How to determine MW in free radical polymerization

**Kinetic Chain Length**

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

\[ \nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[M]}{2(\beta k_d k_c [I])^{1/2}} \]

\[ p_n = \nu \text{ if termination is by disproportionation process} \]

\[ p_n = 2\nu \text{ if termination is by coupling} \]

Generally, (if no chain transfer):

\[ p_n = 2a\nu \text{ where } \frac{1}{2} \leq a \leq 1 \]

\[ 100\% \text{ disproportionation} \quad 100\% \text{ disproportionation} \]

\[ M_n = M_a \cdot p_n \]

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:

\[ \text{or if: } \beta\text{-hydrogens are more reactive:} \]

Citation: Professor Paula Hammond, 10.569 Synthesis of Polymers Fall 2006 materials, MIT OpenCourseWare (http://ocw.mit.edu/index.html), Massachusetts Institute of Technology, Date.
Consider

\[ v = \frac{k_p [M]}{2(k_d k_I)^{1/2}} \]

\[ R_p = k_p \left( \frac{f k_p [I]}{k_I} \right)^{1/2} [M] \]

Increase \( R_p \) by: \([M]↑, [I]↑\)
But increase \( ν \rightarrow [M]↑, [I]↓\)
Thus you want to increase \([M]\)

**Chain Transfer**

1.

\[ \text{Mn} \cdot + X\cdot Y \xrightarrow{k_{\text{tr}}} \text{Mn} - X + Y \]

\( k_{\text{tr}} \) = transfer constant

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

\( k_p \gg k_{\text{tr}} \) and \( k_p \approx k_a \) ⇒ \( R_p \) is the same \( \overline{p_n} \downarrow \)

slightly – moderately
depending on CTA

\( k_p \ll k_{\text{tr}} \) and \( k_p \approx k_a \) ⇒ \( R_p \) – same \( \overline{p_n} \downarrow \) dramatically

\( k_p \gg k_{\text{tr}} \) and \( k_a < k_p \) ⇒ \( R_p \downarrow \) slightly and \( \overline{p_n} \downarrow \) slightly

\( k_p \ll k_{\text{tr}} \) and \( k_a < k_p \) ⇒ \( R_p \downarrow \) drastically and \( \overline{p_n} \downarrow \) drastically

**Transfer Types:**

1. to monomer: \( k_{\text{tr,m}} \)
   \[ Mn\cdot + M \rightarrow Mn + M \cdot \]

2. to solvent or impurity
   \( k_{\text{tr,s}} \)
   \[ Mn\cdot + S \rightarrow Mn + S \cdot \]
or CTA

3. to initiator: \( k_{tr, I} \) \( M_n + I \rightarrow M_n + I \)

All act to decrease \( p_n \) : (assume coupling)

\[
\frac{1}{p_n} = \frac{R_p}{R_i + R_{tr,m} + R_{tr,s} + R_{tr,f}} = \frac{R_p}{R_i + k_{tr,m}[M][M] + k_{tr,s}[M][S] + k_{tr,f}[M][I]}
\]

Use resistor analogy: (resistors in series)
\( C \) = transfer constant
\( C_m = k_{tr,m} \frac{k_p}{k_p} \)
\( C_S = k_{tr,s} \frac{k_p}{k_p} \)
\( C_I = k_{tr,f} \frac{k_p}{k_p} \)

since \( R_p = k_p[M][M] \)

\[
\frac{1}{p_n} = \frac{R_i}{2R_p} + C_m + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]}
\]

\[
\left( \frac{1}{p_n} \right)_a \leftrightarrow \frac{1}{2v}
\]

Often only have transfer to CTA (or impurity)

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

\[
\frac{\left( k_{tr} k_f [I] \right)^{1/2}}{k_p [M]} = \frac{1}{2v}
\]
For a given amount of initiator [I] and monomer [M]

\[
\frac{1}{p_n} = \left( \frac{1}{p_n} \right) + C_s \frac{[S]}{[M]} 
\]

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

Increasing radical stability

\[
\text{weakest} < \text{alkanes} < \text{cyclic hydrocarbons} < \text{benzenes, aromatics}
\]

High C_s values:
- weak C—H bonds
- stabilized by conjugation

- \( \text{weak C—Cl, C—Br, C—I} \)
weak S–S bonds, S–H

weakest
largest $C_S$

<table>
<thead>
<tr>
<th>CTA (chain-transfer-agents)</th>
<th>$C_S \times 10^4$ for styrene</th>
<th>$C_S \times 10^4$ for Vinyl acetate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.023</td>
<td>1.2</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.031</td>
<td>7.0</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.42</td>
<td>17.0</td>
</tr>
<tr>
<td>n-butyl alcohol</td>
<td>1.6</td>
<td>20.0</td>
</tr>
<tr>
<td>CHCl$_3$ (chloroform)</td>
<td>3.4</td>
<td>150.0</td>
</tr>
<tr>
<td>Tri-methyl amine</td>
<td>7.1</td>
<td>370</td>
</tr>
<tr>
<td>n-butyl mercaptan</td>
<td>210,000</td>
<td>480,000</td>
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