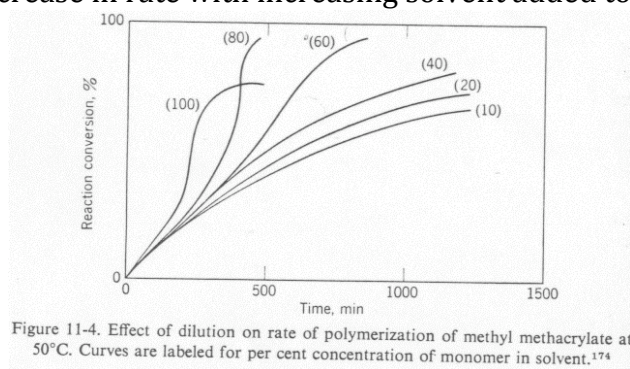


Introduction to Polymers Quiz 7 090225

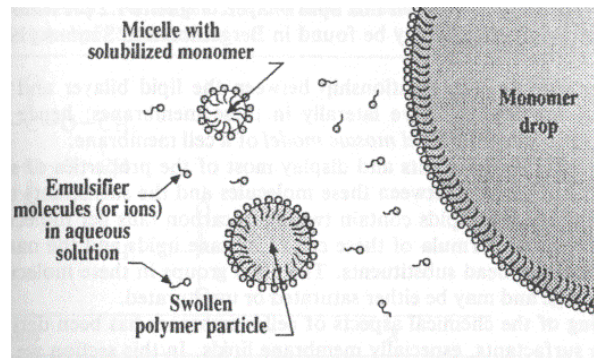
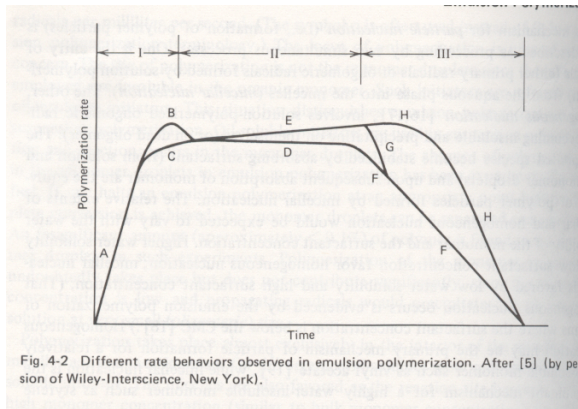
This week we discussed chain growth polymerization using free radical initiators. We performed two syntheses for Polystyrene involving bulk polymerization and emulsion polymerization.

- 1)
 - a) What are the three main stages of chain growth polymerization?
 - b) Is an initiator a catalyst?
 - c) Write an expression for the rate of propagation for chain growth polymerization in terms of the monomer concentration and the initiator concentration.
 - d) Obtain an exponential expression for the monomer concentration from part c and show that this is linear for early stages of the reaction.
 - e) Obtain an expression for the kinetic chain length for chain growth polymerization in terms of the monomer concentration and the initiator concentration.
- 2)
 - a) List and draw the monomer, initiator, reaction temperature, and solvent for bulk polymerization of styrene.
 - b) When adding solvent to polymerization of MMA, below, the conversion versus time shows several characteristic features. Write an equation that explains the decrease in rate with increasing solvent added to the reacting system.



From R. W. Lenz's book.

- c) Why does the plot show a change in shape of the conversion vs time curve for 80 and 100% concentrations? (A steep increase after about 1/2 of the reaction time and plateau).
 - d) How was polystyrene purified after the bulk polymerization?
 - e) What are the disadvantages of bulk polymerization?
- 3)
 - a) List and draw the monomer, initiator, reaction temperature, solvent for emulsion polymerization of styrene.
 - b) Describe other materials needed for emulsion polymerization and why they are needed.
 - c) Obtain an expression for the rate of polymerization and the kinetic chain length for emulsion polymerization.
 - d) How does emulsion polymerization overcome the disadvantages of bulk polymerization (see question 2e).



Figures from Heimenz *Colloid Science*.

e) The figure above (left) shows three regimes for emulsion polymerization and a schematic of the structure of the reaction media. Explain the difference between regimes I, II, and III in terms of the presence of a droplet phase, the change in the number of micelles with time, and the fraction of micelles with an active radical from what you know from class. (Explain the polymerization.)

ANSWERS: Introduction to Polymers Quiz 7 090225

- 1) a) Initiation, propagation and termination.
 b) A catalyst is not consumed in a reaction but plays a part in facilitating the reaction. Initiators are consumed and generally lead to one end group of the chain polymerized polymer. So an initiator is not a catalyst even though it is used in a small amount to facilitate a reaction.

$$c) R_p = -\frac{d[M]}{dt} = k_p \sqrt{\frac{fk_d}{k_t}} \sqrt{[I]} [M] = K \sqrt{[I]} [M]$$

$$\int_{[M]_0}^{[M]} \frac{d[M]}{[M]} = -K \sqrt{[I]} \int_0^t dt$$

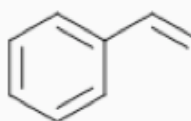
$$d) \ln \left(\frac{[M]}{[M]_0} \right) = -K \sqrt{[I]} t$$

$$[M] = [M]_0 \exp(-K \sqrt{[I]} t)$$

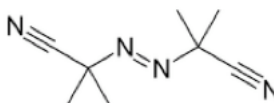
The exponential can be expanded, $\exp -x = 1 - \frac{x}{1!} + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \dots$

For short times we can consider only the first two terms so, $[M] \approx [M]_0 (1 - K \sqrt{[I]} t)$

$$e) \bar{v} = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p \sqrt{\frac{fk_d}{k_t}} \sqrt{[I]} [M]}{fk_d [I]} = \frac{k_p [M]}{k_t \sqrt{fk_d [I]}}$$



- 2) a) monomer: Styrene



initiator: AIBN Azobisisobutyronitrile

Temperature: 80°C (degradation of AIBN at 60°C)

Solvent: Bulk polymerization i.e. no solvent

$$b) R_p = K \sqrt{[I]} [M] \text{ and } [M] = [M]_0 \exp(-K \sqrt{[I]} t)$$

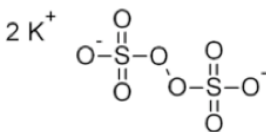
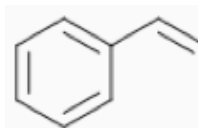
c) This is a manifestation of the Trommsdorf (gel) effect. The increase in rate occurs because termination is primarily by combination and two chains cannot reach each other when the system gels so that termination stops. Propagation continues since monomers can still diffuse to the growing chain. The system is viscous so the heat generated by propagation increases the temperature rapidly.

d) The bulk polymerization product was dissolved in a small amount of toluene and this solution was precipitated by adding to an excess of propanol while stirring. The polymer was washed several times with propanol.

e) The disadvantages of bulk polymerization are poor heat transfer from the reaction that leads to overheating of the polymerizing system and the Trommsdorf effect. Polydispersity is high due to backbiting of the radical on the chain. Chain transfer is prominent due to the high density of chains. Reducing $[I]$ increases molecular weight but only at the expense of

lowering the rate of polymerization. You can not get high molecular weight and high rate of polymerization.

3) a) monomer: Styrene

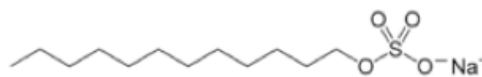


initiator: Potassium persulfate

Temperature: ~80C (degradation of Potassium persulfate at ~60C)

Solvent: There is no solvent. The reaction occurs in the bulk within micelles that are suspended in water.

b) Micelles are made from sodium dodecyl sulfate



Water is used to suspend the micelles and as a medium to form free radicals with potassium persulfate.

The micelles are broken with NaCl after the reaction is complete.

c) The micelles are active (growing free radical) half of the time and are dormant (no growing free radical) half of the time. The rate of polymerization depends on the number of micelles, N and the monomer concentration $[M]$.

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

The micelles grow half of the time. The rate of the micelles being turned on and off is given by the rate of initiation, R_i , divided by the number of micelles, N , $\rho = \frac{R_i}{N} = \frac{2fk_d[I]}{N}$. The kinetic

chain length is the rate of propagation divided by this rate of switching on and off, $\bar{v} = \frac{k_p[M]N}{2fk_d[I]}$.

d) By increasing N both the degree of polymerization and the rate can be increased. This can be achieved by adding more SDS. Decreasing $[I]$ will only effect the degree of polymerization. This overcomes the problem with bulk polymerization that for high molecular weight products you need to slow the reaction rate.

e) Droplet phase is present in I and II but not in III this leads to depletion of monomer in the water phase and the decline in polymerization rate in regime III. The number of micelles is very large at the start of the reaction but only a very few are initiated. The initiated growing polymer micelles require more surfactant to stabilize the polymer particles that they obtain from non-initiated micelles. When an equilibrium number of polymer/micelle particles form for the system initiation and termination of micelles offset each other and the micelles are either on or off in terms of growth. This is regime II.