

Supporting material for students registered to subject:

Macromolecular chemistry S112003

Teacher: Jan Merna, Department of Polymers, Institute of Chemical Technology ,Prague



Lecture authored by Jan Merna is licensed under a [Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported License](https://creativecommons.org/licenses/by-nc-nd/3.0/)

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

COORDINATION POLYMERIZATION

(Ziegler-Natta polymerization, polyinsertion,
stereospecific polymerization)

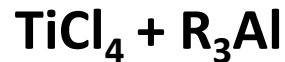
Monomers: non-polar

- ethene, 1-alkenes, dienes, cycloalkenes, alkynes

Z.-N. catalysts:

combination of group IV. – VIII. transition metal compounds
and organometallic compounds of group I. – III. metals

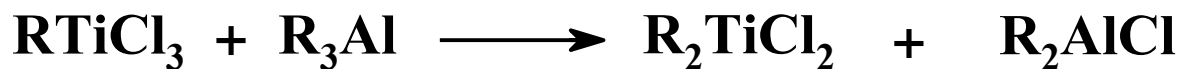
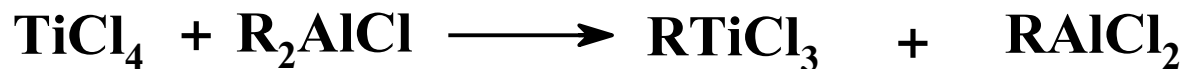
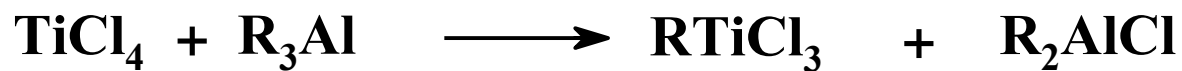
Example:



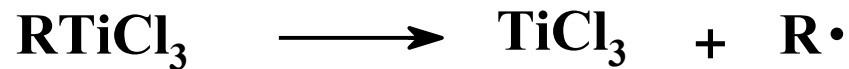
Substitution and reduction reactions, catalyst maturation

Catalyst maturation

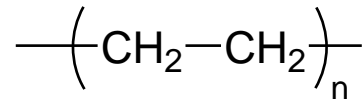
Alkylation:



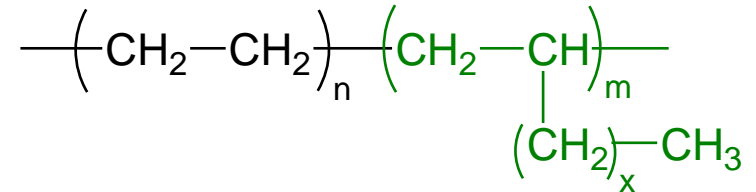
Reduction:



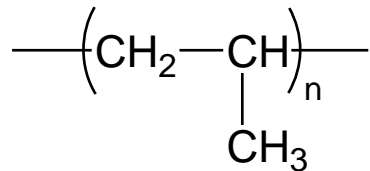
Commercial olefin thermoplastics



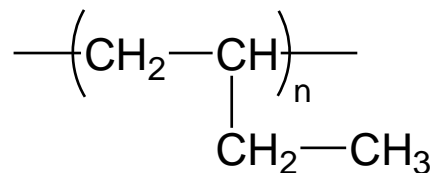
Polyethylene homopolymer
High-density PE (HDPE)



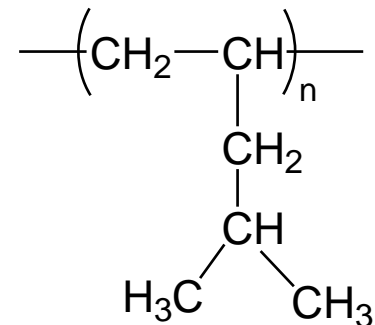
Ethylene + 1-alkene copolymers
Linear low density PE (LLDPE)



Polypropylene

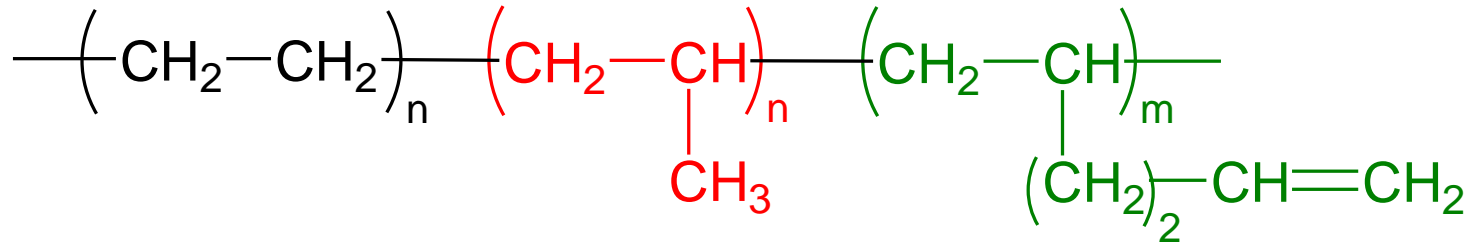


Poly(but-1-ene)

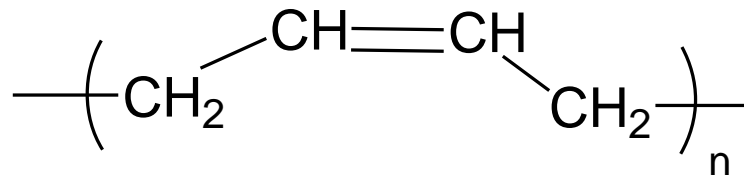


Poly(4-methylpent-1-ene)

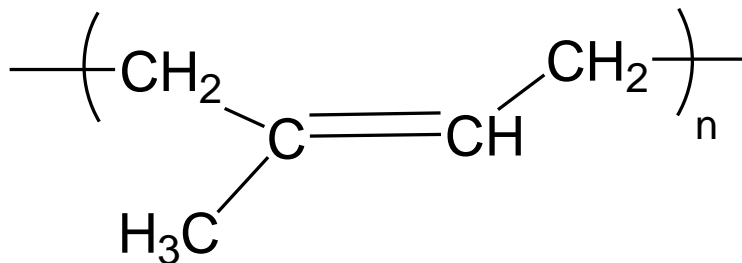
Commercial olefin elastomers



ethylene+propylene+nonconjugated diene



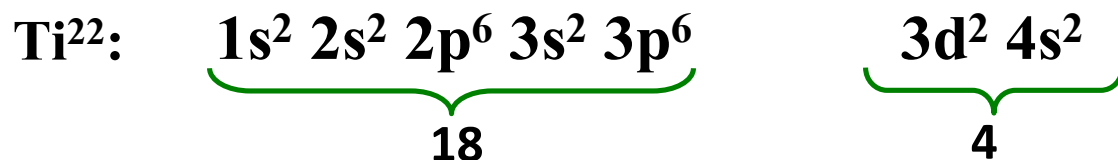
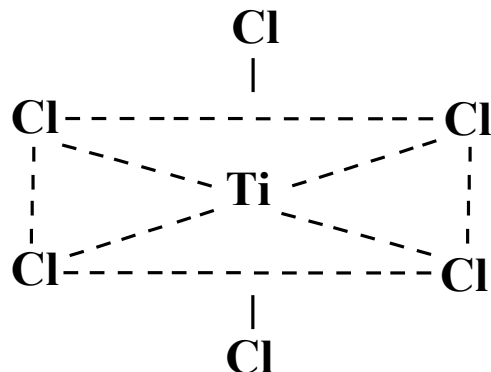
Polybutadiene



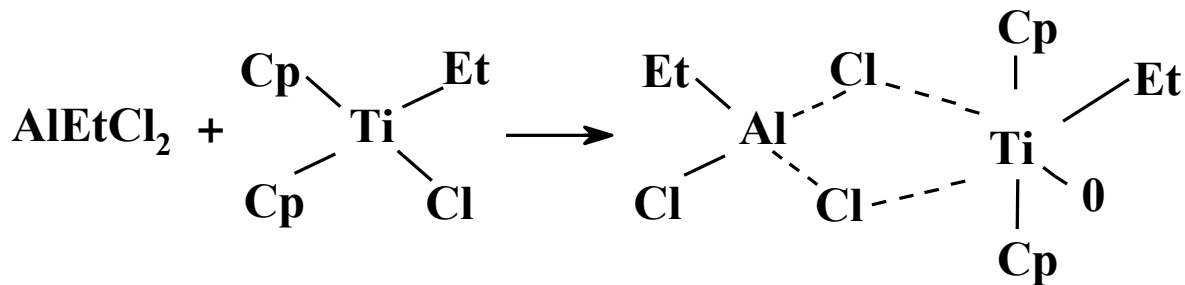
Polyisoprene

Chlorides of transition metals

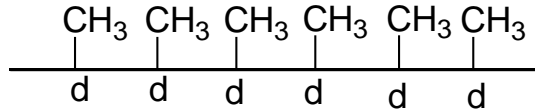
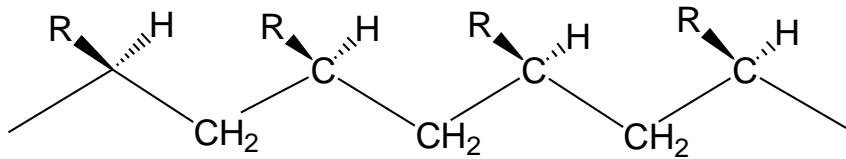
-octahedral coordination of metal in crystal lattice



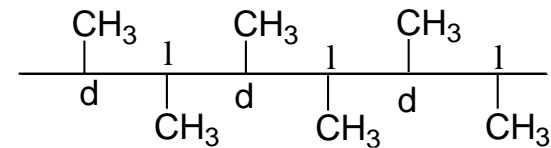
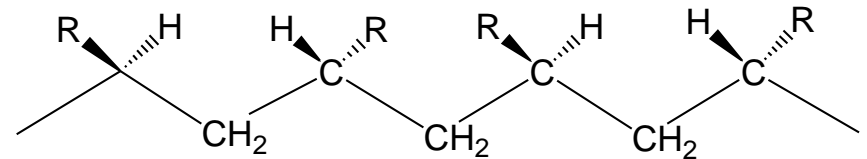
**Structure of growing center in Z.-N. polymerization
(soluble Z.-N. catalyst)**



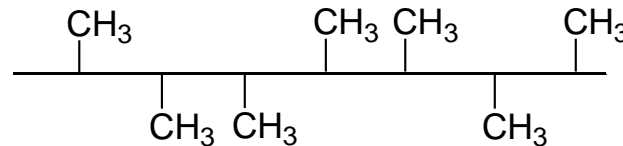
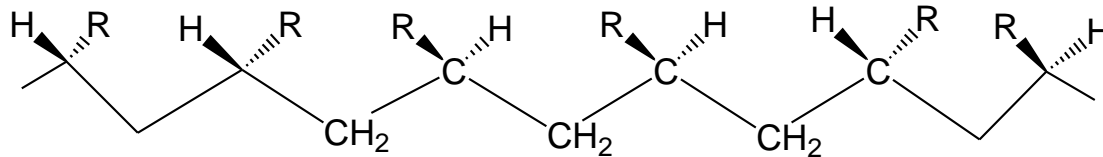
Stereoselectivity of polymerization process



Isotactic PP
 $T_m=170^\circ\text{C}$



Syndiotactic PP
 $T_m=130^\circ\text{C}$



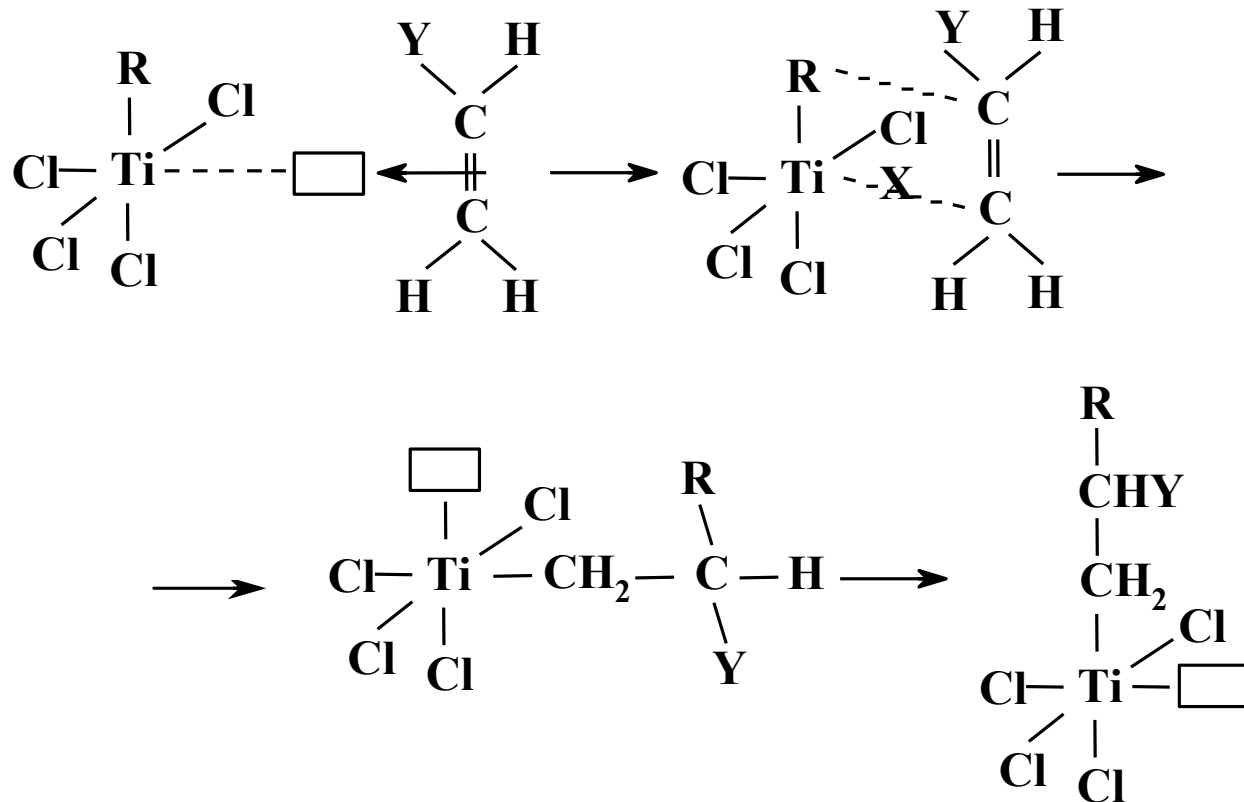
Atactic PP
no crystallinity

Mechanism of growth reaction in Z.-N. polymerization

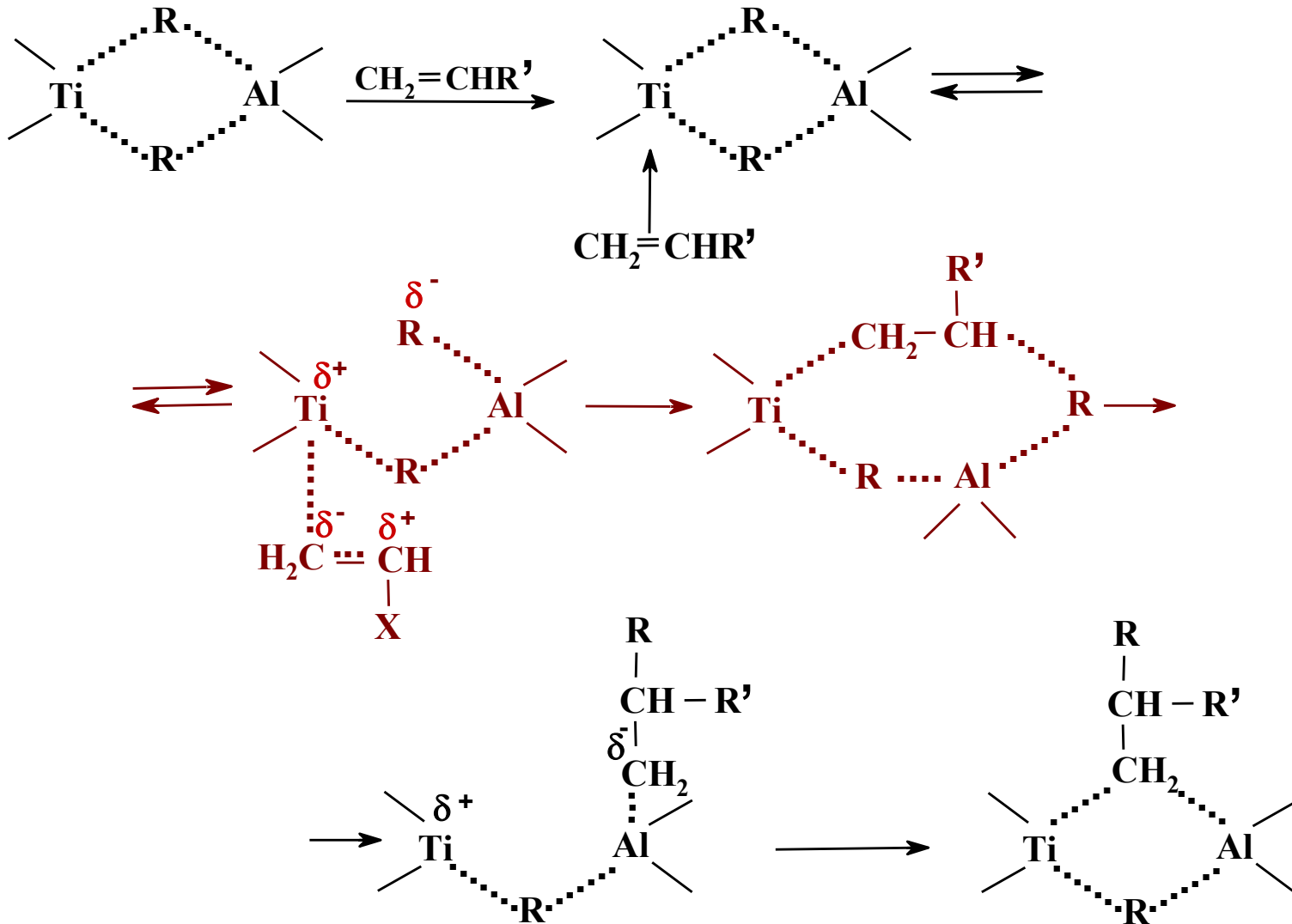
- monometallic

- bimetallic

Monometallic mechanism of growth reaction



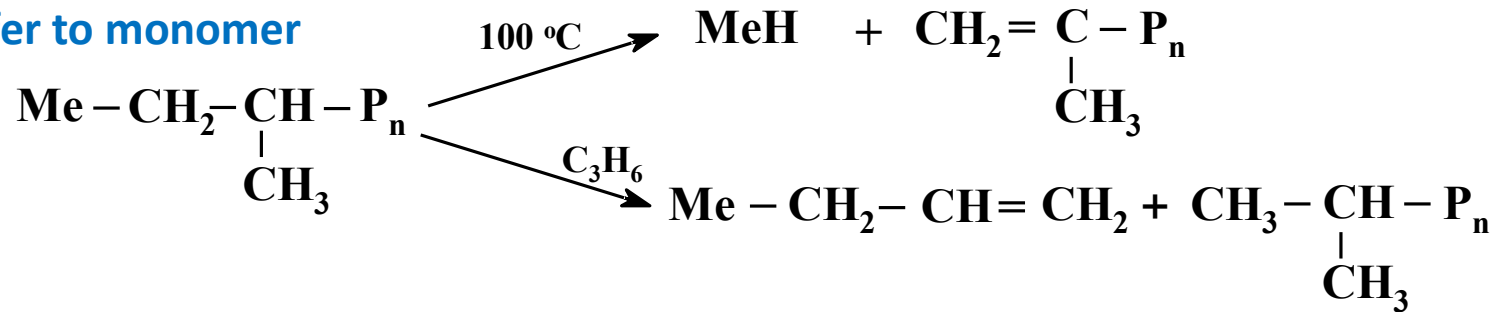
Bimetallic mechanism of growth reaction



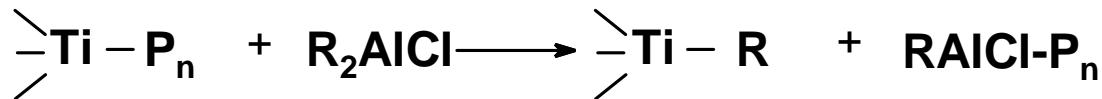
Termination in Z.-N. polymerization

β -H elimination

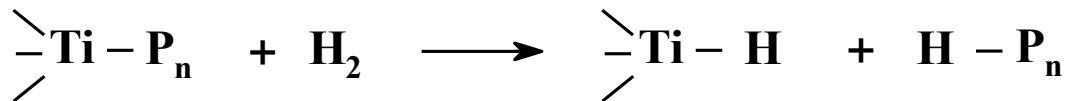
Transfer to monomer



Reaction with alkylating agents:

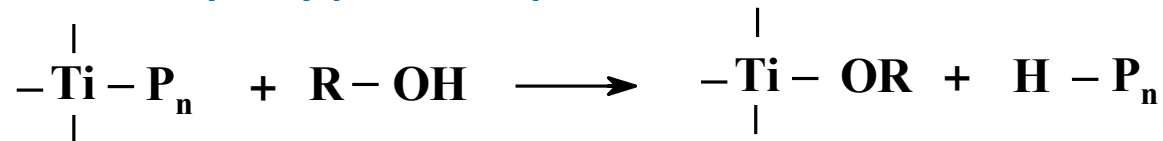


Transfer to hydrogen:

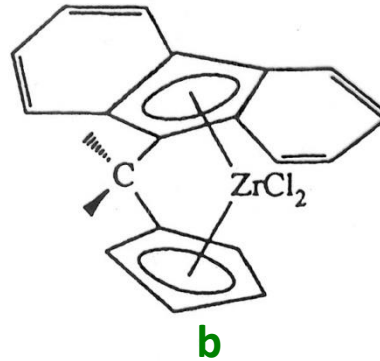
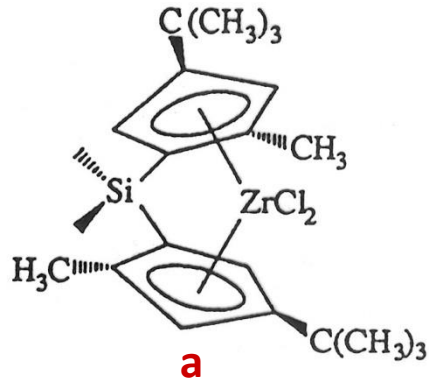


MeH + olefin \rightarrow new Me-C bond

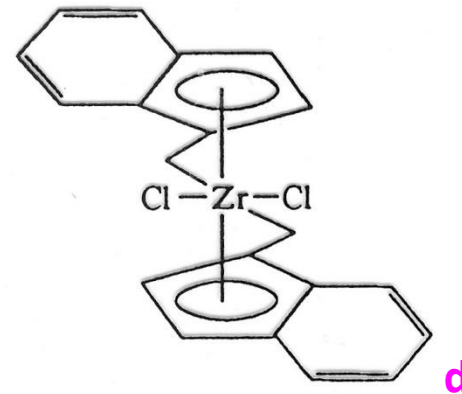
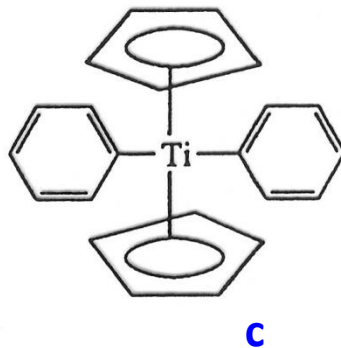
Decomposition of catalyst by polar compounds:



Metallocene catalysts

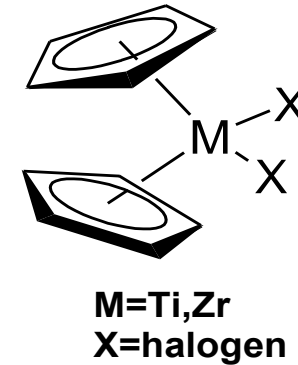
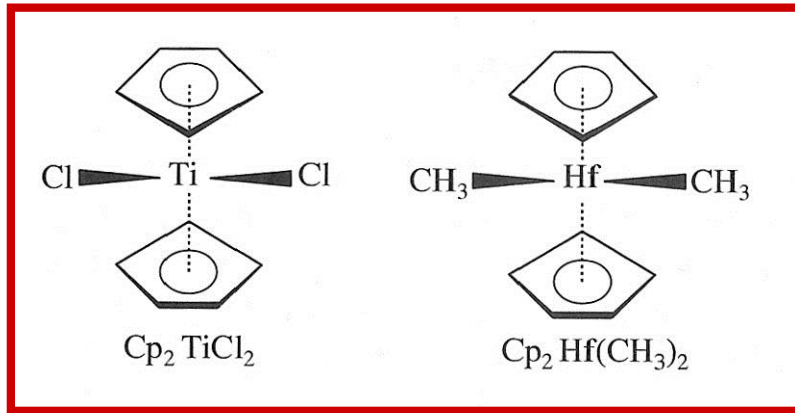


Catalyst: **a** isotactic, **b** syndiotactic polypropylene



Catalyst: **c** isotactic stereoblock polypropylene,
d isotactic polypropylene

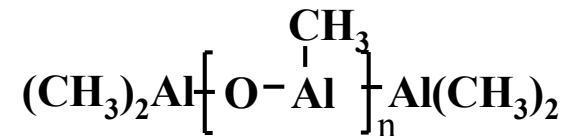
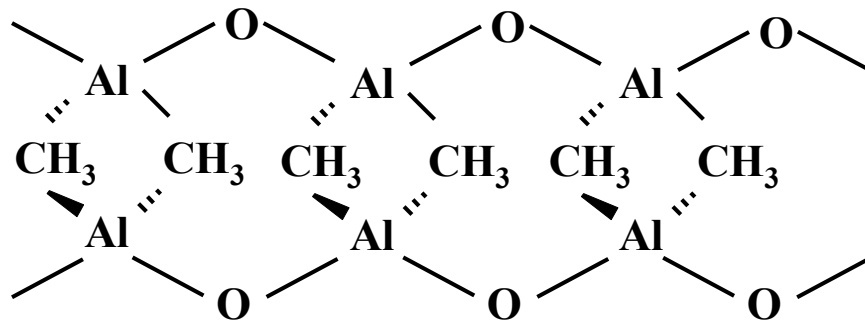
Metallocene catalysts



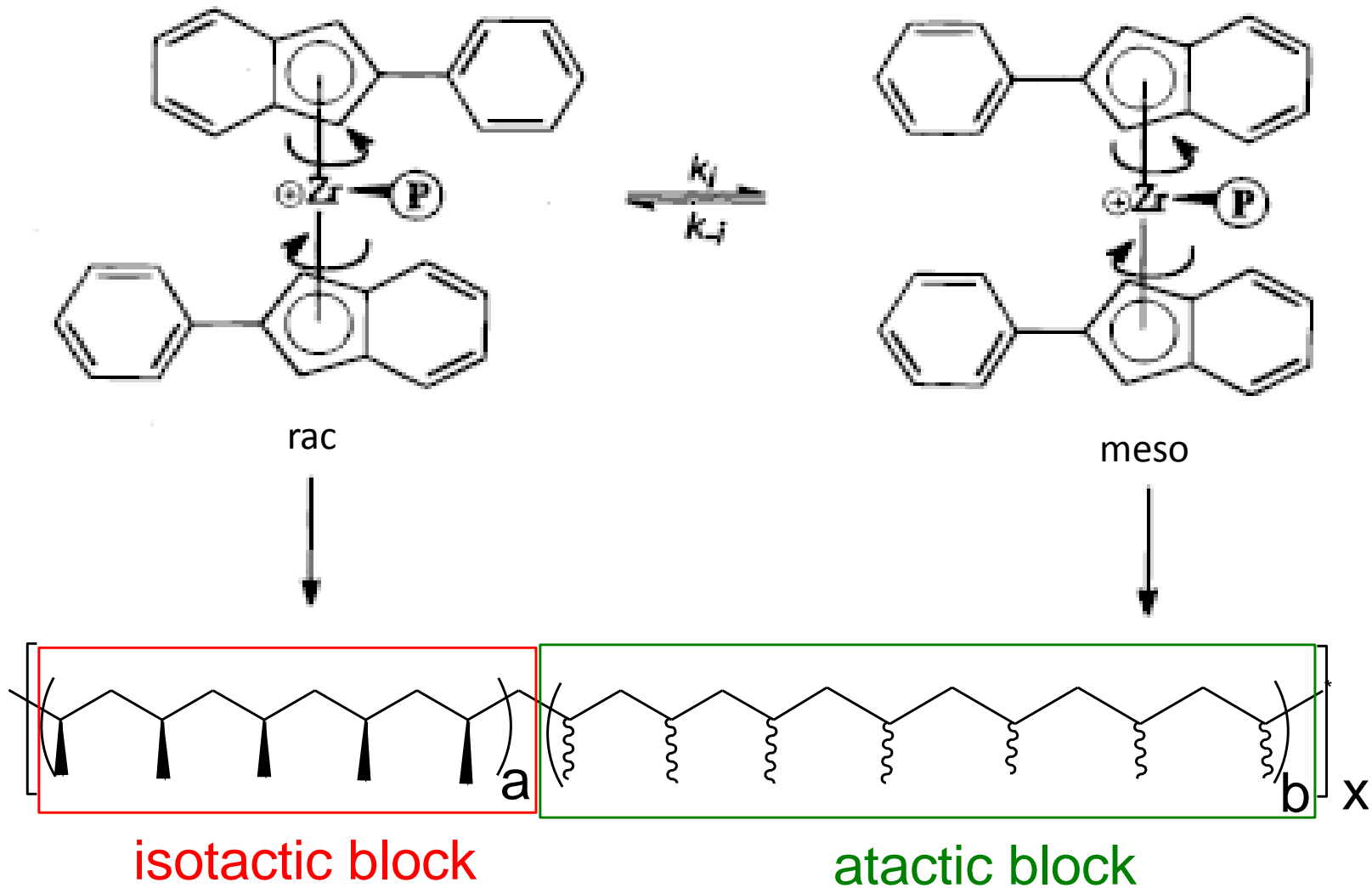
Significant increase of catalytic activity in presence of water:

Formation of alkylaluminumoxane

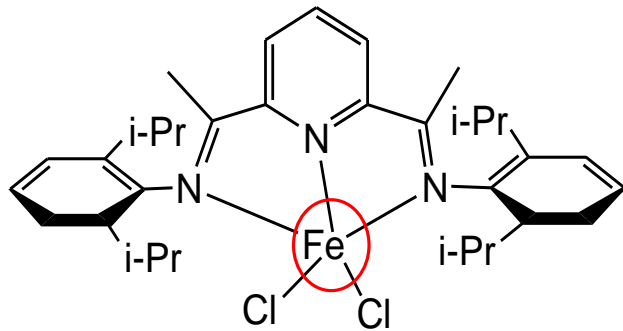
MAO (methylaluminoxane)



Oscillating catalysts



Post-metallocene Non Cp structures



Bis(imino)pyridyl catalyst
BIP (Fe, Co)

Late metal complexes



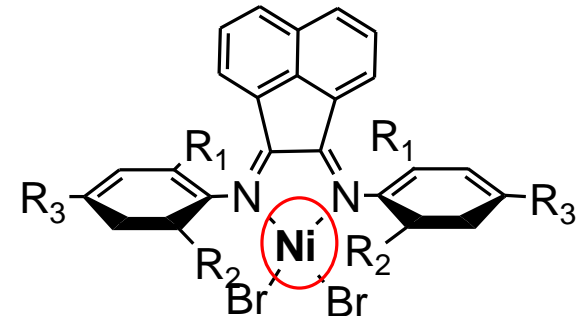
Less oxophilic



less sensitive

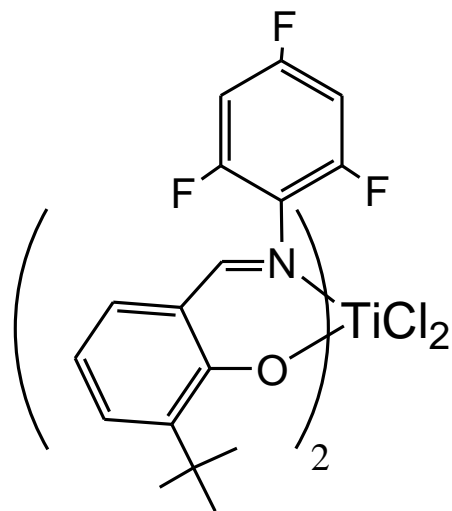


more tolerant
to functional monomer



Diimine catalysts
(Ni, Pd)

+living polymerization
+ chain-walking



Early metal complexes

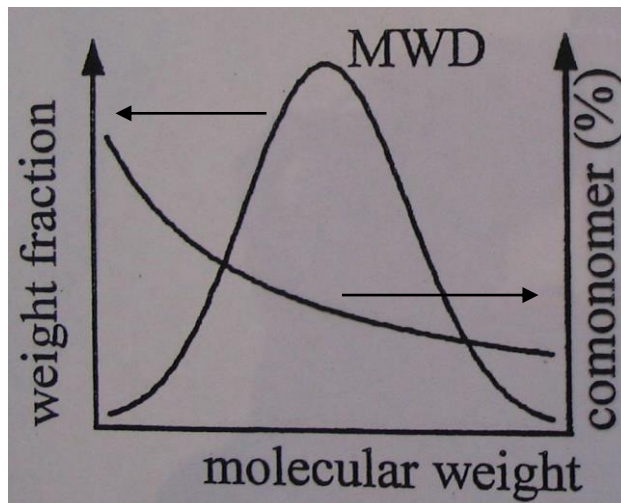
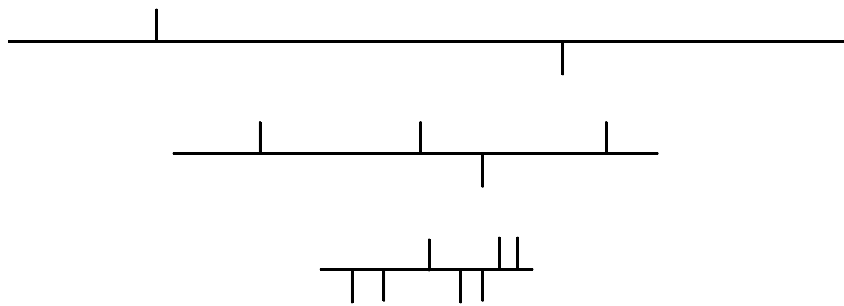
Phenoxy-imine catalysts
FI catalyst (Ti, Zr, Hf)

+living polymerization

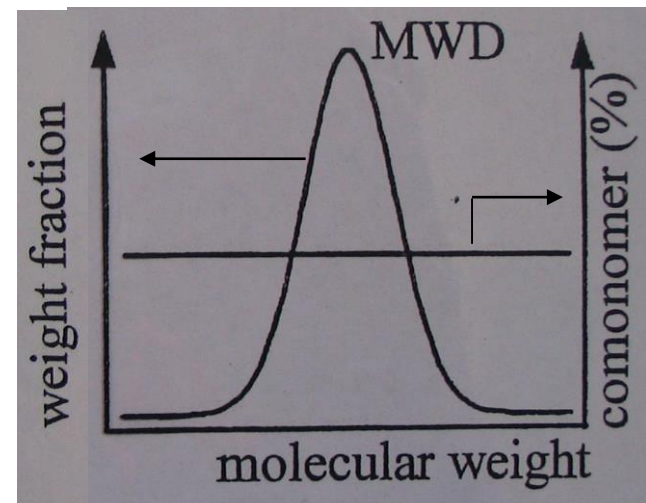
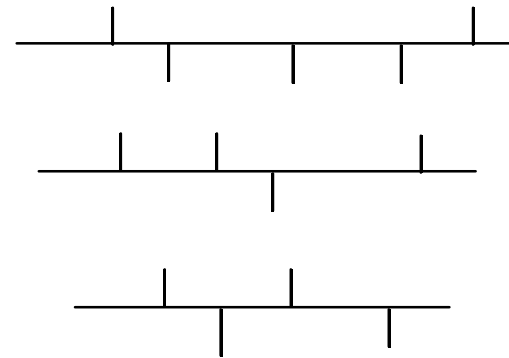
$M_w/M_n < 1.2$

Comparison of conventional and metallocene catalyst in olefin copolymerization

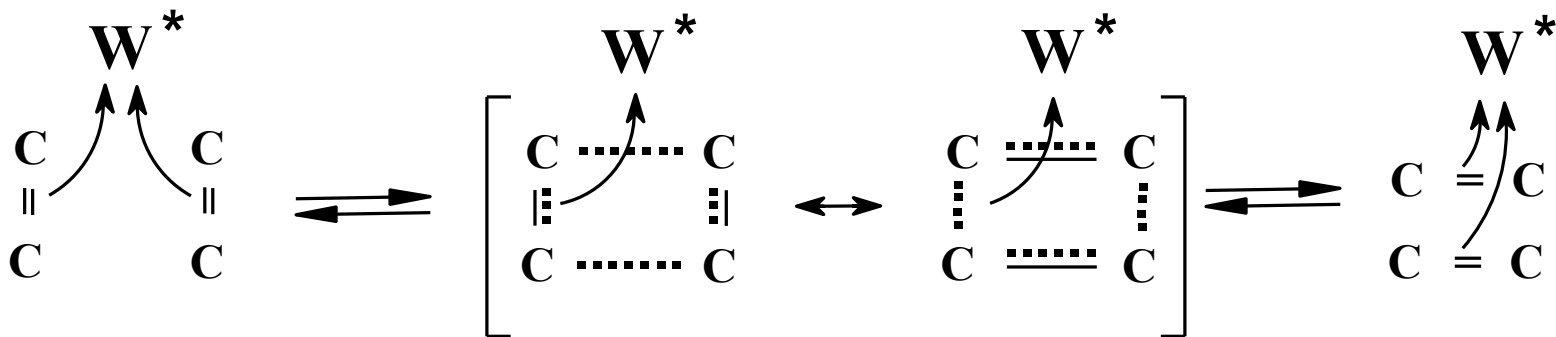
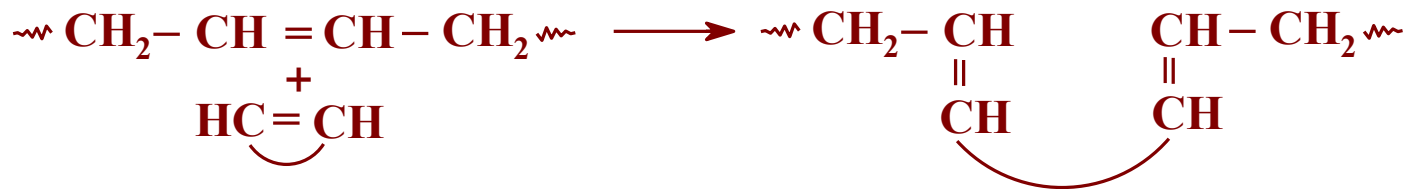
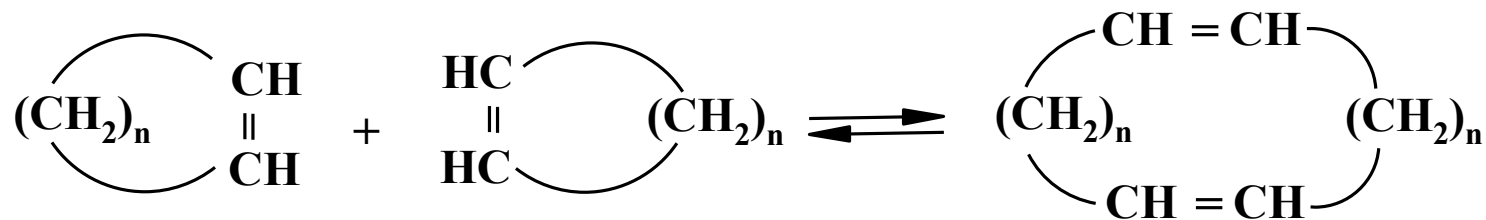
Conventional Z.N. catalyst



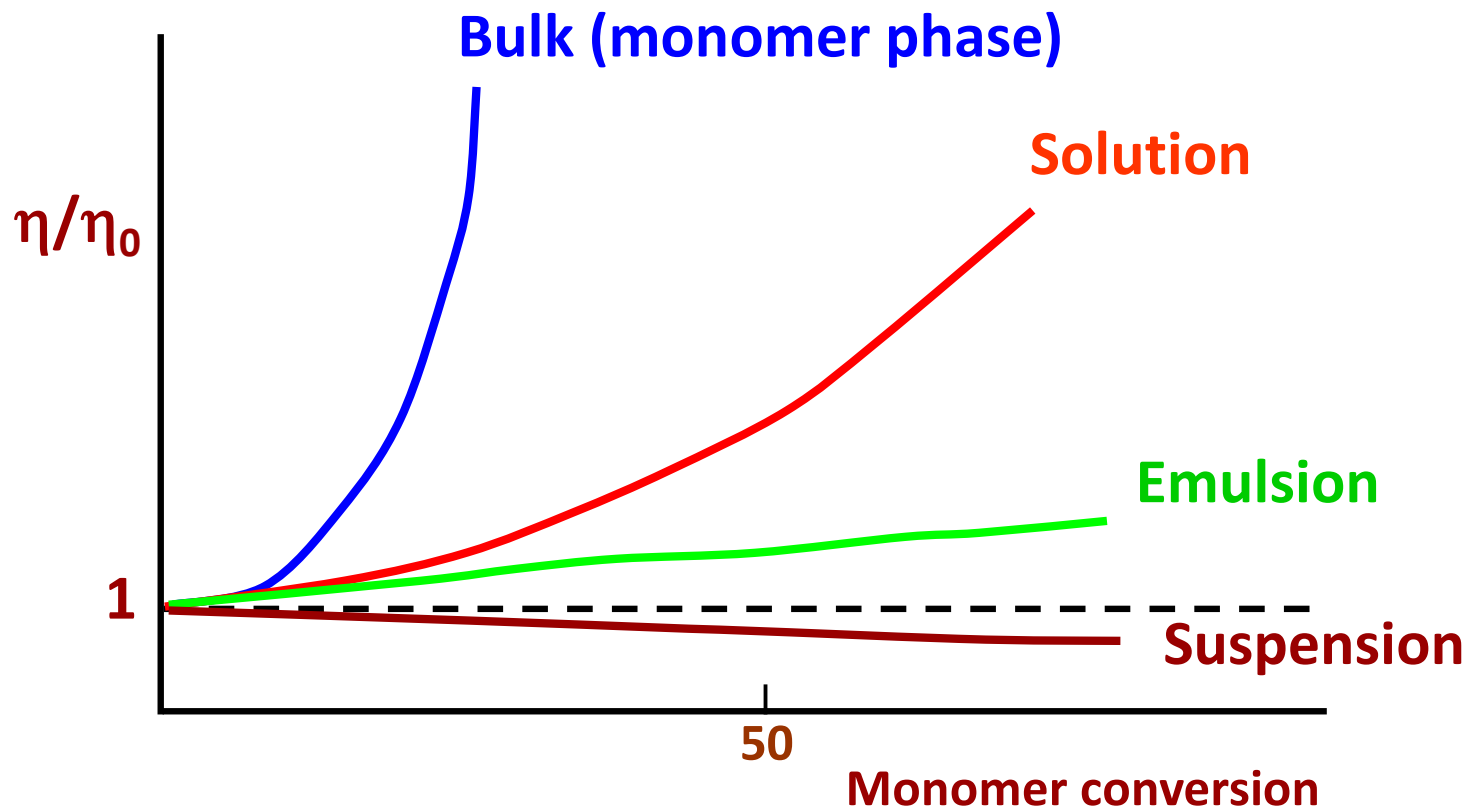
Metallocene



Metathesis (rearrangement of double bonds)



Polymerization techniques



Bulk polymerization

- feed composition: monomer, initiator, ev. MM regulator

! Exclusion of O_2

↑↑ highly pure, non-contaminated polymer

↑↑ possibility of polymerization in mould (product obtained directly)

↓↓ high viscosity of reaction system ⇒ difficult stirring ⇒ difficult reaction heat transfer



possibility of local overheating ⇒ local degradation of product (coloration), more transfer reactions ⇒ widening of molar mass distr.
boiling of monomer ⇒ formation of bubbles



! gel-effect !
popcorn polymerization

Solution polymerization

- Elimination of problems with reaction heat transfer

Presence of solvent

↑↑ easy mixing– transfer of reaction heat
max. effective cooling: solvent boiling

↓↓ economical and ecological aspects

↓↓ lower polymerization degree compared to bulk p.
(dilution of reaction mixture, ev. transfer to solvent, transfer to polymer suppressed)

Solution polymerization:

homogeneous – polymer soluble in the solvent

heterogeneous (precipitation) – polymer insoluble in the solvent

Presence of solvent residues after polymer isolation can deteriorate its properties

Suspension (bead, pearl) polymerization

- Proceeds in heterogeneous mode from beginning

Monomer with dissolved initiator dispersed in immiscible liquid (water, resp. solution of inorg. salts)

Monomer phase : water phase = 1:1 to 1:4

Diameter of dispersed droplets 0.01 – 1 mm (depends on T and mixing rate)

Droplets cooled by water \Rightarrow good transfer of reaction heat

Droplet \equiv small polymerization reactor

To avoid agglomeration of droplets suspension stabilizer is added

a) water soluble polymers

b) water insoluble powdery inorg. compounds

Further suspension stabilization: pH regulators

Polymers contaminated by stabilizer's residues \Rightarrow negative influence on optical properties mainly

Emulsion polymerization

- Heterogeneous reaction system

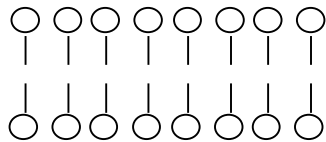
Dispersion media: water

Initiator: soluble in water

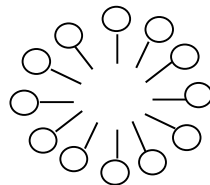
Monomer: dispersed in water phase with emulgator

Emulgator: org. compounds – molecules with both hydrophilic and hydrophobic part

Micelles: associates of emulgator molecules (spherical– 20-100 molecules)



a)



b)

○ Hydrophilic part of molecule
– Hydrophobic part of molecule

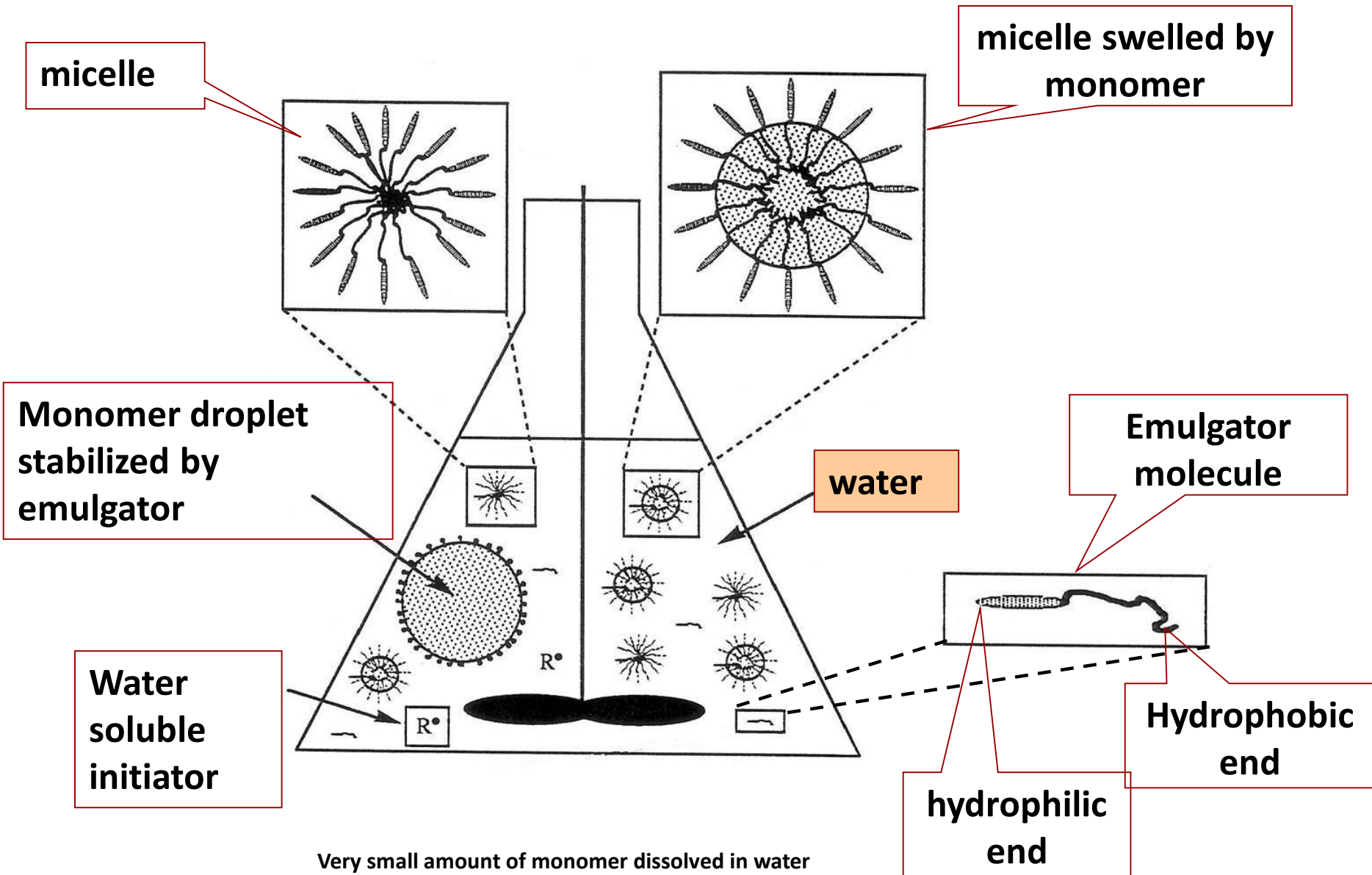
Scheme of rod-like (a) and spherical (b) micelles from emulgator molecules in water

Monomer droplets: diameter 1 – 10 μm

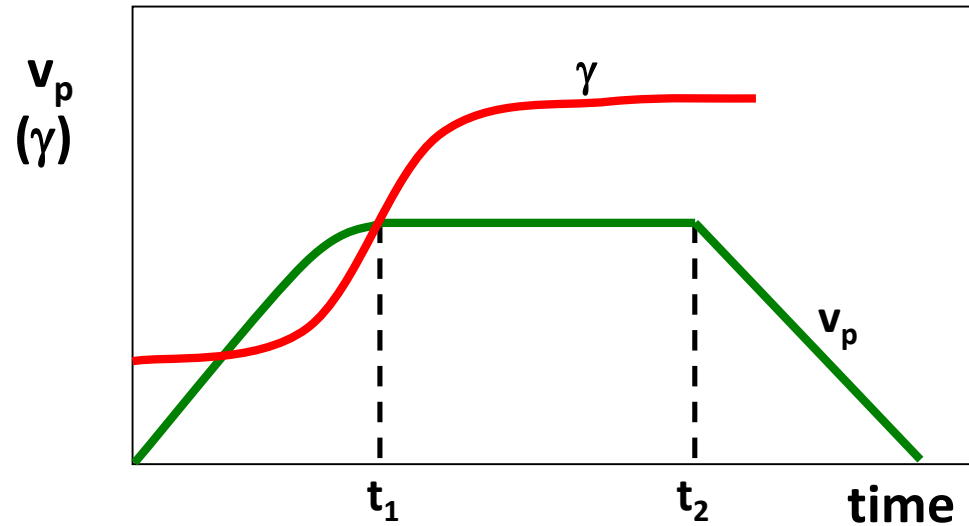
Spherical micelles: diameter 10^{-3} – 10^{-4} μm

Latex particles : diameter $5 \cdot 10^{-2}$ – $5 \cdot 10^{-1}$ μm

Emulsion polymerization



Emulsion polymerization



Schematical representation of polymerization rate v_p and surface tension γ in emulsion polymerization system

Kinetics and polymerization degree in emulsion radical polymerization

$$v_p = k_p [M] \frac{N}{2}$$

$$v_t = r_i = \frac{\rho}{N}$$

ρ -rate of radical formation from initiator
 r_i =rate of a radical entry to one of N micelles

$$P_n = \frac{k_p [M] N}{\rho}$$