Oxirane-carbon dioxide copolymers

\[
\text{O} = \text{C} = \text{O} + \text{O} = \text{C} = \text{O} \text{[cat]} \rightarrow \text{[copolymer]} \]

\[
\begin{align*}
\text{[copolymer]} & = \text{[polyester]} \\
\text{[polyester]} & = \text{[ester]} \\
\text{[ester]} & = \text{[monomer]} \\
\end{align*}
\]
Oxirane-carbon dioxide copolymers

Bimetallic mechanism.
ROP – cocatalyst assisted
Acyclic Diene Metathesis (ADMET)
Ring Opening Metathesis Polymerization (ROMP)
Olefin metathesis polymerization

Schrock type

Grubbs type
Olefin metathesis polymerization

ADMET – Cross metathesis polymerization

Polyolefins by step growth polymerization (polycondensation).
Olefin metathesis polymerization

Ring opening metathesis polymerization

Chemical reaction diagram
3 homopolymerizes norbornene but does not homopolymerize cyclooctene. However, 3 does copolymerize norbornene and cyclooctene.

Why does 3 copolymerize these monomers and what is the structure of the copolymer?

A is sterically less hindered than D.

A B C D will only occur when severe ring strain is released since finally a sterically more hindered species is formed.

D E F A will occur also for non-strained cyclic olefins since finally a sterically less hindered species is formed.
Coordination polymerization – acrylates

- Metal mediated Michael addition
- Migratory reaction
- MMA is prochiral which leads to tacticity

Coordination intermediate

Resting state

Chirality
Coordination polymerization – olefins

- Migratory insertion
- propylene is prochiral which leads to tacticity

\[
\text{Cp}_2\text{Zr} \rightarrow \text{Cp}_2\text{Zr} + \text{CH}_3
\]

Chirality
Coordination polymerization – olefins - MMA

1-olefins polymerization

In 1-olefin polymerizations monomer prochirality is committed at the moment of enchainment

Acrylates polymerization

In acrylate polymerizations monomer prochirality is committed one step after enchainment
Homogeneous single-site catalysts

Applied for i-PP, s-PP, HDPE, LLDPE, VLDPE, ....

- Group 4 metal (Ti, Zr, Hf) based
- Co-catalysts: MAO, boranes, borates, ....
- Uniform active species yielding narrow molecular weight distribution
- In general improved product quality
- In principle easier product/catalyst tailoring
- Depending on the process the catalysts are supported on SiO$_2$ or MgCl$_2$
Homogeneous single-site catalysts

Advantages of well-defined single-site catalysts.

- Tunability of the catalyst performance through designed ligand modification
- Enhanced stereo control
- Uniform, random and tunable comonomer incorporation
Early metallocene catalysis

- **Titanocene dichloride (16 VE)**
- **Ferrocene (18 VE)**

**Breslow, 1955**

Reaction: \( \text{Cl}_{2}\text{TiCl}_{2} + \text{AlEt}_2\text{Cl} \rightarrow \text{HDPE} \)

- Limited activity
- Propene; only dimerization
- Active species unclear

HDPE: very low yield
Inactive in ethylene polymerization unless a small amount of water is added.

Careful hydrolysis of AlMe₃ yields methylaluminoxane (MAO) with unprecedented cocatalyst abilities.
Metalloocene catalysts – $C_v$ symmetric

$C_2v$ symmetric – no stereo control
Metalloocene catalysts – $C_v$ symmetric

No preference for the position of the polymer chain.
Metalloocene catalysts – $C_2$ symmetric

$C_2$-symmetric – stereo control

Ziegler-Natta catalyst
Metallocene catalysts – $C_2$ symmetric

Growing chain preferentially points away from the steric bulk of the ligand system.

Growing chain is responsible for "indirect stereo control". Without growing chain, there is no stereo control.
Metalloocene catalysts – $C_2$ symmetric

- Isospecific

- Isospecific

- Isospecific

- Isospecific
Metalloocene catalysts – $C_s$ symmetric

$C_s$-symmetric – stereo control
Metallocene catalysts – $C_s$ symmetric

Growing chain preferentially points away from the steric bulk of the ligand system.

Growing chain is responsible for "indirect stereo control". Without growing chain, there is no stereo control.
Metallocone catalysts – $C_s$ symmetric

syndiospecific

syndiospecific

syndiospecific
Metalloocene catalysts

By designing the catalyst's ligand system, various including some unprecedented types of polypropylene are available.

- $D_h$ (atactic)
- $C_2$ (isotactic)
- $C_s$ (syndiotactic)

What if we remove the symmetry?
Metalloocene catalysts – $C_1$ symmetric

The effective steric hindrance of the methyl group is comparable to that of the fused aryl group.

![Image of Metalloocene catalysts]

hemi-isotactic PP
Metallocene catalysts – $C_1$ symmetric

-aspecific-

- specific-

- aspecific-
One side is sterically too crowded for the polymer chain. As a result, directly after insertion of a propylene molecule the polymer chain skips back to the less crowded side.
Metalloocene catalysts – $C_1$ symmetric

- Metalloocene catalysts
- $C_1$ symmetric
- Isospecific
- Insertion
- Back skipping
Different ligand structures lead to different types of polypropylene.

Development of metallocene catalysts
Mechanism – initiation

\[
\text{Cp}^*\text{ZrMe}_2 + [\text{R}_3\text{NH}]^+ [\text{B(C}_6\text{F}_5)_4]^\text{−} \rightarrow \text{Cp}_2\text{M} + \text{CH}_4
\]


\[
\text{Cp}^*\text{ZrMe}_2 + \text{B(C}_6\text{F}_5)_3 \rightarrow \text{Cp}^*\text{ZrCH}_3 \rightarrow [\text{MeB(C}_6\text{F}_5)_3]^\text{+}
\]

\[
\text{Cp}^*\text{ZrMe}_2 + [\text{Ph}_3\text{C}]^+ [\text{B(C}_6\text{F}_5)_4]^\text{−} \rightarrow \text{Cp}^*\text{ZrCH}_3 \rightarrow \text{B(C}_6\text{F}_5)_4]^\text{−} + \text{Ph}_3\text{CCH}_3
\]
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\textsuperscript{III}, Ti\textsuperscript{IV}/Zr\textsuperscript{IV}/Hf\textsuperscript{IV}, Ni\textsuperscript{II}/Pd\textsuperscript{II}...

...but it did result in another modification of the Cossee-Arlman mechanism.
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
- $k_{\text{ins}} \gg k_{\beta-H}$
- $E_{M-C} \approx E_{M-H}$
- Highly oxophilic
- Low tolerance to polar groups

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

β-alkyl elimination/transfer to monomer

\[
\text{Termination Mechanism} \quad \rightarrow \quad \text{β-alkyl elimination/transfer to monomer}
\]
Propagation versus termination

Termination requires more room than propagation
Mechanism – chain transfer processes

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
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.

H-X is already polarized, which facilitates the reaction.
Main group metal alkyls can also function as chain transfer agents.

\[ \text{M} \rightarrow \text{R} \quad \rightarrow \quad \text{M} \rightarrow \text{R} \rightarrow \text{R} \quad \rightarrow \quad \text{M} \rightarrow \text{R} \rightarrow \text{R} \quad \rightarrow \quad \text{M} \rightarrow \text{R} \rightarrow \text{R} \]

\[ \text{M}'\text{R}_x = \text{AlMe}_3, \text{MgBu}_2, \text{ZnEt}_2, \ldots \]
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.