Cationic Polymerization

Some differences between cationic and anionic polymerization
- Rates are faster for cationic (1 or more orders of magnitude faster than anionic or free radical)
  - $\text{C}^\oplus$ is very reactive, difficult to control and stabilize
    - more transfer occurs
    - more side reactions
    - more difficult to form "living" systems
      - hard to make polymers with low PDI or block copolymers
- Living cationic only possible for a specific subset of monomers
- Most industrial cationic processes are not living
  - recent developments are improving this

Kinetic Steps for Cationic Polymerization

Initiation: Use Acids
- Protonic Acids (Bronsted): HA
  - strong, but without nucleophilic counterion
    - $\text{HClO}_4$, $\text{CF}_3\text{SO}_3\text{H}$, $\text{H}_2\text{SO}_4$, CFCOOH
    - $\rightarrow \text{ClO}_4^-$

$$H^\oplus_A^\ominus + H_2C=CH\text{R} \rightarrow H_3C=CH^\oplus_A^\ominus$$

want to avoid recombination through counterion

- Lewis Acids
  - Often as initiator/coordination complexes
  - helps stabilize counterions and prevent recombination

$$\begin{align*}
\text{BF}_3 + \text{H}_2\text{O} & \leftrightarrow [\text{H}^+\text{BF}_3^-\text{OH}] \\
\text{AlCl}_3 + \text{RCl} & \leftrightarrow [\text{R}^+\text{AlCl}_4^-] \\
\text{SbF}_5 + \text{HF} & \leftrightarrow [\text{H}^+\text{SbF}_6^-] \\
\end{align*}$$

Equilibrium between anion-cation pair
Carbenium salts with aromatic stabilization

\[
\begin{align*}
\text{H}_2\text{C} & - \text{C}^+ \Theta_A \times \text{SbCl}_5 \\
\text{H}_2\text{C} & - \text{C}^+ \Theta_A \times \text{SbCl}_5
\end{align*}
\]

Propagation

\[
\text{H}_2\text{C} - \text{C}^+ \Theta_A \times \text{H}_2\text{C} = \text{CHR} \rightarrow \text{H}_2\text{C} - \text{C}^+ \Theta_A
\]

initiation species

vinyl monomer

Note: rearrangements can occur, especially if a more stable carbocation can be formed (e.g. tertiary carbocation) (most common for 1-alkenes, \(\alpha\) olefins)

\[\text{e.g. 2 methyl butene} \]

\[
\begin{align*}
\text{H}_2\text{C} & = \text{CH} \\
\text{H}_3\text{C} & \text{CH} \text{CH}_3
\end{align*}
\]

Secondary carbocation

Tertiary carbocation

This occurs via intramolecular hydride (H\(^{-}\)) shifts

Usually slow: If \(R_p \leq\) rearrangement rate, will get rearranged product

If \(R_p >\) rearrangement rate, will get random copolymer

As \(T \uparrow, m \uparrow\) (less rearrangement)

Rate of rearrangement does not increase as fast as rate of propagation.

Hydride shift NOT common for conjugated monomers like: styrene, vinyl ethers and isobutylene and other tertiary carbocations.
Termination and Transfer (Several Possibilities)

A) Termination with counterion: kills propagating cation, kinetic chain ($k_t$)
   
   i) Combination
   \[
   \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{C}} + \text{CF}_3\text{COO}^\Theta \xrightarrow{k_{t,\text{comb}}} \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{O}} \overset{\text{O}}{\overset{\text{C}}{\text{C}}} \overset{\text{CF}_3}{\text{C}}
   \]

   ii) Anion Splitting
   \[
   \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{C}} + \text{BF}_3\Theta\text{OH} \xrightarrow{k_{t,s}} \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{O}} + \text{BF}_3
   \]

B) Transfer or termination to impurity or solvent

   To H$_2$O, ROR, NR$_3$, C-OR, etc.

   \[
   \text{Initiator} \quad \overset{\Theta}{\text{M}(\text{IZ})} + \text{XA} \xrightarrow{k_{t,r,s}} \overset{\Theta}{\text{M}(\text{MA})} + \overset{\Theta}{\text{X(IZ)}}
   \]

   e.g.

   \[
   \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{A}} + \text{ROR} \rightarrow \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{C}} \overset{\Theta}{\text{A}}
   \]

   more stable than
   \[
   \overset{\text{H}}{\overset{\text{R}}{\text{C}}}
   \]

   not as reactive,
   acts as retardant
   - will not propagate further

   or

   \[
   \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{A}} + \text{R-OH} \rightarrow \overset{\text{H}}{\overset{\text{R}}{\text{CH_2}}} \overset{\Theta}{\text{C}} \overset{\Theta}{\text{A}} + \overset{\Theta}{\text{H}} \overset{\Theta}{\text{A}}
   \]

   weak acid
   will not initiate

All these processes kill chain length.
Transfer (Kinetic Chain Maintained)

A) Proton transfer to monomer

\[
\begin{align*}
\text{CH}_2\text{C}^{\Theta_A} + \text{H}_2\text{C}=&\text{CH} & \rightarrow & \text{CH}_2\text{C}^{\Theta_A} + \text{H}_3\text{C}^{\Theta_A} \\
\text{propagates}
\end{align*}
\]

B) Hydride ion transfer from monomer

\[
\begin{align*}
\text{CH}_2\text{C}^{\Theta_A} + \text{H}_2\text{C}=&\text{C} & \rightarrow & \text{CH}_2\text{C}^{\Theta_A} + \text{H}_2\text{C}^{\Theta_A} \\
\text{propagates}
\end{align*}
\]

In general, chain transfer to monomer is favorable so \( C_m \rightarrow \frac{k_{tr,M}}{k_p} \) can be sizeable.

C) Proton transfer to counterion

("spontaneous termination")

\[
\begin{align*}
\text{CH}_2\text{C}^{\Theta_A} \xrightarrow{k_{tr,cl}} \text{CH}_2\text{C}^{\Theta_A} + \text{H}^{\Theta_A} & \rightarrow & \text{CH}_2\text{C}^{\Theta_A} + \text{H}^{\Theta_A} \\
\text{propagating continues} & \rightarrow & \text{usually goes on to initiate again} \\
\text{protic acid initiators are possible} & \rightarrow & \text{+Lewis acids are less likely}
\end{align*}
\]

Usually propagates (does NOT kill chain)
Kinetic Expressions

Initiation: Assume Lewis Acid Pair

1. \[ I + ZY \xrightarrow{\Theta} Y(IZ) \Theta \quad \Rightarrow \quad K = \frac{[Y^+(IZ)^-]}{[I][ZY]} \]

2. \[ Y(IZ)^\Theta + M \xrightarrow{k_i} YM(IZ)^\Theta \quad \text{often rate limiting} \]

If step 2 is rate determining, then
\[ R_i = k_i [Y^+(IZ)^-][M] = k_i K[I][ZY][M] \]

*R_i could be determined based on step 1. Then the expressions would be different.

Propagation

Some number of monomer
\[ YM(IZ)^\Theta + M \xrightarrow{k_p} YM_{j+1}(IZ)^\Theta \quad \text{Assumption: chain length has little effect on reactivity} \]

Let \([M^+] = \text{total concentration of all-size propagating carbocations (ion pairs + free ions)} \]

Termination

Must determine primary means of termination (solvent, impurities, counterion combinations, or all?)

Example case: termination by counterion combination
\[ YM(IZ)^\Theta \xrightarrow{k_{t,comb}} YMIZ \quad \Rightarrow \quad R_t = k_{t,comb} [YM^+(IZ)^-] = k_{t,comb} [M^+] \]

If we assume steady state \([M^+]\)
\[ R_t = k_t [M^+] = k_t K[I][ZY] = R_i \quad \text{Steady state assumption is that } R_t = R_i \]

Going back to \(R_p\) with \([M^+] = \frac{R_i}{k_t}\)
\[ R_p = \frac{R_i k_p [M]}{k_i} = \frac{K k_t k_p [I][ZY][M]^2}{k_i} \quad \text{second order in } [M] \]

First order in \(R_i\)
Unlike free radical,

\[ \overline{P_N} : \text{No transfer (to monomer, solvent, counterion)} \]
\[ \overline{P_N} = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t} \]

\[ \overline{P_N} : \text{If transfer occurs} \]
- \( R_{tr,M} \): to monomer \( \rightarrow \) create new propagating chain
- \( R_{tr,S} \): to solvent \( \rightarrow \) create new cationic species
- \( R_{tr,CI} \): to counterion \( \rightarrow \) recreate initiation

\[ \overline{P_N} = \frac{R_p}{R_t + R_{tr,CI} + R_{tr,M} + R_{tr,S}} \]
with
\[ R_{tr,CI} = k_{tr,CI} [M^+] \]
\[ R_{tr,M} = k_{tr,M} [M^+][M] \]
\[ R_{tr,S} = k_{tr,S} [M^+][S] \]

\[ \frac{1}{\overline{P_N}} = \frac{k_t}{k_p[M]} + \frac{k_{tr,CI}}{k_p[M]} + C_M + C_S \]
\[ \frac{k_{tr,M}}{k_p} + \frac{k_{tr,S}}{k_p} \]

Suppose transfer to solvent or impurity does not result in further propagation.
E.g. \( \text{NR}_3 \Rightarrow \)

\[ \text{HM}_n\text{M} (\text{IZ})^\oplus + \text{NR}_3 \rightarrow \text{HM}_n\text{M} \]

This must be included in steady state \([M^+]\) expression
\[ R_p = \frac{Kk_p[M][Z][Y][M]}{k_t + k_{tr,S}[S]} \]

*Does not effect \( \overline{P_N} \) expression (do not include in \( \overline{P_N} \) calc)

*Note: all of the above assumes the 2nd initiation step is rate determining.

**Validity of Steady State Assumption**
Not really valid
- rxn rates very rapid (seconds – minutes)
- often \( R_t > R_t \)
- $[M^+]$ slowly increases with time
- $[M^+]$ reaches maximum late in polymerization
  then decreases with further conversion

Application of equations is merely an approximation of what really happens.