

Introduction to Macromolecular Chemistry

aka polymer chemistry

Mondays, 8.15-9.45 am, NC 02/99

Controlled radical polymerization (CRP)

Synthesis of block copolymers (AABBAABBAABB)

... is difficult with free radical polymerization (FRP) due to the statistic nature of the chain growth step

➤➤ Living Polymerization

Characteristics:

- Initiation faster than growth reaction
- Degree of polymerization: $\bar{P}_n = \frac{[M]_0}{[InIn]_0}$
- Very narrow mass distribution (PDI ~ 1.1)
- „Infinite“ lifetime of growing chain end:
polymerization stops when all monomer is consumed.

➤ There should not be a living radical polymerization as chains can easily be terminated

Controlled radical polymerization (CRP)

How to drive a free radical polymerization towards a living polymerization?

➤ Prevent termination reactions.

Another look at the kinetics:

Chain growth $v_p \sim [M_i^\cdot]$

Termination $v_t \sim [M_i^\cdot]^2$

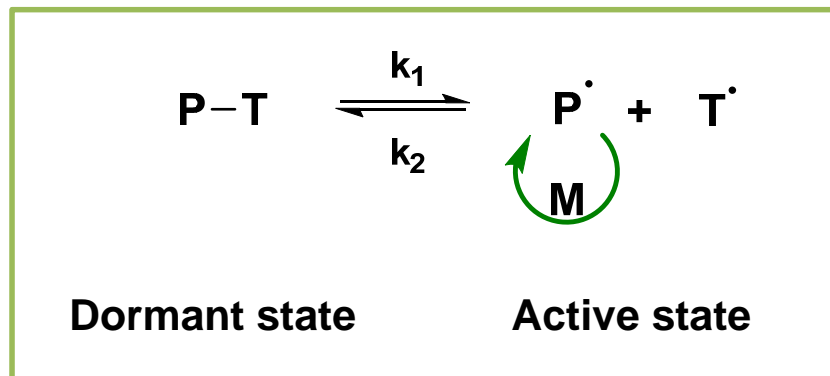
Termination rate decays faster than desired growth rate

Strategy:

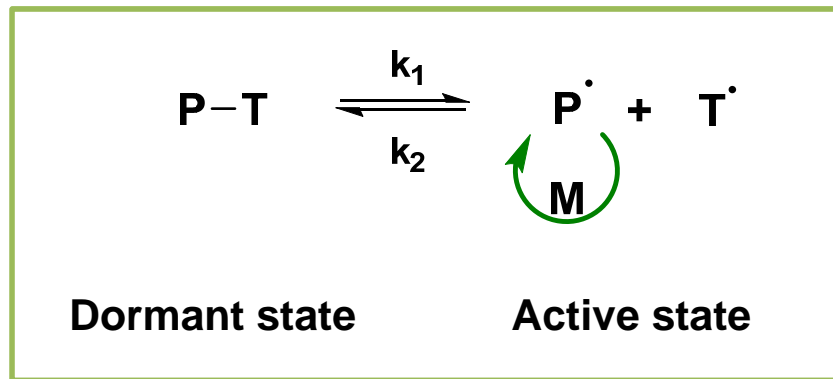
Add stable radical T*, which can add to active chain end

T* can be split off again

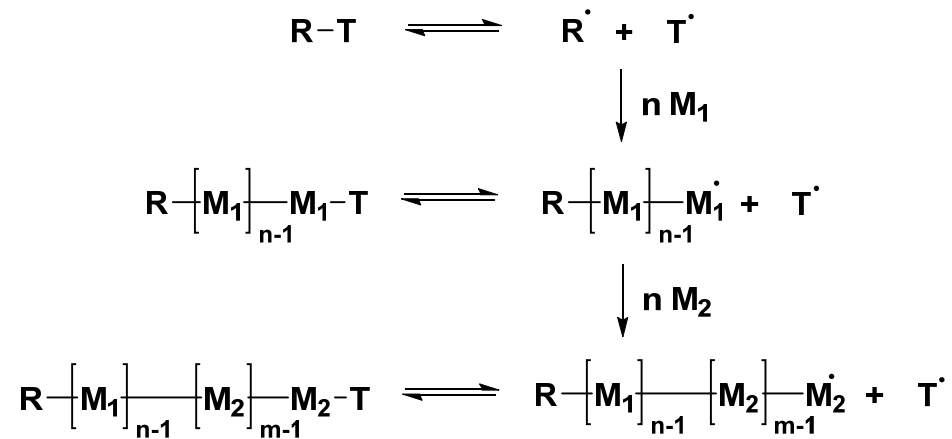
T* should not be able to react with monomers



Controlled radical polymerization (CRP)



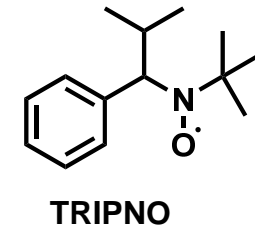
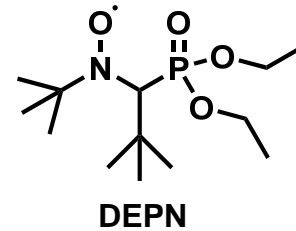
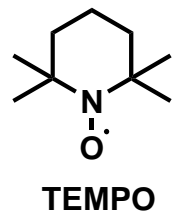
If the exchange between dormant and active state is fast, only few monomers can be added before it goes to sleep again.



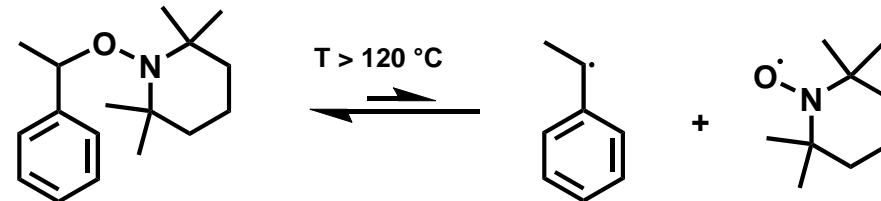
CRP: The N-oxide mediated polymerization (NMP method)

Nitroxid radicals

are the most important types of T*:



Regular initiation with DBPO or special alcoxy amines:

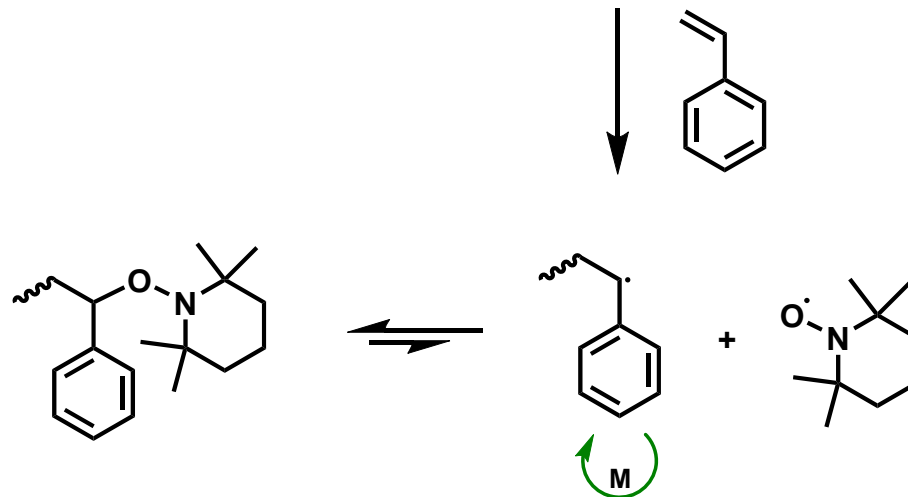


Polymerization conditions vary with the employed NMP:

TEMPO $\geq 120\text{ °C}$

TRIPNO, DEPN $\geq 80\text{ °C}$

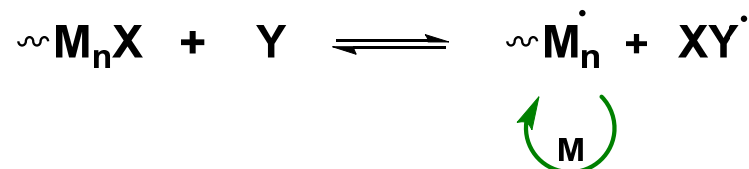
aqueous phase or emulsion



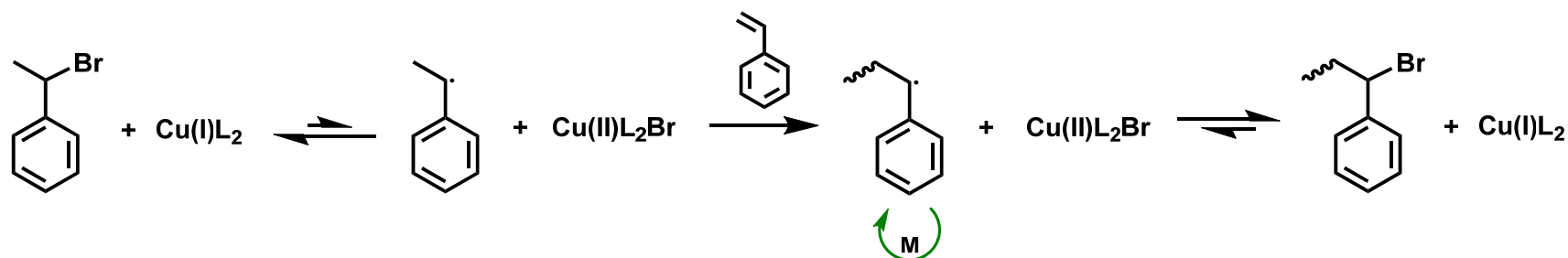
CRP: Atom transfer radical polymerization (ATRP)

Bimolecular activation:

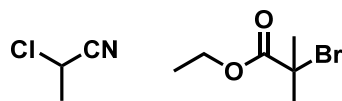
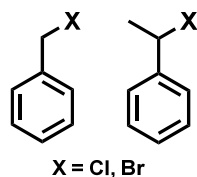
Y can be Cu(I), Ru(II), Fe(II), Ni(II), Ni(0)



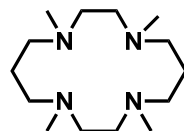
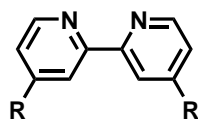
A typical example:



Typical initiators:



Typical ligands:

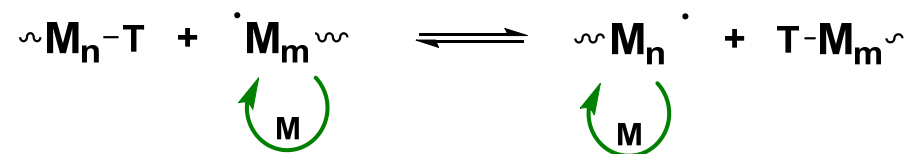


Mass distribution determined by $[M]/[In]$

Temperatures slightly higher than FRP

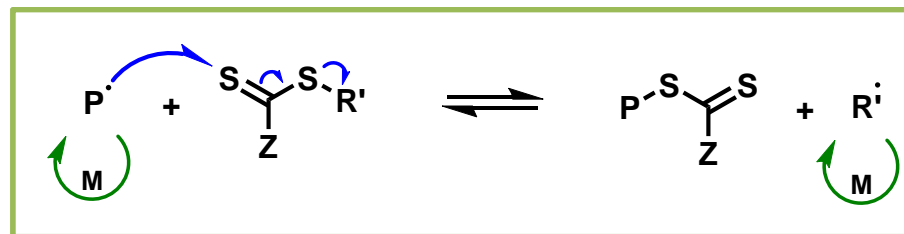
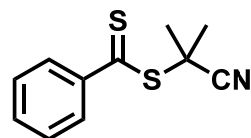
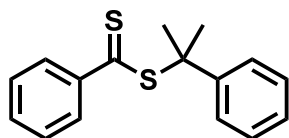
Disadvantage: Color and toxicity of metal salts

CRP: Reversible Addition Fragmentation and Transfer (RAFT)



Advantages over ATRP: no metals, mild conditions

Most known RAFT utilized dithioester transfer agents (T):



- Applicable to variety of vinyl monomers, but finding optimal dithioester is challenging.
- Dithioester are difficult to remove or replace with more interesting end groups
- Dithioesters are little stable against elevated temperatures or light.

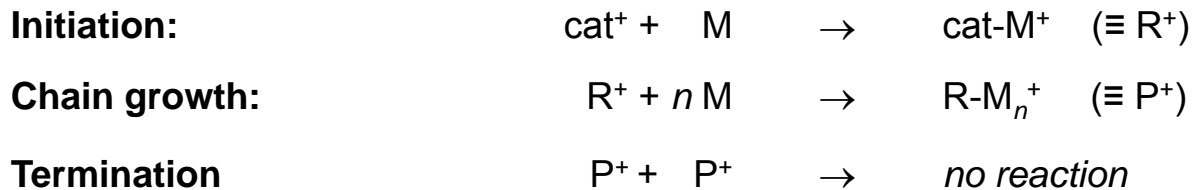
CRP: Comparison of NMP, ATRP, and RAFT

Generally, all methods have pros and cons:

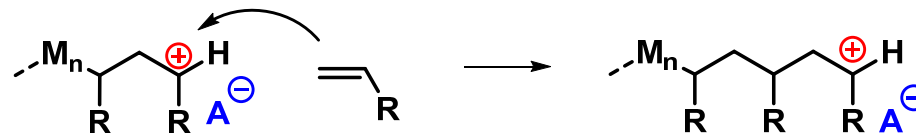
	pro	con
NMP	<ul style="list-style-type: none">▪ Purely organic▪ Applicable to many types of monomers incl. acids	<ul style="list-style-type: none">▪ High temperatures▪ Little chemistry for end groups
ATRP	<ul style="list-style-type: none">▪ Catalytic amounts of metal salts▪ Many monomers polymerizable▪ End group (X=Br) easily substituted▪ Initiators cheap and commercially available	<ul style="list-style-type: none">▪ Color▪ Toxicity▪ Removability of metal salts
RAFT	<ul style="list-style-type: none">▪ Universal as the others	<ul style="list-style-type: none">▪ Few dithioesters commercially available▪ Color and toxicity

Major drawbacks for industrial applications: slow and expensive

Cationic polymerization: General aspects



Highly suitable and selective for monomers with donor functionalizes which stabilize charge at growing chain end



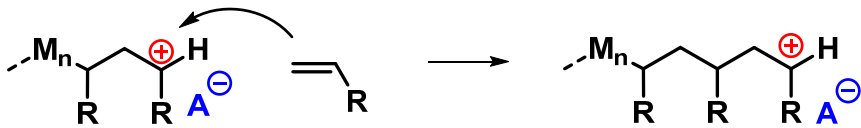
Active species (carbocation) very sensitive:

- Careful choice of solvent, often preferred: DCM, CH_3Cl , CHCl_3 , benzene, toluene
- Traces of water can be problematic
- Carried out at low temperatures to avoid side reactions of cation

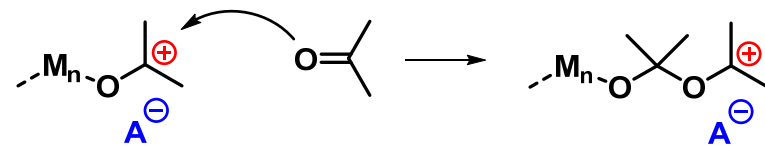
Cationic polymerization

Suitable monomers and reaction schemes:

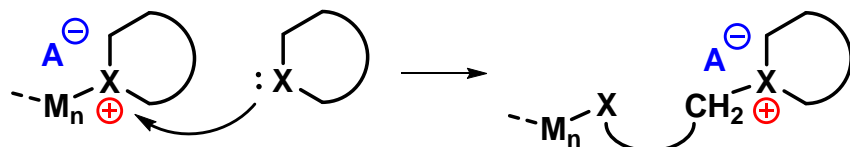
Vinyl monomers (isobutene, vinyl ether)



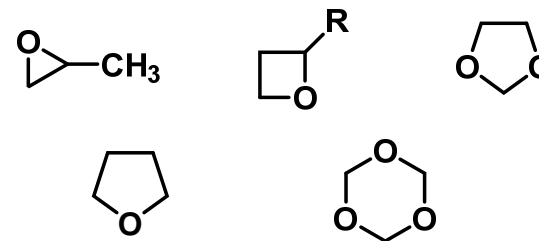
Carbonyl monomers (formaldehyd, acetaldehyd)



Heterocycles



Typical oxygen-containing heterocycles for cationic polymerization

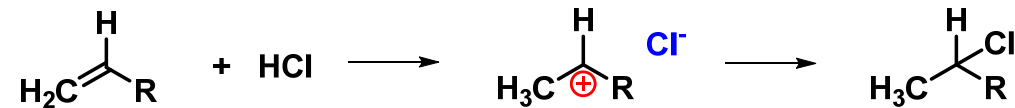


Cationic polymerization: Initiation

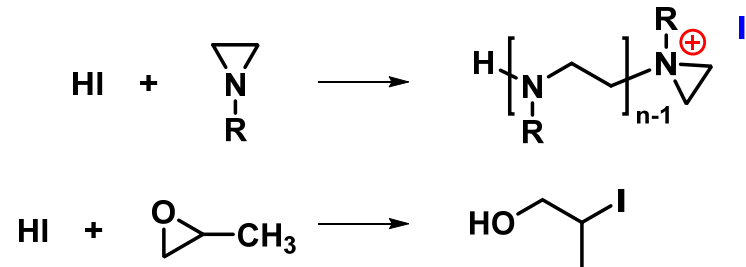
Brönsted acids

... add easily to C=C double bonds, but:

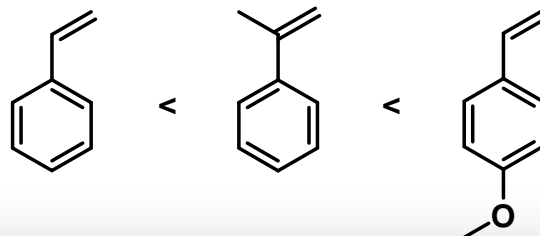
- If resulting anion is more nucleophilic than monomer, formation of covalent bond



- HI can polymerize azirine but not oxirane



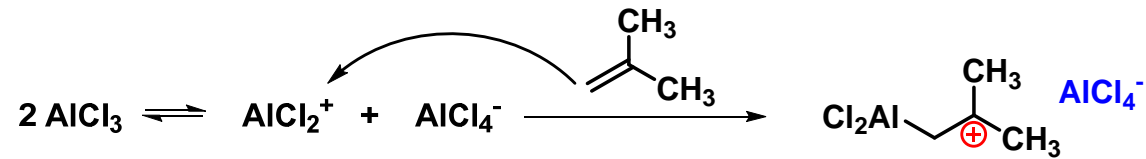
- Hence, reactivity increases with nucleophilicity:



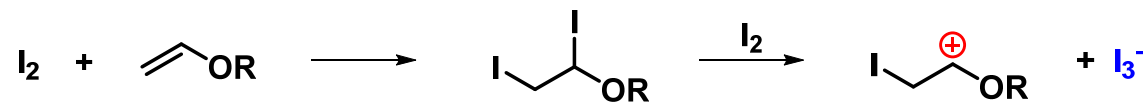
Cationic polymerization: Initiation

Lewis acids

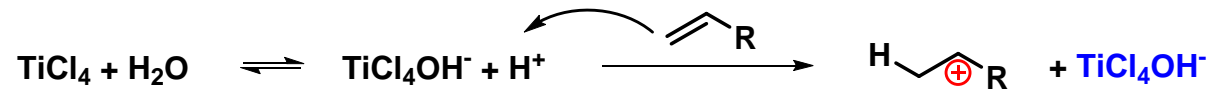
- Typical Lewis acids for initiation: AlCl_3 , BF_3 , TiCl_4 , SnCl_4 , SbCl_5



- Elementary iodine can be used as well



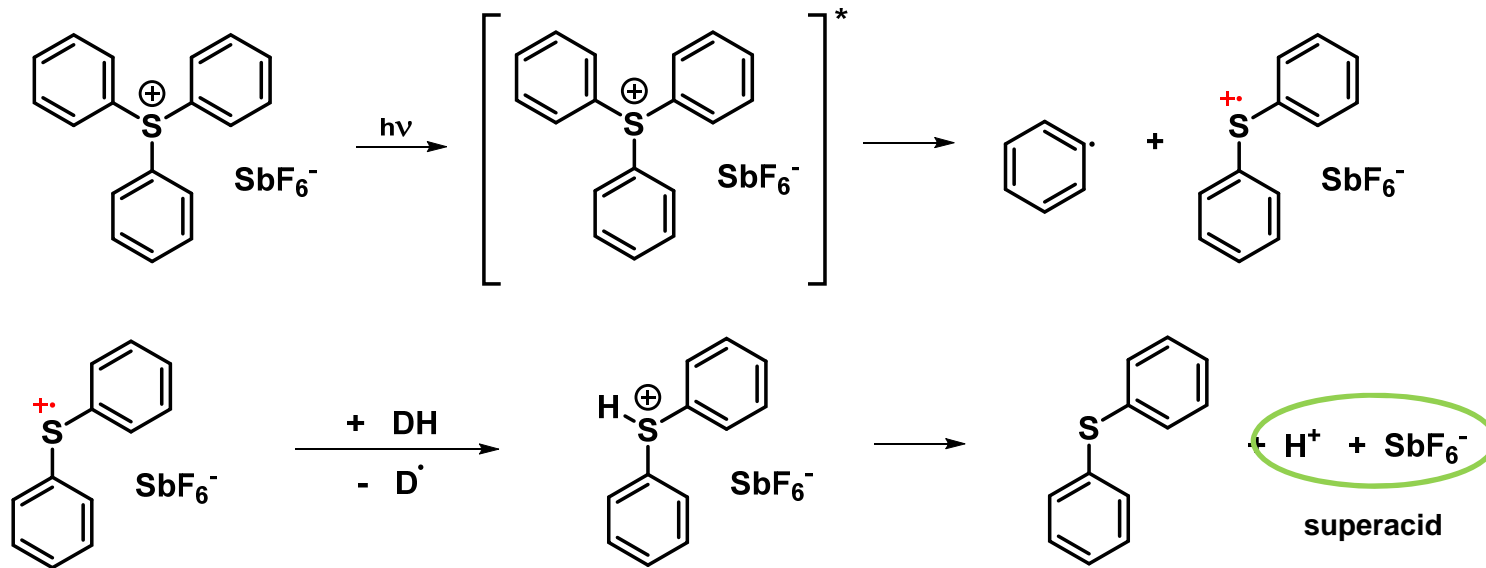
- Industrially most relevant: Co-initiation with $\text{TiCl}_4/\text{H}_2\text{O}$



Cationic polymerization: Initiation

Lewis acids

- Iodonium- and sulfonium salts (photoacids), which can photochemically initiate polymerization reactions if proton donors like H₂O are present:

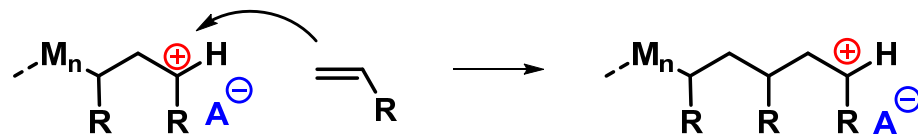


Technically relevant for inks, coatings and in the production of multilayer OLEDs.

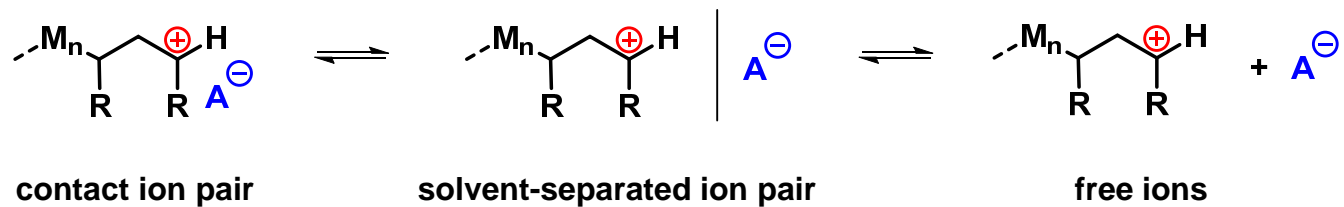
Cationic polymerization: Chain growth

Most important for chain growth:

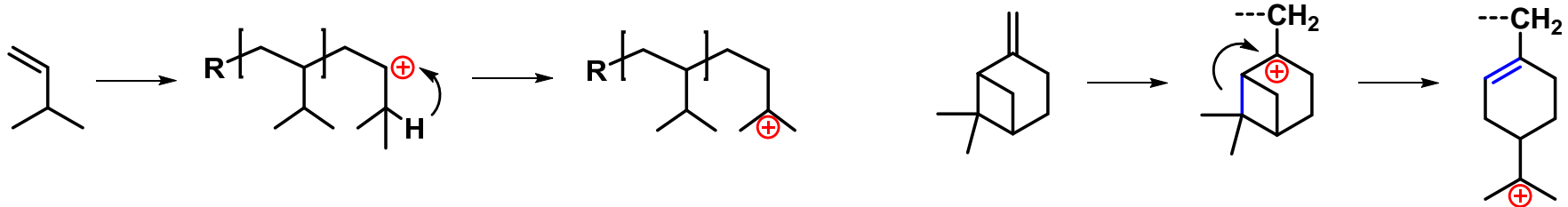
Stability and reactivity of cationic intermediate



- Solvation plays important role:



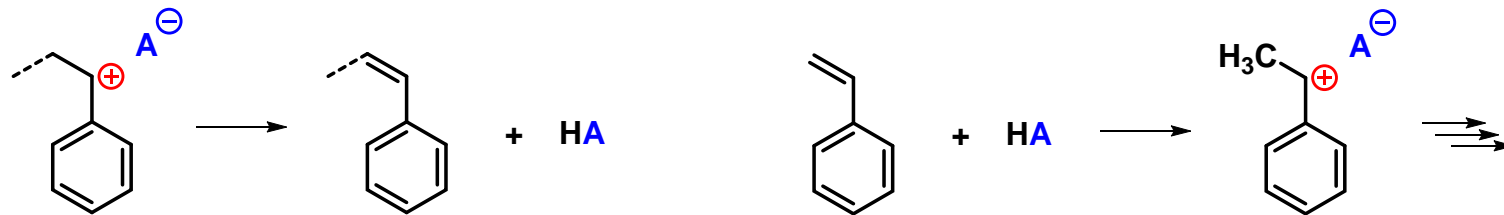
- Side reactions due to rearrangements



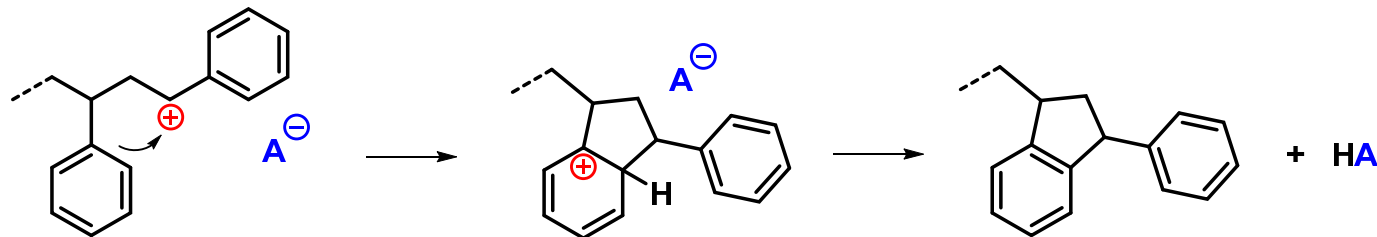
Cationic polymerization: Chain transfer and termination

Termination reactions

- β-elimination



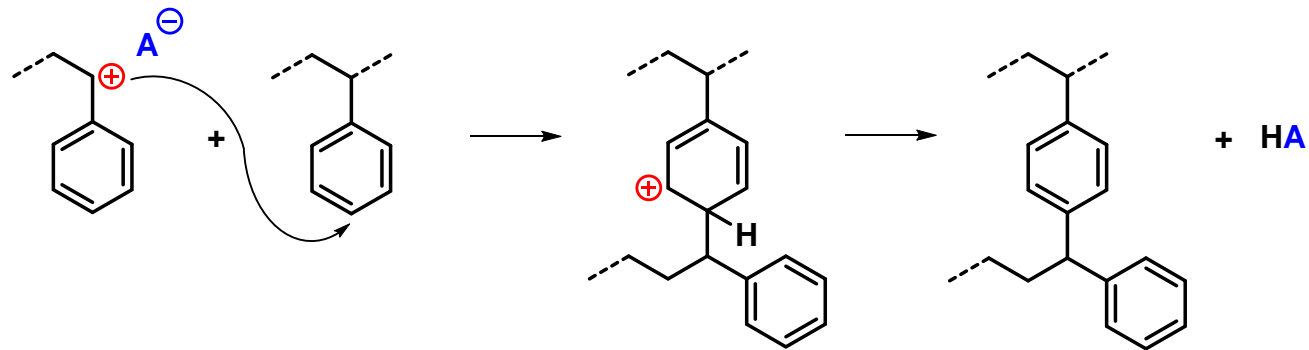
- In presence of aromatic groups, intramolecular Friedel Crafts alkylation are often observed as well



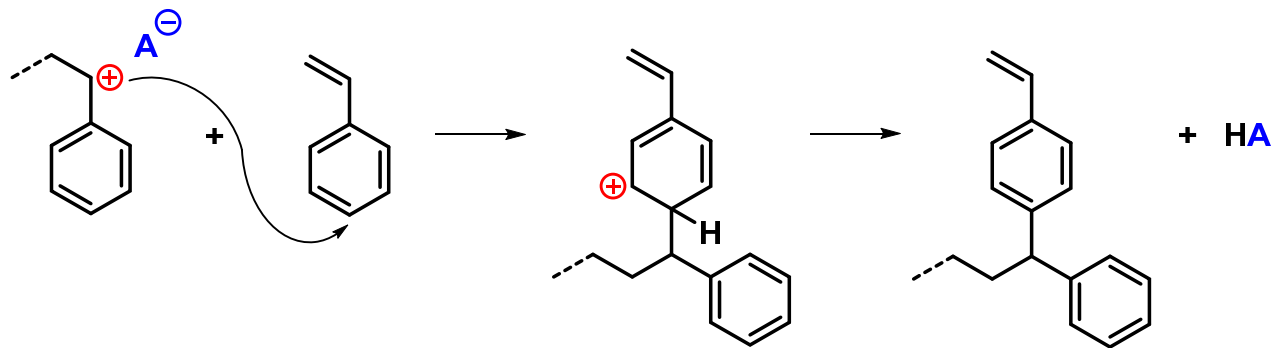
Cationic polymerization: Chain transfer and termination

Transfer reactions

- Intermolecular Friedel Crafts reactions are also observed, but lead to crosslinking



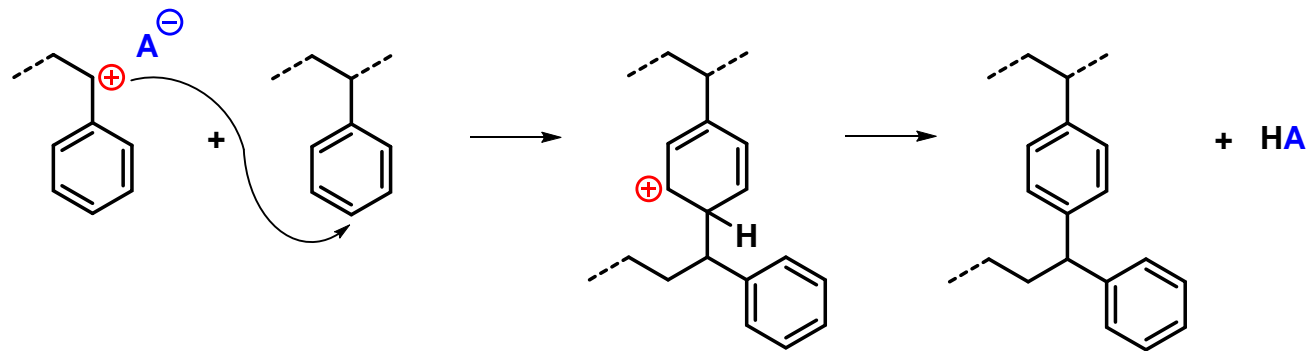
- or macromonomers



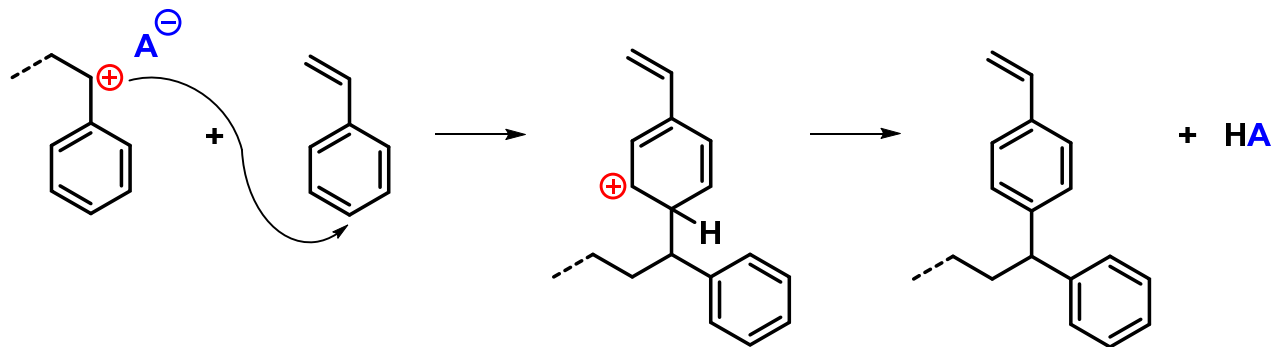
Cationic polymerization: Chain transfer and termination

Transfer reactions

- Intermolecular Friedel Crafts reactions are also observed, but lead to crosslinking



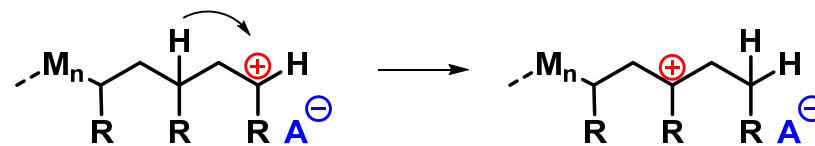
- or macromonomers



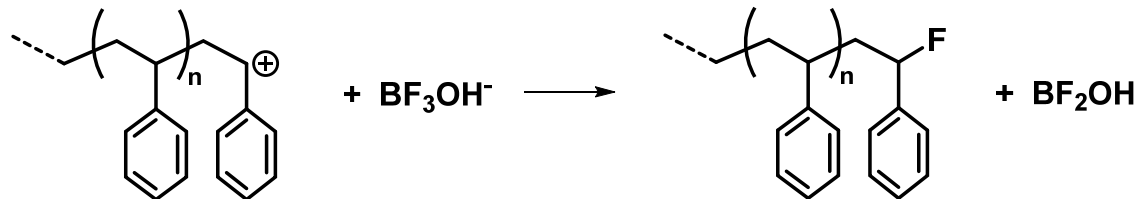
Cationic polymerization: Chain transfer and termination

Termination

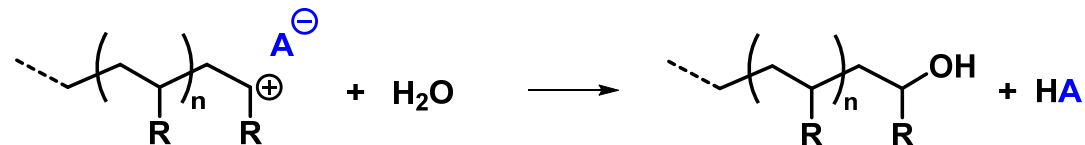
- Hydride shift



- Anion splitting



- Termination reagents (impurities)



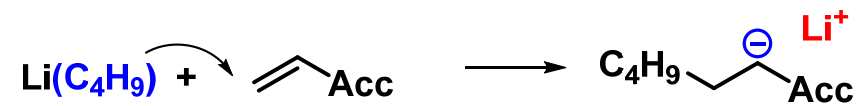
Anionic polymerization: Initiation

Nucleophilic initiation

Choice of initiator depends on monomers:

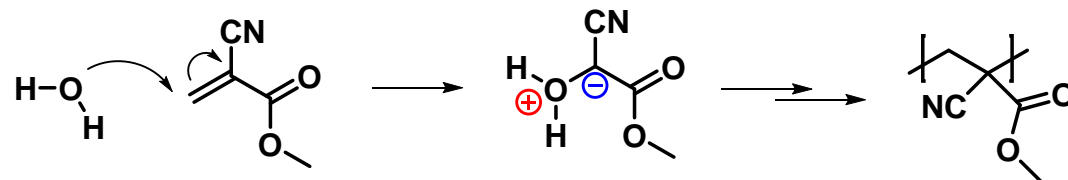
styrene/ 1,3-butadiene need strong nucleophiles, acrylnitrile / methyl methacrylate work with alkoxides

- With lithium organic compounds or Grignard compounds (e.g. PhMgBr):



- Neutral nucleophiles

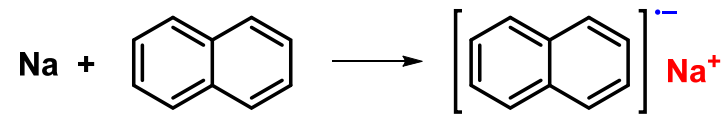
e.g. water in polymerization of cyano acrylate



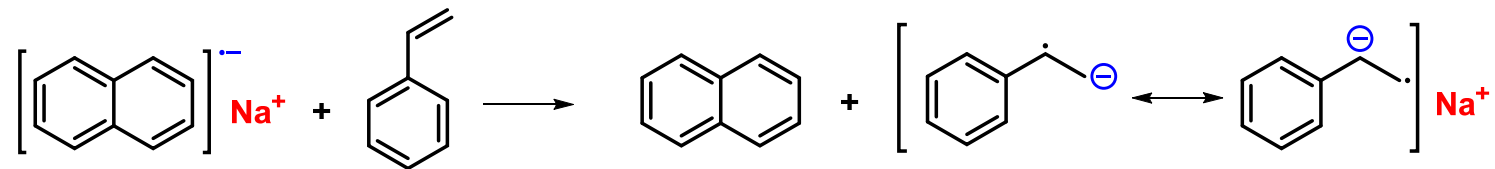
Anionic polymerization: Initiation

Electron transfer

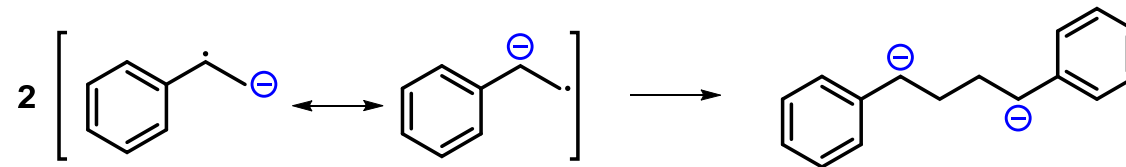
- Reaction of naphthalene with sodium leads to radical anion



... which can initiate polymerization of styrene



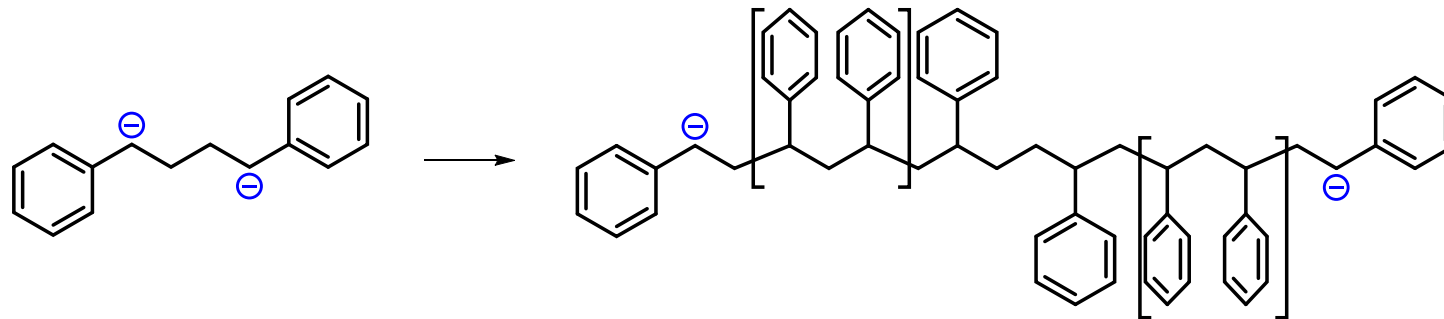
- Styryl radical dimerizes:



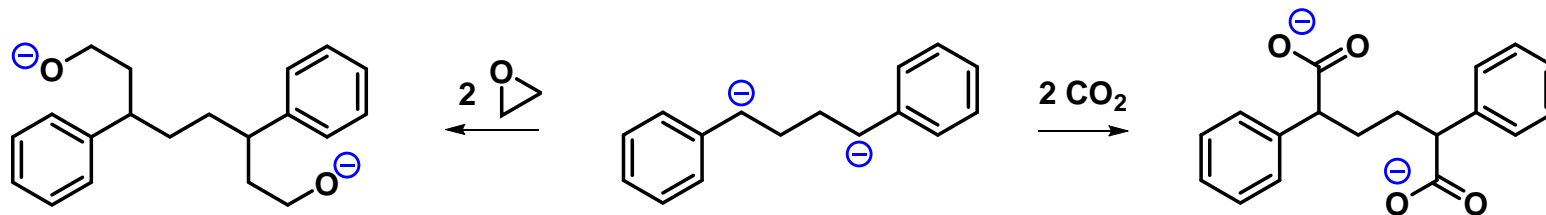
Anionic polymerization: Initiation

Electron transfer

- Anion dimer polymerizes in two directions:



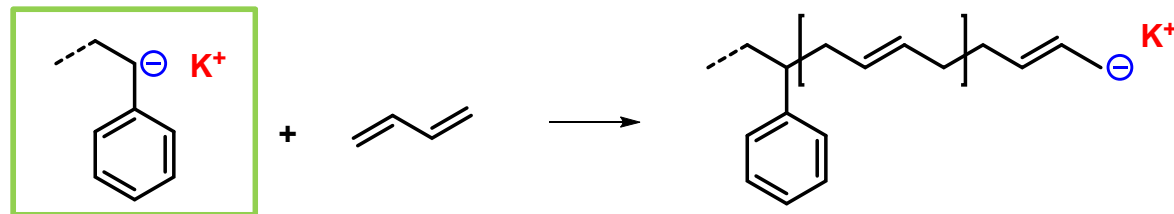
- Allows end group functionalization



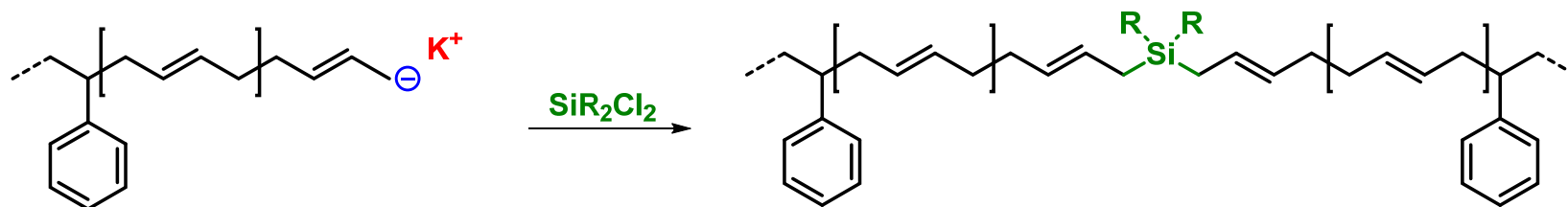
Anionic polymerization: Living polymerization

Via electron transfer initiation

- Styrenyl salts are bottleable when avoiding humidity
 - Continue polymerization by addition of styrene
 - Preparation of block copolymers (here: Styrene Butadiene Rubber, in 2012 production of 5.4 tons)



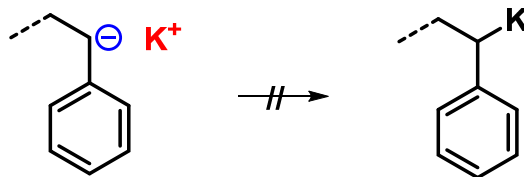
- Preparation of ABA block copolymer by addition of bifunctional termination agent



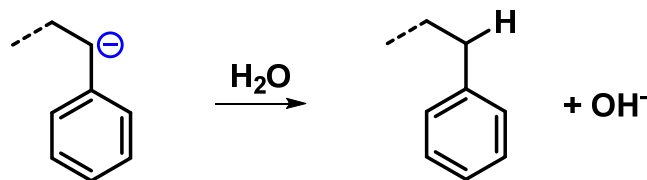
Anionic polymerization: Termination

Termination

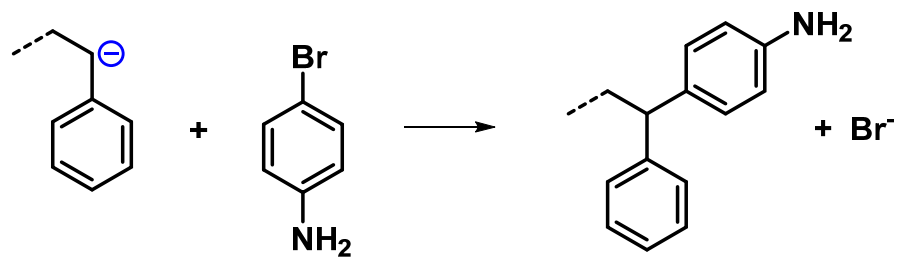
- Collaps is not possible



- Addition of water



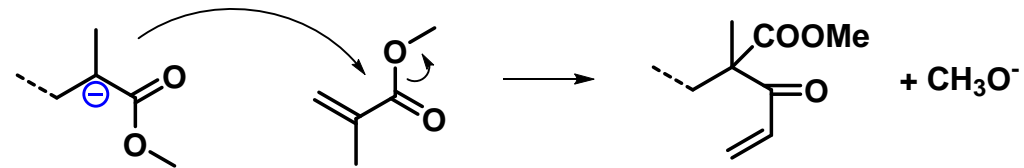
- Other termination reagents yielding end group functionalization



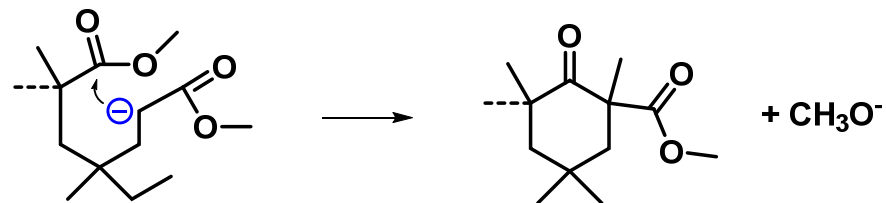
Anionic polymerization: Termination

Termination of methacrylate polymerizations

- Nucleophilic attack of polymer on carbonyl of monomer



- Intramolecular backbiting










- Termination reactions can be kept under control by selection of less reactive initiators, lower temperatures and polar solvents.

Ring opening polymerizations

Typical monomers for ROP

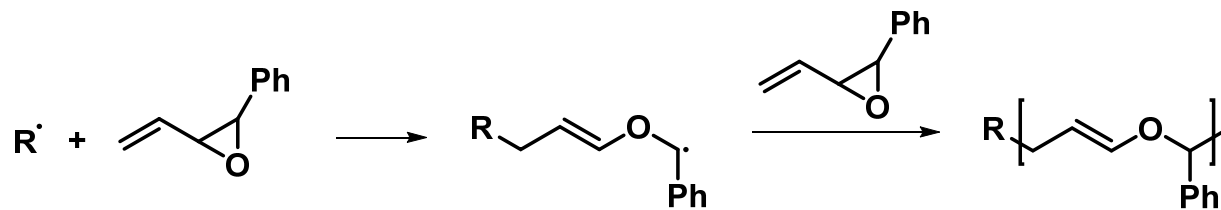
- No low molecular weight side products (e.g. leaving groups)
- No driving force from ΔH which can make up the entropy loss during regular step or chain growth
- Common to all ROP: Monomers are rings (who would have thought so?)
- Important driving force for ring size 3-5, but less for 7-8 membered rings: **release of ring strain**
- Entropy gain important for disulfides, silicones and carbonates: additional degrees of rotation

	radical	cationic	anionic
	✓		
		✓	✓
		✓	✓
		✓	
		✓	✓
		✓	✓
		✓	✓
			✓
			✓

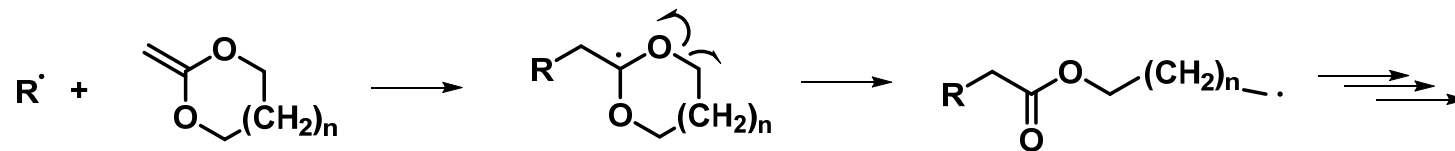
Ring opening polymerization: Radical ROP

Initiation process: see free radical polymerization

Vinyl-substituted cyclic monomers



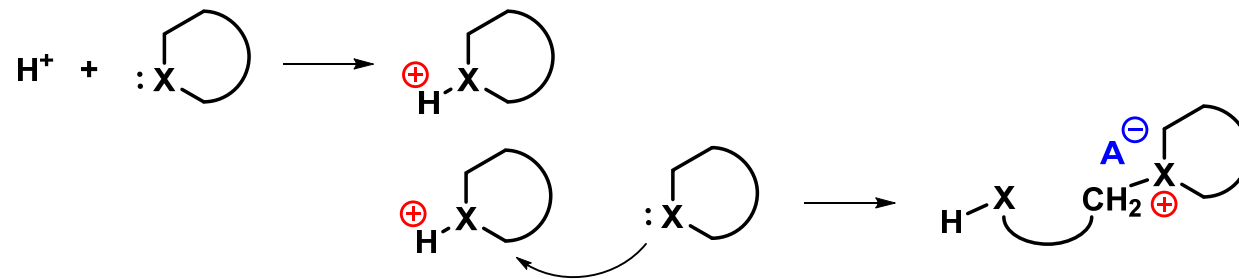
Methylene-substituted cyclic monomers



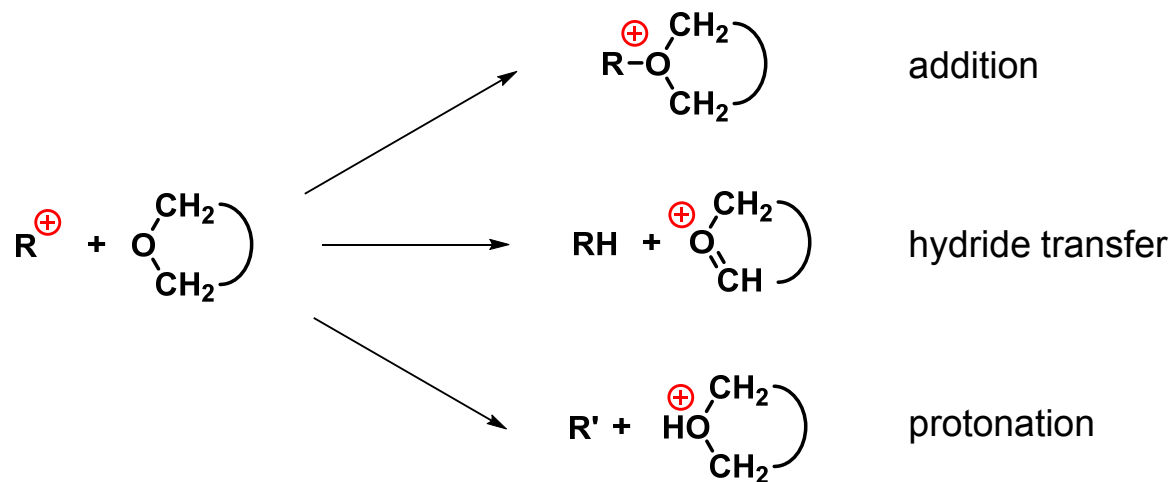
Ring opening polymerization: Cationic ROP

Initiation

(a) „activated monomer“ – proton initiation (e.g. from photoacid)



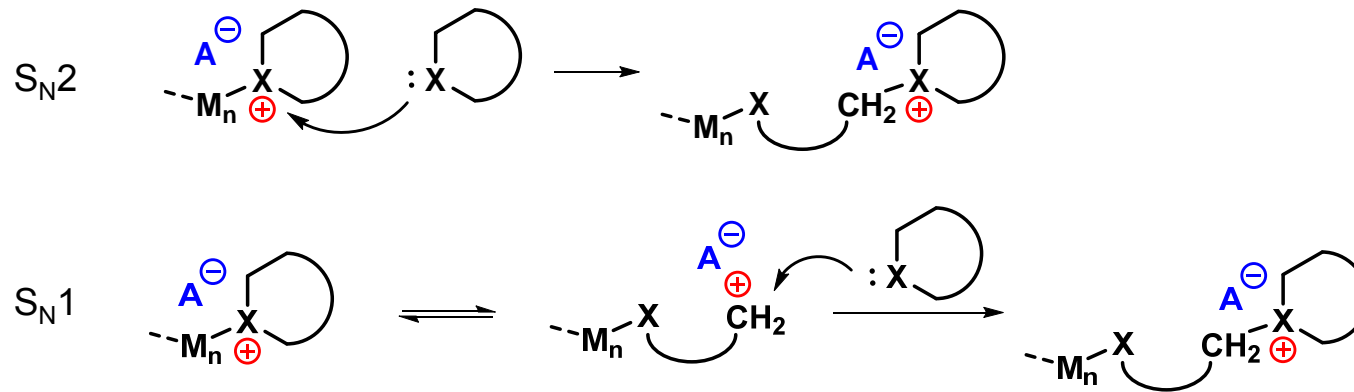
(b) Via carbenium ions



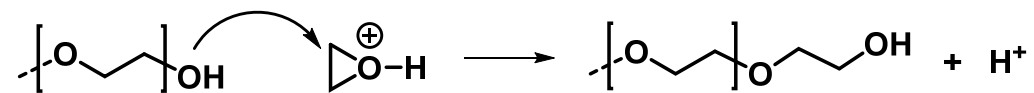
Ring opening polymerization: Cationic ROP

Mechanisms

(a) S_N2 or S_N1 mechanism with active positively charged chain end

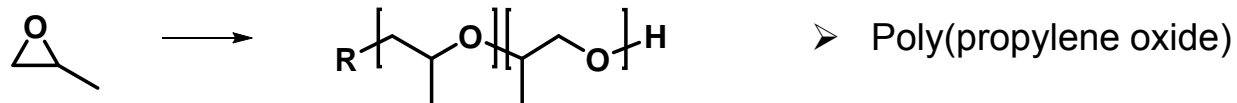


(b) „activated monomer“

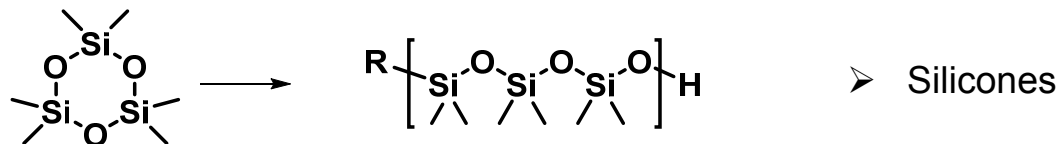
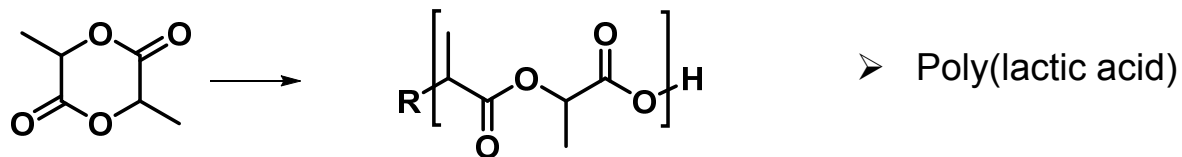


Ring opening polymerization: Anionic ROP

Important monomers for anionic ROP and their polymers



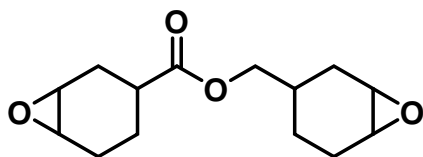
- Often: copolymers of EO and PO
- Base materials for polyurethanes, but also used in cosmetics
- Endgroup functionality (i.e. number of OH end groups) depends on starting material



Exercise: Cationic ROP

Example: 3,4-Epoxyhexylmethyl-3',4'-epoxycyclohexane carboxylate

Write the reaction mechanisms for the ringopening polymerization with a superacid (HSbF_6).



(A) **What materials properties do you expect?**

Rubber like, brittle, strong, soft, low/high melting points?

(B) **How do the properties change if it is co-polymerized with propylene oxide?**

For you to think about it at home.