Polymers: Synthesis by Alkene Chemistry

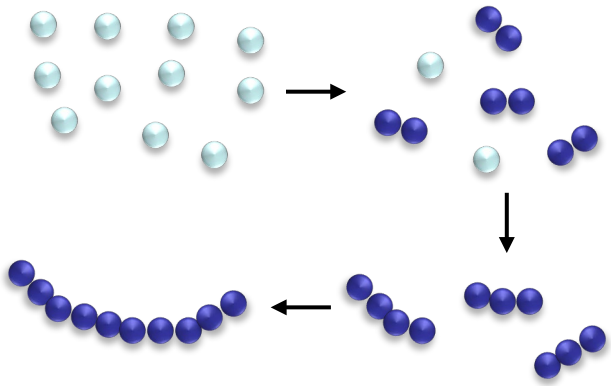
Contents

- Ionic polymerization
  - Propagation by Anionic Species
  - Propagation by Cationic Species
- Propagation by Radical Species
  - Free Radical
  - Reversible Activation-Deactivation Polymerization
    - *See special topics for additional details*

Classification by Mechanism

Step

$$A + B \longrightarrow AB$$
$$AB + A \longrightarrow ABA$$
$$AB + AB \longrightarrow ABAB$$
$$ABA + BA \longrightarrow ABABA\ (etc.)$$
$$\downarrow\downarrow$$
$$(AB)_n$$



Chain

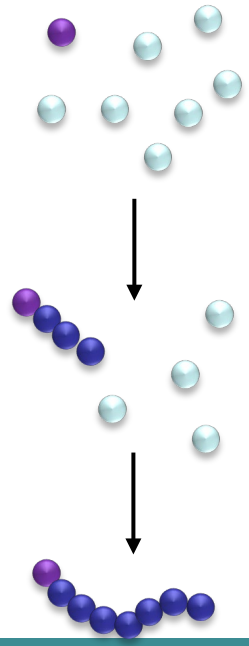
1) Initiation $\quad I + M \longrightarrow IM^*$

2) Propagation $\quad IM^* + nM \longrightarrow I(M)_nM^*$

} Living

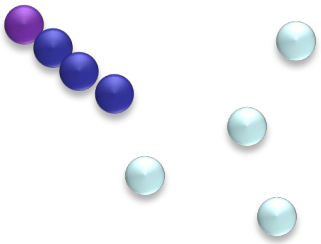
3) Transfer $\quad I(M)_nM^* + X \longrightarrow P + X^*$

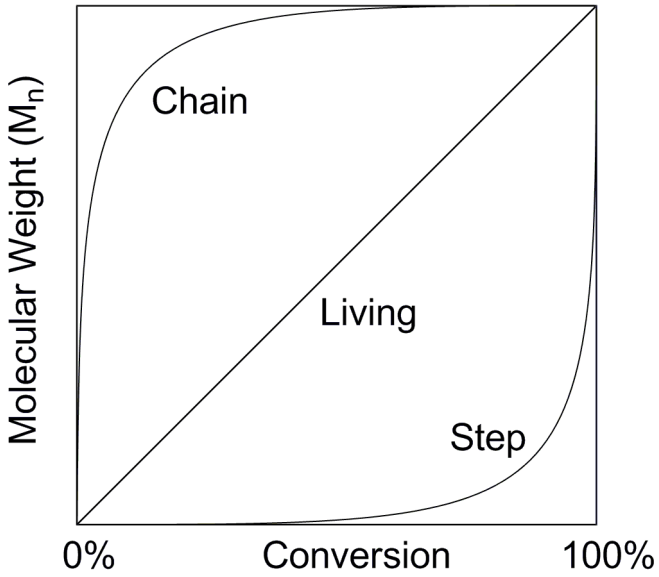
4) Termination $\quad I(M)_nM^* + X \longrightarrow P + Y$



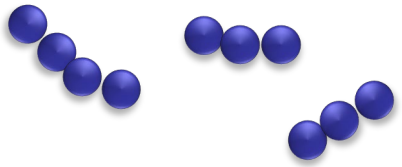
Molecular Weight vs. Conversion

Chain polymerization:
High polymer + monomer in flask between 0-100% conv.



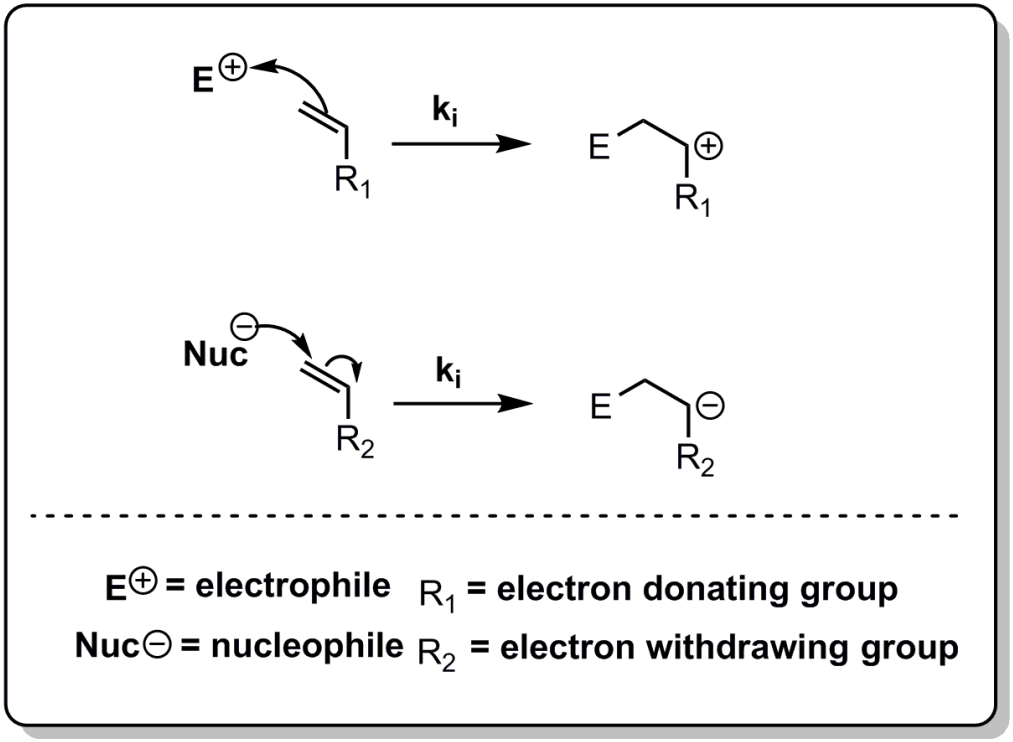


Step polymerization:
Oligomers in flask between 0-100% conv.



Conversion is the percent of polymerizable functional groups that have been converted into backbone functional groups.

Chemistry of Ionic Polymerizations

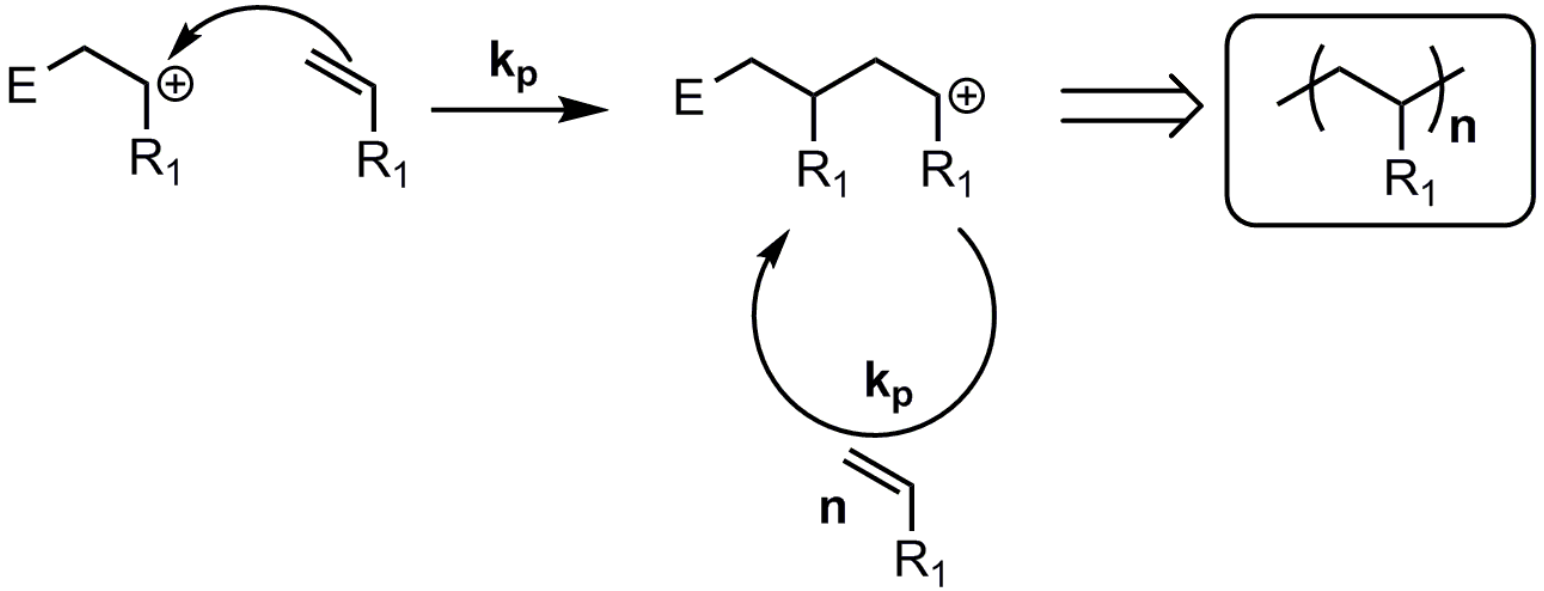


Alkenes can act as nucleophiles, with the propagating species a carbocation. The R_1 group should be capable of stabilizing the charge.

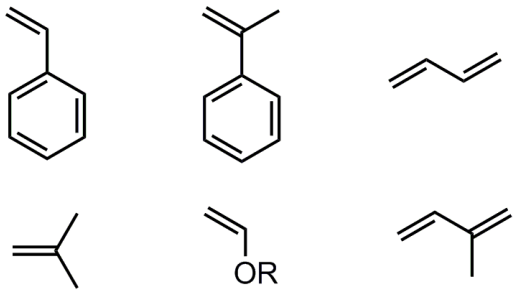
Alkenes can also act as electrophiles, with the propagating species a carbanion. The R_2 group should be capable of stabilizing the negative charge.

Looking ahead: what might be examples of E+ and Nuc- suitable for the reaction steps above?

Cationic Polymerization



monomers suitable for cationic polymerization



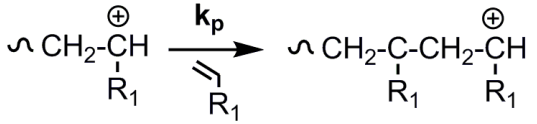
examples of initiating systems for cationic polymerization

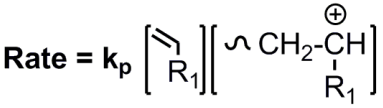
RCl / Lewis Acid

Ex) $SnCl_4$, $TiCl_4$, $AlCl_3$, etc….

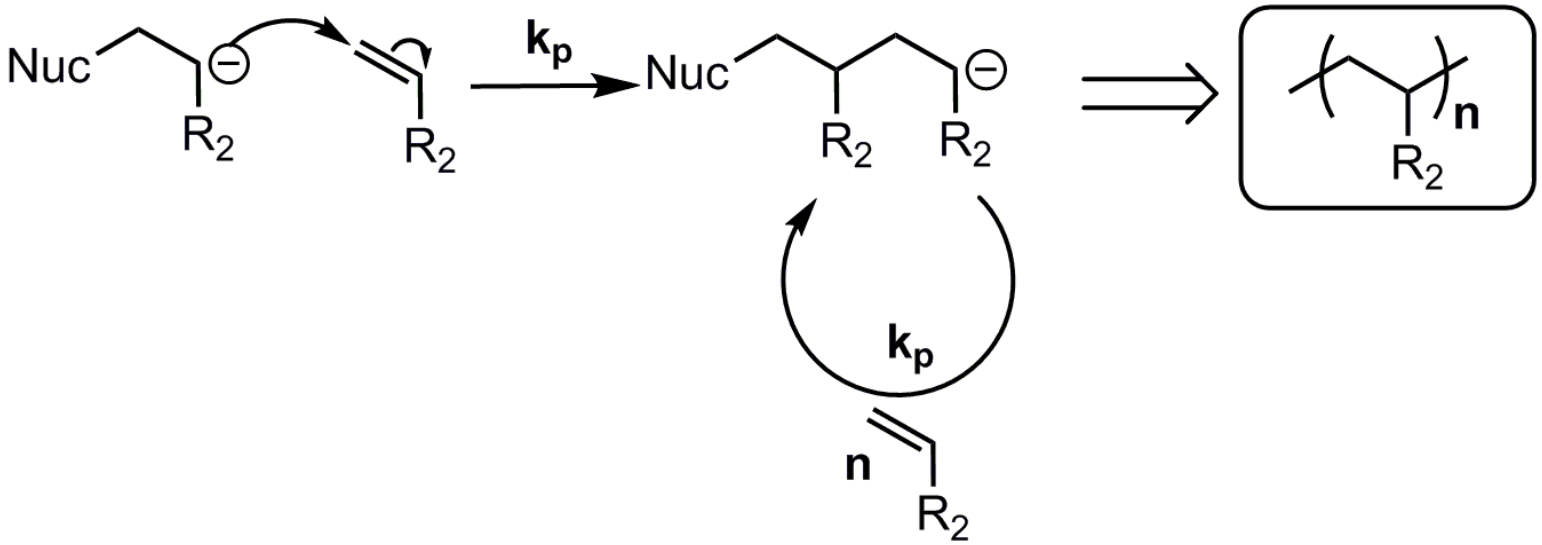
Protic acids

Ex) CF_3SO_3H, H_2SO_4, ClO_4

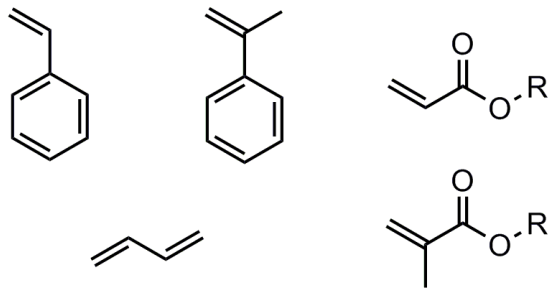




Anionic Polymerization



monomers suitable for anionic polymerization

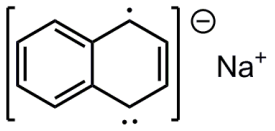


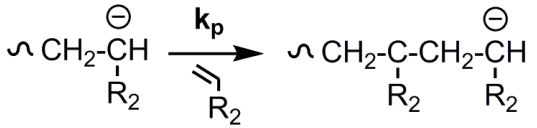
examples of initiating systems for anionic polymerization

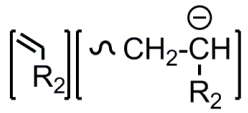
RLi

Ex) *t*BuLi, *n*BuLi

$NaNH_2$



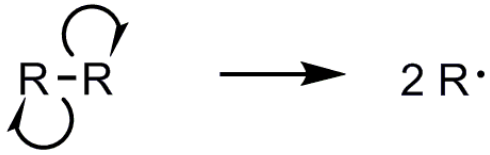


Rate = k_p 

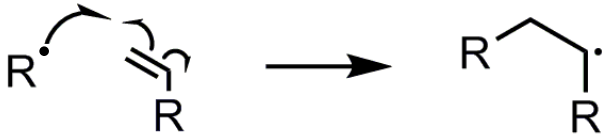
Basics of Radical Chemistry

- Apply same fundamental steps as radical halogenation to polymerization
- All of these steps are happening at the same time
- Additional step
  - Transfer

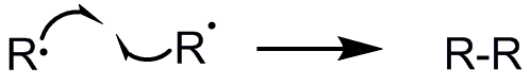
1) Initiation - "create radicals"



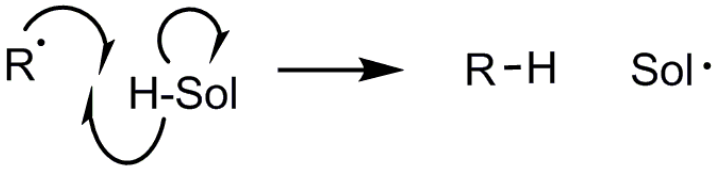
2) Propagation - "move radical"



3) Termination - "kill radicals"



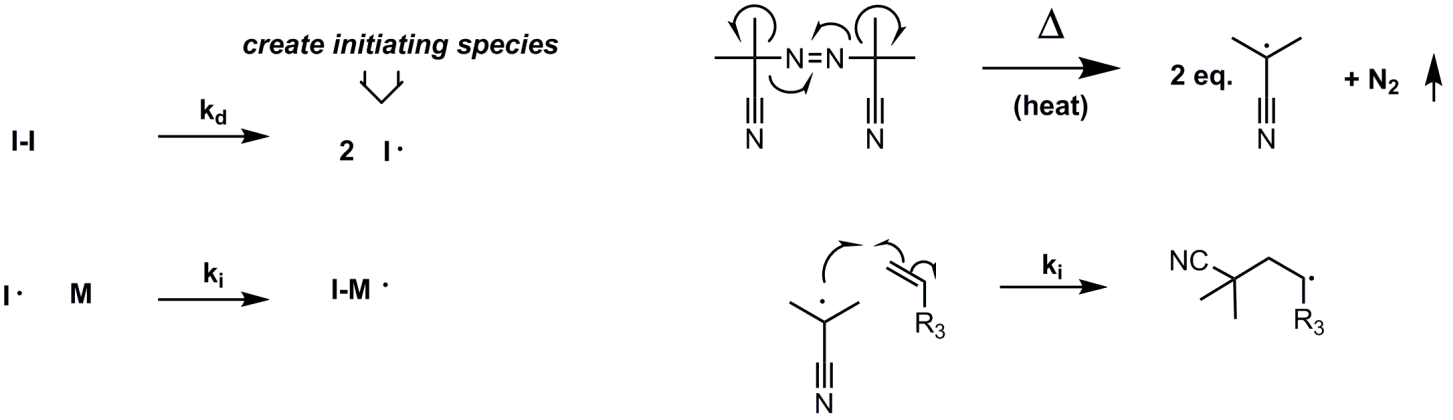
4) Transfer - "move radical to something new"



Free Radical Polymerization

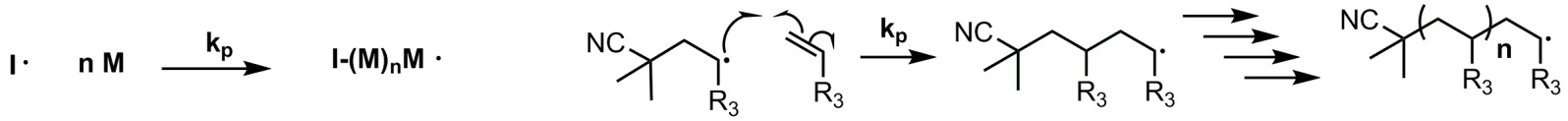
- Just like any radical chain reaction, the first step is initiation. “make radicals”
- Note the difference in the k_d, k_i, and k_p
  - Each step has a different rate and lead to complex mechanism questions
- Common initiators are azo compounds and peroxides

Initiation - "make radicals"



Propagation - "move radical"

This step is repeated many times over



Free Radical Polymerization

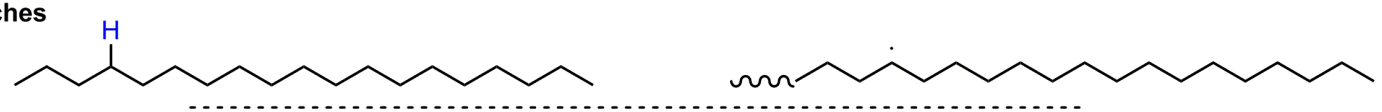
Transfer - "move radical to something new"

Can transfer to monomer, solvent or polymer.
Each route affects the end product differently

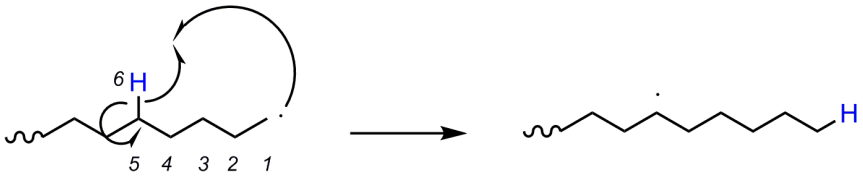
Monomer:
(and solvent)

Limits molecular weight

Polymer (intermolecular):
Large branches

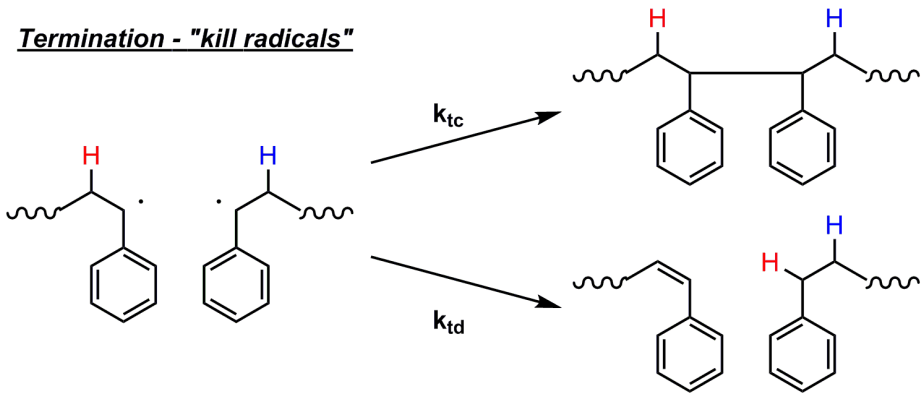


Polymer (intramolecular):
Small branches
"backbiting"



Leads to branching
and affects molecular weight

Termination - "kill radicals"

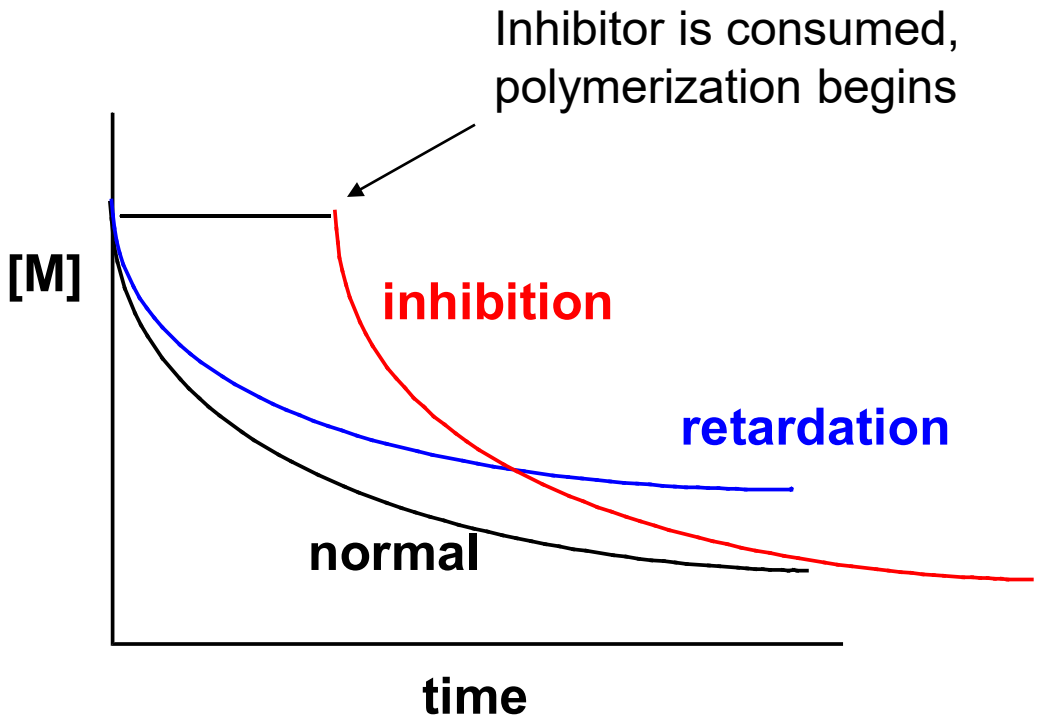


k_{tc} : *Combination - molecular weight is twice as large*

k_{td} : Disproportionation - *leads to branching*

Inhibition and Retardation

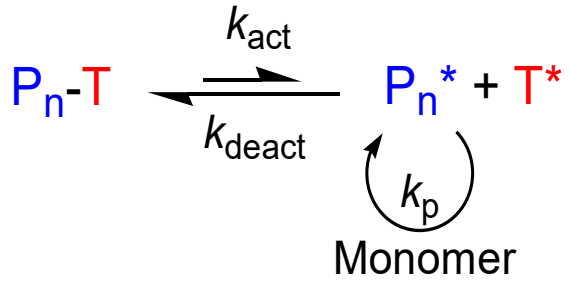
- Inhibitors stop the reaction
- Retarders slow down the reaction



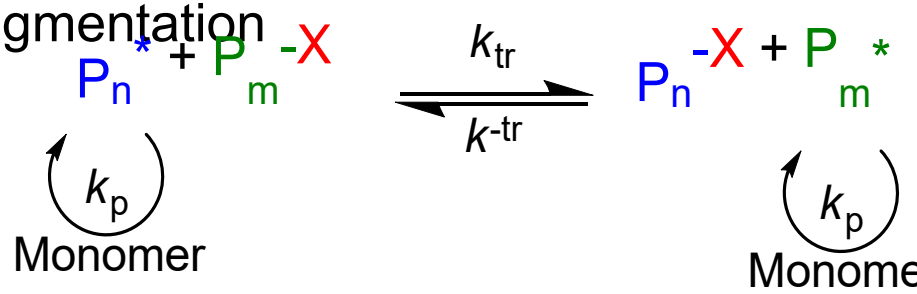
Reversible Activation-Deactivation Polymerization

Control achieved by minimizing radicals and therefore side reactions

- Reversible deactivation by coupling
  - e.g. Nitroxide-mediated polymerization



- Reversible transfer
  - Degenerative transfer / Addition-fragmentation
    - Alkyl iodides
    - Methacrylate macromonomers
    - Dithioesters / trithiocarbonates



- Reversible deactivation by atom transfer
  - e.g. Atom transfer radical polymerization