Introduction to Macromolecular Chemistry

aka polymer chemistry

Mondays, 8.15-9.45 am, NC 02/99

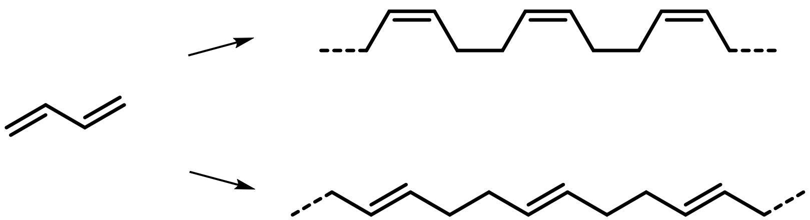
Dr. Christian Merten, Ruhr-Uni Bochum, 2019

www.ruhr-uni-bochum.de/chirality

Stereoisomerism

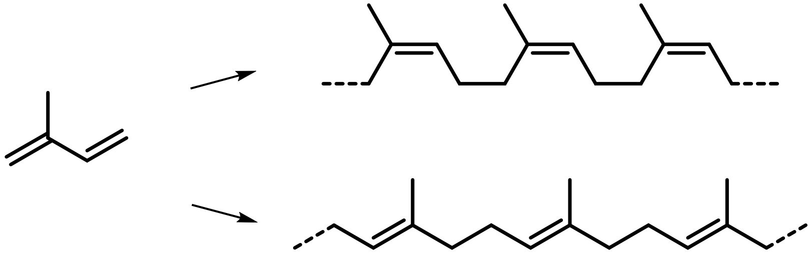
Similar to low-molecular weight molecules, polymers can feature stereoisomerism:

- Cis/trans isomerism:



cis-1,4-polybutadiene
amorphous, sticky

trans-1,4-polybutadiene
semi-crystalline, high melting point



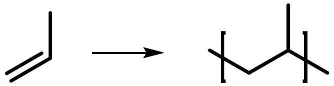
cis-1,4-polyisoprene (natural rubber)
amorphous, sticky

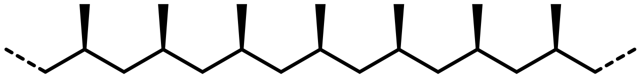
trans-1,4-polybutadiene (Gutapercha)
semi-crystalline, high melting point

Stereoisomerism

Similar to low-molecular weight molecules, polymers can feature stereoisomerism:

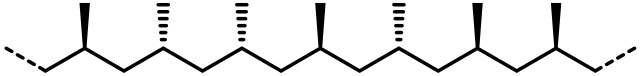
- Tacticity





Isotactic polypropylene (*it*-PP)
Highly crystalline (T_M ~ 160°C)

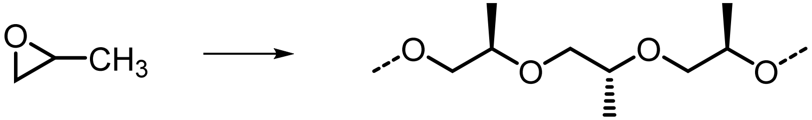
Syndiotactic polypropylene (*st*-PP)



Atactic polypropylene (*at*-PP)
amorphous, sticky

Note: Although high stereoregularity, no optical activity (mirror plane due to long chain length)!

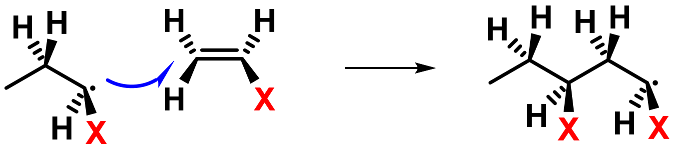
…but: *it*-PO does not have a mirror plane anymore:



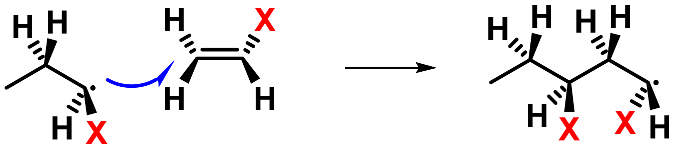
Controlling tacticity: Radical polymerizations

In free radical polymerization, monomer addition can take place from both sides of C_{sp2} :

- Isotactic bond formation



- Syndiotactic bond formation



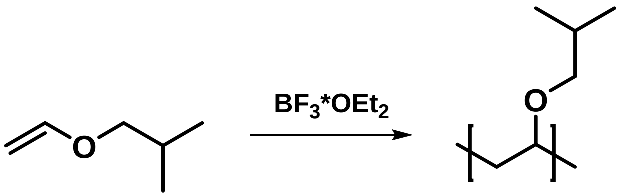
For steric reasons, the *st*-bond formation is preferred.

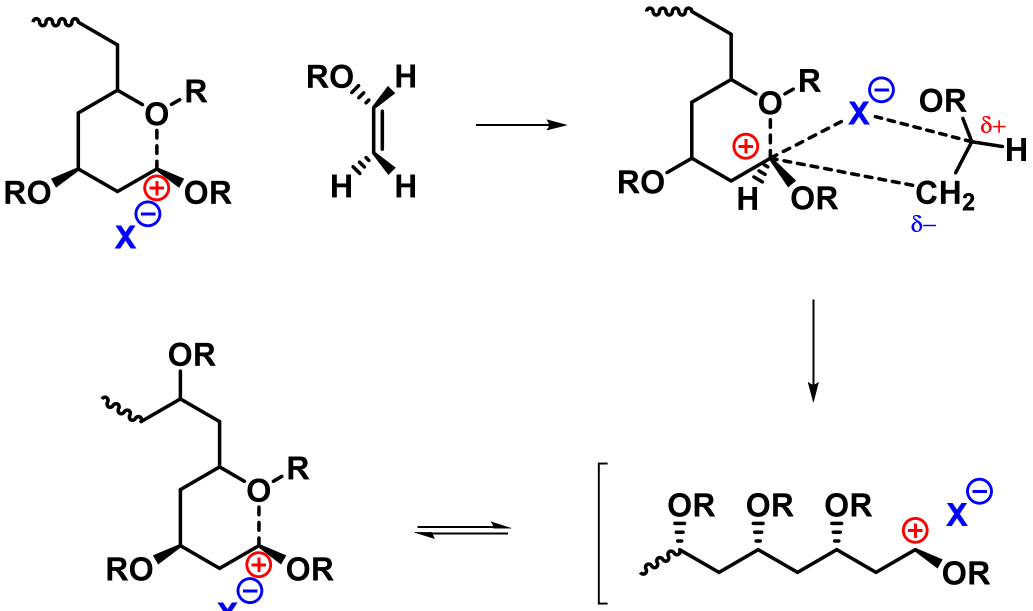
Low temperatures further increase this preference.

Controlling tacticity: Cationic polymerizations

First example for stereospecific cationic polymerization:

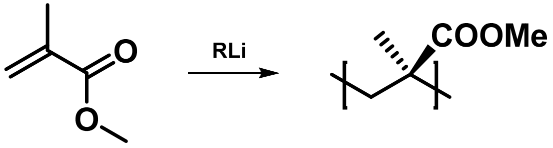
- Steric hindrance of one side of C=C
- Cyclic transition state which promotes attack on C2





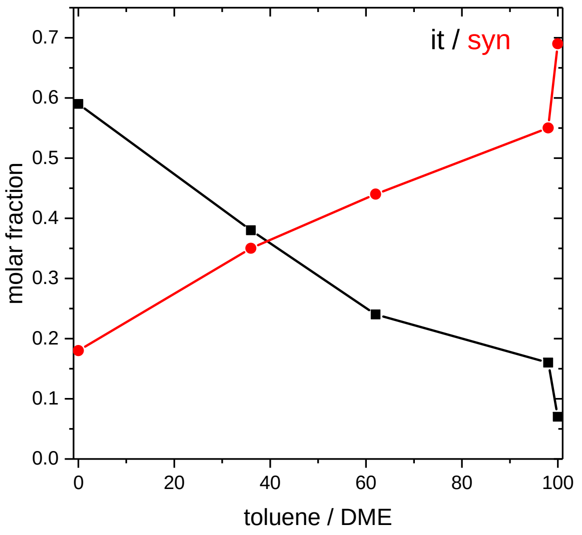
Controlling tacticity: Anionic polymerizations

Factors determining the stereoregularity of anionic polymerizations:



- Polarity of the solvent (degree of dissociation of RLi)
- Low temperature facilitate regularity
- Initiator

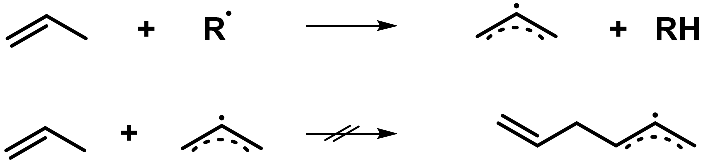
Generally very similar to radical polymerization, i.e. syndiotactic addition preferred.



Example:
PMMA (BuLi, 243K) in toluene/dimethoxyethan(DME)
from Tieke, Makromolekulare Chemie, 2nd edition

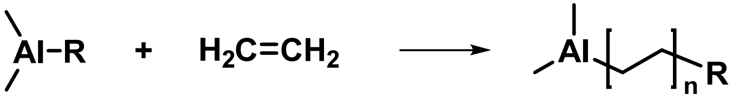
Catalytic polymerizations: Ziegler‘s „Aufbaureaktionen“

Simple α-olefines cannot be polymerized by free radical or anionic polymerizations due to formation of resonance stabilized radical:



Karl Ziegler
(1898 – 1973)

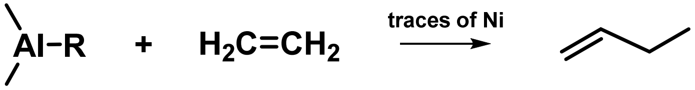
In the early 1950s, Ziegler was interested in oligomerization of ethene by aluminium alkyles



$R = H, CH_3, C_2H_5$

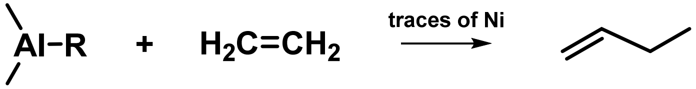
$n << 100$

… and found that trace amounts of nickel can prevent it (only dimerization):



Catalytic polymerizations: Ziegler‘s „Aufbaureaktionen“

- ➢➢ The „nickel effect“ (K. Fischer et al., Angew. Chem. Int. Ed. 12 (1973) 943-1026)



This made him curious about the role of transition metals on oligomerization, and finally lead to the discovery of a highly potent reaction system:

Ti-compound + Al-alkyl

- ➢➢ Mixture was capable of polymerizing ethene at room temperature and atmospheric pressure yielding polymers of high molecular weights which precipitated from solution (as opposed to radical polymerization which requires 300°C/ 2kbar)

Catalytic polymerizations: Ziegler‘s „Aufbaureaktionen“

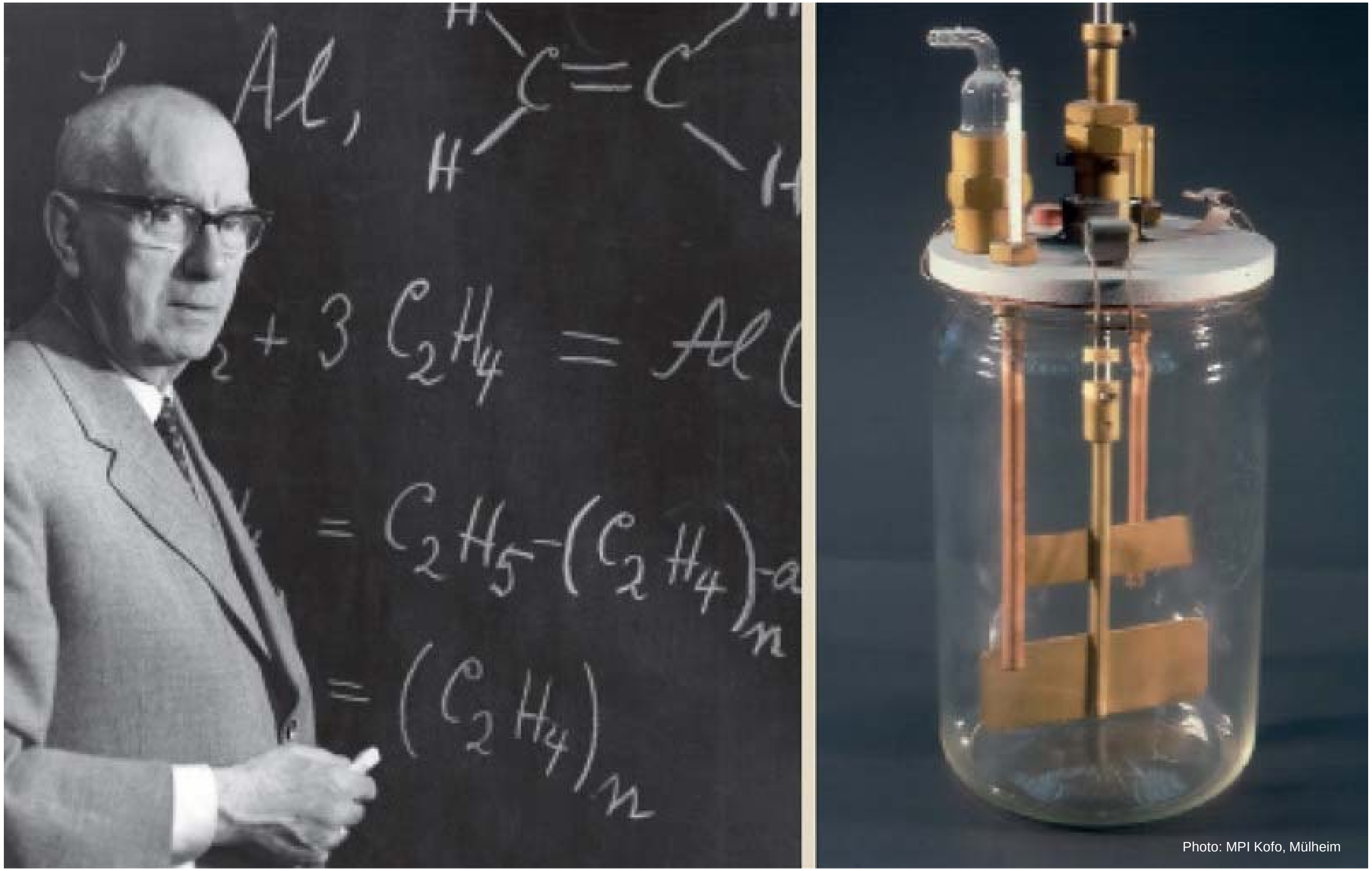


Photo: MPI Kofo, Mülheim

Ziegler was so proud of his discovery, that he used to demostrate the experiment in a jar – just to show that it works at ambient pressure!

Catalytic polymerizations: Ziegler‘s „Aufbaureaktionen“

Reaction mechanism

Common starting materials for catalyst preparation:

- Al-organic compound: $AlEt_3$, $AlEt_2Cl$, $Al(OEt)Et_2$, $AlH(iC_4H_9)_2$
- Transition metal compound: $TiCl_4$, $TiCl_3$, $Ti(OC_4H_9)_2$, $VOCl_3$, VCl_4, $ZrCl_4$, $NiCl_2$, WCl_6, $MnCl_2$
- Water-free non-polar solvent like hexane or benzene

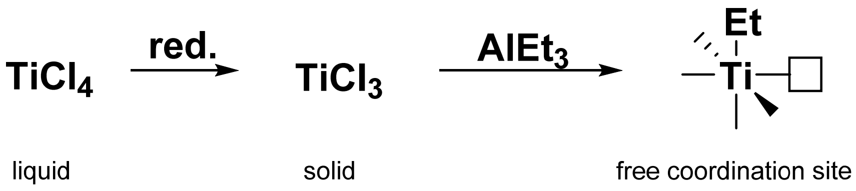
Mixing of these compounds leads to complex activation reactions, with Ti^{IV} being the most important species for polymerization:

$$\left.\begin{aligned}
&TiCl_4 + AlEt_3 &&\rightarrow EtTiCl_3 + AlEt_2Cl \\
&TiCl_4 + AlEt_2Cl &&\rightarrow EtTiCl_3 + AlEtCl_2 \\
&EtCl_3 + AlEt_3 &&\rightarrow Et_2TiCl_2 + AlEt_2Cl \\
&EtTiCl_3 &&\rightarrow TiCl_3 + Et^* \\
&Et_2TiCl_2 &&\rightarrow EtTiCl_2 + Et^* \\
&Et^* + TiCl_4 &&\rightarrow TiCl_3 + EtCl
\end{aligned}\right\}\ \text{heterogenous catalysis}$$

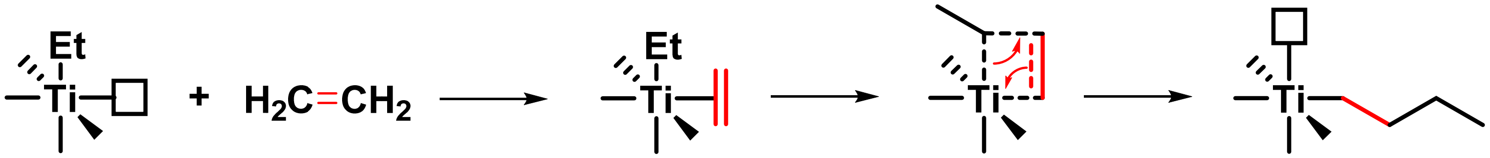
Catalytic polymerizations: Ziegler‘s „Aufbaureaktionen“

Reaction mechanism

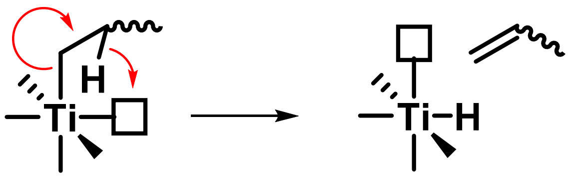
- Initiation



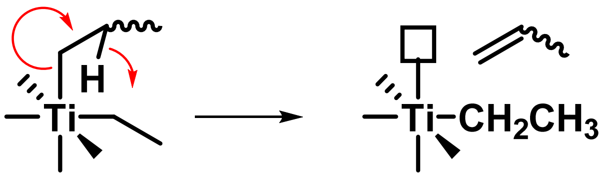
- Chain growth (➢ chain migration mechanism)



- Termination resp. chain transfer



β-hydride elimination



β-hydride transfer

Catalytic polymerizations: Ziegler‘s „Aufbaureaktionen“

Molecular weight distribution

Like radical or ionic polymerization, M_n depends on kinetic chain length:

- Increase in T, β-H elimination and transfer are becoming more favored
- Increase in T hence leads to decrease of M_n

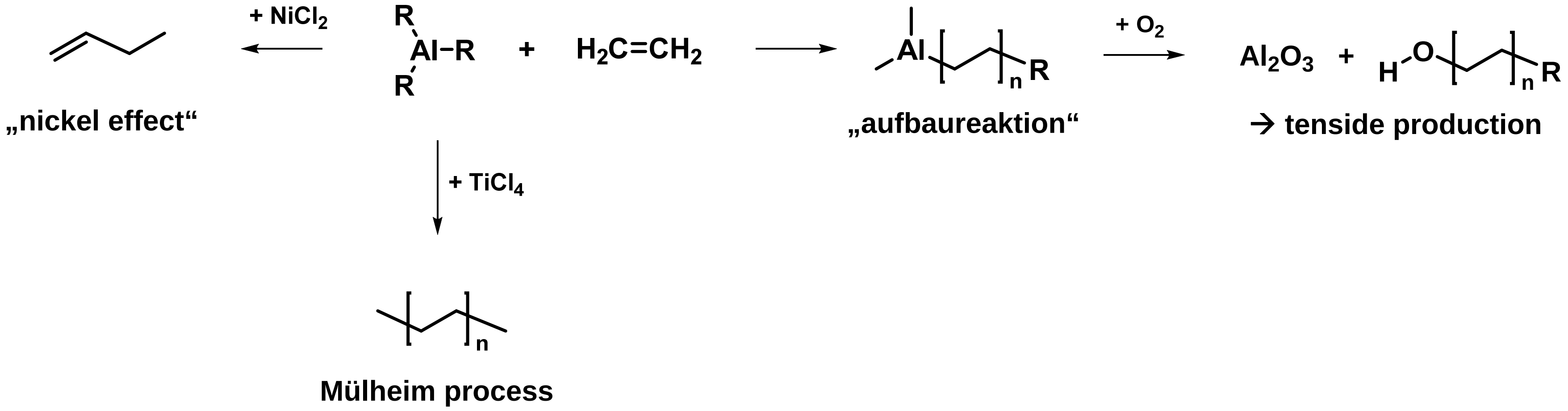
Addition of hydrogen allows control of molecular weight (hydrogenolysis):

$$\mathrm{Ti{-}CH_2}\sim \quad + \quad \mathrm{H_2} \longrightarrow \mathrm{Ti{-}H} \quad + \quad \mathrm{H{-}CH_2}\sim$$

$$\mathrm{Ti{-}H} \quad + \quad \mathrm{H_2C{=}CH_2} \longrightarrow \mathrm{Ti{-}CH_2CH_3}$$

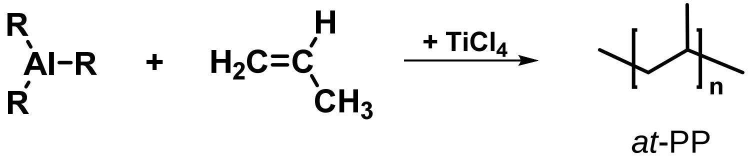
Catalytic polymerizations: Ziegler‘s „Aufbaureaktionen“

Summary of Ziegler‘s „Aufbaureaktionen“



time for

Giulio Natta (1903-1973)



Why has it been overlooked by Ziegler?

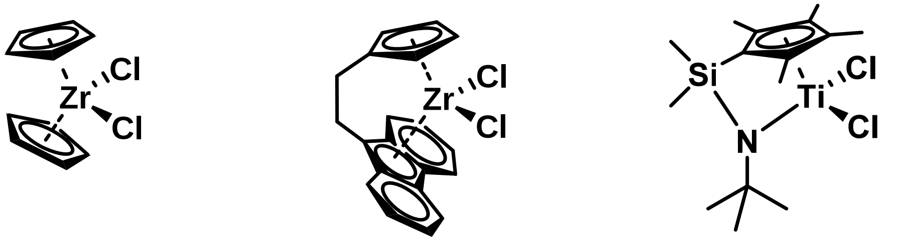
HDPE is insoluble in reaction medium

at-PP is soluble!

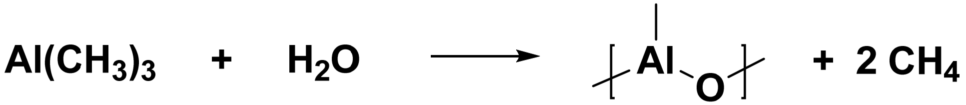
Catalytic polymerizations: Ziegler-Natta catalysts

Homogeneous Ziegler-Natta catalysis

Most homogeneus catalyst are sandwich or half-sandwich complexes of Ti or Zr.



Aluminum co-catalyst: methyl aluminoxane (*MAO*, n~20)



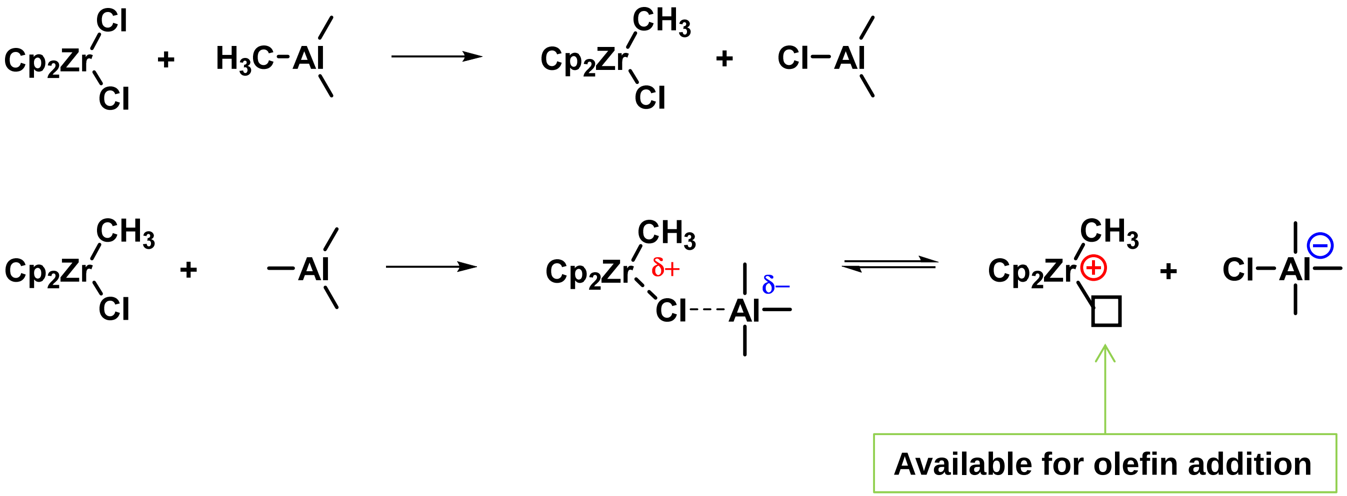
$$Al(CH_3)_3 + H_2O \longrightarrow \left[\overset{|}{Al} - O \right] + 2\,CH_4$$

Mechanistic assumption: (Di)methylation of TM species followed by removal of chloride (methyl) anion.

Catalytic polymerizations: Ziegler-Natta catalysts

Homogeneous Ziegler-Natta catalysis

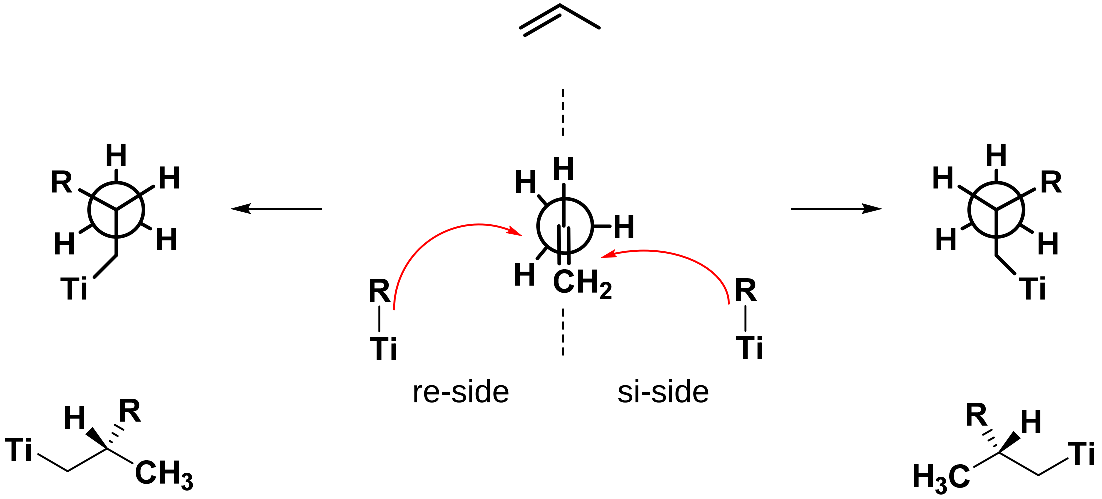
These soluble systems could be used to confirm the initially proposed mechanism:



Catalytic polymerizations: Ziegler-Natta catalysts

Stereoregulation in the polymerization of propene

Stereochemistry of the addition of a titanium alkyl compound to propene:



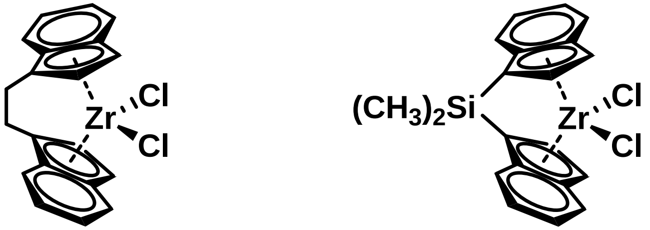
A stereoregular polymer is obtained if

(A) The polymerization always takes place from the same side (re or si) → isotactic

(B) If the sides are alternated for each step → syndiotactic

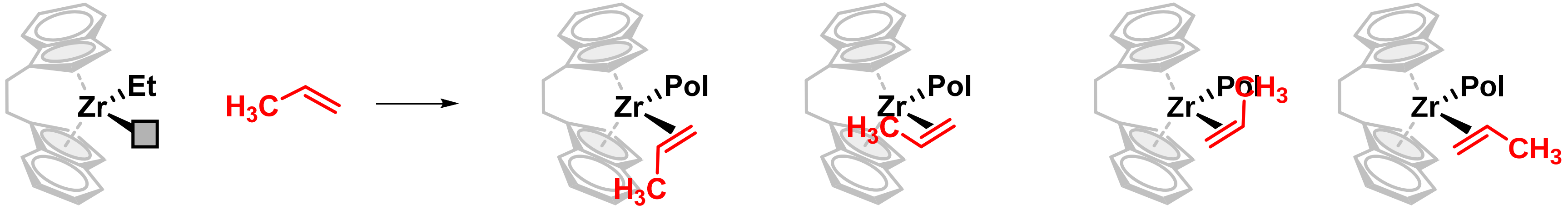
Catalytic polymerizations: Ziegler-Natta catalysts

Catalysts for isotactic PP

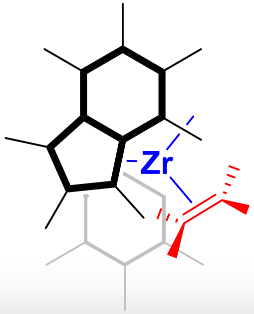


Key: C_2 symmetry!

Isoselectivity achieved by selecting only specific binding orientations:



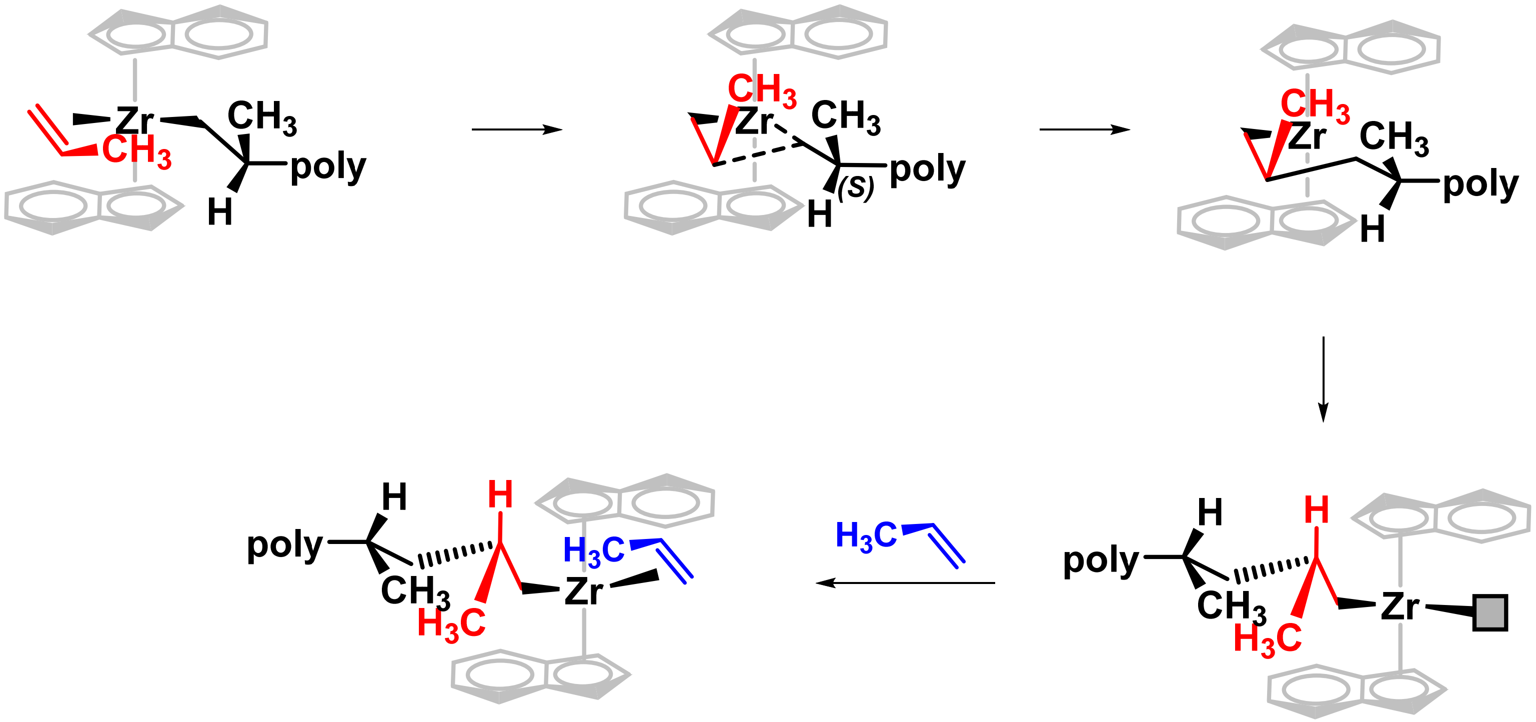
The interactions of the CH_3 group with the indenyl rings are minimized ➢ **Preferred binding orientation**



Catalytic polymerizations: Ziegler-Natta catalysts

Catalysts for isotactic PP

Step by step:

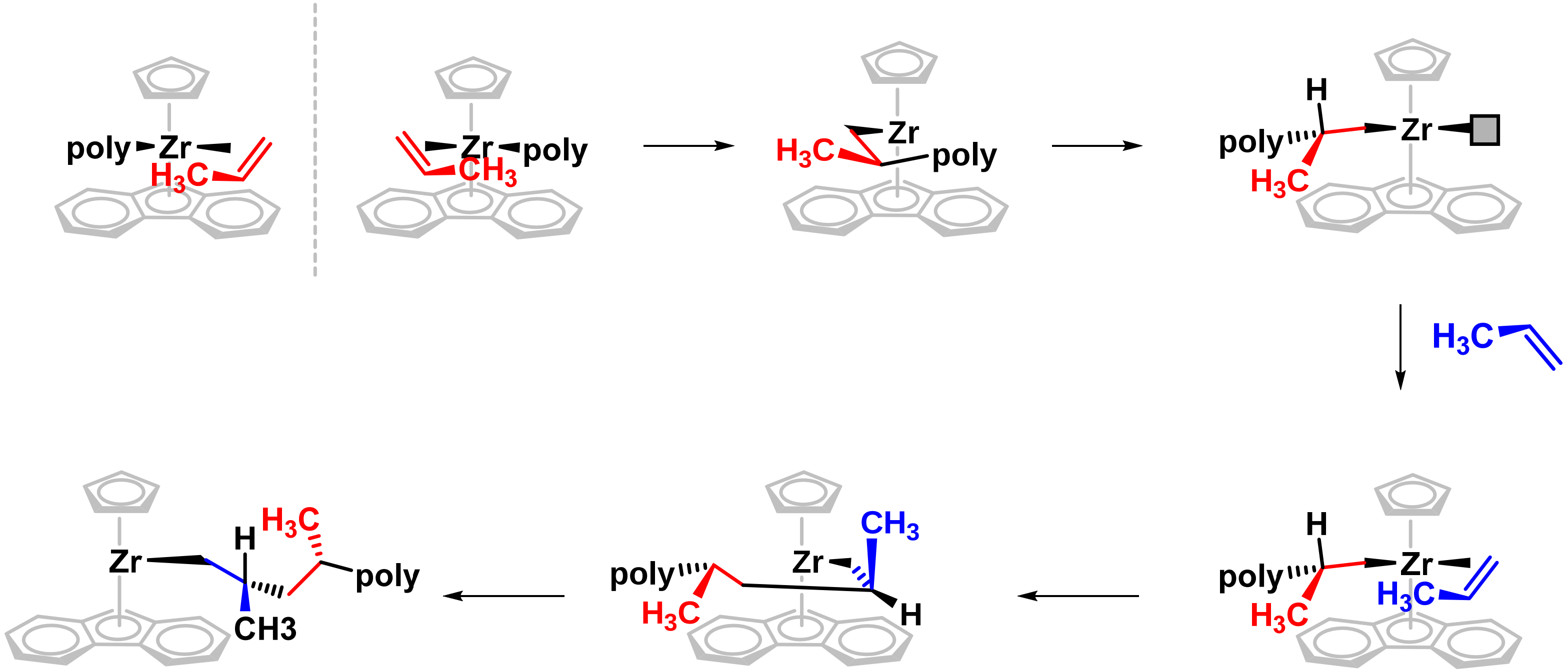


More details on the stereoregularity of the mechanism:
Angermund et al., *Chem Rev.* **100** (2000) 1457-1470

Catalytic polymerizations: Ziegler-Natta catalysts

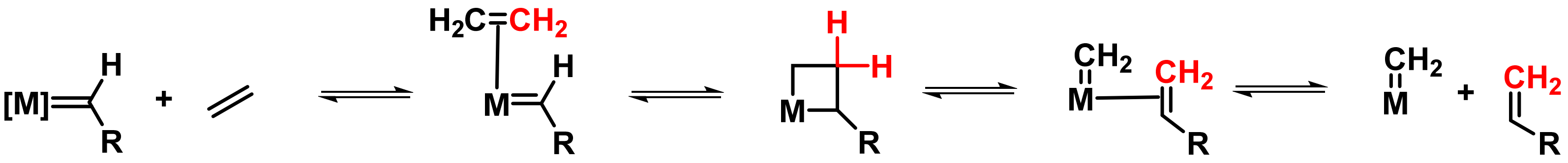
Catalysts for syndiotactic PP

While both binding position were identical in the C2-symmetric catalysts, syndiotactic catalysts need to feature enantiotop positions:



Catalytic polymerizations: Olefin metathesis

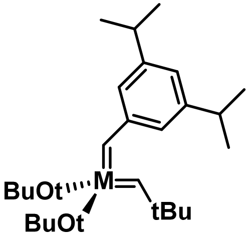
Olefin metathesis : Formal exchange of alkylidene groups between two olefins



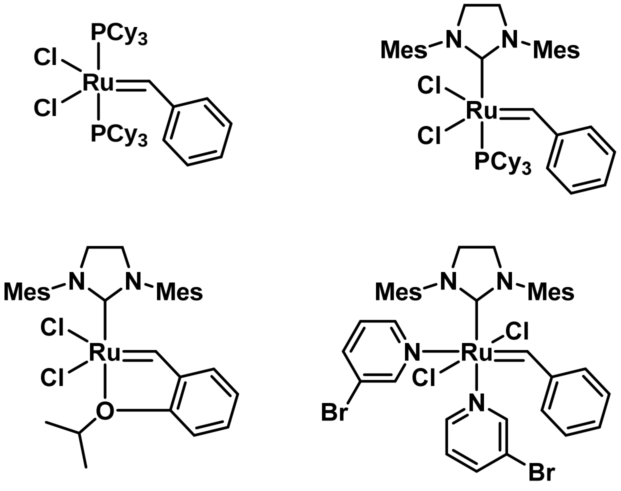
Catalysts can be devided into three groups:

Homogeneous

Schrock / Grubbs



M = W, Mo

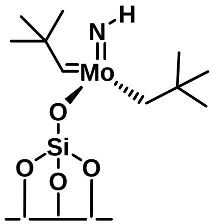


Ru: highest functional group tolerance

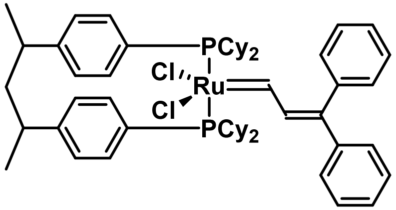
Heterogeneous

WO_3/Al_2O_3 at 400°C or MoO_3/ZrO_2 at RT)

Immobilized



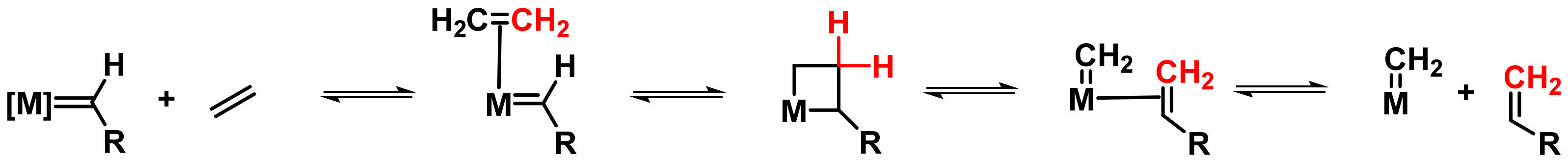
on silicate



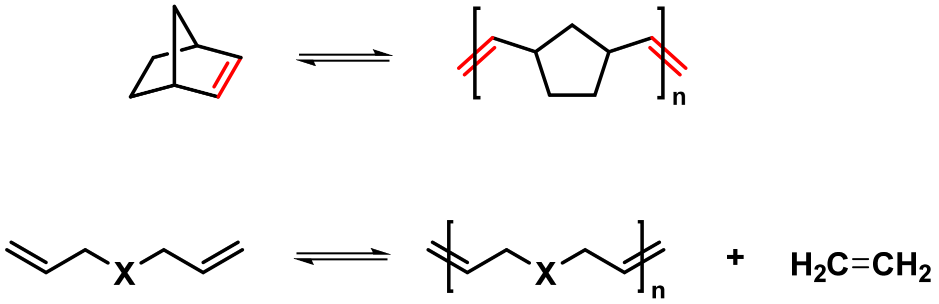
on polystyrene

Catalytic polymerizations: Olefin metathesis

Olefin metathesis : Formal exchange of alkylidene groups between two olefins



How can metathesis be used in polymerization reactions?

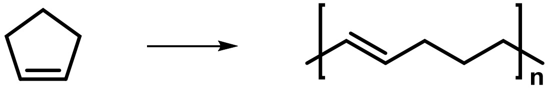


Ring opening metathesis (ROMP)

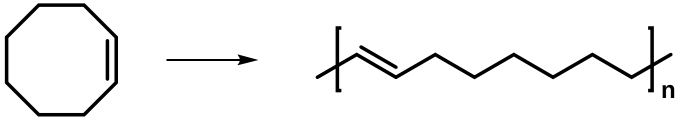
Acyclic diene metathesis (ADMET)

Catalytic polymerizations: Olefin metathesis

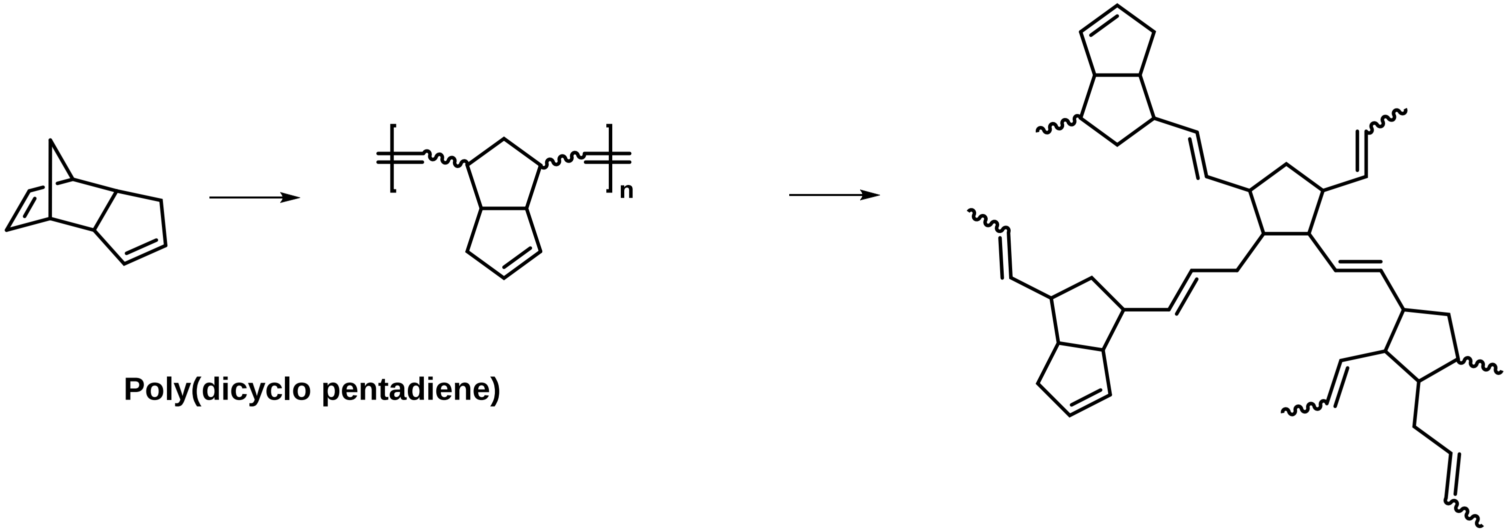
Important polymers from ring opening metathesis :



Poly(cyclopentene) [Polypenteneamer®]



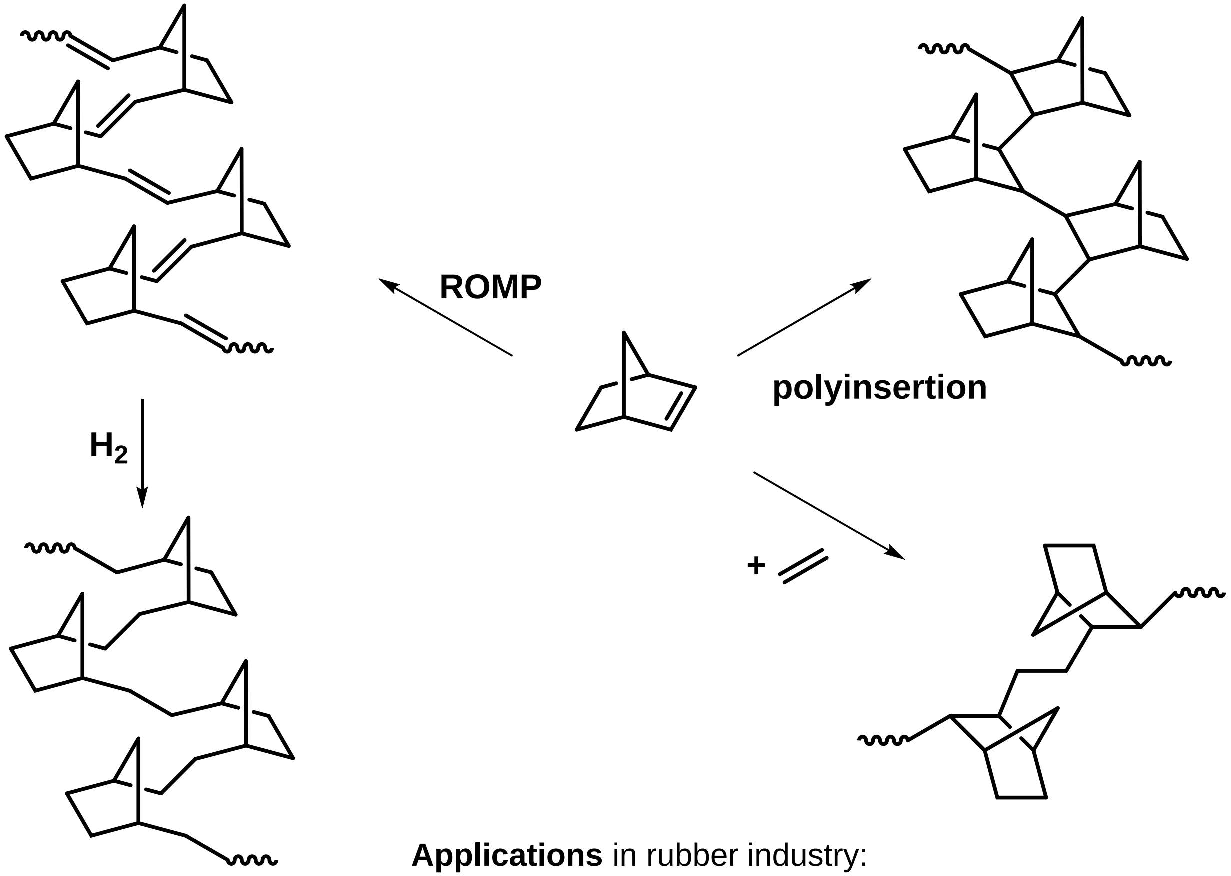
Poly(cyclooctene) [Vestenamer®]



Poly(dicyclo pentadiene)

Catalytic polymerizations: Olefin metathesis

Norbornene polymers:

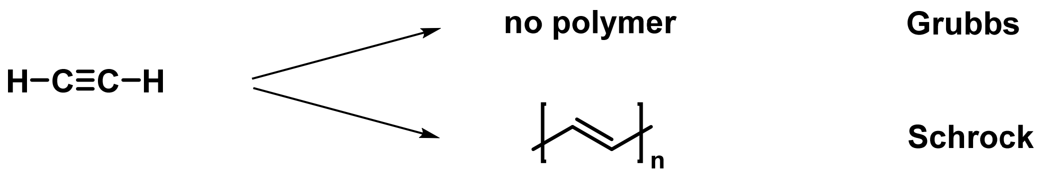


Applications in rubber industry:

- anti-vibration (rail, building, industry)
- anti-impact (personal protective equipment, shoe parts, bumpers)
- grip improvement (toy tires, racing tires, transmission systems, transports systems for copiers, feeders, etc.)

Catalytic polymerizations: Olefin metathesis

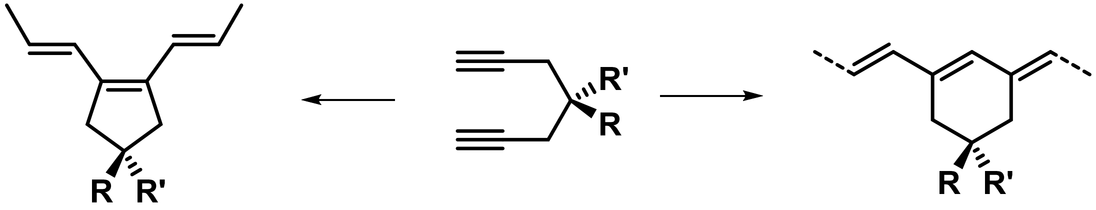
Special monomer: Acetylene



Poly(acetylene):

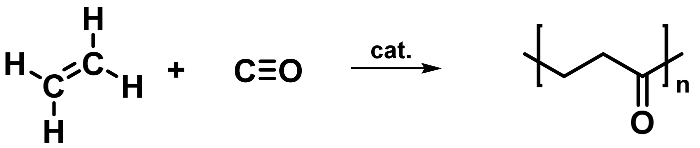
- C=C along backbone → conjugated sp^2-π system
- Doping → electrically conductive
- Disadvantage: sensitive to oxidation, insoluble, not meltable

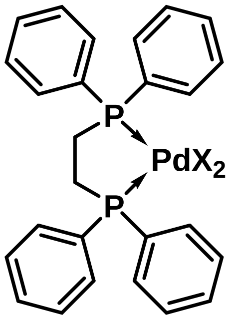
Other interesting architectures are possible:



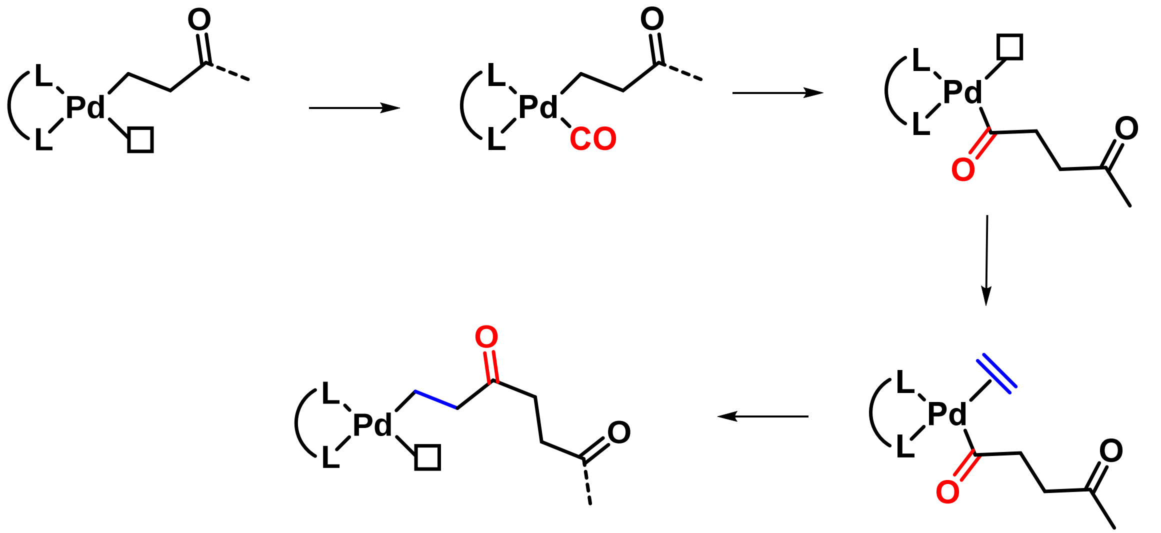
Catalytic olefine polymerizations: polar comonomers

Olefin-CO co-polymerization





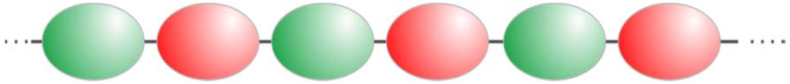
Mechanistic insight:



Binding Pd-CO not favorable, but incorporation of CO in polymer is fast.
Binding of ethene favorable, but insertion is slow.

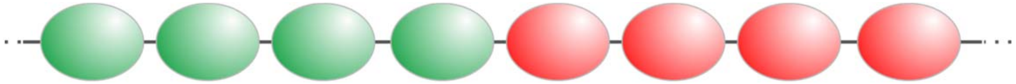
Copolymers

alternating copolymer
poly(A-*alt*-B)

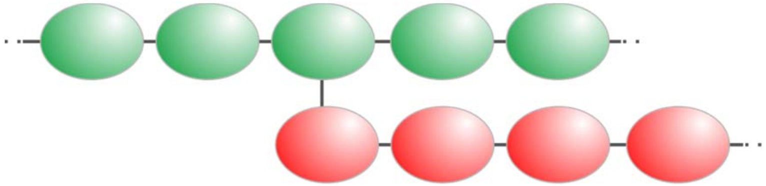


statistical copolymer poly(A-*stat*-B)

block copolymer
poly(A)-*block-poly(*B)



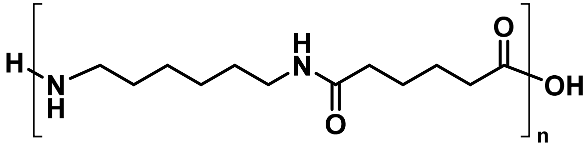
graft copolymer
poly(B)-*graft-poly(*A)



Copolymers

alternating copolymer
poly(A-*alt*-B)

via step growth reactions

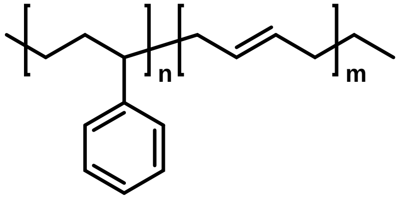


statistical copolymer poly(A-*stat*-B)

via mixing two monomers
with same polymerizable group

block copolymer
poly(A)-*block-poly(*B)

via living polymerization



graft copolymer
poly(B)-*graft-poly(*A)

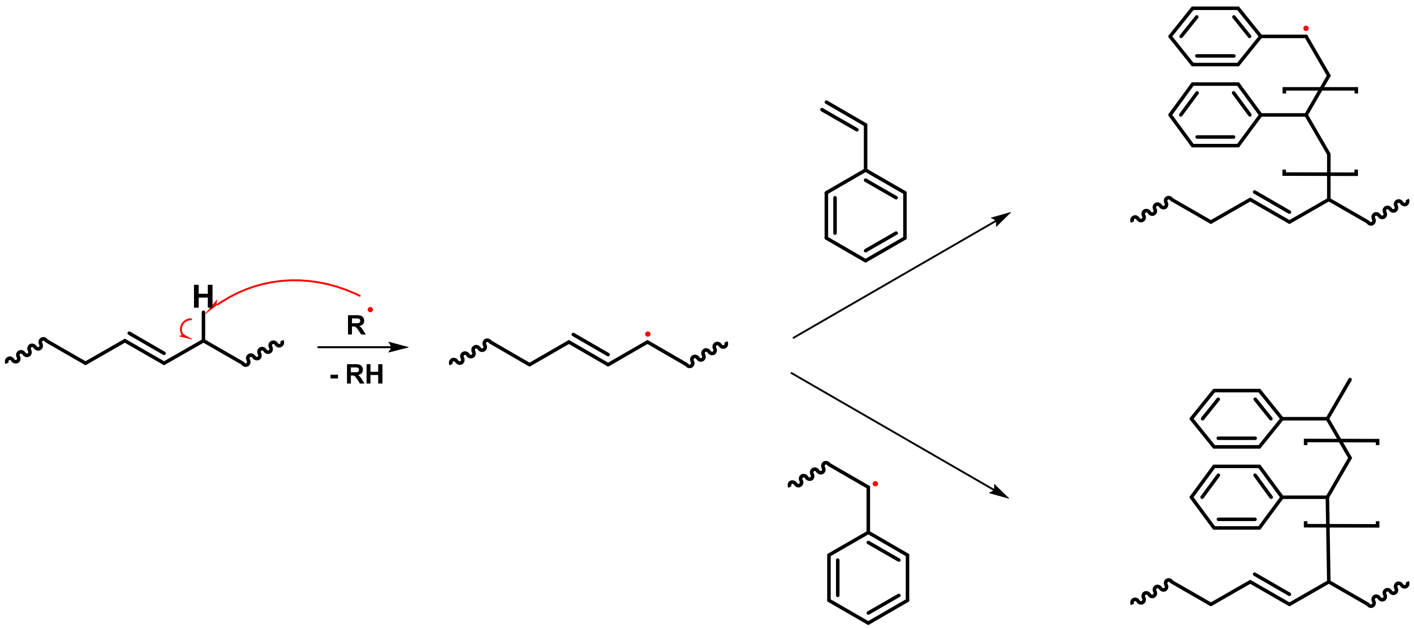
via post-modification of an exististing polymer / macromonomer

Graft copolymers

„Grafting onto“ approach

Modification of an existing polymer by

attaching another polymer to it

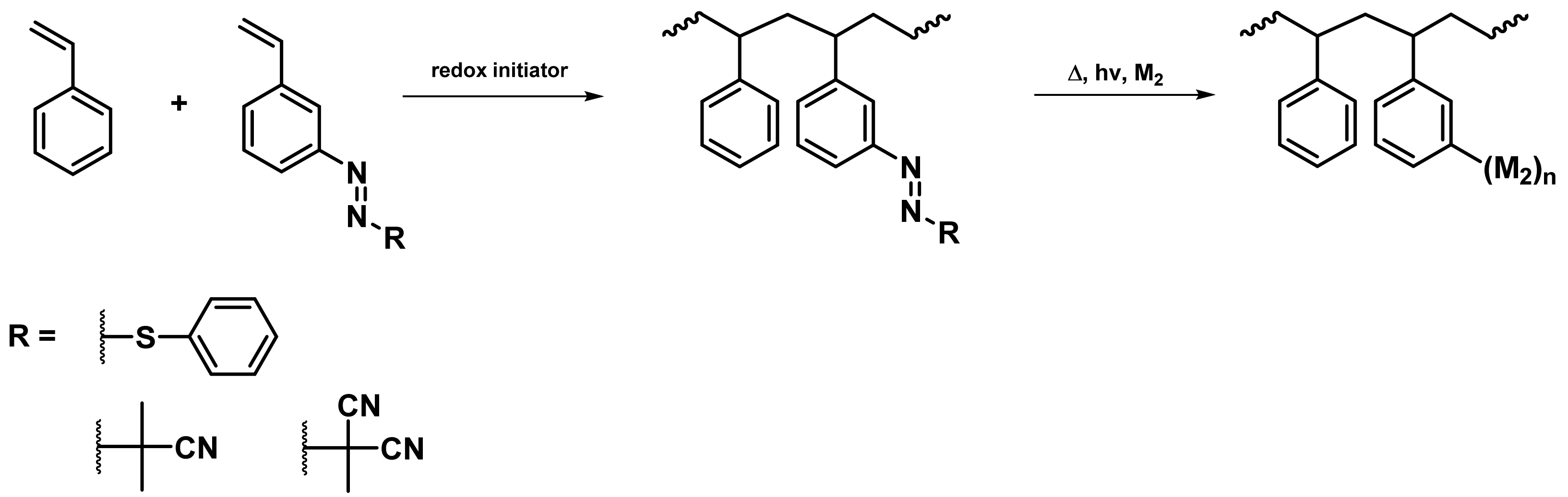


Graft copolymers

„Grafting from“ approach

Use of polymers with independent initiator group in the side chains

(A) Radical polymerization

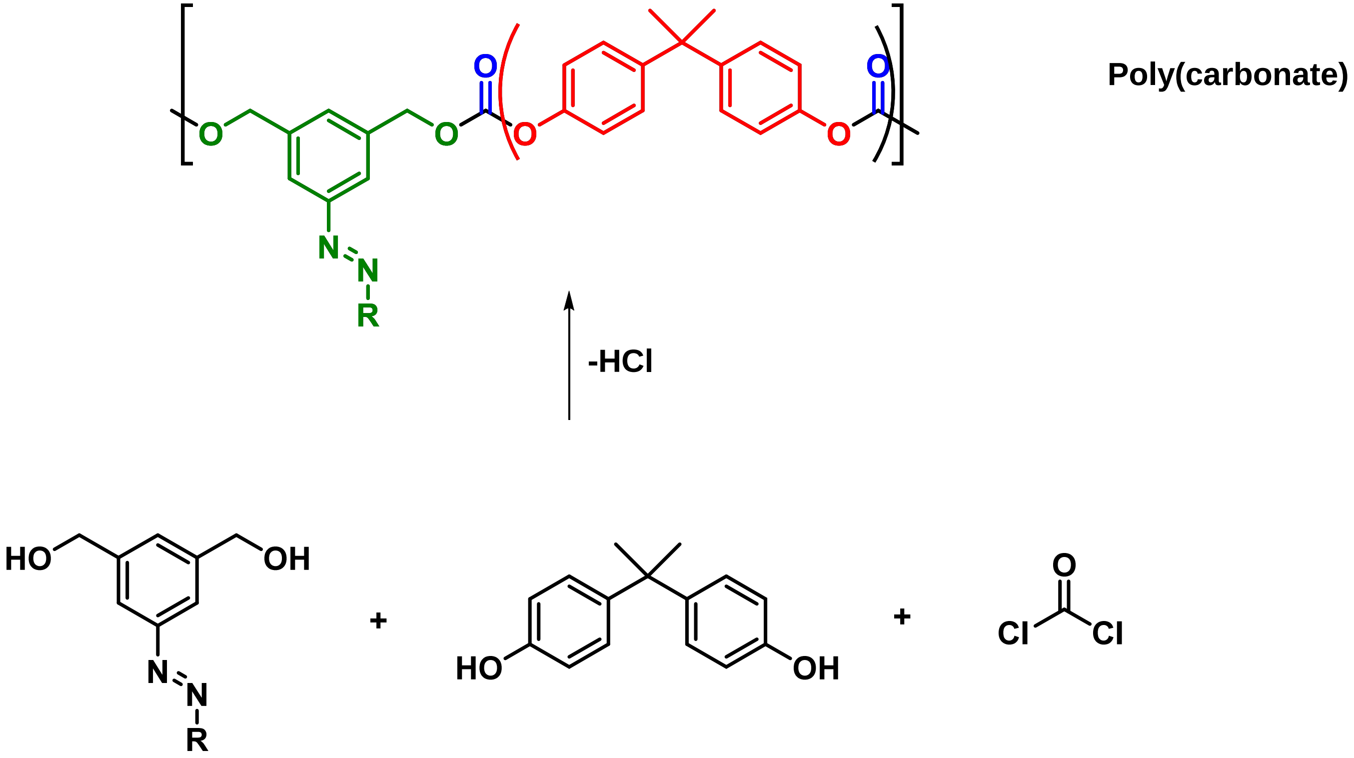


Graft copolymers

„Grafting from“ approach

Use of polymers with independent initiator group in the side chains

(B) Step growth reaction



Graft copolymers

„Macromonomer“ approach

Oligomers with unsaturated chain ends

- Base polymer accessible by radical, anionic or cationic polymerization
- Introduction of end group functionalisation by initiator, chain transfer or terminating reagent
- … or by modification of chain end: