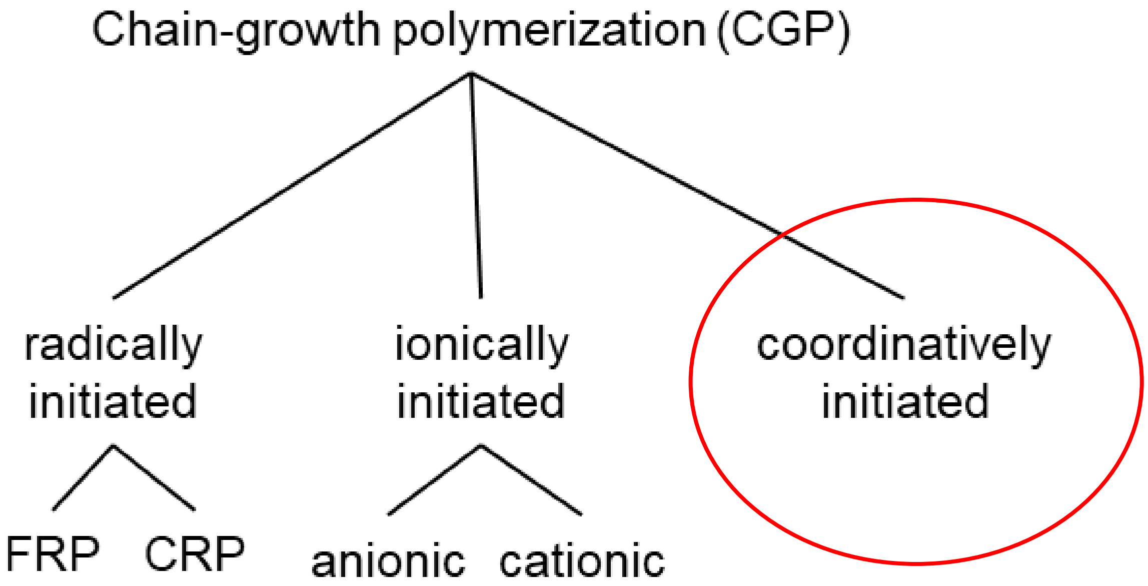
Polimerizzazioni a Catena
(chain-growth polymerizations)



Chain-growth polymerization (CGP)

radically initiated

FRP

CRP

ionically initiated

anionic

cationic

coordinatively initiated

Ziegler Natta Polymerizations

Ziegler-Natta Polymerization

- Synthesis of PE by I.C.I. Process

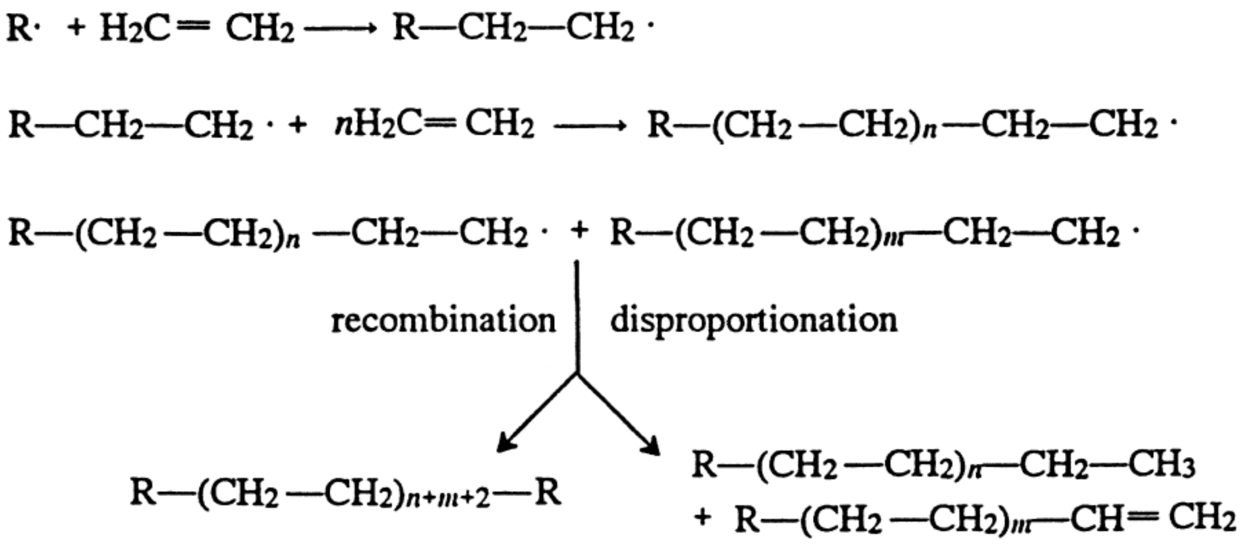
- From Ziegler’s *Aufbaureaction* to the first transition metal catalyst

- Mechanism of ZN polymerization for the synthesis of PE

- Stereospecific polymerization of PP

Ziegler-Natta Polymerization

I.C.I. Process: Free Radical Polymerization of Ethene (180-350 Mpa)



$R\cdot + H_2C{=}CH_2 \longrightarrow R{-}CH_2{-}CH_2\cdot$

$R{-}CH_2{-}CH_2\cdot + nH_2C{=}CH_2 \longrightarrow R{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_2\cdot$

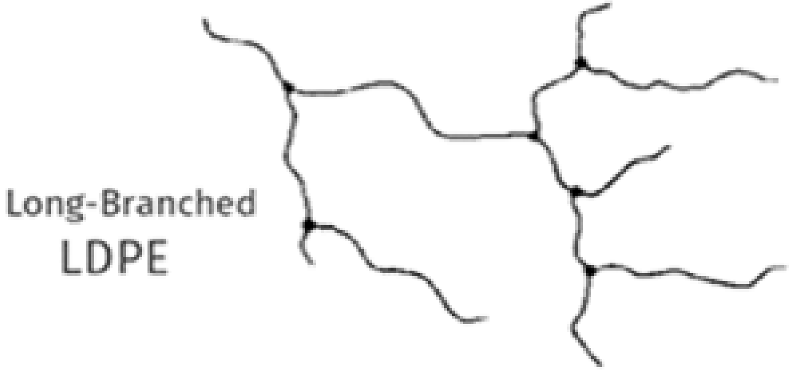
$R{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_2\cdot + R{-}(CH_2{-}CH_2)_m{-}CH_2{-}CH_2\cdot$

$R{-}(CH_2{-}CH_2)_{n+m+2}{-}R$

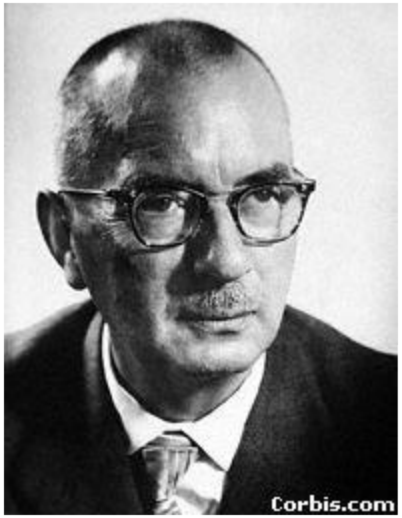
$R{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH_3 + R{-}(CH_2{-}CH_2)_m{-}CH{=}CH_2$

d = 0.91 g/cm^3
Crystallinity ~ 60%
Mp = 105°C

10-50 branches per 1000 C atoms



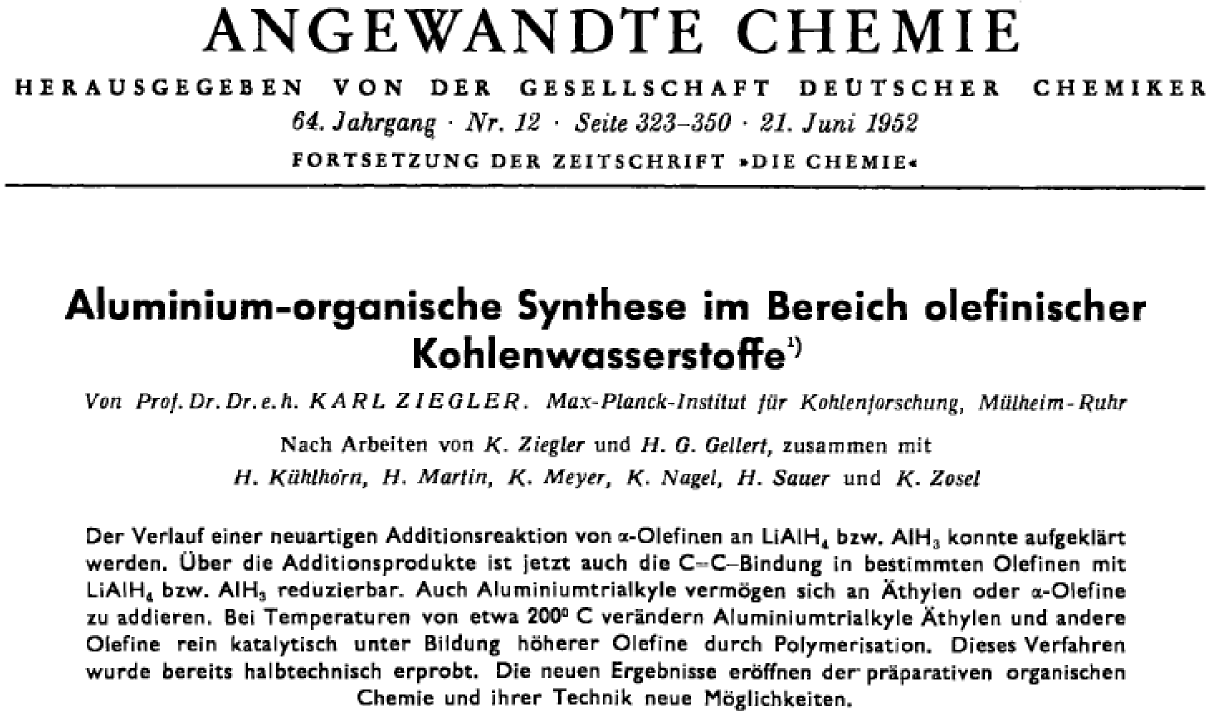
Ziegler-Natta Polymerization



Karl Ziegler, 1952

Aufbaureaction:

can be modified in the presence of transition metals



ANGEWANDTE CHEMIE
HERAUSGEGEBEN VON DER GESELLSCHAFT DEUTSCHER CHEMIKER
64. Jahrgang · Nr. 12 · Seite 323–350 · 21. Juni 1952
FORTSETZUNG DER ZEITSCHRIFT »DIE CHEMIE«

Aluminium-organische Synthese im Bereich olefinischer Kohlenwasserstoffe 1)

Von Prof. Dr. Dr. e. h. KARL ZIEGLER, *Max-Planck-Institut für Kohlenforschung, Mülheim-Ruhr*

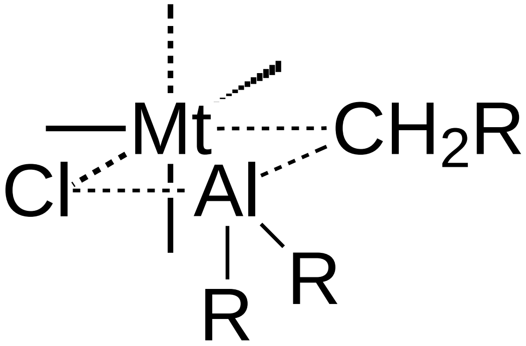
Nach Arbeiten von *K. Ziegler* und *H. G. Gellert*, zusammen mit
H. Kühlhorn, H. Martin, K. Meyer, K. Nagel, H. Sauer und *K. Zosel*

Der Verlauf einer neuartigen Additionsreaktion von α-Olefinen an $LiAlH_4$ bzw. AlH_3 konnte aufgeklärt werden. Über die Additionsprodukte ist jetzt auch die C=C–Bindung in bestimmten Olefinen mit $LiAlH_4$ bzw. AlH_3 reduzierbar. Auch Aluminiumtrialkyle vermögen sich an Äthylen oder α-Olefine zu addieren. Bei Temperaturen von etwa 200° C verändern Aluminiumtrialkyle Äthylen und andere Olefine rein katalytisch unter Bildung höherer Olefine durch Polymerisation. Dieses Verfahren wurde bereits halbtechnisch erprobt. Die neuen Ergebnisse eröffnen der präparativen organischen Chemie und ihrer Technik neue Möglichkeiten.

Ziegler-Natta Polymerization

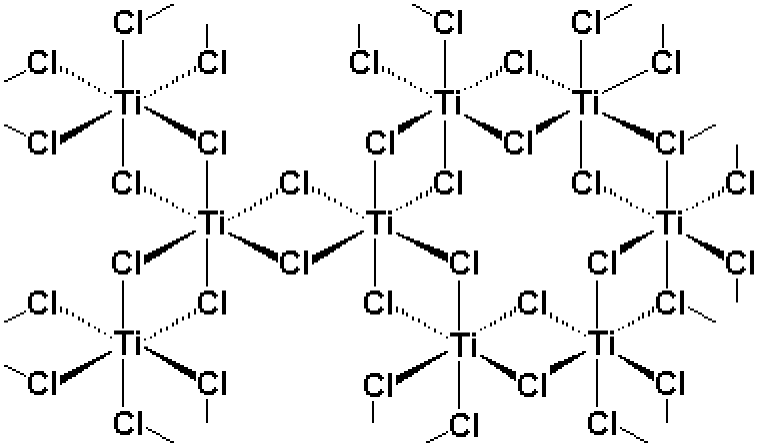
Site activation

$Cl_3Ti^{III}\text{-}Cl + AlEt_3 \longrightarrow Cl_3Ti^{III}\text{-}Et + AlEt_2Cl$



Natta proposed α-$Ti^{III}Cl_3 + AlEt_3$

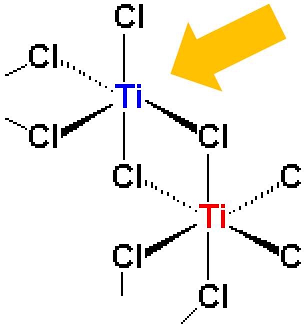
Ziegler-Natta Polymerization: PE

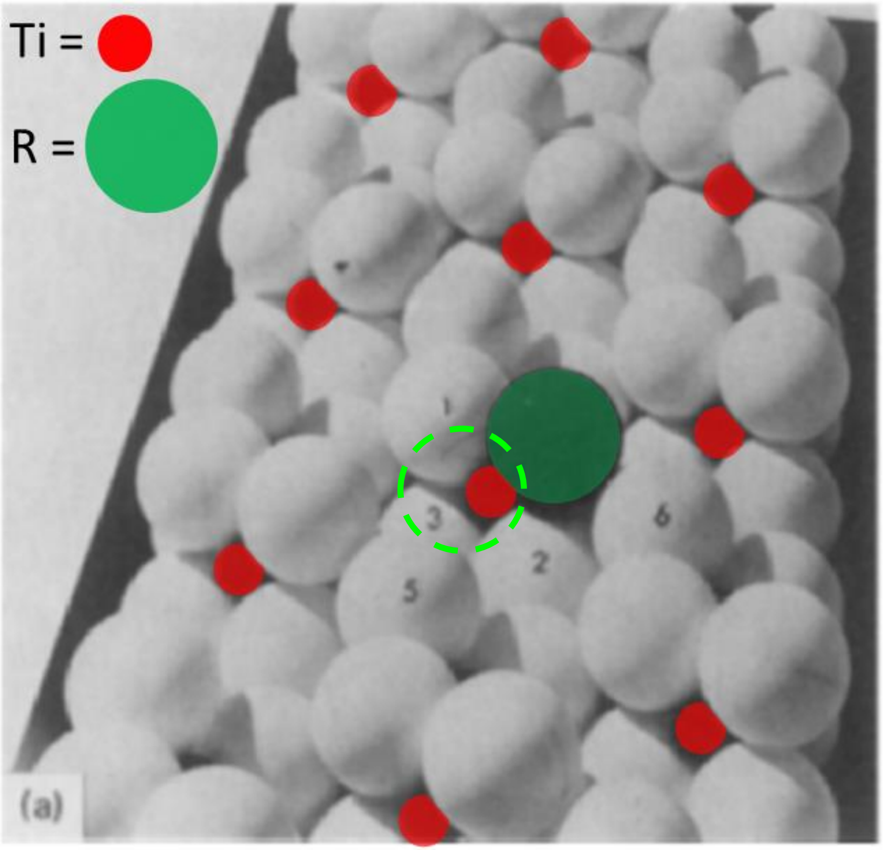


α-$TiCl_3$

$AlEt_3$ + α-$TiCl_3$:

At the edge of the crystal:

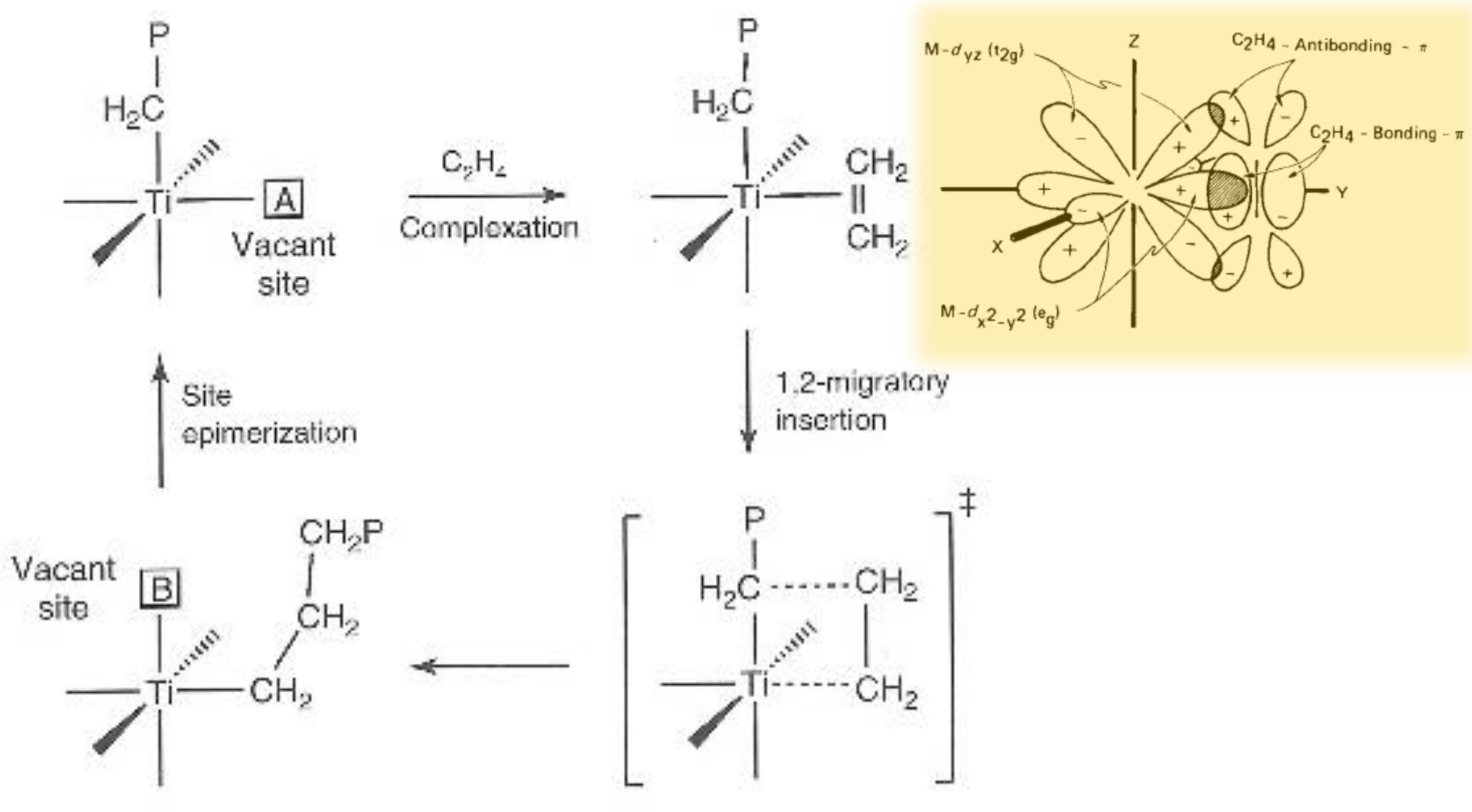




P. Cossee and E.J. Arlman *J. Catal.* **1964**, *3*, 80-88, 89-98, 99-104
woorking at Royal Dutch Shell

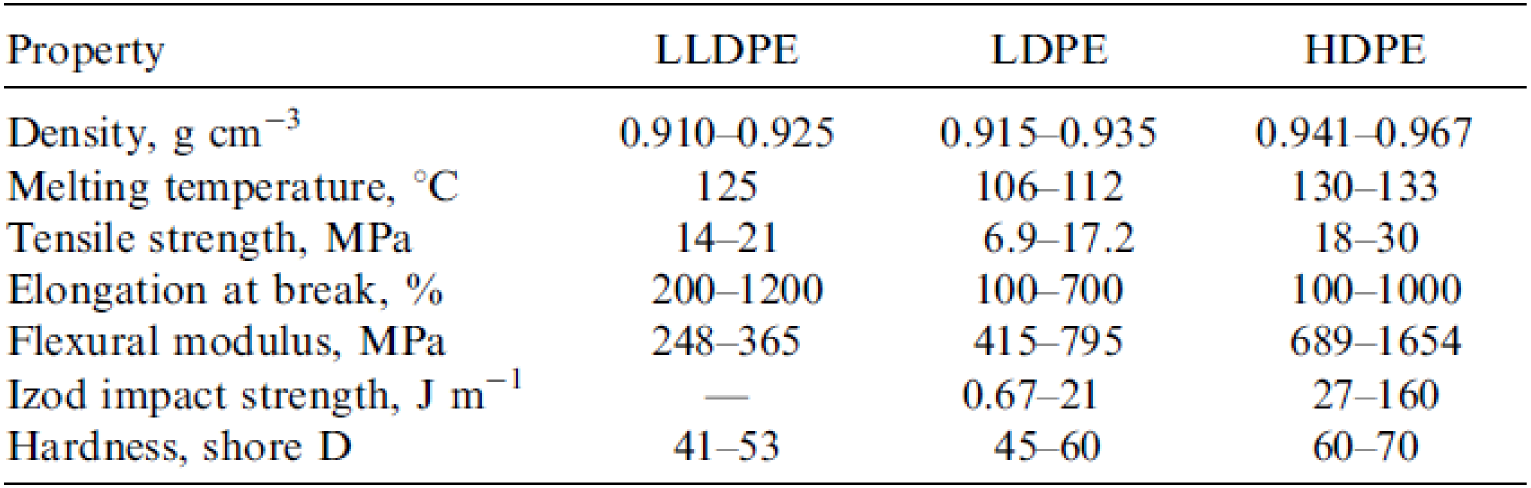
Ziegler-Natta Polymerization: PE

According to P. Cossee and E.J. Arlman (*J. Catal.* **1964**, *3*, 80-88, 89-98, 99-104)

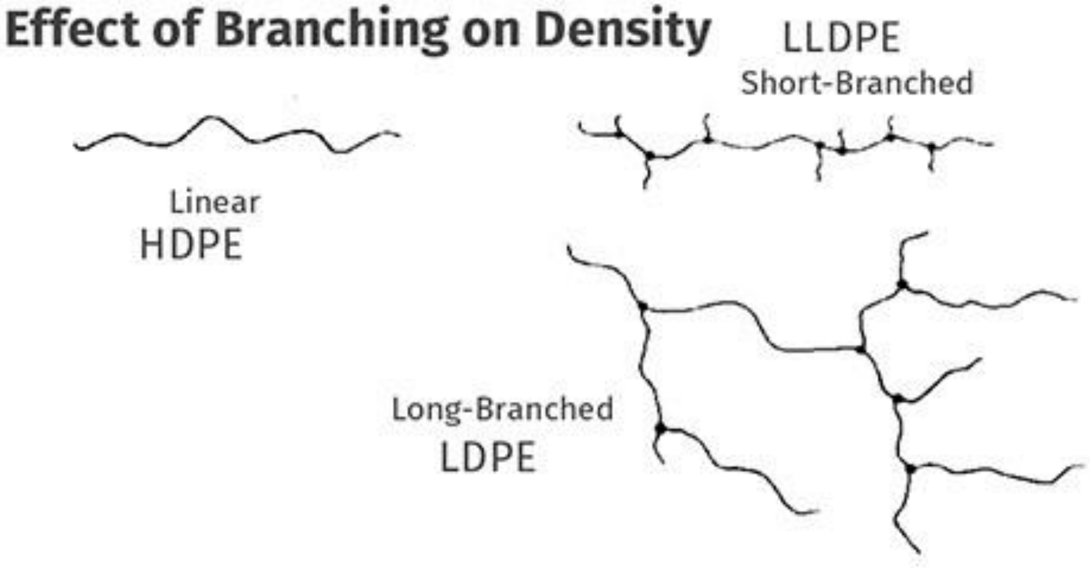


cis-insertion / *cis*-ligand migration

Ziegler-Natta Polymerization: PE



Property	LLDPE	LDPE	HDPE
Density, g cm^{-3}	0.910–0.925	0.915–0.935	0.941–0.967
Melting temperature, °C	125	106–112	130–133
Tensile strength, MPa	14–21	6.9–17.2	18–30
Elongation at break, %	200–1200	100–700	100–1000
Flexural modulus, MPa	248–365	415–795	689–1654
Izod impact strength, J m^{-1}	—	0.67–21	27–160
Hardness, shore D	41–53	45–60	60–70



Ziegler-Natta Polymerization: UHMWPE

Dyneema® Fiber

The world's strongest fiber™

BRIGHT SCIENCE. BRIGHTER LIVING.™

The Dyneema® Secret

DSM's super-strong ultra-high molecular weight polyethylene (UHMwPE) fiber branded as Dyneema® offers maximum strength with minimum weight. This makes the number of possible applications virtually unlimited.

Dyneema® fiber is produced in a patented gel spinning process in which the fibers are drawn, heated, elongated, and cooled. Stretching and spinning leads to molecular alignment, high crystallization, and low density. Dyneema® has extremely long molecular chains that transfer load more effectively to the polymer backbone. So it's stronger at the same weight or lighter at the same strength than alternatives.

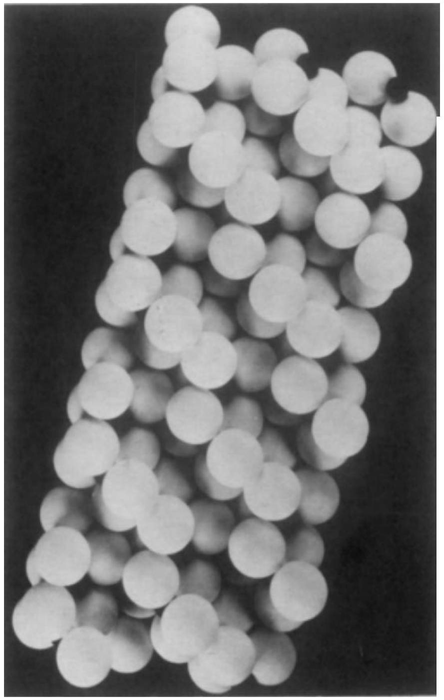
Dyneema® fiber is 15x stronger than steel at the same weight, with a tensile strength up to 43 cN/dtex. As well as its extraordinary strength, Dyneema® excels in cut and abrasion resistance and has a high resistance to chemicals and UV. Dyneema® fiber is so light that it floats on water and furthermore has a very high modulus (resistance against deformation). Dyneema® is available in a wide range of titers (fiber thickness), from 50 to 6600 dtex, making the fiber suitable for many applications.

Ziegler-Natta Polymerization: UHMWPE

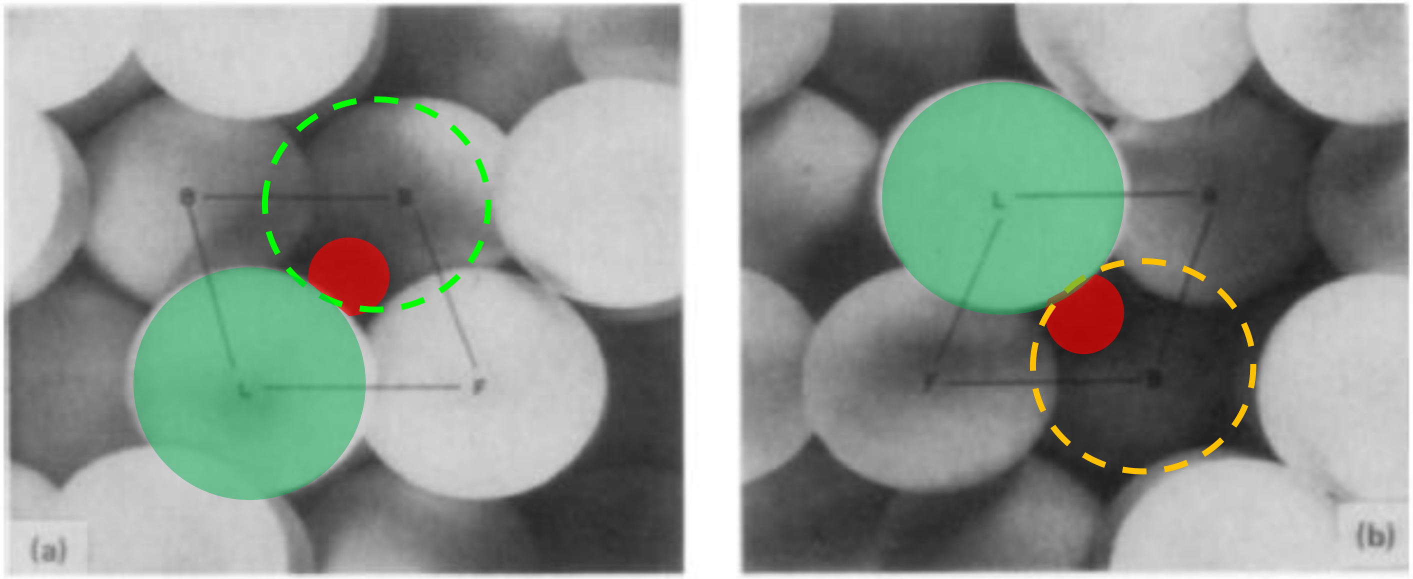
UHMWPE fiber applications (Dyneema, a product of DSM)

http://www.dyneema.com/emea/explore-dyneema/downloads

Ziegler-Natta Polymerization: iPP *G. Natta (1954)*



The crystal edges of α-$TiCl_3$ are inherently noncentrosymmetric *i.e.* chiral (two enantiomeric forms)

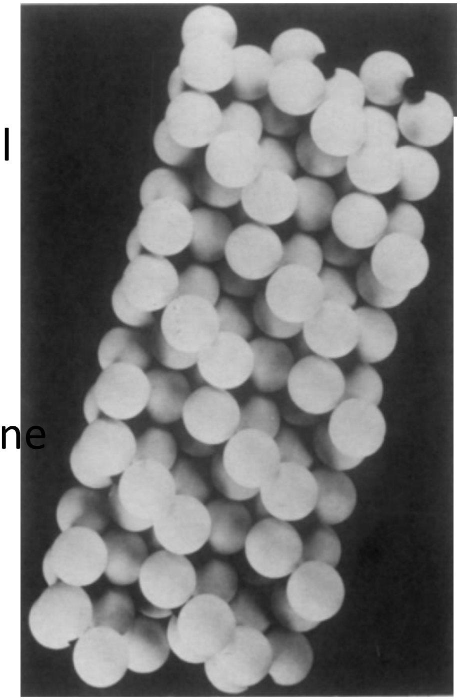


- All active centers features a square base of 4 Cl ions around a Ti(III) which is in oblique position with respect to the crystal plane

- Cl ions are not equivalent; two are sterically blocked (B), one is bound to two Ti(III) (F) and one is bound to one Ti(III) (L). This last might be exchanged.

- L and the vacancy are not equivalent

Ziegler-Natta Polymerization: iPP *G. Natta (1954)*



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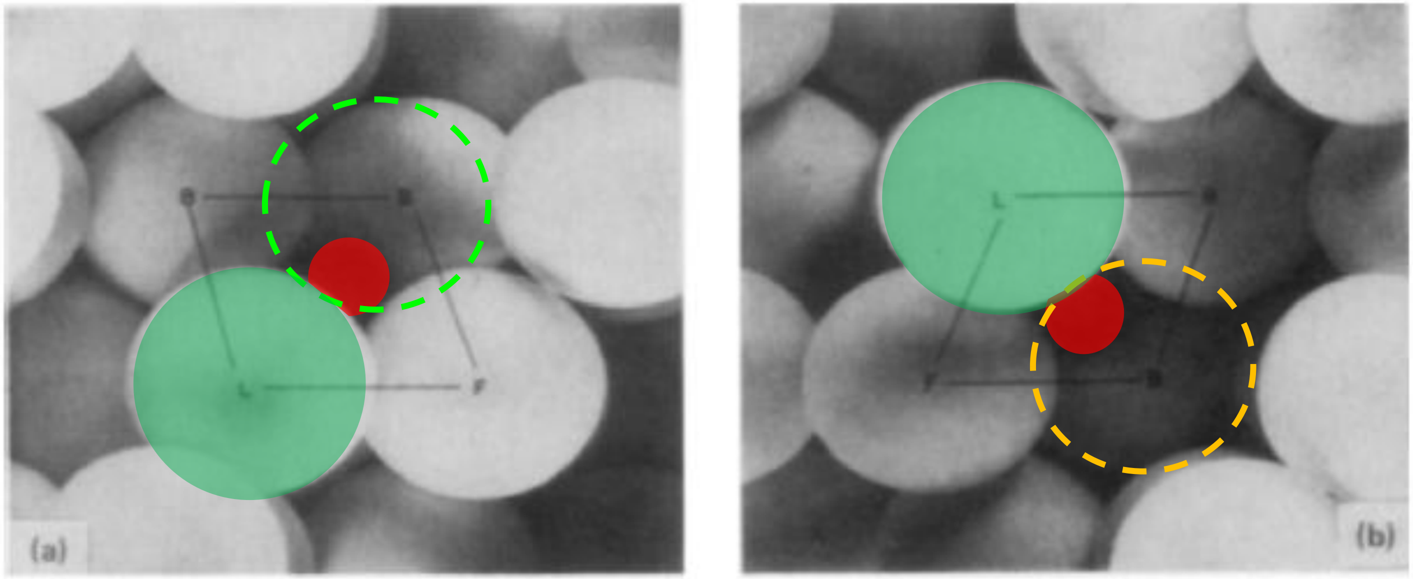
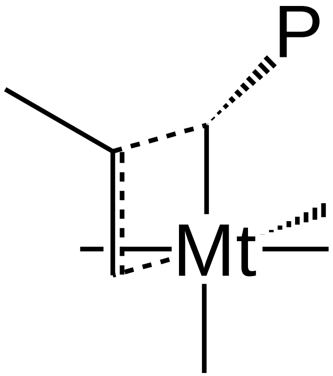
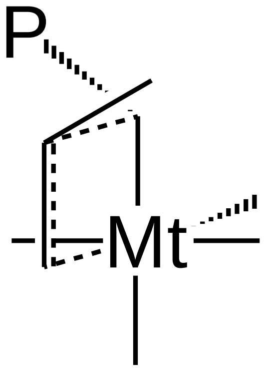


propylene (prochiral) will add to the metal centre via one or the other enantioface:

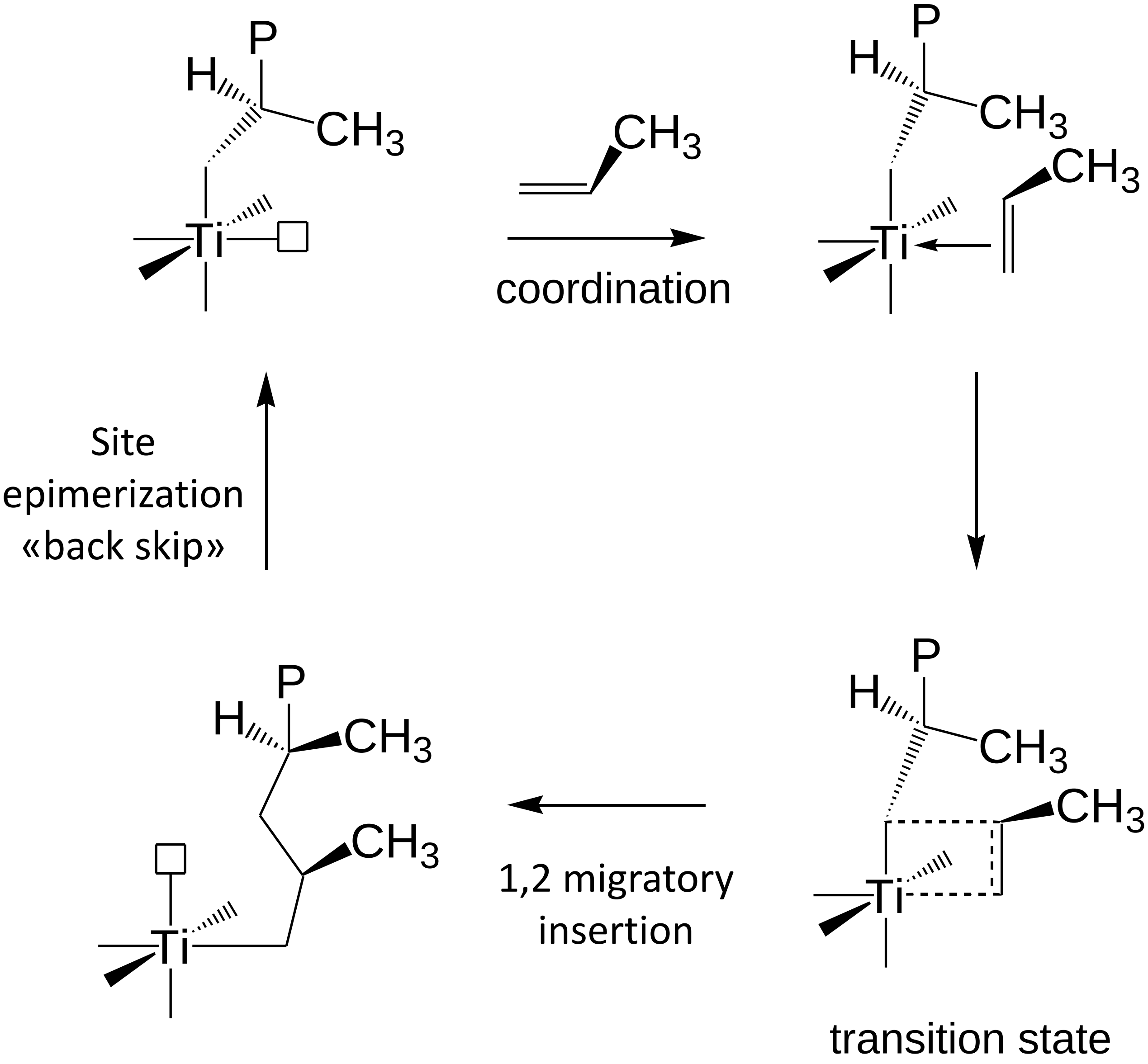


si



re

Ziegler-Natta Polymerization: iPP



coordination

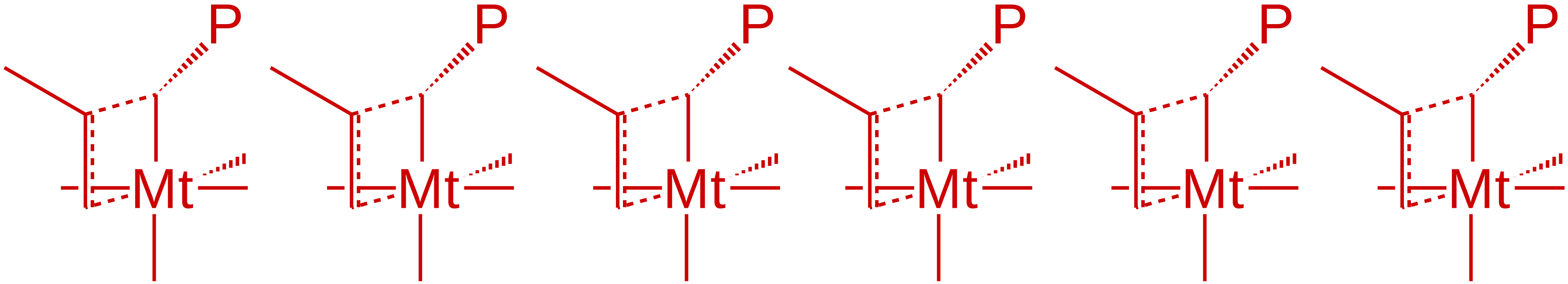
transition state

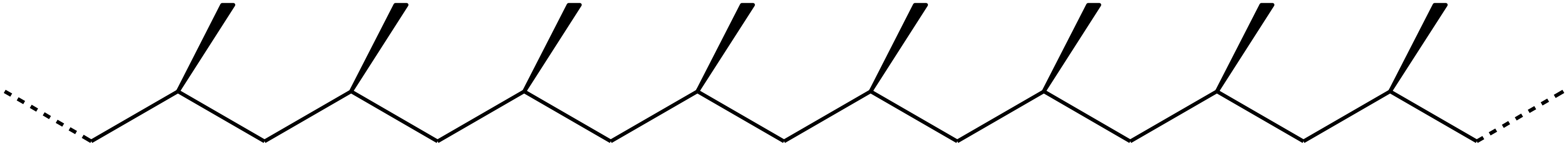
1,2 migratory insertion

Site epimerization «back skip»

Ziegler-Natta Polymerization

Multiple insertions of the same enantioface
produce an isotactic polymer

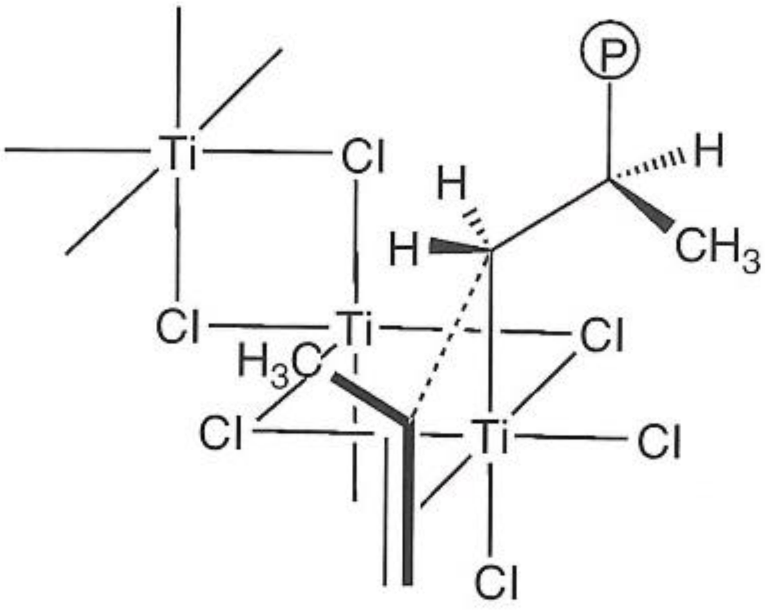




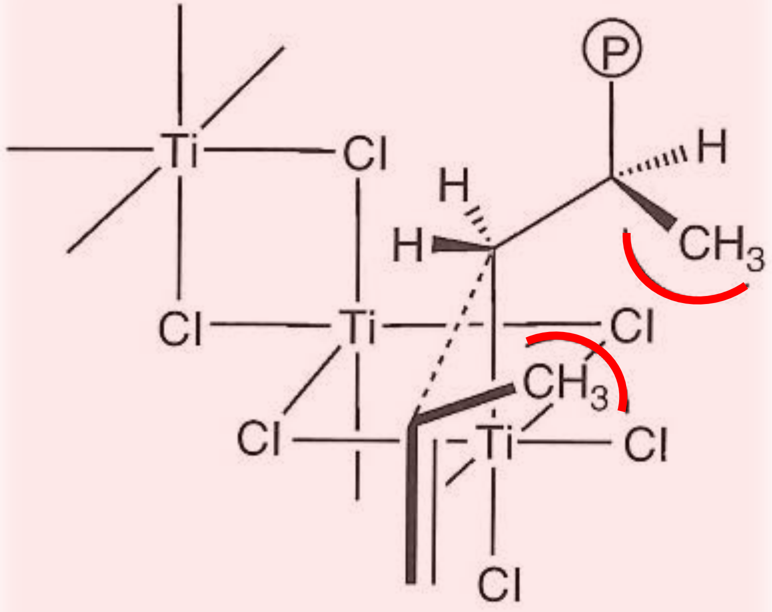
iPP is finally formed. This has high crystallinity and T_m 160-166°C
(up to 95% of isotactic fraction)

Ziegler-Natta Polymerization: iPP

steric interactions around the coordination site



si-addition



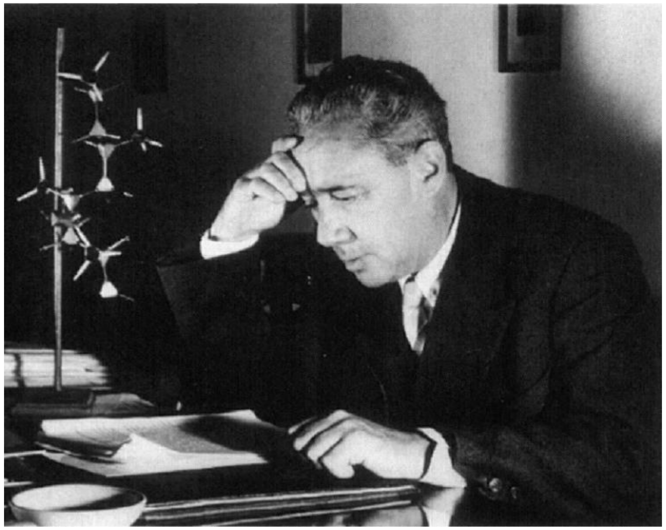
re-addition

Side reactions...

Ziegler-Natta Polymerization: iPP

Advertisement of MOPLEN^{TM} from 60s

Giulio Natta, 1954



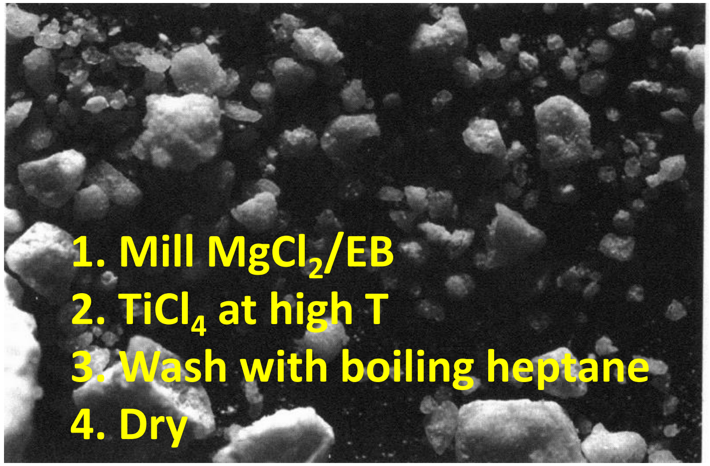
"Professor Natta. You have succeeded in preparing by a new method macromolecules having a spatially regular structure. The scientific and technical consequences of your discovery are immense and cannot even now be fully estimated."

(Nobel Prize with K. Ziegler 1963)

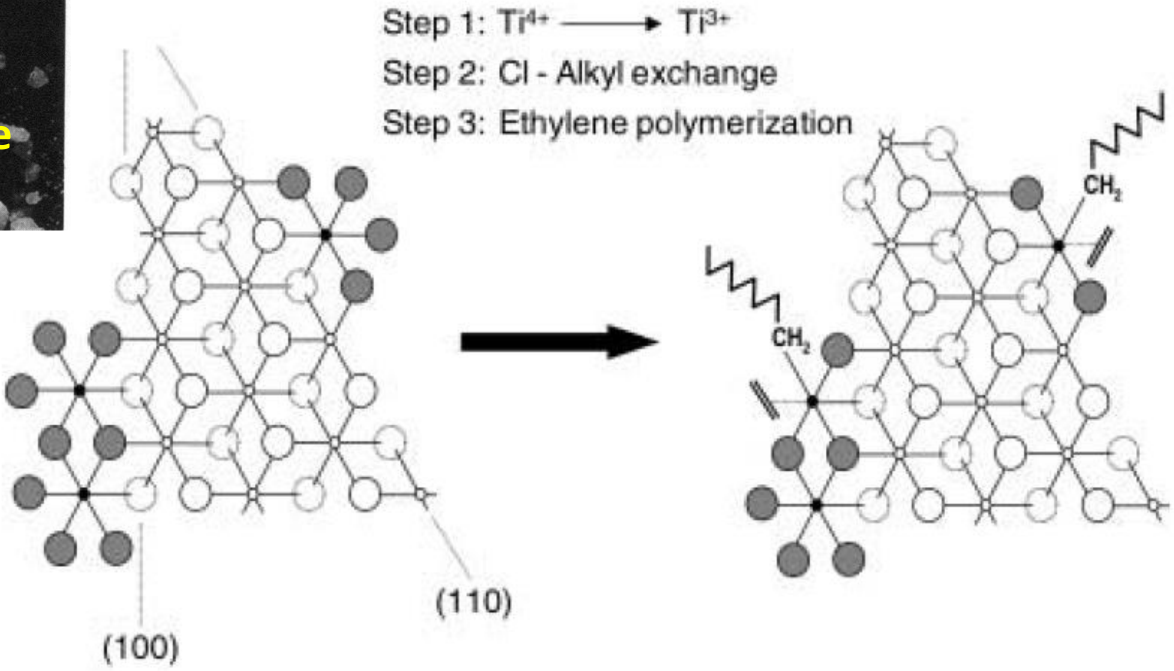
Ziegler-Natta Polymerization

	Generat. (year)	Catalyst composition	Productivity (KgPP/gCat)	X.I. (%)
$TiCl_3$	1st (1954)	$\delta\text{-}TiCl_3 \cdot 0.33AlCl_3$ + $AlEt_2Cl$	2-4	90-94
	2nd (1970)	$\delta\text{-}TiCl_3$ + $AlEt_2Cl$	10-15	94-97
$MgCl_2$ / $TiCl_4$	(1968)	$MgCl_2/TiCl_4$ + AlR_3	15	40
	3rd (1971)	$MgCl_2/TiCl_4$/Benzoate + AlR_3/Benzoate	15-30	95-97
	4th (1980)	$MgCl_2/TiCl_4$/Phthalate + AlR_3/Silane	40-70	95-99
	5th (1988)	$MgCl_2/TiCl_4$/Diether + AlR_3/Silane (opt.)	70-130	95-99
	“Next” (1999)	$MgCl_2/TiCl_4$/Succinate + AlR_3/Silane	40-70	95-99

Ziegler-Natta Polymerization *latest catalyst's generations*



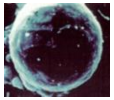
1. Mill $MgCl_2$/EB
2. $TiCl_4$ at high T
3. Wash with boiling heptane
4. Dry



Step 1: $Ti^{4+} \longrightarrow Ti^{3+}$

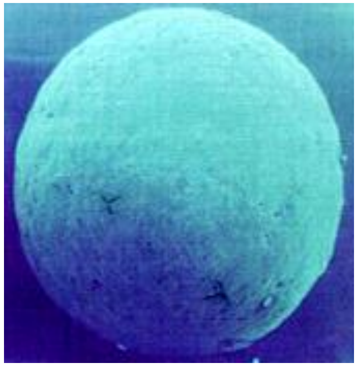
Step 2: Cl - Alkyl exchange

Step 3: Ethylene polymerization



Catalyst

(<100 μm)



Polymer

Final
Polymer Particle
(1000 μm)

Remarks on the history of ZN polymerization

Everything started with the *Aufbaureaktion*, which is an insertion of ethylene into Al-H and Al-C bonds under pressure.
The first step of this reaction is a hydroalumination, which is continued as carbalumination (in analogy to carbopalladation a.k.a. Heck reaction). At higher temperature β-hydride elimination leads to the formation of α-olefins. Alternatively, under oxidative conditions long-chain alcohols are formed.
Already in late 1940s it was observed that low molar mass PE could be obtained after long reaction times.

$TiCl_3$ is a solid, thus ZN polymerization using $TiCl_3/AlEt_3$ is heterogeneous, with advantages and disadvantages.

Advantages – Catalyst supports can be engineered such thata they disintegrate during polymerization (expose more catalytic sites). Catalyst is suspended, polymerization takes place on the catalyst particles: better heat dissipation, no adhesion on reactor walls by the polymer (as in the case of homogeneous systems).

Disadvantages – Catalyst has different active sites and planes. This causes a broad molar mass distribution ($Đ$ = 2-10). Dehashing (*i.e.* removal of catalyst) is needed (however not in the latest ZN catalyst generations).

ZN synthesis of iPP

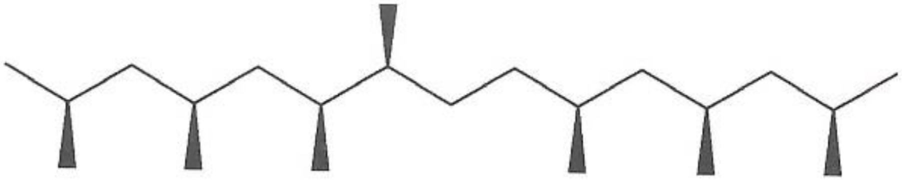
- The growth step involves complexing of the olefin to an open site of an octahedral coordination environment around the Ti atom.

- A *cis 1,2* migratory insertion transfers the polymeryl group to the coordinated olefin through a four-centered transition state.

- Relocation of the polymer chain back to its original position re-esteblishes the original vacant coordination site through site epimerization (back skip).

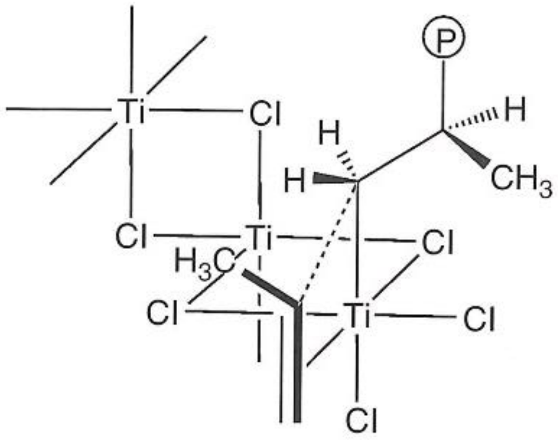
To be kept in mind:

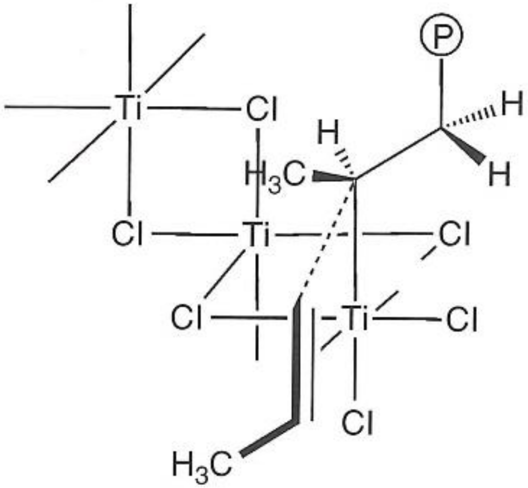
Primary (1,2) *vs* secondary (2,1) insertion determines the regioregularity of the obatined PP. Head-to-tail propagation is typically occurring. Occasionally, head-to-head regioerrors may take place.



The diving forces for isotactic propagation are steric in nature. The asymmetric nature of each center in the heterogeneous catalyst forces the popylene to always add either in the ***si*** or ***re*** configuration and thus isotactic chains are eventually formed.

Ziegler-Natta Polymerization





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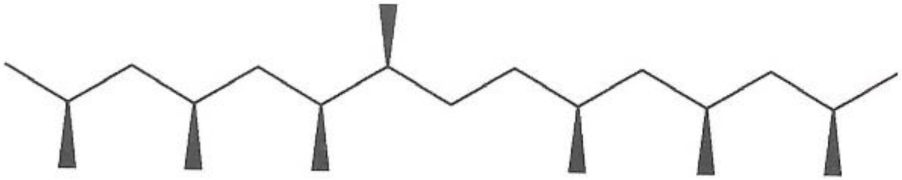

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