

Ring Opening Polymerization(ROP)

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CH392N

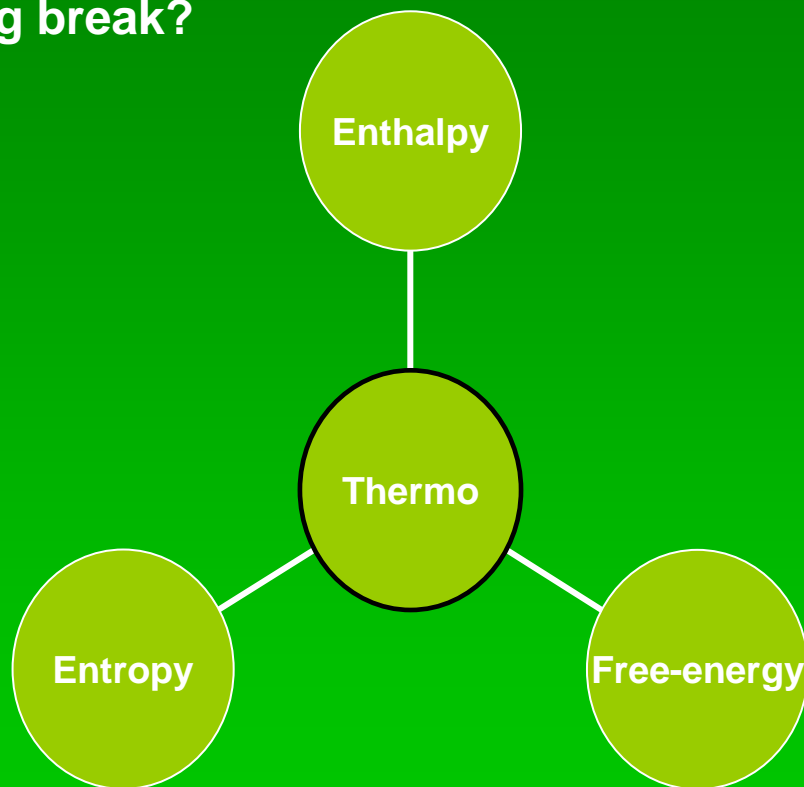
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Outline

- Polymerizability
- Anionic ROP
- Cationic ROP
- Free Radical ROP
- N-carboxyanhydrides
- Questions

Polymerizability

What makes the ring break?

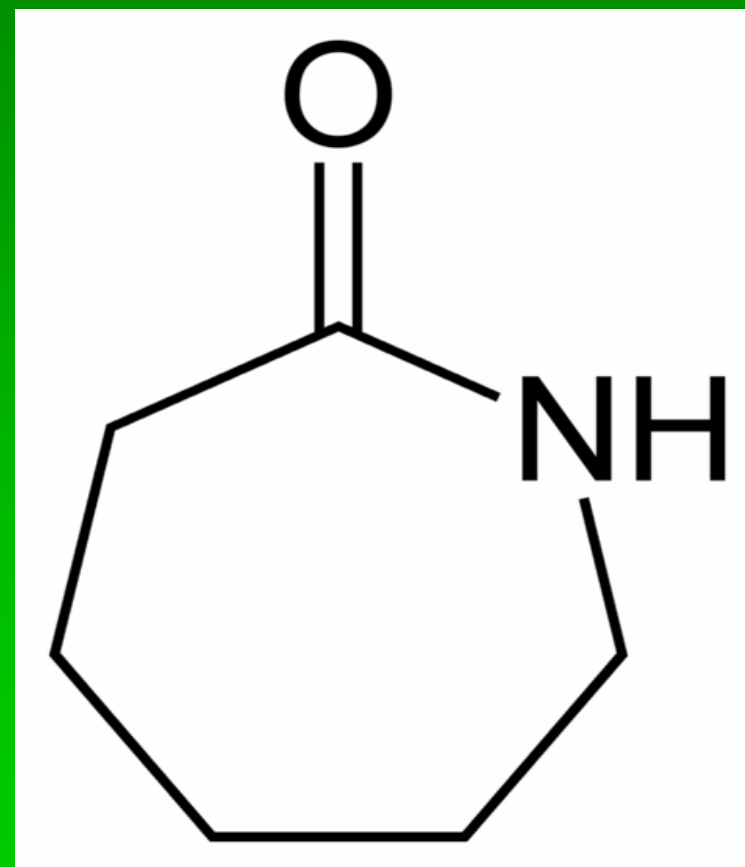


Cyclic Monomer ←-----→ **Linear Polymer**

Odian, G., *Principles of Polymerization*, Wiley and Sons, 2004.

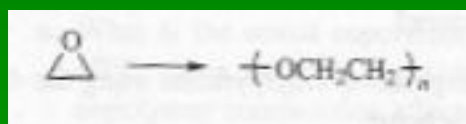
Polymerizability

- Thermodynamic Feasibility $3,4 > 8 > 5,7$
- Recall Sec. 2-5c, bond angle strain, eclipsed conformational strain, and transannular strain
- Are kinetics important?
- 6 membered rings do not generally undergo ROP, what about.... Nylon 6?



*Image from Wikipedia

Mechanism Review?

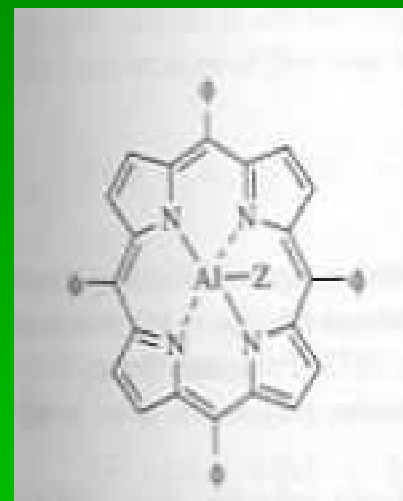


- Most ROPs proceed using the same type ionic initiators that we have studied previously...cationic, anionic, radical
- ROP is a chain polymerization (initiation, propagation, termination) where only monomer adds to the chain and no branching
- R_p lower than typical C=C and C=O polymerizations-kinetics
- Solvent and counterion effects are similar to non-cyclic systems

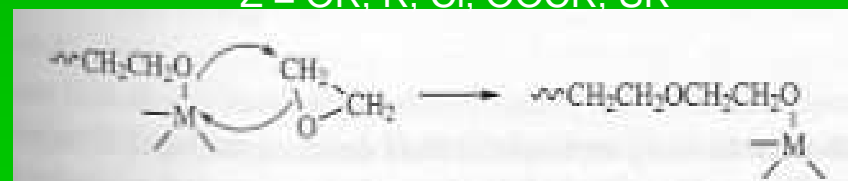
Anionic Polymerization



- Initiated by metal hydroxides, alkoxides, oxides, amides, metal alkyls, radical-anion species (Na Naphthalene)
- Anionic Coordination
Mechanism: Pruitt-Baggett
Initiator yields a covalent propagation where monomer is inserted into the metal-oxygen bond
- Increase R_p by 10^2 - 10^3 because of sterically hindered Lewis Acids
- Most proceed as “living” polymerizations



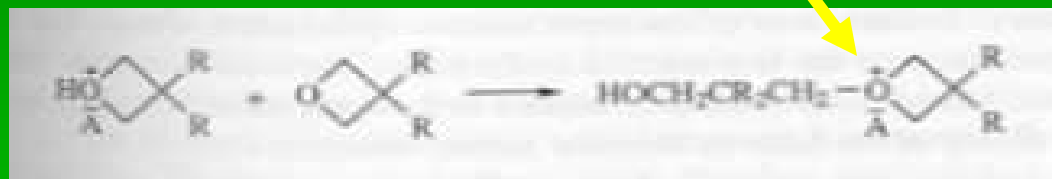
Z = OR, R, Cl, OOCR, SR



Cationic Polymerization

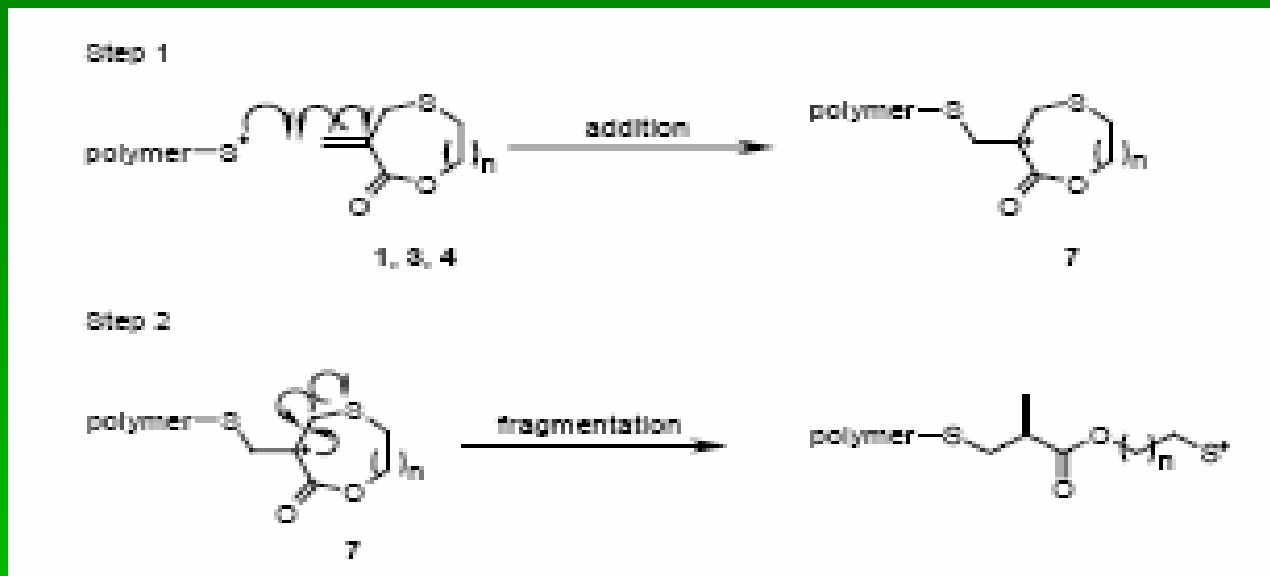


- Same initiators (protonic acids) as alkenes react to produce tertiary oxonium ions



- Can be hindered by the nucleophilicity of the counterion or water
- Also “living” if bonds are of a covalent nature...lower reactivity, “dormant”
- Highly Regioselective

Free Radical Polymerization

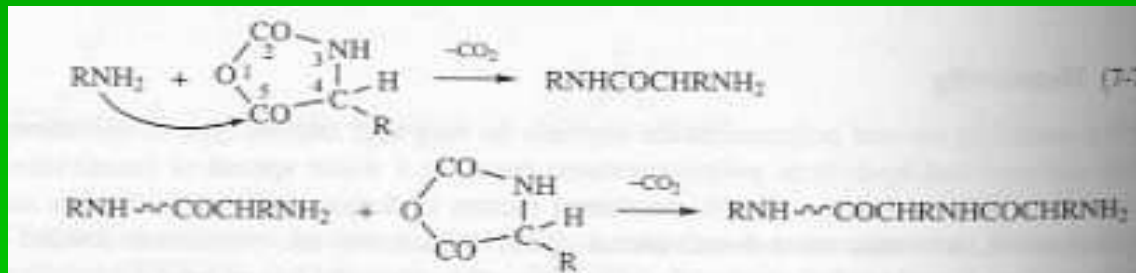


- Sulfonated allylic lactone radical polymerization to form a polyester
- Allows for introduction of functional groups into backbone
- Sulfur, as opposed to N or O, allows for less chain transfer due to H abstraction along the chain

Phelan, et al., Mechanism and Kinetics of the Free Radical Polymerization of Cyclic Allylic Sulfide Lactones, *Polymer*, 46(2005), p. 12046-12056.

N-Carboxyanhydrides

- Polyamide synthesis by decarboxylation
- Polymerized by bases and transition metal complexes (also weaker nucleophiles like water and aromatic primary amines)
- N as a nucleophile...



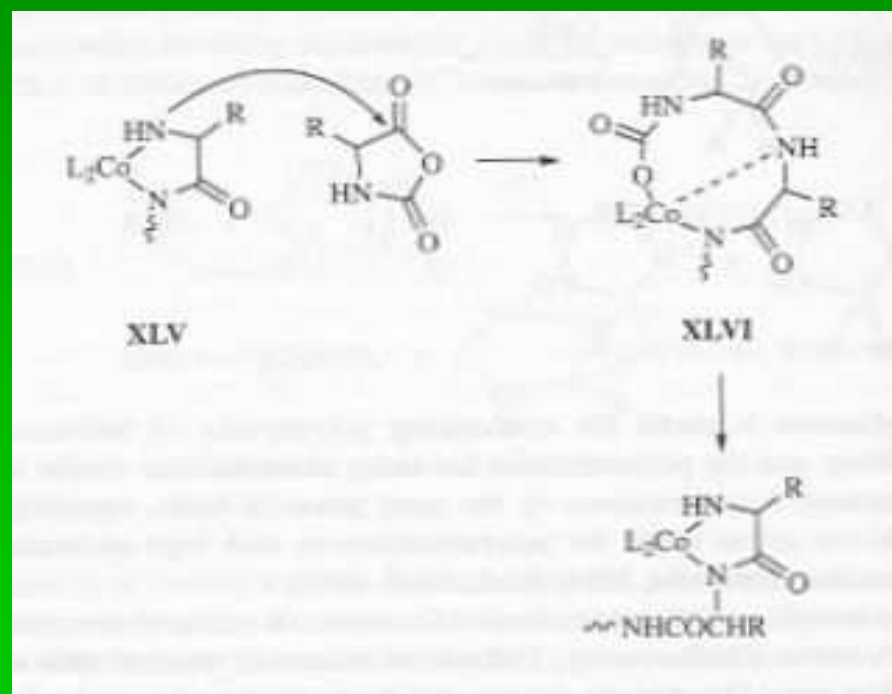
- R_p dependent on monomer and amine concentrations
So, what about the transition metal complex?

Odian, G., *Principles of Polymerization*, Wiley and Sons, 2004.

Shalitin, Y. In *Kinetics and Mechanisms of Polymerizations*, Vol. 2, Marcel, London, 1969, p. 421-496.

N-Carboxyanhydrides(NCA)

- Transition Metal Complexes
- Typically “late” transition metals work best (Ni, Co)
- Forms a 5 membered amido-amidate metallacyclic complex which acts as a nucleophile at C-5 of NCA
- Why do we do such a complex reaction?...



L₂Co = bpyNi(COD)
bpy= 2,2-bipyridyl
COD=1,5- cyclooctadiene

QUESTIONS