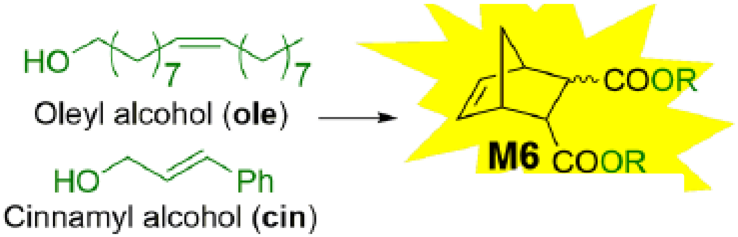
Catalysis for polymerization

Synthesis of
new polymers

Tailoring of new monomers
Multistep organic synthesis

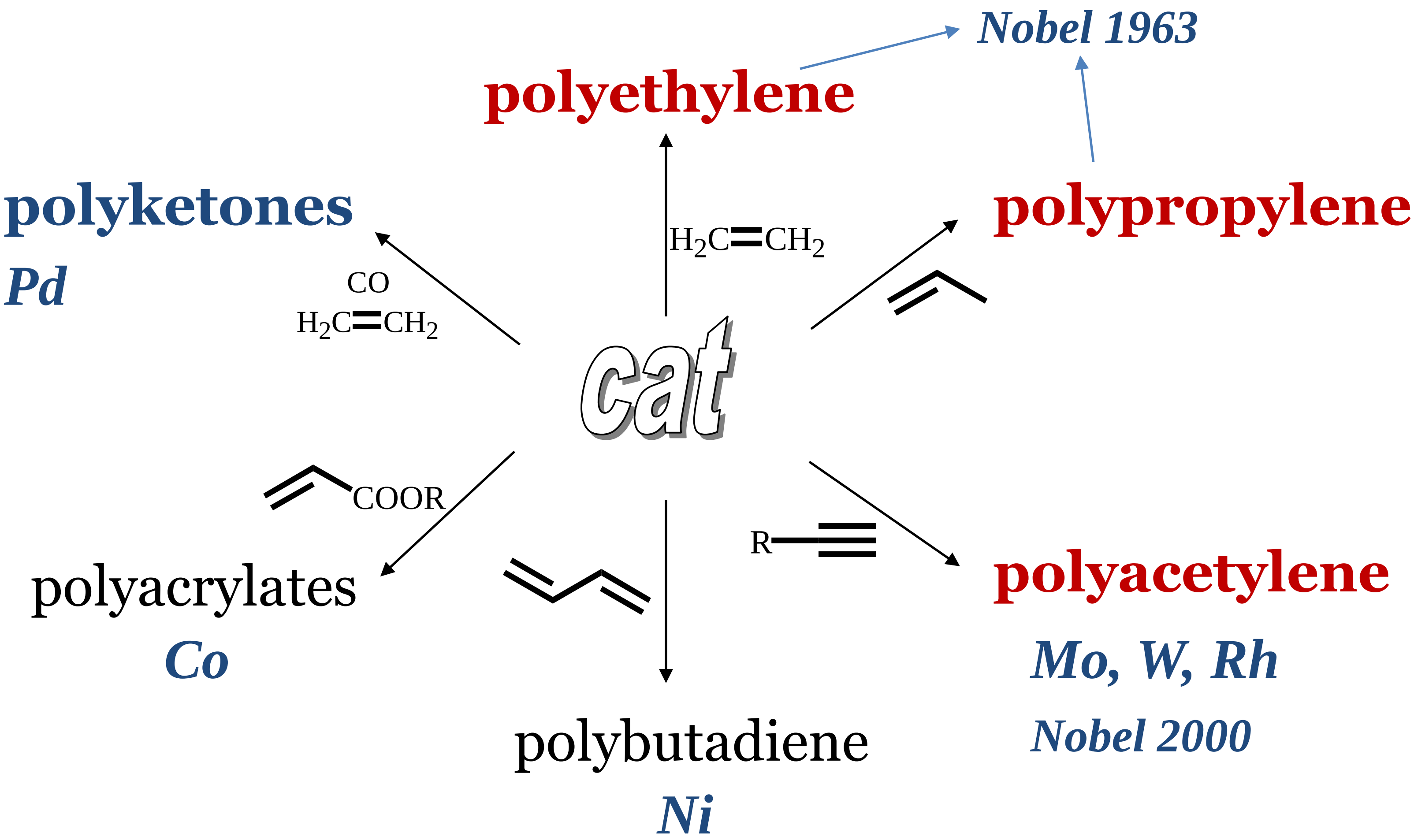


Development of new catalysts able to polymerize in a new fashion simple and commercially available monomers

Precision Polymerization

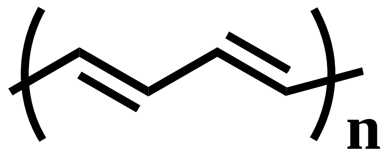
G. Chen, X. S. Ma, Z. Guan *J. Am. Chem. Soc.* 2003, *125*, 6697.

Catalysis for polymerization



[1]S. Kobayashi, *Catalysis in Precision Polymerisation* **1997**, Ed. Wiley.

Polyacetylene and substituted polyacetylene

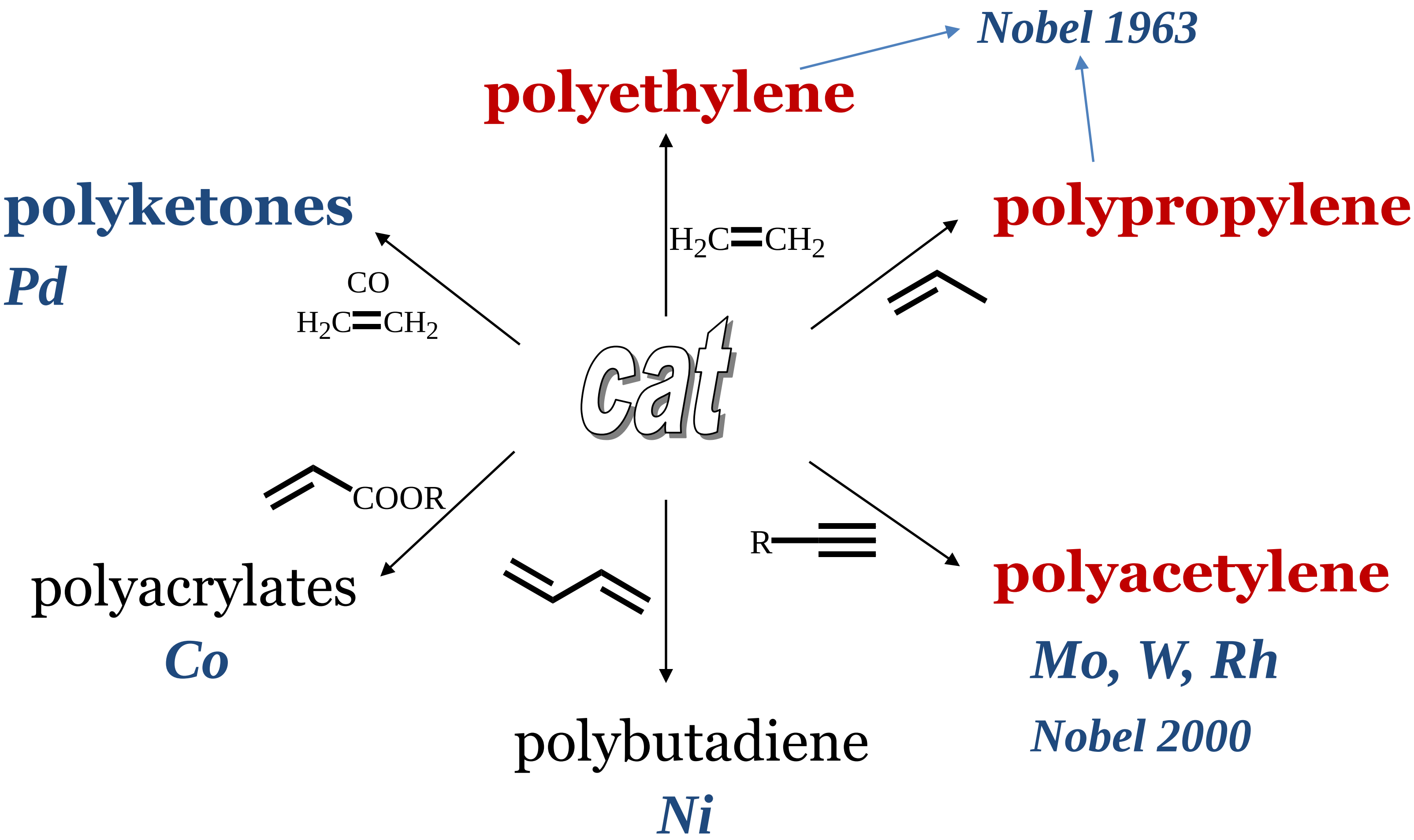


The polymers are featured by **conjugated** *C-C* double bonds. Thus, they show peculiar properties not found in polyolefins. The most important is the conductivity of electricity.

Polyacetylene is a **black solid**, **unstable** in air. It behaves like a **semiconductor**, but when properly **dopped** with AsF_5 or I_2 it shows the **conductivity** like a metal.

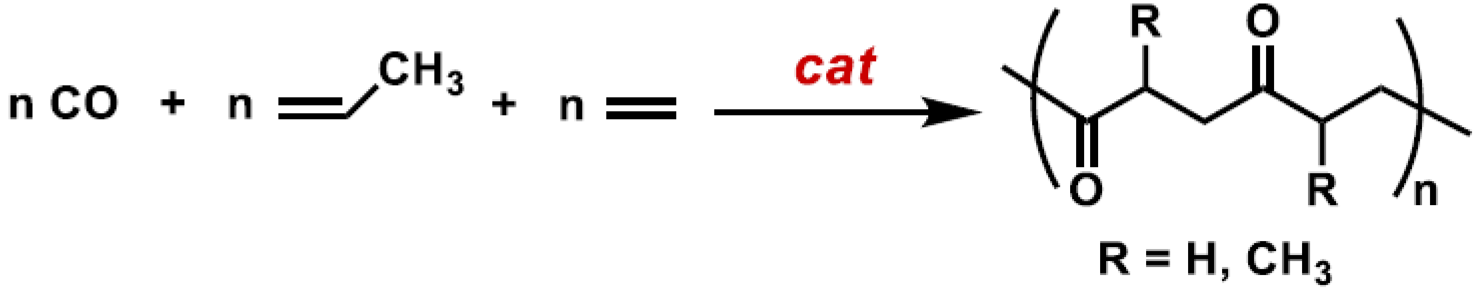
Substituted polyacetylenes have different **colors** depending on the number and the nature of the substituents; they are **soluble** in common organic solvents, they are **stable** in air for long time and they are **insulators**.

Catalysis for polymerization



[1]S. Kobayashi, *Catalysis in Precision Polymerisation* **1997**, Ed. Wiley.

CO/terminal alkene copolymerization



Commercialized by Shell Chemicals

Drent, E. et al. *J. Organomet. Chem. Soc.* **1991**, *417*, 235; Drent, E. et al. *Chem. Rev.,* **1996**, *96*, 663; Alperwicz, N., *Chem. Week.* **1995**, 22.

Innovative engineering plastics we have dreamed of

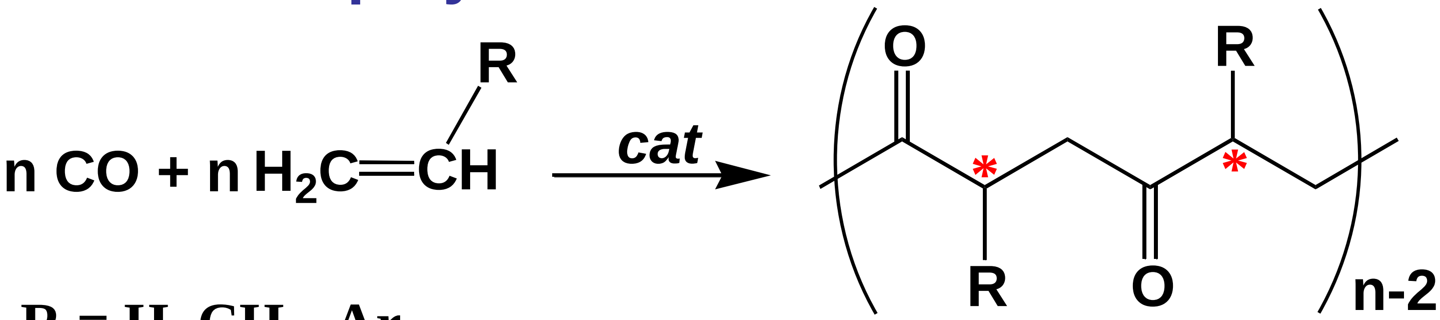
POKETONE is a new eco-friendly thermoplastic made of CO and olefins.
With its unique balance of excellent properties,
it will bring you various innovations for diverse applications.

Commercialized by Hyosung

http://www.poly-ketone.com/utl/web/mediadownload.do?subpath=/download/catalogEn/poketone_catalogue2017_en.pdf.

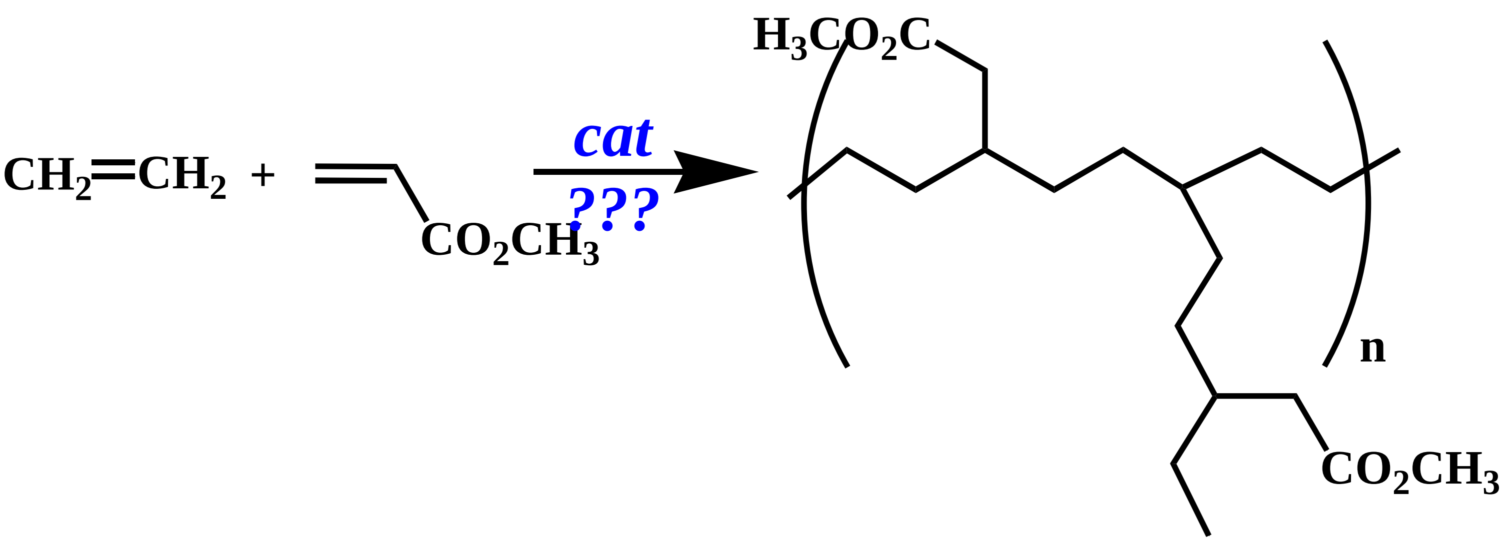
Synthesis of copolymers

CO/alkene Copolymers



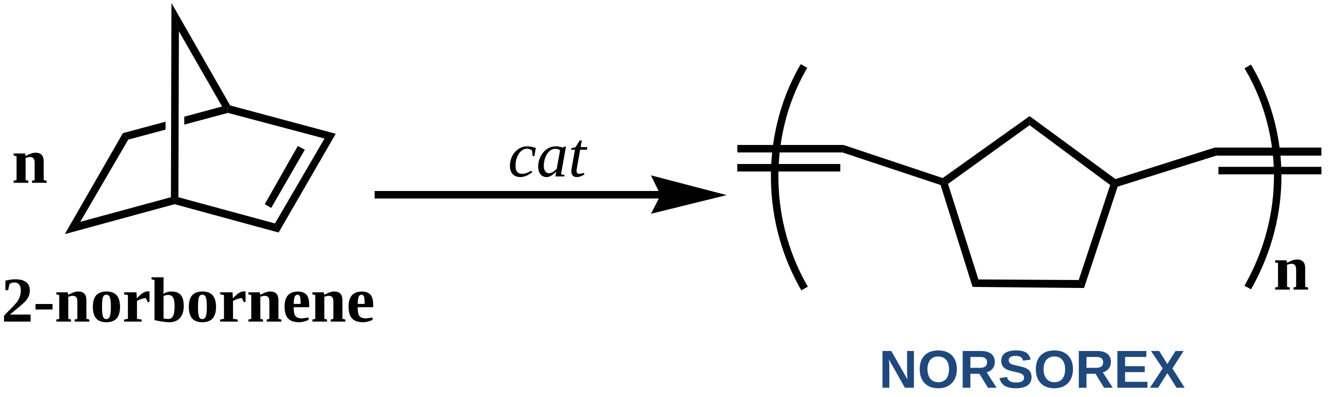
R = H, CH_3, Ar

Ethylene/polar vinyl monomers Copolymers



Ring-opening metathesis polymerization

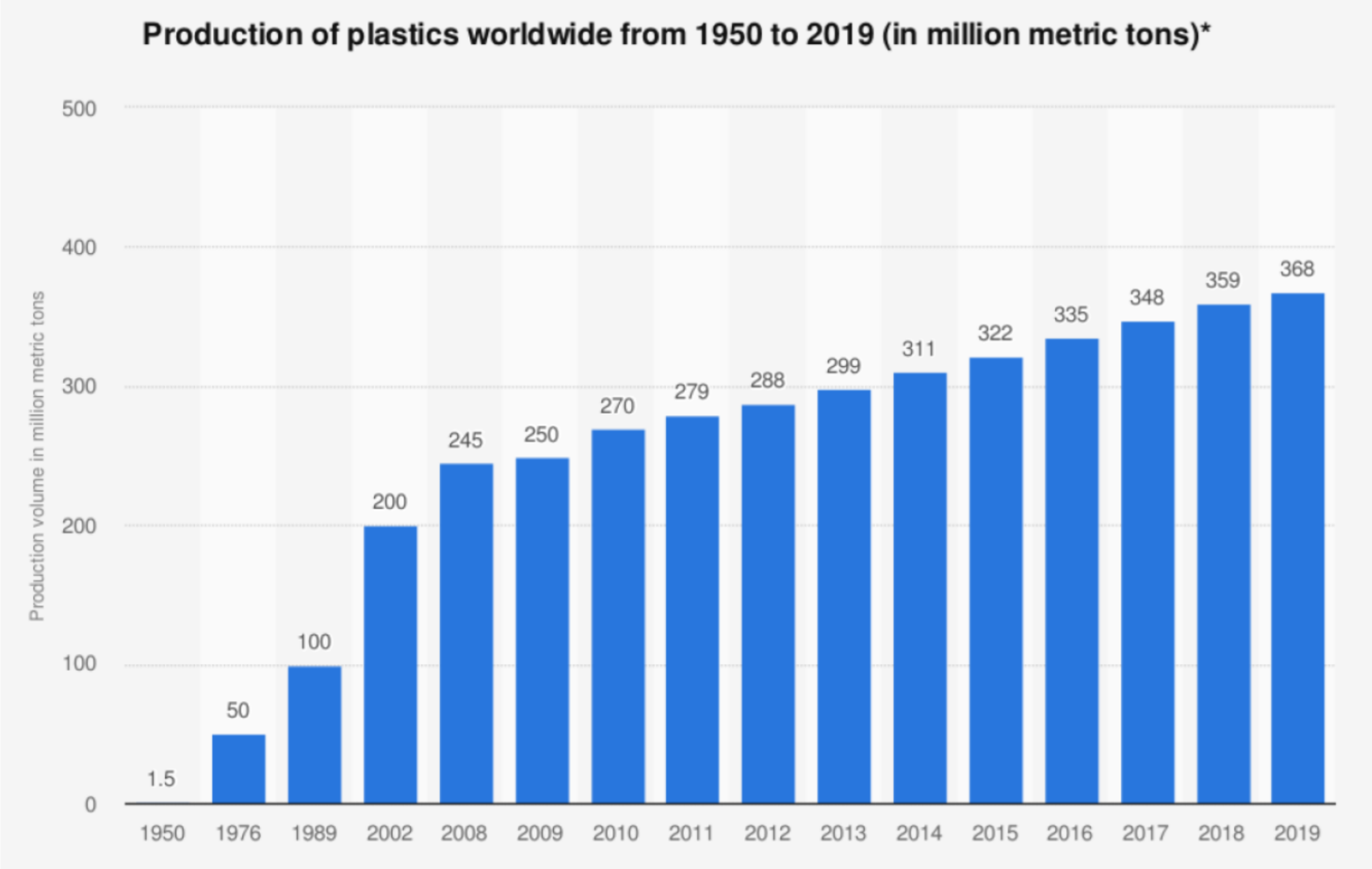
ROMP



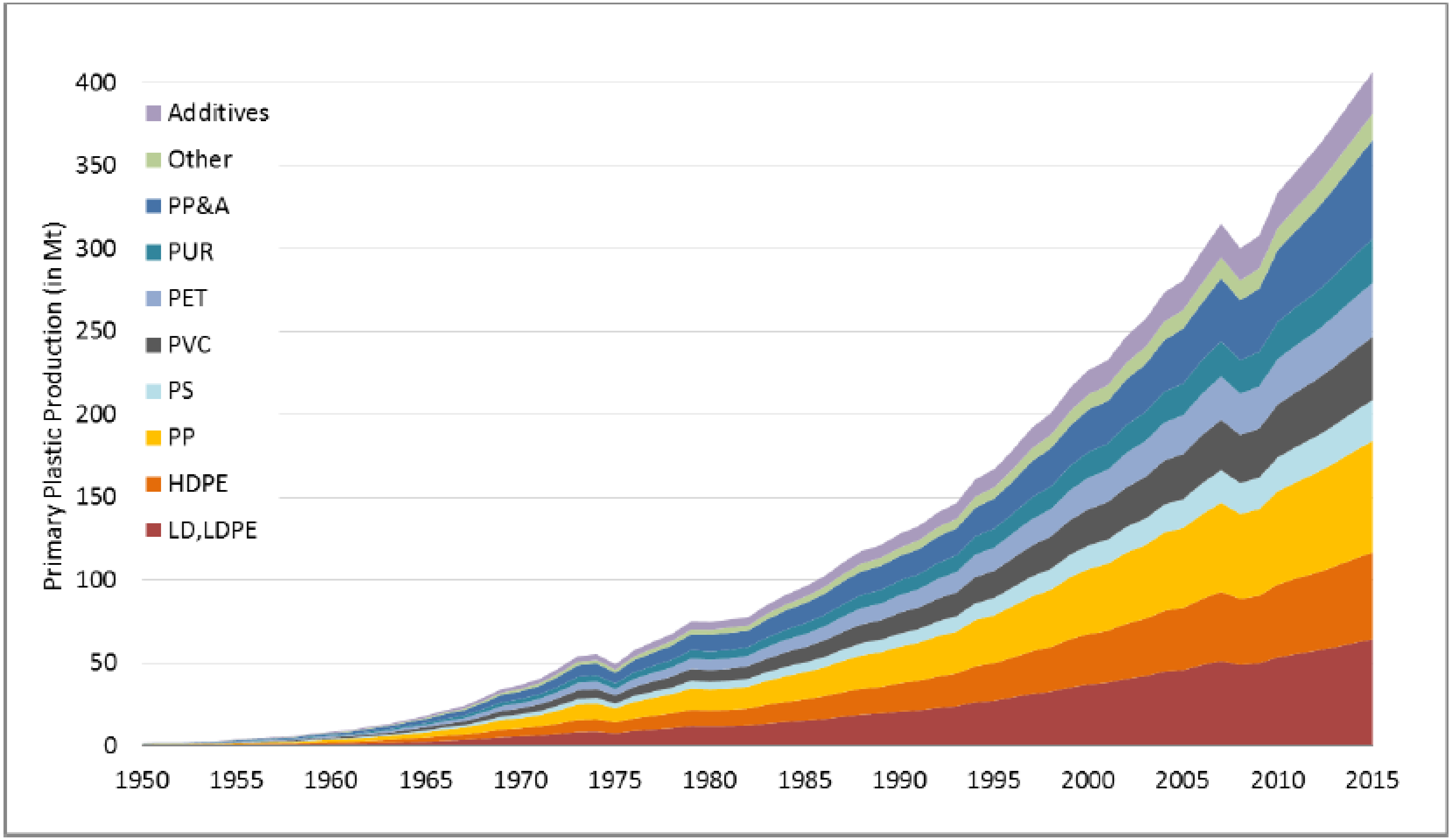
Polymerization with retaining of the functional groups.

https://youtu.be/KzzkYYYPNxI

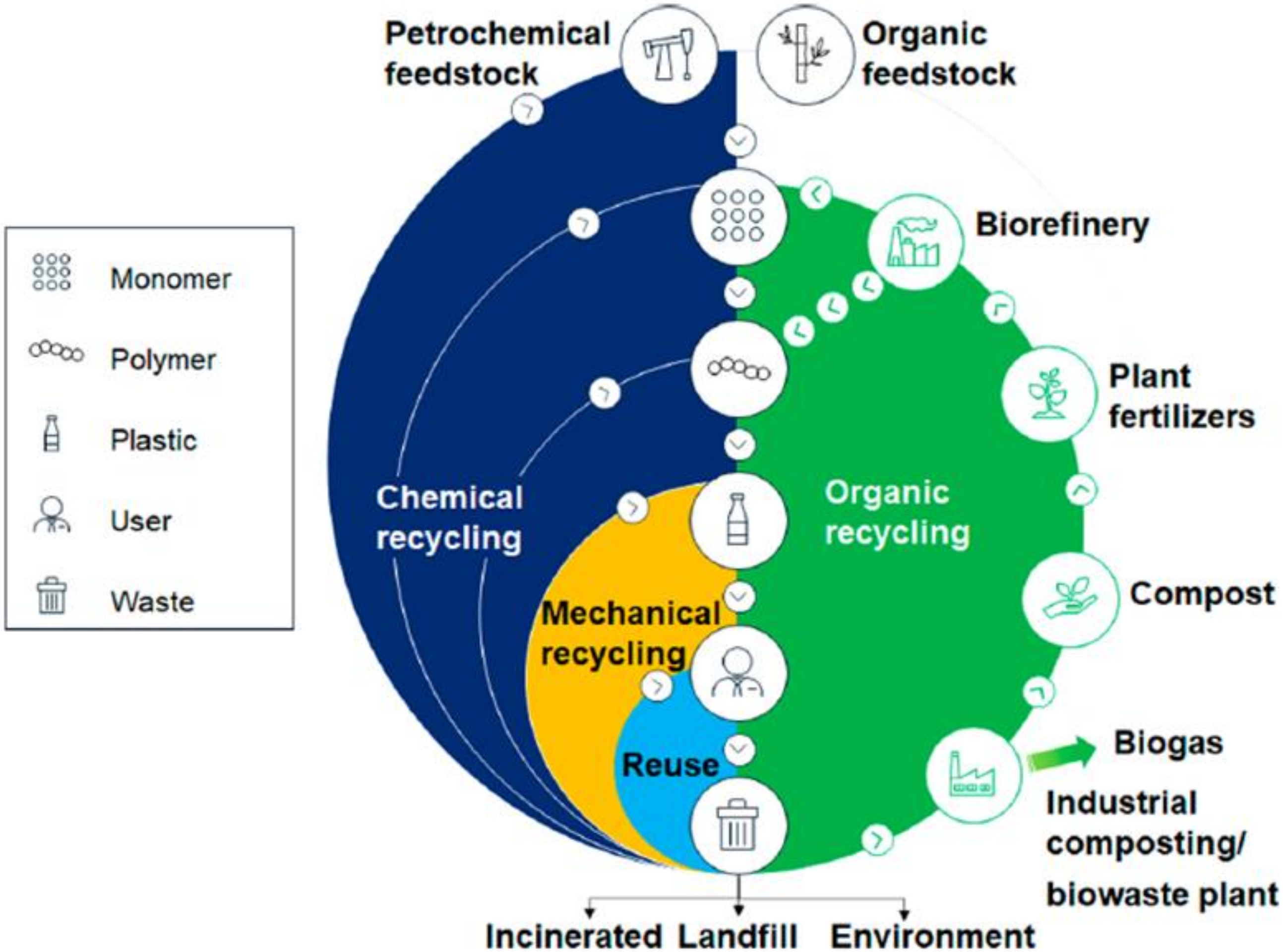
Plastic: is the abbreviative of **thermoplastic**, a type of material that can be melted when heated and solidified when cooled. This process can be repeated almost indefinitely.



Global primary plastic production according to polymer type

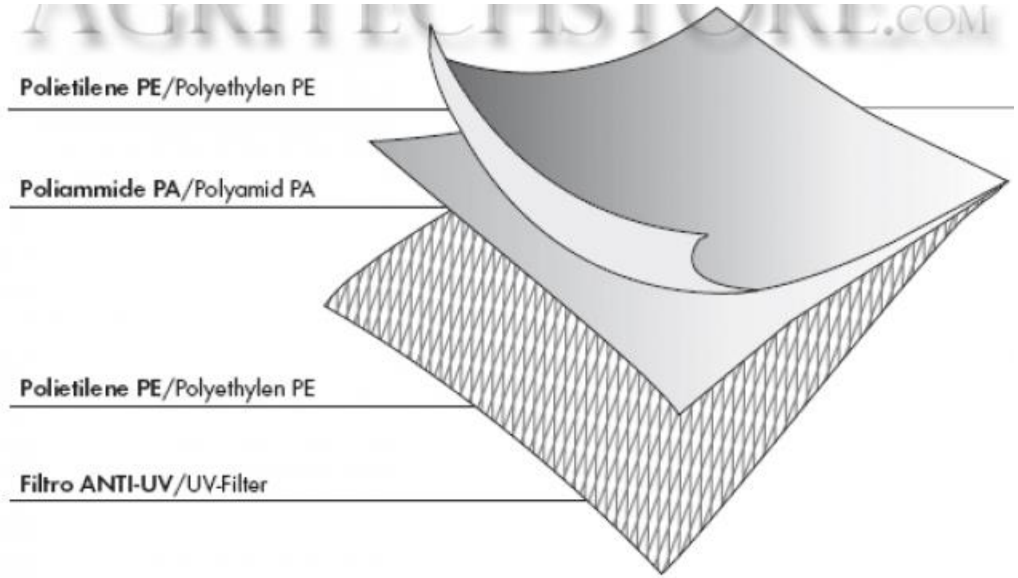


The problem of polyolefin environmental pollution.

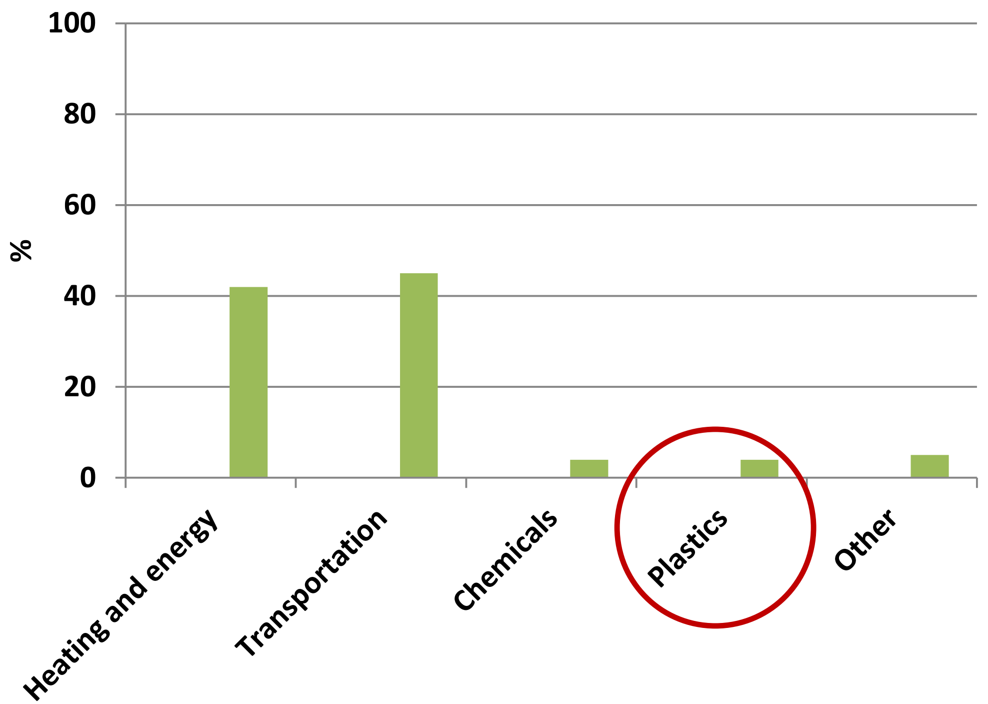


Moving from the linear end-of-life to the circular end-of-life.

Multimaterials



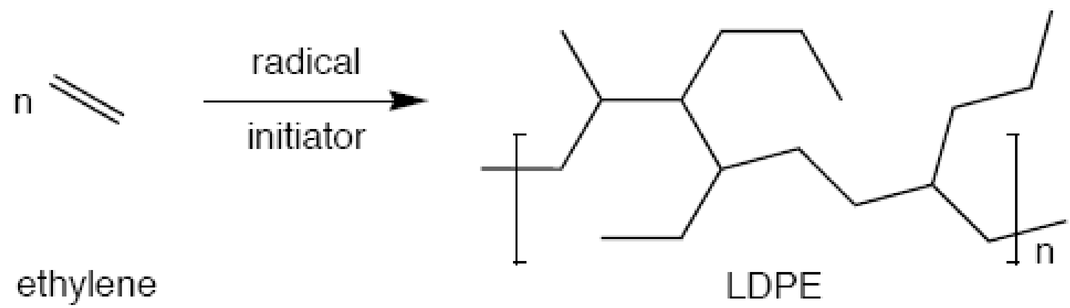
Use of oil



Kind of polyolefins

	LLDPE	LDPE	HDPE	UHMWPE	iPP
Density (g cm^{-3})	0.90-0.94	0.91-0.94	0.94	0.930-0.935	0.88-0.92
Melting point (°C)	100-125	98-115	125-132	130-136	160-166
Cristallinity (%)	22-55	30-54	55-77	39-75	30-60

LDPE

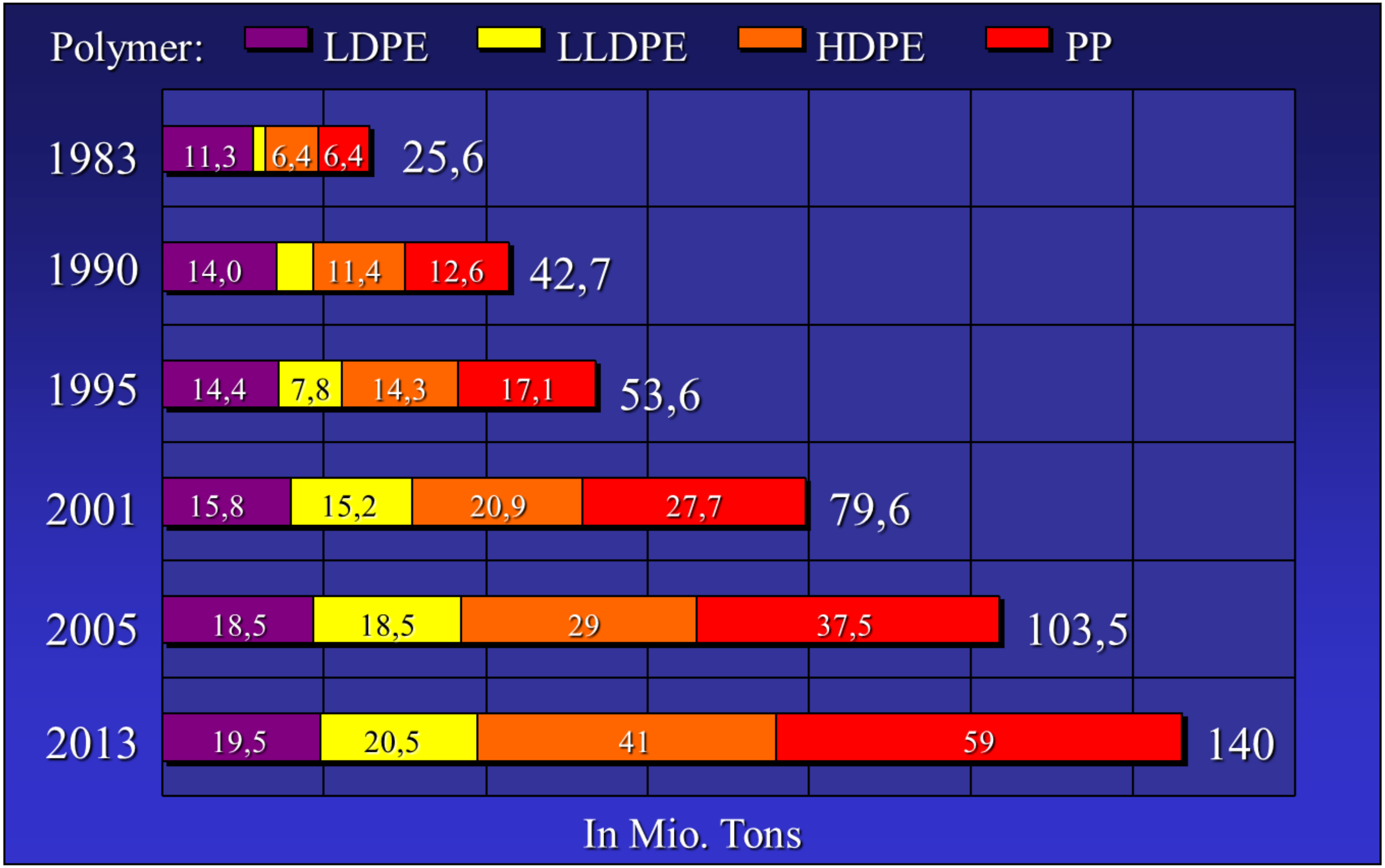


- LDPE: Low density polyethylene
- Highly branched material
- Properties and usage:

Stretchable before tearing
Used for flexible plastic bags
Recycled material: trash bags, grocery sacks

4
LDPE

Global production of polyolefins (10^6 ton)



W. Kaminsky, *personal communication.*

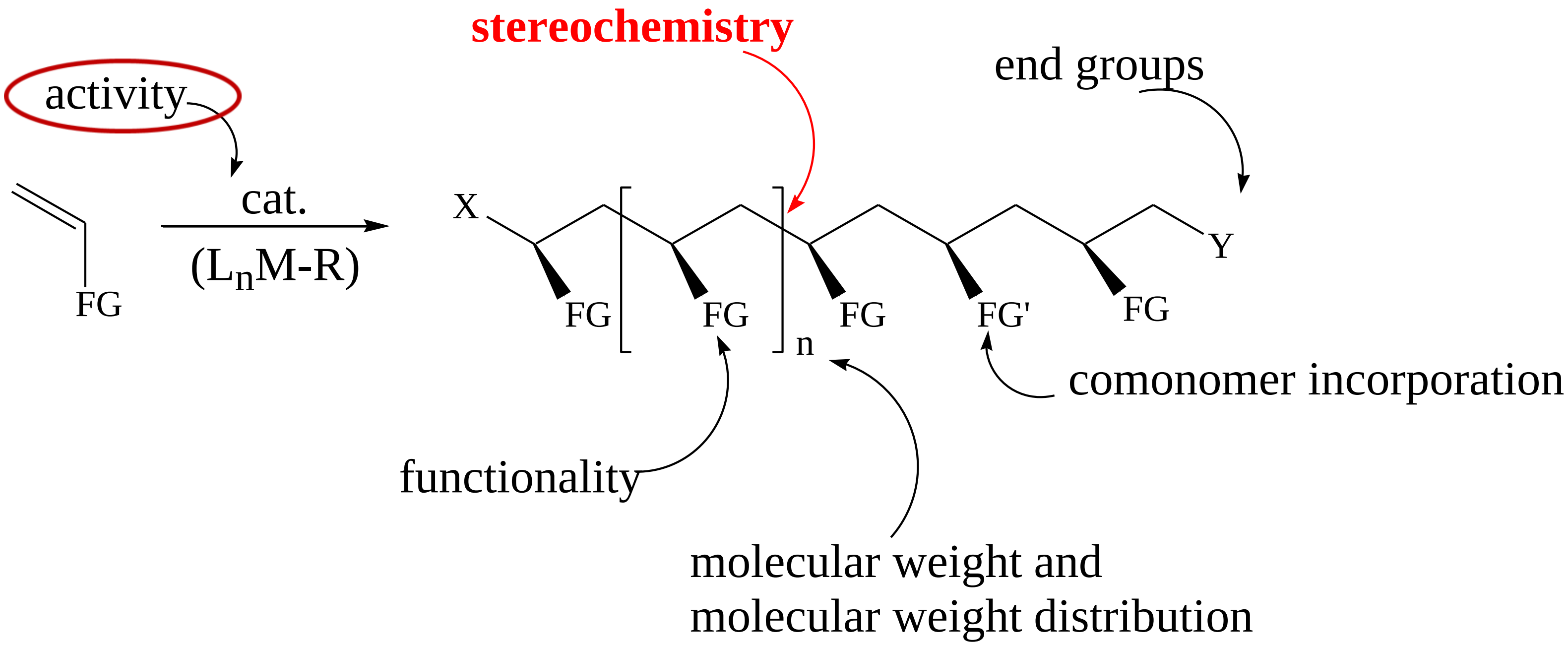
Worldwide production of polyolefins in 2005 (10^6 ton/year)

Total production in 2010: 120 10^6 ton.*

W. Kaminsky *Macromol. Chem. Phys.* **2008**, *209*, 459.
* Barzan, C.; Gianolio, D.; Groppo, E.; Lamberti, C.; Monteil, V.; Quadrelli, E. A.; Bordiga, S. *Chem.-Eur. J.* **2013**, *19*, 17277.

Methods of polymerization

Radical Anionic Cationic Coordination-Insertion



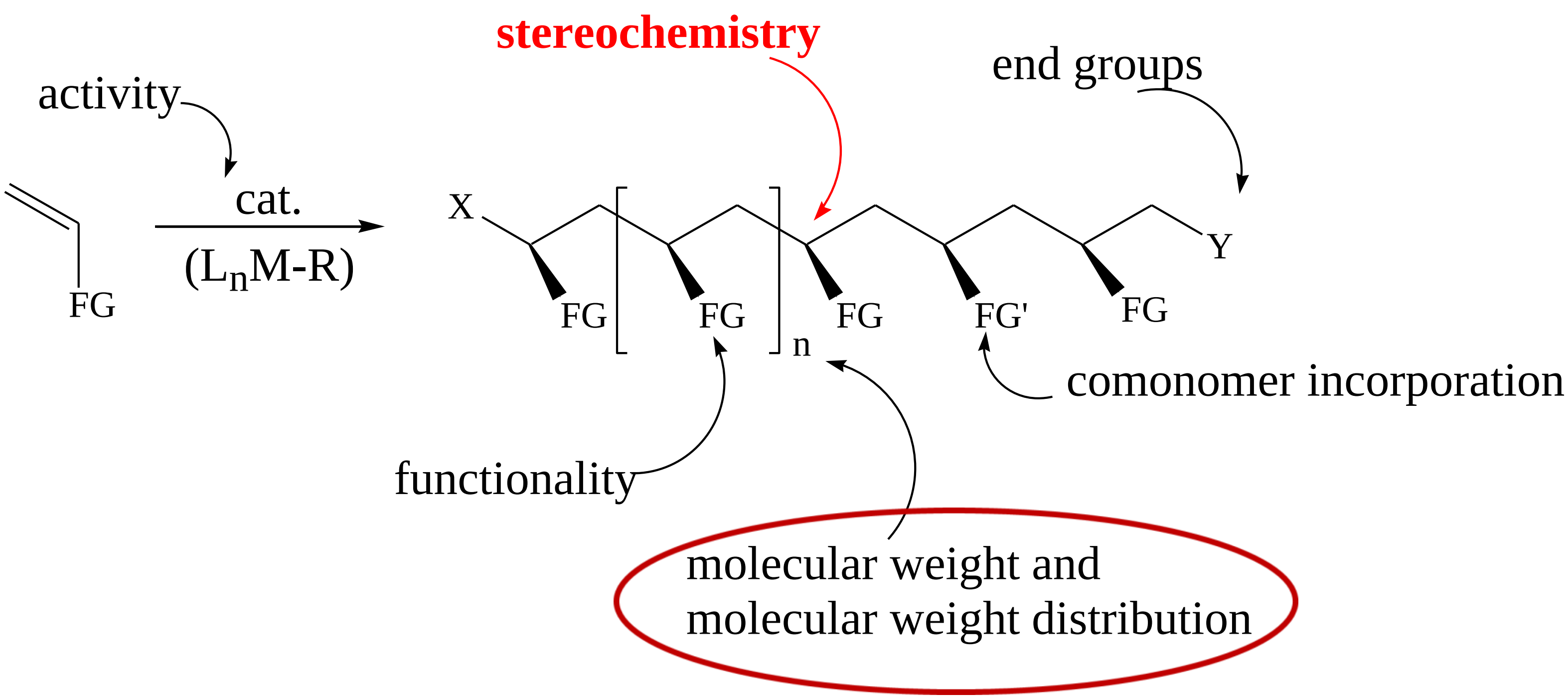
G. W. Coates et al. *Angew. Chem. Int. Ed.* **2002**, *41*, 2236.

Rating effectiveness of a catalyst for polyolefin production

Rating	Very low	Low	Moderate	High	Very high
Activity (g P/mmol cat · h · bar)	< 1	10 - 1	100 - 10	1000 - 100	> 1000

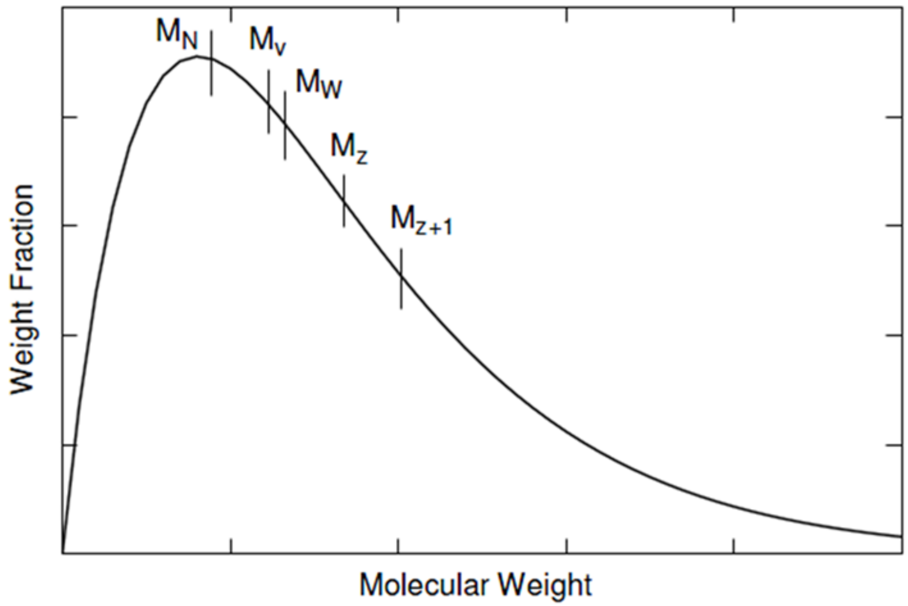
Gibson, V. C. et al. *Angew. Chem. It. Ed.* **1999**, *38*, 429.

Coordination – Insertion Polymerization (*CIP*)



G. W. Coates et al. *Angew. Chem. Int. Ed.* **2002**, *41*, 2236.

Molecular Weight and Molecular Weight distribution



$$\langle M_n \rangle = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i}$$

$$\langle M_w \rangle = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i}$$

- In a polydisperse polymer, Mw ≥ Mn.
- The polydispersity and breadth of plot, has bearing on the mechanism of polymerization and the properties of the resulting polymer.

The polydispersity index

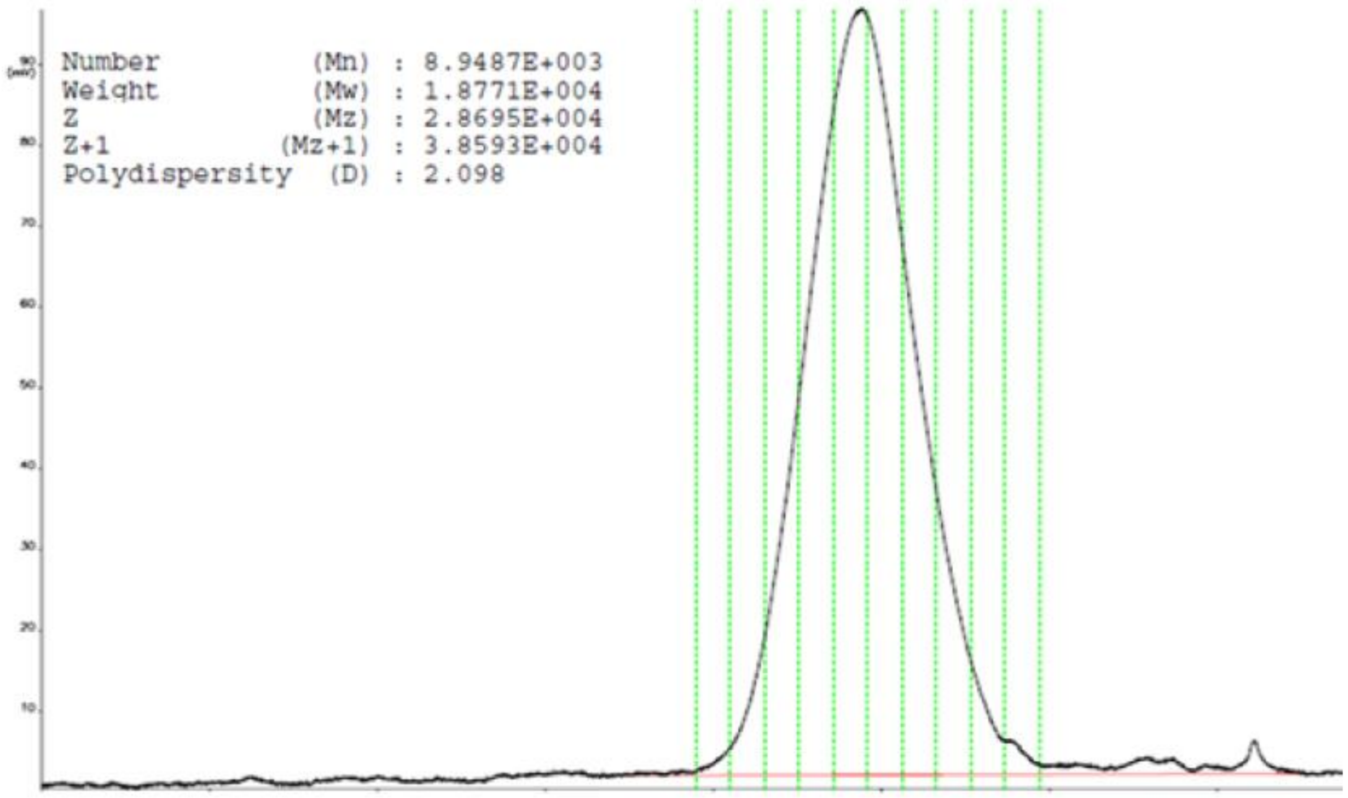
$$\frac{Mw}{Mn}$$

- $\gg 10$ Radical polym.
- $\cong 10$ Heterogeneous catalyst
- $\cong 2$ Single site catalyst
- $\cong 1$ Living polym.

Examples of analytical techniques applied for polymer characterization

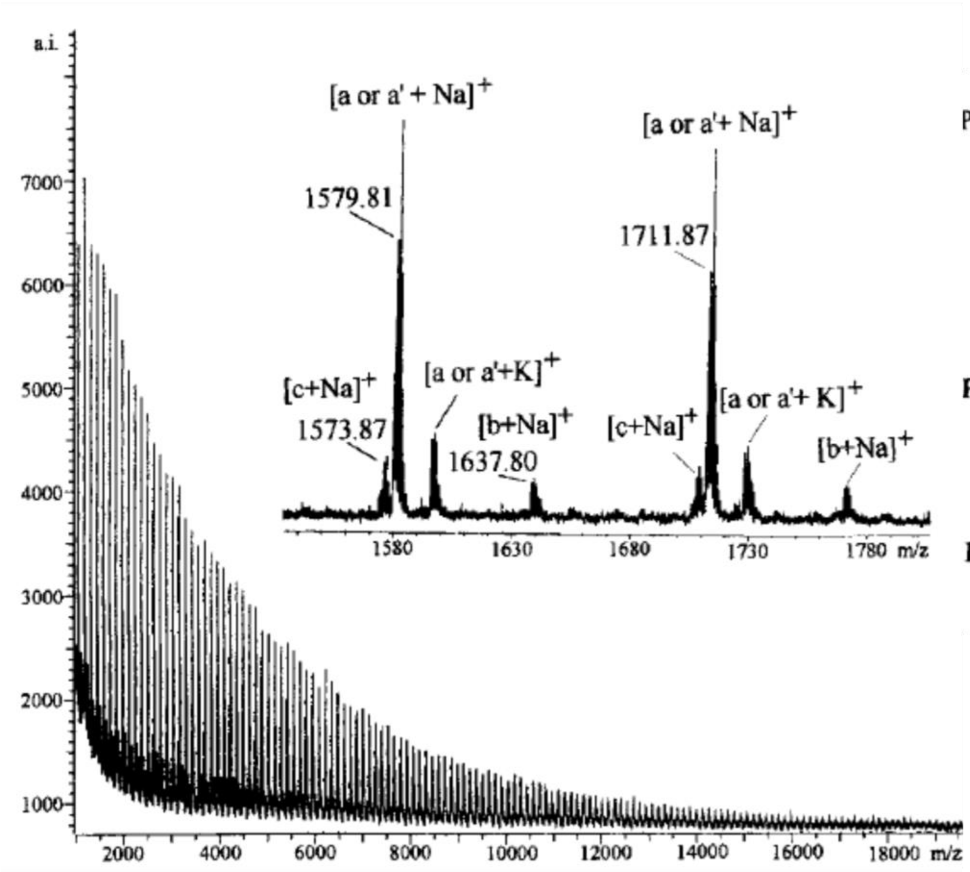
Gel Permeation Chromatography

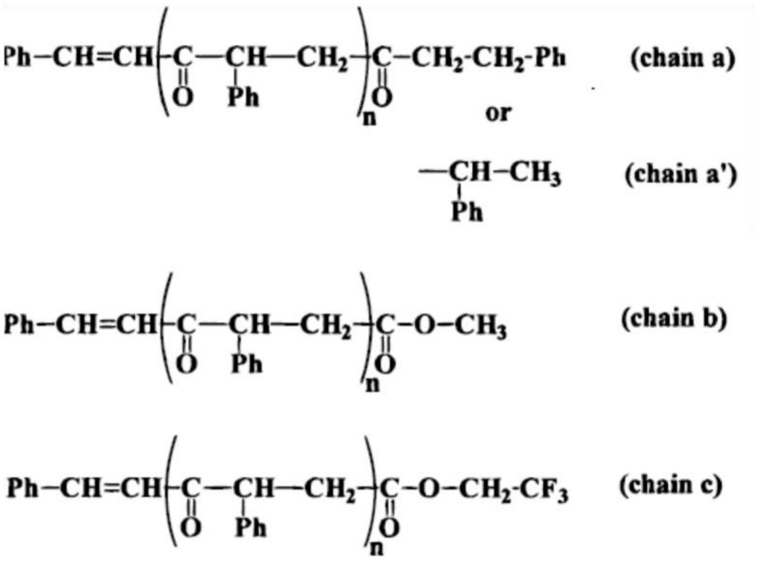
Size Exclusion Chromatography



Examples of analytical techniques applied for polymer characterization

MALDI-TOF





Milani, B. et al. *Organometallics* **2000**, *19, 3435.*

Examples of analytical techniques applied for polymer characterization

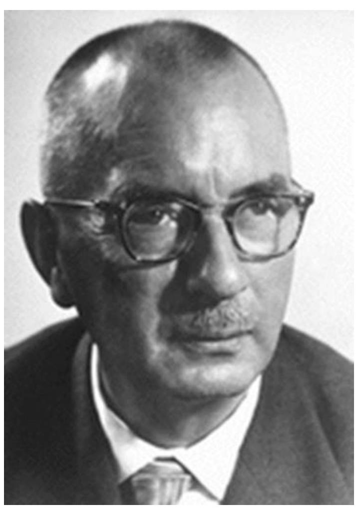
NMR Spectroscopy in solution allows to characterize macromolecules:

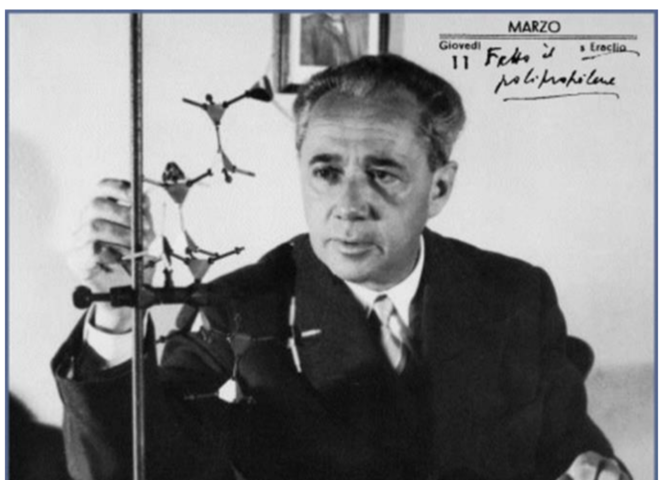
- ✓ **microstructure: e.g. linear or branched chains;**
- ✓ **regiochemistry: head to tail, tail to tail, head to head enchainments;**
- ✓ **stereochemistry: different microtacticity;**
- ✓ **end groups: to gain information about initiation and termination steps;**
- ✓ **content of comonomers;**
- ✓ **comonomer distribution: random, block, alternate;**
- ✓ **comonomer position: into the main chain; in the branches.**

Coordination – Insertion polymerization: The starting point.

1953. POLYETHYLENE is synthesized via catalysis for the first time under mild reaction conditions. Ziegler.

1954. STEREOREGULAR POLYPROPYLENE is synthesized for the first time. The principle of STEREOSPECIFIC POLYMERIZATION is introduced. Natta.





1963. Ziegler and Natta were awarded with the Nobel Prize for Chemistry

Synthesis of polyolefins

Ziegler Natta Catalysts

1950

Heterogeneous Catalysts

Catalysts based on **Ti or V**

Metallocene Catalysts

1980

Homogeneous Catalysts

Catalysts based on **Ti or Zr**

early *transition metals*

Brookhart's Catalysts

1995

Homogeneous Catalysts

Catalysts based on **Fe or Co or Ni or Pd**

late *transition metals*

The Ziegler – Natta catalytic system

Heterogeneous Catalysts:

$TiCl_4$-AlR_3 $TiCl_3$-AlR_3

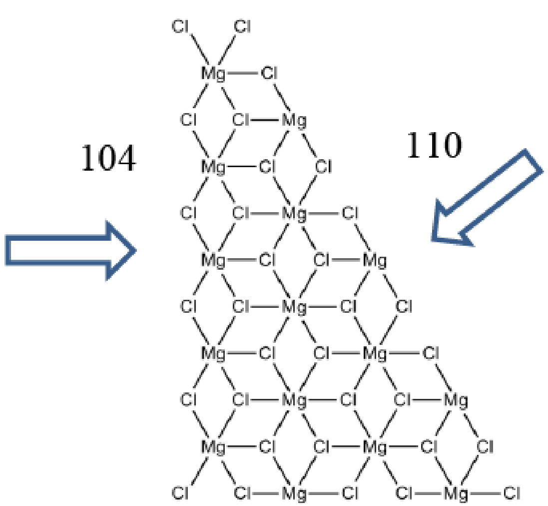
$MgCl_2$/ $TiCl_4$-AlR_3 ⟶ 1 000 kg PE/g Ti

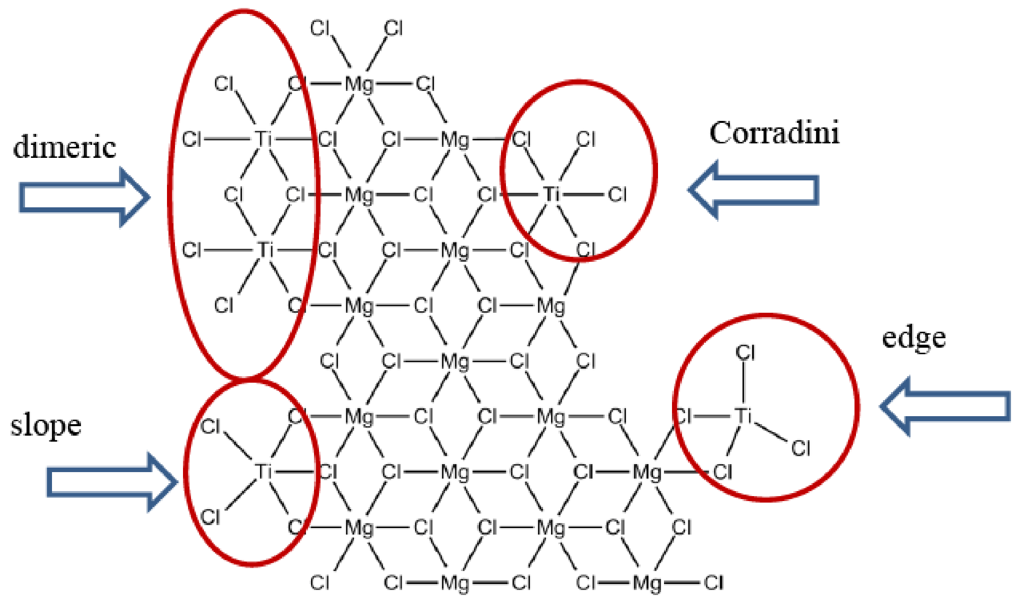
R = Et, *i*-But

$P_{ethylene}$ ≈1 atm;

T ≤ 0°C

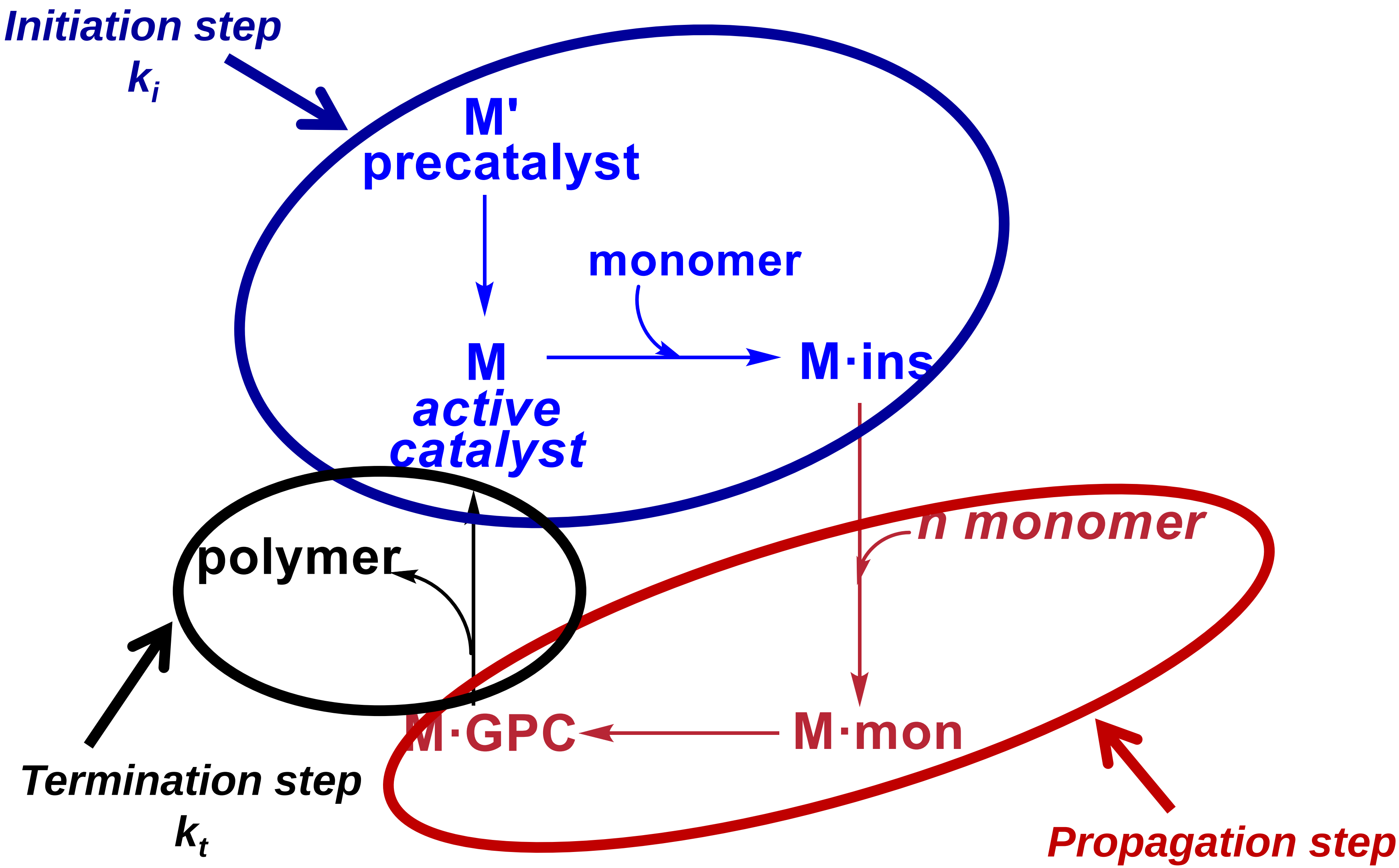
Highly exothermic process: 93.6 kJ/mol.





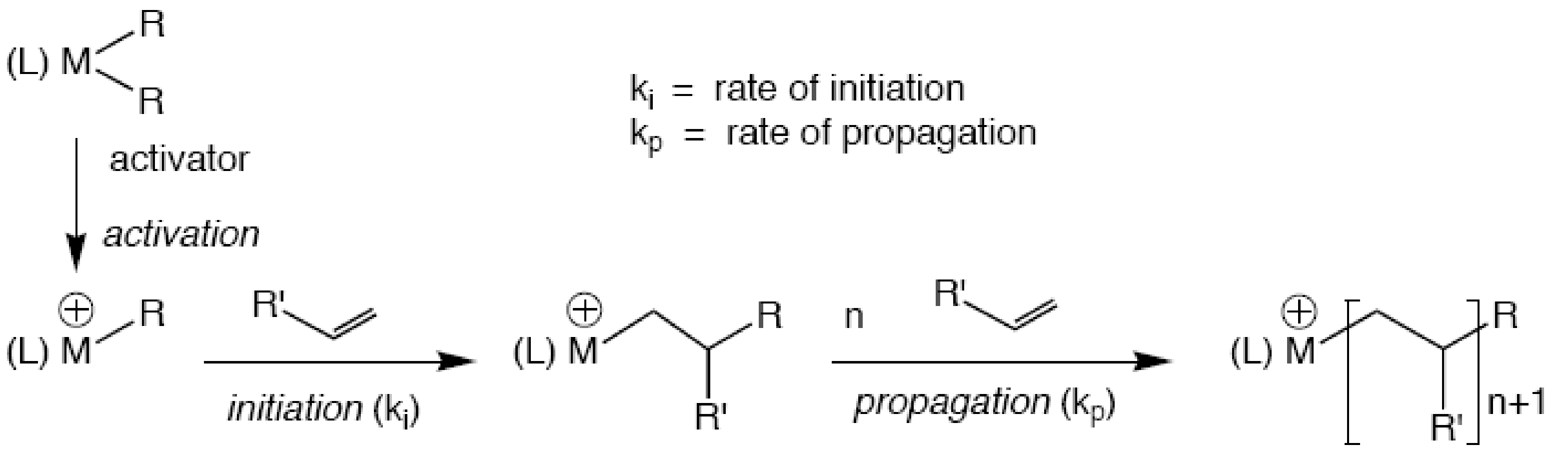
T. Masuda, *Catalysis in Precision Polymerisation* **1997**, Ed. Wiley, pg. 18.

CIP Mechanism: the fundamental steps



Molecular weight $\propto \frac{k_p}{k_t}$

Living polymerization: A special case



• Initiator and intermediates are stable under reaction conditions;
• There is **no chain termination**;
• **ki ≥ kp**: this means that the rate of initiation is greater than rate of propagation and that all the metal centers are initiated before propagation takes place;
• Polymers with **narrow molecular weight distributions** are obtained.

Polymerization Mechanism

Initiation step

$\mathbf{k_i}$

- ❖ active species formation;
- ❖ reaction with the first monomer units;

Propagation step

$\mathbf{k_p}$

- ❖ growth of polymer chain on the metal centre;

Termination step

$\mathbf{k_t}$

- ❖ stop of the growth of the polymer chain;
- ❖ the active species is formed again.

Polymerization Mechanism

Initiation step

$$TiCl_4 + Al(C_2H_5)_3 \longrightarrow (C_2H_5)TiCl_3 + (C_2H_5)_2AlCl$$ *Alkyl.*

$$(C_2H_5)TiCl_3 \longrightarrow TiCl_3 + C_2H_5^{\bullet}$$ *Reduct.*

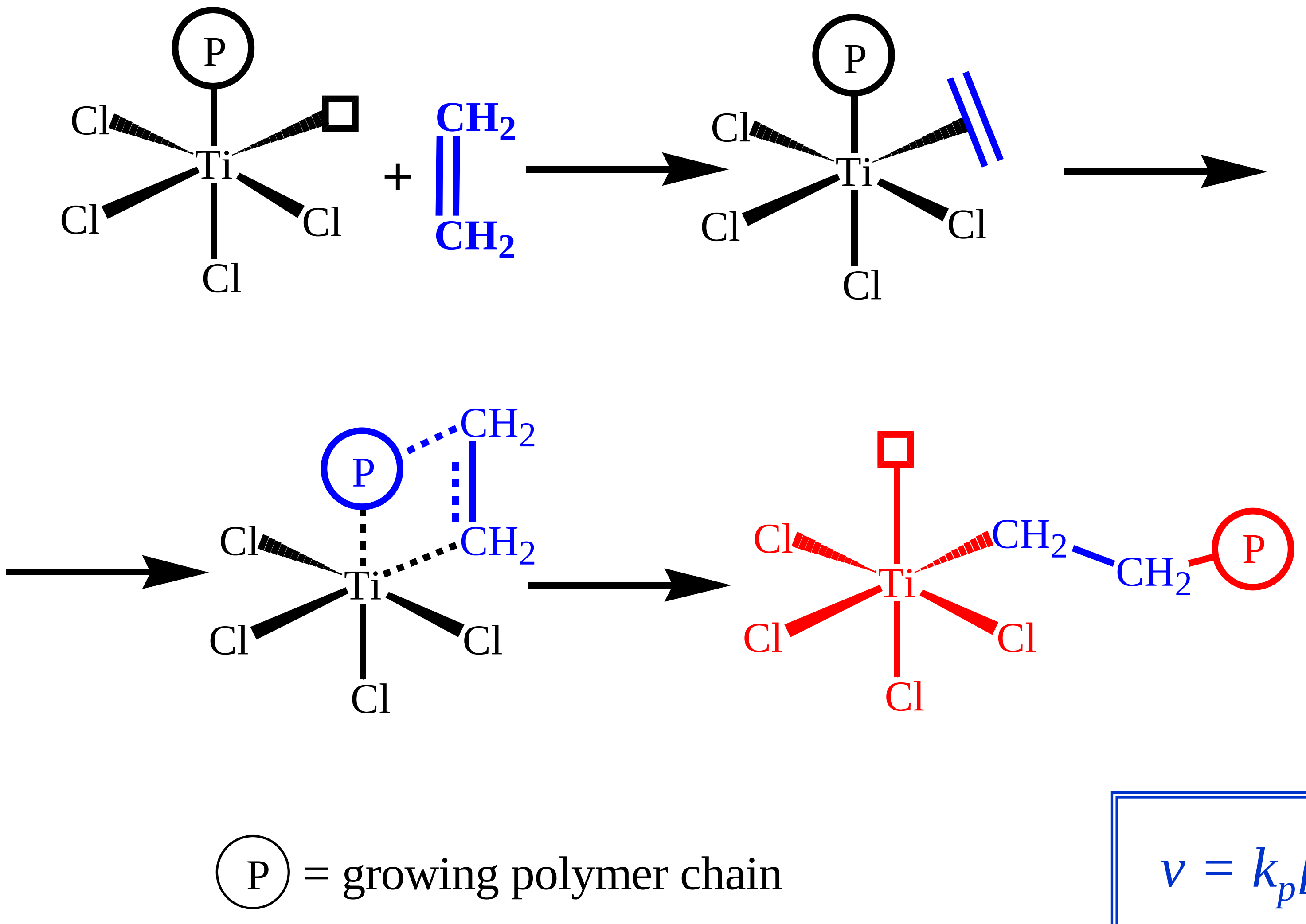
$$TiCl_3 + Al(C_2H_5)_3 \longrightarrow (C_2H_5)TiCl_2 + (C_2H_5)_2AlCl$$ *Alkyl.*

$$(C_2H_5)TiCl_2 \longrightarrow TiCl_2 + C_2H_5^{\bullet}$$ *Reduct.*

$$(C_2H_5)TiCl_n \xrightarrow{C_2H_4} Cl_nTi\text{-}CH_2CH_2\text{-}C_2H_5$$ *Insert.*

Polymerization Mechanism:
(Cossee-Arlman)

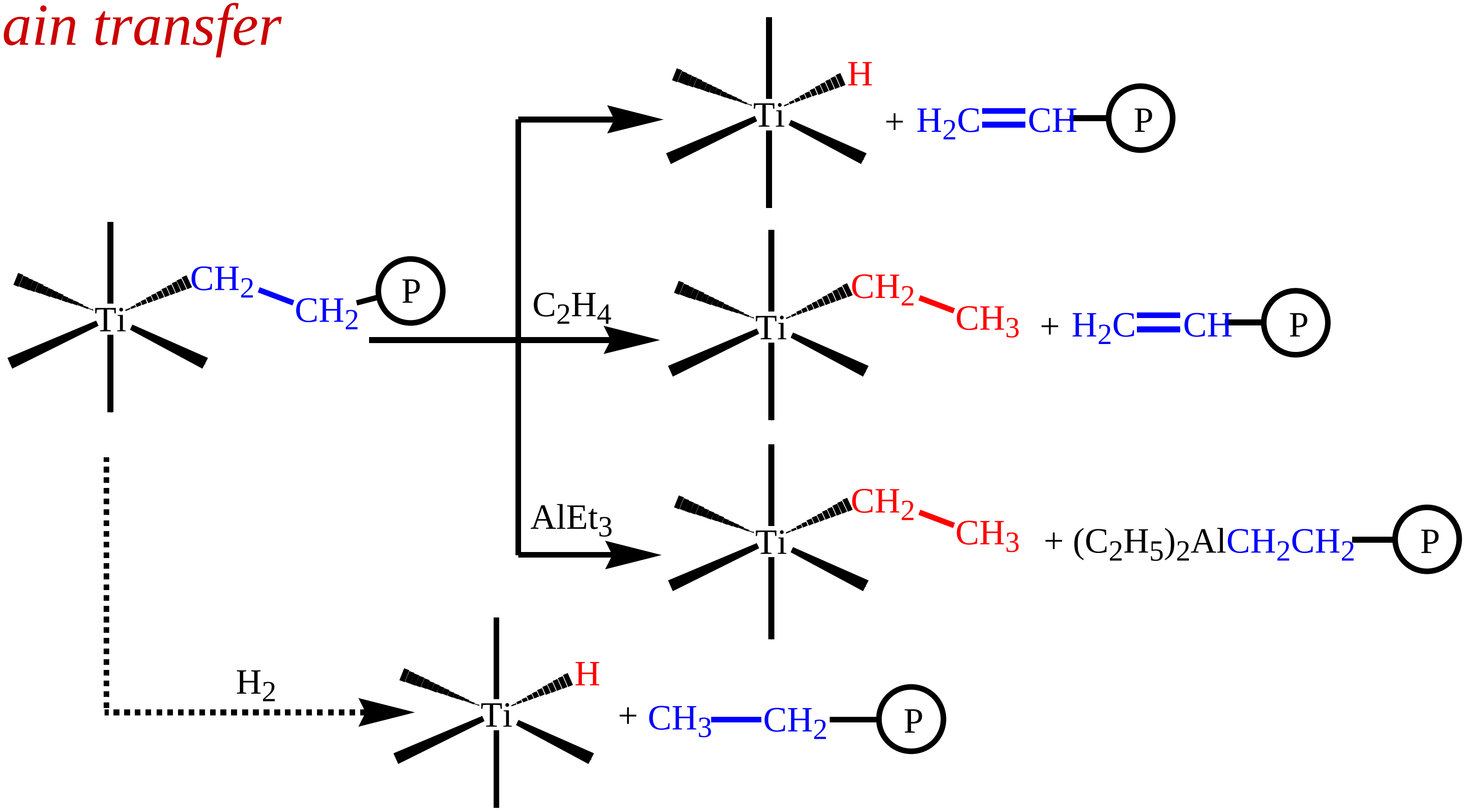
Propagation step



$$v = k_p[C^*][M]$$

Polymerization Mechanism

Termination step:
chain transfer



Limits of Ziegler Natta catalysts

- low amount of active sites: 1 – 20 % of Ti;

- 5 – 50 ppm of Cl_2 coming from the $MgCl_2$ support remain in the polymer, leading to potential corrosive phenomena during the polymer processing;

- it is possible to copolymerize with ethylene only a few terminal alkenes, and not in a random way;

- 3 – 4 % of oligomers remain in the polymer, which are released with time;

- it is difficult to have a control of the microstructure of the macromolecules.