Cationic Polymerization

$$R_p = \frac{K k_i k_p [I][ZY][M]^2}{k_t}$$

Energetics of Cationic Polymerization
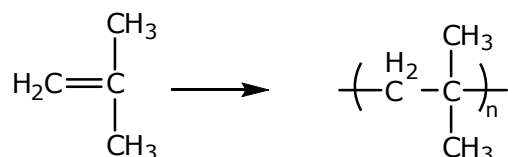
$$R_p \propto \frac{k_i k_p}{k_t} \Rightarrow \frac{A_p A_i}{A_t} \exp\left(\frac{-E_p - E_i + E_t}{RT}\right)$$

$-E_p-E_i+E_t = E_{RP} \sim$ 5-10 kcal/mol
smaller impact of T than in free radical

- More directly impacted by T: transfer rates
    $C_M \downarrow$ by 100x for ΔT from -30°C to -60°C
    (isobutene)
    Often use refrigeration for commercial processes

$$E_{\overline{pn}} = -E_p + E_t + \underbrace{\sum E_{tr}}$$

energy of transfer rxns

Example: Cationic Polymerization of Polyisobutylene (PIB)

temp of polymerization: -100°C to -30°C
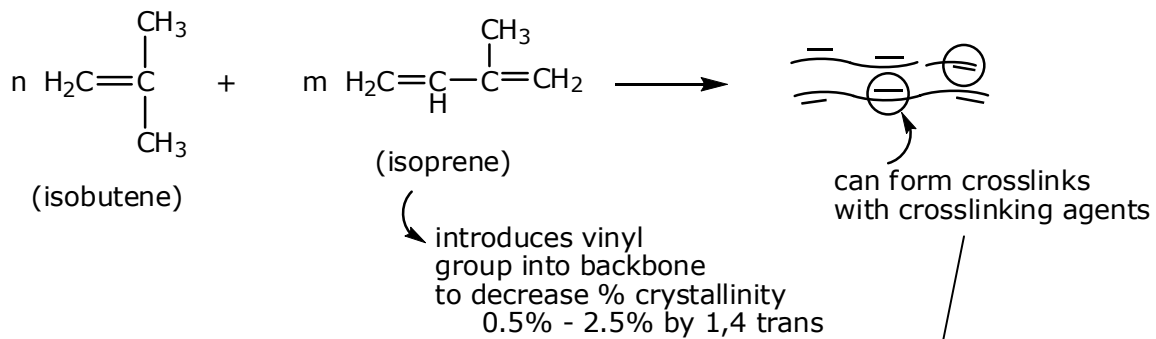need a lot of refrigeration!

$\rightarrow$ high rate of heat release
want R_p to be lower for control
(cationic is very rapid, faster than other polymerization methods)

- If used a good solvent for PIB $\rightarrow$ high viscosity early on (problem!)
- Thus, choose a decent solvent for monomer but poor solvent for polymer PIB
- Precipitation occurs as polymer is generated
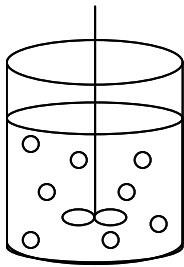
Porous crystal particles
  ⇒ allow precipitation of monomer
  ⇒ continued chain growth
  ⇒ low η slurry
     low T's } η, T control

Example: To Form Butyl Rubber

(isobutene)   (isoprene)

introduces vinyl
group into backbone
to decrease % crystallinity
0.5% - 2.5% by 1,4 trans

can form crosslinks
with crosslinking agents

Doesn't crystallize
even at low T
→ stiff and brittle
app: space shuttle

Solvent: $CHCl_3$
    (also precipitant of polymer)

Butyl rubber: solvent resistant
      Ex: gloves
   - doesn't break down in ozone (O_3)
      → chemically stable
   - chem tank liners
   - chem tubes

Cationic: very rapid, high MW
    Difficult to control, PDI affected

Living Cationic Polymerization

    - must have $R_i \gg R_p$
     (steady state is not a very good assumption)
    - must eliminate cross-transfer processes (that limit chain growth)
    1. carbocation reactivity is lowered
    2. deter combination of counterion
    3. eliminate other impurities
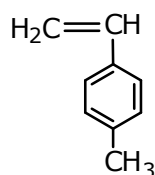
Examples

Vinyl ethers

$$H_2C{=}CH$$
$$|$$
$$OR'$$
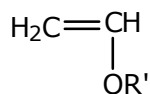
Initiator: $HI + ZnI_2$
Solvent: toluene
        -40 to -25^oC

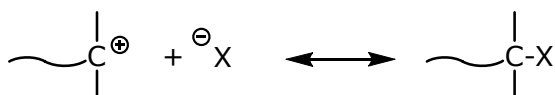Ethyl styrene

$$H_2C{=}CH$$

(aromatic ring with CH_3)

Initiator: CH_3COClO_4
Solvent: CH_2Cl_2/Toluene, -78^oC

- Counterion choice is important
    e.g. Bulky counterion that cannot recombine or counterion attacks reversibly

$$\sim{\overset{|}{\underset{|}{C}}}^{\oplus} \quad + \quad {}^{\ominus}X \quad \longleftrightarrow \quad \sim{\overset{|}{\underset{|}{C}}}{-}X$$
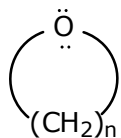
- Styrenes, vinyl ethers, vinyl carbazoles, isobutylene

        can attach side groups

"Living" or "Quasi-living" b/c never completely get rid of transfer
    PDI $\sim$ 1.1 to 1.2   but good enough to get
                                             high yield polymers
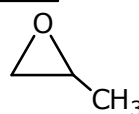
Ring-Opening of Cyclic Ethers

            (best example of ring-opening family)

$$\overset{\ddot{O}}{\underset{(CH_2)_n}{\bigcirc}}$$

$(n{=}2) \Rightarrow$ oxirane or epoxide
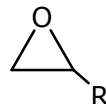monomers: ethylene oxide

            propylene oxide

                CH_3

            or other epoxide rings

                R

where R does not affect polymerization
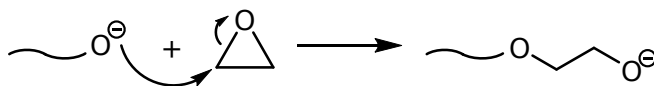
$(n=3) \Rightarrow$ oxetane, trimethylene oxide

$(n=4) \Rightarrow$ oxolane, tetrahydrofuran

n=6   keep increasing

(for anionic polymerization: only epoxides can be polymerized)
b/c it has a huge angle strain, will open using anionic or cationic initiation

anionic

can be done in controlled environment (living polymerization)

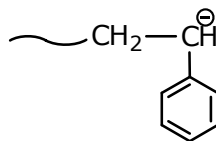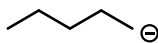$\overline{p_n} \uparrow$ slowly with conversion
Rate, kinetics indicate living system

$$R_p = k_p^{app}[M][M^-]$$

$$\parallel$$
$$[I]$$

$$\overline{p_n}(t) = \frac{[M]_o - [M]_t}{[I]} \Rightarrow \overline{p_n} = \frac{[M]_o}{[I]}$$

Can initiate with any oxyanion: CH3O-
                                          and its analogs
                          carboanion

$$\sim\!\!CH_2-\overset{\ominus}{CH}$$
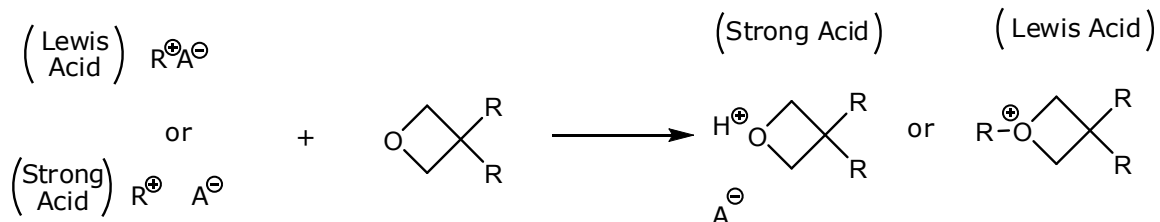

- all other cyclic ethers only go by cationic initiation

Examples: oxetanes
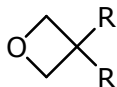
Initiators: strong acids: H_2SO_4, CF_3COOH
                          or Lewis acid with counterions that don't combine

$\left(\begin{array}{c}\text{Lewis}\\\text{Acid}\end{array}\right)$ $R^{\oplus}A^{\ominus}$

or

$\left(\begin{array}{c}\text{Strong}\\\text{Acid}\end{array}\right)$ $R^{\oplus}$ $A^{\ominus}$

$+$ (oxetane with R, R) $\longrightarrow$ $\left(\text{Strong Acid}\right)$ $H^{\oplus}O$(ring with R, R) $A^{\ominus}$ or $\left(\text{Lewis Acid}\right)$ $R-O^{\oplus}$(ring with R, R)

Propagation Step

$H^{\oplus}O$(ring with R, R) $+$ $:O$(ring with R, R) $\longrightarrow$ $HO-\overset{H_2}{C}-\overset{R_2}{C}-\overset{H_2}{C}-O^{\oplus}$(ring with R, R)
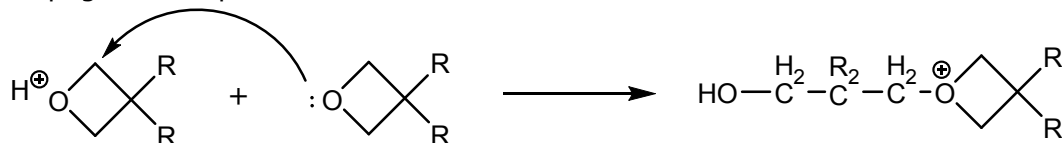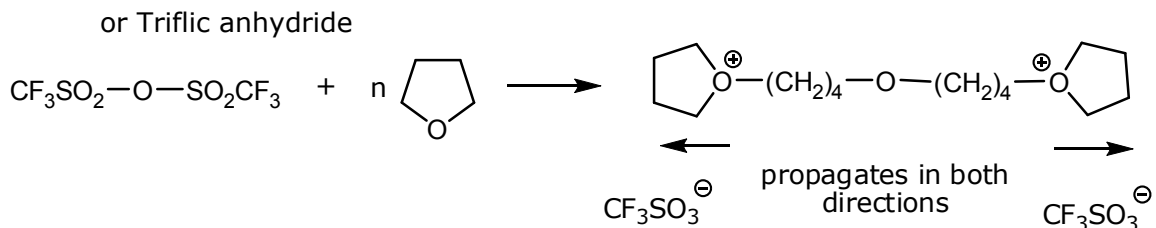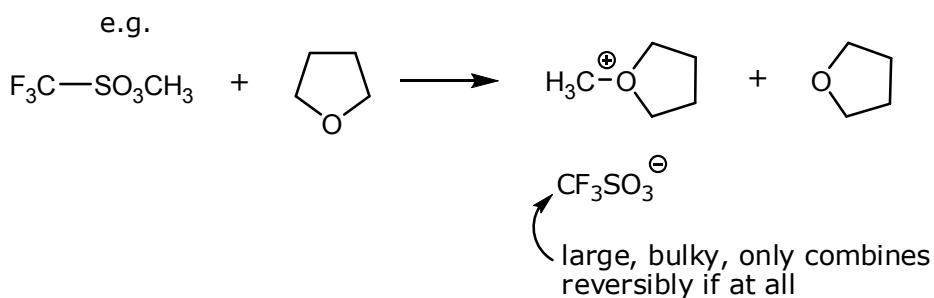
Termination Step

- Will happen if A^- is nucleophilic $\rightarrow$ counterion combination
(bad if irreversible)
If H_2O is present (very good nucleophile)
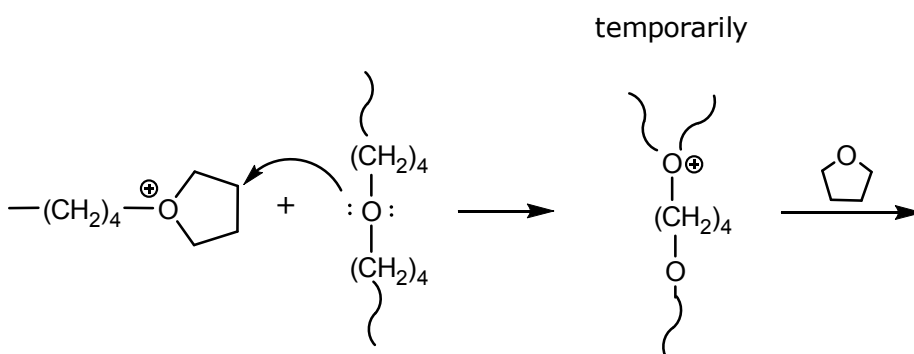If $:NH_2$ is present

Use counterions that are stable
AsF_6^-, PF_6, $SbCl_6^-$

Or very strong fluorosulfonic acids
$CF_3SO_3^-H^+$
Only combine reversibly and rapidly

Initiate with mono- and bifunctional initiators

e.g.

$F_3C-SO_3CH_3$ $+$ (THF ring with O) $\longrightarrow$ $H_3C-\overset{\oplus}{O}$(THF ring) $+$ (THF ring with O)

$CF_3SO_3^{\ominus}$

large, bulky, only combines
reversibly if at all

or Triflic anhydride

$CF_3SO_2-O-SO_2CF_3$ $+$ n (THF ring) $\longrightarrow$ (ring)$\overset{\oplus}{O}-(CH_2)_4-O-(CH_2)_4-\overset{\oplus}{O}$(ring)

$\longleftarrow$ propagates in both $\longrightarrow$
directions

$CF_3SO_3^{\ominus}$ $\qquad$ $CF_3SO_3^{\ominus}$

want to avoid: $\left\{ \begin{array}{l} BF_3/H_2O \\ AlCl_3/HCl \end{array} \right\}$

temporarily

→ causes shuffling ⇒ Flory distribution, hurts PDI

Best Living Systems
      Pre-existing carbenium ions

      $C_6H_5\text{-}C^+\text{=}O$ SbF_6^-

      Carbenium ions

      $CH_3CH_2\text{-}C^+\text{=}O$ PF_6^-
      $(C_6H_5)_2C^+H$ B^-F_4
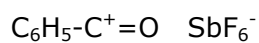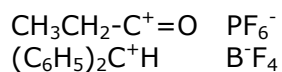
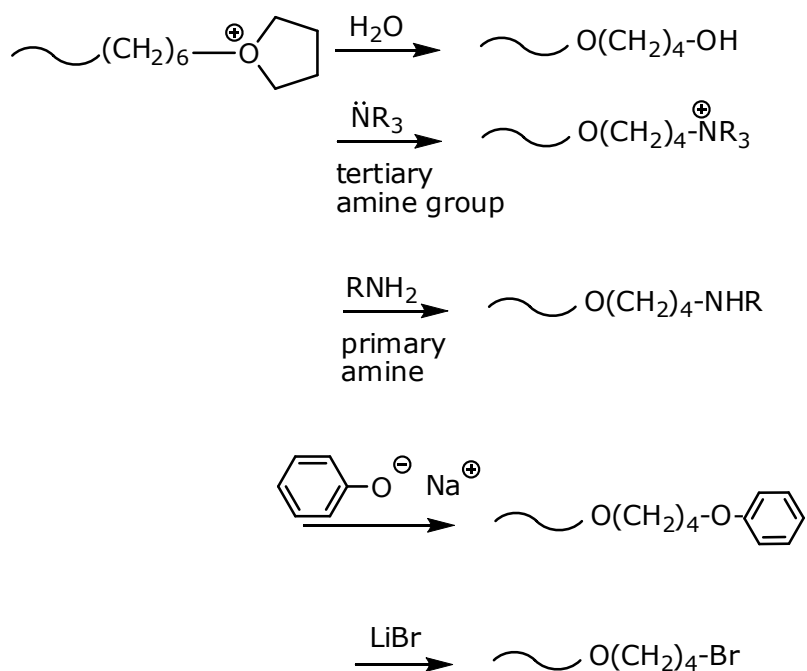Triflic systems
      $CF_3\text{-}SO_2\text{-}O\text{-}CH_3$, etc

Avoid: ROH
      RNH_3
      ROR
      Other ethers (check relative reactivities)

Can intentionally terminate to get o-functionalities

$\sim\sim$(CH$_2$)$_6$—$\overset{\oplus}{O}$⟨ ⟩ $\xrightarrow{\text{H}_2\text{O}}$ $\sim\sim$O(CH$_2$)$_4$-OH

$\xrightarrow{\ddot{\text{N}}\text{R}_3}$ $\sim\sim$O(CH$_2$)$_4$-$\overset{\oplus}{\text{N}}R_3$

tertiary
amine group

$\xrightarrow{\text{RNH}_2}$ $\sim\sim$O(CH$_2$)$_4$-NHR

primary
amine

⟨ ⟩—O$^{\ominus}$ Na$^{\oplus}$

$\xrightarrow{\hspace{2cm}}$ $\sim\sim$O(CH$_2$)$_4$-O—⟨ ⟩

$\xrightarrow{\text{LiBr}}$ $\sim\sim$O(CH$_2$)$_4$-Br

Ch. 7 Odian: Ring strain
Diff impacts of ring sizes