Lecture 11: Radical Polymerization, Homogeneous Reaction Rate Kinetics

---

How to determine MW in free radical polymerization

Kinetic Chain Length

ν = # of monomers added per effective free radical

$$\nu = \frac{\text{rate of chain growth}}{\text{rate of chain initiation}} = \frac{\text{rate of chain growth}}{\text{rate of chain termination}}$$

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[M]}{2(fk_d k_t[I])^{\frac{1}{2}}}$$

$\overline{p_n} = \nu$ if termination is by disproportionation process

$\overline{p_n} = 2\nu$ if termination is by coupling

Generally, (if no chain transfer):

$\overline{p_n} = 2a\nu$ where ½ ≤ a ≤ 1

100% disproportionation

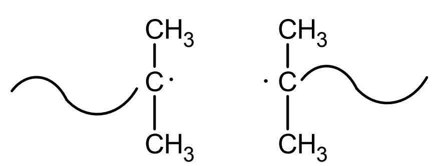
100% disproportionation

$\overline{M_n} = M_n \cdot \overline{p_n}$

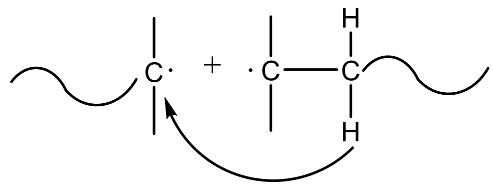
molecular weight of vinyl monomer unit

What happens more often?

- Coupling usually greater than disproportionation
- Percent of coupling increases if: steric factors prevent effective coupling:



or if: β-hydrogens are more reactive:



Consider $$\nu = \frac{k_p[M]}{2(fk_d k_t[I])^{\frac{1}{2}}}$$

$$R_p = k_p\left(\frac{fk_p[I]}{k_t}\right)^{\frac{1}{2}}[M]$$

Increase R_p by: [M]↑, [I]↑
But increase $\nu \rightarrow$ [M]↑, [I]↓
Thus you want to increase [M]

Chain Transfer

1.

$$Mn\cdot + X'\!-\!Y \xrightarrow{k_{tr}} Mn\!-\!X' + Y\cdot$$

k_{tr} = transfer constant

$$R_{tr} = \frac{d[Y\cdot]}{dt} = k_{tr}[M\cdot][X'-Y]$$

Chain transfer can occur when there are solvent impurities.
But sometimes using chain transfer can be advantageous.

2.

$$Y\cdot + M \xrightarrow{k_a} YM\cdot$$

3.

$$YM\cdot + M \xrightarrow{k_p} YMn\cdot$$

Chain transfer agent → CTA
Used to decrease MW in polymerization

$k_p >> k_{tr}$ and $k_p \approx k_a \Rightarrow R_p$ is the same $\overline{p_n}\downarrow$ slightly – moderately depending on CTA

$k_p << k_{tr}$ and $k_p \approx k_a \Rightarrow R_p$ ~ same $\overline{p_n}\downarrow$ dramatically
$k_p >> k_{tr}$ and $k_a < k_p \Rightarrow R_p\downarrow$ slightly and $\overline{p_n}\downarrow$ slightly
$k_p << k_{tr}$ and $k_a < k_p \Rightarrow R_p\downarrow$ drastically and $\overline{p_n}\downarrow$ drastically

Transfer Types:

1. to monomer: $k_{tr,m}$ $\qquad M_n\cdot + M \rightarrow M_n + M\cdot$
2. $\left.\begin{array}{l}\text{to solvent}\\ \text{or impurity}\end{array}\right\}$ $k_{tr,s}$ $\qquad M_n\cdot + S \rightarrow M_n + S\cdot$

or CTA

3. to initiator: $k_{tr,I}$ $M_n\cdot + I \rightarrow M_n + I\cdot$

All act to decrease $\overline{p_n}$: (assume coupling)

$$\overline{p_n} = \frac{R_p}{\frac{R_t}{2} + R_{tr,m} + R_{tr,s} + R_{tr,I}} = \frac{R_p}{\frac{R_t}{2} + k_{tr,m}[M\cdot][M] + k_{tr,s}[M\cdot][S] + k_{tr,I}[M\cdot][I]}$$

Use resistor analogy: (resistors in series)

C = transfer constant

= relative rate const vs. R_p

$$C_m = \frac{k_{tr,m}}{k_p}, \quad C_S = \frac{k_{tr,S}}{k_p}, \quad C_I = \frac{k_{tr,I}}{k_p}$$

since $R_p = k_p[M\cdot][M]$

$$\frac{1}{\overline{p_n}} = \frac{R_i}{2R_p} + \underbrace{C_m + C_S\frac{[S]}{[M]} + C_I\frac{[I]}{[M]}}_{\text{Additive effect of each constant}}$$

$$\downarrow$$

$$\frac{R_t}{2R_p}$$

$$\downarrow$$

$$\left(\frac{1}{\overline{p_n}}\right)_o \leftrightarrow \frac{1}{2\nu}$$

Often only have transfer to CTA (or impurity)

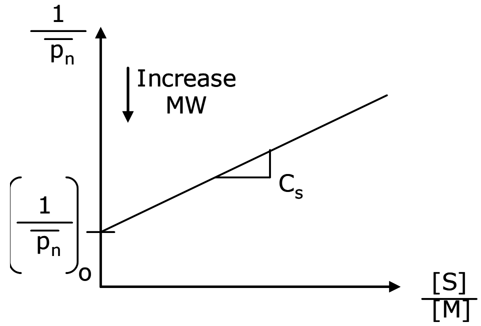
$$\frac{1}{\overline{p_n}} = \frac{R_i}{2R_p} + C_S\frac{[S]}{[M]}$$

$$\updownarrow$$

$$\frac{(fk_d k_t[I])^{\frac{1}{2}}}{k_p[M]} = \frac{1}{2\nu}$$

For a given amount of initiator [I] and monomer [M]

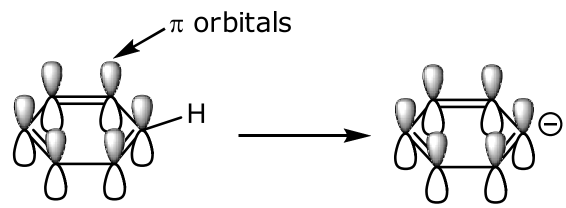
$$\frac{1}{\overline{p_n}} = \left(\frac{1}{\overline{p_n}}\right)_o + C_S \frac{[S]}{[M]}$$



Useful to control MW is free radical with high k_p and/or really low k_t

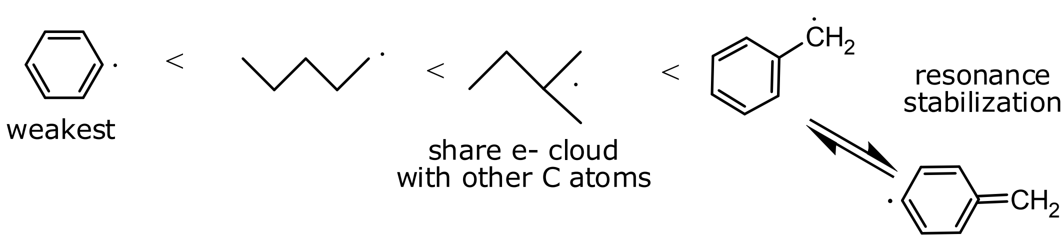
C_s values for different compounds:

- alkanes (weakest)
- cyclic hydrocarbons
- benzenes, aromatics



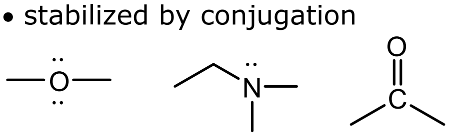
unstable negative charge → H- extraction unlikely

Increasing radical stability

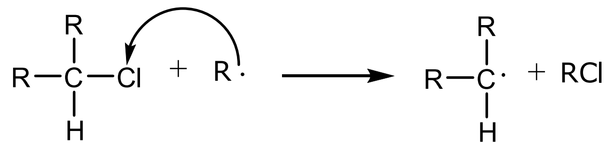


High C_s values:

- weak C—H bonds
- stabilized by conjugation



- weak C—Cl, C—Br, C—I



- weak S—S bonds, S—H

weakest
largest C_S

CTA (chain-transfer-agents)	$C_S \times 10^4$	$C_S \times 10^4$
	For styrene	Vinyl acetate
Benzene	0.023	1.2
Cyclohexane	0.031	7.0
Heptane	0.42	17.0
n-butyl alcohol	1.6	20.0
$CHCl_3$ (chloroform)	3.4	150.0
Tri-methyl amine	7.1	370
n-butyl mercaptan	210,000	480,000