Radical Polymerizations I

Chain Growth Basics

Devon A. Shipp
Department of Chemistry, &
Center for Advanced Materials Processing
Clarkson University
Potsdam, NY 13699-5810

Tel. (315) 268-2393, Fax (315) 268-6610
dshipp@clarkson.edu
Chain Polymerizations

- **Typical chain reaction**
  - $I \rightarrow I^*$ Initiation
  - $I^* + M \rightarrow IM^*$ ($=P_1^*$)
  - $P_n^* + M \rightarrow P_{n+1}^*$ Propagation
  - $P_n^* + P_m^* \rightarrow D_{n+m}$ Termination
  - $P_n^* + P_m^* \rightarrow D_n + D_n$
  - $P_n^* + A \rightarrow D_n + A^*$

- $^*$ = reactive species
  - Radical
  - Anion
  - Cation

Chain Growth (Addition)
## Olefinic Monomers

<table>
<thead>
<tr>
<th>Monomers</th>
<th>Type of Initiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Radical</td>
</tr>
<tr>
<td>Ethylene</td>
<td>+</td>
</tr>
<tr>
<td>1-Alkyl olefins (α-olefins)</td>
<td>-</td>
</tr>
<tr>
<td>1,1-Dialkyl olefins</td>
<td>-</td>
</tr>
<tr>
<td>1,3-Dienes</td>
<td>+</td>
</tr>
<tr>
<td>Styrene, α-methyl styrene</td>
<td>+</td>
</tr>
<tr>
<td>Halogenated olefins</td>
<td>+</td>
</tr>
<tr>
<td>Vinyl esters (CH₂=CHCOR)</td>
<td>+</td>
</tr>
<tr>
<td>Acrylates, methacrylates</td>
<td>+</td>
</tr>
<tr>
<td>Acrylonitrile, methacrylonitrile</td>
<td>+</td>
</tr>
<tr>
<td>Acrylamide, methacrylamide</td>
<td>+</td>
</tr>
<tr>
<td>Vinyl ethers</td>
<td>-</td>
</tr>
<tr>
<td>N-Vinyl carbazole</td>
<td>+</td>
</tr>
<tr>
<td>N-Vinyl pyrrolidone</td>
<td>+</td>
</tr>
<tr>
<td>Aldehydes, ketones</td>
<td>-</td>
</tr>
</tbody>
</table>
Initiators and Solvents

- **Initiators**
  - Peroxides
  - Azo compounds
  - Redox
  - Thermal
  - UV
  - $\gamma$-rays

- **Solvents**
  - Danger of radical transfer to solvent
    - E.g. $C_6H_6$ is better than $C_6H_5CH_3$
  - Water is okay
  - Remove $O_2$
    - Formation of stable peroxide radicals
      - $\sim\sim\sim O-O\cdot$ (relatively stable)
Some Typical Conditions

• **Styrene**
  – Bulk, under N\textsubscript{2}
  – 125\degree C, 1-7 days, M\textsubscript{n} \approx 150,000

• **Methyl methacrylate (MMA)**
  – Solution, 0.5% AIBN
  – 1-2 days, 60\degree C, M\textsubscript{n} \approx 100,000

• **Acrylonitrile**
  – Emulsion, H\textsubscript{2}O, N\textsubscript{2}, surfactant
  – K\textsubscript{2}S\textsubscript{2}O\textsubscript{8}/NaHSO\textsubscript{3} (redox)
  – 35\degree C, 24 hrs, M\textsubscript{n} \approx 50,000
Elementary Reactions …1

• **Initiation**
  - $R^\cdot = \text{primary radicals}$
  - $R_d = 2k_d[I] \ll R_i = k_i[R^\cdot][M]$

• **Propagation**
  - $R_p = k_p[R^\cdot][M]$

\[
\begin{align*}
M_1^\cdot + M & \xrightarrow{k_{p1}} M_2^\cdot \\
M_2^\cdot + M & \xrightarrow{k_{p2}} M_3^\cdot \\
M_3^\cdot + M & \xrightarrow{k_{p3}} M_4^\cdot \\
\end{align*}
\]

\[
\begin{align*}
I & \xrightarrow{k_d} 2R^\cdot \\
R^\cdot + M & \xrightarrow{k_i} M_1^\cdot (R-M^\cdot) \\
M_n^\cdot + M & \xrightarrow{k_p} M_{n+1}^\cdot \\
\end{align*}
\]
Elementary Reactions ...

- **Termination** (radical–radical)
  
  \[
  \begin{align*}
  \text{(CH}_2\text{-CH)}_n\text{CH}_2\cdot \text{CH} & \xrightarrow{k_{ic}} \text{(CH}_2\text{-CH)}_n\text{CH}_2\text{-CH} \cdot \\
  \cdot \text{CH} \text{-CH}_2(\text{CH}_2\cdot \text{CH})_m & \xrightarrow{k_{id}} \text{(CH}_2\text{-CH)}_n\text{CH}_2\text{-CH} \cdot \text{CH}_2(\text{CH}_2\cdot \text{CH})_m
  \end{align*}
  \]
  
  Combination

- **Transfer**
  - E.g. to monomer
  
  \[
  \begin{align*}
  M_n^\cdot & + \text{H}_2\text{C} \equiv \text{C} \xrightarrow{k_{tr}} M_n\text{-H} + \text{H}_2\text{C} \equiv \cdot \text{C} \\
  \text{R} & \text{R}
  \end{align*}
  \]
  - Solvent
  - Polymer
  - Additives
Initiation

• **Rate of radical formation**
  – \(\frac{d[R]}{dt} = 2 \ k_d \ [I]\)
  – Typical values
    • \(k_d \sim 10^{-6} - 10^{-4} \text{ s}^{-1}\)
    • \([I] \sim 0.01 \text{ M (0.1%)}\)
  – \(\frac{d[R]}{dt} \sim 10^{-8} - 10^{-6} \text{ M s}^{-1}\)

• **Temperature at which half lifetime = 10 hrs**
  – Depends on initiator structure
  – \(\tau_{1/2} = (\ln 2)/k_d\)
Thermal Initiators … 1

- **Peroxides**
  - Dialkyl peroxides
    
    \[
    \begin{align*}
    \text{H}_3\text{C} - \overset{\text{CH}_3}{\text{C}} - \overset{\text{CH}_3}{\text{O}} - \overset{\text{CH}_3}{\text{O}} - \overset{\text{CH}_3}{\text{C}} - \overset{\text{CH}_3}{\text{CH}_3} & \rightarrow 120 - 140 ^\circ \text{C} \quad 2 \text{H}_3\text{C} - \overset{\text{CH}_3}{\text{C}} - \overset{\text{O^*}}{\overset{\text{CH}_3}{\text{CH}_3}} \\
    \text{H}_3\text{C} - \overset{\text{CH}_3}{\text{C}} - \overset{\text{CH}_3}{\text{O}} - \overset{\text{CH}_3}{\text{O}} - \overset{\text{CH}_3}{\text{C}} - \overset{\text{CH}_3}{\text{CH}_3} & \rightarrow 70 - 90 ^\circ \text{C} \quad 2 \text{H}_3\text{C} - \overset{\text{C}}{\text{O^*}} \rightarrow 2 \text{CH}_3 + 2 \text{CO}_2 \\
    \text{Ph} - \overset{\text{O}}{\text{C}} - \overset{\text{O}}{\overset{\text{C}}{\text{Ph}}} & \rightarrow 80 - 95 ^\circ \text{C} \quad 2 \text{Ph} - \overset{\text{C}}{\text{O^*}} \rightarrow 2 \text{Ph}^* + 2 \text{CO}_2
    \end{align*}
    \]
Thermal Initiators …2

- **Hydroperoxides**
  - Low efficiency

\[
\begin{align*}
\text{H}_3\text{C} & \text{C} \text{O} \text{H} & \text{Ph} & \rightarrow & 2\text{H}_3\text{C} & \text{C} \text{O} \cdot & + & \cdot \text{OH} & \rightarrow & \text{H}_3\text{C} & \text{C} \text{O} \cdot & + & \text{H}_2\text{O} \\
\end{align*}
\]

- **Azo initiators**
  - AIBN
    - Azobisisobutyronitrile
  - Others
    - **R-N=N-R**
    - **R = Me (250°C), isopropyl (200°C), PhC(H)Me (110°C), Me_2(CN)C (60°C), Ph_2CH (30°C)**
Redox Initiators

• **Advantages**
  – Lower temperatures
  – Good solubilities
  – High initiation efficiency
  
  • One mole radicals per mole initiator

\[
\text{HO} - \text{OH} + \text{Fe}^{2+} \rightarrow \text{HO}^\cdot + \text{OH}^- + \text{Fe}^{3+}
\]

\[
\text{RO} - \text{OH} + \text{Fe}^{2+} \xrightarrow{15\text{ - }30^\circ\text{C}} \text{RO}^\cdot + \text{OH}^- + \text{Fe}^{3+}
\]

\[
\text{R}_3\text{N} \quad \text{R}^' - \text{C} - \text{O} - \text{O} - \text{C} - \text{R}^' \rightarrow \text{R}_3\text{N}^\cdot + \text{R}^' - \text{C} - \text{O}^\cdot - \text{O} - \text{C} - \text{R}^'
\]

\[
\text{O} - \text{S} - \text{O} - \text{O} - \text{S} - \text{O}^- + \text{Fe}^{2+} \rightarrow \text{O}^\cdot - \text{S} - \text{O}^- - \text{O} - \text{S} - \text{O}^- + \text{Fe}^{3+}
\]
Photochemical Initiator

• **Advantages**
  – Spatially directed polymerization
  – Easy to turn on/off
  – Initiation rates can be controlled

• **Absorb light > 300 – 350nm**
  – Dye-sensitized

\[ D + h\nu \rightarrow D^* \]

\[ \text{radicals} \]

\[ (DA)^* \rightarrow \text{radicals} \]

\[ \text{exciplex} \]
Radiation & Pure Thermal

- **Radiation**
  - Neutrons, $\alpha$-particles, $\beta$-rays, $\gamma$-rays, x-rays
  - Homolytic cleavage

- **Pure thermal**
  - Styrene

![Chemical Reaction Diagram]

\[ \text{Ph} + \text{Ph} \rightarrow \text{PhPh} \]
Initiation Efficiency

- **Cage effect**
  - $f = \text{initiator efficiency} \sim 0.3 - 0.8$
  - Dependent on conversion (viscosity)

- **No cage effect for redox**
  - One radical generated
Kinetics of Initiation

- Rate of initiation
  - Generation of radicals through thermal initiation
    - $R_d = 2 f k_d [I]$
  - Rate of change in primary radical concentration
    - $\frac{d[R\cdot]}{dt} = 2 f k_d [I] - k_i [R\cdot] [M] = 0$
      - Steady-state assumption
      - Assumes $f$ is invariant
  - Rearranging for $[R\cdot]$
    - $[R\cdot] = \frac{(2 f k_d [I])}{(k_i [M])}$
  - Assume decomposition is slowest step:
    - $R_i = 2 f k_d [I]$
Kinetics of Propagation

• **Rate of propagation**
  
  \[-R_p = \frac{d[M]}{dt} = k_p [M•] [M]\]
  
  • Assumes that monomer only consumed during propagation

  \[-\frac{d[M•]}{dt} = k_i [R•] [M] - 2 k_t [M•]^2 = 0\]
  
  • Assumes steady state for radical concentration

  \[-2 f k_d [I] - 2 k_t [M•]^2 = 0\]

  \[-[M•] = \left(f k_d [I] / k_t\right)^{0.5}\]

\[
\begin{align*}
R_p &= \frac{d[M]}{dt} = k_p [M] \sqrt{\frac{2 f k_d [I]}{2 k_t}} \\
R_p &= \frac{d[M]}{dt} = k_p [M] \sqrt{\frac{R_i}{2 k_t}}
\end{align*}
\]
Rate of Polymerization

- **Predictions:**
  - 1st order in monomer
  - ½ order in initiator

- **Plot of** $R_p$ vs. $[I]^{0.5}$
  - Linear

- Classical kinetics justified (?)

---

Assumptions Made in Kinetic Analysis

- **Propagation rate constant is constant**
  - $k_p$ is independent of chain length

- **Termination rate constant is constant**
  - $k_t$ is independent of chain length

- **Very long chains**
  - Monomer only consumed in propagation

- **One type of active site**
  - Only head-to-tail addition
    - Otherwise (at least) 2 types of active sites

- **Steady state**
  - $[M\cdot] = \text{constant (polymer)}$
  - $[R\cdot] = \text{constant (primary)}$
Kinetics for Photoinitiation …1

• **Rate of initiation**
  
  - \( R_i = 2 \Phi I_a \)
  
  - \( I_a = I_0 \varepsilon [A] b \)
    
    • \( \Phi \) = quantum yield for initiation
    
    • \( I_a \) = intensity of light absorbed
    
    • \( I_0 \) = intensity of incident light
    
    • \( \varepsilon \) = extinction coefficient of A
    
    • \( A \) = molecule absorbing light
    
    • \( b \) = total thickness of reaction flask

• **If absorbance does not vary with thickness**

\[
R_p = k_p [M] \sqrt{\frac{R_i}{k_t}} = k_p [M] \sqrt{\frac{2 \Phi I_a}{k_t}} = k_p [M] \sqrt{\frac{2 \Phi \varepsilon I_0 [A] b}{k_t}}
\]
Kinetics for Photoinitiation ...2

• If appreciable absorption
  – Beer-Lambert law
    • \( I = I_0 \left( 10^{-\varepsilon[A]b'} \right) \)
      – \( b' \) = distance into reaction flask
      – \( I = \) intensity at distance \( b' \) into flask

  – \( I_a = I_0 - I \)
  – Therefore:
    \[
    R_p = k_p [M] \sqrt{\frac{2 \Phi I_0 (1-10^{-\varepsilon[A]b'})}{k_t}}
    \]
Dead-End Polymerization

- **Measures** $k_d$
- **Low** [Initiator]
  - Initiator is consumed before polymerization is complete
  - $p = \text{extent of monomer conversion}$
  - $p_\infty = \text{limiting extent of monomer conversion}$

\[-\ln \left[ 1 - \frac{\ln(1-p)}{\ln(1-p_\infty)} \right] = \frac{k_d t}{2}\]

Non-Steady State Kinetics

• **Steady state kinetics**
  – Gives coupled form of \( k_p^2/k_t \)

• **Non-steady state kinetics**
  – Gives coupled form of \( k_p/k_t \)

• **Combine both methods**
  – Gives \( k_p \) and \( k_t \) individually

• **Rotating sector method**
  – Most common non-steady state method (until recently)
  – Determines average lifetime of a growing radical (\( \tau_s \))
  – Complex analysis yields \( k_p/k_t \)
Pulsed Laser Polymerization ...

- Obtains $k_p$ by itself
- Periodic initiation established by laser flashes
  - Initiation effectively instantaneous (10 ns)
- Propagation occurs between pulses
- Most termination occurs at time of laser pulses
  - Chains tend to start growth at laser pulse and terminate at a subsequent pulse
Pulsed Laser Polymerization …2

- **Average time for a propagation event**
  - \( \text{Avg. time} = \frac{1}{(k_p[M])} \)

- **Number of propagation events in time \( t_f \)**
  - \( \nu_p = k_p [M] t_f \)

- **Measure \( \nu_p \) from GPC, know \( t_f \) & [M] (low conversion)**
  - Estimate \( k_p \)

- **From PLP of MMA**
  - From \( \nu_p^{(1)} \)
    - \( k_p = 331 \text{ M}^{-1}\text{s}^{-1} \)
  - From \( \nu_p^{(2)} \)
    - \( k_p = 328 \text{ M}^{-1}\text{s}^{-1} \)
  - From \( \nu_p^{(3)} \)
    - \( k_p = 329 \text{ M}^{-1}\text{s}^{-1} \)

- **Lit. value**
  - \( k_p = 323 \text{ M}^{-1}\text{s}^{-1} \)
Termination Rates

• **Radical-radical termination**
  – Fast; usually diffusion-controlled
  – $k_t \sim 10^6 – 10^9 \text{ M}^{-1}\text{s}^{-1}$
    • low conversion & viscosity
  – $k_t$ decreases with monomer conversion
    • From $\sim 10^9$ to $10^2$ or less

• **No method of unambiguously determining** $k_t$
  – Viscosity dependent
  – Chain length dependent
    • $k_t(i,j)$ where $i, j =$ radical chain lengths
How $k_t$ Varies During Polymerization

Fig. 6. Conversion dependence of $k_t$ for the free-radical polymerization of methyl methacrylate. The experimental data are: (○) from ref. 8) (for 0°C) and (△) from ref. 9) (for 50°C). The full line represents $k_t$ from Eq. (11) with the rate coefficients and kinetic parameters given in the text.

Termination Chemistry

- Two mechanisms
  - Combination (or coupling)
  - Disproportionation

- Proportions of both depend on monomer

<table>
<thead>
<tr>
<th></th>
<th>%D</th>
<th>%C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile</td>
<td>~0</td>
<td>~100</td>
</tr>
<tr>
<td>Styrene</td>
<td>~10</td>
<td>~90</td>
</tr>
<tr>
<td>Vinyl acetate</td>
<td>~10</td>
<td>~90</td>
</tr>
<tr>
<td>MMA</td>
<td>~60</td>
<td>~40</td>
</tr>
</tbody>
</table>

- More H’s available ⇒ more disproportionation
Kinetic Chain Length

- **Kinetic chain length** = \( \nu \)
  - Number of monomer molecules per radical
  - \( \nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} \) (steady state)

\[
\nu = \frac{k_p [M]}{2k_t \text{[radical]}} = \frac{k_p^2 [M]^2}{2k_t R_p}
\]

- For thermolysis:

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

- Increase \( R_p \) (through increase [radical])
  - Decrease in \( \nu \)
Molecular Weights … 1

• **Average degrees of polymerization**
  – Dependent on mode of termination
    • Disproportionation
    • Combination

• **Define:**
  – \( p = \text{probability of propagation over termination or transfer} \)

\[
p = \frac{R_p}{R_p + R_{tr} + R_t}
\]
Molecular Weights …2

• **Disproportionation**
  - \( X_n = \) number average degree of polymerization = \( \nu \)
  
  \[
  X_n = \frac{1}{1-p} \quad X_w = \frac{1+p}{1-p}
  \]

  \[
  \frac{X_w}{X_n} = 1 + p
  \]

• **Combination**
  - \( X_n = 2\nu \)
  
  \[
  X_n = \frac{2}{1-p} \quad X_w = \frac{2+p}{1-p}
  \]

  \[
  \frac{X_w}{X_n} = \frac{2+p}{2}
  \]
Chain Transfer ...1

- Transfer may occur to:
  - Monomer (M)
  - Polymer (P)
  - Solvent (S)
  - Impurity
  - Chain transfer agent (A)

\[
M_n^\cdot + XA \xrightarrow{k_{tr}} M_nX + A^\cdot
\]
\[
A^\cdot + M \xrightarrow{k_a} M_1^\cdot
\]

<table>
<thead>
<tr>
<th>Case</th>
<th>Relative Rates</th>
<th>Effect</th>
<th>(R_p)</th>
<th>(X_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(k_p \gg k_{tr}) (k_a \sim k_p)</td>
<td>Normal</td>
<td>None</td>
<td>↓</td>
</tr>
<tr>
<td>2</td>
<td>(k_p \ll k_{tr}) (k_a \sim k_p)</td>
<td>Oligomerization</td>
<td>None</td>
<td>Large ↓</td>
</tr>
<tr>
<td>3</td>
<td>(k_p \gg k_{tr}) (k_a &lt; k_p)</td>
<td>Retardation</td>
<td>↓</td>
<td>↓</td>
</tr>
<tr>
<td>4</td>
<td>(k_p \ll k_{tr}) (k_a &lt; k_p)</td>
<td>Degradative Chain Transfer</td>
<td>Large ↓</td>
<td>Large ↓</td>
</tr>
</tbody>
</table>
Chain Transfer …2

- **Transfer constants = C**
  - Defined by the ratio of $k_{tr}/k_p$ for a particular transfer agent
  - E.g. monomer ($C_M = k_{tr,M}/k_p$), solvent ($C_S = k_{tr,S}/k_p$), etc.

- **Redefine $X_n$:**
  - Rate of polymerization divided by all chain-terminating processes
  - \[
  X_n = \frac{R_p}{R_t + R_{tr,M} + R_{tr,S} + \ldots} = \frac{k_p [M^\cdot] [M]}{k_{tc} [M^\cdot]^2 / 2 + k_{tr,M} [M^\cdot] [M] + k_{tr,S} [M^\cdot] [S] + \ldots}
  \]
  - Then rearrange ……
Chain Transfer …3

• After rearranging …

\[
\frac{1}{X_n} = \frac{k_t[M\cdot]}{2k_p[M]} \left( \frac{k_p[M]}{k_p[M]} \right) + \frac{k_{tr,M}}{k_p} + \frac{k_{tr,S}[S]}{k_p[M]} + \ldots
\]

\[
\frac{1}{X_n} = \frac{k_tR_p}{k_p^2[M]^2} + C_M + C_S \frac{[S]}{[M]} + C_I \frac{k_tR_p^2}{k_p^2 f_k[M]^3}
\]

• For transfer to monomer
  – \( C_S[S]/[M] \) & other terms vanish
  – Plot \( 1/X_n \) vs. \( R_p \)
    • Intercept yields \( C_M \)
    • Slope yields \( k_p^2/k_t \)
• **Added transfer agent (A)**
  – Dominates any transfer events

• **Mayo equation:**

\[
\frac{1}{X_n} = \left( \frac{1}{X_n} \right)_0 + C_A \frac{[A]}{[M]}
\]

– \((1/X_n)_0 = \text{value of } (1/X_n) \text{ in absence of } A\)
– Plot \(1/X_n \text{ vs. } [A]/[M]\)
  • Slope = \(C_S\)

---

**Fig. 3-10** The effect of various chain-transfer agents on the degree of polymerization of styrene at 100°C. After Gregg and Mayo [1948] (by permission of American Chemical Society, Washington, D.C.).

Transfer Agents & Constants

- Transfer agents and constants for styrene polymerization at 60°C

<table>
<thead>
<tr>
<th>Transfer Agent</th>
<th>$C_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$1.05 \times 10^{-5}$</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>$6.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>$t$-Butyl alcohol</td>
<td>$6.7 \times 10^{-4}$</td>
</tr>
<tr>
<td>CBr$_4$</td>
<td>1.8</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>$8.4 \times 10^{-3}$</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>$5 \times 10^{-5}$</td>
</tr>
<tr>
<td>1-Octanethiol</td>
<td>19</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>$1.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>Water</td>
<td>0</td>
</tr>
</tbody>
</table>

- Alkyl thiols often used to control molecular weight
Gel Effect - Autoacceleration

- Expect rate to decrease with time
  - Monomer is consumed
    - $R_p = k_p [M\cdot] [M]$
- But, rate usually increases

- Cause
  - Decrease in $k_t$
    - Diffusion-controlled process
  - $R_p$ increases

$$R_p = \frac{d [M]}{dt} = k_p [M] \sqrt{\frac{R_i}{2 k_t}}$$

Figure 3.4: Plot of conversion vs. time, for the free radical polymerization of methyl methacrylate at 50°C using benzoyl peroxide at various concentrations in benzene. Redrawn from the data of G.W. Schultz and G. Harborth, Macromol. Chem., 110:67 (1967).
Ceiling Temperature

- Propagation as an equilibrium
  \[ \text{M}\cdot + M \rightleftharpoons \text{MM}\cdot \]
  \[ k_p \]
  \[ k_{dp} \]
  \[ \Delta G = \Delta G^o + RT \ln K \]
  \[ K = k_p/k_{dp} = \frac{[\text{~~MM}\cdot]}{[\text{~~M}\cdot][\text{M}]} = \frac{1}{[\text{M}]} \]

- At equilibrium ($\Delta G = 0$)
  \[ \Delta H^o + T\Delta S^o = -RT \ln K \]
  \[ T_c = \frac{\Delta H^o}{\Delta S^o + R \ln[M]_c} \]
  \[ \ln[M]_c = \frac{\Delta H^o}{RT_c} - \frac{\Delta S^o}{R} \]
  \[ T_c = \text{ceiling temperature} \]
  \[ [M]_c = \text{equilibrium monomer conc.} \]

- For $\alpha$-methyl styrene
  - Neat, $T_c = 61^\circ C$
  - $T = 25^\circ C$, $[M]_c = 2.2$ M
Heterogeneous Radical Polymerizations

- Particle-forming polymerizations
  - Emulsion polymerizations
    - Mini-emulsion, micro-emulsion and emulsion
  - Dispersion polymerizations
  - Suspension polymerizations

![Image of polymerization process]
Heterogeneous Polymerization ... 1

- Advantages
  - Bulk – batch
    • Reduces effect of impurities
  - Bulk – continuous
    • Better temperature control
  - Solution
    • Temperature control

- Suspension
  • Temperature control
  • Low viscosity
  • Isolation
  • Size control

- Emulsion
  • Temperature control
  • Low viscosity
  • Latex product
  • High molecular weight & polymerization rate
Heterogeneous Polymerization ...2

- **Disadvantages**
  - Bulk – batch
    - Temperature control difficult
    - High viscosity
    - Incomplete conversion possible
  - Bulk – continuous
    - Isolation
    - Agitation required
    - Recycling

- **Solution**
  - Isolation
  - Chain transfer to solvent
  - Solvent removal

- **Suspension**
  - Agitation required to maintain suspension
  - Washing, drying
  - Removal of suspending agents (stabilizers)

- **Emulsion**
  - Sensitive to impurities
  - Removal of emulsifier maybe required
  - Cost
## Suspension vs. Emulsion

### Comparison of suspension and emulsion polymerizations

<table>
<thead>
<tr>
<th></th>
<th>Suspension</th>
<th>Emulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer</td>
<td>35.7</td>
<td>Monomer</td>
</tr>
<tr>
<td>H₂O</td>
<td>64.2</td>
<td>H₂O</td>
</tr>
<tr>
<td>Poly(vinyl alcohol)</td>
<td>0.0143</td>
<td>H(CH₂)₇CO₂⁻NH₄⁺</td>
</tr>
<tr>
<td>Laurel peroxide</td>
<td>0.0714</td>
<td>K₂S₂O₈</td>
</tr>
<tr>
<td>Size of monomer droplet (φ)</td>
<td>0.1-5 mm</td>
<td>Size of monomer droplet (φ)</td>
</tr>
</tbody>
</table>
Emulsion Polymerizations

- **Nucleation**
  - Micellar
    - Radicals from \( \text{H}_2\text{O} \) into micelle
  - Homogeneous
    - Polymer radicals precipitate from \( \text{H}_2\text{O} \)

Suspension Polymerization

- **Monomer**
  - Discontinuous suspension in a continuous phase (usually water)

- **Initiators**
  - Monomer-soluble

- **Surfactants**
  - Determine monomer droplet size
  - Control agglomeration

- **Polymerizing droplets**
  - Diameter of 50 – 500 micron
  - Heat removed easily

- **Monomers**
  - Styrene/divinyl benzene
  - Vinyl chloride, vinyl acetate
  - Methacrylic esters
  - Tetrafluoro ethylene
    - Homo- and co-polymers
Mini- & Micro-Emulsions, Precipitation

• **Mini-emulsion polymerization**
  • Similar to emulsions but droplet nucleation

• **Micro-emulsion polymerization**
  • An emulsion that is thermodynamically stable
  • Usually particles are 10-50 nm

• **Precipitation polymerization**
Dispersion Polymerizations

• **Monomer**
  - Homogeneous monomer phase in solvent (usually water)
  - Polymer is insoluble in solvent, therefore becomes heterogeneous

• **Initiators**
  - Monomer-soluble

• **Surfactants**
  - Stabilize polymer particles
  - Control agglomeration

• **Polymerizing particles**
  - Diameter of 1–10 micron
  - Heat removed easily

• **Monomers**
  - Vinyl acetate
  - Methacrylates, acrylates
    • Homo- and co-polymers