

Lecture 14: Processing Approaches: Emulsion Polymerization Processes

Tromsdorff Effect (or Auto-acceleration)

- Auto-acceleration usually occurs in radical chain polymerizations and normally in bulk polymerization.
- As conversion (π) increases, the viscosity (η) increases so much that the ends cannot find each other to terminate polymerization. This in turn lowers the effective termination rate ($k_{t,eff}$) and termination rate (R_t) and thus, the average number weight of polymerization \overline{P}_n increases. In other words:

$$\pi \uparrow \rightarrow \eta \uparrow \rightarrow k_{t,eff} \downarrow \rightarrow R_t \downarrow \rightarrow \overline{P}_n \uparrow$$

- In auto-acceleration,
 - There is no change in k_d because there are small molecules
 - There is no change in k_p because of small molecules as well
 - But for k_t , the rate of termination decreases because the two growing chain ends cannot find each other.
- We know from previous lecture that the rate of polymerization is:

$$R_p = k_p \left(\frac{2k_d f [I]}{k_t} \right)^{1/2} [M]$$

And the number average degree of polymerization is:

$$\overline{P}_n = 2a\nu \quad \text{where } 1/2 \leq a \leq 1$$

$a = 1$ for coupling
 $a = 1/2$ for disproportionation

Where ν is the number of monomers added per effective free radical and given by:

$$\nu = \frac{k_p [M]}{(2k_d f d_t [I])^{1/2}}$$

- See Figure 3-15 in Odian for a plot that demonstrates autoacceleration.

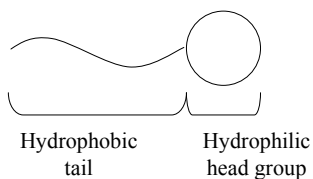
Emulsion Polymerization

(See handout: Ch. 12)

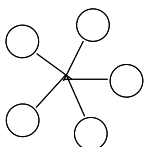
- In emulsion polymerization there are some key “ingredients”:
 - The monomer must be insoluble in water and polymerizable by free radicals
 - Water-soluble initiator
 - Water
 - Surfactant

Formation of micelles

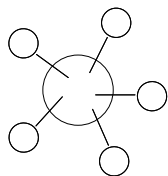
In water, soap (e.g. sodium palmitate) is added to the aqueous phase.
For example: $\text{CH}_3(\text{CH}_2)_n - \text{COO}^- \text{Na}^+$



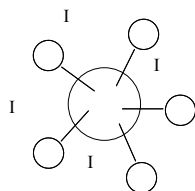
The surfactant forms micelles at high concentrations:



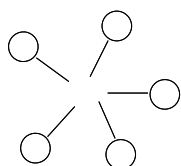
Add monomer and disperse as droplets



large monomer drops ($\sim\text{mm}$)



micelle with monomer (1\AA to $0.1\mu\text{m}$)
and initiator (I)



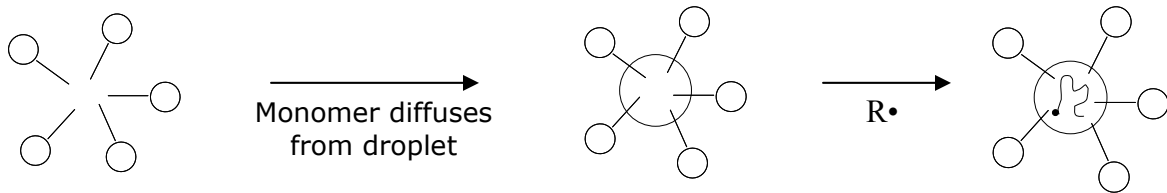
empty micelle

- The initiator (I) can diffuse into the micelle particle and polymerize the monomer
- More monomer from the droplet diffuses over and polymerizes
- Thus the particle size increases

The three stages of emulsion polymerization:

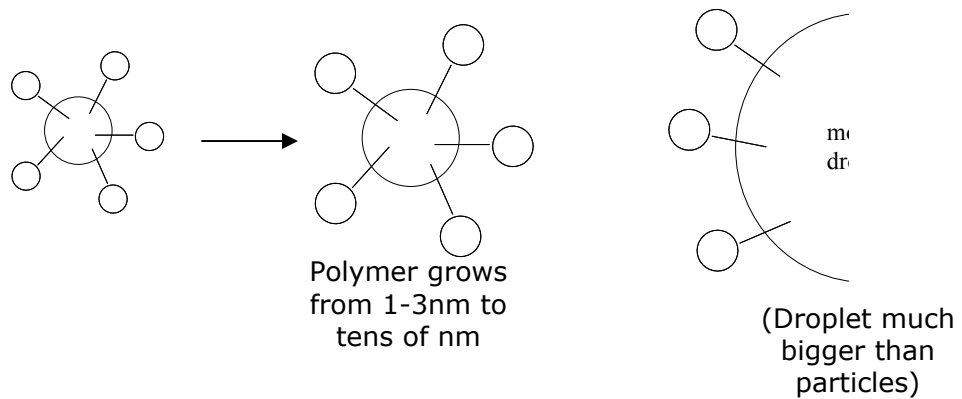
Stage I:

- The monomer diffuses to the empty micelle from droplet
- Polymerization initiated in micelles to become polymer particles
- New particles are generated as micelles are consumed
- This stage lasts for conversion $\pi \sim 0-15\%$



Stage II:

- No more surfactant available to generate new particles
- Monomer diffuses into now a constant number of particles to maintain some equilibrium $[M]$ with the particle
- The monomer reservoir drops get slowly consumed



- An equilibrium between increasing interfacial tension within micelle and monomer/polymer dilution leads to a constant volume fraction where Φ_2 is the volume fraction of the polymer and Φ_1 is the volume fraction of the monomer

$$[M] = [M]_0(1 - \Phi_2)$$

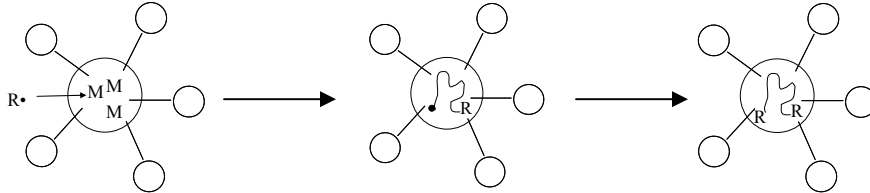
Stage III:

- This stage occurs when conversion $\pi \sim 40-60\%$
- All the monomers exist in particles

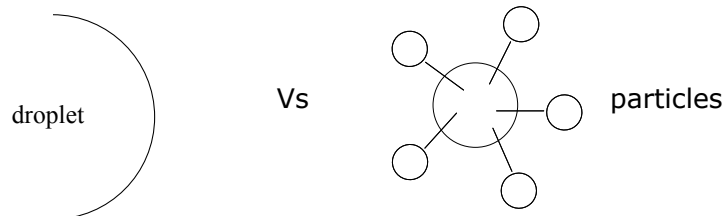
- The monomer droplets are exhausted
- $[M]$ in particles continually decreasing as π increases
- Particle size is constant
- Conversion rate can reach up to 80-100%

Smith-Ewart Model

- The Smith-Ewart model states that one radical diffuses into a particle at a time and termination occurs when another radical $R\bullet$ diffuses in:



- There is 1-100 seconds between radical entry events



- Why does polymerization happen in the particle rather than the droplet? Answer: Large polymer particles have a much lower surface area to volume ratio than the small droplets. The probability of a free radical entering a droplet versus a micelle particle is very small.

Kinetics:

- Assumptions:
 - All radicals enter the micelle
 - When radical enters a particle, there is instant initiation if there are no other radicals present. If there is a radical already present, termination occurs
- The number of monomer molecules converted to polymer per second per particle is given by:

$$-\frac{dm}{dt} = \frac{1}{2}k_p[M] = \frac{\text{monomers}}{\text{sec} \cdot \text{radical}}$$

½ because the chain grows half the time (the other ½ is to terminate the polymer)

Initiators

(Ch. 12.1.3, p. 251 in handout)

- Rate of production of initiator radicals is given by:

$$\rho = \frac{N_A}{10^3} (1 - \Phi) k_{d,r} [X][Y] = \frac{\text{radicals}}{\text{cm}^3 \cdot \text{sec}}$$

Where Φ is the organic (monomer) volume fraction
 $k_{d,r}$ is the k_d for the radical
 $[X]$ and $[Y]$ are the concentration of the redox

initiators

- The number of particles in solution is given by:

$$n = (\# \text{ of particles})/\text{cm}^3$$

$$n = (0.53)(c_s a_s)^{3/5} \rho^{2/5} \left(\frac{dV}{dt} \right)^{-2/5}$$

Where c_s is the concentration of the surfactant
 a_s is the area of the surfactant head group

- Define Δt as the time between $R\bullet$ entry:

$$\Delta t = \frac{n}{\rho} \text{ is usually } 1\text{-}100 \text{ sec}$$

$$\bar{p}_n = k_p [M] \Delta t = k_p [M] \frac{n}{\rho}$$