Cationic Polymerization

Concepts

General Mechanism

Initiation

\[ \text{E}^* + \text{R} \rightarrow \text{E}^*\text{R} \]

Propagation

\[ \text{E}^*\text{R} + \text{R} \rightarrow \text{E}^*\text{R}_2 \]

Termination

\[ \text{E}^*\text{R}_n \rightarrow \text{E}^*\text{R}_n^\text{Nu} \]

\[ \text{E}^*\text{R}_n \rightarrow \text{E}^*\text{R}_n^\beta \text{-elim} \]

Chemistry

Initiators

1. Proton Acids
   
   \[ \text{CF}_3\text{SO}_3\text{H}, \text{H}_2\text{SO}_4, \text{H}_3\text{PO}_4 \]
   
   \( \text{e.g.} \)
   
   (want a counterion that’s not nucleophilic)
2. Lewis Acids

e.g.  AlCl₃, BF₃, SbCl₅, TiCl₄, ZnCl₂, RAlCl₂

With Lewis acid initiators, you most often need a co-initiator
e.g. a “protogen”

$$\text{BF}_3 + \text{H}_2\text{O} \rightarrow \text{H}^+\text{[BF}_3\text{OH]}$$

or a “cationogen”

$$\text{AlCl}_3 + (\text{CH}_3)_3\text{CCl} \rightarrow (\text{CH}_3)_3\text{C}^+ + (\text{AlCl}_4)^-$$

3. Photoinitiators

(activated by UV)

$$\text{N}_2^+\text{(BF}_4^-)$$

1

$$\text{I}_2$$

2

$$\text{Y}^-\text{H}$$

(e.g. S-H)

$$\text{S}^-\text{(BF}_4^-)$$

3
Cationic Polymerization

Kinetics: Initiation

1. Single Cation Initiator
\[ Y^+Z^- + M \xrightarrow{k_i} YM^+Z^- \]
\[ R_i = k_i [M] [Y^+Z^-] \]

2. Cation Initiator Complex
\[ I + ZY \rightleftharpoons Y^+ (IZ)^- \]
\[ R_i = k_i [M] \text{[complex]} \]
\[ BF_3 + H_2O \rightarrow H^+BF_3OH^- \]
\[ K = \frac{[H^+BF_3OH^-]}{[BF_3][H_2O]} \]
therefore:\n\[ \text{complex} = [H^+BF_3OH^-] = K [BF_3][H_2O] \]
\[ R_i = k_i [M] \{K [BF_3][H_2O]\} \]

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Propagation

\[ YM_n^+(IZ)^- + M \xrightarrow{k_p} YM_{n+1}^+(IZ)^- \]
\[ R_p = k_p [M] [M^+] \]

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Regiochemistry

Markownikov addition – form the most stable carbocation
\[ E^+ \xrightarrow{\text{H}} \text{H} \quad \text{E}^+ \xrightarrow{\text{R}} \text{H} \]
\[ e^- \text{donating R groups stabilize a cation thus increasing reactivity,} \]
and affect regiochemistry by directing the cation α to the donating group:
\[ R = \text{alkyl, aryl, halide, OR} \]
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Propagation

Factors affecting rate:

1. R groups: rate of propagation (and rate of initiation) fastest with monomer that yields most stable carbocation

\[
\text{OMe} \quad \text{Me} \quad \text{H} \quad \text{Cl} \quad \text{H} \quad \text{Cl}
\]

Note: most stable carbocation reacts fastest

2. Counterion: larger and less tightly bound counterions give larger \( k_p \)

\[
\text{ClO}_4^- \quad \text{TiCl}_4H_2O \quad \text{I}^- \quad \text{I}^-
\]

Examples

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \varepsilon )</th>
<th>Catalyst</th>
<th>( k_p ) (dm(^3)mol(^{-1})sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2\text{Cl}_2 )</td>
<td>9.72</td>
<td>HClO(_4)</td>
<td>17.0</td>
</tr>
<tr>
<td>( \text{CH}_2\text{Cl}_4 )</td>
<td>9.72</td>
<td>TiCl(_4)H(_2)O</td>
<td>6.0</td>
</tr>
<tr>
<td>( \text{CH}_2\text{Cl}_3 )</td>
<td>9.72</td>
<td>I(^-)</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Cationic Polymerization

Propagation

3. Solvent Effects

Species

\[
\begin{align*}
\text{covalent} & \quad \text{intimate} \\
\text{solvent separated} & \quad \text{free ions}
\end{align*}
\]
**Cationic Polymerization**

### Propagation

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ε</th>
<th>Catalyst</th>
<th>$k_p$ (dm$^3$/mol$^{-1}$sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC$_4$I</td>
<td>2.3</td>
<td>HClO$_4$</td>
<td>0.012</td>
</tr>
<tr>
<td>40/60 : CC$_4$I/CH$_2$Cl$_2$</td>
<td>5.16</td>
<td>HClO$_4$</td>
<td>0.44</td>
</tr>
<tr>
<td>40/60 : CC$_4$I/CH$_2$Cl$_2$</td>
<td>7.0</td>
<td>HClO$_4$</td>
<td>3.20</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>9.72</td>
<td>HClO$_4$</td>
<td>17.0</td>
</tr>
<tr>
<td>CH$_3$CCl$_2$</td>
<td>9.72</td>
<td>TiCl$_4$/H$_2$O</td>
<td>6.0</td>
</tr>
<tr>
<td>CH$_3$CCl$_2$</td>
<td>9.72</td>
<td>$t_5$</td>
<td>0.003</td>
</tr>
</tbody>
</table>

4. Temperature: $E_a$ only 2-3 kcal/mole; that's low therefore reaction is fast and side reactions have higher $E_a$ — use low temps for polym.

### Rearrangements:

aka Isomerization Polymerization

Not so good: low DP when rearrangements are complex:

\[ E^+ \xrightarrow{H^-} \xrightarrow{H^-} \xrightarrow{H^-} \]

Both cations can propagate, the lower the temp, the more tertiary formed.
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Termination

Recombination of Ion Pairs – can control with solvent polarity

\[ \begin{array}{c}
Y^+ M_n^- (IZ) + M \xrightarrow{k_r, M} Y^+ M_{n+1} + M^- (IZ)
\end{array} \]

\[ R_t = k_r [M^+] \]

Chain Transfer

Cationic Polymerization

Chain Transfer to Monomer: most frequently encountered

A. β-Proton transfer

\[ \begin{array}{c}
Y \xrightarrow{H} R_1 R_2 (+IZ) + \xrightarrow{k_{r, M}} R_1 R_2 (+IZ) + H
\end{array} \]

B. Hydride Transfer

\[ \begin{array}{c}
Y \xrightarrow{H} R_1 R_2 (+IZ) + \xrightarrow{k_{r, M}} R_1 R_2 (+IZ) + H
\end{array} \]

\[ R_{r, M} = k_{r, M} [M] [M^+] \]

Chain Transfer

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Chain Transfer to Polymer: EAS or hydride transfer

1. Electrophilic Aromatic Substitution: “backbiting”

2. Hydride Transfer
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Chain Transfer

Spontaneous: aka: Chain Transfer to Counterion; this is actually termination

\[ \begin{align*}
\frac{d[Y]}{dt} & = -k_tC[Y][M] \\
\frac{d[M]}{dt} & = k_tC[Y][M] - k_p[Y(M^+I-Z^-)] - k_t[Y(M^+I-Z^-)] \\
\end{align*} \]

Chain Transfer

Transfer Agents, impurities, Solvent (S) (e.g. \(H_2O\))

\[ \begin{align*}
\frac{d[M]}{dt} & = k_p[Y(M^+I-Z^-)][A^-] - k_t[Y(M^+I-Z^-)] \\
\end{align*} \]

\[ \begin{align*}
HML^+_2M^+(I-Z)^- + [X] & \rightarrow HML^+_2 + [X(I-Z)^+] \\
\end{align*} \]

Kinetics

Overall (first considering unimolecular termination)

\[ \begin{align*}
R_i & = K_i[I][Z][Y][M] \\
R_p & = k_p[Y(M^+I-Z^-)][M] \\
R_t & = k_t[Y(M^+I-Z^-)] \\
\end{align*} \]

Apply steady state: \( R_i = R_p \)

\[ \begin{align*}
[Y(M^+I-Z^-)] = \frac{K_i[I][Z][Y][M]}{k_t} \\
\end{align*} \]

\[ \begin{align*}
DP & = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t} \\
\text{Note: Increase in } I, \text{ no change to } DP \\
\end{align*} \]
Cationic Polymerization

Kinetics

Overall with Chain Transfer

\[ R_m = k_m [YM+\{IZ}\}] \]

\[ R_p = k_p [YM+\{IZ\}] [M] \]

\[ R_{ts} = k_{ts} [YM+\{IZ\}] [S] \]

\[ DP = \frac{R_p}{R_m + R_{ts} + R_{tr, S}} \]

\[ = \frac{k_p [M]}{k_t + k_m + k_{tr, M}[M] + k_{tr, S}[S]} \]

Cationic Polymerization

Energetics

Composite activation energy for rate of polymerization:

\[ E_R = E_i + E_p - E_t \]

And for DP (= kinetic chain length)

\[ E_{DP} = E_p - E_t \]

Often:

\[ E_p \ll E_i, E_t \text{ or } E_m \]

Therefore,

\[ E_R = \text{negative} \]

When this is the case, there is an increase in rate with a decrease in temp. Because, \( R = A e^{\frac{-E_R}{RT}} \) becomes \( R = Ae^{\frac{-E_i}{RT}} \)

Cationic Polymerization

Living Polymerization

Polymerizations in which propagating centers do not undergo termination or transfer; i.e. propagating center has low reactivity such that termination and transfer reactions are effectively suppressed.

1. If you add more monomer, polymer keeps growing
2. Propagating center should persist throughout polymerization.

For Cationic, need to balance the stability of the carbocation with counterion, solvent polarity, and temperature.

For optimum conditions = HI, toluene, -40°C
Cationic Polymerization

Telechelic Polymers via Cationic Polymerization

Telechelic Polymers: have relatively low mass ($M_n \leq 20,000$) with functional end groups. These can be used for further reaction to form block or network polymers.

How do you make these? With cationic polymerization, a good technique is by the “Inifer” method. Inifer is short for initiation-chain transfer.

New polymer

Types of Polymers Produced via Cationic Polymerization

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyisobutylene Polybutenes</td>
<td>Adhesives, Sealants, Insulating oils, Lubricating oil, Moisture barriers</td>
</tr>
<tr>
<td>Isobutylene-Isooctene Copolymer</td>
<td>Inner tubes, Engine mounts, Chemical tank liners, Hoses, Gaskets</td>
</tr>
<tr>
<td>Isobutylene-Cyclopentadiene Copolymer</td>
<td>Ozone resistant rubber</td>
</tr>
<tr>
<td>Polyterpene Resins (Natural Product Based)</td>
<td>Inks, Varnishes, Paints, Adhesives</td>
</tr>
<tr>
<td>Coumarone-Indene Resins (Coal Based)</td>
<td>Flooring, Coatings, Adhesives</td>
</tr>
<tr>
<td>Poly(vinyl ethers)</td>
<td>Polymer modifiers, Tackifiers, Adhesives</td>
</tr>
</tbody>
</table>

Examples
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Examples