Last week we made polyacrylamide by concentrated solution (similar to bulk) and by solution polymerization.

1) a) Give the chemical structure of the monomer and explain why it is soluble in the solvent used.
   b) What initiator can be used to polymerize this monomer and under what conditions?
   c) Compare the extent of reaction “p” that is needed to make a high molecular weight polymer for this chain growth polymerization compared to that needed for high molecular weight in a step growth polymerization.
   d) How was the polymer separated from the reaction solution? (Why was a small amount of HCl used?)
   e) Compare the reaction when the monomer concentration was very high to the reaction when the monomer concentration was moderate in terms of scale-up to an industrial synthesis (consider heat, ability to separate polymer and waste solvent byproduct).

2) a) For a solution reaction such as the polymerization of polyacrylamide, write the reaction equation for the propagation reaction and the rate equation for propagation.
   b) Write the reaction equations and the rate equation for initiation.
   c) Write the reaction equations and rate equation for termination.
   d) Sketch the overall conversion rate versus time for such a free radical chain growth reaction and state the relationship between the rates of termination and initiation for most of this reaction.
   e) Calculate an expression for the kinetic chain length based on the monomer concentration and the initiator concentration.

3) In addition to single phase polymerizations we considered two phase reactions.
   a) Describe the reaction scheme for a suspension polymerization (give number of phases, phase composition, process that determines droplet size, location of initiator, kinetic chain length compared to solution polymerization).
   b) Describe the reaction scheme for an emulsion polymerization (give number of phases, phase composition, process that determines droplet size, location of initiator, kinetic chain length compared to solution polymerization).
   c) Write the rate of propagation for an emulsion polymerization.
   d) Calculate the kinetic chain length for an emulsion polymerization.
   e) How does the kinetic chain length equation for an emulsion polymerization differ from that of a suspension polymerization?
1) a) $c = 0 \text{ mol}$

b) A free radical initiator we used was:

- Hydrogen peroxide
- As the reduction of $H_2O_2 \rightarrow HO^- \cdot OH^-
- By the oxidation of $Fe^{+2} \rightarrow Fe^{+3}$

2) For a step growth you need almost 100% conversion to achieve high molecular weight polymer.
d) The polymer precipitated out of the dropwise addition to propanol with a slight trace of HCl. HCl neutralized off and removed HSO₃⁻ & CO₂⁻ from the system terminating the reaction.

e) For high concentrations the reaction got very warm. In scale-up the reaction might become hectic & uncontrolled chain reactions might occur since termination becomes difficult in a high concentration system. That is, long chains cannot rapidly diffuse while monomers can easily approach the growing chain so low termination rates result in a runaway reaction (Flory-Stockmayer effect). The dilute system did not heat.

For high concentration, the reaction resulted in a solid gel & the water could not be separated from the polymer. For dilute, the polymer was
easily separated by precipitation or idihed procedure.

The concentrated system used little solvent but the dilute system produced about 5X as much solvent as polymer.

2) a) 

\[ \text{C} + \text{C} \rightarrow \text{C} \]

\[ \text{NH}_2 \]

\[ \text{M} + \text{M}_n \overset{k_p}{\rightarrow} \text{M}_{n+1} \]

\[ R_p = K_p [M] [M^\bullet] \]

Propagating Radical Concentration

b) 

\[ \text{HO} - \text{OH} \rightarrow \text{HO}^- + \text{H}^+ \]

Fe^{3+} \rightarrow Fe^{2+}

\[ R_e = K_e [E]^\bullet \]

c) 

\[ \text{C}=\text{C} + \text{C}=\text{C} \rightarrow \text{C}=\text{C} \]

\[ \text{C}=\text{O} \]

\[ \text{NH}_2 \]
\[ \text{ disproportionation at } t \quad \text{y} \]

\[ R_t = K_f [M_0]^2 \]

**d)**

\[ R_{\text{final}} = R_\infty \]

For most of the reaction \( R_2 = R_\infty \)

**e)**

\[ \bar{y} = \frac{R_T}{R_t} = \frac{R_T}{R_1} = \frac{K_p [m_0]}{K_f [M_0]^2} \]

From \( R_2 = R_\infty \) we have

\[ [M_0] = \sqrt{\frac{K_f [I]}{K_p}} \]

\[ \bar{y} = \frac{K_p [m_0]}{\sqrt{K_f K_2 [I]}} \]
3) a) Suspension:

2 phase
Monomer & Solvent

Particle size is determined by strength of agitation, presence of polymer/alcohol

Kinetics: Mark Blak Polymerization

\[
\bar{D} = \frac{Kp [M]}{K_k [I]^2}
\]

b) Emulsion:

2 phase
Monomer & Solvent

Particle size is fixed by surfactant

No. of particles is determined by surfactant concentration

Initiator is soluble in solvent (water)

Kinetics differ from bulk/solution

\[
\bar{D} = \frac{N_k p [M]}{2 f K_k [I]}
\]
c) \[ R_p = N_k p [m] \]
   where \( N_k \) is the number of micelles.

\[ \text{rate of micelles} \]

\[ \bar{v} = \frac{N_k p [m]}{P_r} \]

\[ P_r \text{ is the probability for a micelle} \]

\[ p = \frac{2 + k d [I]}{N} \]

\[ \bar{v} = \frac{N_k p [m]}{2 + k d [I]} \]

\[ \bar{v} \text{ is controlled by } N \text{ and concentration of surfactant in emulsion phase.} \]

Stronger dependence on [I] for Emulsion Polymers than \( \text{polymers.} \)