10 µm) **Droplets** of monomer and initiator are suspended in the continuous phase, then polymerized. The droplets are prevented from coalescing by:
   - agitation (also determines size)
   - use of a stabilizer (called surfactant or dispersant and often emulsifier)

Components:

1. Monomer (aka: discontinuous phase)
2. Continuous phase (usually water)
3. Initiator-soluble in monomer
4. Stabilizer (often less than 0.1 wt% - no micelle emulsion)



Emulsion Polymerization

Overview

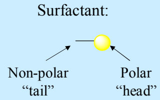
Phase Separated Polymerizations

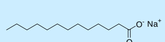
3. Emulsion Polymerization: (0.01-10 µm) Polymerization is propagated in micelles, which are stable structures of stabilizer (aka: surfactant or emulsifier) that surround monomer, usually in a water continuous phase.

Components:

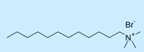
1. Monomer
2. Continuous phase (usually water)
3. Initiator-soluble in water (continuous phase)
4. Surfactant (often 1-5 wt%)

Surfactant:





Sodium laurate

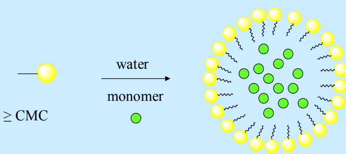


Dodecyl trimethyl ammonium bromide

Emulsion Polymerization

Concepts

Key to Emulsion and Emulsion Polymerization = Micelles



Conc. ≥ CMC

CMC = Critical micelle concentration

Emulsion Polymerization

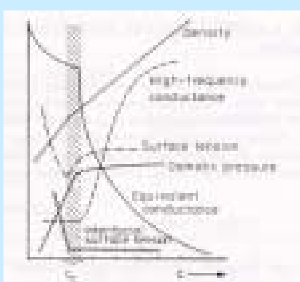
Concepts

CMC

Emulsion Polymerization

Concepts

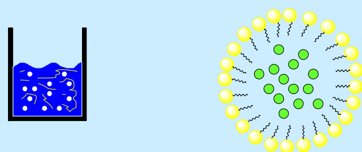
CMC



Emulsion Polymerization

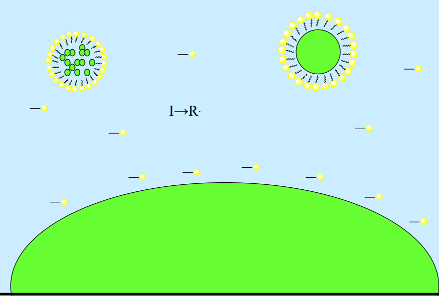
Concepts

Droplet vs. Micelle



Emulsion Polymerization

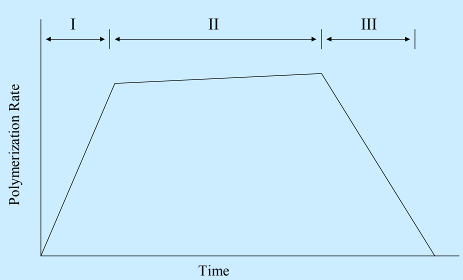
Mechanism



Emulsion Polymerization

Mechanism

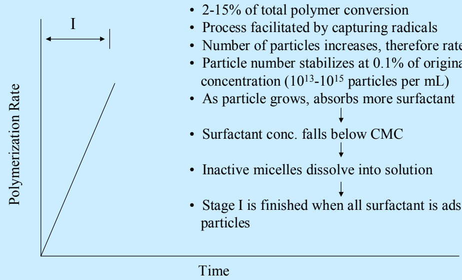
Stages of Emulsion Polymerization



Emulsion Polymerization

Mechanism

Stages of Emulsion Polymerization

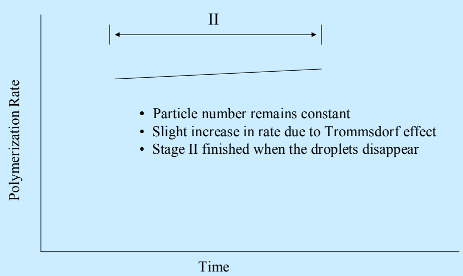


- 2-15% of total polymer conversion
- Process facilitated by capturing radicals
- Number of particles increases, therefore rate increases
- Particle number stabilizes at 0.1% of original micelle concentration (10^{13}-10^{15} particles per mL)
- As particle grows, absorbs more surfactant
  ↓
- Surfactant conc. falls below CMC
  ↓
- Inactive micelles dissolve into solution
  ↓
- Stage I is finished when all surfactant is adsorbed to particles

Emulsion Polymerization

Mechanism

Stages of Emulsion Polymerization

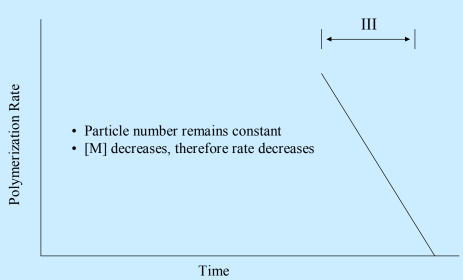


- Particle number remains constant
- Slight increase in rate due to Trommsdorf effect
- Stage II finished when the droplets disappear

Emulsion Polymerization

Mechanism

Stages of Emulsion Polymerization



- Particle number remains constant
- [M] decreases, therefore rate decreases

Emulsion Polymerization

Kinetics

Rate of Polymerization

Once inside a particle, a radical propagates according to:

radical propagation = $r_p = k_p$ [M]

note: k_p is the same as bulk radical polym.

Overall rate of polymerization:

$R_p = r_p [P\cdot] = kp [M] [P\cdot]$

Emulsion Polymerization

Kinetics

Rate of Polymerization (cont.)

$[P\cdot]$ can be substituted by:

$$[P\cdot] = \frac{10^3 N'ñ}{N_A}$$

Therefore:

$$R_p = \frac{10^3 N' ñ k_p [M]}{N_A}$$

- In stage I, N' steadily decreases as surfactant is used up
- ñ increases
- Overall, N'ñ increases

Emulsion Polymerization

Kinetics

Rate of Polymerization (cont.)

$$R_p = \frac{10^3 N' ñ k_p [M]}{N_A}$$

Note:

k_p, [M], and ñ are (more or less) constant for any particular Monomer.

So:

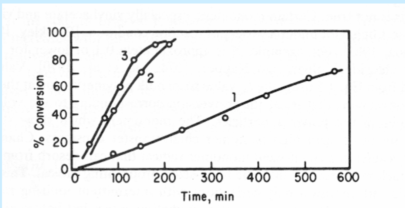
To increase Rate, need to increase N

→ You can increase N by:
- Increasing Surfactant
- Increasing R_i by increasing Initator Concentration [I]

Emulsion Polymerization

Kinetics

Rate of Polymerization → You can increase N by:
Increasing Surfactant

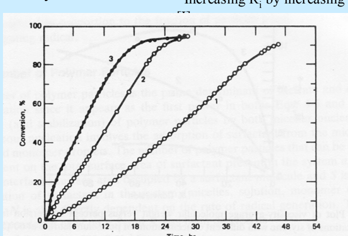


Conversion vs. time for emulsion polymerization of styrene with different concentrations of potassium laurate at 60◦C. Moles of emulsifier: 1 = .0035; 2 = .007; 3 = .014

Emulsion Polymerization

Kinetics

Rate of Polymerization → You can increase N by:
Increasing R_i by increasing



Conversion vs. time for emulsion polymerization of vinyl chloride at 50◦C with different concentrations of initiator: 1 = .0012%; 2 = .0057%; 3 = .023%.

Emulsion Polymerization

Kinetics

Rate of Polymerization: 3 Cases depending on ñ (stages II and III only)
Note: ñ is monomer dependent

Case 2: ñ = 0.5 : THIS APPLIES TO MOST CASES
- no desorption of radical (or faster absorption vs. desorption)
- 1 radical per particle
- since $r_i = r_t$, half particles have radicals, half don't (ñ = 0.5)

Case 1: ñ < 0.5
- significant desorption; often due to chain transfer to monomer, which makes a small $P^{\cdot}$ that can easily desorb
- slow absorption relative to desorption

Case 3: ñ >0.5
- 2 or more radicals per particle, therefore you need a large particle
- low termination facilitates large size
- faster absorption versus desorption

Emulsion Polymerization

Kinetics

Degree of Polymerization

Rate of radical entering particle = "particle initiation"

$= r_i = R_i/N = r_t$

$DP = r_p/r_t = r_p/r_i$

Note: this is the same as the kinetic chain length for bulk:
R_p/R_i

And:
$r_p = k_p [M]$

So:
$r_p/r_i = N\, k_p [M] / R_i$

Emulsion Polymerization

Kinetics

Comparison with Bulk

For Emulsion Polymerization:

$$R_p = \frac{10^3\, N'\, \tilde{n}\, k_p [M]}{N_A}$$

And:

$$DP = r_p/r_i = N\, kp\, [M] / R_i$$

Therefore:
You can increase the rate of polymerization by increasing N
And:
You can increase DP by increasing N, which is increased by increase in surfactant

Recall for Bulk Polymerization:

$$R_p = k_p [M] /(R_i/2k_t)^{1/2}$$

And:

$$DP = k_p [M] / [2 (f\, k_d\, k_t [I])^{1/2}]$$

Therefore:
You can**not** increase the rate of polymerization
Without:
Decreasing DP

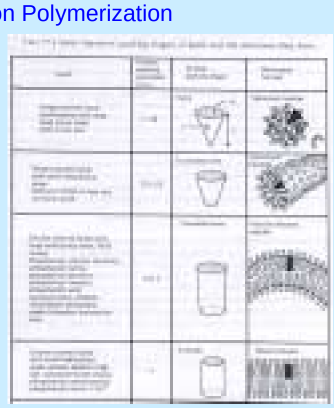
Emulsion Polymerization

Chemistry

Surfactant Structure

Israelachvili Packing Parameter:

$$P = \frac{v}{(a_0)\ (l_c)}$$



Emulsion Polymerization

Chemistry

Phase Diagrams