

Chem 466

Lecture ~~#~~ 21

04/08/2014

• Exam III Thursday !

• Quiz #9 $\bar{x} = 6.1$
S.D. = 3.7

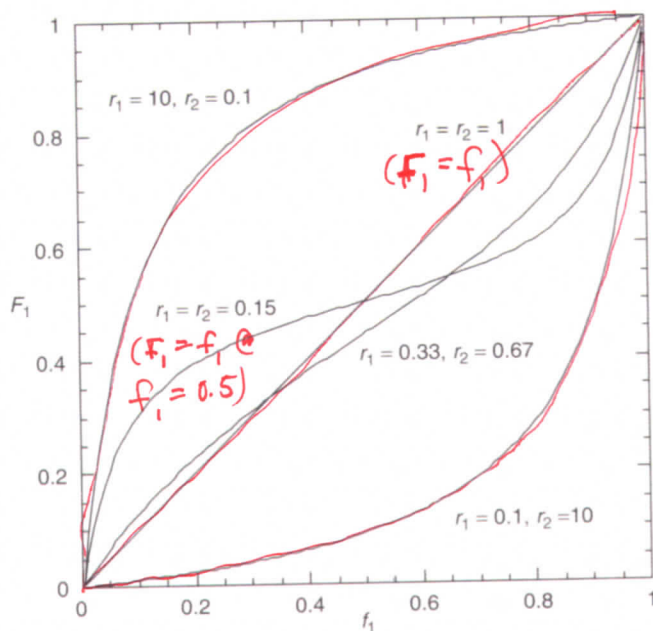


Figure 5.1 Mole fraction of component 1 in the copolymer as a function of feedstock composition for various reactivity ratios.

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:

$$\left(\frac{[M_1]}{[M_2]} \right)_{\text{cross}} = \frac{1 - r_2}{1 - r_1} \quad (5.2.20)$$

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 (rxn mixture)

$$\frac{d[M_1]/dt}{d[M_2]/dt} = \frac{[M_1]}{[M_2]} \left(\frac{r_1 [M_1] + [M_2]}{[M_1] + r_2 [M_2]} \right) \quad \left(\begin{array}{l} \text{eqn} \\ 5.2.15 \\ \text{text p. 168} \end{array} \right)$$

ratio of monomer repeat units in poly (i.e. consumed during polym)

depends upon reactivity ratios + monomer concentrations

see Figure 5.1 (text p. 169)

- when $r_1 \cong r_2 \cong 1 \Rightarrow$ no pref. + random copolymer

$r_1 \cong r_2 \cong 0 \Rightarrow$ no homopolymer + alternating copoly

$r_1 \gg 1; r_2 \cong 0 \Rightarrow M_1$ homopolymer

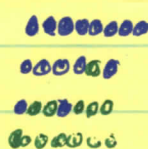
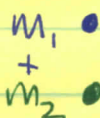
can lead to big differences in poly structure

$r_1 \gg 1; r_2 > 0 \Rightarrow$ initially high M_1 polymer then M_2 polymer

if traditional vs. controlled radical polymer.

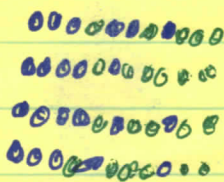
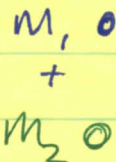


traditional:



mixture of polys of Δ chain lengths + Δ compositions

controlled:



polys of similar chain lengths + Δ compositions along the backbone

(I) practical polym. conditions

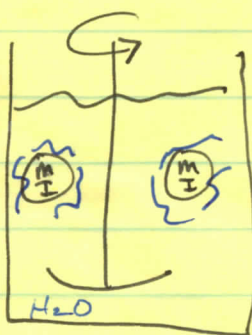
1. bulk polym.

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

2. solution polym.

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

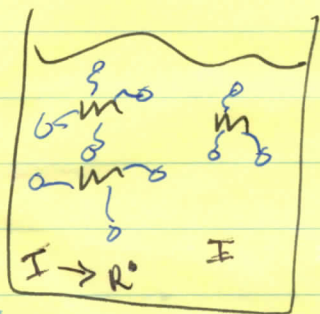
3. suspension polym.



- stirring required
- monomer droplets (10-1000 μm diameter) suspended in H_2O
- initiator dissolved in monomer
- suspending agents added
 - H_2O insoluble inorganics, e.g. ^{magnesium silicate} barium sulfate
 - if H_2O soluble poly + H_2O soluble initiator \Rightarrow dispersion polym.

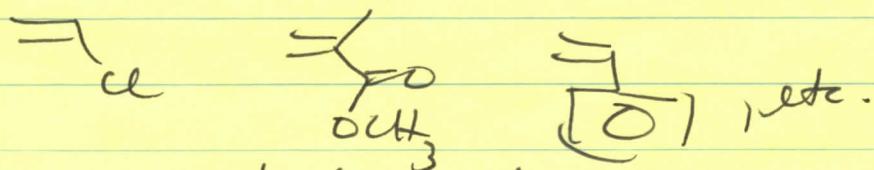
- polymer proceeds like many individual bulk polymer. (same kinetics)
- gives large particles 10-1000 μm
- size + size dist. dependant on suspending agent + stirring rate

4. Emulsion polymer



- monomer droplets (50nm-1 μm) suspended in H_2O as micelles
- initiator (I) dissolved in H_2O
- surfactants (emulsifier) added
- polymer occurs inside micelles
 - diffusion controlled
 - rate of diffusion of $\text{M} + \text{R}^\bullet$ into micelles

Both methods 3 + 4 can be used for most H_2O insoluble monomers



particularly good for $\text{CF}_2=\text{CF}_2$.

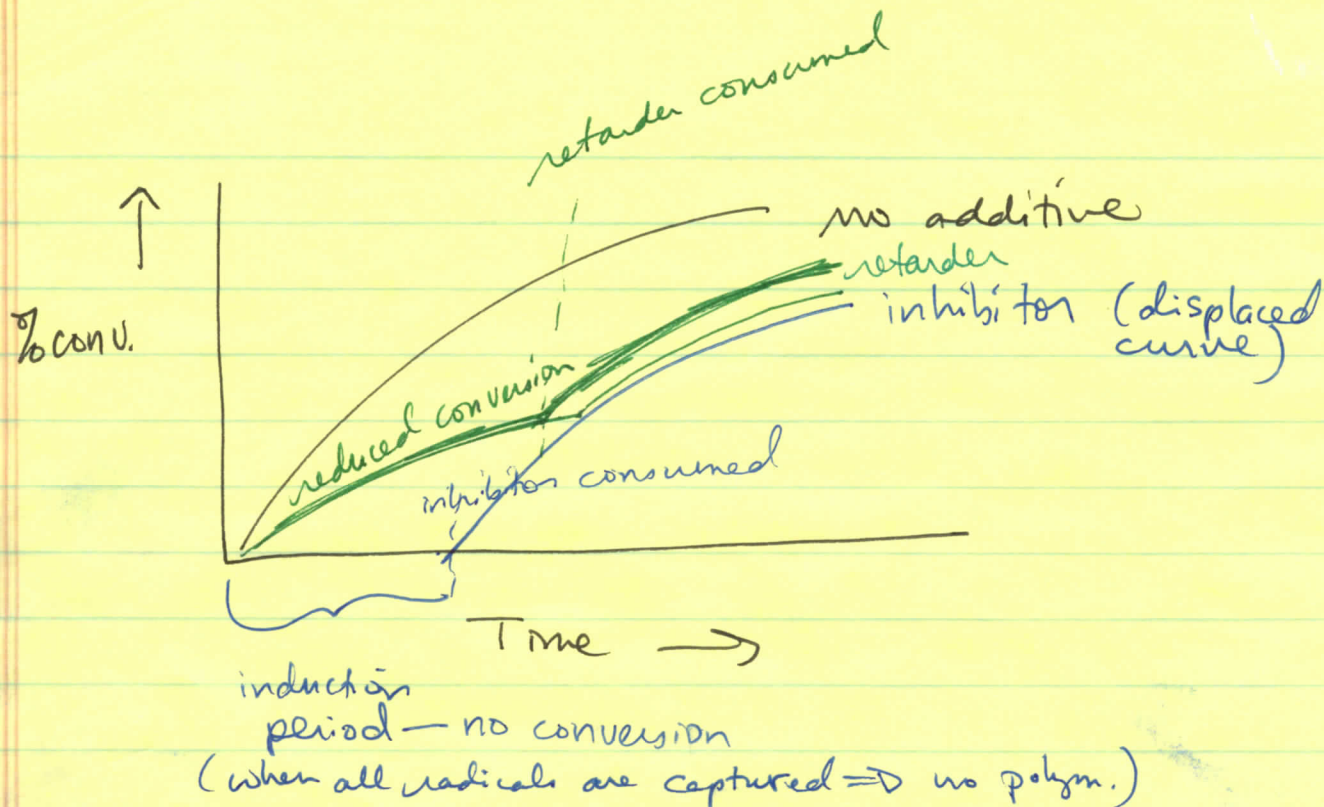
(J) Inhibitors + Retarders

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

Inhibition constant, $z = \frac{k_z}{k_p} = \frac{\text{rate constant for trapping}}{\text{rate constant for prop.}}$

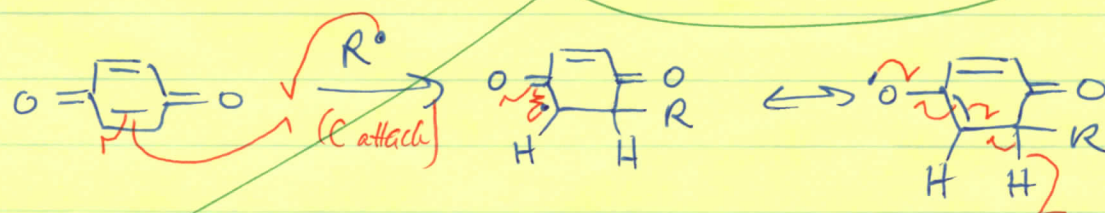
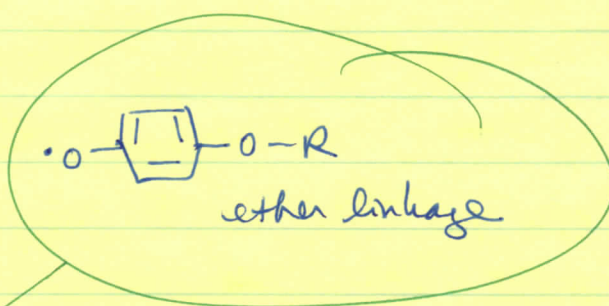
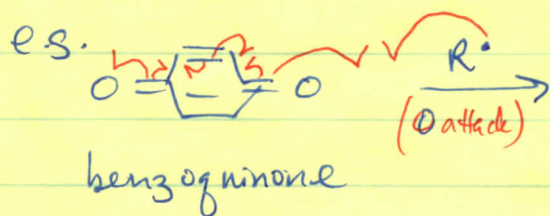
polym. rate
(takes into
acct. k_i ,
 $k_p + k_z$) $\rightarrow \frac{1}{R_{\text{polym.}}} \propto z \therefore \text{as } z \uparrow, R_{\text{polym.}} \downarrow$

- species with high z (>10) are inhibitors
- species with low z (<1) are retarders



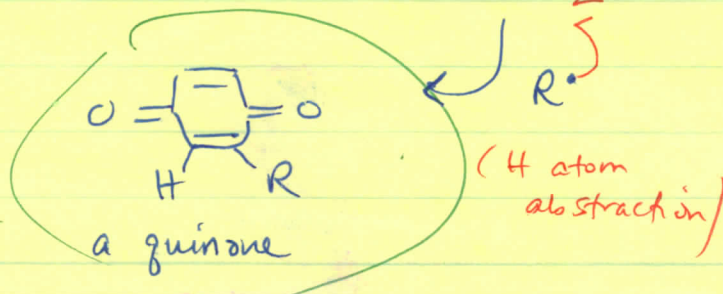
• Inhibitor — prevents polym. as long as it is present (induction period, $\frac{k_z}{k_p} > 10$),

but once consumed, polym. occurs as w/out inhibitor



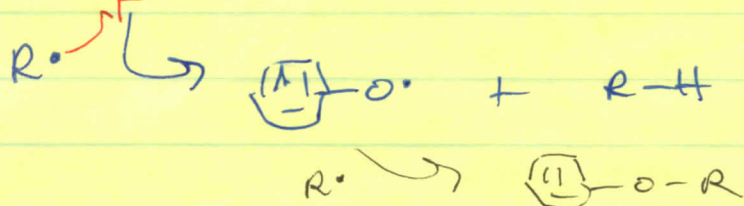
• these species can undergo rxn further w/ additional radicals

$R-H +$

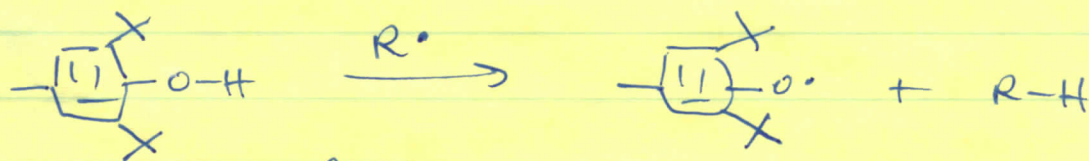


Phenol

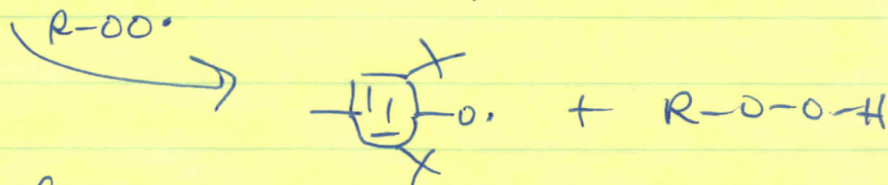
c1ccccc1O is a poorer inhibitor



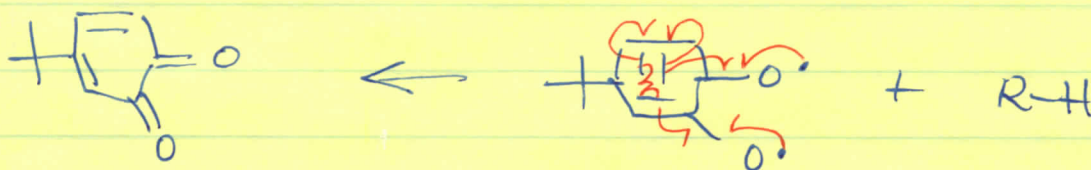
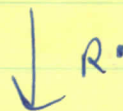
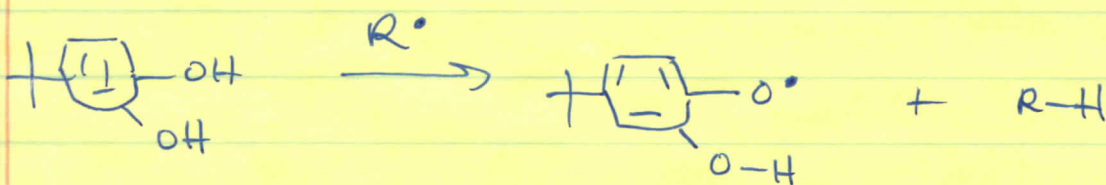
BHT - used as a food antioxidant
(2,6-di-tert-butyl-4-methyl phenol)



• good at scavenging peroxy radicals



t-butyl catechol - is often used as inhibitor
(e.s. when purchase styrene from Aldrich)



an o-quinone

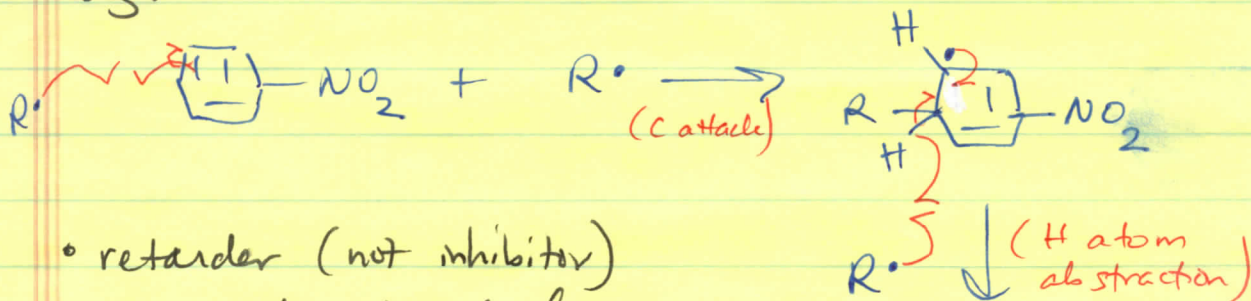
(which can undergo further radical scavenging)

- Retarder — decreases the amt. of polym. by trapping some of the unwanted radicals ($z < 1$; $k_{prop} > k_z$)

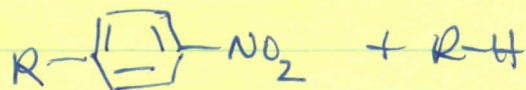
— no induction period b/c no complete trapping of radicals

— once retarder is consumed, polym. occurs as w/out retarder

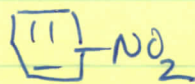
e.g.



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



- combo of monomer + additive det'ms whether inhibitor or retarder:

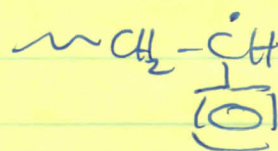
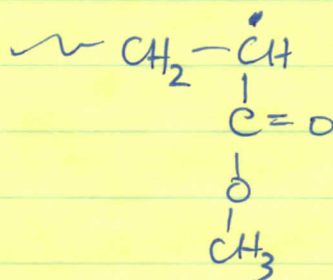
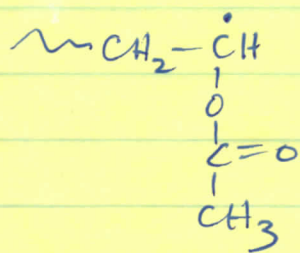


e^- deficient Ar ring — reacts more readily with e^- rich radicals + more reactive radicals

eg. vinyl acetate

methyl acrylate

styrene



Reactivity:

①

②

③

ee richness:

③

②

①

$\text{[O]}-\text{NO}_2$ z:

11.2

0.00464

0.326

inhibits

little effect

retards

- Inhibitors + retarders must be removed prior to polym. of monomer (by chromatography, distillation, extraction, rex, 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.