

Supporting material for students registered to subject:

Macromolecular chemistry S112003

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Sources:

Prokopová I.: Makromolekulární chemie, VŠCHT Praha, 2007. (educational text in Czech)

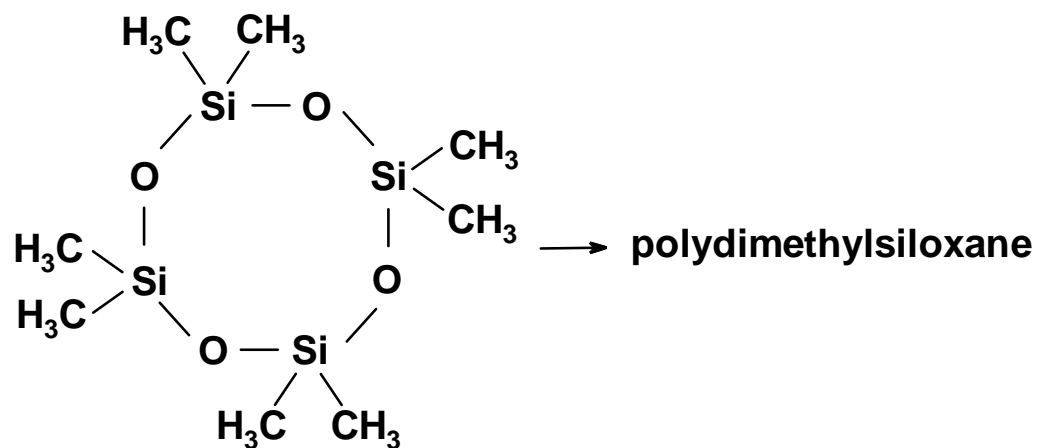
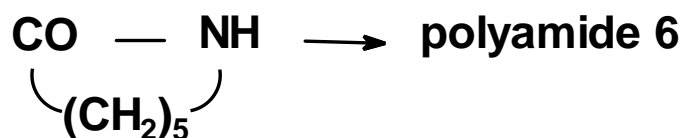
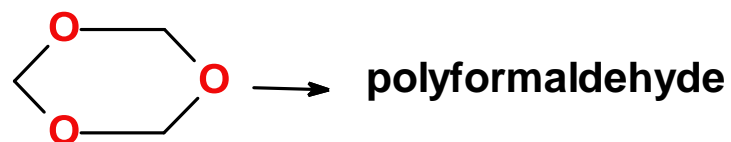
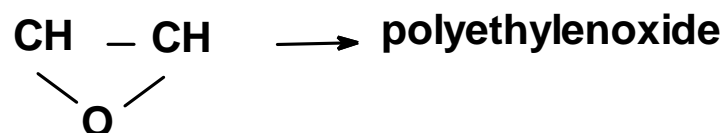
Merna J.: Polymers Instantly, educational text in English, freely accessible from

<http://merna.eu/teaching/macromolecular-chemistry/>

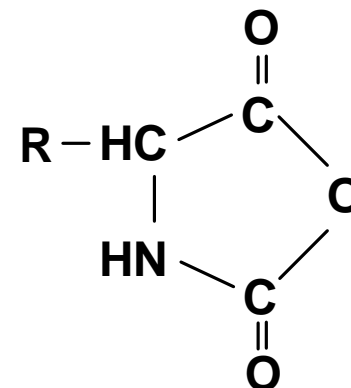
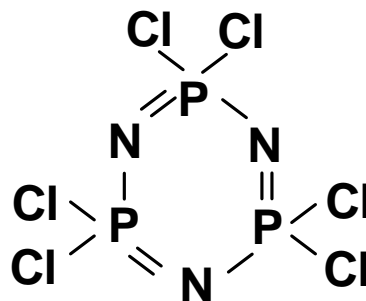
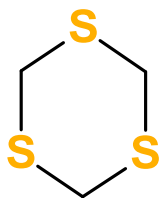
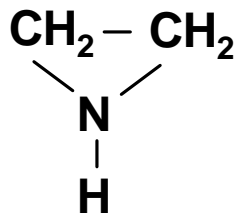
Encyclopedia of Polymer Science and Technology, J.Wiley Sons, Interscience, Publ., New York, 1964-1991

Ring opening polymerizations (ROP)

Industrially important cyclic monomers:



Other monomers:



Polymerizability of cyclic monomers

Depends on:

strain of cycle

used initiation system

reactivity of functional groups

ring substitution

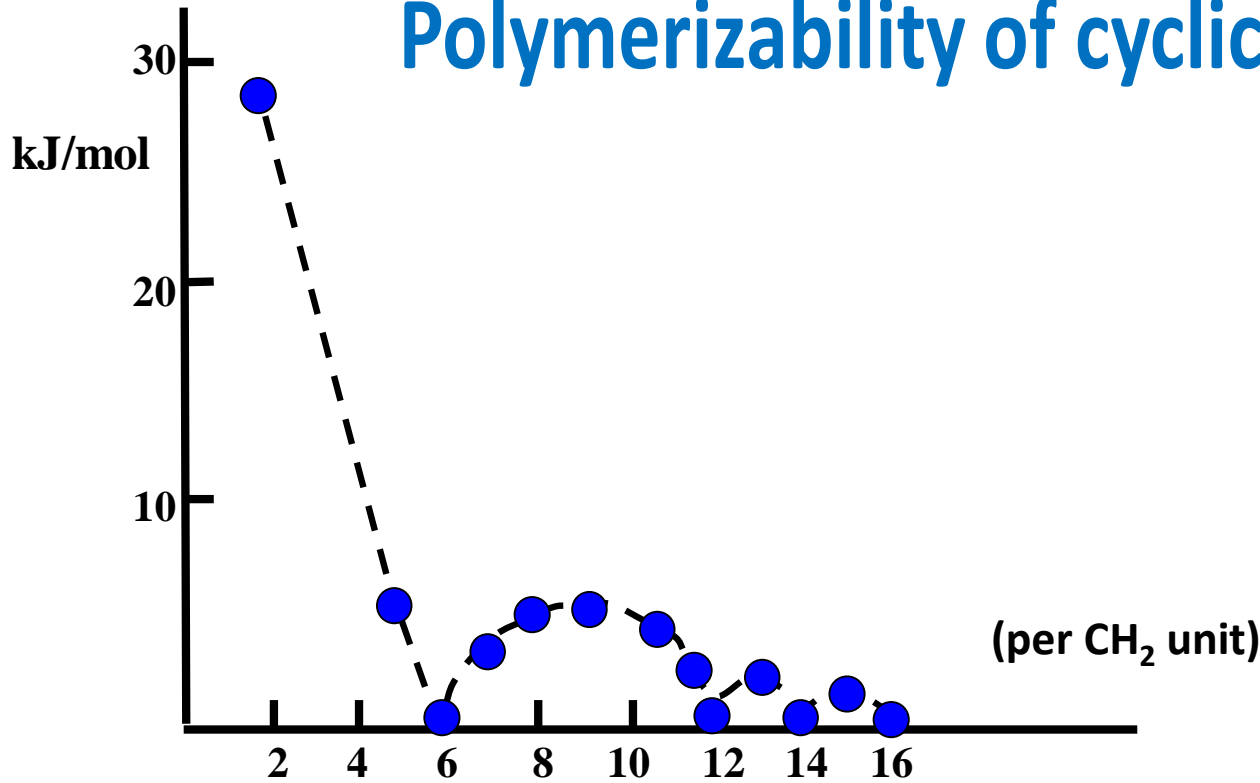
Polymerizable monomers:

heterocycles (ionic initiators)

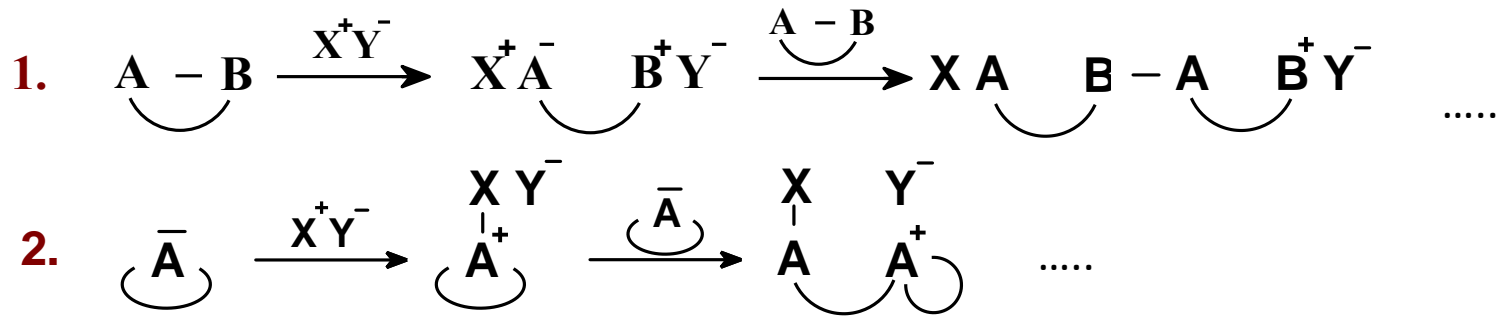
cykloalkenes (metathesis)

Cykloalkanes do not polymerize

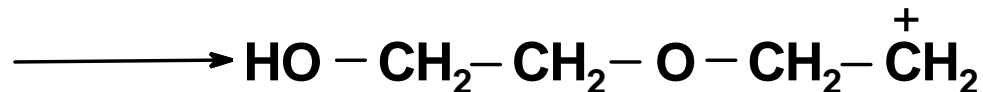
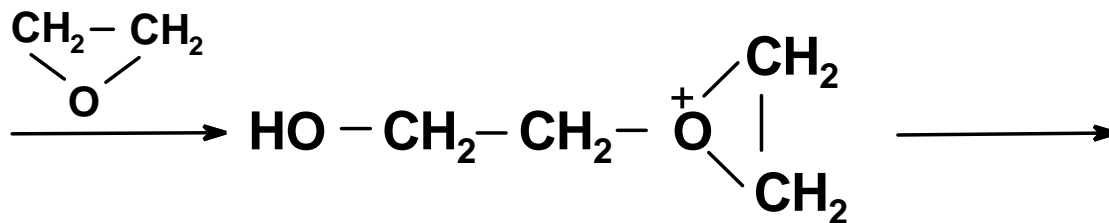
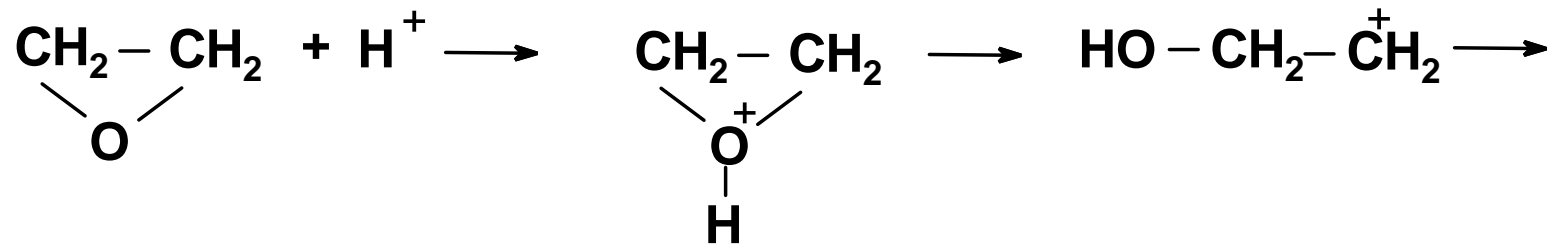
Polymerizability of cyclic monomers



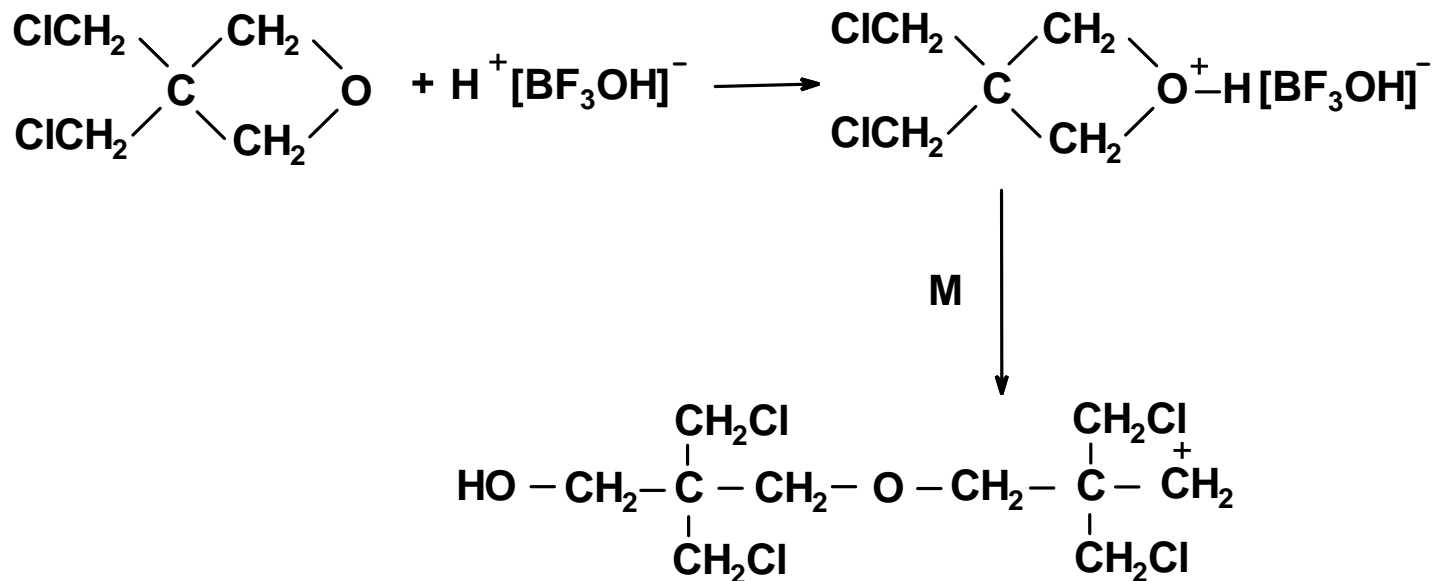
Mechanisms of initiation of cyclic monomers polymerization:



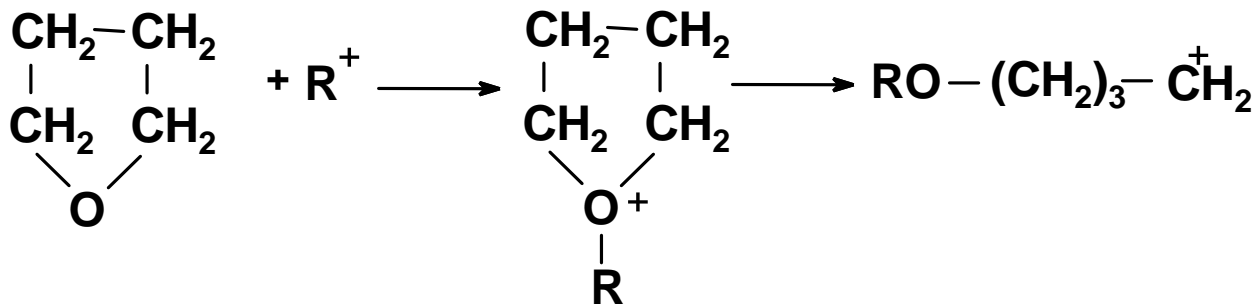
Cationic polymerization of oxirane



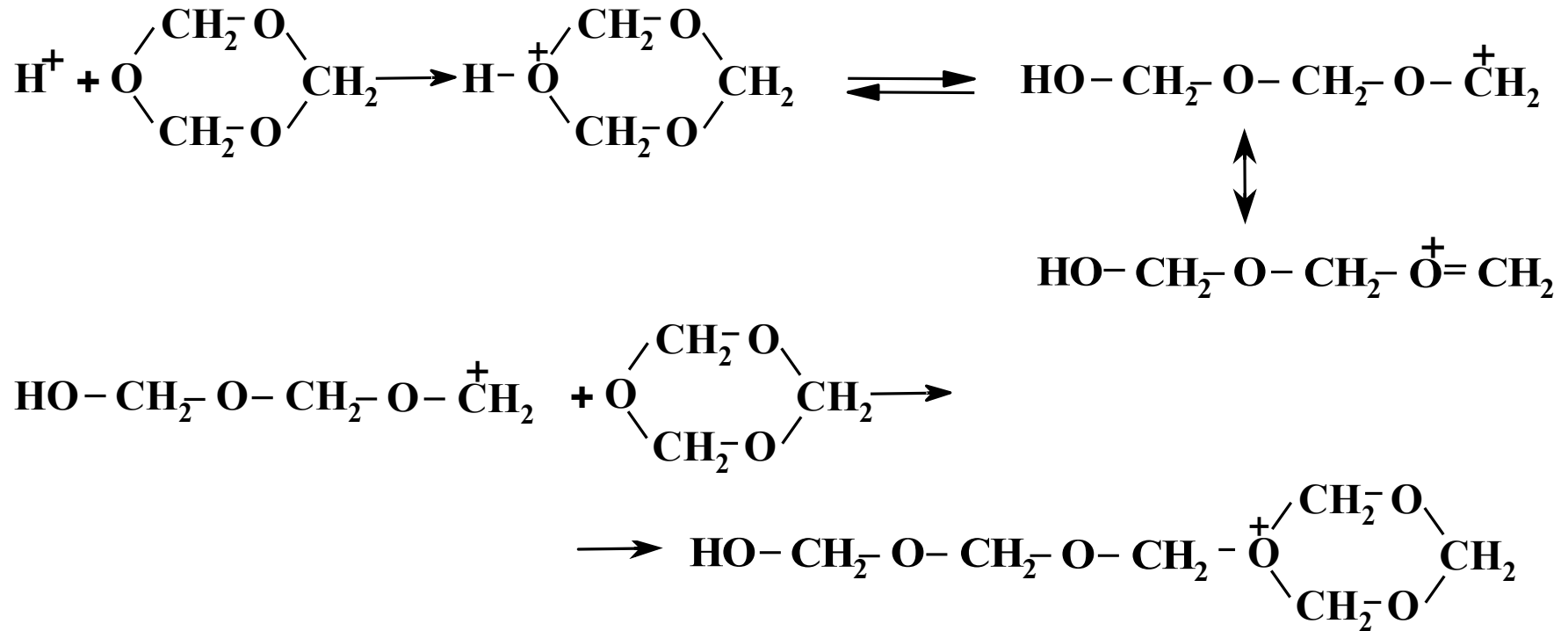
3,3-bis(chloromethyl)oxacyklobutane



THF:



Cationic polymerization of trioxane



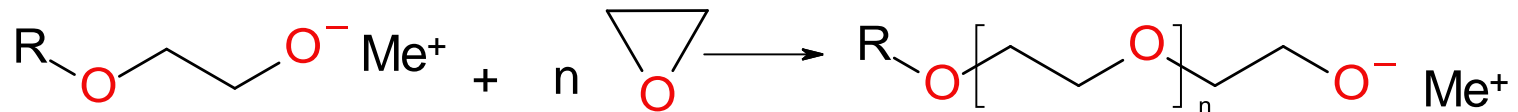
Cationic polymerization: active centers are highly reactive



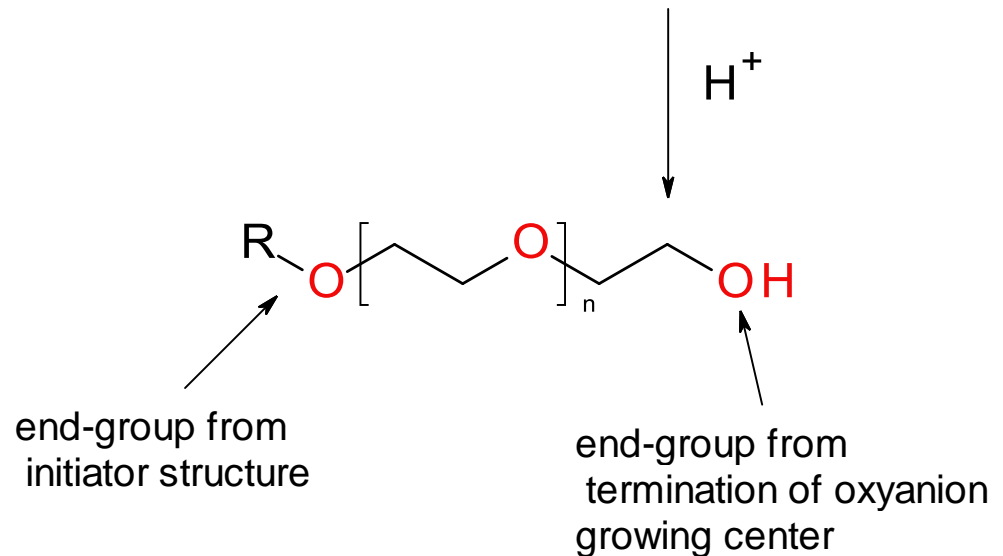
transfer

Anionic polymerization of oxirane

Allowed due to high cycle strain - despite the nucleophilic character of the monomer

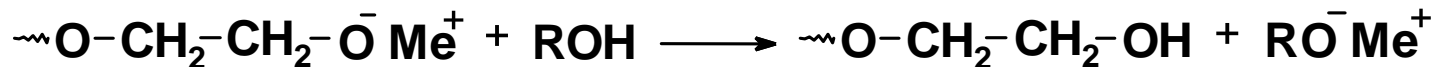


Me⁺ = alkaline,
alkaline earth metal

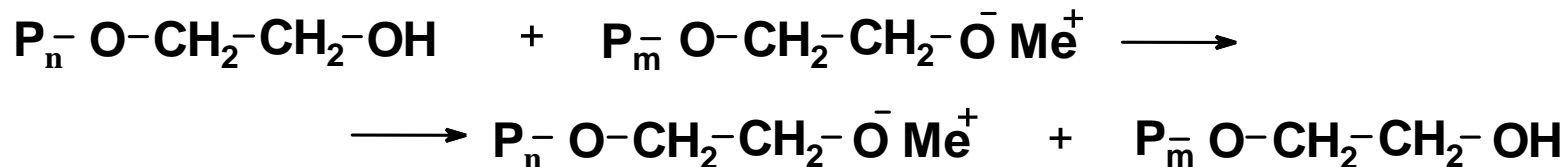


Transfer reactions in anionic oxirane polymn.:

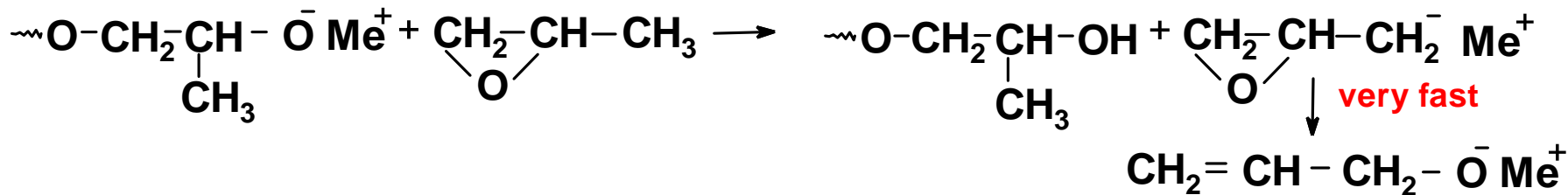
a) to solvent



b) to polymer

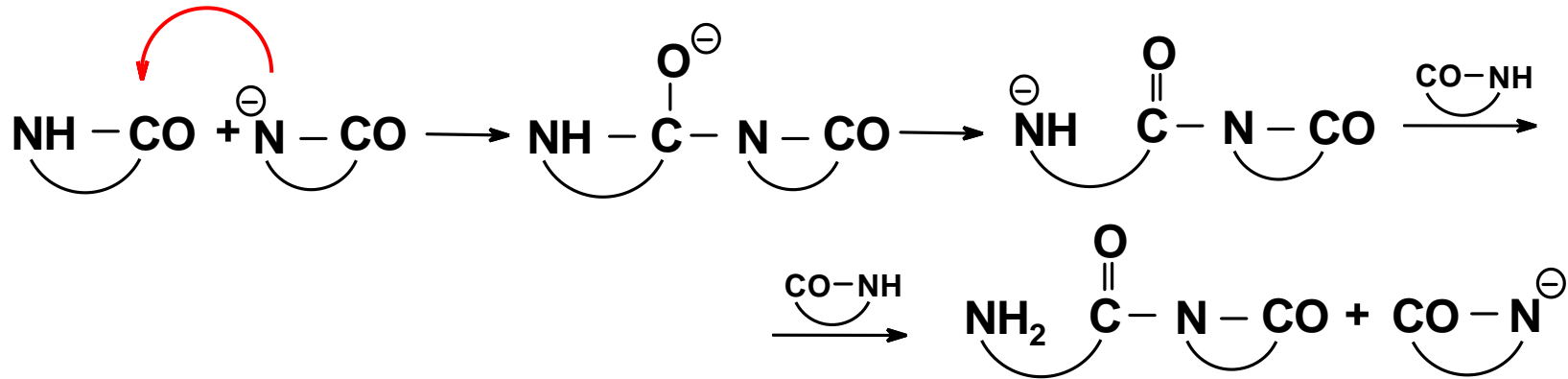


c) To monomer (substituted cycles)

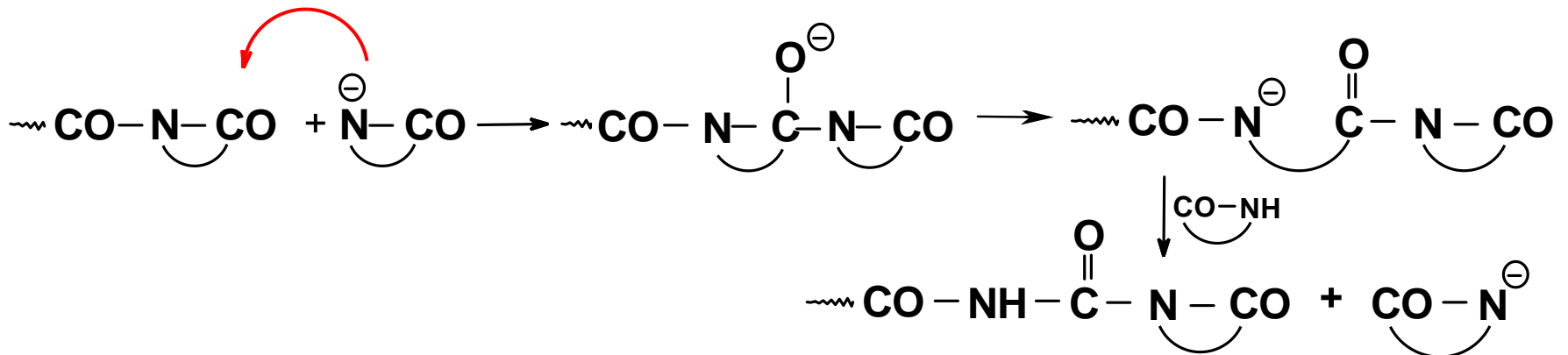


Anionic polymerization of lactams

(Activated monomer mechanism)



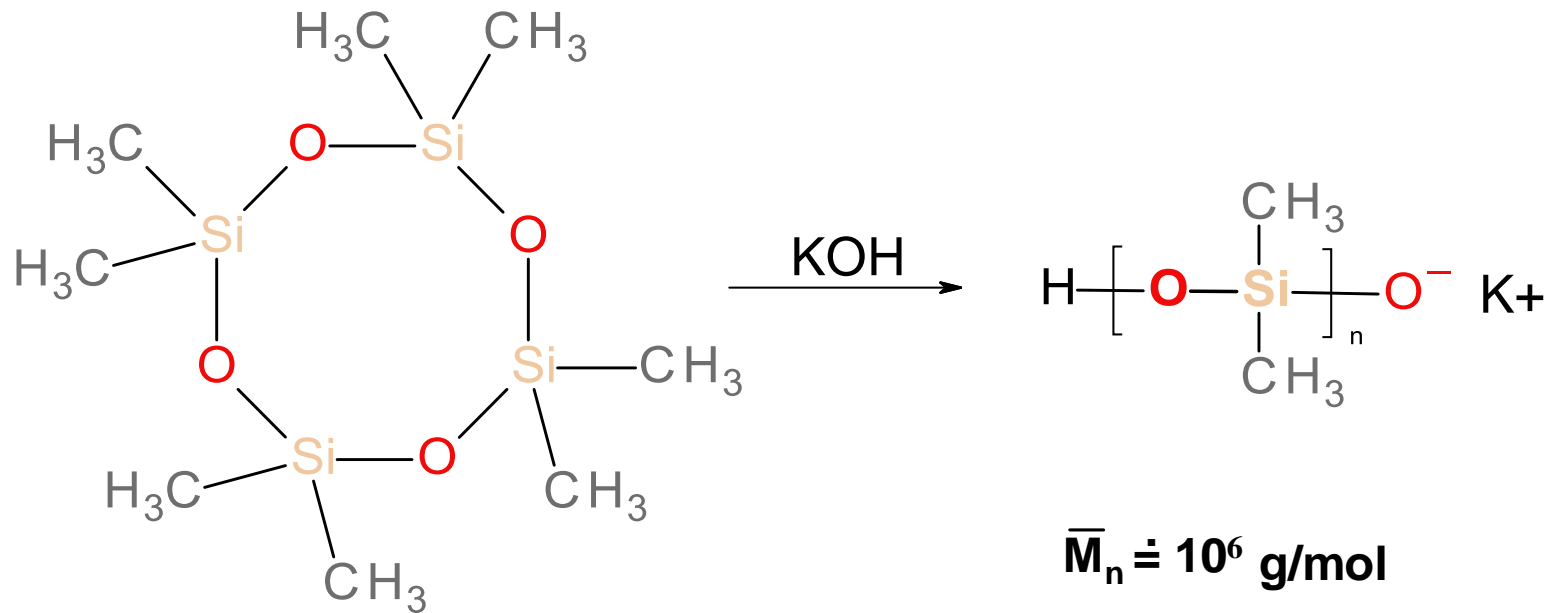
N-acyllactam growing center formation (RLS)



Neutral chain-end

Anionic monomer

Anionic polymerization of cyclic siloxanes



$$\Delta H_p \doteq 0 \text{ kJ/mol}$$

$$\Delta S_p = + 6,7 \text{ J/molK}$$

Driving force = increase of entropy !!