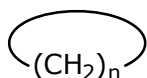


### **Issues of Equilibria (Ring-Opening Polymerization)**

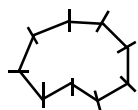
- particularly relevant with long lived polymerization processes
- "living" systems: step growth → revert to equilibrium

Ch 7 Odian

### **Effects of Ring Strain**

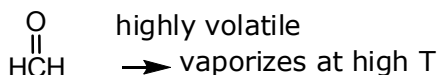
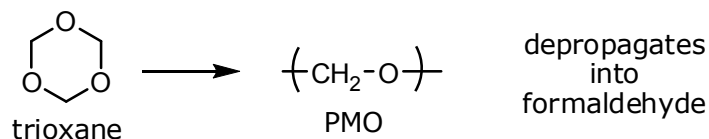
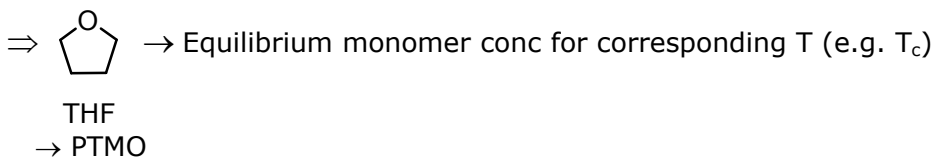


- 3-4 atoms → angle strain
- 5,7 atoms → torsional strain b/c of eclipsed conformations on neighboring atoms (not a planar condition, → chair conformation (6))
- 6 atoms → perfect situation (no angle, torsional strain, have chair conformation)
- 8-11 atoms → transangular strain (due to repulsive interactions w/in ring from H atoms) → much more pronounced when things are bigger than H-atoms



- 13 atoms → eliminate strains but difficult to make ends meet for polymerization

In general, 5 and 6 membered rings are more likely to undergo depropagation due to cyclic nature, or in non-ring opening polym, it's a temperature effect



Because of possible depropagation,

- for "Quasi-living" systems

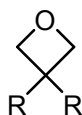
→ living behavior to approach of  $[M]_e$

But for more strained systems, have full conversion

e.g. Ethylene oxide

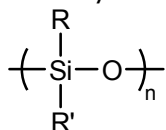


oxitanes

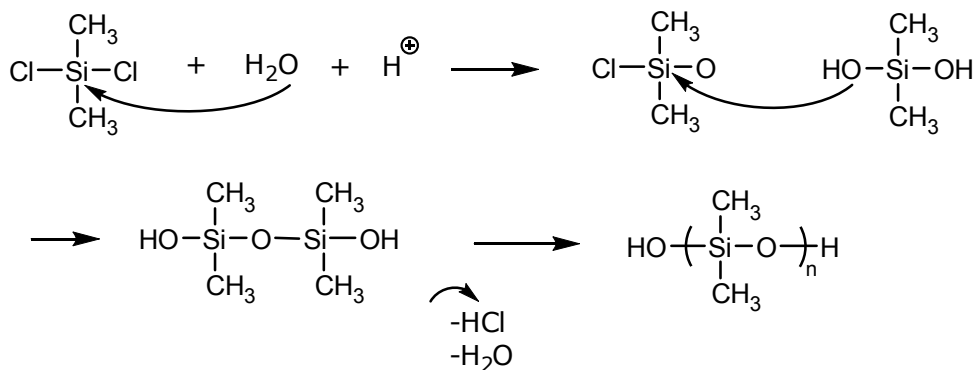


## Siloxanes

- Accessible by anionic or cationic means



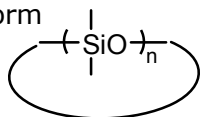
Step growth is also possible



Siloxanes form stable ring compounds

→ alleviate ring strains

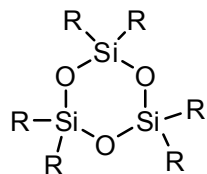
→ also form



n=3-5 most common  
(favored in equilibrium)

Note: most stable cycle is n=4 (8 atoms) for Si-O bond

Anionic Ring Opening



trimer

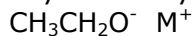
e.g. R=CH<sub>3</sub> ⇒

dimethyltrisiloxane

"D<sub>3</sub>"

D<sub>3</sub> and other trimers like it can be initiated by

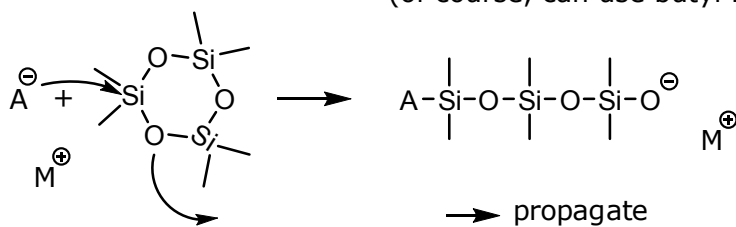
- alkyl metal hydroxide



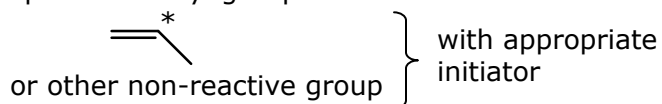
or HO<sup>-</sup> M<sup>+</sup> metal hydroxide

or CH<sub>3</sub>-Si-O<sup>-</sup> M<sup>+</sup> silanolate anion

(of course, can use butyl Li, strong initiators)

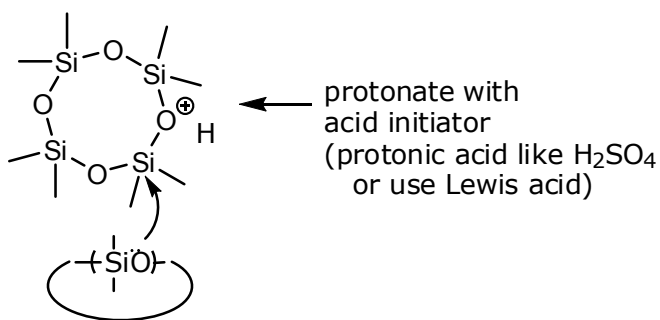


- R group can be alkyl, cannot be H  
(because Si-H is acidic → termination)
- R group can be vinyl group



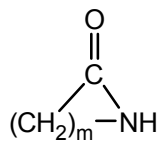
## Cationic Propagation

Can use D<sub>3</sub> or D<sub>4</sub> ← too stable to be made by anionic      NOTE: D<sub>4</sub> is cheaper commercially  
 only D<sub>3</sub> can be made by anionic



## Lactams

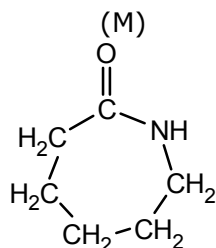
form polyamids via "activated monomer" mechanism  
(cyclic amide)



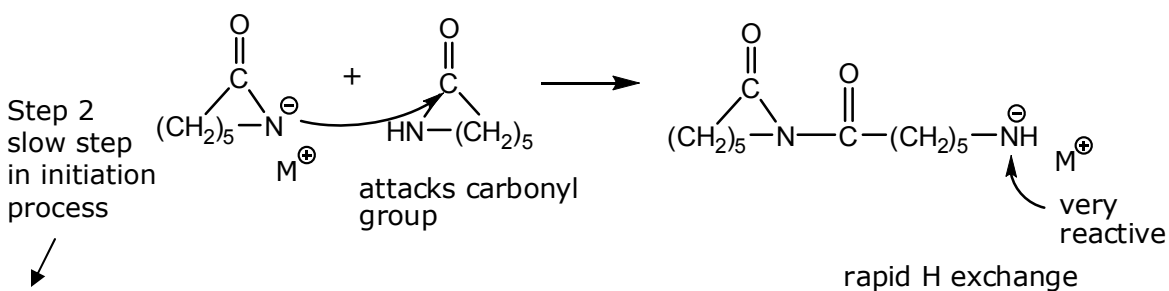
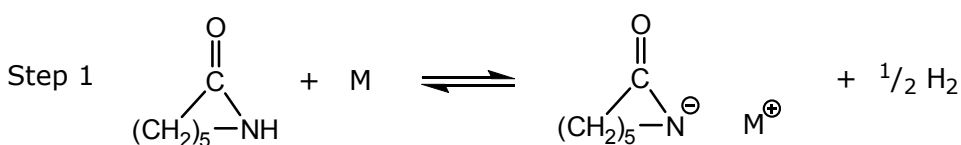
most common: m=5  
(ε-caprolactone)  
can go by anionic or cationic mechanisms

## Anionic

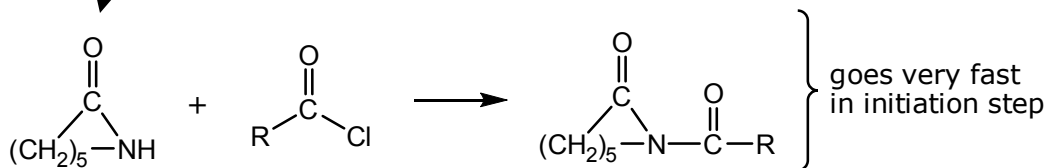
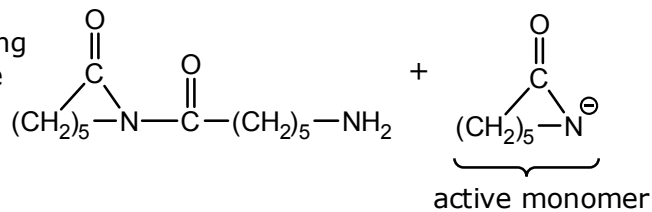
- Use metal or metal hydride as initiator



Initiation



can be sped up by introducing a more reactive group (acyl lactam)



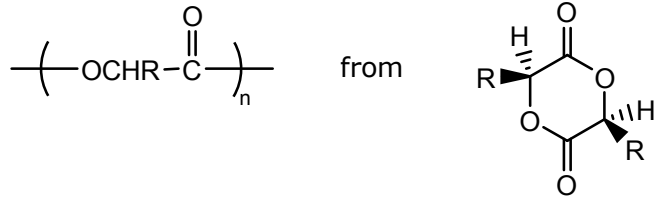
$$R_i \gg R_p \Rightarrow \text{living system}$$

Can be used to create block copolymers

Can have well-defined blocks with other vinyl monomers.

# Polyesters as Biodegradable Polymers

## Poly( $\alpha$ -hydroxy acids)

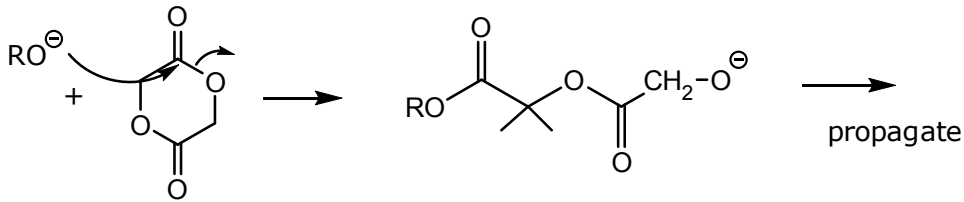


R=H  $\Rightarrow$  polyglycolic acid (PGA)  
(polyglycolide)

R=CH<sub>3</sub>  $\Rightarrow$  polylactic acid  
 $\rightarrow$  poly (L-lactide) (PLLA)  
poly (D-L-lactide) (PDLLA)

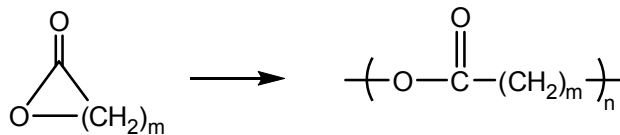
copolymers: "PLGA" (vary composition to change T<sub>m</sub>)  
and other mechanical properties

- can proceed by anionic or cationic means  
most common: anionic  
initiated by oxyanions



- Details - can achieve living polymerization
- commonly add catalyst that accelerates esterification  
e.g. stannous octanoate
  - can also change conditions to achieve step growth-like conditions  
(e.g. initiator, solvent conditions)  
condensation nature  
 $\rightarrow$  control MW with alcohol endcappers

## Poly lactones



Anionic or cationic  
Initiate with CH<sub>3</sub>O<sup>-</sup>  
m=3,4,5 (5 most common)  
 $\epsilon$ -caprolactone