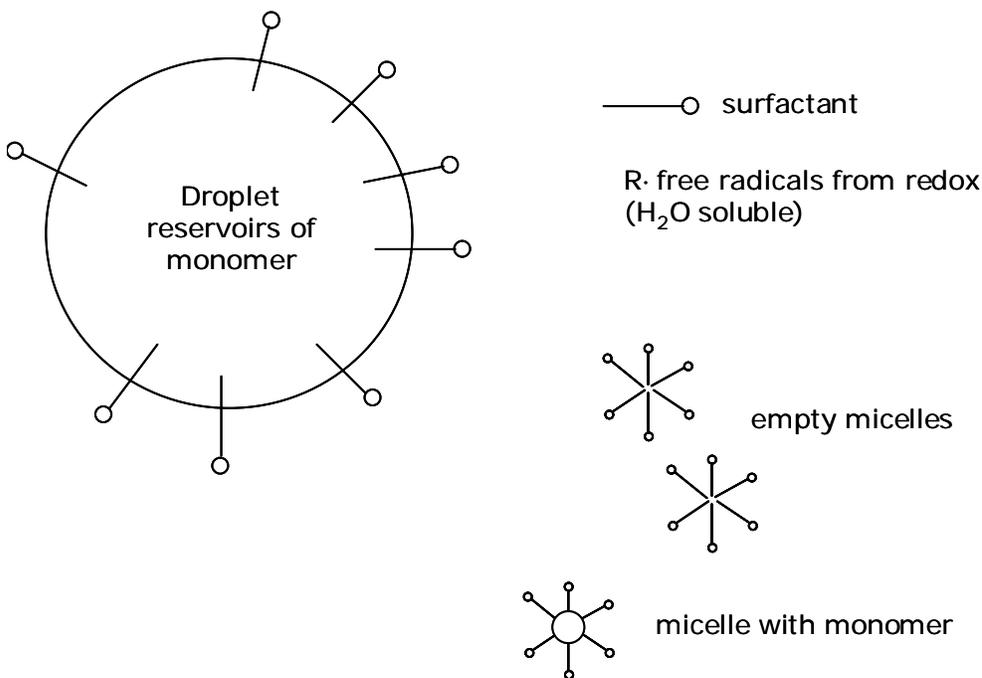**Lecture 15: Processing Approaches: Suspension (bead) Polymerization
Processes, Polyvinyl Chloride via Precipitation Polymerization, Polyethylene
via Radical Polymerization**

——o surfactant

R· free radicals from redox
(H_2O soluble)

empty micelles

micelle with monomer

Rate of conversion, emulsion polymerization

$$\overline{p_n} = k_p[M]\Delta t = k_p[M]\frac{n}{\rho}$$

In general,

$$R_p = \frac{n}{2}$$

} handout

$$-\frac{dm}{dt} = \frac{1}{2}k_p[M]$$

$$R_p = \frac{n}{2}k_p[M]$$

ρ (radicals)

$$\overline{p_n} = k_p[M]\Delta t = k_p[M]\frac{n}{\rho}$$

Emulsion Polymerization: monomer $\rightarrow$ porous particles

introduce plasticizer
more readily processible, aerodyn. in powder form
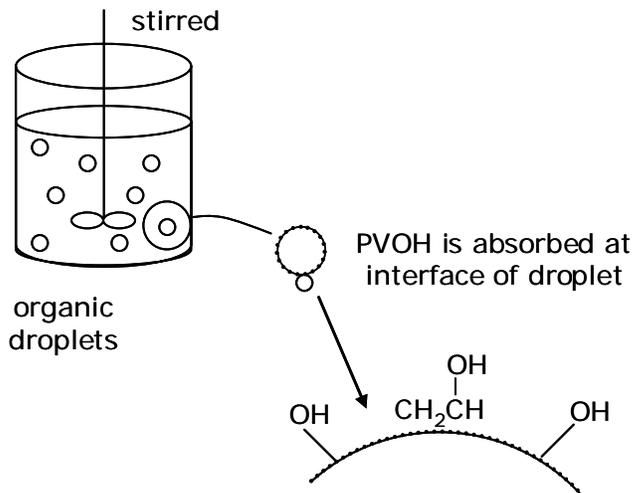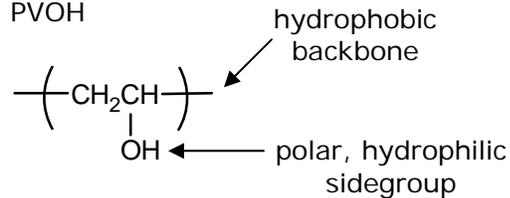
Common emulsion polymers:
        styrene + copolymers
        vinyl chlorides   ex. Pleather
        butadiene
        vinylidene chloride
        vinyl acetate
        vinyl acrylates (acrylics)
        methyl acrylates

Advantages:
        - low η (viscosity)
        - great T control
        - final product $\rightarrow$ fine powder
                        or water form $\Rightarrow$ coatings

Disadvantages:
        - a lot of soap as impurity
        ex. In medical applications, can be irritant

Suspension Polymerization:

(Pearl of Bead)
"Ingredients"
monomer – organic phase
aqueous phase
initiator (soluble in monomer phase)
stabilizer, often a polymer, such as PVOH

$$-(-CH_2CH-)-$$

hydrophobic backbone

OH ← polar, hydrophilic sidegroup

stirred

organic droplets

PVOH is absorbed at interface of droplet

OH   CH₂CH   OH
         |
         OH

much more soluble in water

Organic droplets: ~ 1 μm – 1 cm
Drop size determined by impeller speed
Within each droplet, have
       - initiator
       - monomer
$\Rightarrow$ Batch reactor within droplet
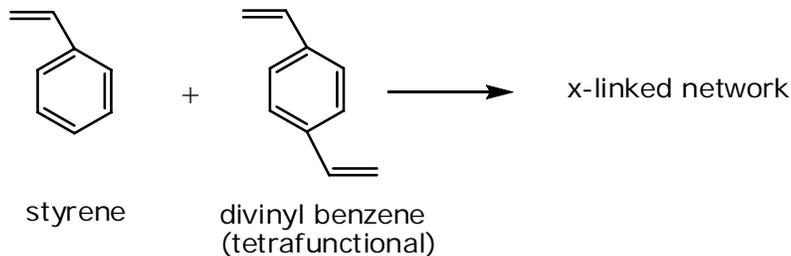   Kinetics are identical to typical large scale free radical polymerization
       • initiation
       • propagation
       • termination
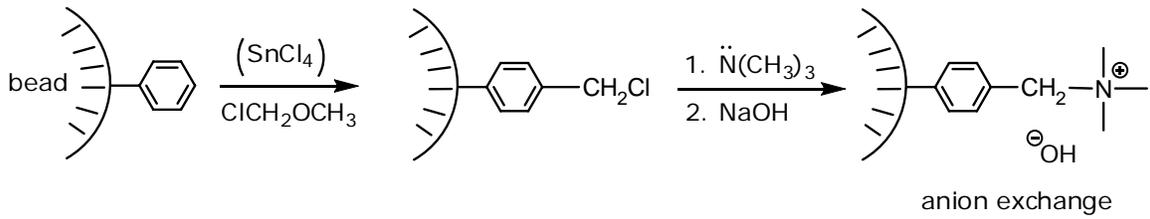   • steady state assumption
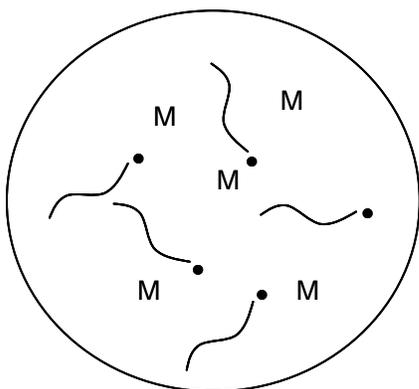
Concerned with avoiding drop coalescence
$\rightarrow$ premix initiator + monomer
$\rightarrow$ agitate H2O phase + add organic phase
       ~ 20 – 30 % vol
$\rightarrow$ adjust impellar speed to get desired drop size
$\rightarrow$ add stabilizer (PVOH)
$\rightarrow$ continue stirring at more gentle speed and increase T to 40°C $\rightarrow$ 80°C depending on which initiator you're using
$\rightarrow$ initiator activation
$\rightarrow$ go to near complete conversion
(may need to increase T for final % π)

Products:
       - glassy rigid beads often called "latex beads"
       - very uniform
       - nice spherical shapes

x-linked network

styrene   divinyl benzene
             (tetrafunctional)

vary surface chain:

bead —⟨benzene⟩ $\xrightarrow[\text{ClCH}_2\text{OCH}_3]{(\text{SnCl}_4)}$ bead —⟨benzene⟩—CH_2Cl $\xrightarrow[\text{2. NaOH}]{\text{1. }\ddot{N}(CH_3)_3}$ bead —⟨benzene⟩—CH_2—$\overset{\oplus}{N}(CH_3)_3$ $\overset{\ominus}{OH}$

anion exchange

or

bead —⟨benzene⟩ $\xrightarrow{\text{H}_2\text{SO}_4}$ bead —⟨benzene⟩—$\overset{\ominus}{SO_3}$ $\overset{\oplus}{Na}$

cation exchange
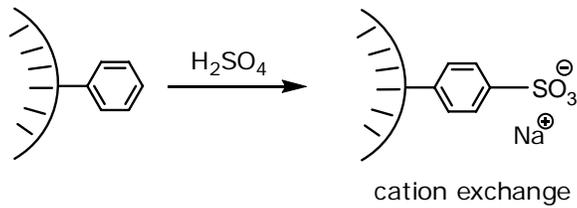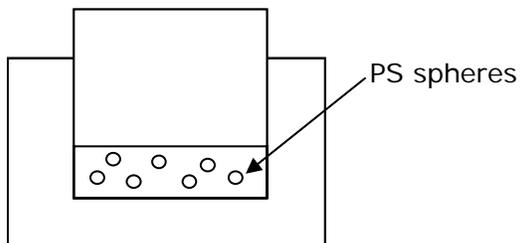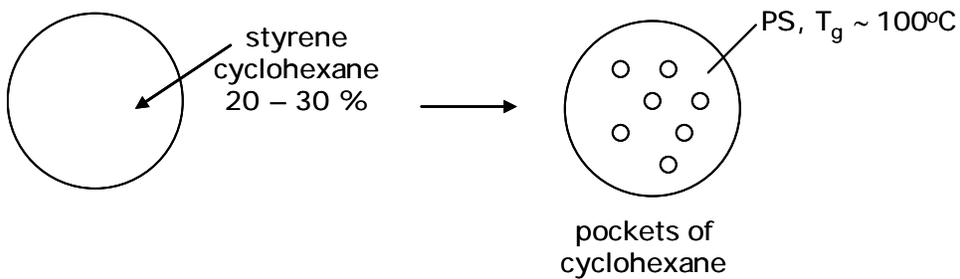
Form Pores:
- add non-solvent + monomer w/organic phase

Form connected channels of non-solvent

$\rightarrow$ go to high π
       flash off non solvent

If monomer (e.g. styrene) is well-dissolved in solvent, but solvent is poor for high MW polymer (e.g. cyclohexane)

styrene
cyclohexane
20 – 30 %

$\longrightarrow$

PS, $T_g \sim 100^o$C

pockets of cyclohexane

PS spheres

Increase T to 120°C
$\Rightarrow$ expansion – foaming effect
  $\rightarrow$ very large increases in size and
decreases in density (mostly air)
$\Rightarrow$ STYROFOAM®

Prof. Paula Hammond   Page 4 of 8

OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.

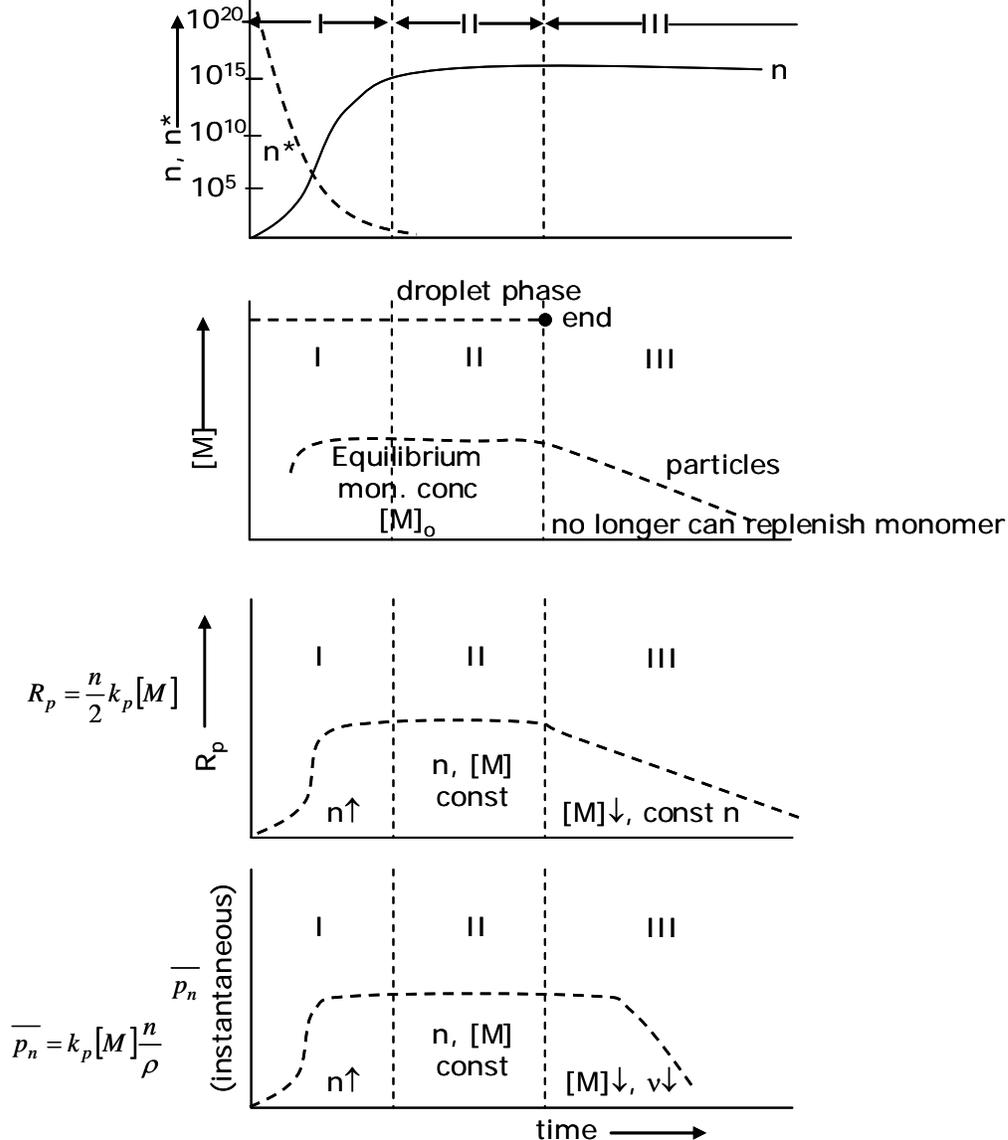The following figures are adapted from page 250 of *Polymer Synthesis*:[1]

Fig 12.2. Diagrams showing the three stages of emulsion polymerization: (I) Micelles increasing; (II) micelles exhausted, droplet phase remains; (III) droplet phase exhausted.

n number of particles per unit volume

n* number of micelles per unit volume

[M] monomer concentration in the droplets and in the particles

R_p overall rate of polymerization

$\overline{p_n}$ instantaneous degree of polymerization

[1] Rempp, P. and Edward W. Merrill. *Polymer Synthesis*. Second Edition. New York, NY: Hüthig and Wepf, 1991. page 250.

Rate of Conversion, Emulsion Polymerization

$$\overline{p_n} = k_p[M]\Delta t = k_p[M]\frac{n}{}$$

rate of production of free radicals

In general:

mol/l

$$R_p = \frac{n}{2}k_p[M] = \quad \text{monomer molecules per sec per cm}^3$$

particles per cm^3 l/mol-sec

* (recall that the rate, -dm/dt of disappearance of monomer molecules **per particle** per second is $\frac{1}{2}k_p[M]$)

In general, for conversion:

$$\frac{d\pi}{dt} = \underbrace{\frac{n}{2}k_p[M]}\cdot\frac{1}{C} = n\cdot\frac{-dm}{dt}\frac{1}{m_o}$$

initial # of monomer molecules charged

=monomers/sec-cm^3

$$C = \frac{\Theta N_A \rho_m}{M_u} = \text{ initial \# of monomers in total volume}$$

How much you've added

where Θ = cm^3 monomer charged/cm^3 of total volume = volume fraction
   ρ = density of monomer (g/cm^3)
   N_A = Avogadro's number = 6.023x10^{23} molecules/mole
   M_u = MW of monomer (repeat) unit

For Stage I:

$$[M] \cong [M]_{eq} = [M]_o(1-\Theta_2)$$

   where $[M]_o$ = pure monomer
      Θ_2 = vol. Fraction of polymer in particles at equilibrium
      n = n(t) b/c number of particles ↑

$$\Rightarrow \int_0^{\pi_I} d\pi = \frac{1}{C}\int_0^{t_I} n(t)\frac{k_p}{2}[M]_o(1-\Theta_2)\,dt$$

For Stage II:

Surfactant consumed, droplets still exist
  Growing particles

$$[M] = \text{constant} = [M]_o (1 - \Theta_2)$$

n = constant

$$\int_{\pi_I}^{\pi_{II}} d\pi = \frac{1}{C} \underbrace{\int_{t_I}^{t_{II}} \frac{n}{2} k_p [M]_o (1 - \Theta_2) \, dt}_{\text{constant}}$$

$$\Rightarrow \boxed{\pi_{II} - \pi_I = \frac{n k_p [M]_o (1 - \Theta_2)}{2C} (t_{II} - t_I)}$$
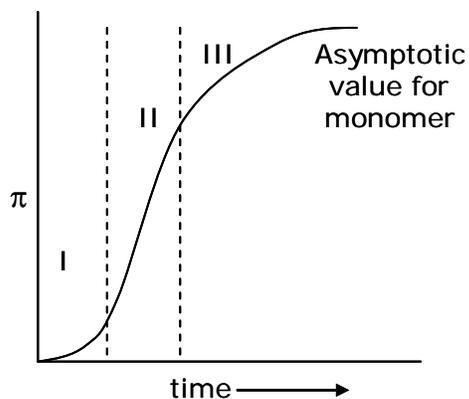
Stage III:

Droplets exhausted, only particles
  On avg, particles all same size, grow at same rate

Here, monomer is consumed w/in particles, as monomer $\rightarrow$ polymer,
$[M] \downarrow$ w/in particle.

$$[M] = [M]_o (1 - \pi)$$

$$\Rightarrow \int_{\pi_{II}}^{\pi} d\pi = \frac{1}{C} \int_{t_{II}}^{t} k_p [M]_o (1 - \pi) \frac{n}{2} \, dt$$

$$\Rightarrow \frac{-\Delta \ln(1 - \pi)}{\Delta t} = \frac{k_p [M]_o n}{2C}$$

Plot: vertical axis labeled π, horizontal axis labeled time →. Curve rises sigmoidally to an "Asymptotic value for monomer". Regions labeled I, II, III separated by dashed vertical lines.

For Stage I:

$$n = f\left(C_s, a_s, \rho, \nu_n, \frac{dm}{dt}\right)$$

where C_s = surfactant concentration
a_s = area of surfactant molecule (of polar head)
ρ = rate of radical production
ν_n = vol of a single repeat
dm/dt = rate of monomer polym.

Empirical expression:

$$n \approx 0.53\left(C_s a_s\right)^{\frac{3}{5}} \rho^{\frac{2}{5}} \left(-\nu_n q \frac{dm}{dt}\right)$$

$$q = \frac{\text{vol polymer} + \text{vol monomer}}{\text{vol polymer}} \left.\right\} \text{ inside the particle (related to [M])}$$