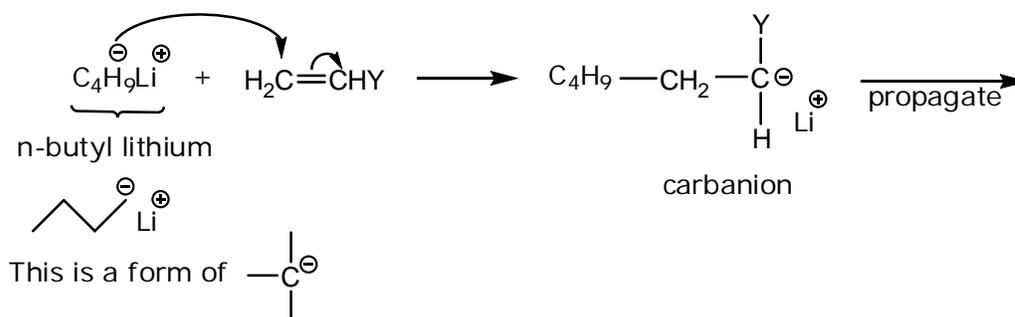


Ionic Polymerization

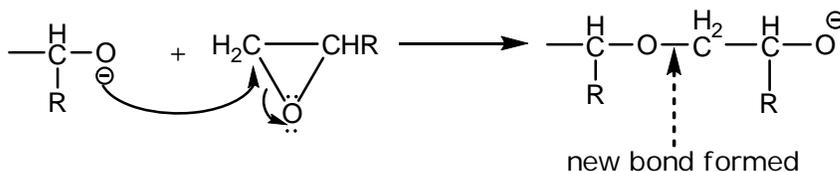
1. Anionic
2. Cationic

Anionic Polymerization

- very aggressively charged negative group



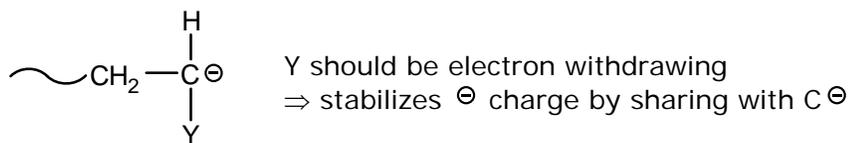
Also have negative charge on other atoms:
 e.g. ring opening:



Monomer Requirements

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

1.



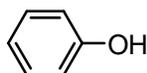
Y can fit a range of electron-withdrawing groups
 How withdrawing impacts monomer reactivity

2. (second requirement for monomer)

monomer should have no protic or acidic hydrogens

No: -COOH carboxyl groups
R-OH alcohols

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



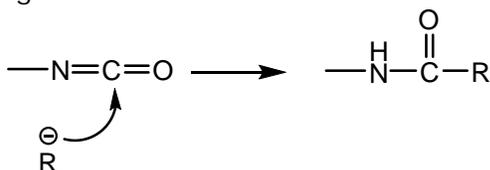
-C≡C-H

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

3. contains no electrophilic groups:

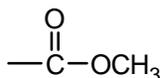
Note: carbanion is a very strong nucleophile

Avoid e.g.



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

e.g.



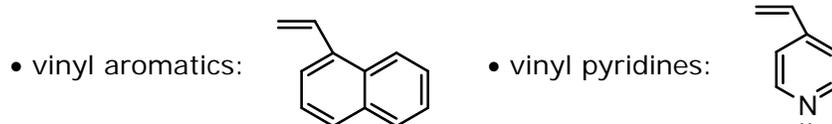
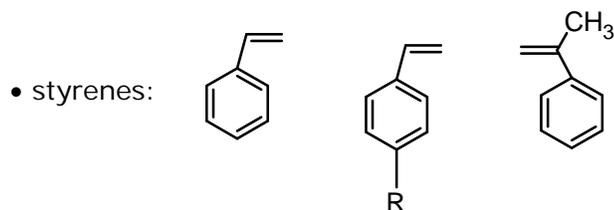
That's why we have ranking of reactive groups

Finally

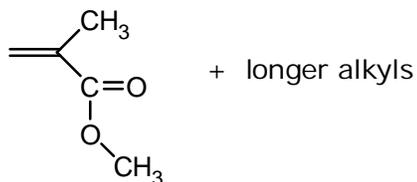
4. Carbanion generated must be able to attack its own monomer

Now, good monomers for anionic polymerizations:

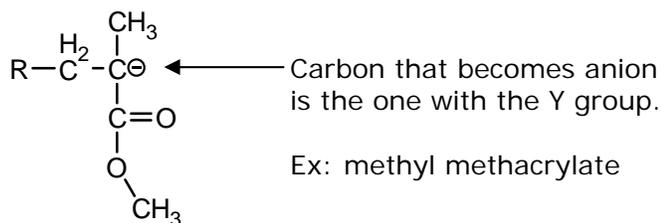
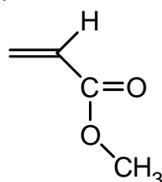
Vinyl:



Alkyl methacrylates:



NOT acrylates:



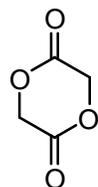
Ring Compounds:

• epoxides:



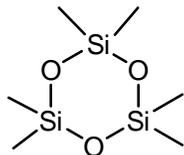
BUT not free radical versions of epoxy

• lactones:



ex: get caprolactone

• siloxanes:



ex: silly putty
silicone oil

Anionic Polymerization Initiators

What about initiators?

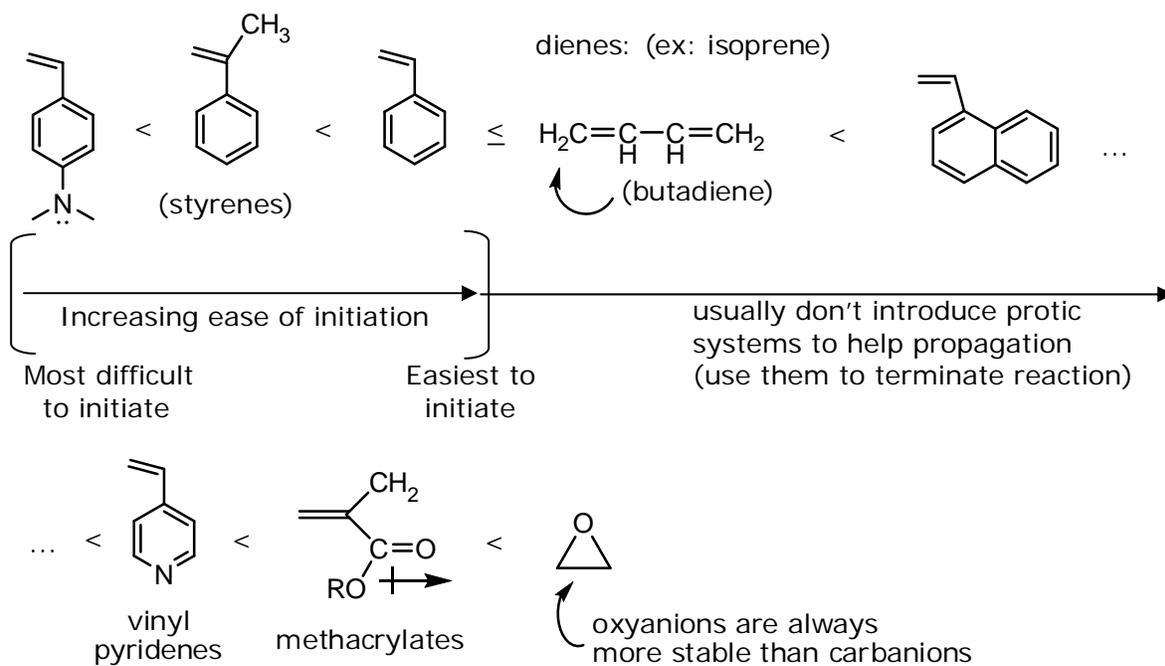
There are rules that govern good initiators as well:

- 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

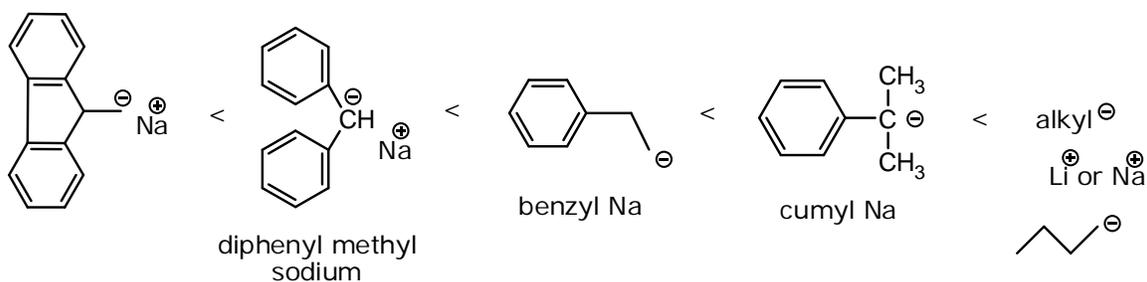
Reactivity trends:



Types of initiators and trends of reactivities

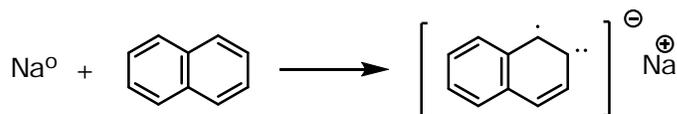
"mild" ————— "strong"

reactivity



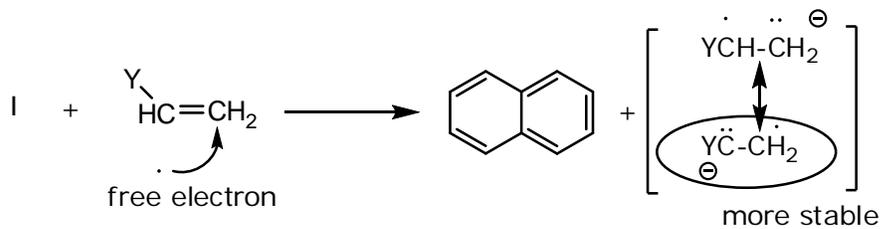
another useful initiator:

Aromatic radical anions:

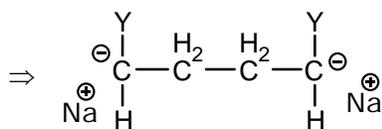


Na "gives" electron to Naphthalene reduction

Na naphthalene I



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



dianionic species propagate
in both directions

