Chem 466
Lecture # 21
04/08/2014

- Exam III Thursday
- Quiz #9 $x = 6.1$
  $SD = 3.7$
Figure 5.1 Mole fraction of component 1 in the copolymer as a function of feedstock composition for various reactivity ratios.

The crossover point. At the crossover point the copolymer and feed mixture have the same composition. The monomer ratio at this point is conveniently solved by Equation 5.2.15:

\[
\left( \frac{[M_1]}{[M_2]} \right)_{\text{cross}} = \frac{1 - r_2}{1 - r_1}
\]

For the case of \( r_1 = 0.33 \) and \( r_2 = 0.67 \) shown in Figure 5.1, \([M_1]/[M_2]\) equals 0.5 and \( f_1 = 0.33 \). This mathematical analysis shows that a comparable result is possible with both \( r_1 \) and \( r_2 \) greater than unity, but is not possible for \( r_1 < 1 \) and \( r_2 < 1 \).

6. When \( r_1 = 1/r_2 \), the copolymer composition curve will be either convex or concave when viewed from the \( F_1 \) axis, depending on whether \( r_1 \) is greater or less than unity. The further removed from unity \( r_1 \) is, the farther the composition curve will be displaced from the 45° line. This situation where \( r_1 r_2 = 1 \) is called an ideal copolymerization. The example below explores the origin of this terminology.

There is a parallel between the composition of a copolymer produced from a certain feed and the composition of a vapor in equilibrium with a two-component liquid mixture. The following example illustrates this parallel when the liquid mixture is an ideal solution and the vapor is an ideal gas.

**Example 5.1**

An ideal gas obeys Dalton’s law; that is, the total pressure is the sum of the partial pressures of the components. An ideal solution obeys Raoult’s law; that is, the partial pressure of the \( i \)th component above a solution is equal to the mole fraction of that component in the solution times the vapor pressure of pure component \( i \). Use these relationships to relate the mole fraction of component 1 in the equilibrium vapor to its mole fraction in a two-component solution and relate the result to the ideal case of the copolymer composition equation.
- Copolymer equation defines ratio of monomer repeat units in poly vs. ratio of monomers in feed (reaction mixture)

\[ \frac{d[M_1]}{dt} = \frac{[M_1]}{[M_2]} \left( \frac{r_1 [M_1] + [M_2]}{[M_1] + r_2 [M_2]} \right) \]

\[ \frac{d[M_2]}{dt} = \frac{[M_2]}{[M_1]} \left( \frac{r_2 [M_2] + [M_1]}{[M_1] + r_1 [M_2]} \right) \]

Ratio of monomer repeat units in poly (i.e., consumed during poly) depends upon reactivity ratios + monomer concentrations. See Figure 5.1 (text p. 169)

- when \( r_1 \approx r_2 \approx 1 \) \( \Rightarrow \) no pref. + random copoly

\[ r_1 \approx r_2 \approx 0 \Rightarrow \text{no homopoly + alternating copoly} \]

\[ r_1 \gg 1; r_2 \approx 0 \Rightarrow \text{initially high } M_1 \text{, then } M_2 \text{ polymer} \]

Can lead to big differences in polymer structure if traditional vs. controlled radical polymer.

Traditional: \( M_1 \) \( + \) \( M_2 \) \( \rightarrow \) mixture of poly of \( \Delta \) chain lengths + \( \Delta \) compositions

Controlled: \( M_1 \) \( + \) \( M_2 \) \( \rightarrow \) poly of similar chain lengths + \( \Delta \) compositions along the backbone
practical polymer conditions

1. bulk polymer
   - no solvent
   - cooling may be required, due to exothermicity of polymer
   - shrinkage occurs
   - monomer/polymer/initiator solubilities are important

2. solution polymer
   - monomer/polymer/initiator solubilities are important
   - dilution of solvent provides for heat transfer + smoother (more homogeneous) run
   - MW can be affected by conc.

3. suspension polymer
   - stirring required
   - monomer droplets (10-1000 um diameter) suspended in H₂O
   - initiator dissolved in monomer
   - suspending agents added: magnesium sulfate, H₂O insoluble inorganics, e.g. barium sulfate
   - if H₂O soluble poly + H₂O soluble initiator \( \rightarrow \) dispersion polymer
- polymer proceeds like many individual bulk
  polym. (same kinetics)
- gives large particles 10-1000 μm
- size & size dist dependent on
  suspending agent & stirring rate

4. Emulsion poly:

- monomer droplets (50nm-1μm)
  suspended in H2O as
  micelles
- initiator dissolved in H2O
- surfactants (emulsifier)
  added
- polymer occurs inside micelles
  - diffusion controlled
  - rate of diffusion of M + R
    into micelles

Both methods 3+4 can be used for
most H2O insoluble monomers

= \frac{\text{M}}{\text{M}_0} \text{ rate} = \frac{1}{3} \text{ etc.}

particularly good for CF₂=CFCF₂.
Inhibitors + Retarders

- used during storage of monomers to reduce polym. (unwanted)

\[ Z = \frac{k_z}{k_p} = \frac{\text{rate constant for trapping}}{\text{rate constant for prop.}} \]

- \( \alpha \propto Z \) as \( z \to 1 \), \( R_{\text{polym.}} \)

- species with high \( Z \) (\( >10 \)) are inhibitors
- species with low \( Z \) (\( <1 \)) are retarders
Inhibitor — prevents polymerization as long as it is present (induction period, \( \frac{k_i}{k_p} > 10 \)), but once consumed polymerization occurs as if without inhibitor.

Examples:

- Benzoguaiine

These species can undergo reaction further by additional radicals.

\[ R - H + O = C - O \quad \text{a quinone} \]

(4 atom abstraction)
**Phenol**

\[
\begin{align*}
\text{Phenol} + \text{O-H} & \rightarrow \text{Phenol-}^\cdot + \text{H}^+ \\
R^\cdot + \text{O-H} & \rightarrow \text{R-}^\cdot + \text{H}^+ \\
R^\cdot + \text{O}^\cdot & \rightarrow \text{R-O-O-H}
\end{align*}
\]

BHT - used as a food antioxidant
(2,6-di-tert-butyl-4-methyl phenol)

\[
\begin{align*}
\text{Phenol} + \text{O-H} & \rightarrow \text{Phenol-}^\cdot + \text{H}^+ \\
R^\cdot + \text{O-H} & \rightarrow \text{R-}^\cdot + \text{H}^+ \\
R^\cdot + \text{O}^\cdot & \rightarrow \text{R-O-O-H}
\end{align*}
\]

- Good at scavenging peroxyl radicals

**t-butyl catechol** is often used as an inhibitor
(es. when purchase styrene from Aldrich)

\[
\begin{align*}
\text{Phenol} + \text{O-H} & \rightarrow \text{Phenol-}^\cdot + \text{H}^+ \\
R^\cdot + \text{O-H} & \rightarrow \text{R-}^\cdot + \text{H}^+ \\
R^\cdot + \text{O}^\cdot & \rightarrow \text{R-O-O-H}
\end{align*}
\]

- An o-quinone
  (which can undergo further radical scavenging)
Retarder — decreases the amt. of polymer by trapping some of the unwanted radicals
\( (Z < 1; k_{\text{prop}} > k_2) \)

- no induction period b/c no complete trapping of radicals
- once retarder is consumed polymer occurs as w/out retarder

\[ \text{ES.} \]

\[ R' - \text{NO}_2 + R^* \xrightarrow{\text{c attack}} R - \text{NO}_2 \]

- retarder (not inhibitor)
b/c reacts w/ radicals
more slowly than k_{prop}

\[ R - \text{NO}_2 + R - H \]

- combo of monomer + additive defines whether inhibitor or retarder:

\[ \text{deficient } A \text{ ring} \text{ reacts more readily with } e^0 \text{ rich radicals} + \text{ more reactive radicals} \]
e.g. vinyl acetate  methyl acrylate  styrene

Reactivity:  ①  ②  ③

e enrichment:  ③  ②  ①

\( [O-O_2 \bigg| 11.2 \] \)
ihibits  \( 0.00464 \)  little effect  \( 0.326 \)

- Inhibitors + retarders must be removed prior to polym. of monomer
  (by chromatography, distillation, extraction, etc.)
  to obtain reproducible + controlled polym.

- Add'\( n \) of excess initiator to consume inhibitor/retarder + then proceed w/ polym. "is done only when purification is not feasible"