“Precipitation Polymerization”

Polymer:  
- semicrystalline
- semicrystalline polymer not soluble in monomer

⇒ crystalline regions insoluble
⇒ amorphous regions remain soluble

Polymerization in bulk monomer
As # of high MW chains ↑, precipitation occurs

also:

occur in polymer chains with enough irregularity to form short chains

-polymer flakes, particles, etc. are porous

-some active sites remain accessible via diffusion through pores

monomer can still diffuse to active sites
Kinetics
- ill-defined and complex
- similar to emulsion polymerization
- can have red light/green light effect with free radicals
⇒ gain advantages
→ more temp/heat control
→ low η (can dilute slurry)
→ no surfactant

<table>
<thead>
<tr>
<th>Common Monomers</th>
<th>$T_{m,crys}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl chloride</td>
<td>140 – 200°C</td>
</tr>
<tr>
<td>Vinyl fluoride</td>
<td>200 – 230°C</td>
</tr>
<tr>
<td>Vinylidene fluoride</td>
<td>200°C</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>317°C</td>
</tr>
<tr>
<td>Tetrafluoroethylene (Teflon)</td>
<td>327°C</td>
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Dispersion Polymerization
- monomer
- organic solvent (good for monomer, bad for polymer)
- initiator
- particle stabilizer: repel sticky polymers, avoid coalescence

As polymerization occurs, form large solid/semisolid particles of polymer

Random copolymers
Incorporating 2 or more different monomer units in chain growth process
(radical, cationic, or anionic polymerizations)

Consider 2 different monomers: 1 and 2

\[
\begin{align*}
\text{M}_1^* + \text{M}_1 &\xrightarrow{k_{11}} \text{M}_1^* \\
\text{M}_1^* + \text{M}_2 &\xrightarrow{k_{12}} \text{M}_2^* \\
\text{M}_2^* + \text{M}_1 &\xrightarrow{k_{21}} \text{M}_1^* \\
\text{M}_2^* + \text{M}_2 &\xrightarrow{k_{22}} \text{M}_2^* \\
\end{align*}
\]

The ratio of rates of monomers entering polymer chains
\[
\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]}{k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]} \quad \text{(relative rates)}
\]

Assume steady state concentration of both \([M_1^*]\) and \([M_2^*]\)

\[\Rightarrow \text{Rate of } M_2^* \rightarrow M_1^* = \text{rate of } M_1^* \rightarrow M_2^*\]

\[k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2]\]

Simplify and combine with \(\frac{d[M_1]}{d[M_2]}\):

\[
\frac{d[M_1]}{d[M_2]} = \frac{[M_1][r_1[M_1] + [M_2]]}{[M_2][r_1[M_1] + r_2[M_2]]}
\]

where \(r_1 = \frac{k_{11}}{k_{12}}\) and \(r_2 = \frac{k_{22}}{k_{21}}\) \quad \text{(reactivity rates)}

reactivity of \(M_1^*\) with \(M_1\) versus \(M_1^*\) with \(M_2\) \quad r_1
reactivity of \(M_2^*\) with \(M_2\) versus \(M_2^*\) with \(M_1\) \quad r_2

Fraction of each monomer:

\[f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad f_2 = \frac{[M_2]}{[M_1] + [M_2]}\]

\[\Rightarrow \text{expressions for monomer composition}\]

Define:

\[F_1 = 1 - F_2 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad \text{instantaneous polymer composition}\]

Combine expressions and definitions:

\[F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad \text{copolymer composition equation}\]
Special Cases:

1. **“Ideal” copolymerization:**

\[
\begin{align*}
\eta_1 \cdot \eta_2 &= 1.0 \\
\frac{k_{12}}{k_{11}} &= \frac{k_{21}}{k_{22}} \\
r_2 &= \frac{1}{r_1}
\end{align*}
\]

probability of \( M_1^* \) or \( M_2^* \) react with \( M_1 \) vs \( M_2 \) is equal

- special case:
  \( r_1 = r_2 = 1.0 \)
  \( \Rightarrow f_1 = F_1 \)

Bernoullian (random) arrangement of monomers
large \( r_1 \) \( \Rightarrow \) monomers want to react with \( M_1 \) much more than \( M_2 \)

Simplified expression for ideal copolymerizations:

\[
F_1 = \frac{\eta_1 f_1}{\eta_1 f_1 + f_2} \quad (r_1 \cdot r_2 = 1.0)
\]

2. \( r_1 = r_2 = 0 \)

neither \( M_1 \) nor \( M_2 \) react with themselves

\[
\begin{align*}
M_1 &\rightarrow M_2^* \\
M_2 &\rightarrow M_1^*
\end{align*}
\]

Perfectly alternating composition:

\( M_1M_2M_1M_2 \ldots \) (not random at all)

Regardless of \( f_1 \): \( F_1 = 0.5 \)
2 extremes:

- perfect Bernoullian (random) case: $r_1 = r_2 = 1$
  $$r_1 r_2 = 1$$
- perfect alternating case: $r_1 = r_2 = 0$
  $$r_1 r_2 = 0$$

As $r_1 r_2$ product goes from $0 \rightarrow 1.0$, move from random to alternating sequencing:

If $r_1 < 1.0$ and $r_2 < 1.0$
Then induce inflection $\Rightarrow$ form an azeotrope:

Find azeotrope condition:

$$f_1 = \frac{(1 - r_2)}{(2 - r_1 - r_2)}$$

azeotrope exists at this monomer composition

- Block polymer: If $r_1 > 1$, $r_2 > 1$
  $$M_1 M_1 M_1 M_2 M_2 M_2 M_2$$

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.
- Consecutive homopolymer if \( r_1 >> r_2 \)

\[
\begin{align*}
M_1 \text{ homopolymerizes} & \quad r_1 >> 1 \\
\text{Then} & \\
M_2 \text{ homopolymerizes} & \quad r_2 << 1
\end{align*}
\]