Chapter 7

Ring-Opening Polymerization

Introduction

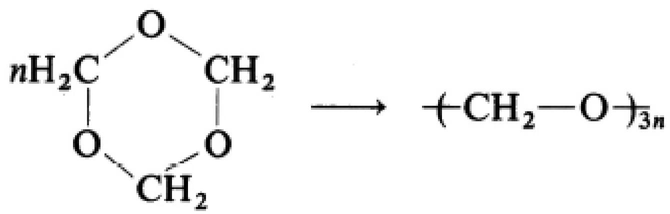
- Z ~ linking group like ether, ester, amide, --- Table 7.1 p170

- ring-opening driven by the relief of
  - angle strain ~ for 3-, 4-membered rings
  - steric repulsion ~ for 8- to 11-membered rings
- 5-, 6-, 7-membered rings ~ hard to polymerize
- ROP typically by cationic or anionic chain polym'n.
  - some by radical or coordination
  - some by opening followed by condensation, eg, nylon 6
- Some ROP steps are reversible; some are not.

Cationic ROP of cyclic ethers

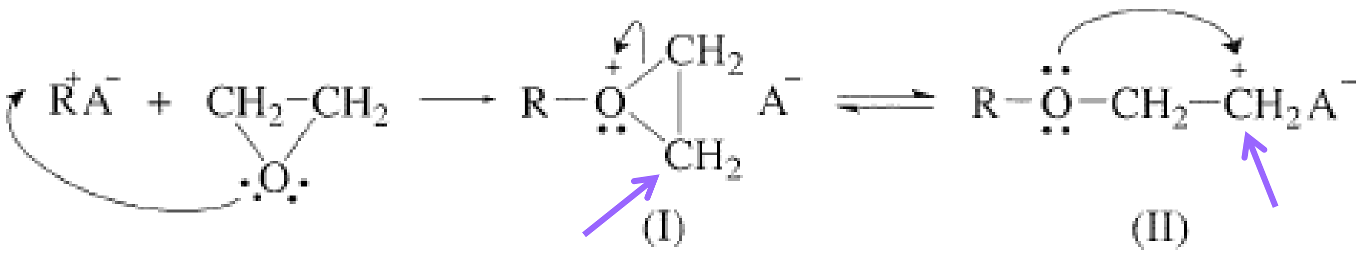
- cyclic ethers
  - strong C-O bond and Lewis-basic O: → cationic ROP
    - except for epoxide ~ both possible ← high ring strain
      - epoxide [oxirane] = 3-membered cyclic ether

    - oxetane (4-), oxolane [THF] (5-), oxepane (7-)
  - Oxanes (6-) do not polymerize.
    - except for trioxane (→ polyacetal [POM])
      - large exotherm due to crystallization/precipitation

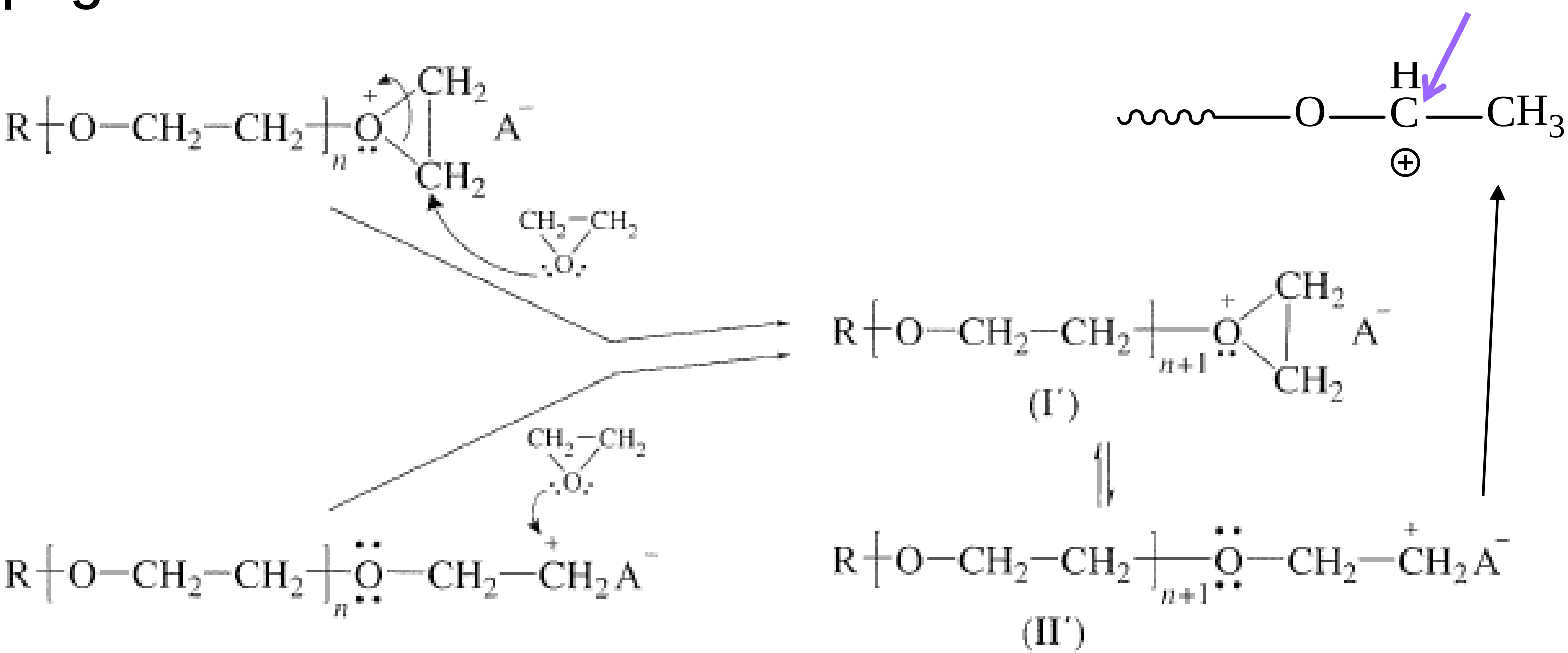


Cationic ROP of epoxide

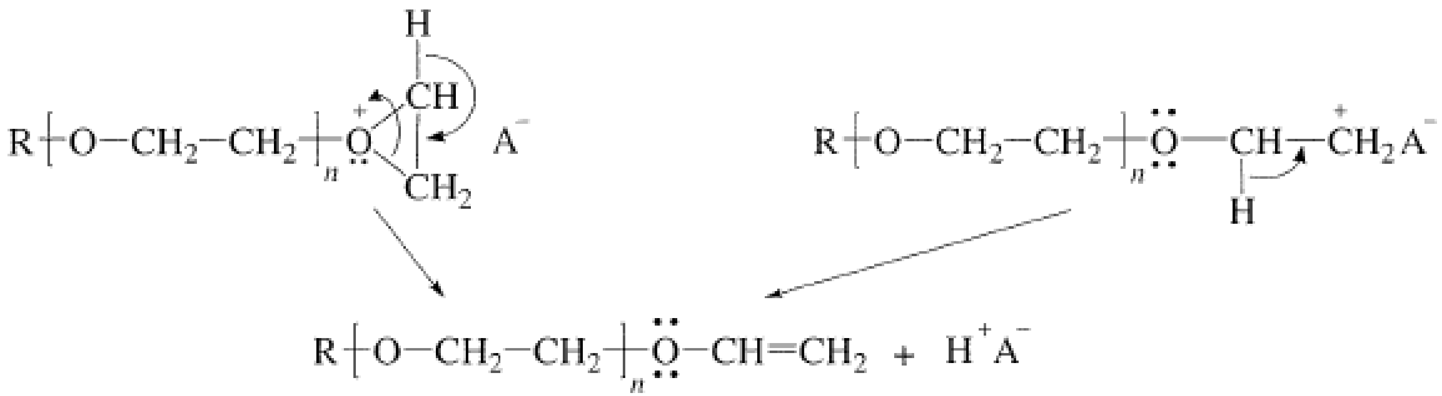
- initiated by protonic acid or Lewis acid/cocatalyst



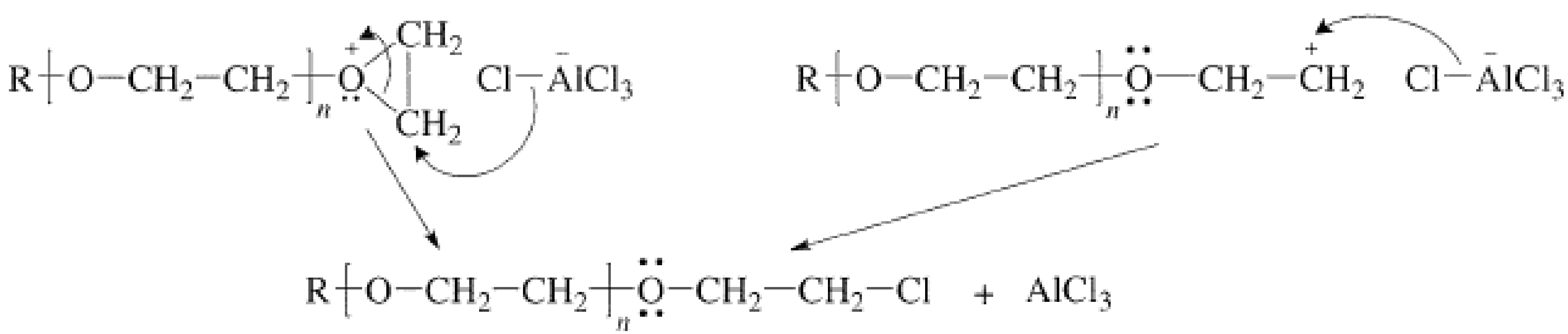
- propagation



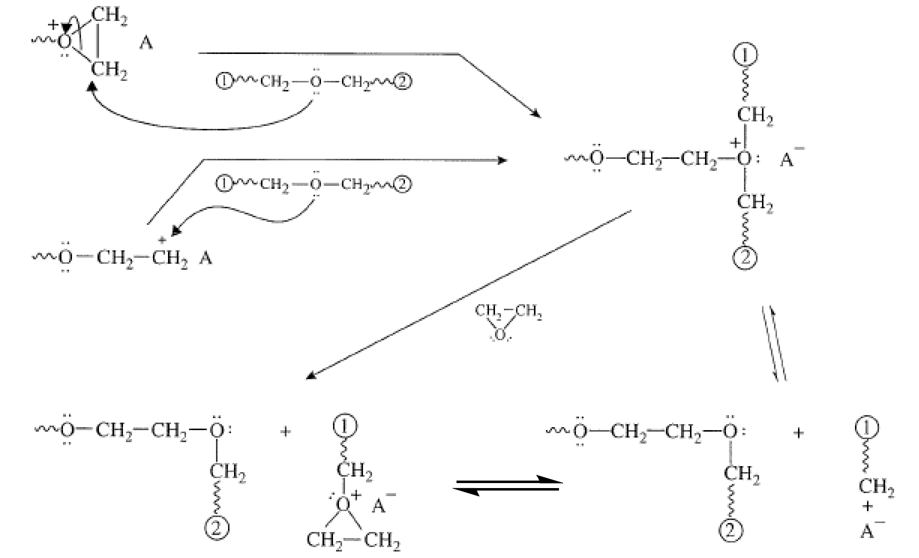
- termination
  - spontaneous ~ CT to counter-ion

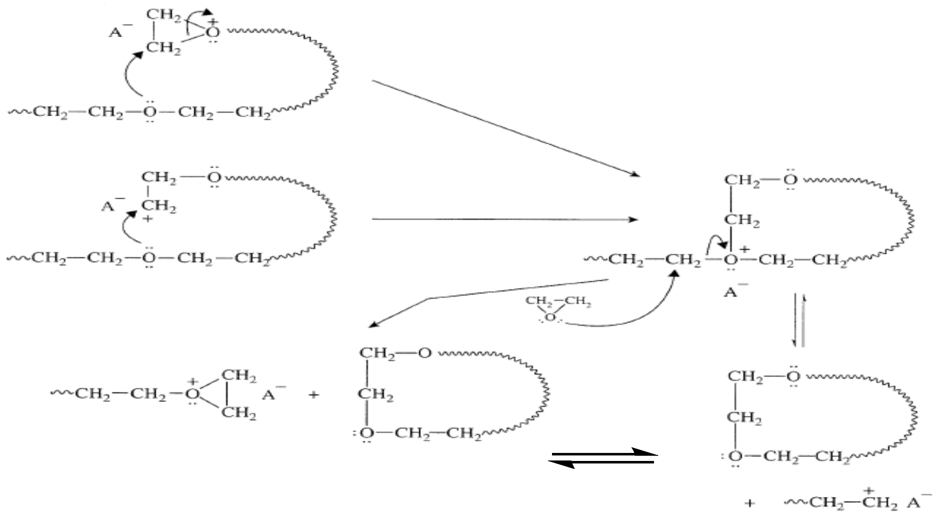


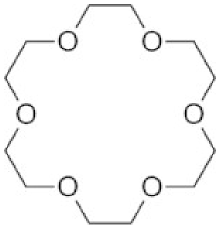
  - ion-pair rearrangement



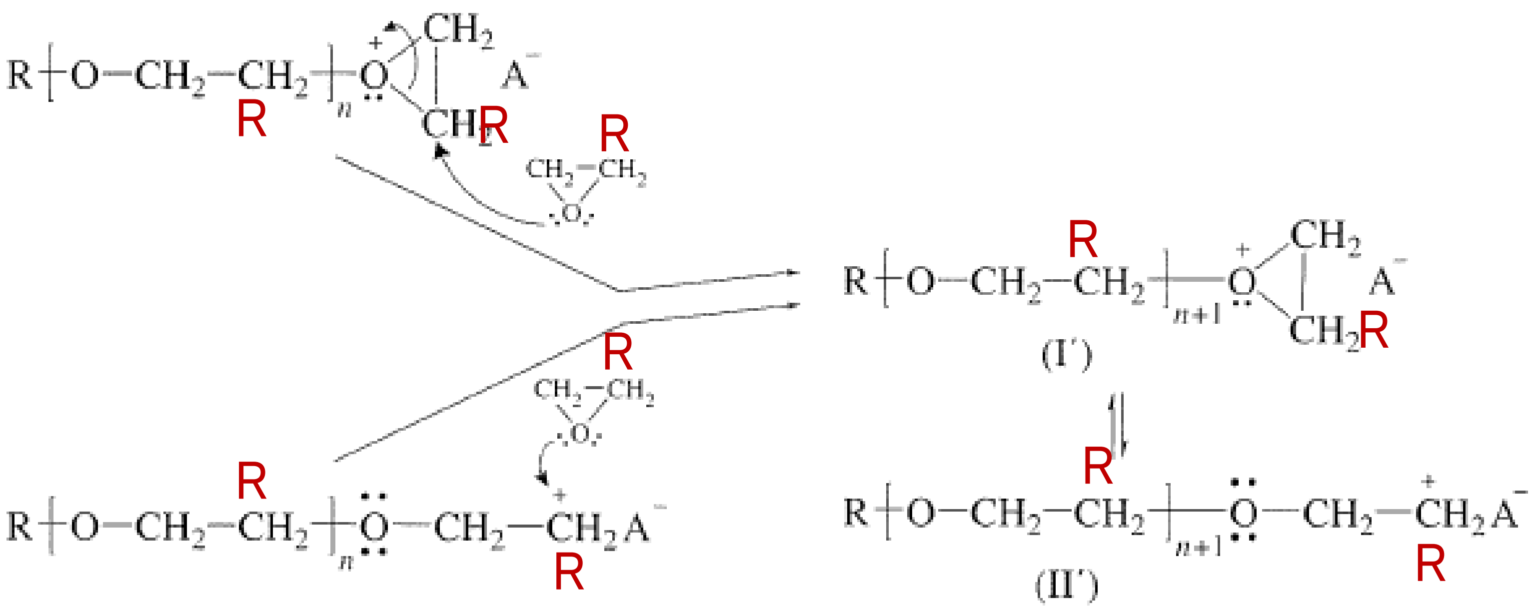
- CT to polymer
  - intermolecular CT
    - breaking chain
  - intramolecular CT
    - back-biting → ring formation
    - compete with propagation → ring-chain equilibria
    - usually, CT wins
    - cationic ROP more useful for crown ether synthesis







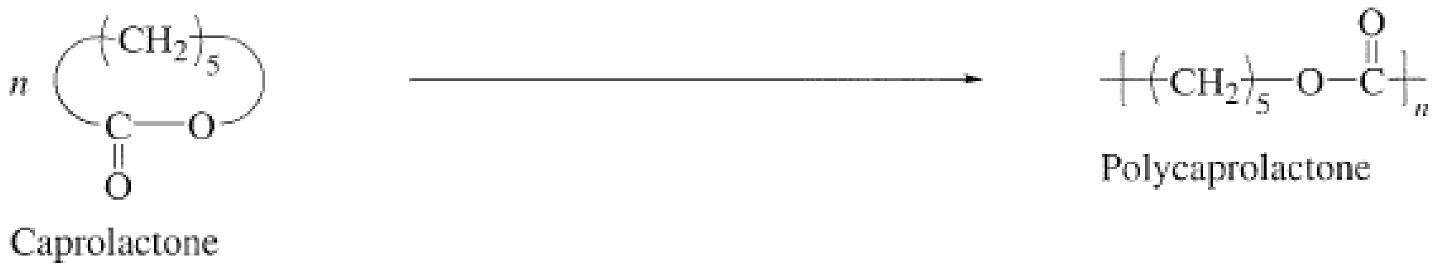
- cationic ROP of substituted EO
  - propylene oxide
    - head-to-tail and head-to-head ← regioselective not specific



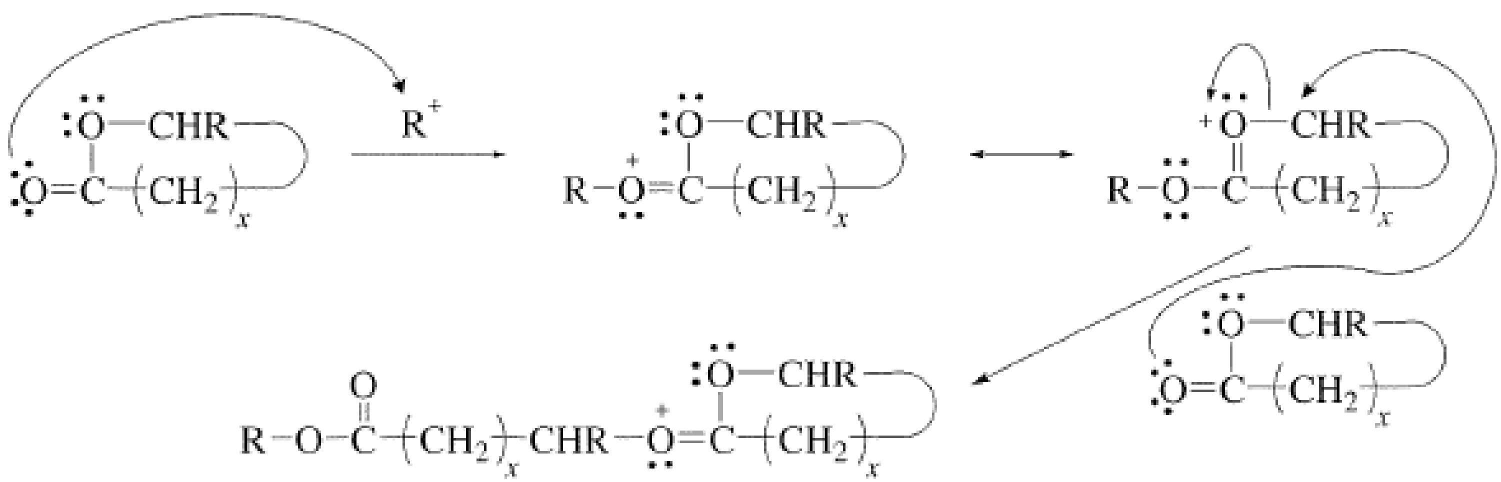
    - stereochemistry
      - ----

Cationic ROP of lactones

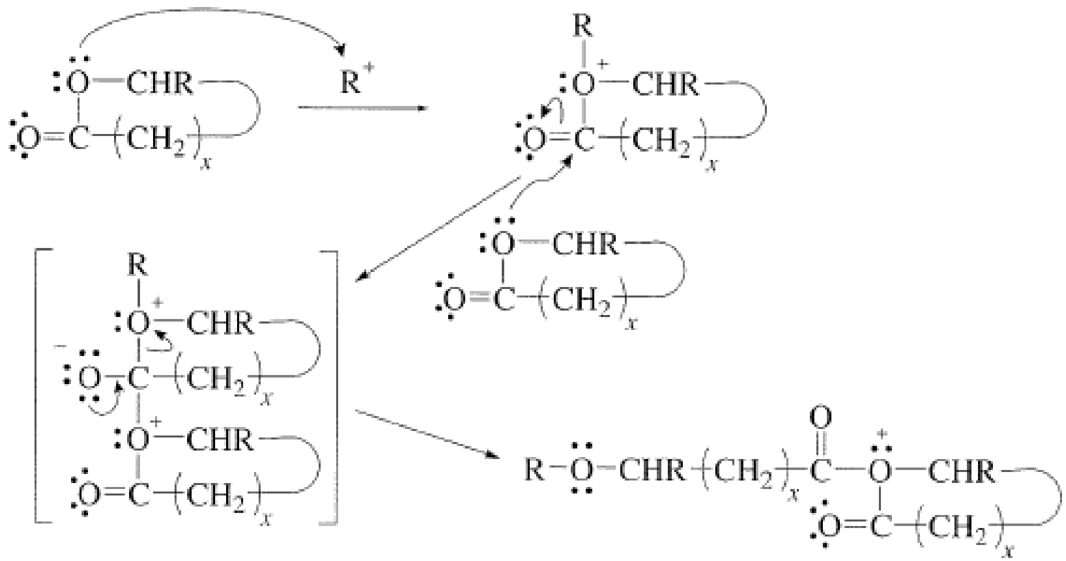
- lactone = cyclic ester



- mechanism



- 2nd mechanism? more probable due to R?

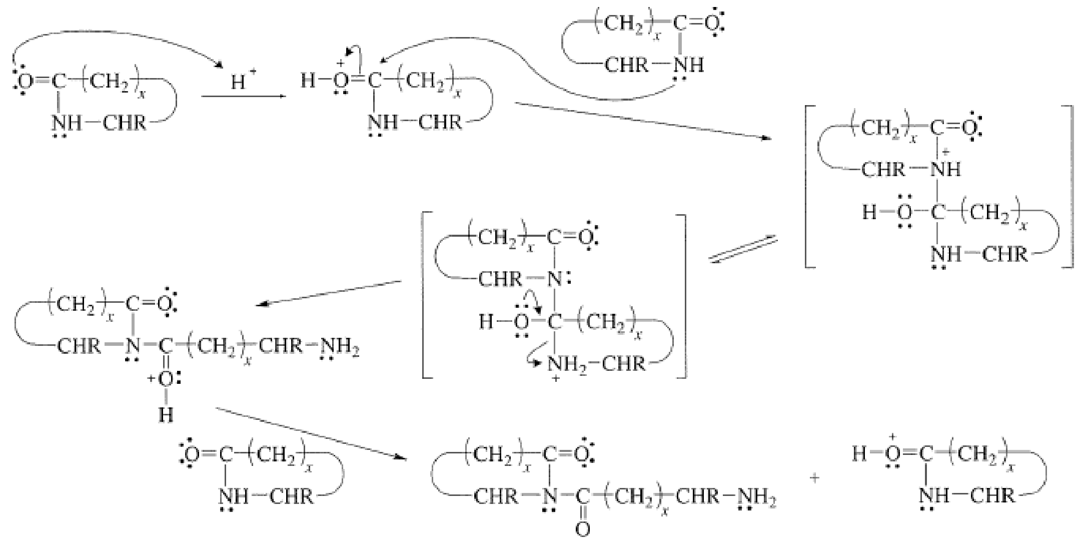


- not useful
  - termination and CT to polymer (similar to EO)
  - only low MM polyester formed

Cationic ROP of lactams

- lactam = cyclic amide

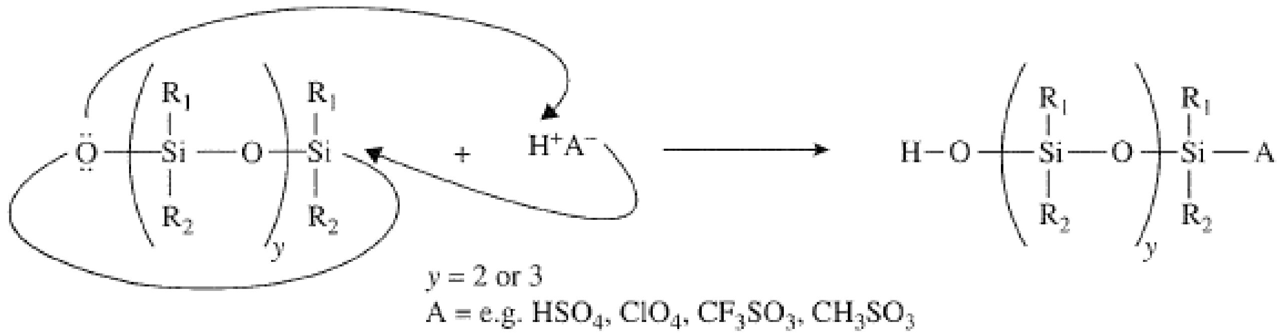
- mechanism



- not useful as it is, ---
  - CROP is the only route for *N*-alkylated lactams, but not used.

Cationic ROP of cyclic siloxanes

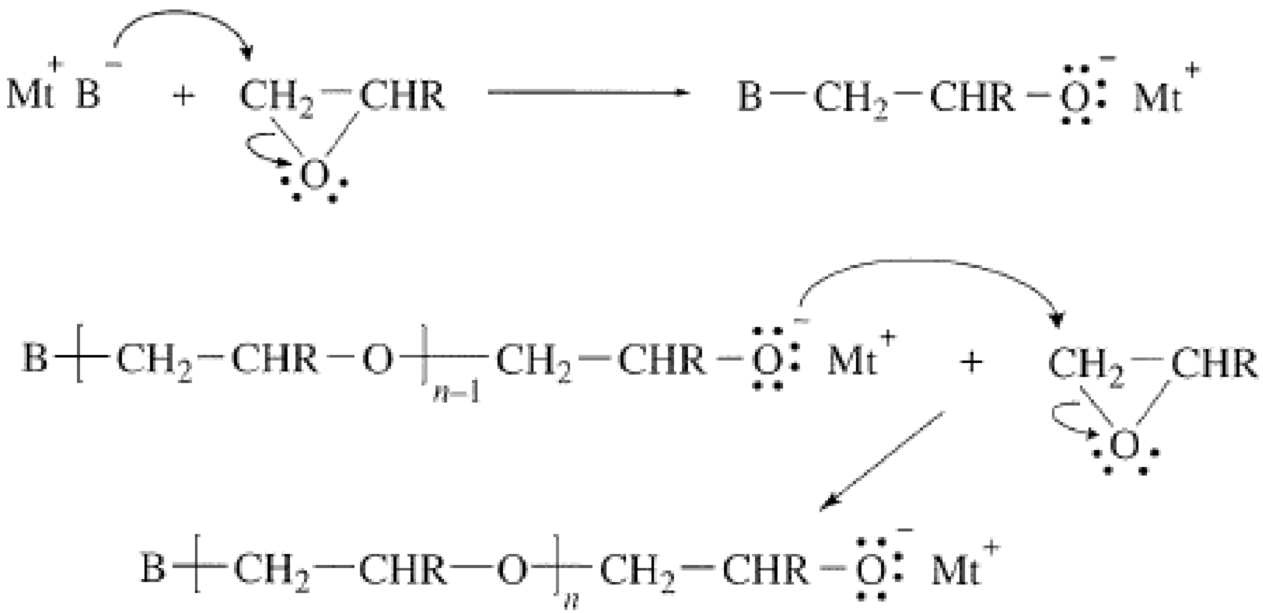
- initiation



- propagation ~ complex (mixed condens'n + addition) p177
- useful only for R that reacts with base

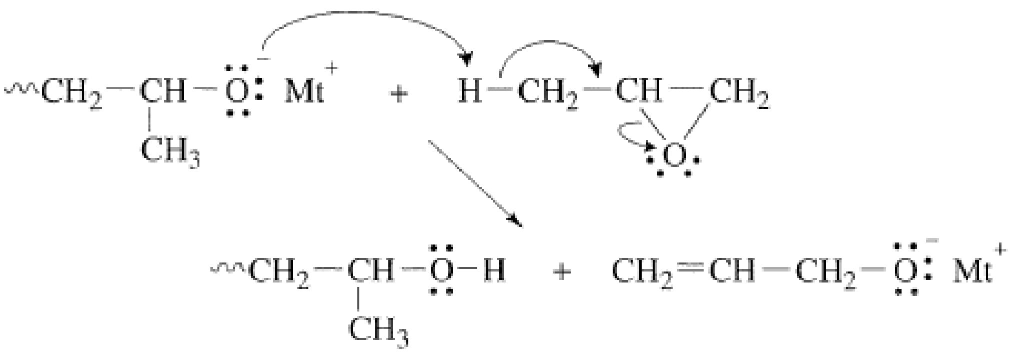
Anionic ROP of epoxides

- initiated by base
  - alkali metal, inorganic base, Mt-OR, Mt-R, e transfer cat
- mechanism



- basic → S_N2 → regiospecific → head-to-tail only

- living polym'n
  - no termination or CT
  - except for CT to monomer in propylene oxide



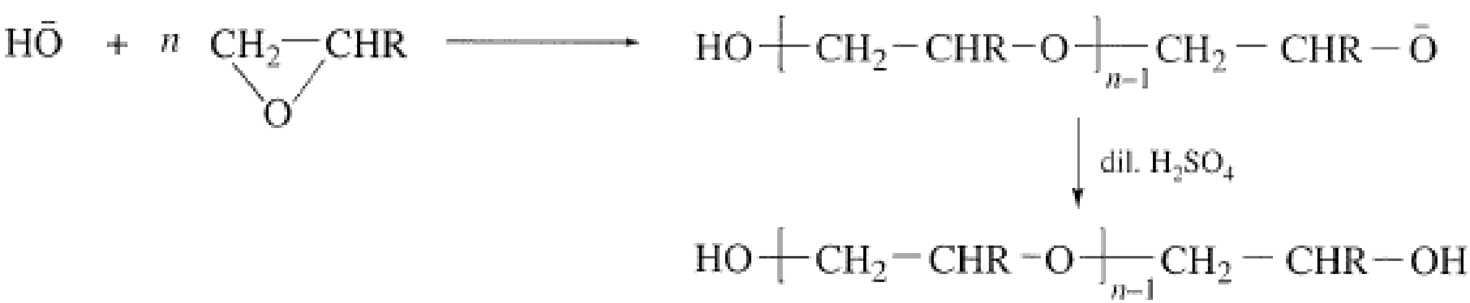
isomerization → lower MM

reinitiate → polymer with =

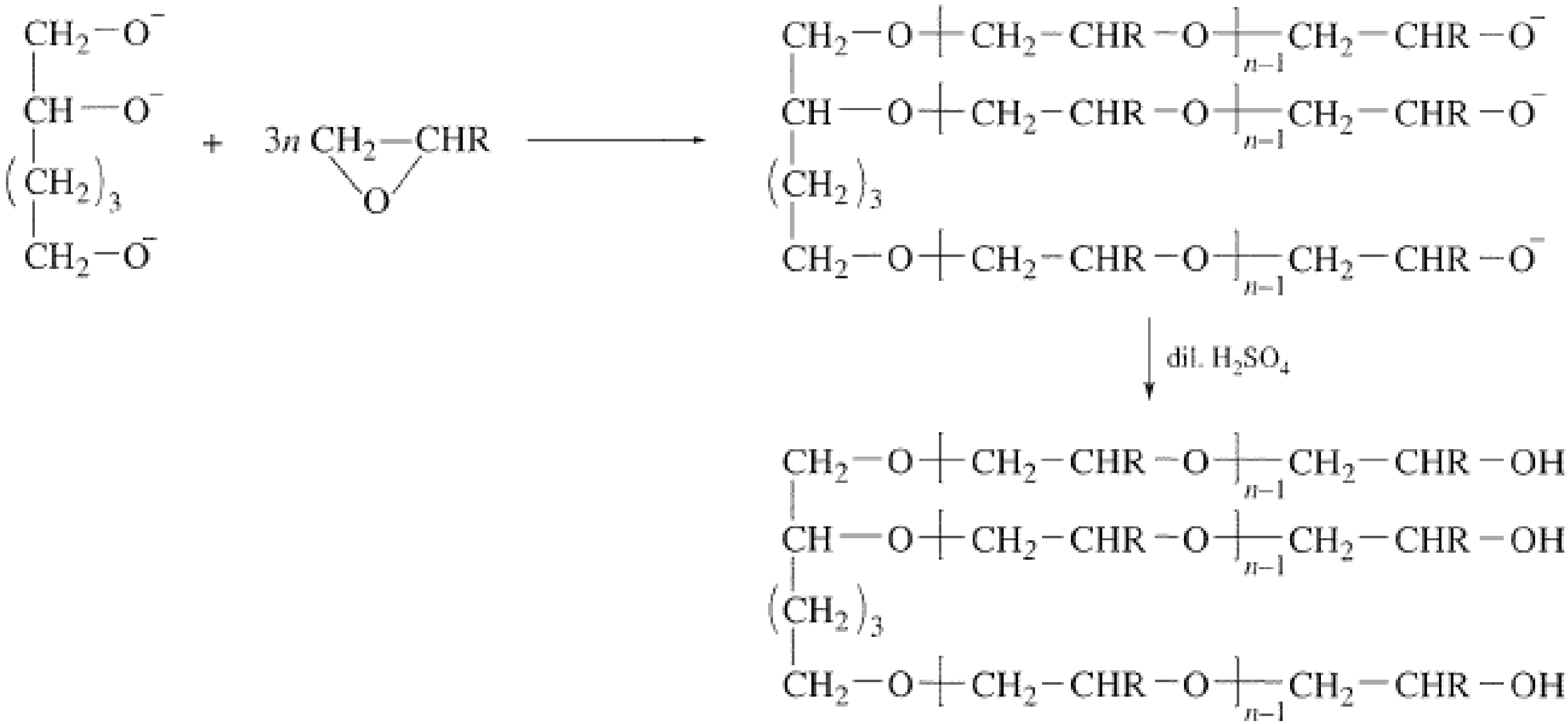
Not too severe

CH_3-CH=CHO^- Mt^+

- functionalization

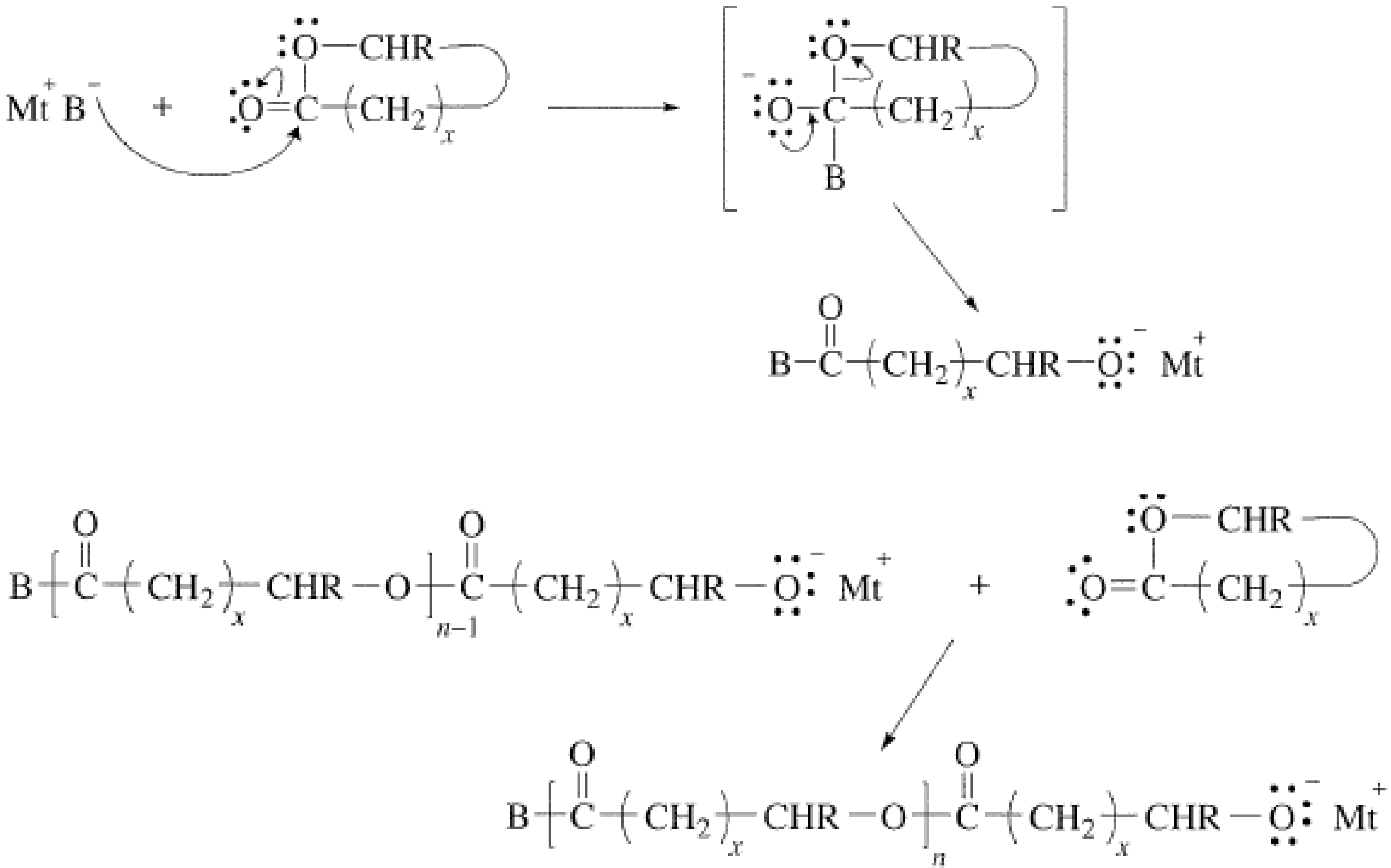


functionalization (cont'd)



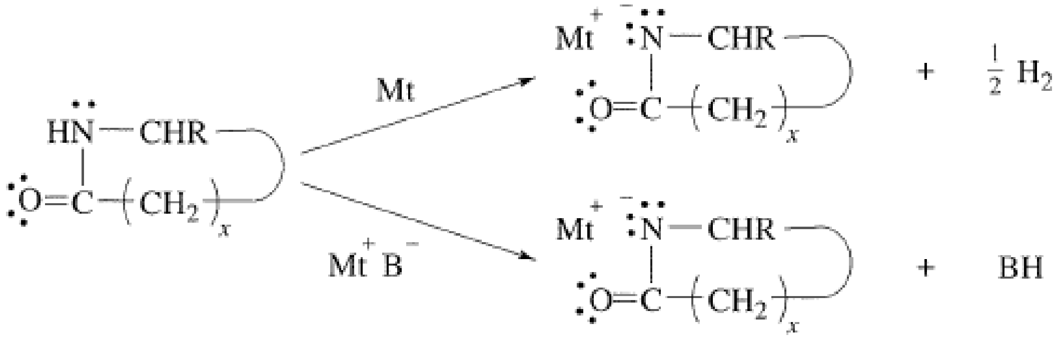
- useful for multifunctional PU elastomer synthesis p45
  - may need to change the end group to CH_2OH

Anionic ROP of lactones

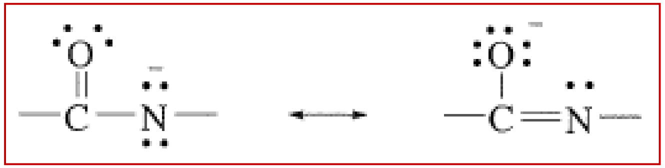


Anionic ROP of lactams

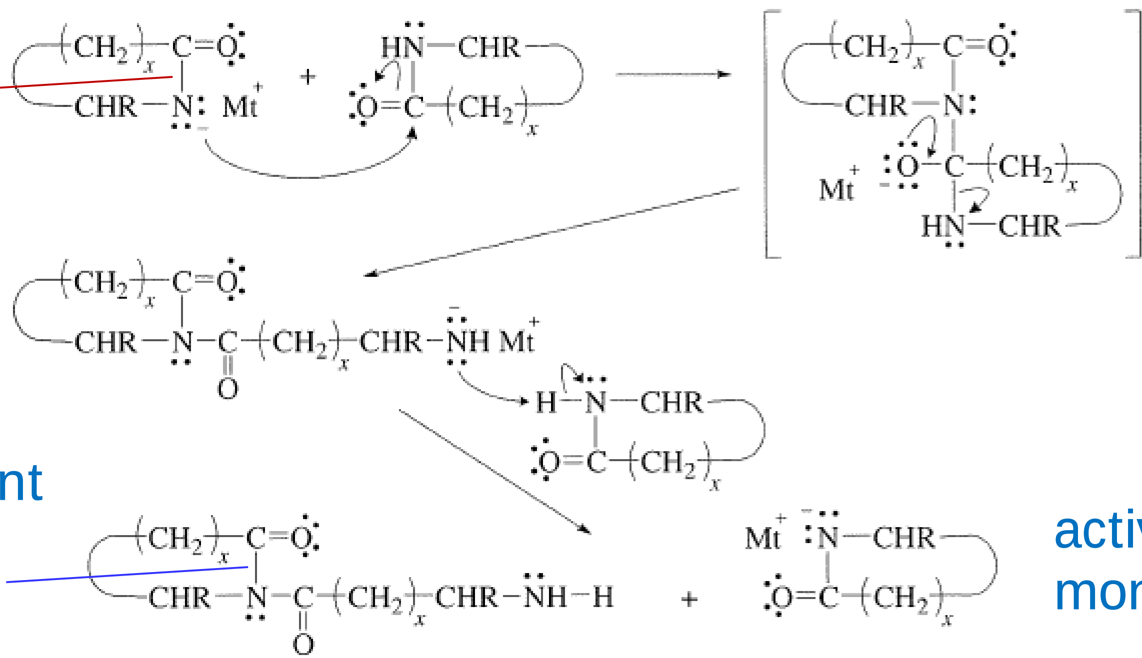
- initiation



- lactamate ion ~ not reactive due to
  - become active by



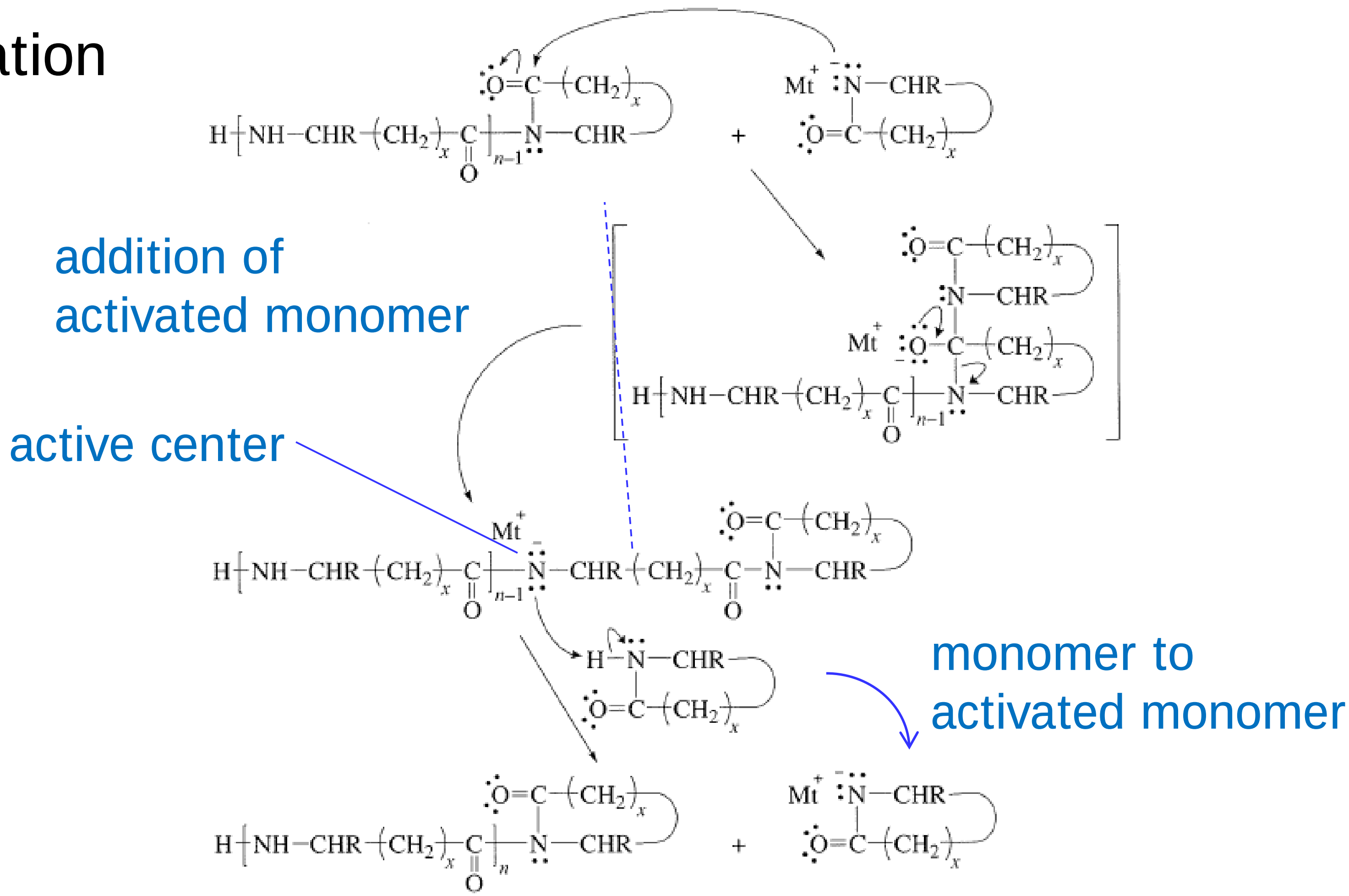
not active



N-acyl lactam:
more e deficient
due to C=O
→ reactive to

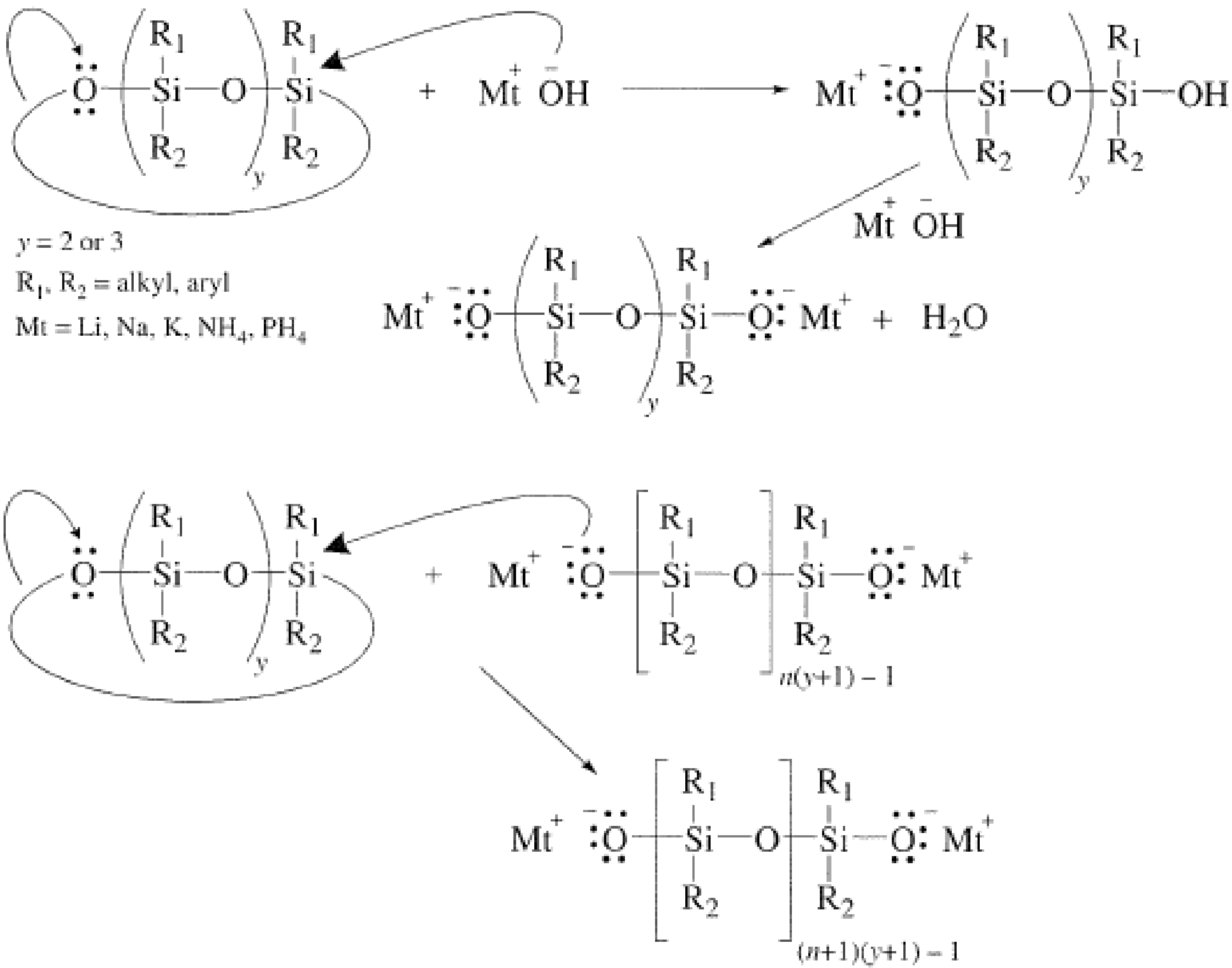
activated
monomer

- propagation



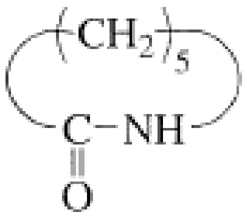
- induction period observed ← formation of *N*-acyl lactam
  - removal of induction period ~ adding acylating agent p181

Anionic ROP of cyclic siloxanes



Hydrolytic ROP

- nylon 6 synthesis

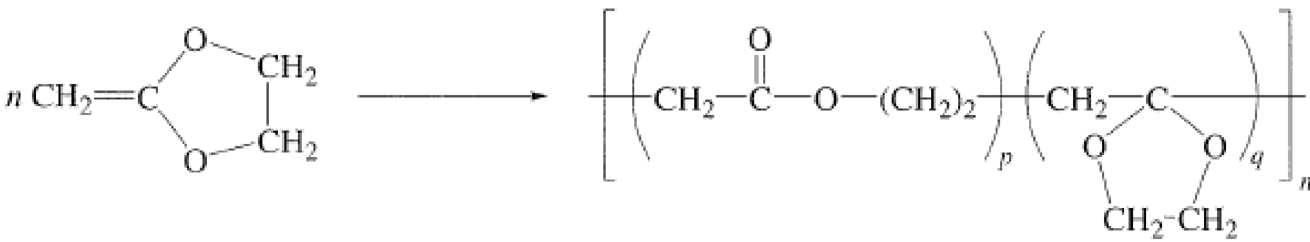


$+ \ H_2O \rightarrow \ HOOC\text{-}(CH_2)_5\text{-}NH_2$ → step polym'n or ROP (cationic)

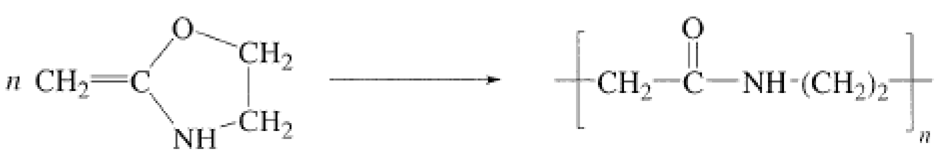
- acid-catalyzed ROP
  - primary amine is not a good initiator (compared to COOH)
  - the major route (much faster)
- step polym'n of aminocaproic acid
  - only a few % contribution
  - determines the final MM
    - removing water at high conversion → high MM

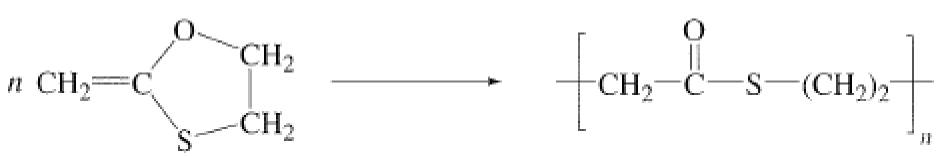
Radical ROP

- monomers with = and ring
  - ring-opening and 'normal' polym'n compete



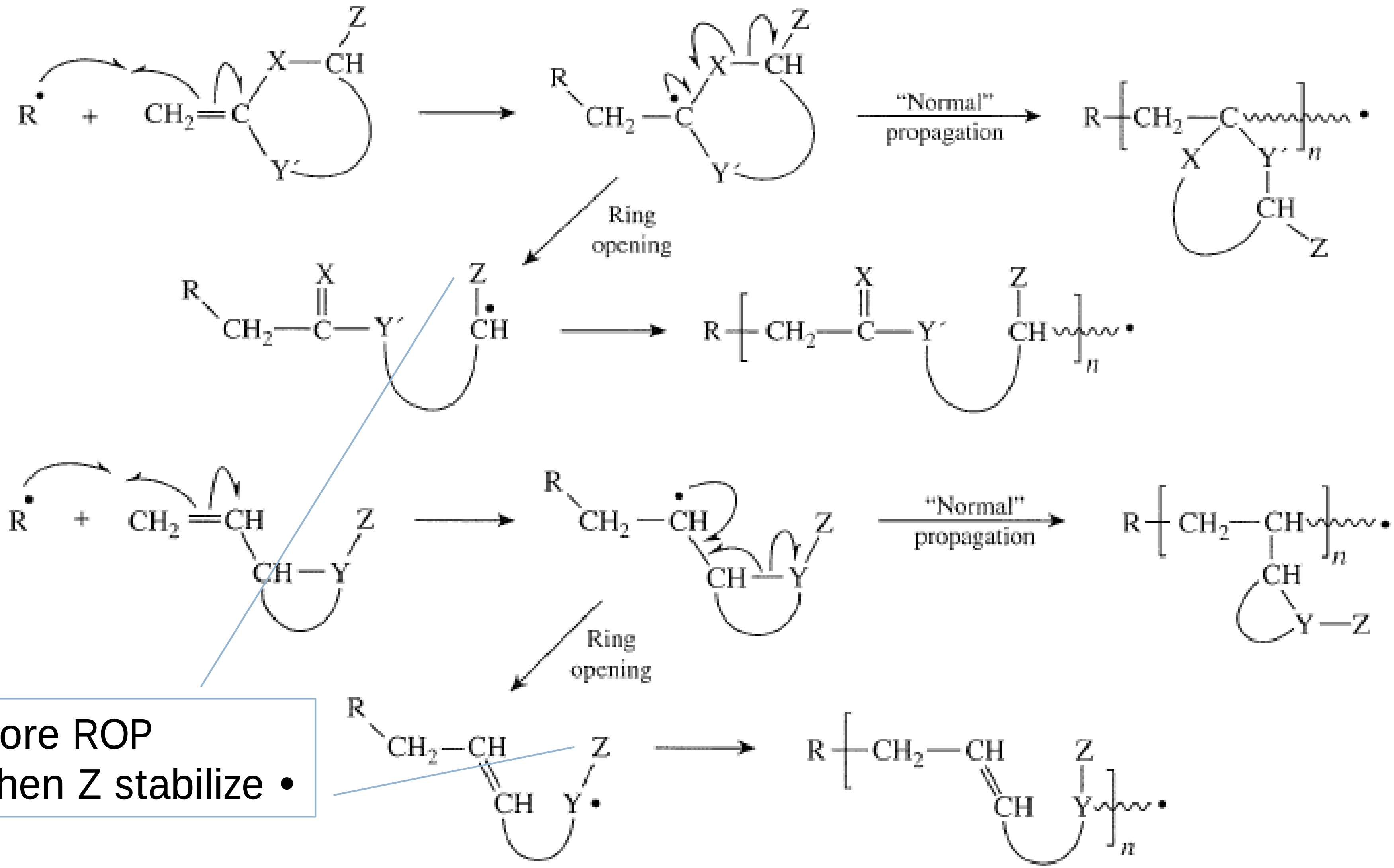
    - composition dep on monomer and Temp
    - ROP more favored at high Temp (σ vs π)





more ROP
amide > ester> thioester

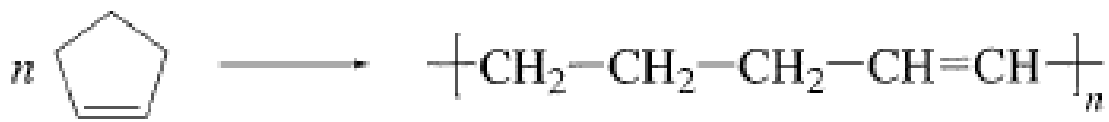
- 2 types of monomers

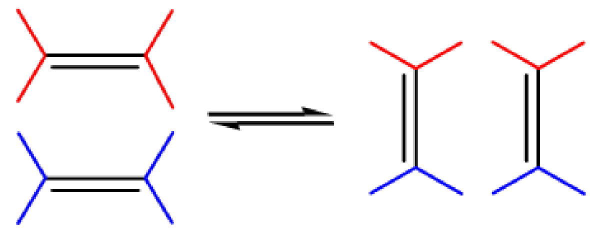


more ROP
when Z stabilize •

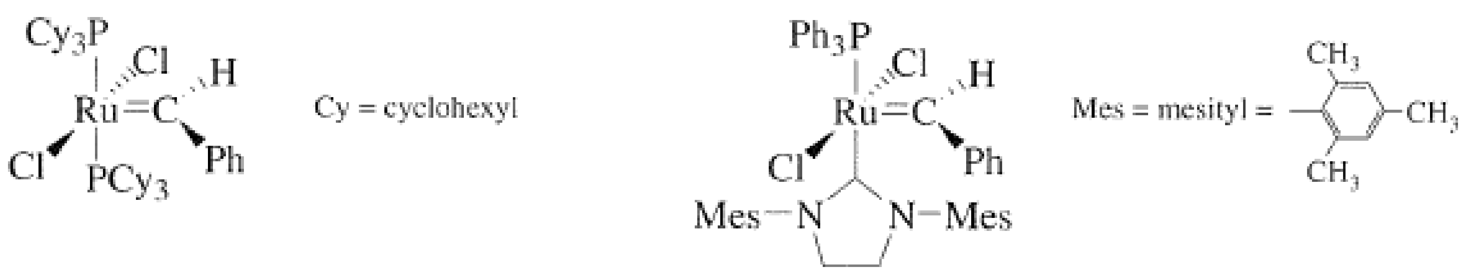
ROMP

- ring-opening metathesis polym'n

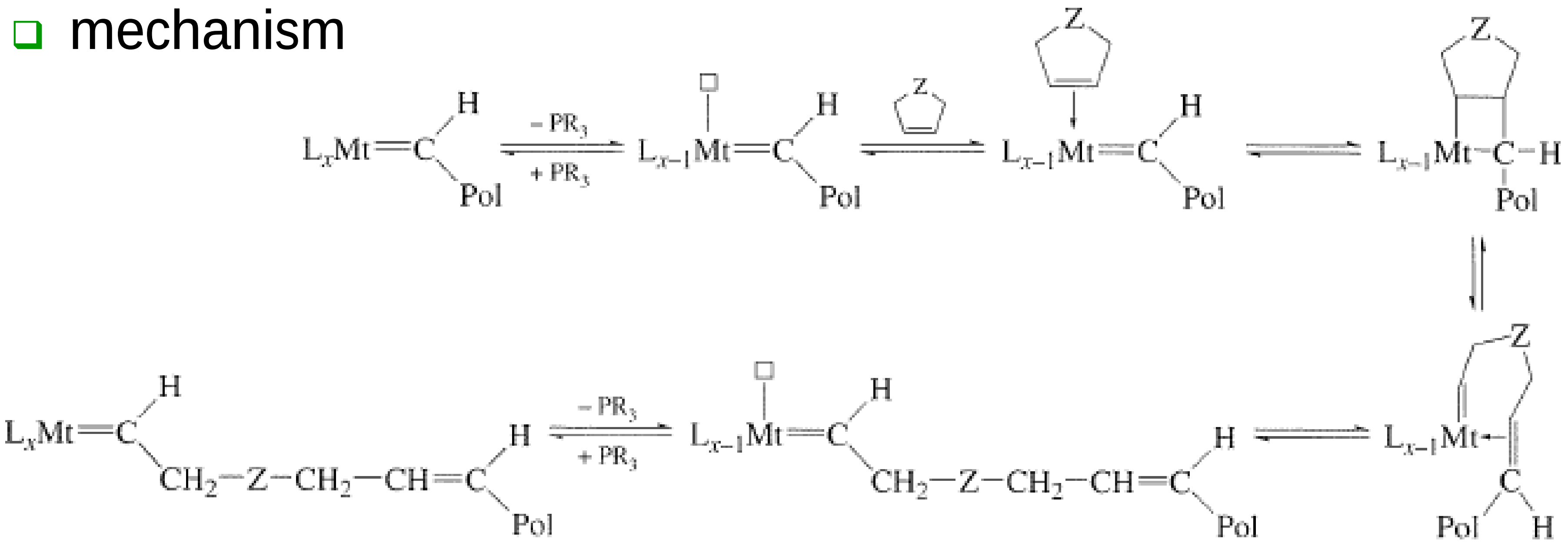




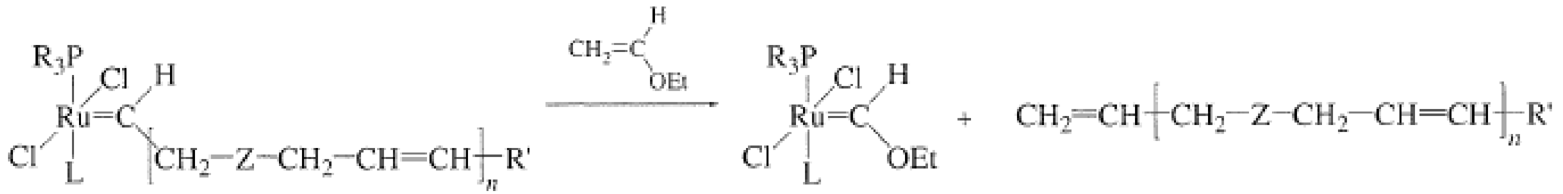
  - using olefin metathesis
    - metathesis ~ exchange of bonds
    - olefin metathesis ~ redistribution of double bonds
  - with 'Grubbs catalyst' (2005 Nobel prize)
    - Ru-based metal carbene [Mt=C], homogeneous



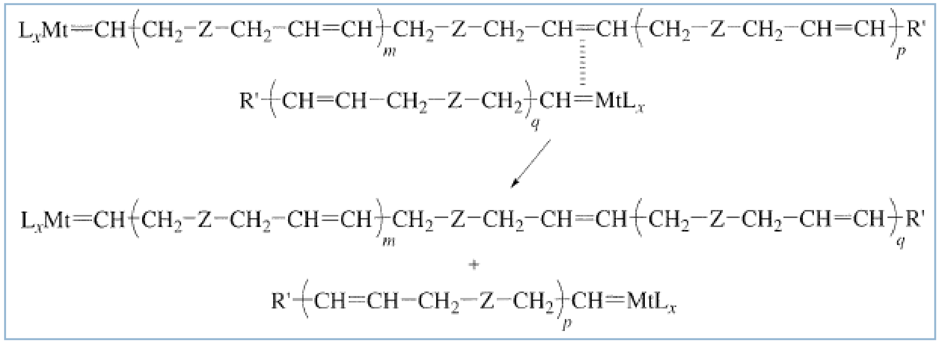
- mechanism

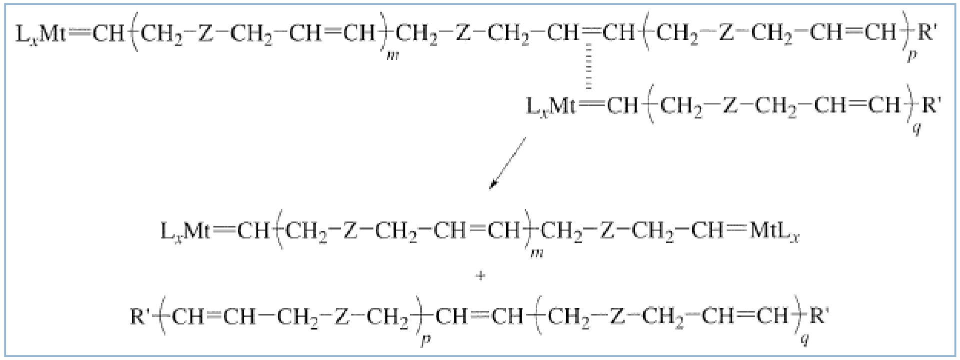


- a living polym'n
  - block copolymer possible
  - deactivation

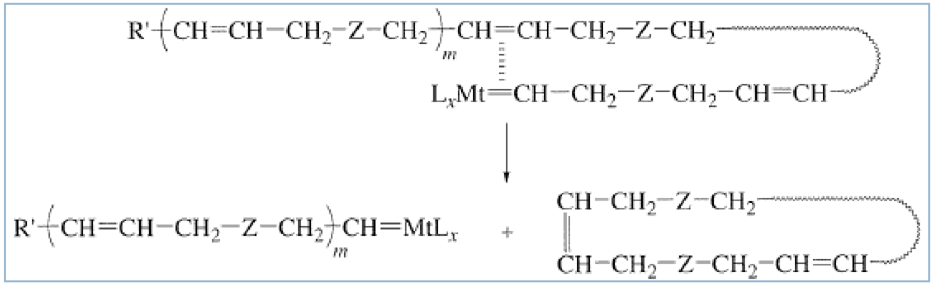


- chain transfer to polymer
  - intermolecular
    - mp+q → mq+p
    - mp+q → m+pq
    - broadening MMD

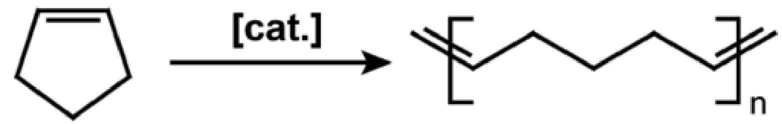




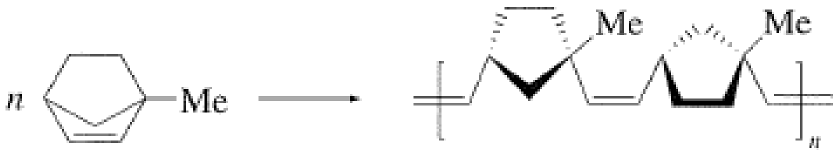
  - intramolecular



- cycloalkene
  - radical polym'n?
  - ZN catalyst?
    - mixture of ROMP and = polym'n
  - Grubbs catalyst → exclusively ROMP



- isomers
  - cis, trans; ditacticity



- conducting polymers