From last lecture

Association Effects

$$[M^-] = K_e^{1/n} [\{M^-\}_n]^{1/n}$$

$$[\{M^-\}_n] \propto [M^-] = [I]$$ can assume conc. of initiator is
equal to conc of propagating anion

$$\approx \frac{1}{n}[I] \ \text{ e.g.}$$

$$\Rightarrow R_p = k_p K_e^{1/n} [M][\{M^-\}_n]^{1/n}$$

Dissociation

$$\alpha \equiv \frac{\text{\# of dissociated (free) ions}}{\text{all ions}}$$

$$K_D = \frac{\alpha^2 [M^-]}{1-\alpha}$$

assuming $1 - \alpha \to 1$ (small α)

$$\Rightarrow \quad \alpha \cong \left(\frac{K_D}{[M^-]}\right)^{1/2}$$

$$k_p = k_{p,apparent} = \alpha k_{p-} + (1-\alpha) k_{pI}$$

remember k_{p-} = propagation rate constant for free ion
k_{pI} =   "   "   "   "   ion pair
$k_{p,app}$ = apparent, or global, or pseudo rate constant

$$\Rightarrow R_P = k_{p,app}[M][M^-]$$

$$\Rightarrow R_P = \underbrace{\left[k_{pI} + \left(\frac{K_D}{[M^-]}\right)^{1/2}(k_{p-} - k_{pI})\right]}_{k_{p,app}}[M^-][M]$$
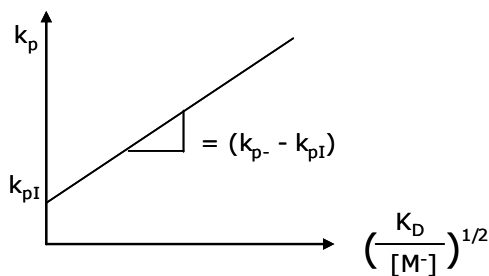
Note: $K_D \sim 10^{-7}$
    $\Rightarrow \alpha \Rightarrow 1\%$ free ions
If you know K_D, you can find k_{PI}, and $k_{p-} - k_{pI}$ by plotting

$$k_p \ \text{ vs } \left(\frac{K_D}{[M^-]}\right)^{1/2}$$
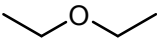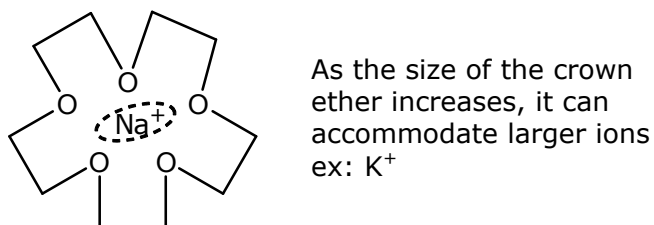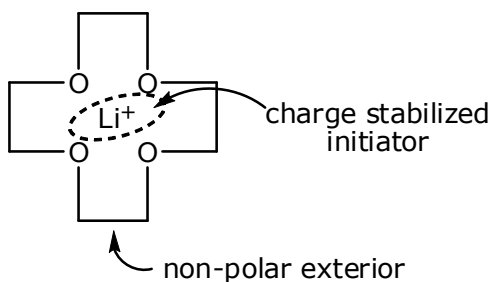
where $[M^-] = [I]$

Effects of Solvent Polarity on Polymerization

Solvent effects in anionic polymerization.

To measure polarity, look at dielectric constant ε, which is a change in polarity.

Examples:

Solvent		dielectric const ε	k_p (L/mol·s) with P.S.
• Benzene		2.2	2
• Dioxane		2.2	5
• THF		7.6	550
• 1,2 dimethyl ether		5.5	3800
			solvation effects are due to ε and chem structure
(the ether group helps solvate system)			

The ether group is very strong ligand for cations:
The best example for this is: crown ethers

charge stabilized initiator

non-polar exterior

As the size of the crown ether increases, it can accommodate larger ions
ex: K^+

• Crown ethers (Odian p. 435) increase the conc of free-ion propagating species, resulting in very large rate increases
• In addition, crown ethers & "glycines" (short PEO chains) are added to non-polar solvents to solvate cations (ex: Li^+ and Na^+)

Ion effects are also observed in ion dissociation/solvation

Ex: Ion Size: larger ions are more soluble in "neutral"
solvents (no specific interaction)

according to $F = \dfrac{Q_- \cdot Q_+ \cdot e^2}{\varepsilon \cdot r^2}$

where r = distance between $\oplus$ and $\ominus$

as ion size $\uparrow$
   r $\uparrow$
   F $\downarrow$
$\Rightarrow$ dissociation becomes easier

There are exceptions through: ether solvents are generally better at solvating smaller ions (Li$^+$)

See Table 5-11: Anionic polymerization of styrene in THF

counterions	k_{pI}	$k_p \times 10^7$		k_{p-}	k_{pI} for dioxene
Li$^\oplus$	160	2.2			0.94
Na$^\oplus$	80	1.5			3.4
K$^\oplus$	60-80	0.8		6.5×10^4 (same k_{p-} value)	19.8
Rb$^\oplus$	50-80	0.1			21.5
Cs$^\oplus$	22	0.02			24.5

Stereospecificity

(affected by both solvent and ion)

Less polar solvents allow coordination effects $\cdot$ closer ion – counterion interactions (association pairs)

$\Rightarrow$ coordination effects w/ion become important
$\Rightarrow$ "   "   often favor isotactic placements
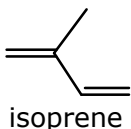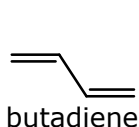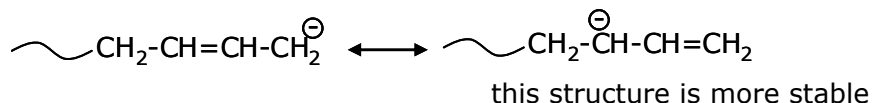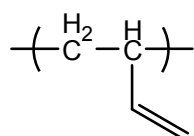$\Rightarrow$ "   "   are greatest for small ions

Ex:

more dissociation
for larger ion

Dienes

In polar solvents in anionic polymerization:
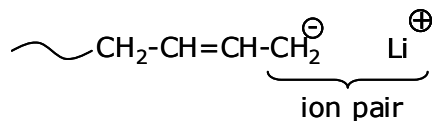

this structure is more stable

A good polar solvent has free ions and "1,2 addition" is preferred in dienes:



and this can be
functionalized

Polymer is similar to PVC
$T_g \sim 30\text{-}40^oC$
Polymer is harder around room T

In a non-polar solvent, coordination effects are strong
Delocalization decreases and thus, localized effects are strong
$Li^\oplus$ in particular directs addition to primary carbon:

ion pair

1,4 addition is favored in this case.

1,4 polybutadiene:
- low T_g
- extremely flexible
- non-crystalline
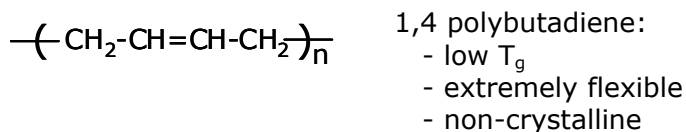
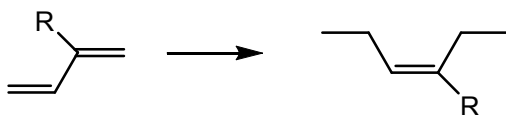## Cis-Trans Considerations

What about –cis and trans?

vs

cis 1,4   trans 1,4

What is the percentage of cis and trans?
- trans form is slightly more favored (more accessible to monomer)
- can get trans over cis using a polar solvent

- can get cis over trans using a non-polar solvent, esp for Li$^\oplus$
  (effect is weaker for larger ions)
- can get preference for cis with substituent on diene:

If we put all the effects together:

For butadiene:

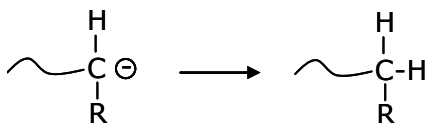| Ion	Solvent	1,4 cis	1,4 trans	1,2
Li$^\oplus$	pentane (non-polar)	35%	50%	15%
Li$^\oplus$	THF	0%	5%	95%
Na$^\oplus$	pentane	7%	25%	67%
K$^\oplus$	pentane	12%	38%	50%
For isoprene				
Li$^\oplus$	pentane	94%	0%	6%

Prob of occurence

Li$^\oplus$ has extreme power in trans coordination: (sacrificing speed for structure)

End Functionalization in Anionic Polymerization

In living polymerization, "lives" until we intentionally "quench" the anion:
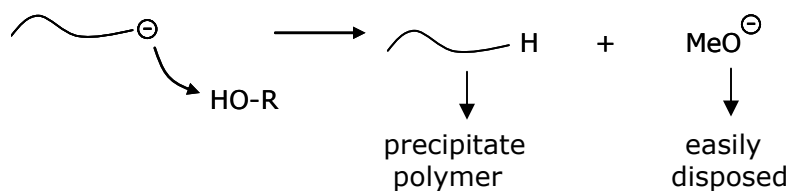
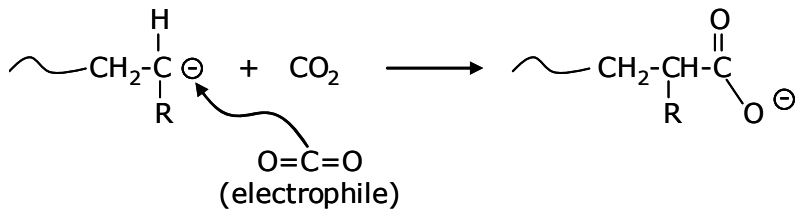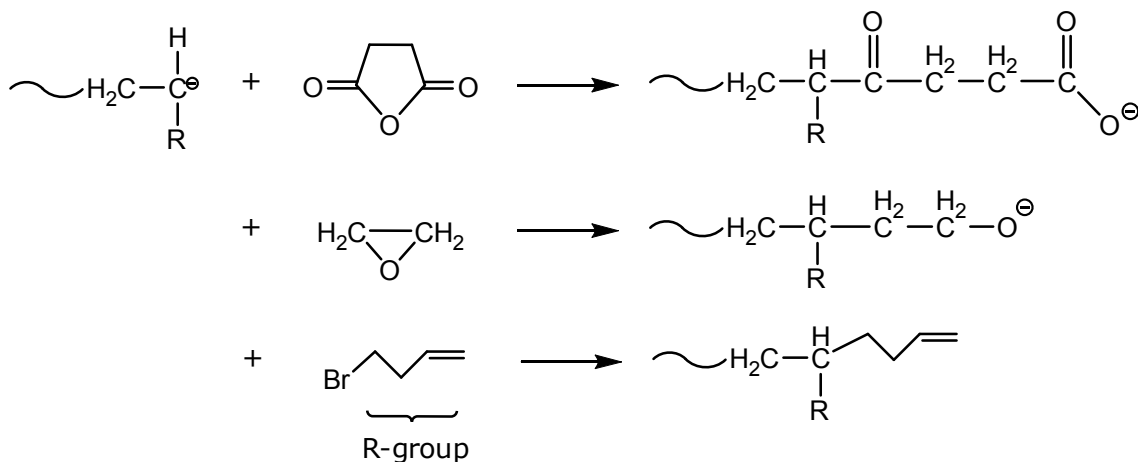But

  is boring…

We can end functionalize with specific terminating agents:

React with anhydride:

Because the reaction goes to end, just add end capper in excess

Can have

or

- dionic initiator with 2 prop directions
- have α, Ω End functionalization