

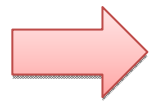
***Ionic* Polymerization:**
***Anionic* and *Cationic* Polymerization**

2009.10.26

Radical versus *Ionic* Chain Polymerizations

- *General Considerations of Polymerizability*

Whether a particular monomer can be converted to polymer depends on both *thermodynamic* and *kinetic* considerations.

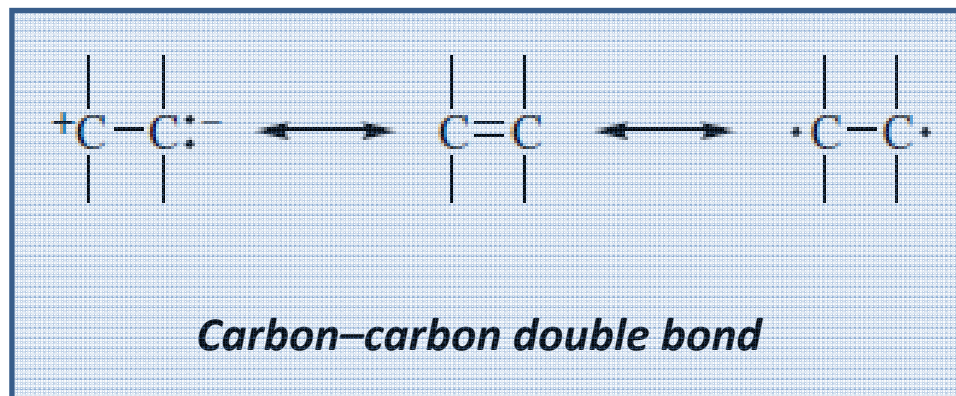
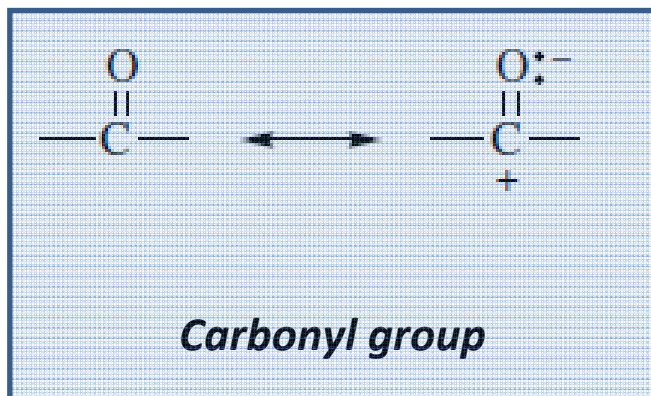


Polymerization is possible only if the *free-energy difference* ΔG between *monomer* and *polymer* is negative. **(Thermodynamic feasibility)**

- The ability to carry out a thermodynamically feasible polymerization depends on its *kinetic feasibility*—on whether the process proceeds at a reasonable rate under a proposed set of *reaction conditions*.

Carbon–carbon double bond undergoes polymerization by both *radical* and *ionic* initiators.

The difference arises because the p-bond of a vinyl monomer can respond appropriately to the initiator species by either *homolytic* or *heterolytic* bond breakage:

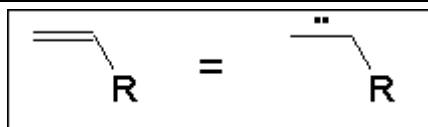


The carbon–carbon double bond in vinyl monomers and the carbon–oxygen double bond in *aldehydes* and *ketones* are the two main types of linkages that undergo *chain polymerization*.

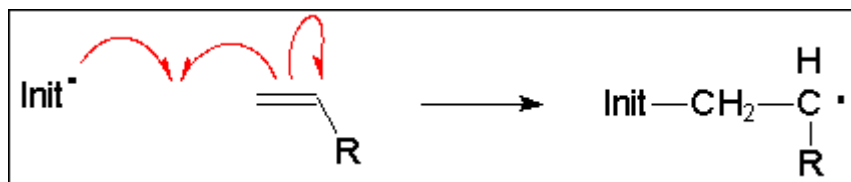
Comparison of *Free Radical* and *Ionic* Polymerizations

"The only difference is the "flow" of the electrons during propagation"

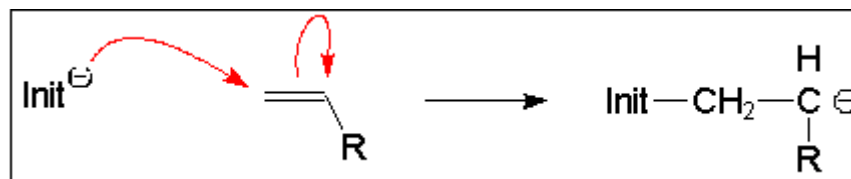
a double bond equals a single bond plus two more electrons



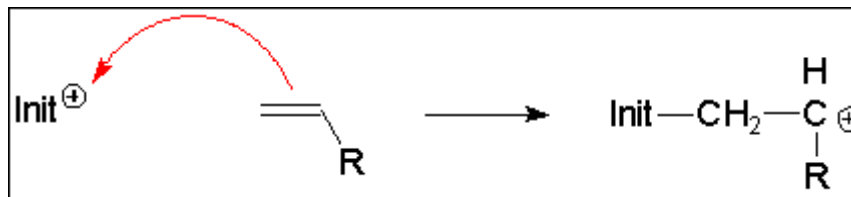
Free radical vinyl polymerization



Anionic vinyl polymerization



Cationic vinyl polymerization

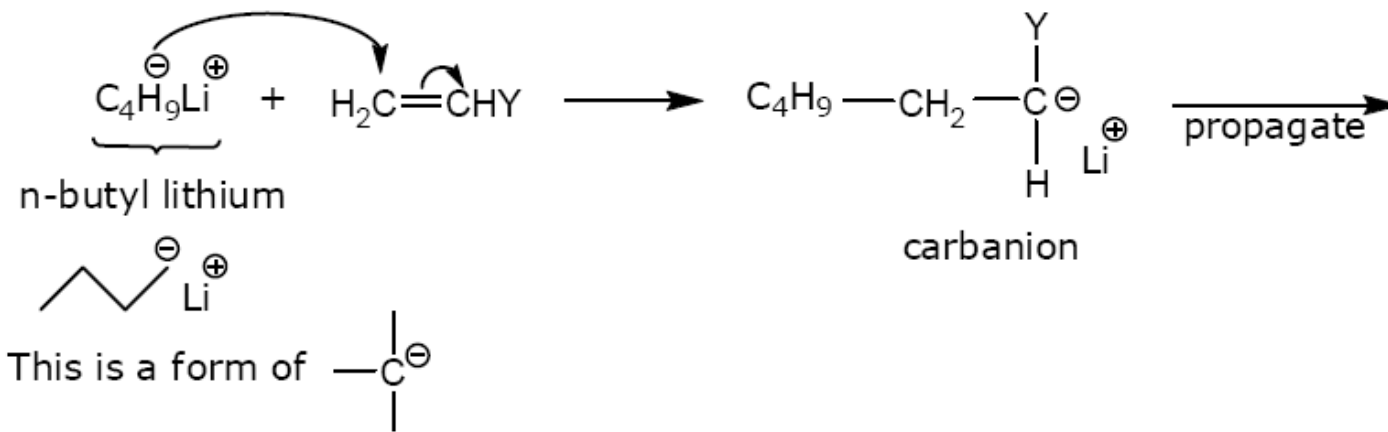


Ionic Polymerization

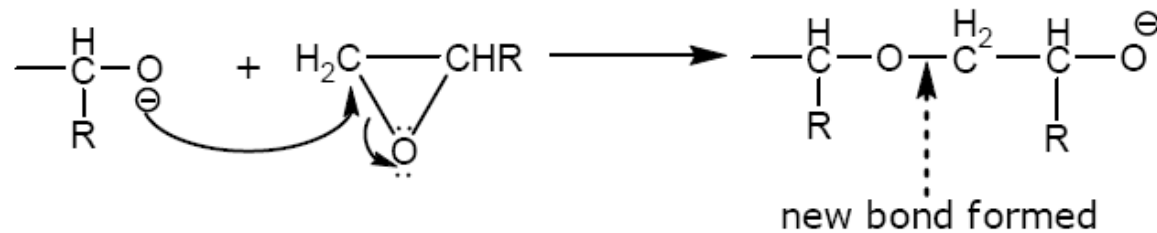
1. Anionic
2. Cationic

Anionic Polymerization

- very aggressively charged negative group

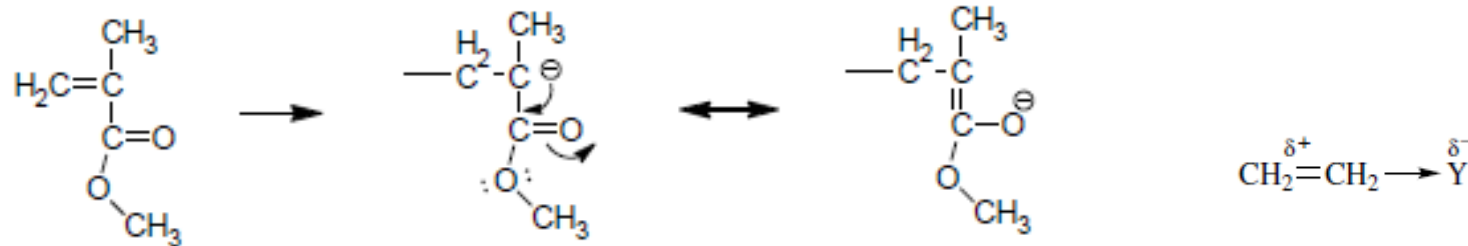


Also have negative charge on other atoms:
e.g. ring opening:



Propagating species stabilized by *resonance*

Anionic Polymerization

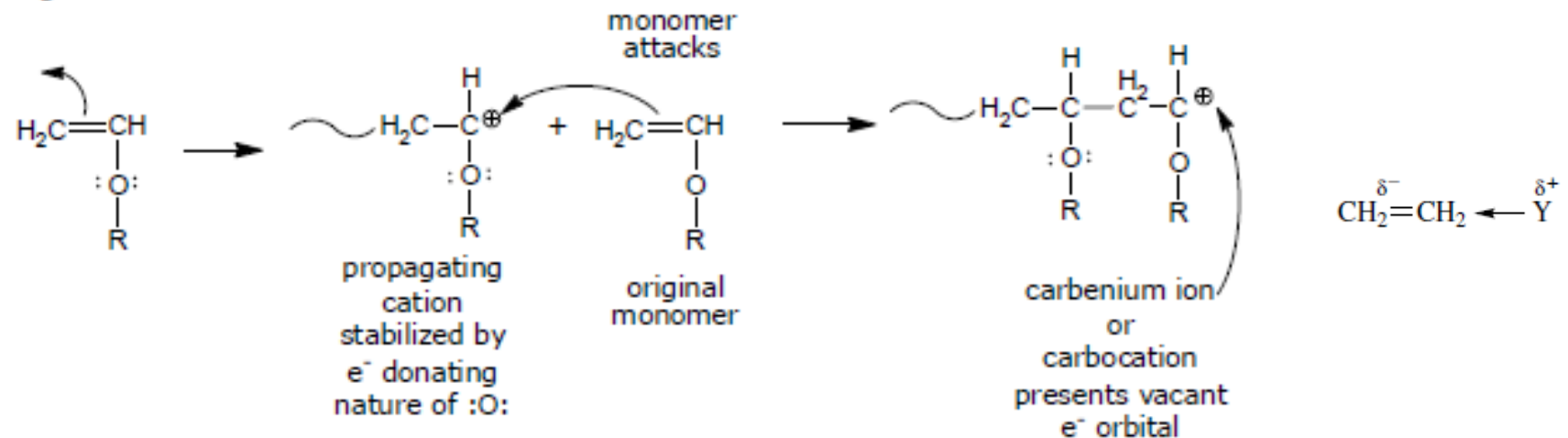


methyl methacrylate
 e^- -drawing group

Cationic Polymerization

- need substituent that is e^- donating

e.g.

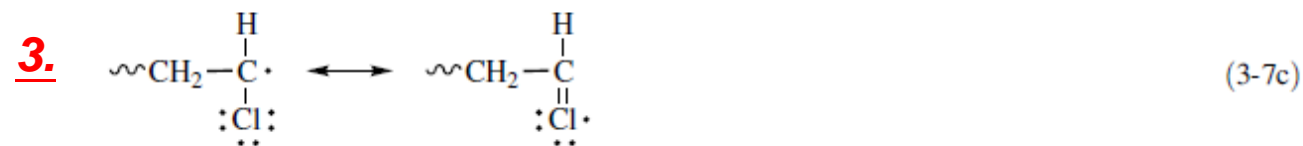
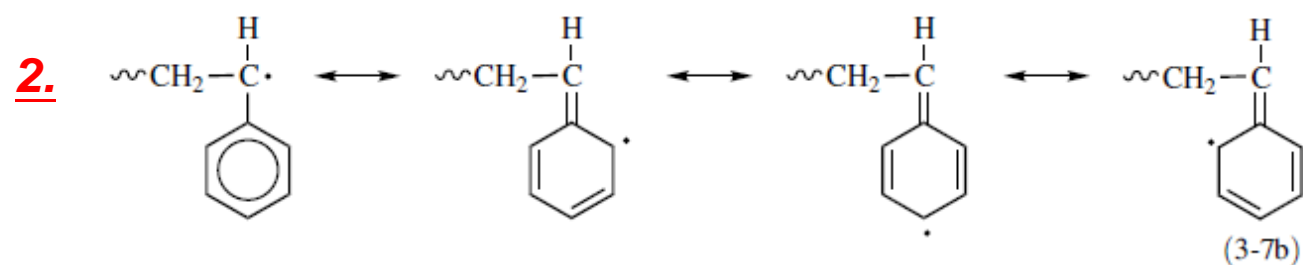
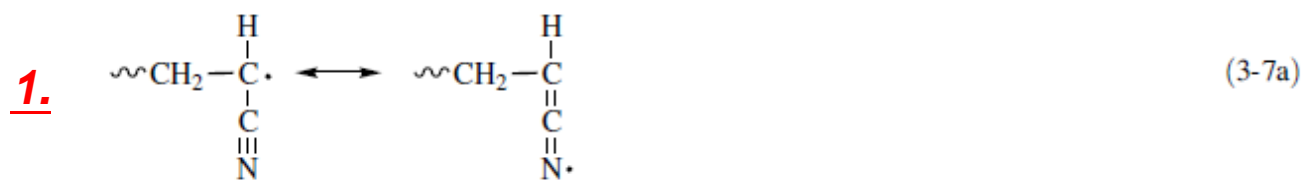


propagating cation stabilized by e^- donating nature of $:O:$

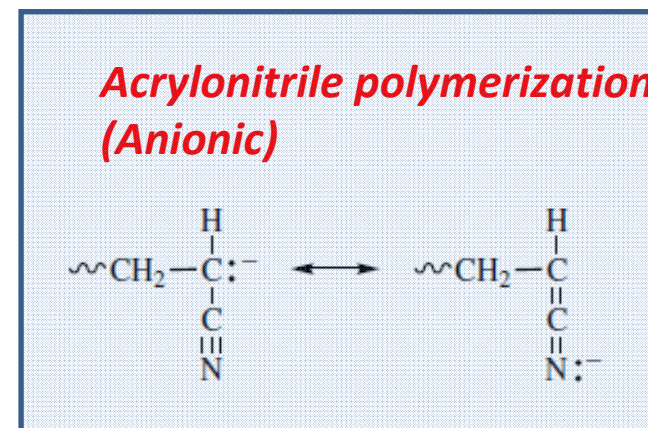
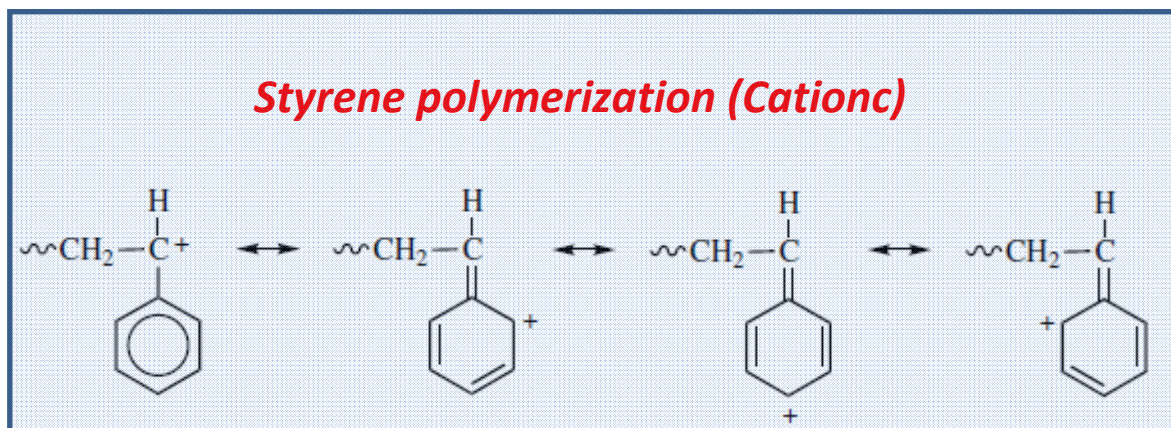
original monomer

carbenium ion or carbocation presents vacant e^- orbital

Resonance stabilization of the propagating radical occurs with almost all substituents



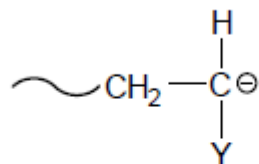
Compare with:



Monomer Requirements (anionic polymerization)

1. In general, for vinyl monomers, need monomer that supports a stable carbanion.

1.



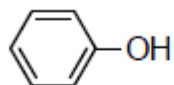
Y should be electron withdrawing
⇒ stabilizes \ominus charge by sharing with C^{\ominus}

Y can fit a range of electron-withdrawing groups
How withdrawing impacts monomer reactivity

2. Monomer should have no protic or acidic hydrogens

No: -COOH carboxyl groups
R-OH alcohols

-NH₂ amide groups
(polyacrylimide in electrophoresis)
for biological experiments

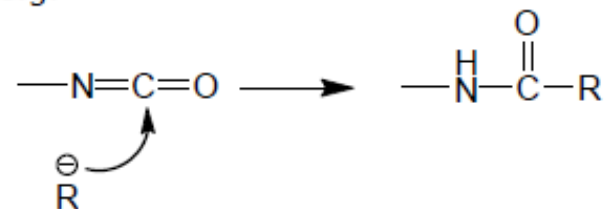


-C≡C-H

and more... basically if it gives a H away easily, it'll be a problem

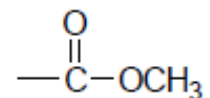
3. contains no electrophilic groups (carbanion is a very strong nucleophile)

Avoid e.g.



There are some exceptions: certain groups are electrophilic but less reactive to carbanion of interest:

e.g.



4. Carbanion generated must be able to attack its own monomer .

Choosing Initiator (for anionic polymerization)

Must be strong enough to initiate monomer, i.e. stronger nucleophile (more aggressive)



- must be reactive enough to attack monomer
i.e. stronger nucleophile
(more aggressive)

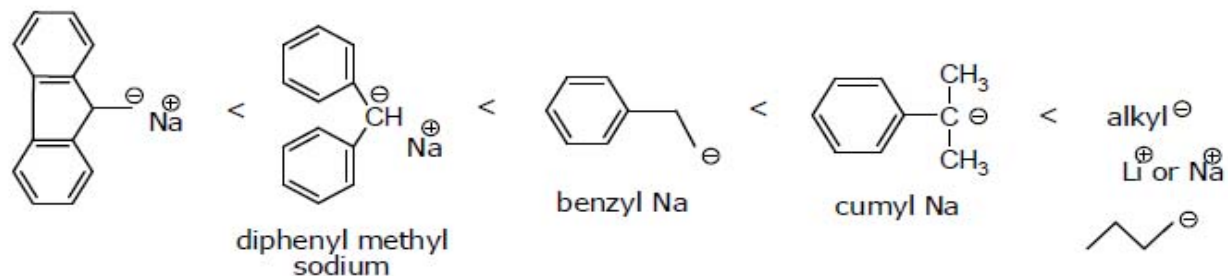
So this depends on the monomer to be initiated:

- If monomer substituent Y is strongly e⁻ withdrawing;
→ then activated monomer is relatively stable
→ relatively weaker nucleophiles can initiate it
ex: epoxy: ethoxyanion
initiate ring polymerization with variety of initiators
- If substituent Y is weakly e⁻ withdrawing:
→ need stronger nucleophile to initiate it:
⇒ need to know reactivity trends in monomers

Types of initiators and trends of reactivities

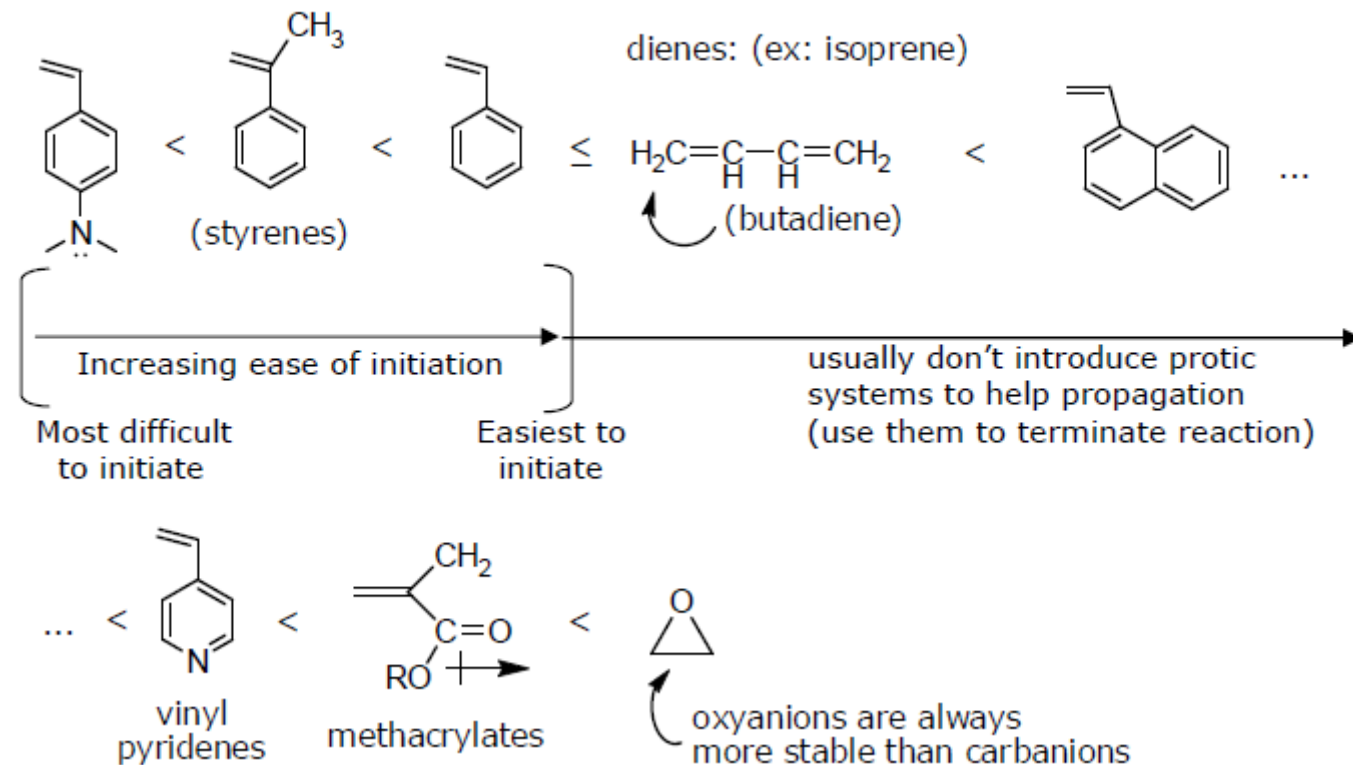
"mild" ————— "strong"

reactivity



Reactivity trends in monomers (in **anionic** polymerization)

Reactivity trends:



Solvent Characteristics

Most common solvents

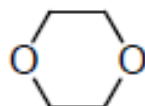
pentane

hexane

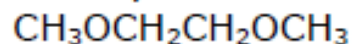
cyclohexane

benzene

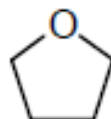
dioxane



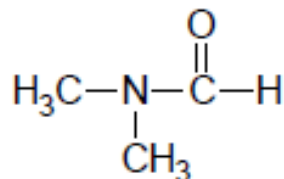
1,2 dimethoxyethane




tetrahydrofuran



dimethyl formamide



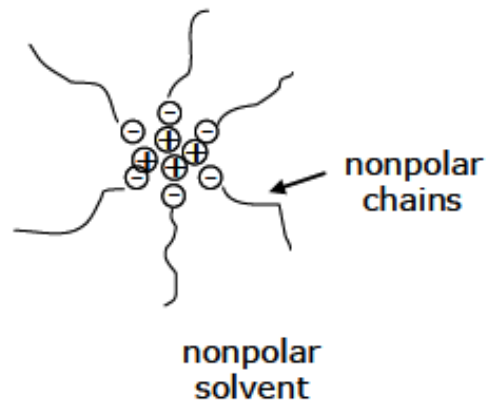
increasing
polarity



- solvent must solvate monomer + polymer
⇒ function of polarity

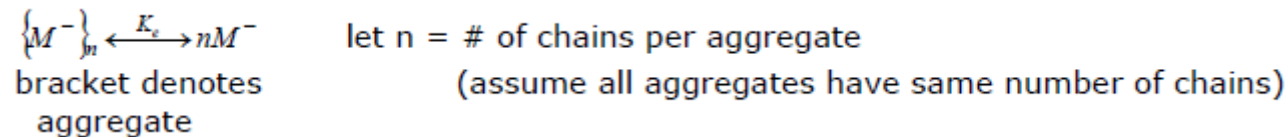
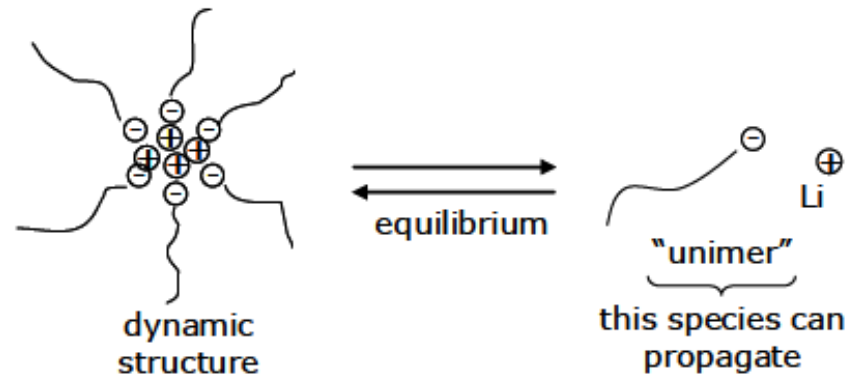
Important *Solvent Effects* in Anionic Polymerization

1. Association Effects : *Low dielectric (nonpolar) solvent* are poor environments for ions; Possible to form micelle-like aggregates.



aggregation probabilities \uparrow
as polarity of solvent \downarrow
and as counterion size \downarrow

dependency on concentration:
as conc \uparrow , agg \uparrow



$$K_e = \frac{[M^-]^n}{[\{M^-\}_n]} \quad \text{equilibrium constant}$$

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

$$R_p = -\frac{d[M]}{dt} = k_p K_e^{1/n} [M] [\{M^-\}_n]^{1/n} \quad \text{see } 1/n \text{ dependency in rate of propagation with respect to } [M^-]$$

$$[\{M^-\}_n] \propto [M^-] = [I]$$

$$\text{can assume } [I] \sim [\{M^-\}_n]$$

$$\Rightarrow R_p \cong k_p K_e^{1/n} [M][I]^{1/n}$$

If aggregation number is 2, ($n=2$)

$$R_p = k_p K_e^{1/2} [M] [\{M^-\}_2]^{1/2} \\ \cong k_p K_e^{1/2} [M][I]^{1/2} \quad \text{aggregate form}$$

2. Degrees of *dissociation* of counterion and chain (happens much more frequently)

different degrees of dissociation:

Free ions:



ions are fully dissociated from
negative charge

⇒ assume full availability of charge to react with monomer

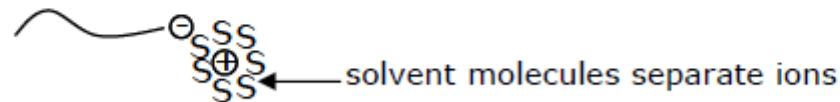
Versus ... 2 types of ion pairs

a) unsolvated ion pairs (tight pairs)



"contact ion pairs"

b) solvent separated ion pairs (loose ion-ion connections)


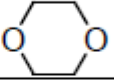

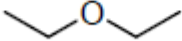


thin layer of solvent that separates counterion from + charge

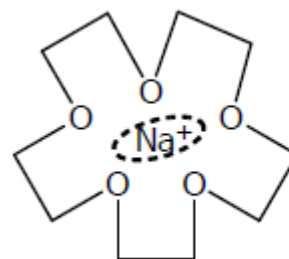
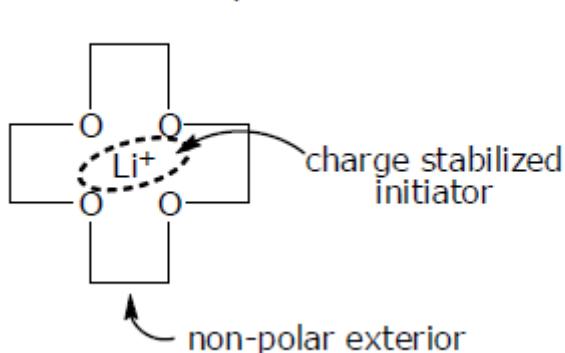
reaction rates of species are going to be different

Effects of *Solvent Polarity* on Polymerization

Solvent effects in anionic polymerization

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 best example for this is: crown ethers



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

- Crown ethers (O'dian 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^+)

Effect of *Counterion* on Anionic Polymerization of Styrene

The decrease in K has a very significant effect on the overall polymerization, since there is a very significant change in the concentration of the highly reactive free ions.

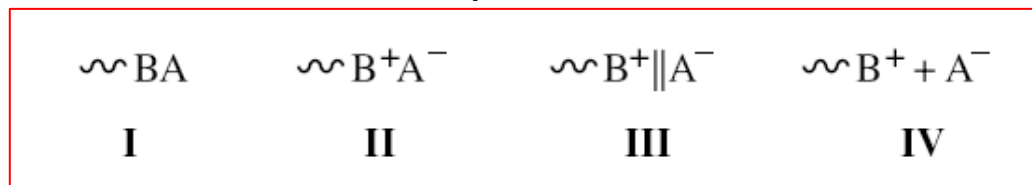
Polymerization in Tetrahydrofuran

Counterion	k_p^\ddagger	$K \times 10^7$	k_p^-	k_p^\ddagger for Dioxane
Li ⁺	160	2.2	} 6.5×10^4	0.94
Na ⁺	80	1.5		3.4
K ⁺	60–80	0.8		19.8
Rb ⁺	50–80	0.1		21.5
Cs ⁺	22	0.02		24.5

^aUnits of K are mol L⁻¹; rate constants are L mol⁻¹ s⁻¹.
^bData from Bhattacharyya et al. [1965a,b].

No detectable dissociation for pair to free ions in dioxane!

contact ion pair

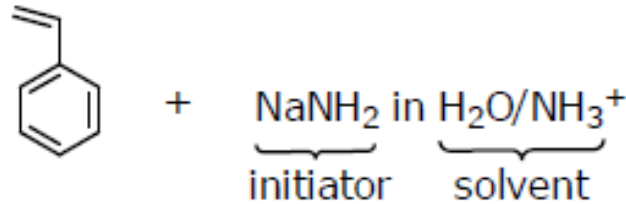


solvent-separated or loose ion pair (III).

K_p^\ddagger = rate constant for all *ion pairs*
 K = dissociation constant
 K_p^- = rate constant for *free ion*

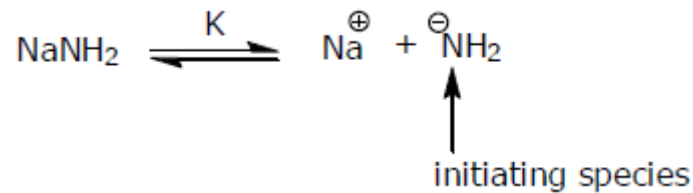
Kinetics of Anionic Polymerization

In protic media:



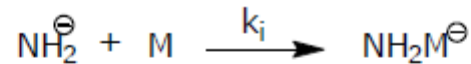
Termination in ionic polymerization
 \Rightarrow only by transfer **or** side rxn
 \Rightarrow no coupling/disproportionation

- ✓ IF transfer leads to anion that is reactive enough to initiate monomer \Rightarrow *transfer*
- ✓ IF transfer leads to anion that won't initiate monomer \Rightarrow *termination*

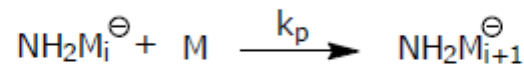


$$[\text{NH}_2^{\ominus}] = \frac{K[\text{NaNH}_2]}{[\text{Na}^{\oplus}]}$$

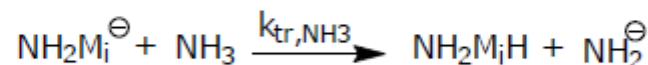
1. Initiation:



2. Propagation:



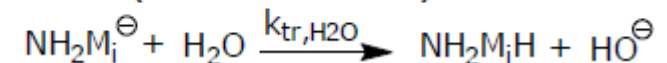
3. Transfer to solvent:



↑
solvent

↑
initiates more monomers
kinetic chain lives BUT
chain length shortens

4. Transfer to water: (termination event)



↑
relatively stable,
will not initiate
styrene

(only thing HO[⊖] will initiate is epoxides)

Living Anionic Polymerizations

1. *No transfer*
2. *No termination events due to other side reactions that might occur due to impurities*

⇒ need solvent with no protic groups (aprotic)

⇒ eliminate H₂O to get dry solvent

O₂

CO₂

Other reactive species like NH₂, anything that can snatch H off

“lifetime” of propagating anion can be very long (~ hours)

3. *Need system with very rapid $R_i \gg R_p$ fast initiation*

start polymerization at same time to get highly controlled MW + polydispersity

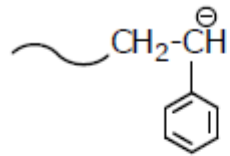
All chains start at the same time and finish the monomer off

~ monodisperse MW distribution

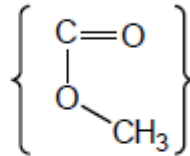
Synthesis of a Diblock Copolymer

want to make *polystyrene-b-poly(methyl methacrylate) PS-b-PMMA*

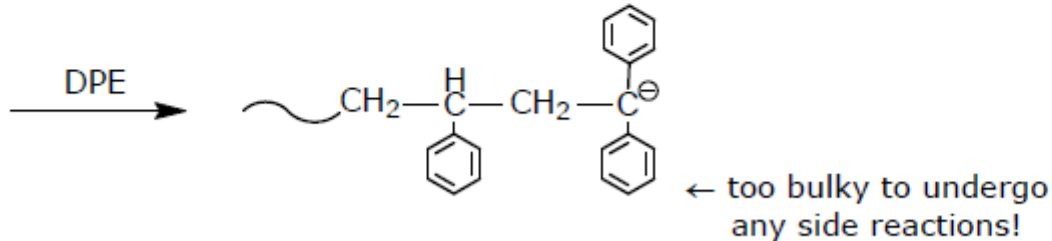
(A) Must start with styrene



But this can react with the carboxylic Ester groups of MMA:

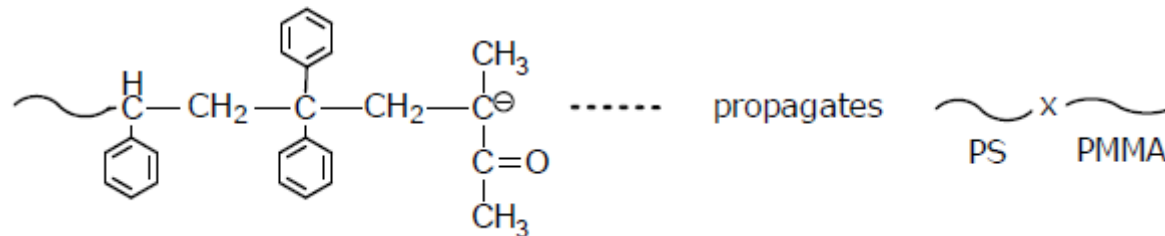


(B) Add DPE



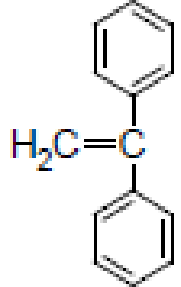

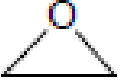
Because only one group of DPE, there is no effect on the properties of copolymer

(C) Add MMA



Short list of monomers, in increasing electrophilicity

most aggressive:

<ul style="list-style-type: none"> • dimethyl amino styrene, p-methoxy styrene, p-methyl styrene, α-methyl styrene 		} almost the same				
• styrene						
• butadiene						
• isoprene						
• vinyl naphthalene					Ease of initiation	
• p-chlorostyrene						
• vinyl pyridine					A monomer in the list can initiate anything equal or below it	
* • diphenyl ethylene (DPE)						
• alkyl methacrylates (MMA)						
• propiolactones						
• ethylene oxide					Ex: ethylene oxide cannot initiate vinyl pyridine but can initiate vinylidene cyanides	
		DPE cannot self-propagate (too bulky)				
propylene sulfide						
• vinylidene cyanide			More reactive monomers → faster polymerization			
• α-cyanoacrylates						

Another useful initiator

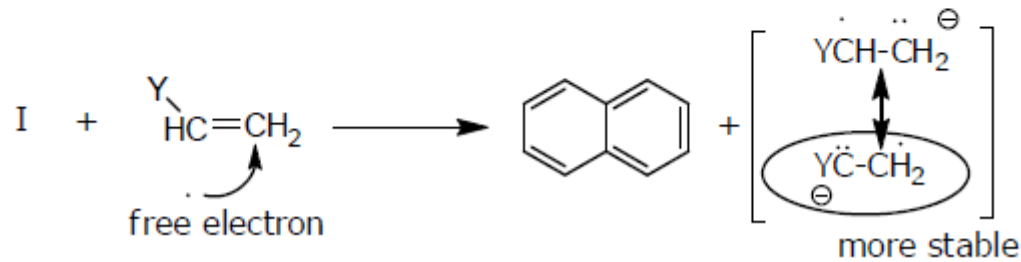
Aromatic radical anions: **Electron transfer**



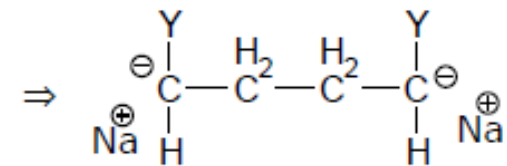
Na "gives" electron to Naphthalene reduction

Na naphthalene
I

$\cdot\text{CH}_2$ can pair with itself
dimerization of (lower)
radical species



Transfers an electron to a monomer.



dianionic species propagate in both directions



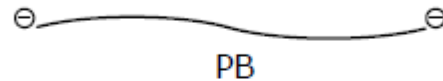
Synthesis of a Triblock Copolymer

Styrene-Butadiene-Styrene triblock
PS-b-PB-b-PS
SBS

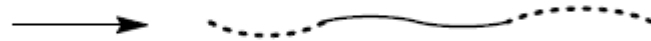
Can make this polymer at least 3 different ways:

- consideration: styrene and butadiene are very close in reactivity
So, butadiene can initiate styrene

1. Difunctional initiator: ex: Na naphthalene
+ butadiene



Consume B completely and then add styrene (S)

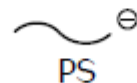


Symmetric triblock b/c same prop. rate and time

2. Add S+B+S in sequence (w/monomer fully consumed by each step)

3. First initiate PS

a)



- b) add butadiene + styrene together in big aliquot
(in anionic polym, do not get alternating copolymers, get blocky behavior)

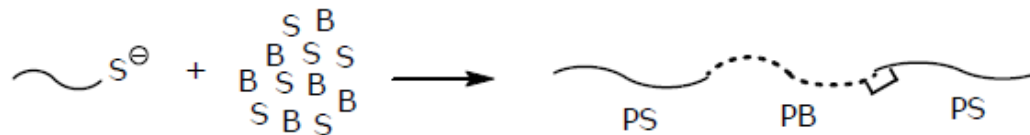
- reactivity rates (anionic)

$$k_{sb} \gg k_{bs}$$

$$r_b = 14$$

$$r_s = 0.03$$

growing B is preferred

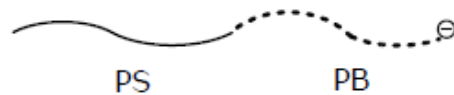


- create block with PB (B preferred over S);
 - then transition (both B and S);
 - then completely PS (all transition left)

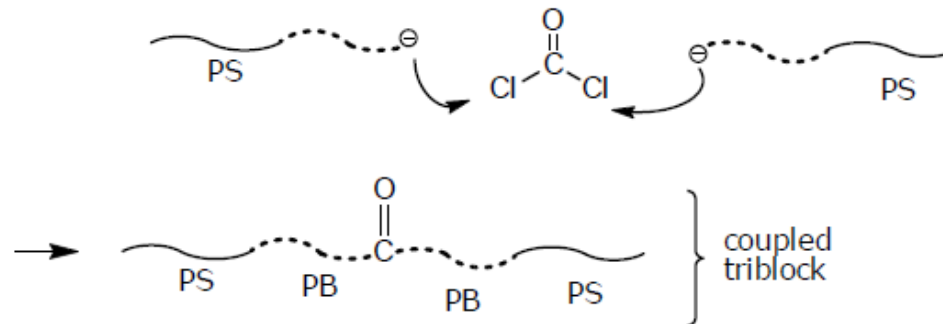
- this is done in industry
 - relatively simple
 - transitional regime enhances surface properties
 - more diffuse interface
 - Better properties

Styrene-Butadiene Rubber (SBR)

4. Use a coupling agent (used for systems with no other options)
 - i) grow diblock of PS-PB



- ii) then add reactive coupling agents e.g. phosgene (extremely reactive)



everytime you introduce a monomer or coupling agent, you risk the chance of impurities (can't get II-block copolymer or high MW copolymer)

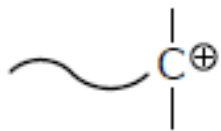
other coupling agents: (Quantitative reactions)

Comparison of Cationic and Anionic Polymerizations

Some differences between cationic and anionic polymerization

1. Rates are faster for cationic

(1. or more orders of magnitude faster than anionic or free radical)



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*

2. Living cationic only possible for a specific subset of monomers

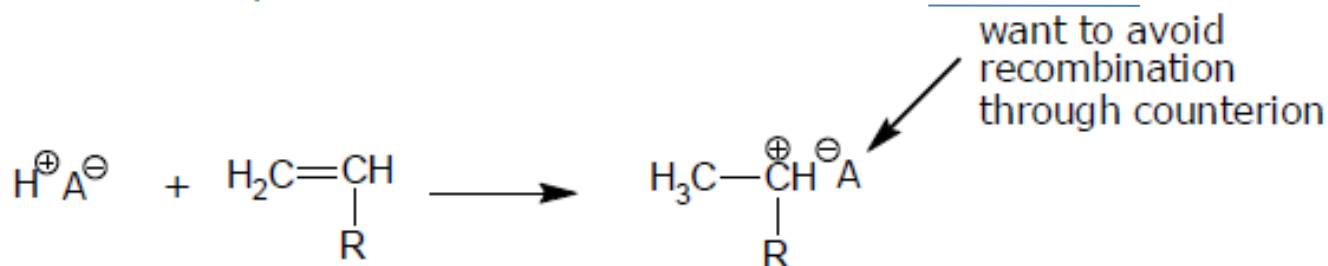
3. Most industrial cationic processes are not living – recent developments are improving this

Kinetic Steps for Cationic Polymerization

Initiation: Use Acids

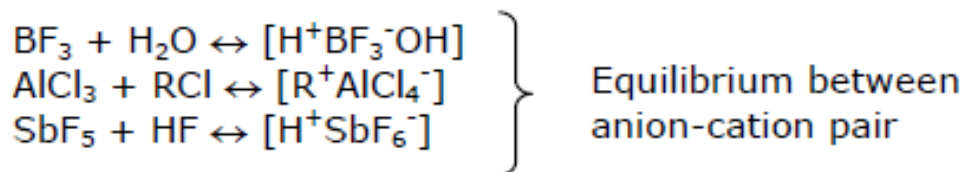
comes off

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



Most important in industry!!

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

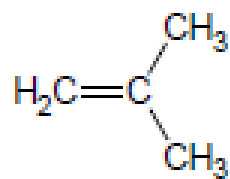
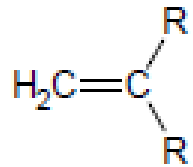


Monomer Requirements (cationic polymerization)

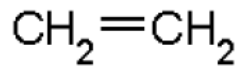
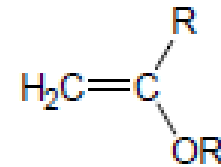
Typical Cationic Monomers:

Butyl rubber—also known as polyisobutylene and PIB

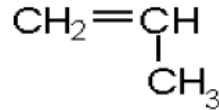
1. alkenes, isobutenes



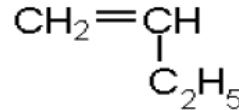
2. Vinyl ethers



−ΔH(kJ/mol) 640

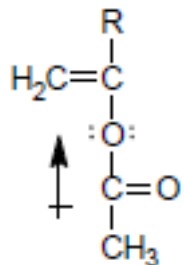


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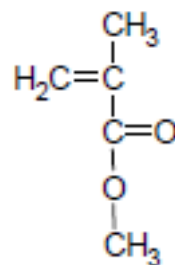


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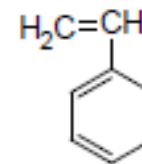
3. Vinyl acetates



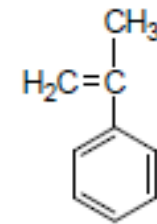
contrast with methyl methacrylate



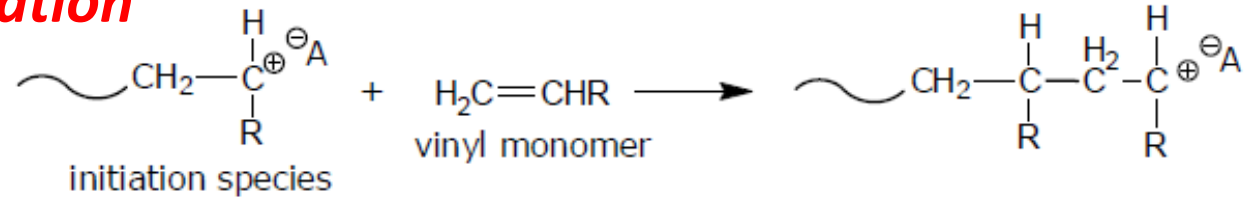
4. Styrene



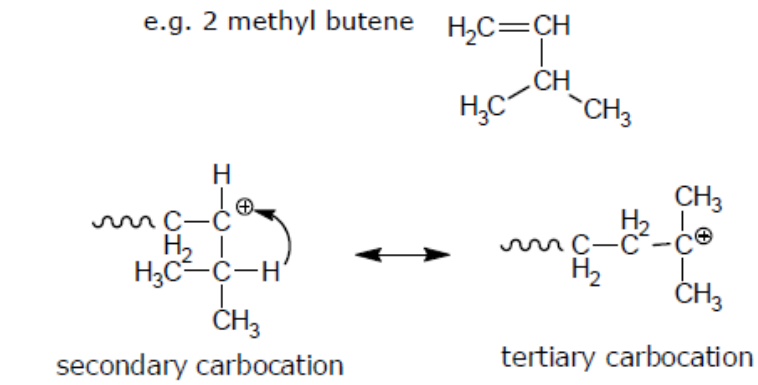
α-methyl*
styrene



Propagation

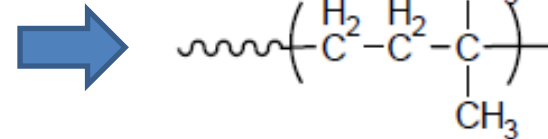


Rearrangements can occur, especially if a more stable carbocation can be formed (e.g. tertiary carbocation) (most common for 1-alkenes, α olefins)

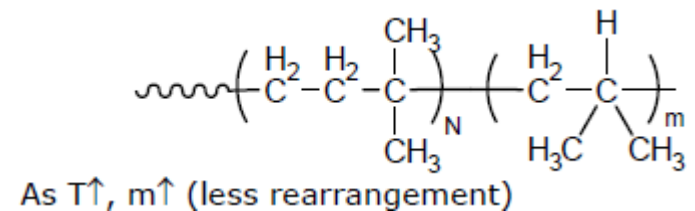


This occurs via intramolecular hydride (H^-) shifts Usually slow:

If $R_p \leq$ rearrangement rate, will get rearranged product



If $R_p >$ rearrangement rate, will get random copolymer

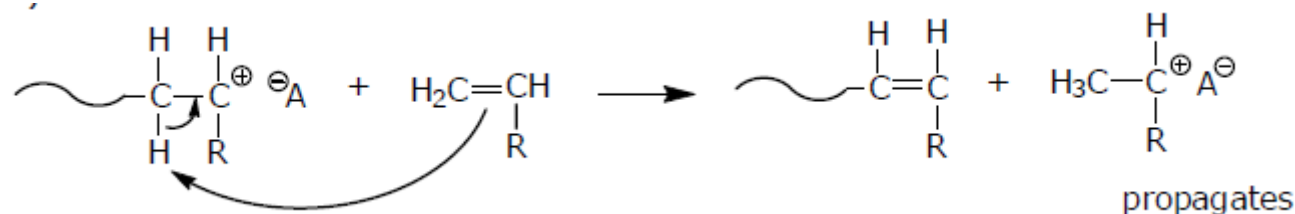


β -Proton Transfer (Kinetic Chain Maintained):

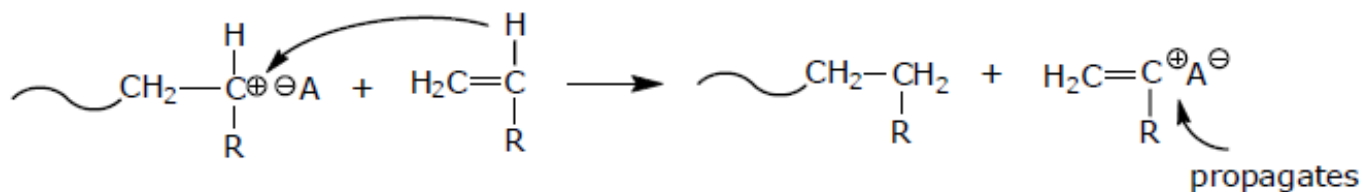
➡ It occurs readily because much of the positive charge of the cationic propagating center resides not on carbon, but on the β -hydrogens because of *hyperconjugation*.

A) Proton transfer to monomer:

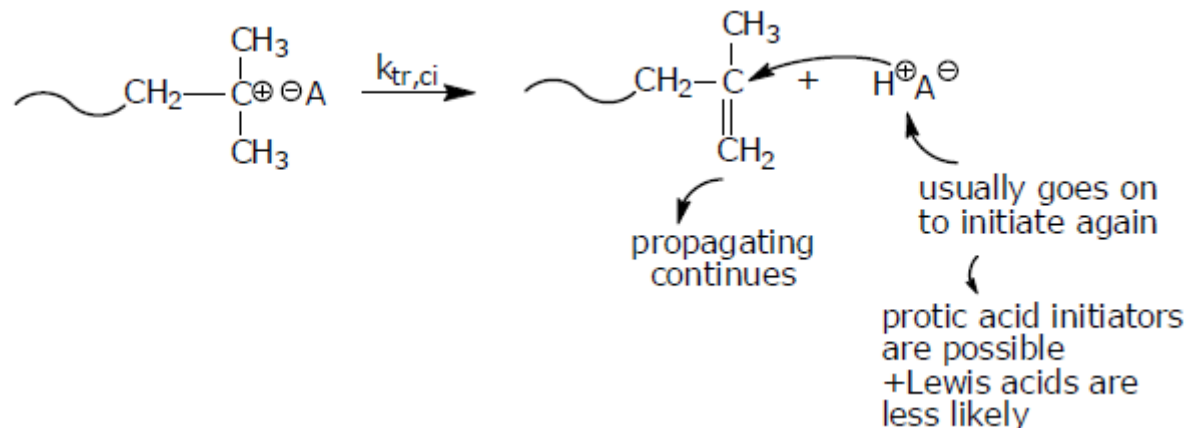
involves transfer of a β -proton to monomer with the formation of *terminal unsaturation in the polymer*



B) Hydride ion transfer from monomer



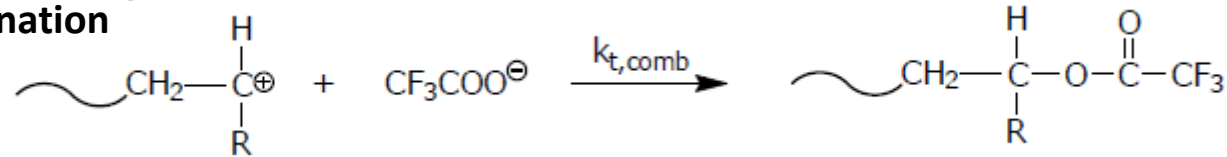
C) Proton transfer to counterion ("spontaneous termination")



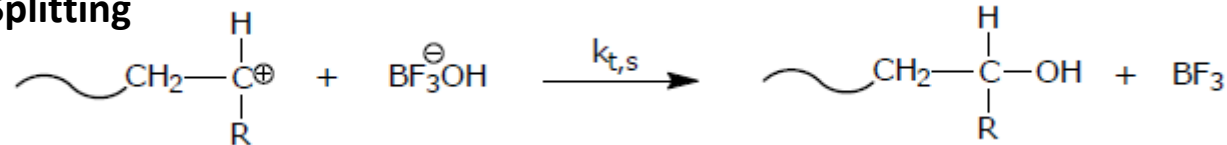
Termination and Transfer (Several Possibilities)

A) Termination with counterion: kills propagating cation, kinetic chain (k_t)

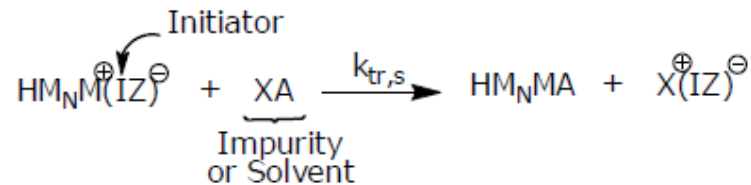
(i) Combination



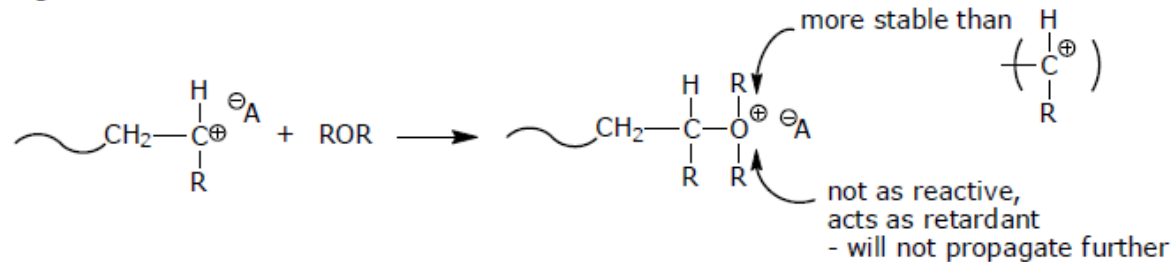
(ii) Anion Splitting



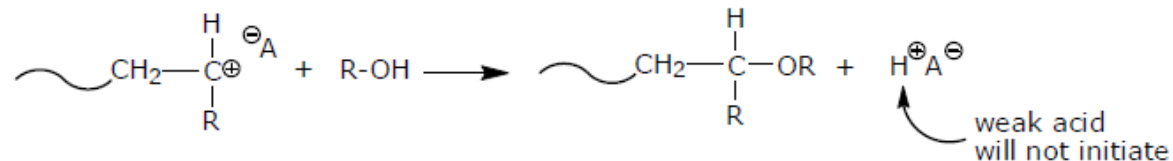
B) Transfer or termination to impurity or solvent To H_2O , ROR , NR_3 , $-\overset{\text{O}}{\parallel}{\text{C}}-\text{OR}$, etc.



e.g.



or



Thanks for you attention