Ziegler-Natta polymerization – mechanism

General reaction mechanism

- **Initiation**
  - Activation of the catalyst precursor

- **Propagation**
  - Chain growth

- **Termination**
  - Chain transfer, catalyst decomposition
Mechanism – poisoning

Problem: sensitivity of the catalysts to oxygen, moisture and other heteroatom containing impurities.

For most catalysts, the solvent and feed should be extremely pure...

...Why is that?

Ziegler's original reactor.
**Problem:** sensitivity of the catalysts to oxygen, moisture and other heteroatom containing impurities.

\[ \text{M-CH}_3 + \text{H}_2\text{O} \rightarrow \text{[M-O-H]}^+ \rightarrow \text{M-OH} + \text{CH}_4 \]

\[ \text{M-CH}_3 + \text{O}_2 \rightarrow \text{[M-O-O]}^+ \rightarrow \text{M-O-M} / \text{M=O} + \text{CH}_3\text{OOCH}_3 \]
Initiation

Generation of an electrophilic metal site that contains a metal-carbon or metal-hydrogen bond.

Catalyst precursors are generally metal halide species.

In most cases the alkylation is done with aluminum alkyls.

Ziegler-Natta precatalyst (MgCl$_2$ / TiCl$_4$ / ester) is treated with AlEt$_2$Cl for activation.

Homogeneous catalyst precursors are generally treated with methylalumoxane.
Strong Lewis acid competes for the electrons of the chloride ion.

If the competing electrophile is Lewis acidic enough, it can even abstract a chloride ion.

Alkylation - chloride ion exchange finally affords the active catalyst consisting of a cationic zirconium alkyl species.
Mechanism – initiation

Mechanism – initiation

C* < [Zr]
TOF > 10^3 s⁻¹
Mechanism – propagation

Propagation

Modified Cossee-Arlman mechanism – migratory insertion

Important for stereospecific polymerization
This mechanism requires a base to scavenge the proton.
This mechanism involves a change in the oxidation state of the metal, which is unlikely for Ln^{III}, Ti^{IV}/Zr^{IV}/Hf^{IV}, Ni^{II}/Pd^{II}…

…but it did result in another modification of the Cossee-Arlman mechanism.
The agostic interaction increases the interaction of the C sp³ with the olefin.
Termination

β-hydrogen elimination

The extreme of agostic interaction is hydrogen transfer to the metal. Depends on relative bond strength of M-C and M-H whether or not this occurs.
Mechanism – termination

Termination

β-hydrogen transfer to monomer

Generally most accepted termination mechanism
Mechanism – Choice of metal

Early transition metals

- Fast insertion
- Slow $\beta$-H elimination
- $k_{\text{ins}} \gg k_{\beta-\text{H}}$
- $E_{\text{M-C}} \approx E_{\text{M-H}}$
- Highly oxophilic
- Low tolerance to polar groups

Late transition metals

- Slow insertion
- Fast $\beta$-H elimination
- $k_{\text{ins}} << k_{\beta-\text{H}}$
- $E_{\text{M-C}} < E_{\text{M-H}}$
- Poorly oxophilic
- High tolerance to polar groups
Termination

- Elimination/transfer to monomer
Mechanism – termination

Propagation versus termination

Termination requires more room than propagation
Besides spontaneous chain transfer processes, chain transfer can be induced by adding chain transfer agents (CTA’s).

Chain transfer agents are used to:
- Control the polymer molecular weight
- Control polydispersity
- Introduce functional groups
- Reactivate dormant sites
Chain transfer – hydrogenolysis

Dihydrogen is the most commonly used chain transfer agent (CTA) to control the molecular weight.

Dihydrogen is a weak Lewis base (like olefins) that can easily be polarized formally producing an acidic proton that can protonate off the polymer chain.
Substrates of the type H-X where X is more electropositive than H can also be used as chain transfer agents. X = H, BR₂, SiR₃, ... H-X is already polarized, which facilitates the reaction.
Chain transfer – CTA’s

Substrates of the type H-X where X is more electronegative than H can also be used as chain transfer agent.

This process only works when M-X is not too strong.

X = NR₂, PR₂
Main group metal alkyls can also function as chain transfer agents.

\[ M'R_x = \text{AlMe}_3, \text{MgBu}_2, \text{ZnEt}_2, \ldots \]
Reactivating dormant sites

Enforced $\beta$-H elimination

Dormant site
Chain transfer to main group metal alkyl CTA's is a relative new way to:

- Control the molecular weight
- PDI
- Produce end-functionalized polyolefins
- Multi-block copolymers.

For this mechanism to be effective, a living catalyst is required.
Chain transfer – multi-block copolymers

Ethylene / 1-alkene copolymers - Shuttle chemistry
A copolymer is obtained with the soft-characteristics of an amorphous random copolymer and the hard-characteristics of a crystalline homopolymer.
How does the reaction of the active catalyst with the olefin take place?

- The **electron rich** olefin is attracted to the **electron poor** metal center.
- The olefin binds to the empty metal orbital.
- The polar M-C bond introduces an induced dipole on the olefin.
- The opposite charges attract each other which leads to σ-bond formation.
- Metal-alkyl with β-agostic interaction as resting state.
- The alkyl group rotates away making space for the new olefin to approach.
How does termination takes place?

**Summary**

- **β-H transfer/elimination (spontaneous)**
- **Hydrogenation by \( \text{H}_2 \) (chain transfer agent)**
Coordination polymerization – market

Polyolefins in the global thermoplastic resins market
Coordination polymerization – market

Polyolefins in the global thermoplastic resins market

- PVC: 20%
- ABS: 4%
- PS: 8%
- PET: 5%
- PP: 22%
- LDPE: 13%
- LLDPE: 10%
- HDPE: 18%
## Coordination polymerization – market

### THERMOPLASTIC RESINS CAPACITIES 2006, KT, WORLD

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34,2 = FIBER, 2,5 = FILM

5,4 = FIBER
Coordination polymerization – market

Quite some plastic per year!

24 km

4 mm
Coordination polymerization – market

Global Unit Consumption Growth

By 2009 capacity is growing @ 2x to 3x historical unit consumption
Coordination polymerization – market
Coordination polymerization – catalyst types

- Ziegler-Natta heterogeneous
- Phillips heterogeneous
- Single-site homogeneous