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

Polymer solution → Precipitated polymer

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)

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

Non-polar "tail" Polar "head"
Emulsion Polymerization

Concepts

Key to Emulsion and Emulsion Polymerization = Micelles

$\text{Water} \rightarrow \text{Monomer}$

Conc. $\geq$ CMC

CMC = Critical micelle concentration
Emulsion Polymerization

Concepts
Droplet vs. Micelle

Emulsion Polymerization

Mechanism

I → R

Emulsion Polymerization

Mechanism
Stages of Emulsion Polymerization

Polymerization Rate

Time
### Emulsion Polymerization

**Mechanism**

**Stages of Emulsion Polymerization**

**Stage I**
- 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

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

**Stage III**
- Particle number remains constant
- [M] decreases, therefore rate decreases
Emulsion Polymerization

Kinetics

Rate of Polymerization

Once inside a particle, a radical propagates according to:

\[
\text{radical propagation} = r_p = k_p [M]
\]

Note: \( k_p \) is the same as bulk radical poln.

Overall rate of polymerization:

\[
R_p = r_p [P] = k_p [M] [P]
\]

Rate of Polymerization (cont.)

\[ [P] \text{ can be substituted by:} \]

\[
[P] = 10^3 N' n
\]

Therefore:

\[
R_p = 10^3 N' n k_p [M] \]

\[\frac{N_a}{N_a}\]

- In stage I, \( N' \) steadily decreases as surfactant is used up
- \( n \) increases
- Overall, \( N' n \) increases

Note: \( k_p \), [M], and \( n \) are (more or less) constant for any particular Monomer.

So:

To increase \( R_p \), need to increase \( N \)

\[\to \]

You can increase \( N \) by:

- Increasing Surfactant
- Increasing \( R_i \) by increasing Initator Concentration [I]

Emulsion Polymerization
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 ñ = 0.5, 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_i 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”

\[ r_i = R_i N = r_i \]

\[ \text{DP} = \frac{r_p}{r_i} = \frac{r_p}{r_i} \]

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

\[ \frac{R_p}{R_i} \]

And:

\[ r_p = k_p [M] \]

So:

\[ \frac{r_p}{r_i} = N \frac{k_p [M]}{R_i} \]

Emulsion Polymerization

Kinetics

Comparison with Bulk

For Emulsion Polymerization:

\[ R_p = 10^3 N' N k_p [M] \]

\[ N' \]

And:

\[ \text{DP} = \frac{r_p}{r_i} = N \frac{k_p [M]}{R_i} \]

Recall for Bulk Polymerization:

\[ R_p = k_p [M] \left( \frac{R_i}{2k_d} \right)^{1/2} \]

And:

\[ \text{DP} = \frac{k_p [M]}{2 \left( \frac{t k_d k_i [I]}{2} \right)^{1/2}} \]

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

Therefore:

You cannot increase the rate of polymerization

Without:

Decreasing DP

Emulsion Polymerization

Chemistry

Surfactant Structure

Israelachvili Packing Parameter:

\[ P = \frac{v_a}{(a_0)(l_c)} \]