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)

- $\underset{\displaystyle \sim}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}^{\oplus}$ 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

comes off ← $\textcircled{H}ClO_4$, CF_3SO_3H, H_2SO_4, $CFCOOH$
    → ClO_4^-

want to avoid
recombination
through counterion

$$H^{\oplus}A^{\ominus} \quad + \quad H_2C{=}\underset{\underset{\displaystyle R}{|}}{CH} \quad \longrightarrow \quad H_3C{-}\underset{\underset{\displaystyle R}{|}}{\overset{\oplus}{C}H} \; \overset{\ominus}{A}$$
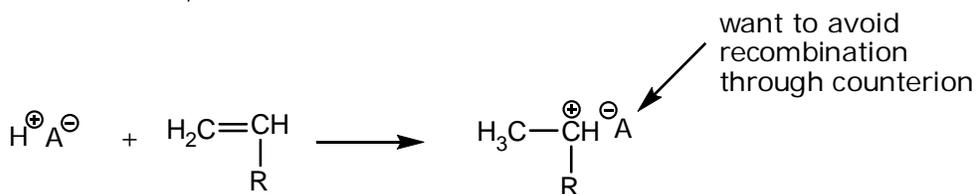
- Lewis Acids
    Often as initiator/coordination complexes
        → helps stabilize counterions and prevent
        recombination

$$\left.\begin{array}{l} BF_3 + H_2O \leftrightarrow [H^+BF_3^-OH] \\ AlCl_3 + RCl \leftrightarrow [R^+AlCl_4^-] \\ SbF_5 + HF \leftrightarrow [H^+SbF_6^-] \end{array}\right\} \quad \begin{array}{l} \text{Equilibrium between} \\ \text{anion-cation pair} \end{array}$$
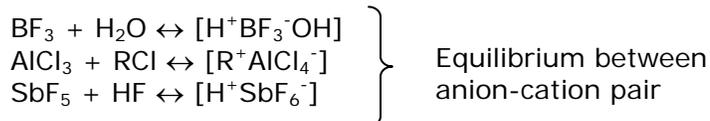
Carbenium salts with aromatic stabilization

Propagation

initiation species   vinyl monomer
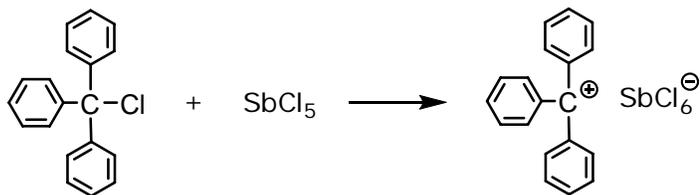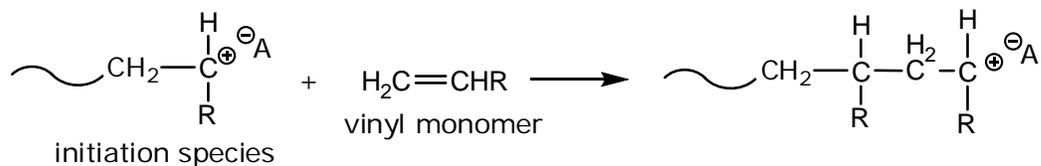
Note: rearrangements can occur, especially if a more stable carbocattion can be formed (e.g. tertiary carbocation)
   (most common for 1-alkenes, α olefins)

e.g. 2 methyl butene

secondary carbocation   tertiary carbocation
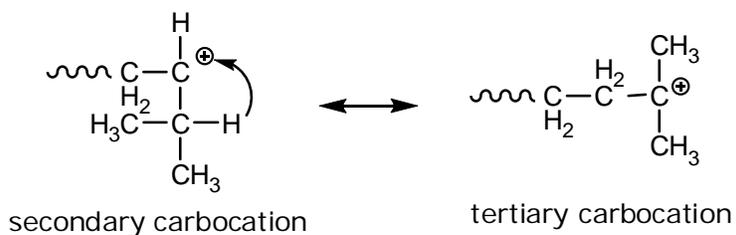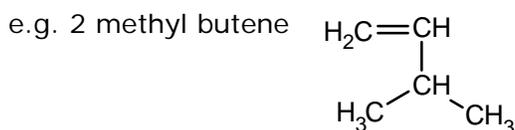
This occurs via intramolecular hydride (H^-) shifts
    Usually slow: If $R_p \leq$ rearrangement rate, will get rearranged product
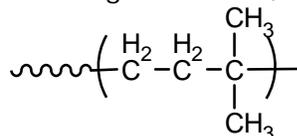
If $R_p >$ rearrangement rate, will get random copolymer
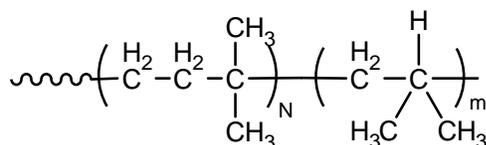
As T↑, m↑ (less rearrangement)
Rate of rearrangement does not increase as fast as rate of propagation.

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
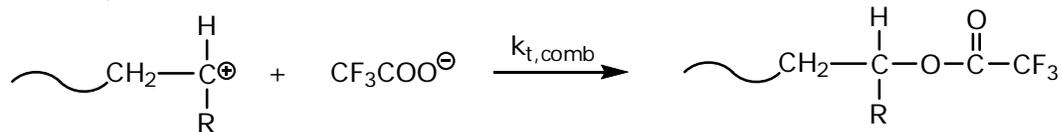
    ii) Anion Splitting
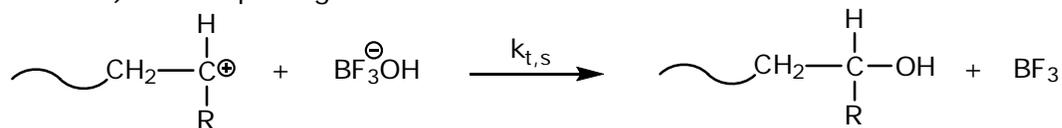
B) Transfer or termination to impurity or solvent

    To H_2O, ROR, NR_3, $-\overset{O}{\overset{\|}{C}}-OR$, etc.

e.g.

    more stable than

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

or

    weak acid
    will not initiate
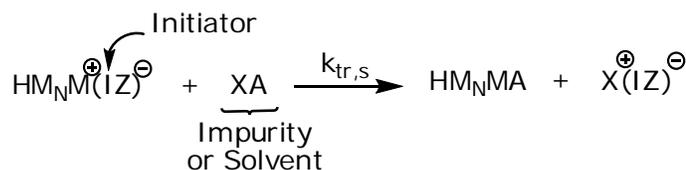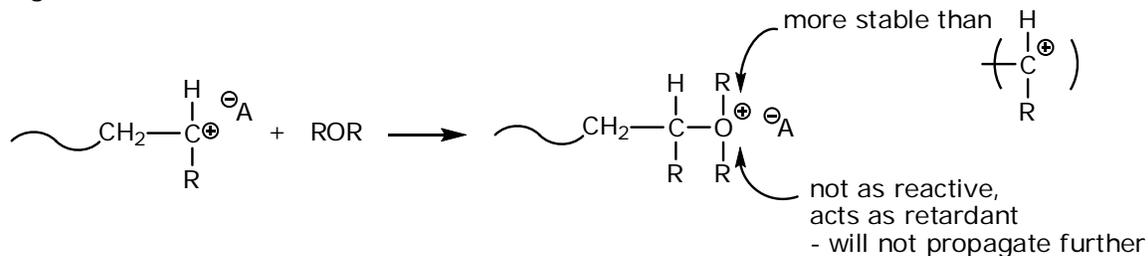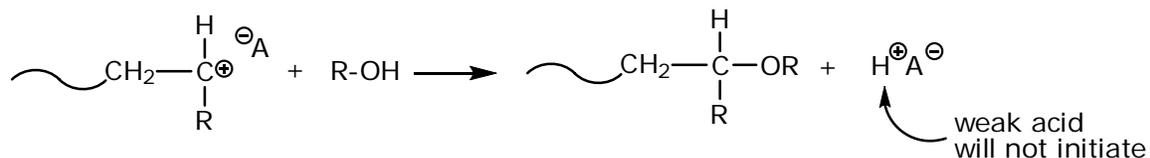
> All these processes
> kill chain length.

Transfer (Kinetic Chain Maintained)

A) Proton transfer to monomer
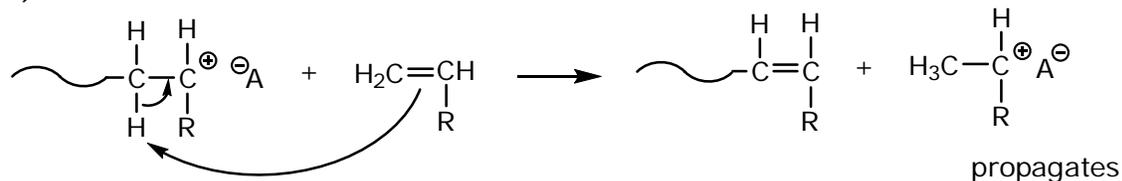
propagates

B) Hydride ion transfer from monomer
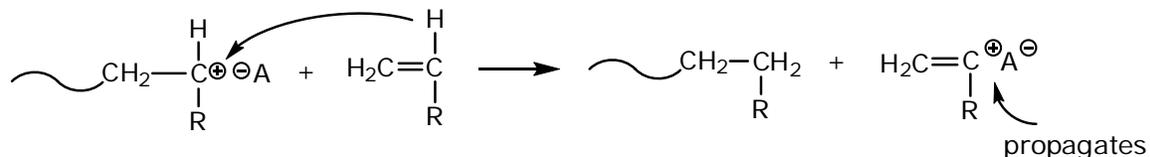
propagates

In general, chain transfer to monomer is favorable so $C_M \to \dfrac{k_{tr,M}}{k_p}$ can be sizeable.

C) Proton transfer to counterion
   ("spontaneous termination")

propagating continues

usually goes on to initiate again

protic acid initiators are possible
+Lewis acids are less likely
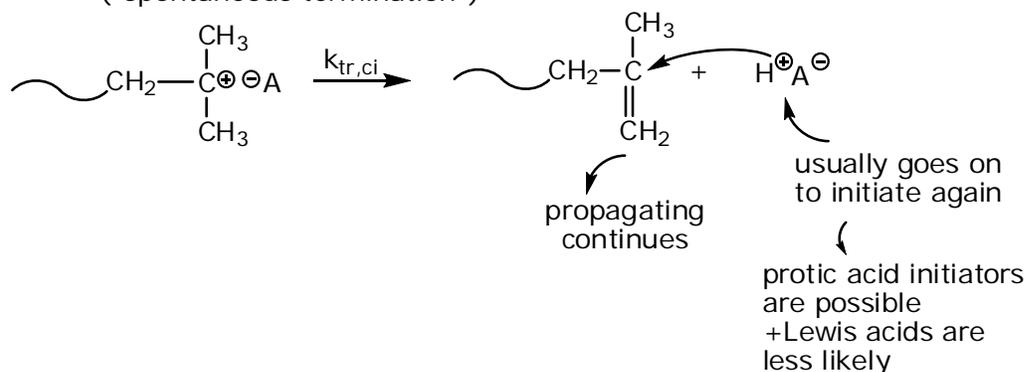
Usually propagates
(does NOT kill chain)

Kinetic Expressions

Initation: Assume Lewis Acid Pair

1. $I + ZY \longleftrightarrow \overset{\oplus}{Y}(IZ)^{\ominus} \Rightarrow K = \dfrac{\left[Y^+ \left(IZ \right)^- \right]}{\left[I \right]\left[ZY \right]}$

2. $\overset{\oplus}{Y}(IZ)^{\ominus} + M \xrightarrow{k_i} YM^{\oplus}(IZ)^{\ominus}$ often rate limiting
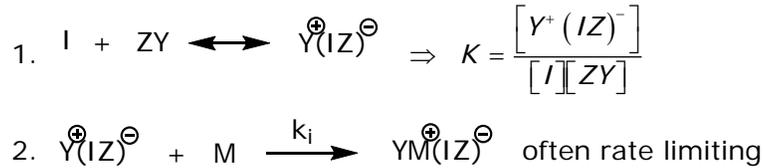
If step 2 is rate determining, then

$$R_i = k_i \left[Y^+ \left(IZ \right)^- \right]\left[M \right]$$
$$= k_i K \left[I \right]\left[ZY \right]\left[M \right]$$

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

Propagation

$YM_j^{\oplus}(IZ)^{\ominus} + M \xrightarrow{k_p} YM_{j+1}^{\oplus}(IZ)^{\ominus}$ Assumption: chain length has little effect on reactivity

some number of monomer

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

$$R_p = k_p \left[YM_j^+ \left(IZ \right)^- \right]\left[M \right] = k_p \left[M^+ \right]\left[M \right]$$
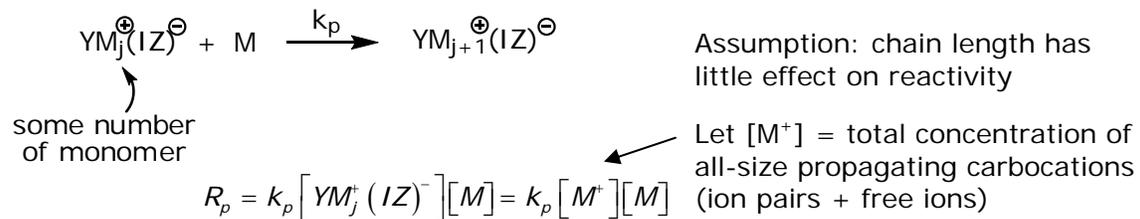
Termination

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

Example case: termination by counterion combination

$YM^{\oplus}(IZ)^{\ominus} \xrightarrow{k_{t,comb}} YMIZ \Rightarrow R_t = k_{t,comb} \left[YM^+ \left(IZ \right)^- \right] = k_{t,comb}\left[M^+ \right]$
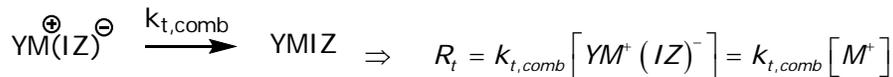
If we assume steady state $[M^+]$

$$R_t = k_t \left[M^+ \right] = k_i K \left[M \right]\left[I \right]\left[ZY \right] = R_i$$ Steady state assumption is that $R_t = R_i$

$$\left[M^+ \right] = \frac{R_i}{k_t} = \frac{k_i K \left[M \right]\left[I \right]\left[ZY \right]}{k_t}$$

Going back to R_p with $\left[M^+ \right] = \dfrac{R_i}{k_t}$

$$R_p = \frac{R_i k_p \left[M \right]}{k_t} = \frac{K k_i k_p \left[I \right]\left[ZY \right]\left[M \right]^2}{k_t}$$ second order in [M]

First order in R_i

(unlike free radical)

$\overline{P_N}$: No transfer (to monomer, solvent, counterion)

$$\overline{P_N} = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t}$$

$\overline{P_N}$: 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

$$\overline{P_N} = \frac{R_p}{R_t + R_{tr,Ci} + R_{tr,M} + R_{tr,S}} \quad \text{with} \quad \begin{aligned} R_{tr,Ci} &= k_{tr,Ci}\left[M^+\right] \\ R_{tr,M} &= k_{tr,M}\left[M^+\right][M] \\ R_{tr,S} &= k_{tr,S}\left[M^+\right][S] \end{aligned}$$

$$\overline{P_N} = \frac{k_p[M]}{k_t + k_{tr,Ci} + k_{tr,M}[M] + k_{tr,S}[S]}$$

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

$$\underbrace{}_{\dfrac{k'_{tr,M}}{k_p}} \qquad \underbrace{}_{\dfrac{k_{tr,S}}{k_p}}$$

Suppose transfer to solvent or impurity does not result in further propagation.
    e.g. NR$_3$ $\Rightarrow$

$$HM_N\overset{\oplus}{M}(IZ)^{\ominus} \;+\; NR_3 \longrightarrow HM_NM\!\!-\!\!\overset{R}{\underset{R}{\overset{\displaystyle |}{\underset{\displaystyle |}{N}}}}\!\overset{\oplus}{\!\!-\!\!R} \;\; (IZ)^{\ominus}$$

                                                   Is stable
                                                   No further propagation
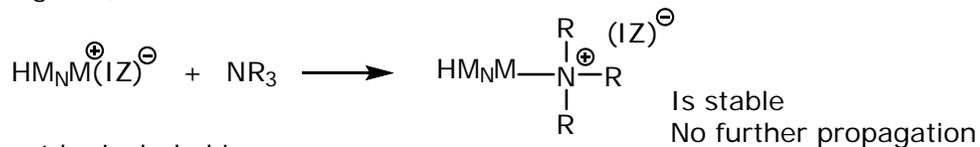
This must be included in
steady state [M$^+$] expression

$$R_p = \frac{Kk_ik_p[I][ZY][M]^2}{k_t + \boxed{k_{tr,S}[S]}} \longrightarrow \text{term from transfer like}$$

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

*Note: all of the above assumes the 2$^{\text{nd}}$ initiation step is rate determining.

Validity of Steady State Assumption

    Not really valid
        - rxn rates very rapid (seconds – minutes)
        - often $R_i > R_t$

- [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.