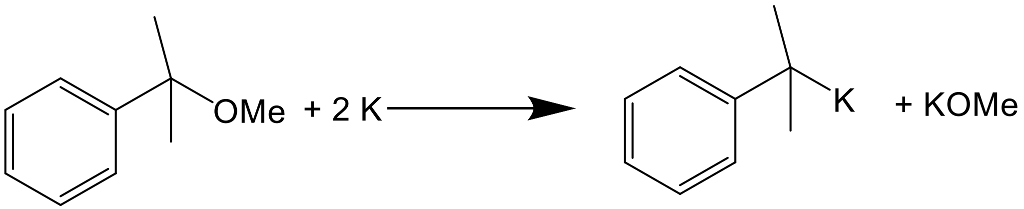
POLYMERIZATION CATALYSTS

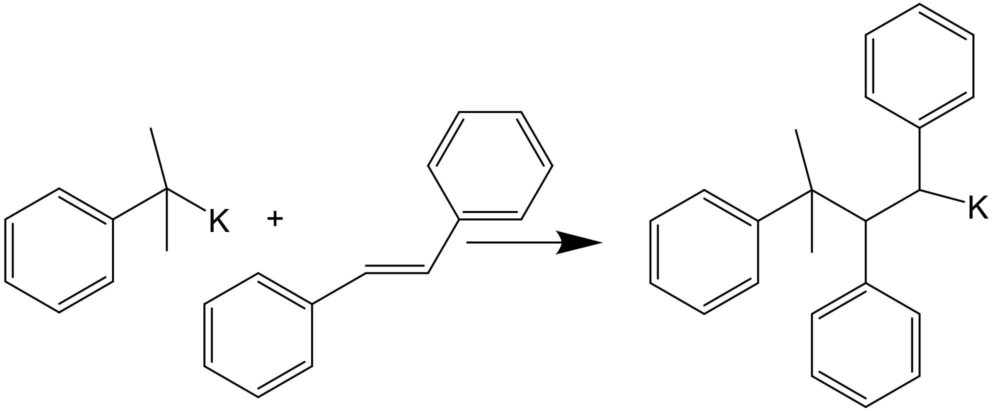
History of olefin polymerization catalysis is personalized to Karl Ziegler.

During 1920s he studied organometallic chemistry of potassium.



Fenyl isopropylpotassium reacts easily with air.

Also C=C double bond of stilbene can react and generates a formal addition product.



This is called generally as “Aufbau” reaction.

POLYMERIZATION CATALYSTS

During 1930s Ziegler and Colonius introduced successful synthesis of BuLi.

$C_4H_9Cl + 2\ Li^{\circ} \rightarrow C_4H_9Li + LiCl$ (35 °C in benzene)

Attempts to purify BuLi by distillation failed and butene and LiH were generated.
(if vacuum is good, this won't happen)

As a good chemist, Ziegler tried the reverse reaction:

$LiH + CH_2{=}CH_2 \rightarrow LiCH_2CH_3$ but failed.

Ziegler's conclusion: LiH is poorly soluble. Why not to use $LiAlH_4$ (discovered few years before)?

100 bar $CH_2CH_2 \rightarrow$ α-olefins ($LiAlH_4$, ether, 200 °C)

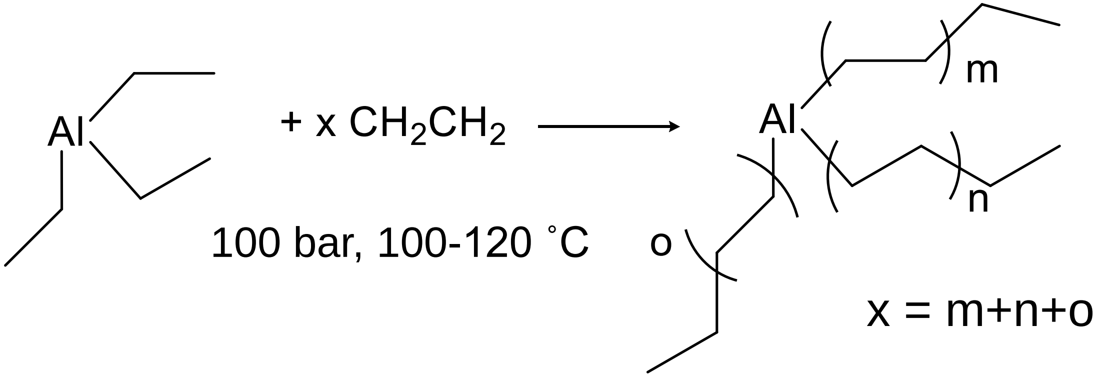
POLYMERIZATION CATALYSTS

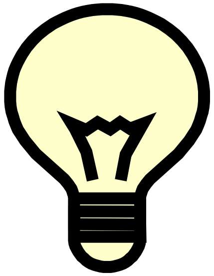
100 bar $CH_2CH_2 \rightarrow$ α-olefins (LiAlH$_4$, ether, 200 °C)

Initial step is the formation of lithiumtetraethylaluminum:

$LiAlH_4 + 4\ CH_2CH_2 \rightarrow LiAl(CH_2CH_3)_4$

Because Li is expensive metal, why not to use only aluminum hydride for oligomerization?





This was the first example of Aufbau –reaction in ethene polymerization.

However, only polymer chains not longer than 100 units is produced.

POLYMERIZATION CATALYSTS

Polyethene chains terminate via β-H elimination:

$R_2\mathbf{Al} – (CH_2CH_2)_{99} – CH_2CH_3 \rightarrow R_2\mathbf{Al}H + CH_2{=}CH - (CH_2CH_2)_{98}\text{-}CH_2CH_3$

Based on this, Ziegler developed a new method to synthesize aluminum alkyls.

$Al^{\circ} + ⅔\, H_2 + CH_2CH_2 \rightarrow (CH_3CH_2)_2AlH \;+ CH_2CH_2 \rightarrow Al(CH_2CH_3)_3$

If Aufbau –reaction can not be used for preparation of good quality PE, could it be used for something else?

$R_2\mathbf{Al} – (CH_2CH_3) + x\, CH_2{=}CH_2 \rightarrow R_2\mathbf{Al} - (CH_2CH_2)_x\text{-}CH_2CH_3 \qquad x = 6\text{-}8$

$R_2\mathbf{Al} - (CH_2CH_2)_x\text{-}CH_2CH_3 + ½\, O_2 \rightarrow \mathbf{Al} –O\text{-} (CH_2CH_2)_x\text{-}CH_2CH_3$

$R_2\mathbf{Al} –O\text{-} (CH_2CH_2)_x\text{-}CH_2CH_3 + H_2O \rightarrow R_2\mathbf{Al}OH + HO\text{-} (CH_2CH_2)_x\text{-}CH_2CH_3$

After insertion of 6-8 monomers aluminum alkyls are hydrolyzed to primary alcohols. Technical application is synthesis of biodegradable detergents.

POLYMERIZATION CATALYSTS

During the 1950s new methods to produce butadiene was looked for. Ziegler tried to synthesized butene via dimerization of ethene.

$\mathbf{Al}\,(CH_2CH_3)_3 + CH_2{=}CH_2 \rightarrow (CH_3CH_2)_2\mathbf{Al} - CH_2CH_2\text{-}CH_2CH_3$

$(CH_3CH_2)_2\mathbf{Al} - CH_2CH_2\text{-}CH_2CH_3 \rightarrow H\mathbf{Al}\,(CH_2CH_3)_2 + CH_2{=}CHCH_2CH_3$

$H\mathbf{Al}\,(CH_2CH_3)_2 + CH_2{=}CH_2 \rightarrow \mathbf{Al}\,(CH_2CH_3)_3$

Because the Aufbau processes were attractive, an Italian company, Montecatini took a license and sent three chemists to Ziegler's lab for training.

All of sudden, the Aufbau-reactions did not work.

The reason was, that the reactors were washed with HNO_3 and traces of Ni-salts were left after washing. Ni salts act as a cocatalyst and caused rapid β-H elimination. As a result, only dimers of ethene were formed.

POLYMERIZATION CATALYSTS

After observation that Ni salts have dramatic effect on Aufbau-reaction, Ziegler studied systematically all other transition metal salts.

Chromium gave first indication that real ethene polymerization is feasible under applied conditions, but real break through game, when Ti and Zr were present.

The combinations of $TiCl_4$ or $ZrCl_4$ together with aluminum alkyls form very efficient polymerization catalysts which are able to produce high molar mass polyethylene even at room temperature and low pressure.

Shortly after Ziegler's invention, in 1954, Giulio Natta applied for a patent for propene polymerization using Ziegler's catalyst system.

The polypropene produced was crystalline and isotactic in nature, although containing some amounts of atactic PP.

These two fundamental observations brought the Nobel Prize to Ziegler and Natta 1963 and started a new era in polymer chemistry initiating a new branch in chemical industry by making possible the inexpensive and easily controlled production of polyethene and polypropene.

[i] (a) Natta, G., *Angew. Chem.*, **1956**, *68*, 393. (b) Natta, G., *Angew. Chem.*, **1964**, *76*, 553.

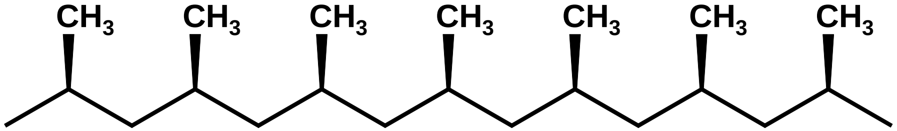
POLYMERIZATION CATALYSTS

Fischer projection of polypropenes
with different stereoregularities.

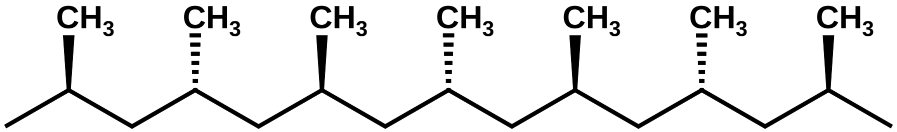
a)In isotactic polypropene all chiral carbon centers have the same relative orientation.

b) In syndiotactic polypropene the chiral carbon centers have alternating configurations along the polymer chain i.e. every second chiral center has the same relative orientation.

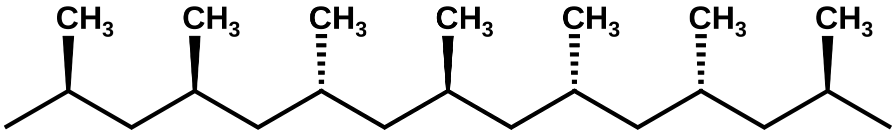
c) In atactic polypropene the chiral carbon centers have random orientation along the polymer chain.



isotactic polypropene



syndiotactic polypropene



atactic polypropene

POLYMERIZATION CATALYSTS

The polyolefins made a break through into everyday life and are now a days important and indispensable materials in our industrialized society.
In 2015 almost 150 million tons of polyolefins were produced.

The research and industrial processes concentrated on catalyst systems containing $TiCl_3$ or $TiCl_4$ together with aluminum alkyls, mainly $AlEt_3$ or $AlEt_2Cl$.
The bare mixture of $TiCl_4$ and $AlEt_3$ produces isotactic polypropene,
which is the most useful stereoisomer of the polymer,
with low activity and stereospecifity.

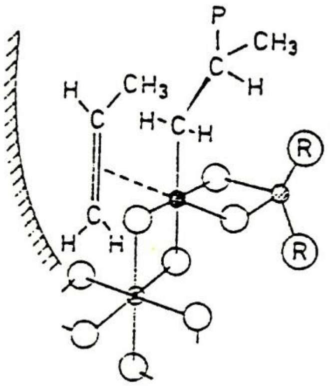
Both the activity and stereospecifity can be substantially improved by the use of crystalline forms of $TiCl_3$.

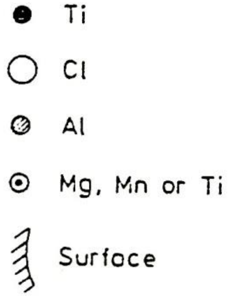
The discovery of activated magnesium chloride as the ideal support for titanium(IV) chloride and its derivatives and introduction of Lewis bases *e.g.* ethyl benzoate started a new chapter in Ziegler-Natta catalysis.

Modern catalysts exceed the activity measured for the original system by 400 times and isotacticity of the formed polymer can reach 99%.

POLYMERIZATION CATALYSTS

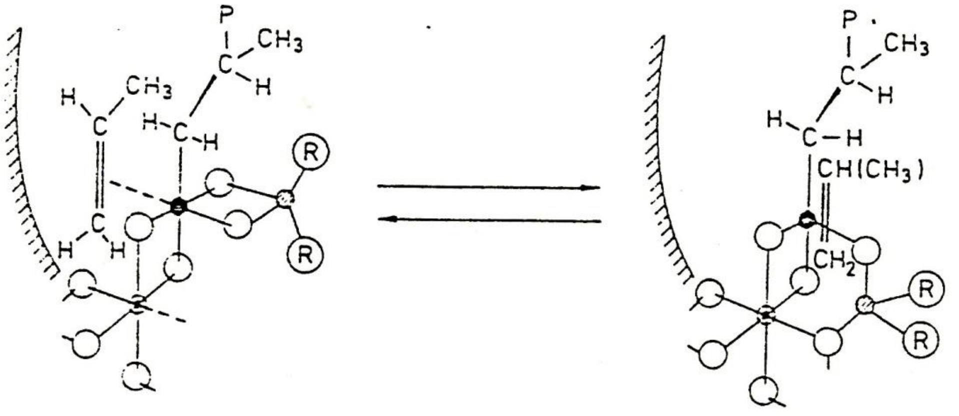
Site A (Isotactic PP)





Isotactic propagation

Site B (Atactic PP)



(B$_6$)
Isotactic propagation

(B$_5$)
Syndiotactic propagation

POLYMERIZATION CATALYSTS

Polyethene was first synthesized by accident in 1898 Hans von

Pechmann, who prepared it by while heating diatzomethane. White,

waxy substance contained long -CH_2- chains and was termed *polymethylene.*

The first industrially practical polyethylene synthesis was discovered (again by accident) by at ICI Chemicals in 1933.

Upon applying extremely high pressure (several hundred atmospheres) to a mixture of ethylene and benzaldehyde, a white waxy material was obtained.

Industrial LDPE production was started in 1939.

The first catalyst was a chromium trioxide based catalyst

discovered in 1951 by Phillips Petroleum followed by Ziegler 1953.

By the end of the 1950s both the catalysts were used in HDPE production.

POLYMERIZATION CATALYSTS

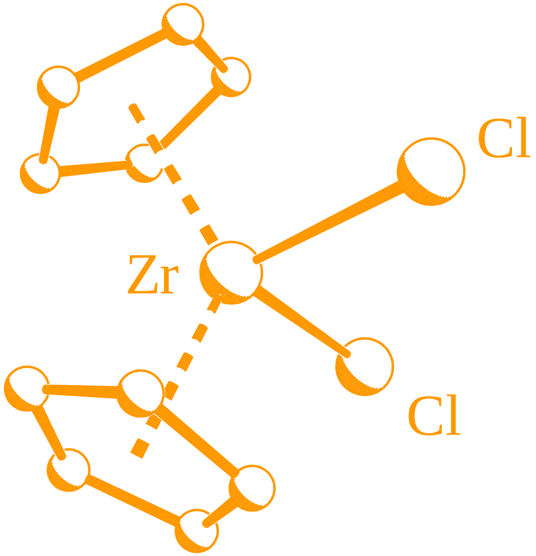
Even though Ziegler-Natta systems are highly active, or probably because of this, the questions concerning the nature of catalytically active species, mechanism how the polymerization occurs and what are the bases for isotactic polymerization in the case of propene, remained unclear for quite a long time. Also the molar mass distribution of the polymers produced are broad indicating that different kind of active centers are participating in polymerization.

Homogeneous models were looked for to simplify the otherwise so complicated mixtures of titanium halides and aluminum alkyls.

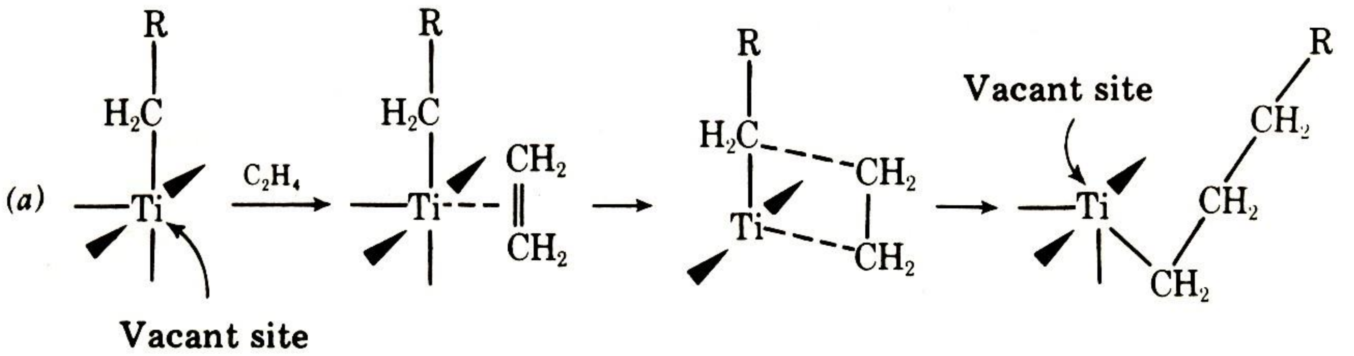
Part of the research interest turned to soluble titanium and zirconium organometallic compounds, metallocenes, which were also published at the same time in 1954.

From these catalyst precursors especially the titanium analogue proved to polymerize ethene, when activated with aluminum alkyls *e.g.* $AlEt_2Cl$.

But for propene polymerization these catalyst systems are inactive. These studies opened a direct view to the catalytically active species and resulted in several mechanistic aspects for ethene polymerization.

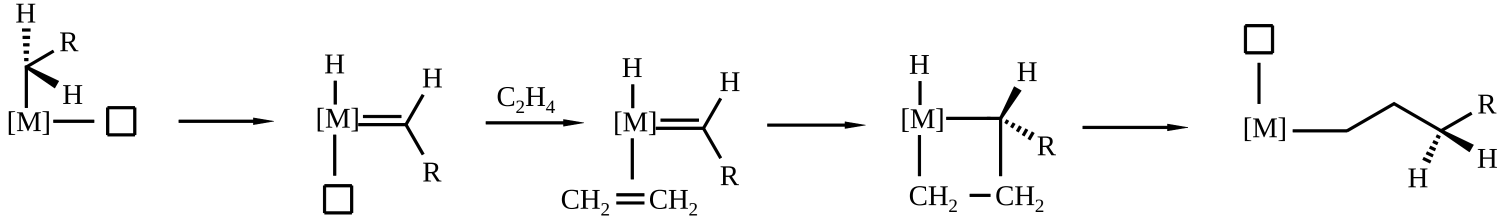


POLYMERIZATION CATALYSTS



According to the Cossee-Arlman mechanism the monomer coordinates to the vacant coordination site and inserts into the metal-carbon bond via four-membered metallocycle intermediate.

A concurrent mechanism for the migration of the alkyl group to the coordinated olefin has been proposed by Rooney and Green. In this model the metal alkylidene hydride, generated by an oxidative 1,2-hydrogen shift from the α-carbon of the polymer chain is responsible for the catalytic activity.

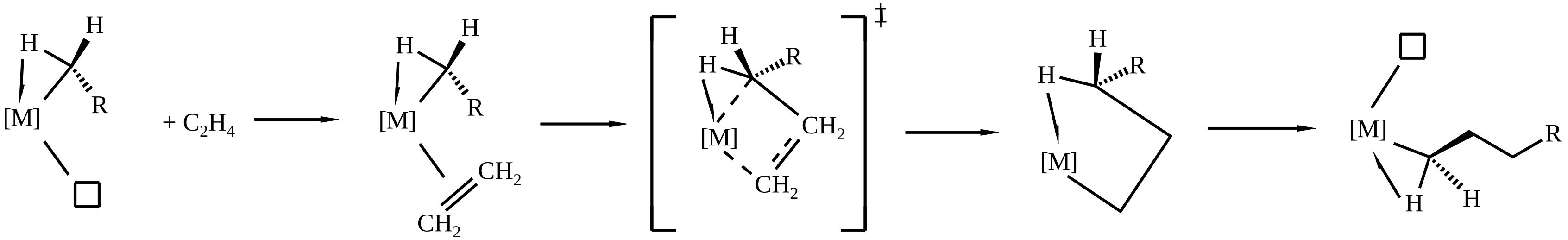


POLYMERIZATION CATALYSTS

Rooney *et al.* introduced later a mechanism, which is a combination of the two previous ones.

In this model the hydrogen atom of the α-carbon interacts with the metal center during the catalytic cycle.

The role of “agostic interaction” is to facilitate the C-C bond forming step.



Since the discovery of methylaluminoxane (MAO) in the middle of 1970s as an effective activator, group 4 metallocenes turned out to be very interesting as catalyst precursors for α-olefin polymerization in general.

Cp_2ZrCl_2 and Cp_2TiCl_2, when activated with MAO, polymerized ethene with high activity, but what was more remarkable was that this new cocatalyst turned out to be able to activate titanocene and zirconocene dichlorides to produce polypropene with high activity.

POLYMERIZATION CATALYSTS

The polypropene obtained consisted of uniform chains with low molar mass and random orientation of methylene groups.

Despite the work with different substitution patterns in Cp-rings the polypropene formed was that time limited only to the atactic material.

The research on heterogeneous Ziegler-Natta catalysts reveal that the stereoregularity of these catalysts is based on individual steps, edges or holes on the catalyst surface inducing chiral metal centers suitable for isospecific polymerization of propene.

Since the discovery of MAO as an effective cocatalyst for Group 4 metallocenes, its structure and function has been a subject of several publications.
Even though MAO is regularly used in polymerization reactions, the structure of MAO and especially the nature of the aluminum species which are responsible for the efficient activation process, are still unknown.

MAO contains different oligomeric products and characteristic behavior for MAO is that compositional modifications take place within time.

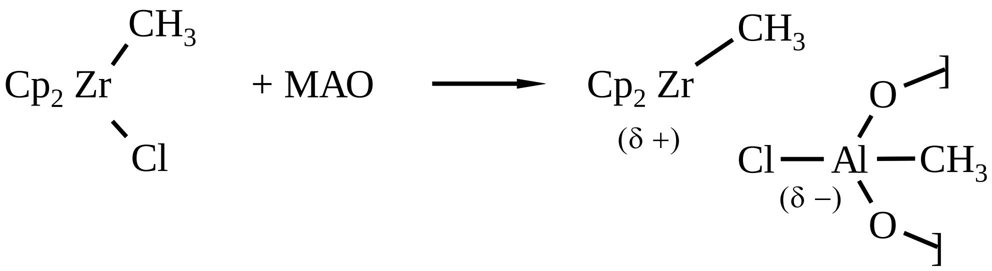
POLYMERIZATION CATALYSTS

The reaction of Cp_2ZrCl_2 with MAO was followed by ^1H NMR.
When the reactants were mixed together, a fast formation of monoalkylated Zr- complex was observed.

In higher concentrations of MAO, which is a stronger methyl acceptor than TMA, the resonance of the methyl group protons shifted slightly to lower field indicating the formation of metal alkyl cations.

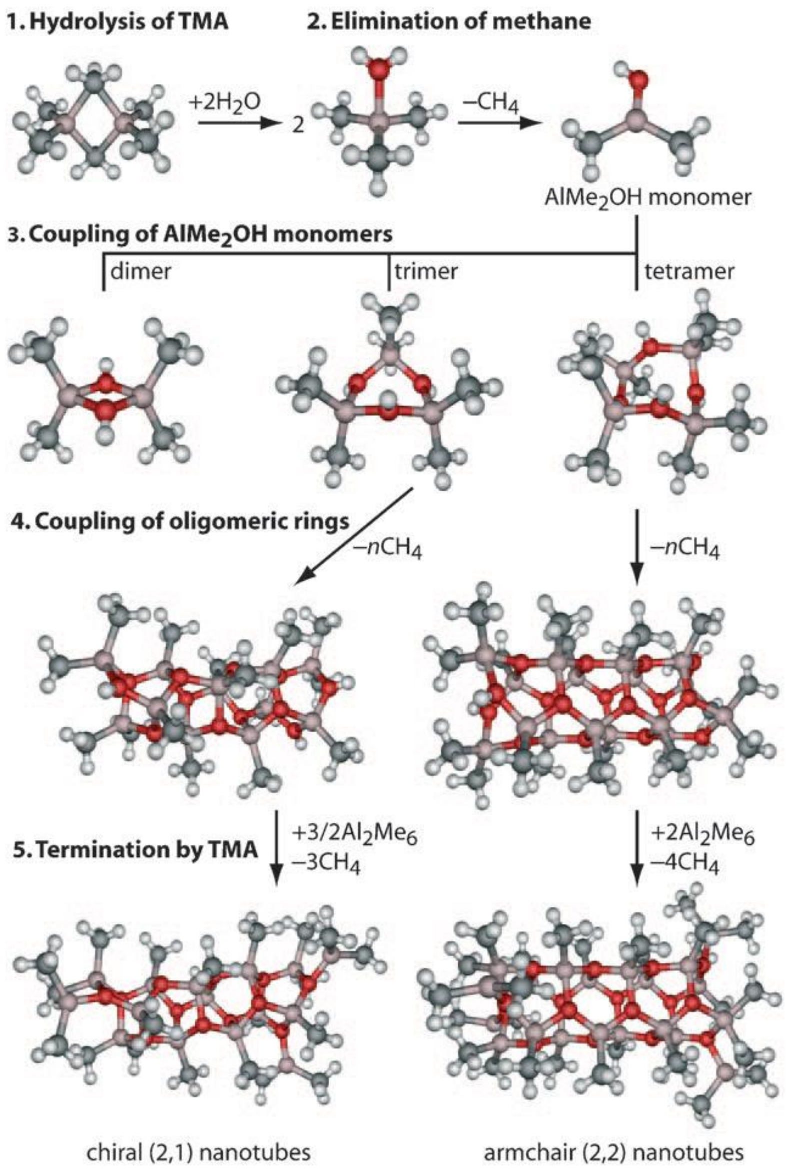
$$Cp_2ZrCl_2 + MAO \cdot x\, Al(CH_3)_3 \longrightarrow$$

$$(1\text{-}x)\, Cp_2ZrCl_2 + x\, Cp_2ZrCH_3Cl + MAO \cdot x\, Al(CH_3)_2Cl$$



It is widely accepted that the cationic, 14-electron metal center $[Cp_2ZrR]^+$ is responsible for the growth of polymer chains.

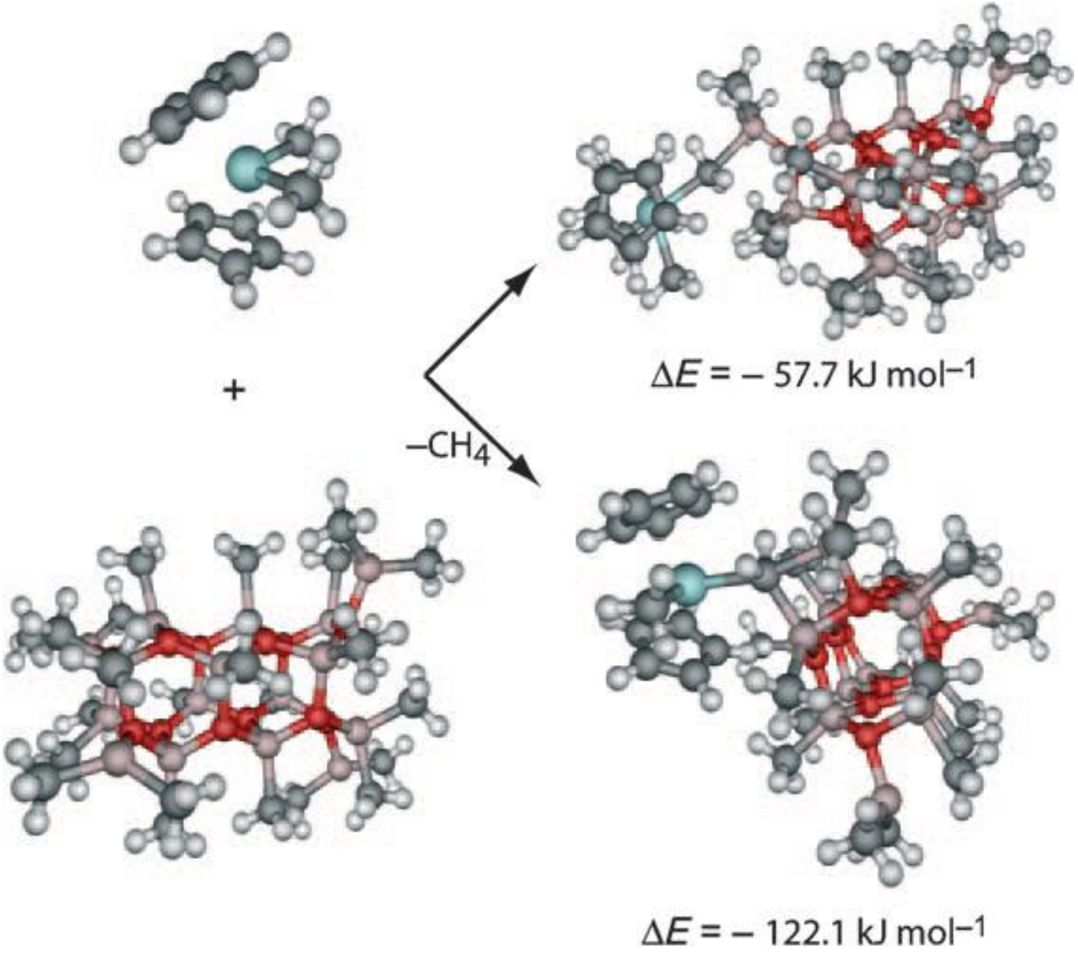
POLYMERIZATION CATALYSTS



Angew. Chem. 2008

POLYMERIZATION CATALYSTS

The role of MAO in the activation process can be thus considered as one assisting in the formation of the loosely coordinated counter ion, which is easily replaced by olefins, even the substituted ones.



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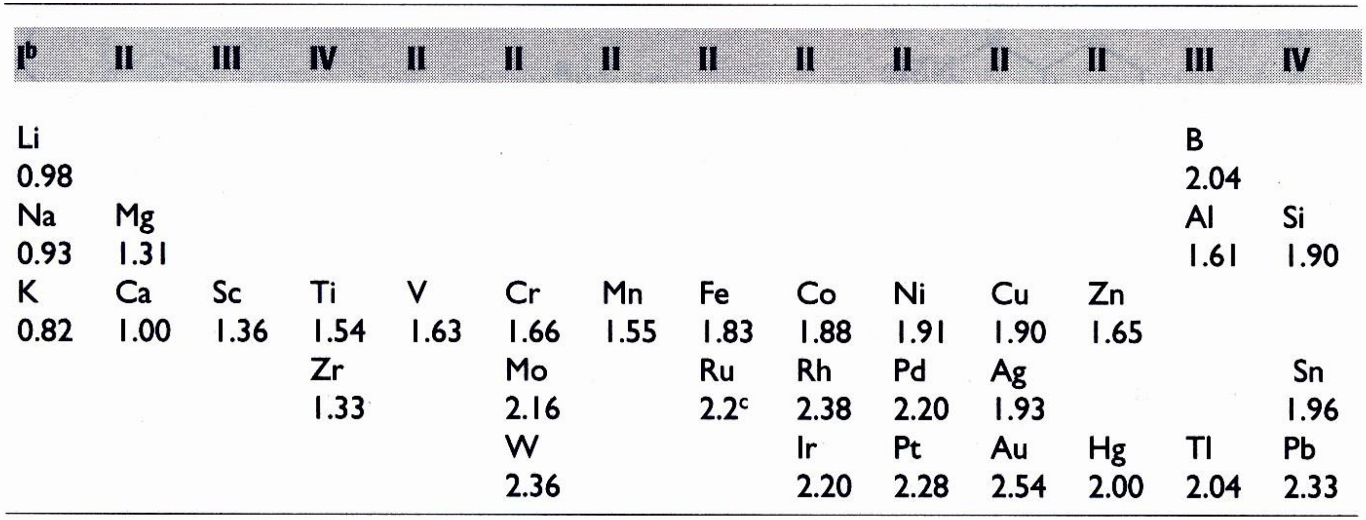
CARBON-CARBON BOND FORMATION

via transmetallation reactions:

M’ - R + M - X ↔ M’ - X + M - R

Transmetallation is an excellent way of introducing σ-bonded hydrocarbon ligands into the coordination sphere of transition metals.

If the electronegativity of M is greater than M’, the reaction (left to right) is thermodynamically favored.



I^b	II	III	IV	II	II	II	II	II	II	II	II	III	IV
Li 0.98												B 2.04	
Na 0.93	Mg 1.31											Al 1.61	Si 1.90
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65		
			Zr 1.33		Mo 2.16		Ru 2.2^c	Rh 2.38	Pd 2.20	Ag 1.93			Sn 1.96
					W 2.36			Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 2.04	Pb 2.33

If an empty orbital is available on both metals, the reaction is kinetically favorable.

POLYMERIZATION CATALYSTS

The reactions lead to metallocene–MAO complexes, in which the bridging pentavalent carbon atoms play a central role. Direct reaction between the methylated zirconocene precursor and MAO breaks the Al-C bond to the bridging carbon atom. The formed three-coordinated aluminum center is capable of partially abstracting the methyl group of the zirconocene, thereby reducing its electron deficiency.

The partially abstracted methyl group appears to be in a delicate balance between the Zr and Al centers; the bond lengths are 2.35 and 2.26 for Zr-C and Al-C, respectively. Under these circumstances, it seems plausible that an incoming monomer can replace the methyl group, thereby forming an olefin-coordinated zirconocene cation and a noncoordinated MeMAO anion in its close proximity.

Within the framework of the current understanding of the single-site olefin polymerization process, a system of this kind would polymerize olefins, and, hence, the ion pair illustrated should be the active species.

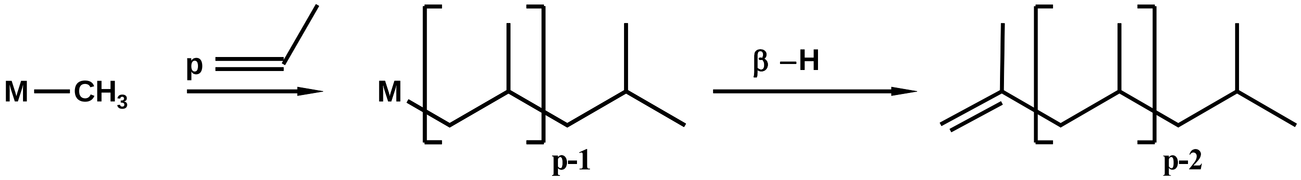
Angew. Chem. 2008

POLYMERIZATION CATALYSTS

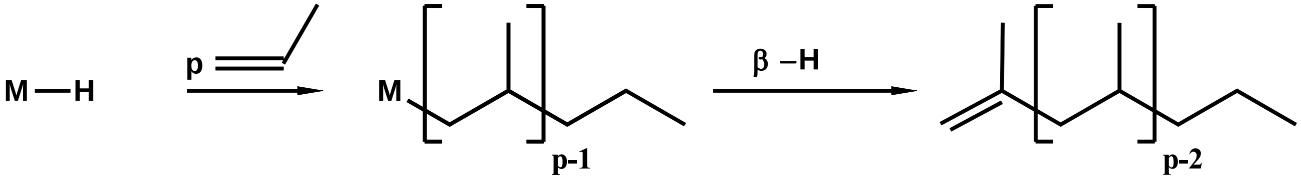
Chain length is depending on two rate factors, the rate of insertion υ_P, and the rate of chain termination υ_T.
The mean degree of polymerization is given as $P_N = \upsilon_P / \upsilon_T$

Modifications in the ligand structure around the metal center allows different kinds of chain termination to be favored. End group analysis has shown that chain transfer mostly occurs via β-H elimination after the primary insertion.

(A)

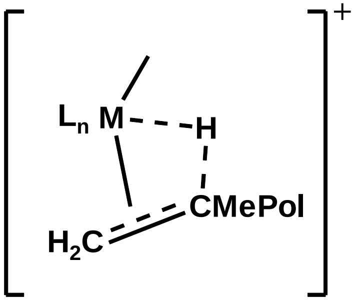


(B)

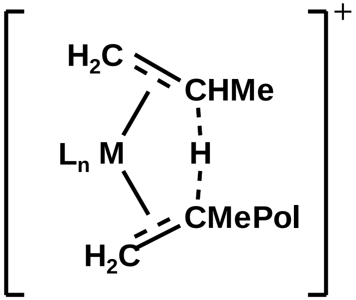


POLYMERIZATION CATALYSTS

A

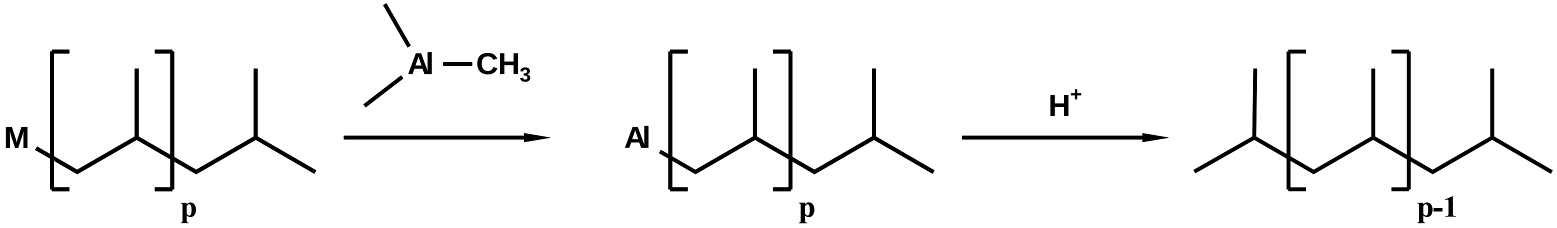


B



A: A schematic picture for the plausable transition state of the β-H transfer to the metal center. ***B**:* A model of the transition state for the chain termination via β-H transfer to the metal coordinated olefin

An increase in molar mass proportional to the monomer pressure indicates that β-H transfer from the growing polymer chain to the metal center is dominant.

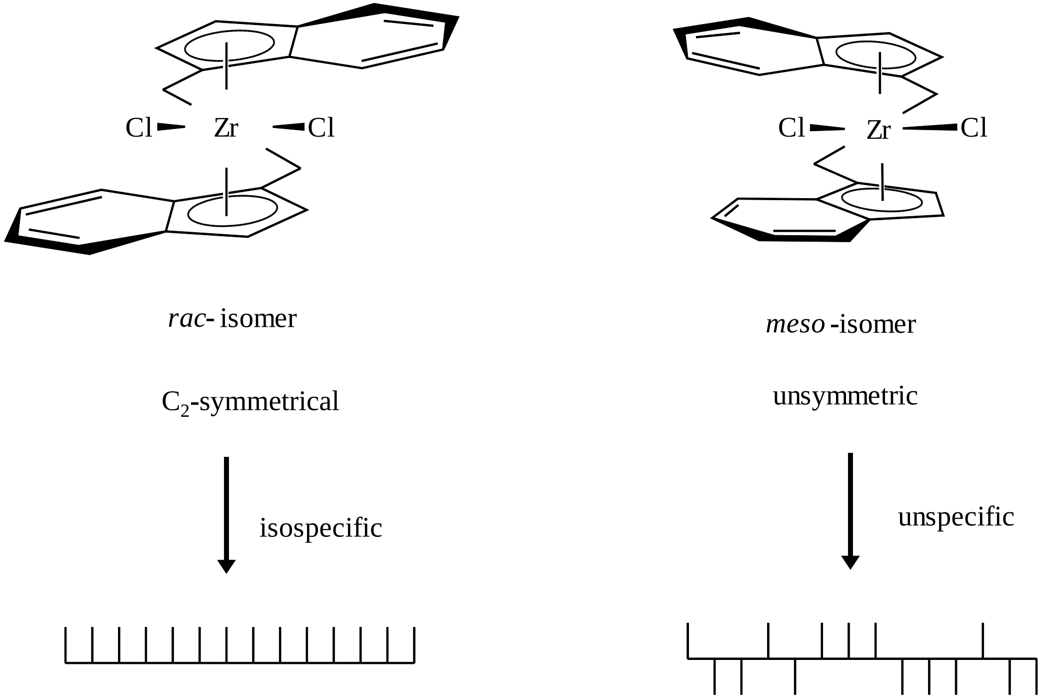


Chain termination via chain transfer to aluminum (transmetallation).

POLYMERIZATION CATALYSTS

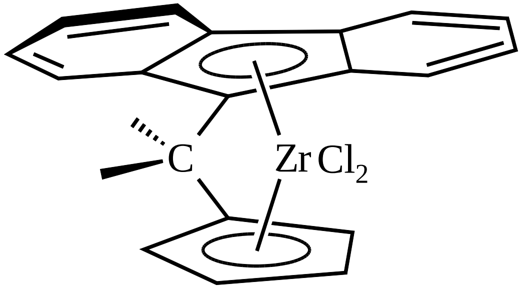
In order to prepare a chiral metallocene complex the torsional mobility of Cp-rings has to be reduced and the ligand framework around the metal center has to obey a certain geometry. To decrease the free rotation of the Cp-moieties, *ansa*-metallocenes were prepared in which Cp-rings are connected together with different manners *e.g.* via an ethylene-bridge

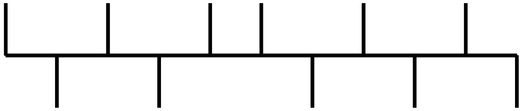
To prepare chiral isospecific metallocene the research focused on C_2-symmetric complexes, in which both chlorides are equally shielded by the substituents on the Cp-rings.



POLYMERIZATION CATALYSTS

While changing the ligand framework of the catalyst precursor from C_2-symmetric to C_S-symmetric, the other stereoregular form of polypropene, syndiotactic polypropene, was obtained



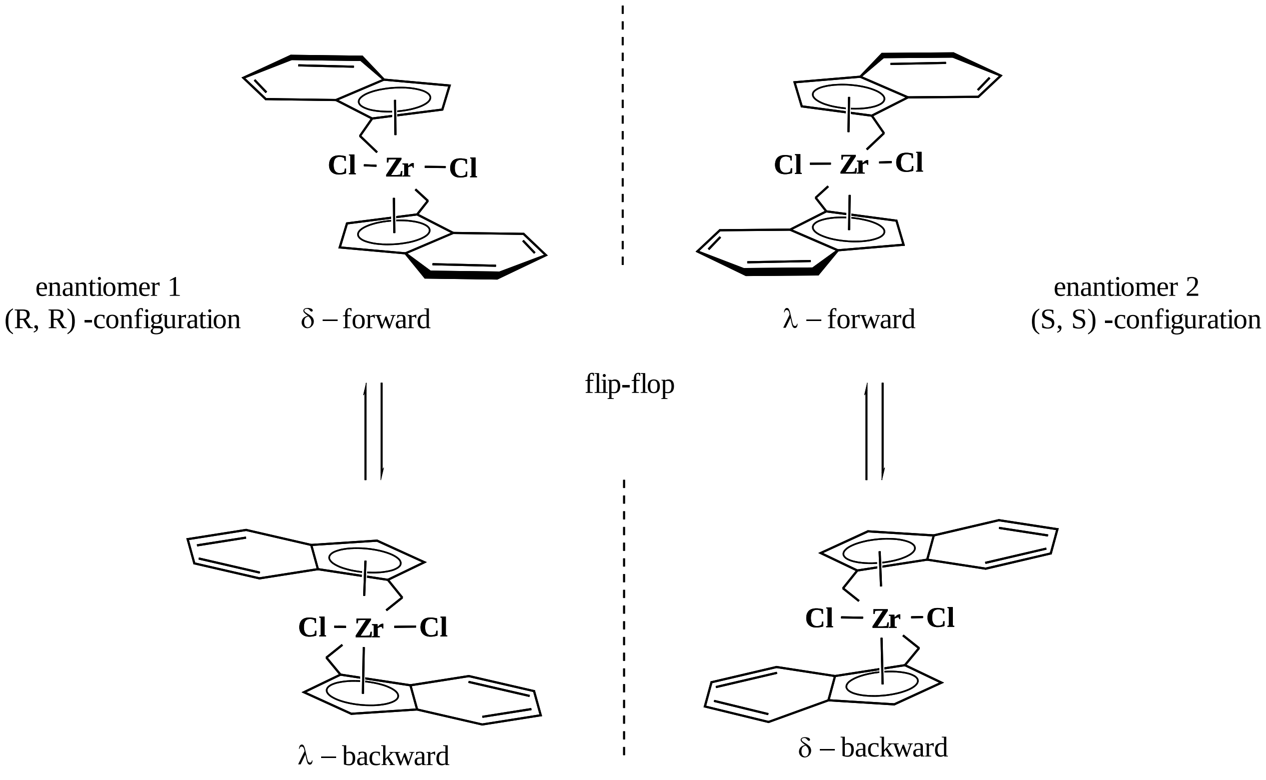


syndiotactic polypropene

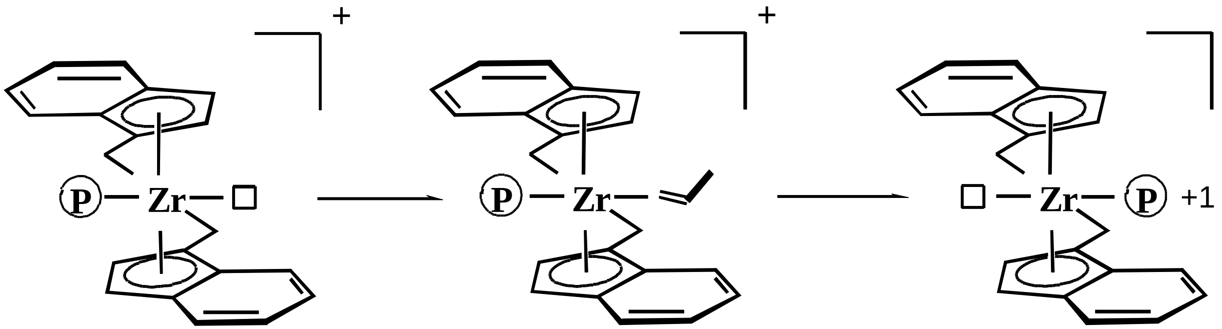
POLYMERIZATION CATALYSTS

Even though *rac*-Et(Ind)$_2$ZrCl$_2$ seems at first look to be quite a simple transition metal complex, it was known from the very beginning that the ethylene-bridge allows a rapid (NMR time scale) interconversion between the two conformations in the *ansa*-titanocene dichloride.

Simultaneously *rac*-Et(Ind)$_2$ZrCl$_2$ is a mixture of two enantiomers which can be separated from each other by crystallization.

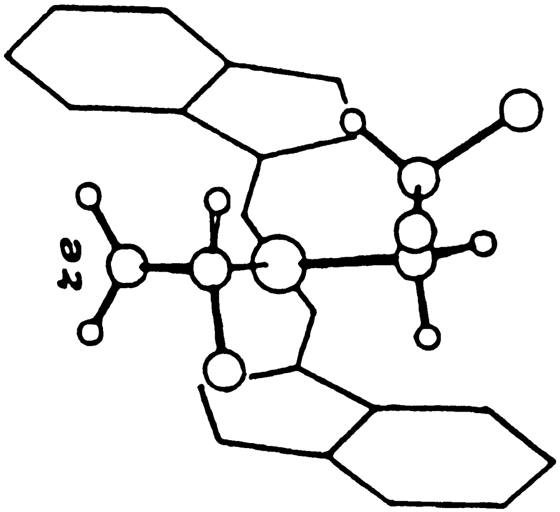


POLYMERIZATION CATALYSTS

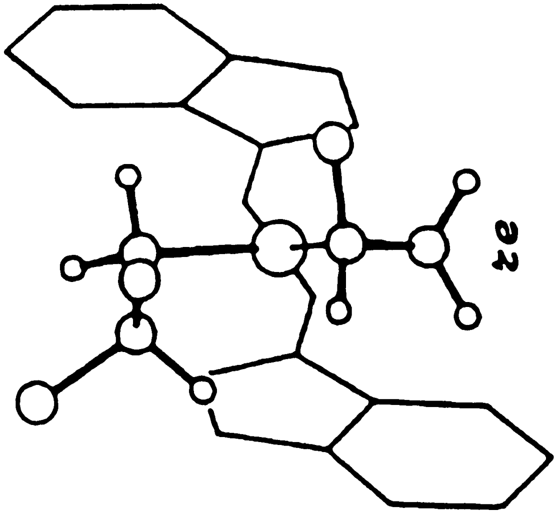


Both coordination positions are homotopic due to C_2-symmetry and thus, the resulting configuration of the complex does not change when transposing the alkyl chain and the free coordination place to each other. Such active species will always discriminate the same enantioface of propene leading to isotactic arrangement.

POLYMERIZATION CATALYSTS



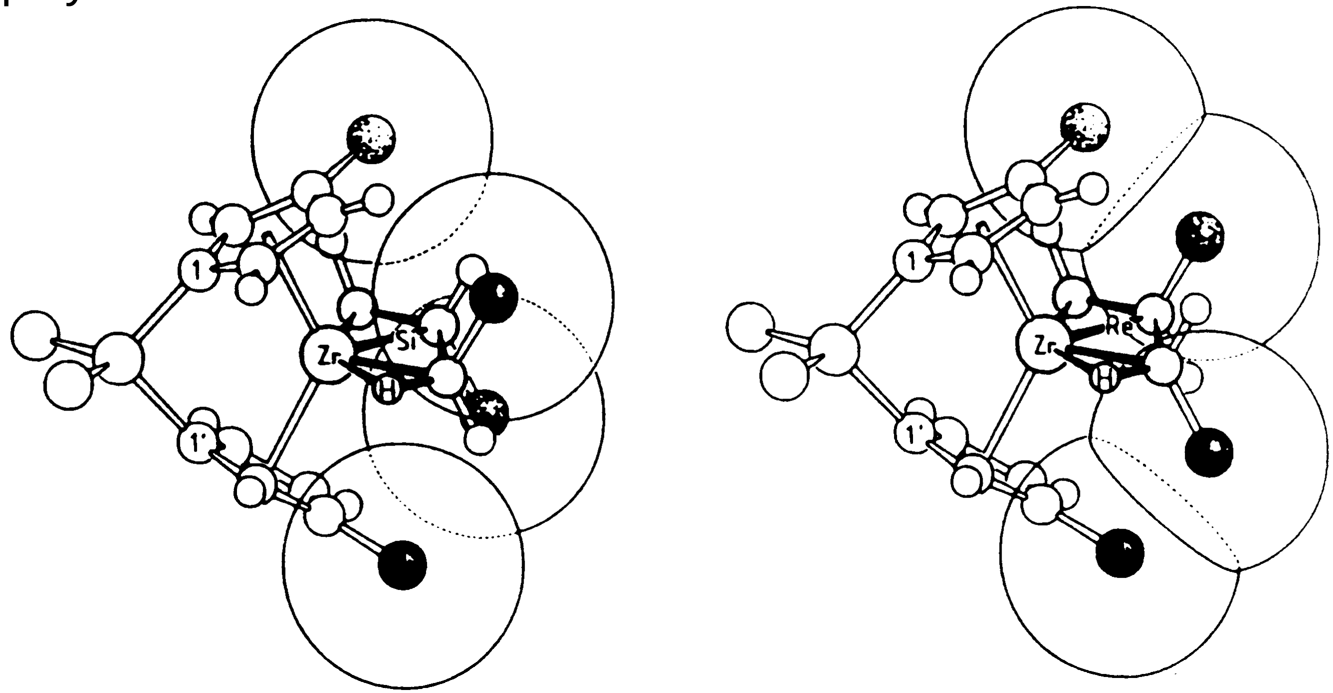
The chiral environment of the metal center forces the growing chain to choose one of the chiral orientations prior to each monomer addition. The C(α)-C(β) chain segment of the polymer tends to orientate itself so that steric interactions with *β*-substituents of the C5 *ring are minimized*



This chiral orientation of the chain in turn guides the monomer to adjust its methyl unit in *trans* position to the C(α)-C(β) segment!

POLYMERIZATION CATALYSTS

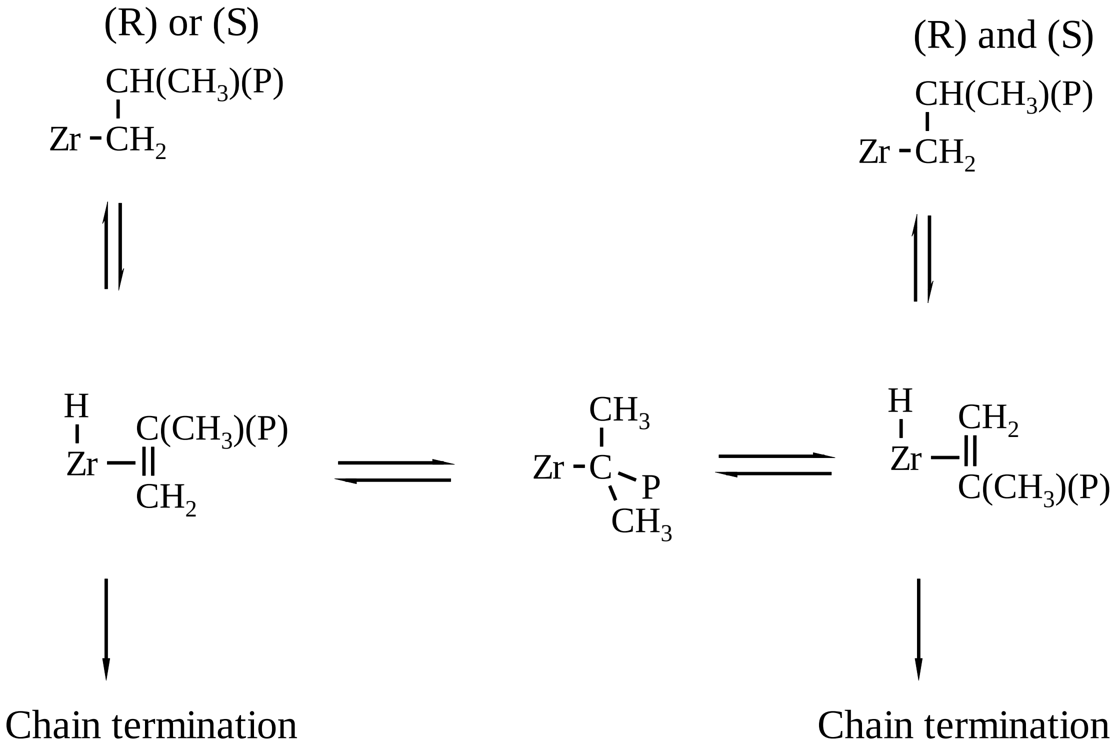
The role of the agostic interaction is to stabilize one of the two conceivable conformers of the Zr-CH_2-unit and thereby to control and assist the orientation of the polymer chain.



The more favorable Zr←H-C interaction prohibits repulsive interactions between the disubstituted β-atom of the chain and the β-substituent of the Cp-ring, while the other possible conformer would lead to severe steric hindrance and is thus inaccessible.

POLYMERIZATION CATALYSTS

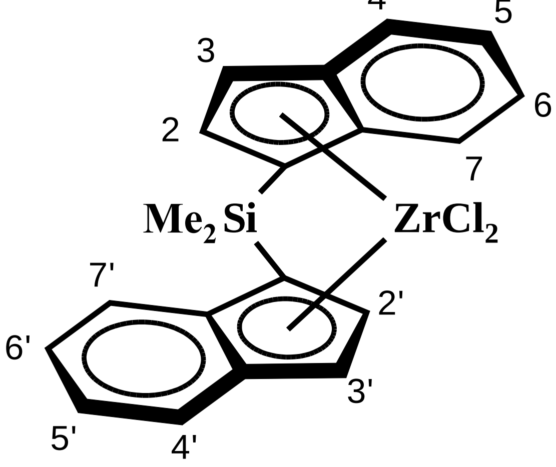
Stereospecifity is strongly depending on polymerization temperature and also on monomer concentration. When the polymerization temperature is increased the number of stereoerrors rises together with the catalytic activity.



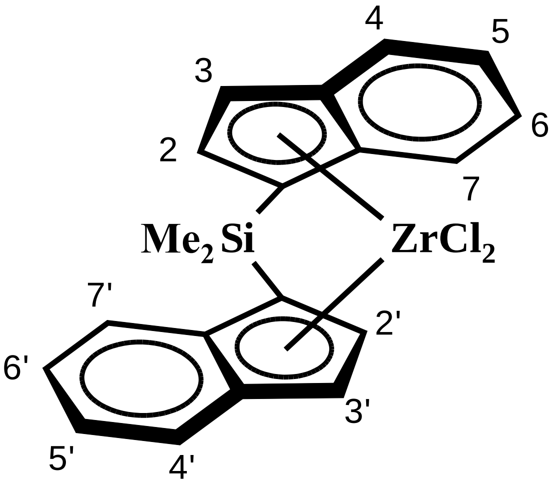
POLYMERIZATION CATALYSTS

The properties of the polypropenes produced by $Et(Ind)_2ZrCl_2$ or $Et(H_4Ind)_2ZrCl_2$ are not satisfactory from the industrial point of view. Both the catalytic selectivity and chain length tend to stay only moderate under technical conditions.

The change of the ethylene-bridge to a silyl-one doubles the molar mass and increases the activity substantially concomitant with improved tacticity.



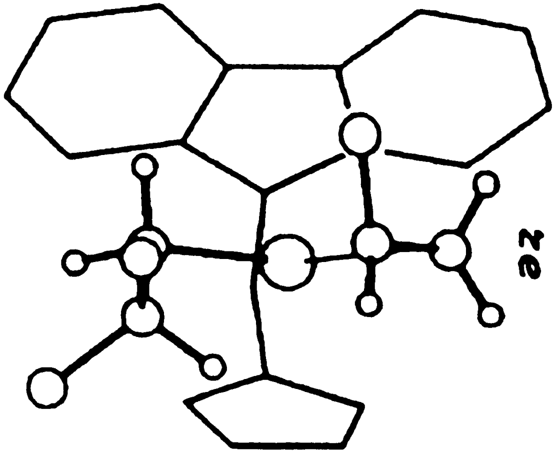
POLYMERIZATION CATALYSTS

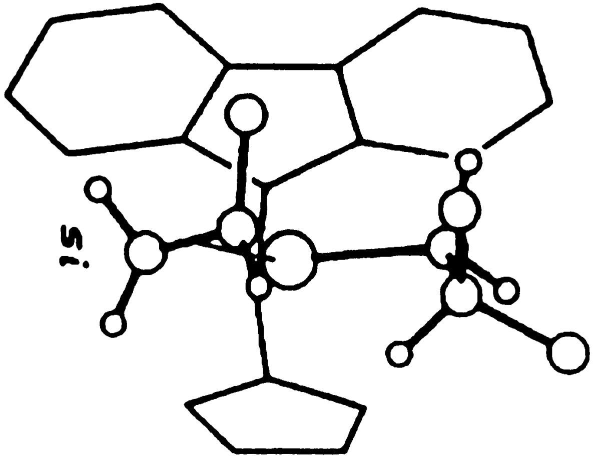


entry	substituents	Activity [kg PP/ (mmol Zr × h)]	M_w kg/mol	m.p. (°C)	[mmmm] (%)
1	none[a]	188	24	132	78.5
2	none	190	36	138	81.7
3	2-Me	99	195	145	88.5
4	2-Me, 4-iPr	245	213	150	88.6
5	2-Me, 4-Ph	553	778	157	95.1
6	2-Me, 4-Naph	875	920	161	99.1
7	4-5 benzo	274	27	138	80.5
8	2-Me, 4-5 benzo	403	330	146	88.7
9	2-Me, 5-Ph	63	188	139	78.1

POLYMERIZATION CATALYSTS

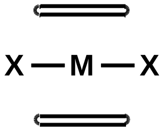
Syndiotactic PP is formed only if propene is coordinated after each insertion from the other enantioface than the previous one.



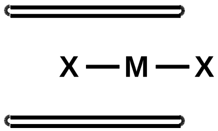


POLYMERIZATION CATALYSTS

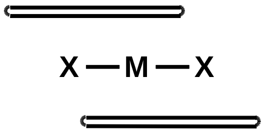
Stereorigid metallocene complexes can be devided into five symmetry classes, based on the relationship between the symmetry of catalytic sites (X) and the local symmetry of the metal atom.



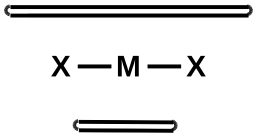
I (C_{2V})



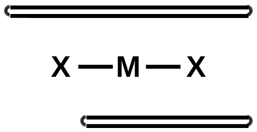
II (C_S)



III (C_2)



IV (C_S)



V (C_1)

POLYMERIZATION CATALYSTS

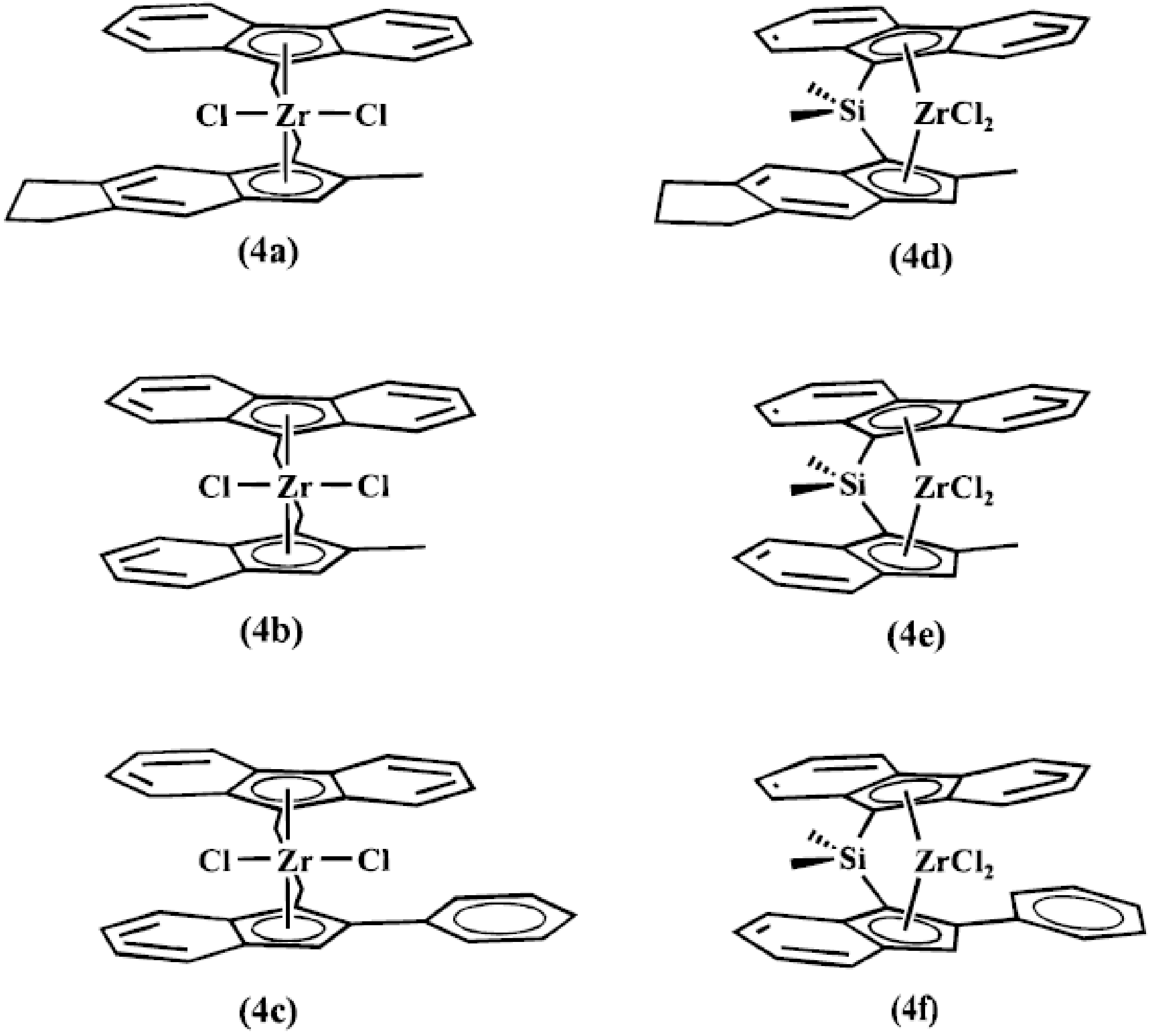
Dual-Side *ansa*-Zirconocene Dichlorides for High Molecular Weight Isotactic Polypropene Elastomers

Jürgen Kukral, Petri Lehmus, Tanja Feifel, Carsten Troll, and Bernhard Rieger*

Organometallics **2000,** *19,* 3767-3775

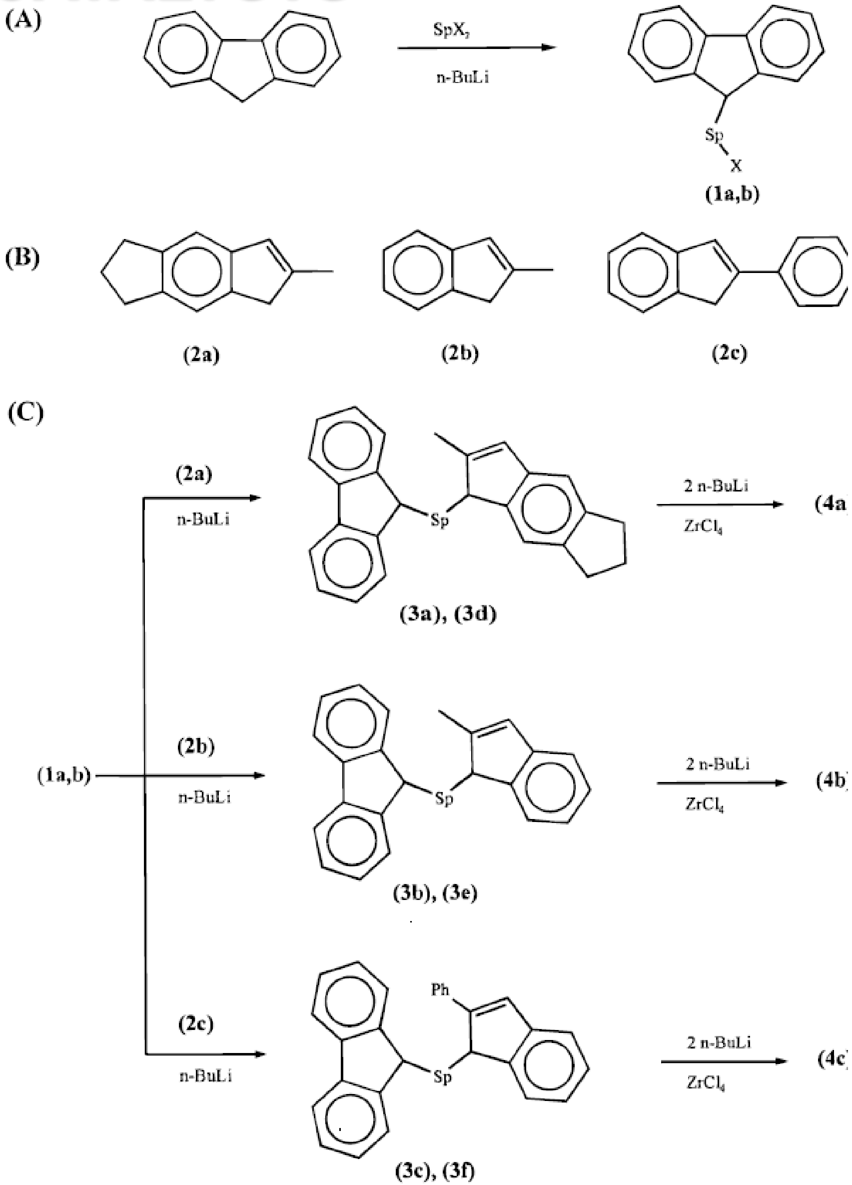
POLYMERIZATION CATALYSTS

Scheme 1



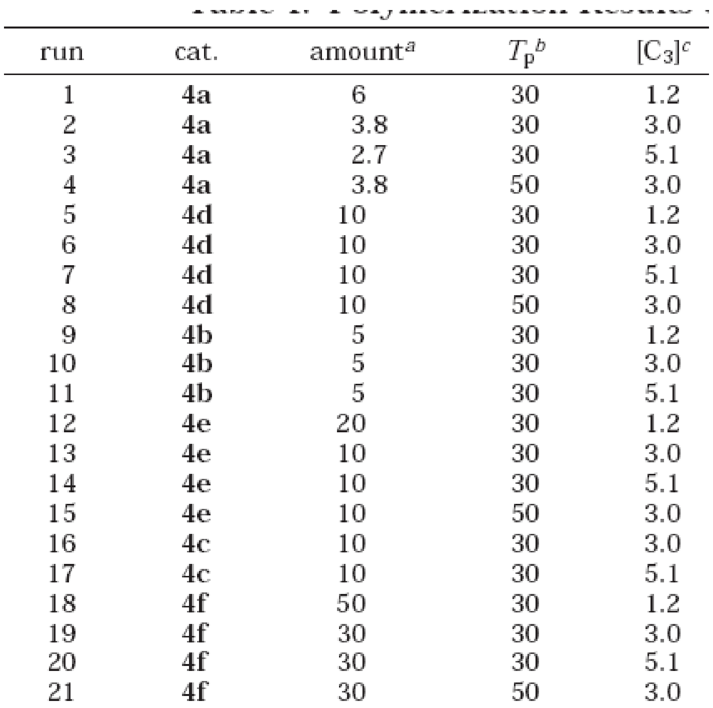
POLYMERIZATION CATALYSTS

Scheme 2

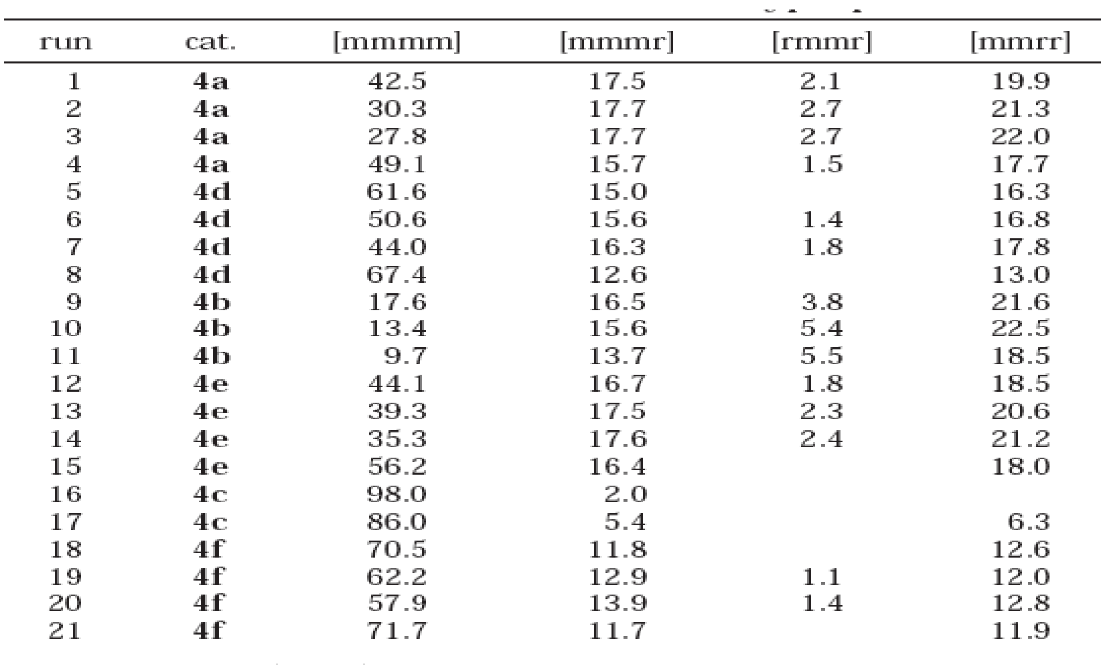


$SpX_2 = C_2H_4Br_2$ or $(CH_3)_2Cl_2Si$
(1a), **(3a)**, **(3b)**, **(3c)**: $Sp = C_2H_4$
(1b), **(3d)**, **(3e)**, **(3f)**: $Sp = (CH_3)_2Si$

POLYMERIZATION CATALYSTS

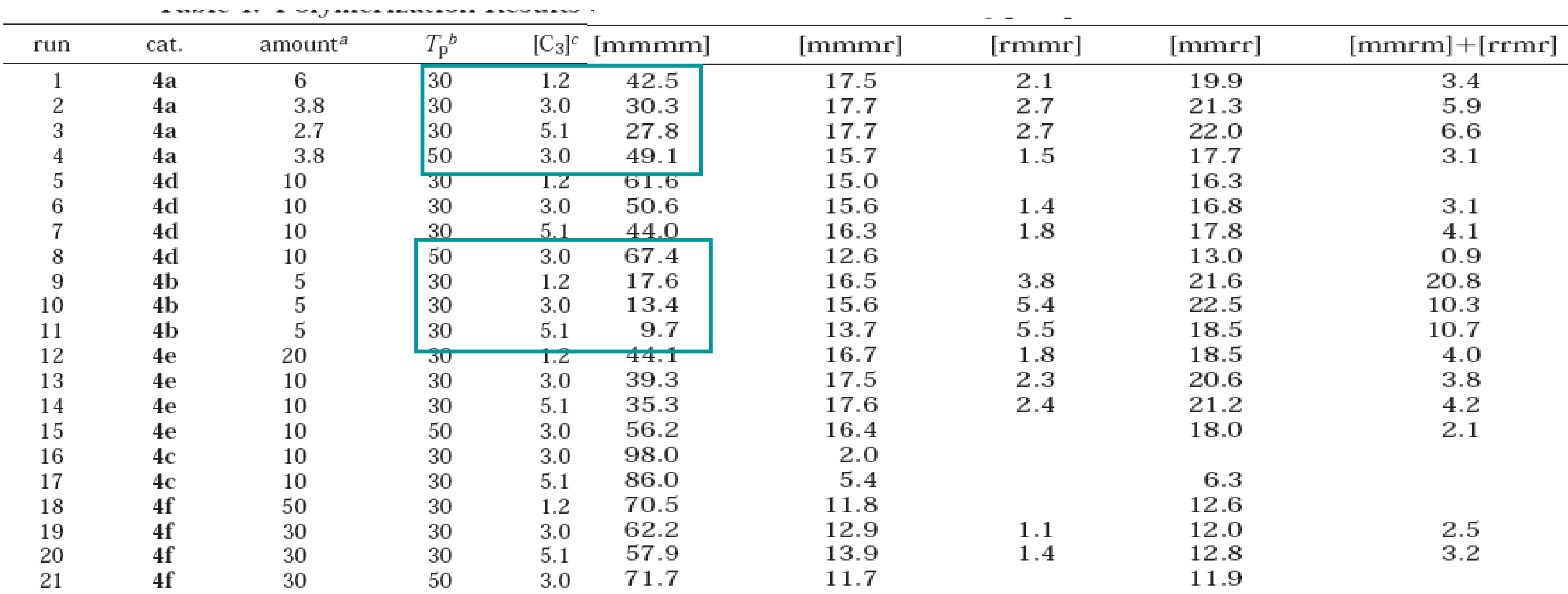


run	cat.	amount^{a}	T_p^{b}	[C$_3$]^{c}
1	**4a**	6	30	1.2
2	**4a**	3.8	30	3.0
3	**4a**	2.7	30	5.1
4	**4a**	3.8	50	3.0
5	**4d**	10	30	1.2
6	**4d**	10	30	3.0
7	**4d**	10	30	5.1
8	**4d**	10	50	3.0
9	**4b**	5	30	1.2
10	**4b**	5	30	3.0
11	**4b**	5	30	5.1
12	**4e**	20	30	1.2
13	**4e**	10	30	3.0
14	**4e**	10	30	5.1
15	**4e**	10	50	3.0
16	**4c**	10	30	3.0
17	**4c**	10	30	5.1
18	**4f**	50	30	1.2
19	**4f**	30	30	3.0
20	**4f**	30	30	5.1
21	**4f**	30	50	3.0



run	cat.	[mmmm]	[mmmr]	[rmmr]	[mmrr]
1	**4a**	42.5	17.5	2.1	19.9
2	**4a**	30.3	17.7	2.7	21.3
3	**4a**	27.8	17.7	2.7	22.0
4	**4a**	49.1	15.7	1.5	17.7
5	**4d**	61.6	15.0		16.3
6	**4d**	50.6	15.6	1.4	16.8
7	**4d**	44.0	16.3	1.8	17.8
8	**4d**	67.4	12.6		13.0
9	**4b**	17.6	16.5	3.8	21.6
10	**4b**	13.4	15.6	5.4	22.5
11	**4b**	9.7	13.7	5.5	18.5
12	**4e**	44.1	16.7	1.8	18.5
13	**4e**	39.3	17.5	2.3	20.6
14	**4e**	35.3	17.6	2.4	21.2
15	**4e**	56.2	16.4		18.0
16	**4c**	98.0	2.0		
17	**4c**	86.0	5.4		6.3
18	**4f**	70.5	11.8		12.6
19	**4f**	62.2	12.9	1.1	12.0
20	**4f**	57.9	13.9	1.4	12.8
21	**4f**	71.7	11.7		11.9

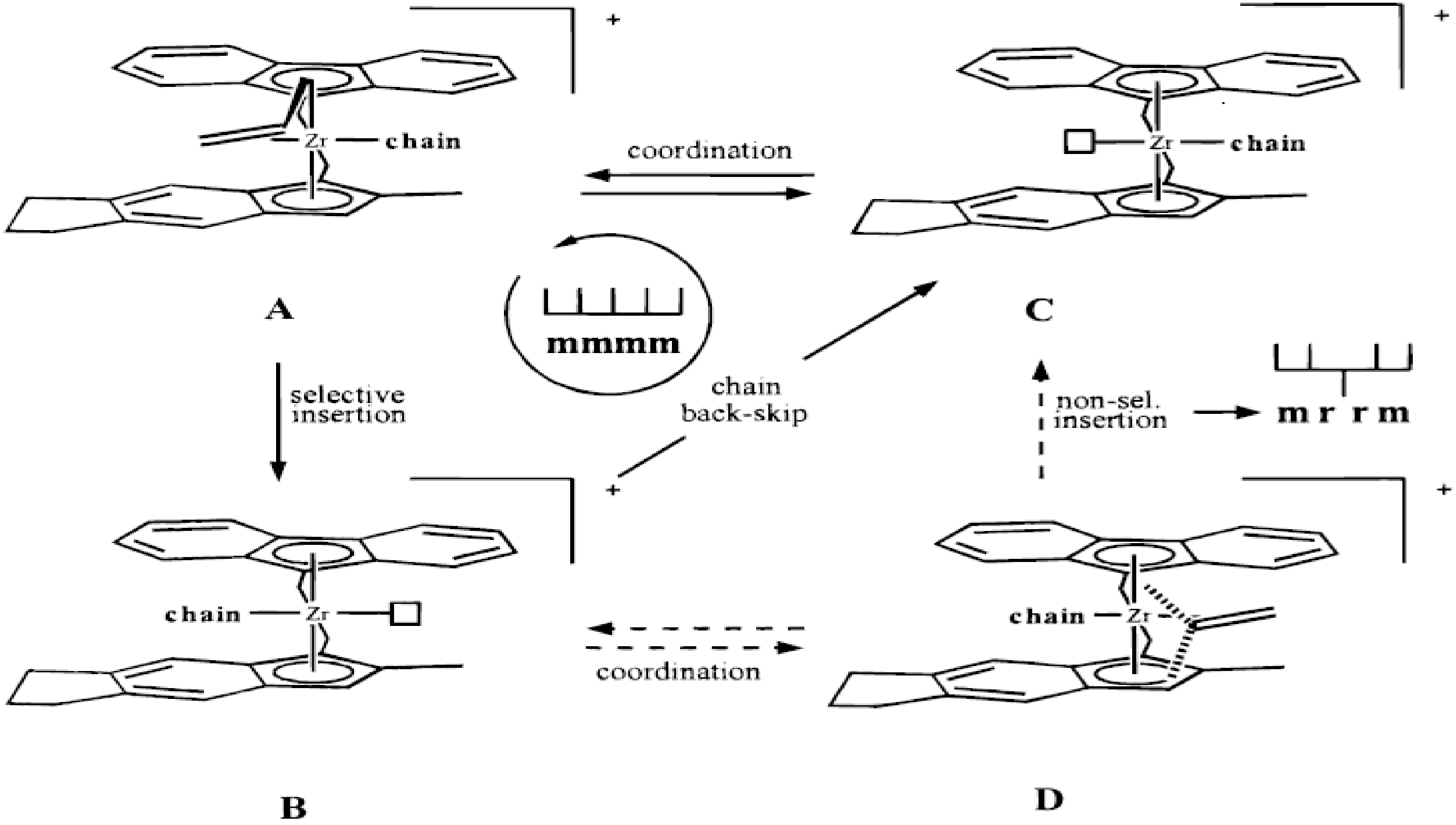
POLYMERIZATION CATALYSTS



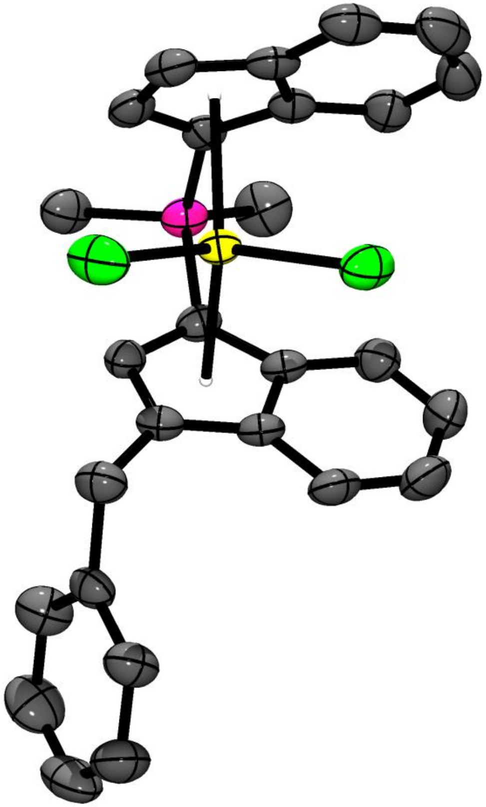
run	cat.	amount[a]	T_p[b]	$[C_3]$[c]	[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mmrm]+[rrmr]
1	**4a**	6	30	1.2	42.5	17.5	2.1	19.9	3.4
2	**4a**	3.8	30	3.0	30.3	17.7	2.7	21.3	5.9
3	**4a**	2.7	30	5.1	27.8	17.7	2.7	22.0	6.6
4	**4a**	3.8	50	3.0	49.1	15.7	1.5	17.7	3.1
5	**4d**	10	30	1.2	61.6	15.0		16.3	
6	**4d**	10	30	3.0	50.6	15.6	1.4	16.8	3.1
7	**4d**	10	30	5.1	44.0	16.3	1.8	17.8	4.1
8	**4d**	10	50	3.0	67.4	12.6		13.0	0.9
9	**4b**	5	30	1.2	17.6	16.5	3.8	21.6	20.8
10	**4b**	5	30	3.0	13.4	15.6	5.4	22.5	10.3
11	**4b**	5	30	5.1	9.7	13.7	5.5	18.5	10.7
12	**4e**	20	30	1.2	44.1	16.7	1.8	18.5	4.0
13	**4e**	10	30	3.0	39.3	17.5	2.3	20.6	3.8
14	**4e**	10	30	5.1	35.3	17.6	2.4	21.2	4.2
15	**4e**	10	50	3.0	56.2	16.4		18.0	2.1
16	**4c**	10	30	3.0	98.0	2.0			
17	**4c**	10	30	5.1	86.0	5.4		6.3	
18	**4f**	50	30	1.2	70.5	11.8		12.6	
19	**4f**	30	30	3.0	62.2	12.9	1.1	12.0	2.5
20	**4f**	30	30	5.1	57.9	13.9	1.4	12.8	3.2
21	**4f**	30	50	3.0	71.7	11.7		11.9	

POLYMERIZATION CATALYSTS

Scheme 3



Polyolefins



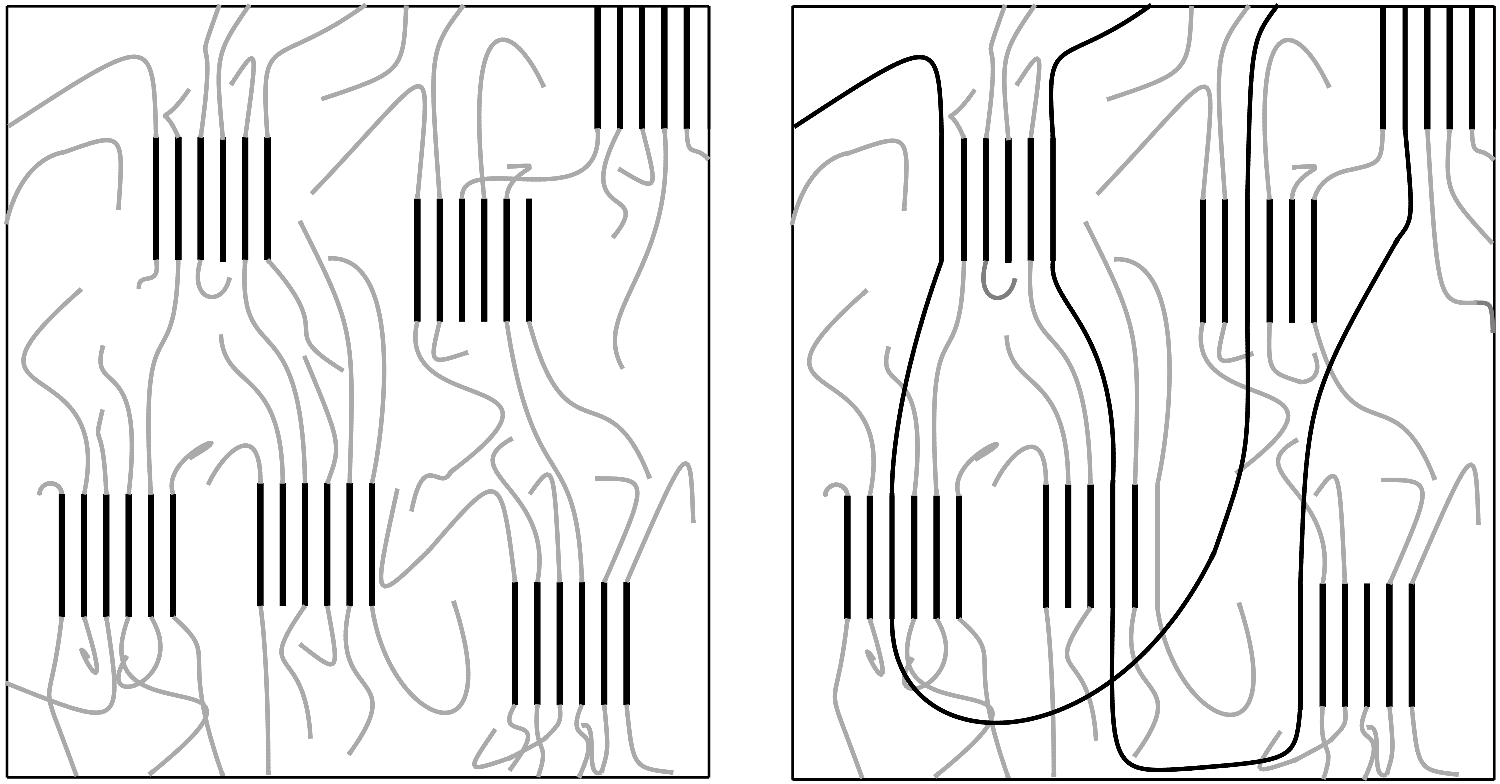
Current trends:

- -Expanding material properties
  - Highly elastic PP
  - High molar mass highly iPP

Goals:

- -Safety
- -More durable products

Polyolefins



OLIGOMERIZATION CATALYSTS

Ziegler’s discovery of Aufbau reaction is the basis of commercial processes.

The most important observation was the “nickel effect”. These two led to an intensive research on organonickel chemistry (see below).

Today linear α-olefins are mainly produced by ethylene oligomerization because of high quality and the good availability of ethylene (from pyrolysis of naphtha, gas-oil or wet natural gases).
(other routes are paraffin wax-cracking, paraffin dehydrogenation and alcohol dehydration).
Paraffin, or paraffin hydrocarbon, is also the technical name for an alkane in general, but in most cases it refers specifically to a linear, or normal alkane — whereas branched, or isoalkanes are also called isoparaffins

The wide application and increasing need for short-chain α-olefins as comonomers for polymers cause the market still to grow.

Main applications:
Comonomers for ethylene (C_4-C_8)
Plasticizers (C_6-C_{10})
Surfactants (C_{12}-C_{20})

OLIGOMERIZATION CATALYSTS

Uses

Gaseous

Fuels

Liquids

Fuels

Paints, Pigments, Dyes and Inks

In leather industry for "pull up finish"

Medicine (Laxative)

Biomedical science (evaporation control during PCR)

Culinary

Fire breathing and fire juggling

Used in toiletries and cosmetics as a moisturiser or emollient.

Paraffin wax

Candle-making

Coatings for waxed paper or cloth

Food-grade paraffin wax:

Shiny coating used in candy-making; although edible, it is nondigestible, passing right through the body without being broken down

Coating for many kinds of hard cheese, like Edam cheese

Sealant for jars, cans, and bottles

Chewing gum additive

Investment casting

Anti-caking agent, moisture repellent, and dustbinding coatings for fertilizers

Agent for preparation of specimens for histology

Bullet lubricant – with other ingredients, such as olive oil and beeswax

Crayons

Solid propellant for hybrid rocket motors.

Component of surfwax, used for grip on surfboards in surfing

Component of glide wax, used on skis and snowboards

Friction-reducer, for use on handrails and cement ledges, commonly used in skateboarding

Ink. Used as the basis for solid ink different color blocks of wax for thermal printers. The wax is melted and then sprayed on the paper producing images with a shiny surface

Microwax: food additive, a glazing agent with E number E905

Forensics aid: the nitrate test uses paraffin wax to detect nitrates and nitrites on the hand of a shooting suspect

Antiozonant agents: blends of paraffin and micro waxes are used in rubber compounds to prevent cracking of the rubber; the antiozonant waxes can be produced from synthetic waxes, FT wax, and Fischer Tropsch wax

Mechanical thermostats and actuators, as an expansion medium for activating such devices.

"Potting" guitar pickups, which reduces microphonic feedback caused from the subtle movements of the pole pieces

Wax baths for beauty and therapy purposes

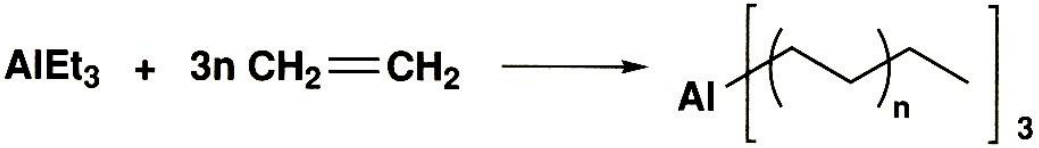
An effective, although comedogenic, moisturiser in toiletries and cosmetics such as Vaseline

Prevents oxidation on the surface of polished steel and iron.

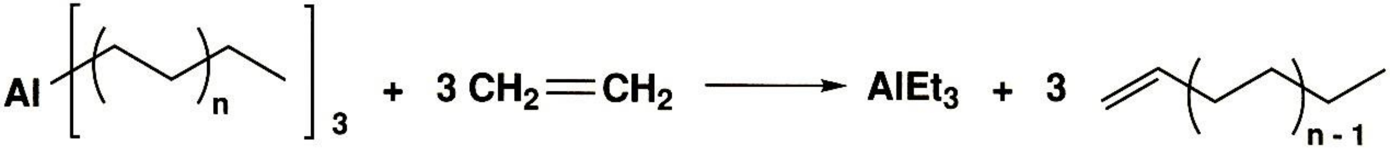
OLIGOMERIZATION CATALYSTS

Alfen Process is carried out in two steps:

The chain growth reaction is first accomplished at 100 ˚C and 100 bar.



In the following high-temperature elimination step the α-olefins are displaced by ethylene at about 300 ˚C and 10 bar.



The main disadvantage is the process is the large amount of aluminum alkyls needed in an industrial plant. The process has been improved by several companies, two most important ones being *Gulf* process and *Ethyl* process.

OLIGOMERIZATION CATALYSTS

Gulf process use one step catalytic procedure, where the chain growth and termination occur simultaneously in the same reactor. About 0.4% of $Al(Et)_3$ is needed, heptane is used as a solvent and the catalyst is destroyed by hydrolysis. The process gives products with Flory-Schultz distribution.

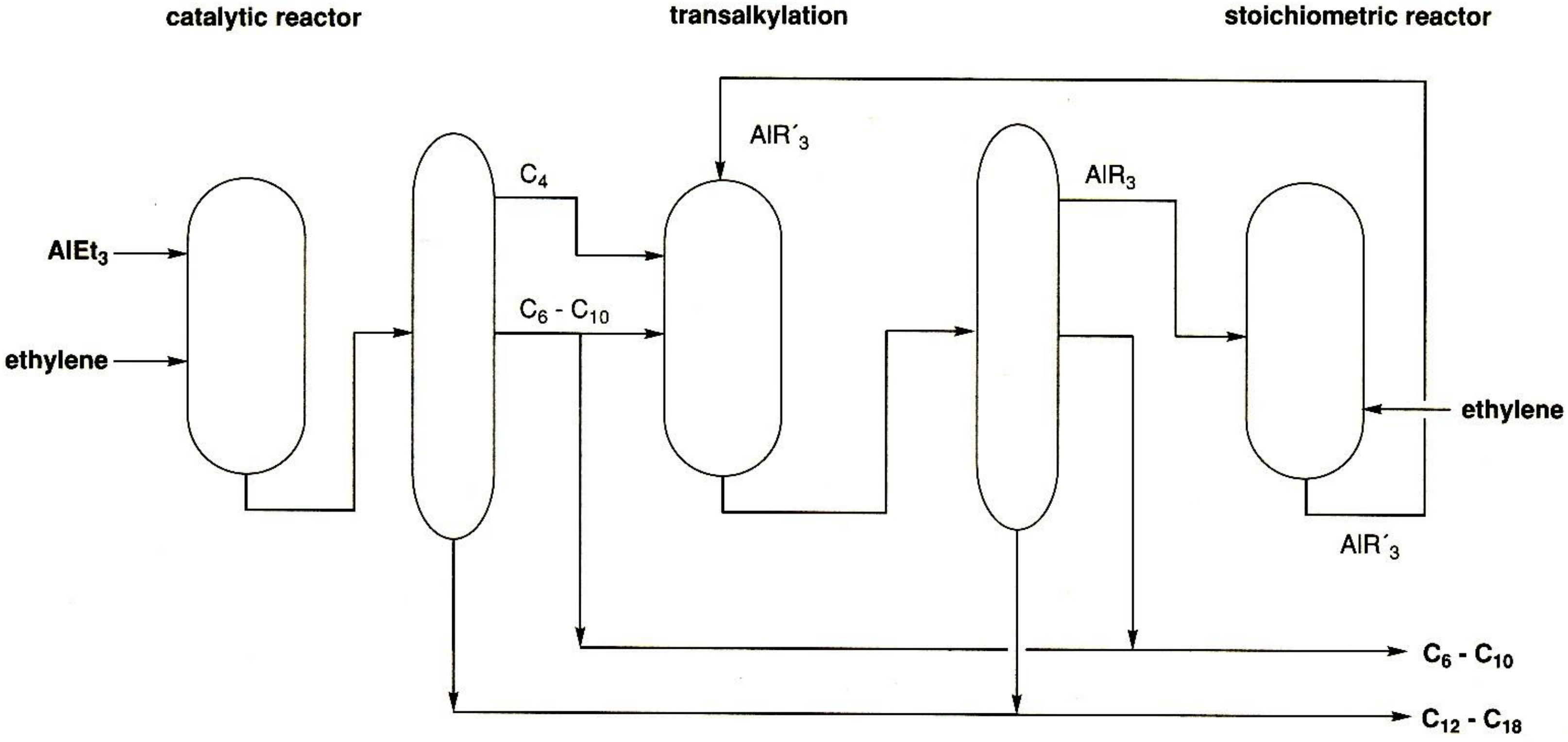
Because α-olefins and aluminum alkyls are present in the same reactor, branched olefins are obtained with increasing chain lenght. Nevertheless, the α-olefins obtained (94-98%) have considerably higher purity than those from wax-cracking.

Ethyl process is a combination of stoichiometric and catalytic chain growth reactions. Unifying these parts with a transalkylation step allows very efficient control of the chain length.

The first oligomerization step is similar to above and is operated at about 160-275 ˚C and 130-270 bar. After the reaction, catalyst is destroyed in hydrolysis and the product mixture (mainly C_4-C_{10}) is distilled and higher olefins are separated (C_{12}-C_{18}). The lower fraction is subject for transalkylation with higher aluminum alkyls, liberating higher olefins (300 ˚C and 100 bar). In the second distillation the olefins are separated from aluminum alkyls.

OLIGOMERIZATION CATALYSTS

The higher alkyls from lower aluminum alkyls were produced in the “stoichiometric” reaction (100 ˚C and 200 bar). Because of the recycle, the copolymerization of the product olefins with ethylene yields branched olefins.

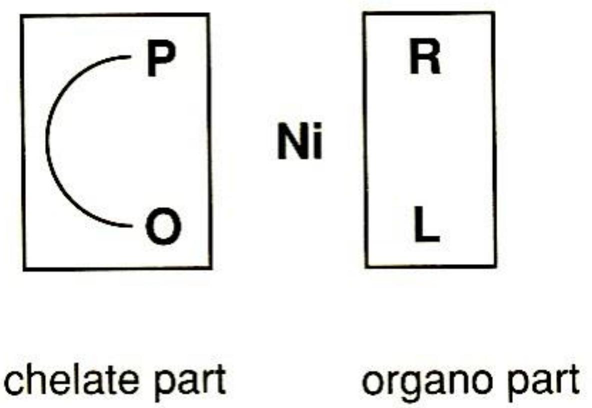


OLIGOMERIZATION CATALYSTS

SHOP Shell Higher Olefin Process

Based on the “nickel effect”. Commercially very important process (1 million tons/year). Takes place in three phases:

* Oligomerization
* Isomerization
* Metathesis



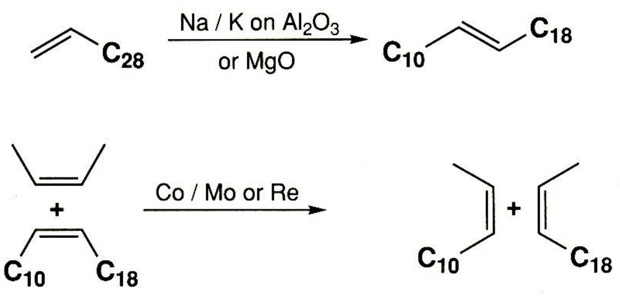
Oligomerization takes place in a polar solvent (e.g. butanediol), where the catalyst is soluble, but the product is not. This is one of the first examples about a biphasic liquid/liquid to be used in catalysis. Suitable ligands are the general type of diorganophosphino acid derivatives.

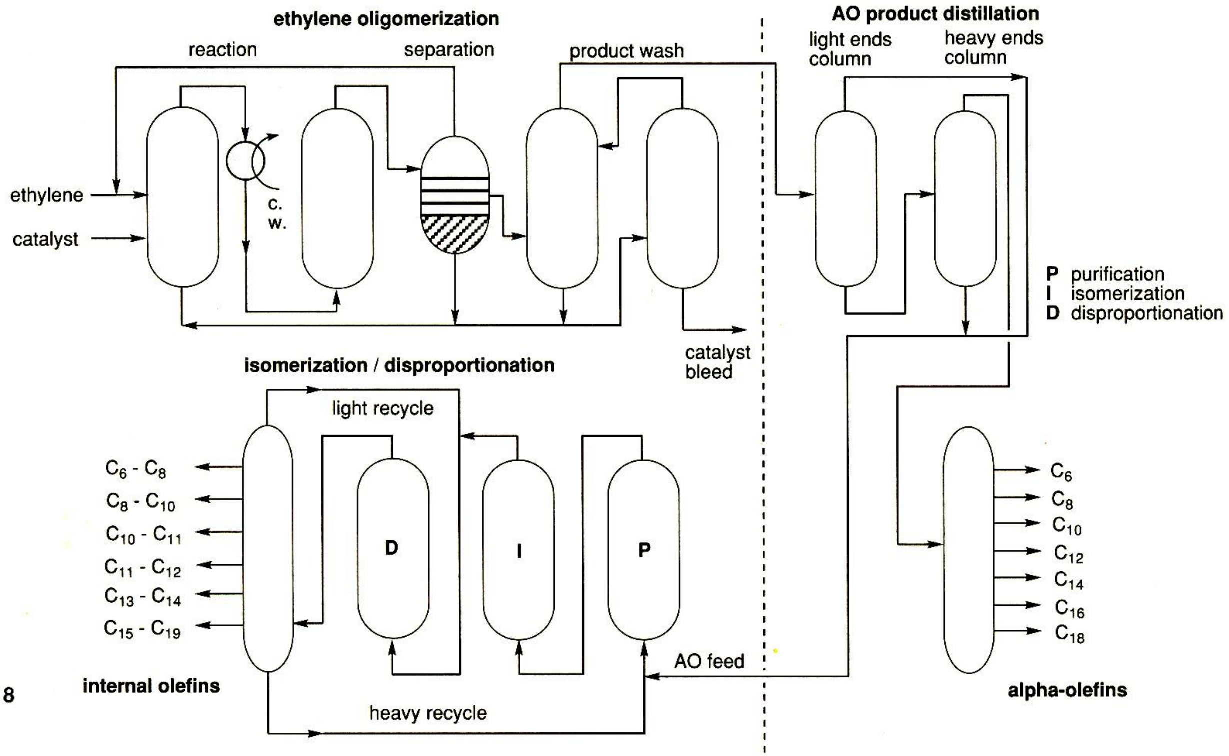
OLIGOMERIZATION CATALYSTS

Heat of the reaction is removed by water cooling (heat exchangers) between the reactors. Insoluble products and the catalyst solution as well as ethene are separated. The catalyst solution and ethylene are fed back into the oligomerization reactor.

Lower C_4-C_{10} olefins and C_{20+} fractions are removed from the desired C_{12}-C_{20} olefins.

Lower C_4-C_{10} olefins and C_{20+} fractions are *isomerized* (90 % yield) to internal linear olefins followed by metathesis.

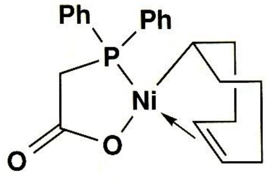




Metathesis produces about 15% of the desired C_{11}-C_{14} linear internal olefins, which are separated. Undesired fractions are recycled: light olefins are fed back to metathesis and heavier ones to isomerization. Because high amount short olefins in the metathesis, the double bonds are in the chain ends.

OLIGOMERIZATION CATALYSTS

Studied catalyst precursors for SHOP. One component catalysts!!
The chelating part of the complex controls selectivity and reactivity, while the organo part stabilize the complex.



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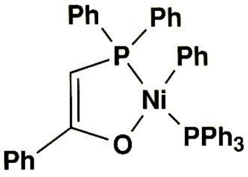

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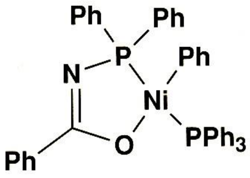

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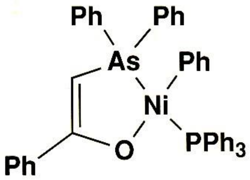

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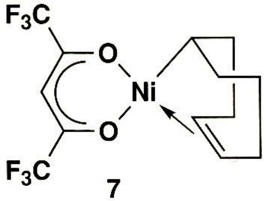
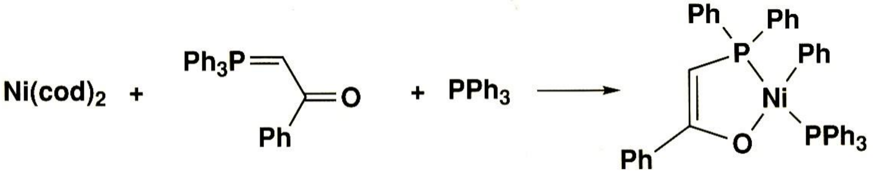


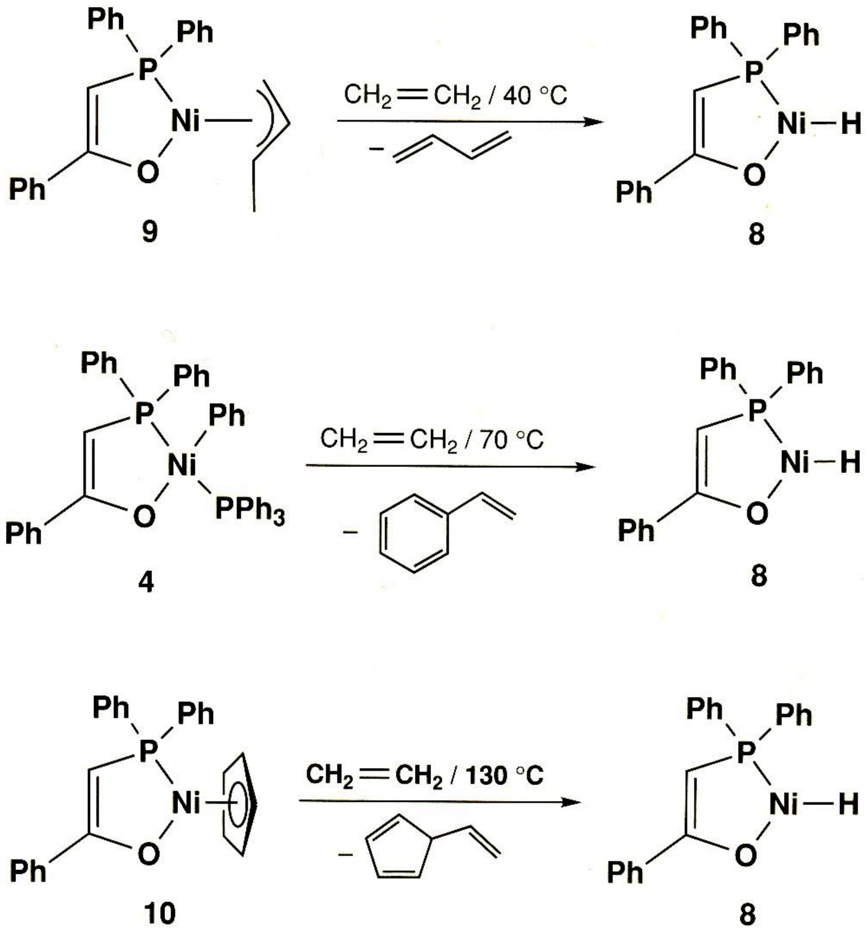
7

Interesting feature of the synthesis of **4** from bis(cyclooctadienyl)Ni and phosphorane is the shift of the one phenyl group from phosphorous to nickel.

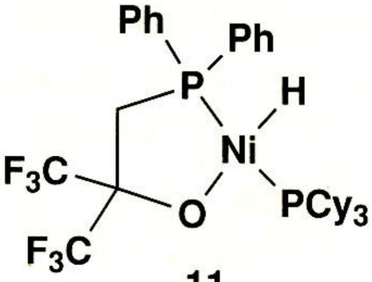


OLIGOMERIZATION CATALYSTS

Activation of the single compound catalysts with ethylene. It is generally agreed that real catalyst is Ni-H species.



OLIGOMERIZATION CATALYSTS



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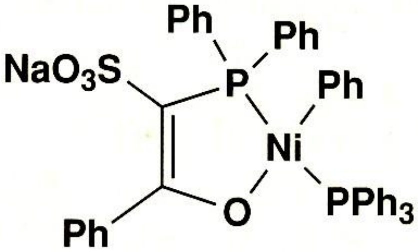

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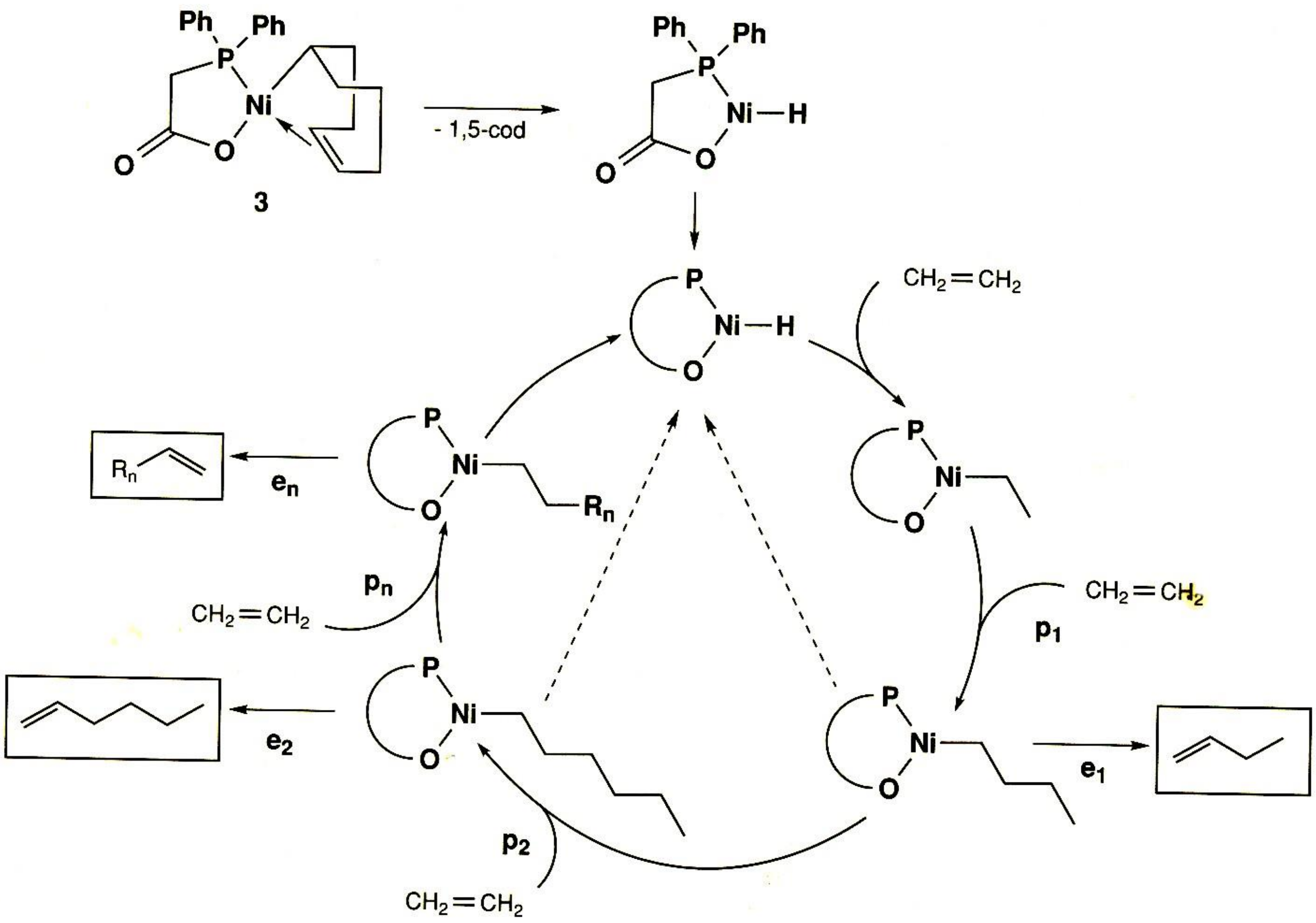
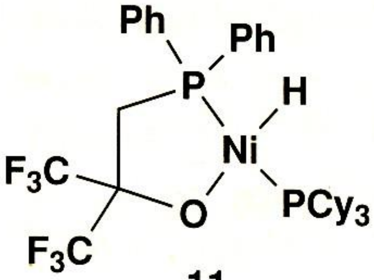
OLIGOMERIZATION CATALYSTS



Mechanism for the nickel hydride SHOP process.
Amount of the catalyst: 0.001-0.005 mol%, 80-140˚C, 70-140 bar. Rate of the reaction is controlled by amount of the catalyst.

OLIGOMERIZATION CATALYSTS



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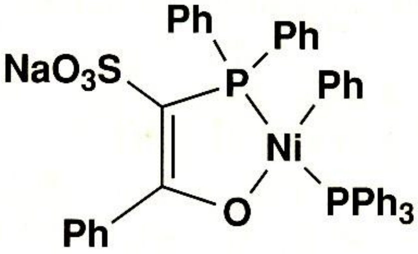

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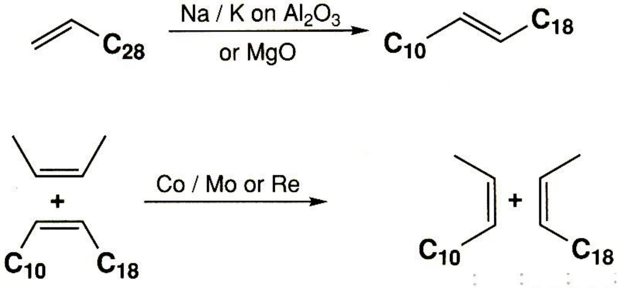
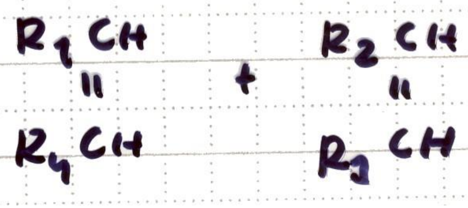
OLIGOMERIZATION CATALYSTS

About the metathesis in SHOP



Low molar mass and high molar mass fractions are combined and methatesis is carried out with e.g. MoO_3/AlO_3

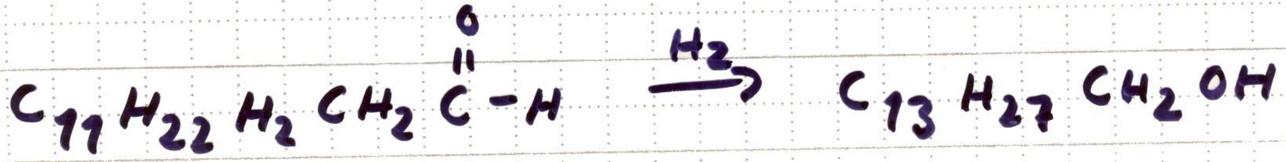
$$R_1CH=CHR_2 + R_3CH=CHR_4 \longrightarrow \begin{matrix} R_1CH \\ \| \\ R_3CH \end{matrix} + \begin{matrix} R_2CH \\ \| \\ R_4CH \end{matrix}$$



$$\begin{matrix} R_1CH \\ \| \\ R_4CH \end{matrix} + \begin{matrix} R_2CH \\ \| \\ R_3CH \end{matrix}$$

Internal olefins can be converted to α-olefins with $HCo(CO)_4$.

If CO and H_2 are present, alcohols and aldehydes can be produced *in situ*.



$$C_{11}H_{22}H_2CH_2\overset{O}{\overset{\|}{C}}-H \xrightarrow{H_2} C_{13}H_{27}CH_2OH$$

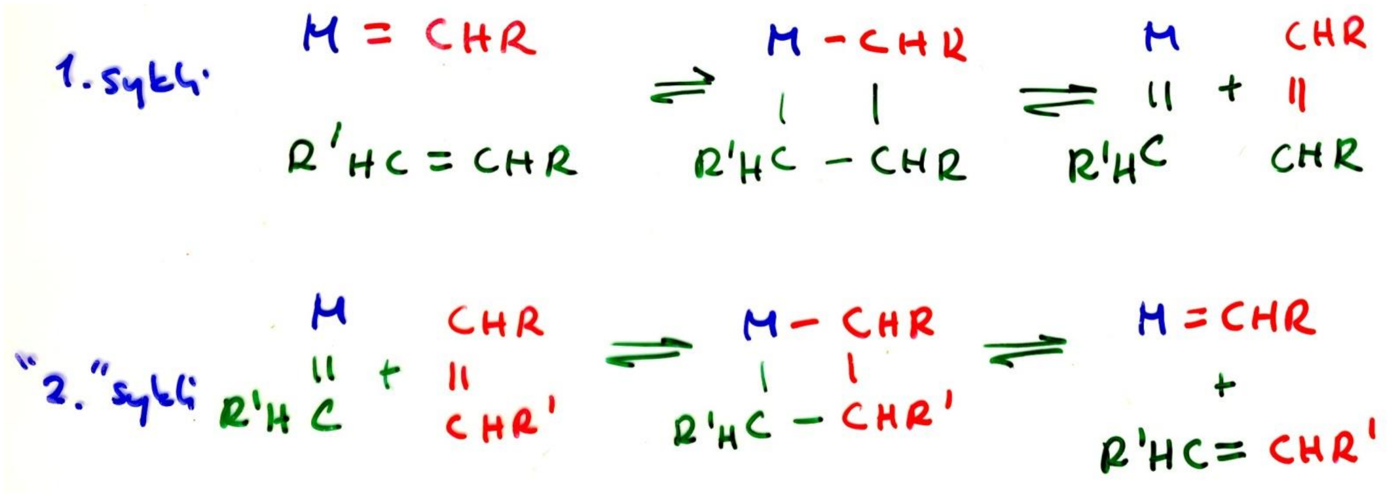
OLIGOMERIZATION CATALYSTS

Metathesis of 2-pentene and 2-heksene produces several alkenes, which ones?

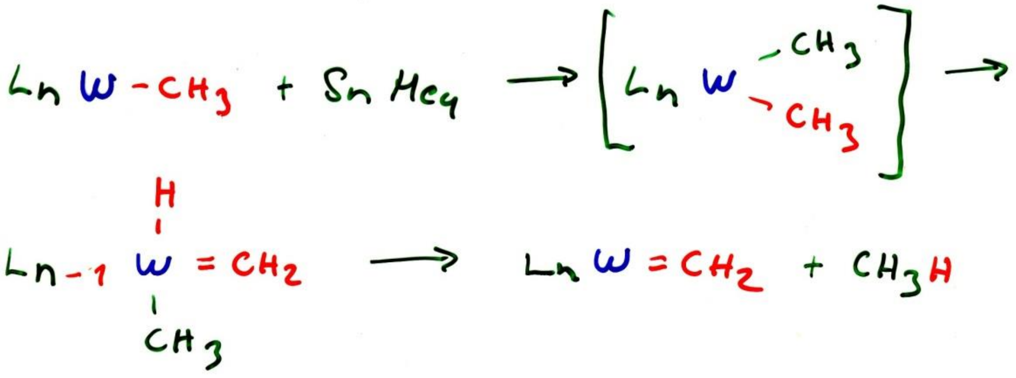
$C-C=C-C-C \quad + \quad C-C=C-C-C-C$

$C-C=C-C$	2-buteeni
$C-C=C-C-C$	2-penteeni
$C-C=C-C-C-C$	2-hekseeni
$C-C-C=C-C-C$	3-hekseeni
$C-C-C=C-C-C-C$	3-hepteeni
$C-C-C-C=C-C-C-C$	4-okteeni

OLIGOMERIZATION CATALYSTS

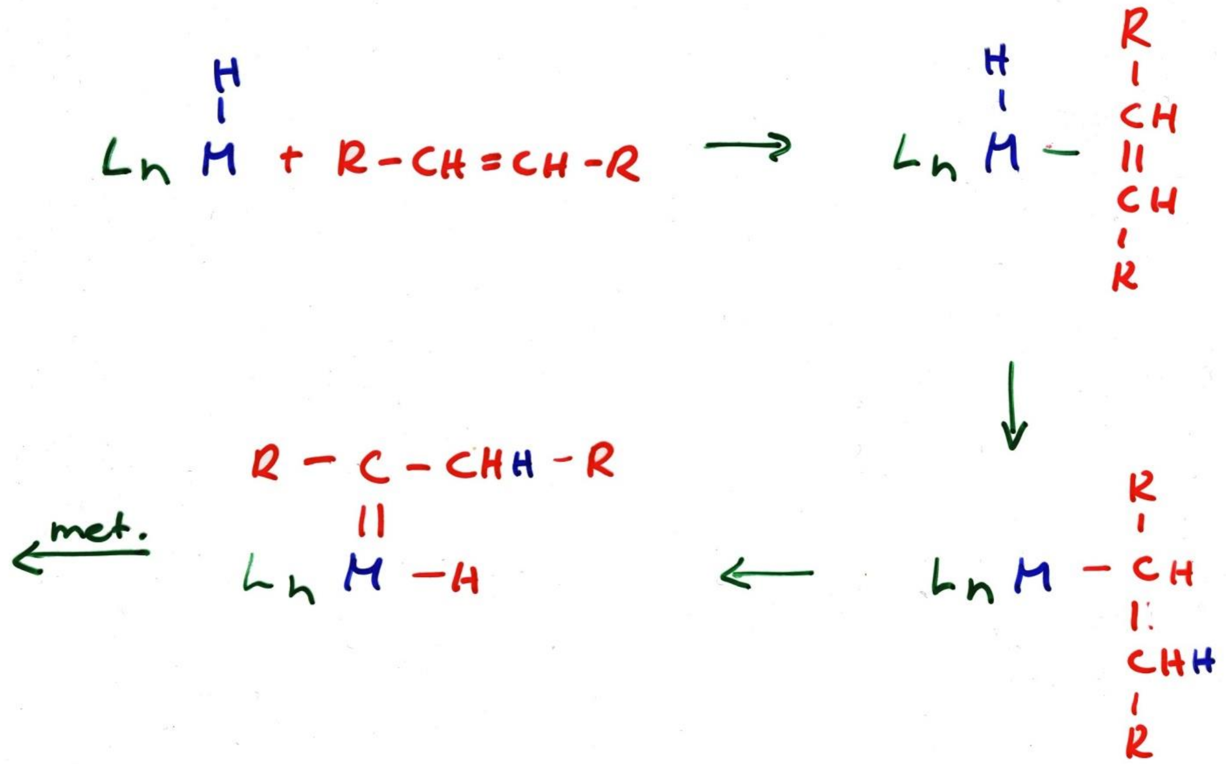


Generating carbene complexes in situ via alkylation (transmetallation)



OLIGOMERIZATION CATALYSTS

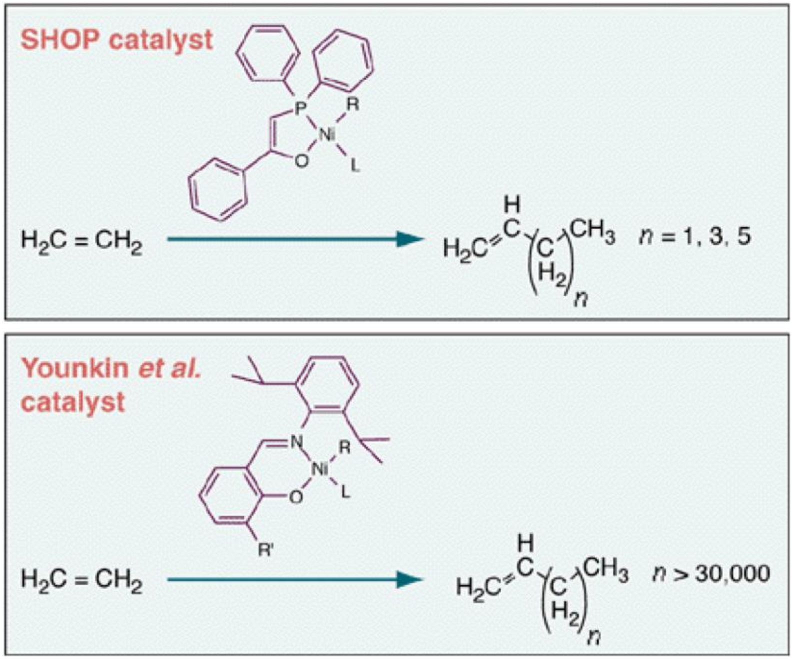
How the carbenes are formed on a heterogeneous catalyst when no alkylation agent is available?



This is a proposed reaction mechanism.

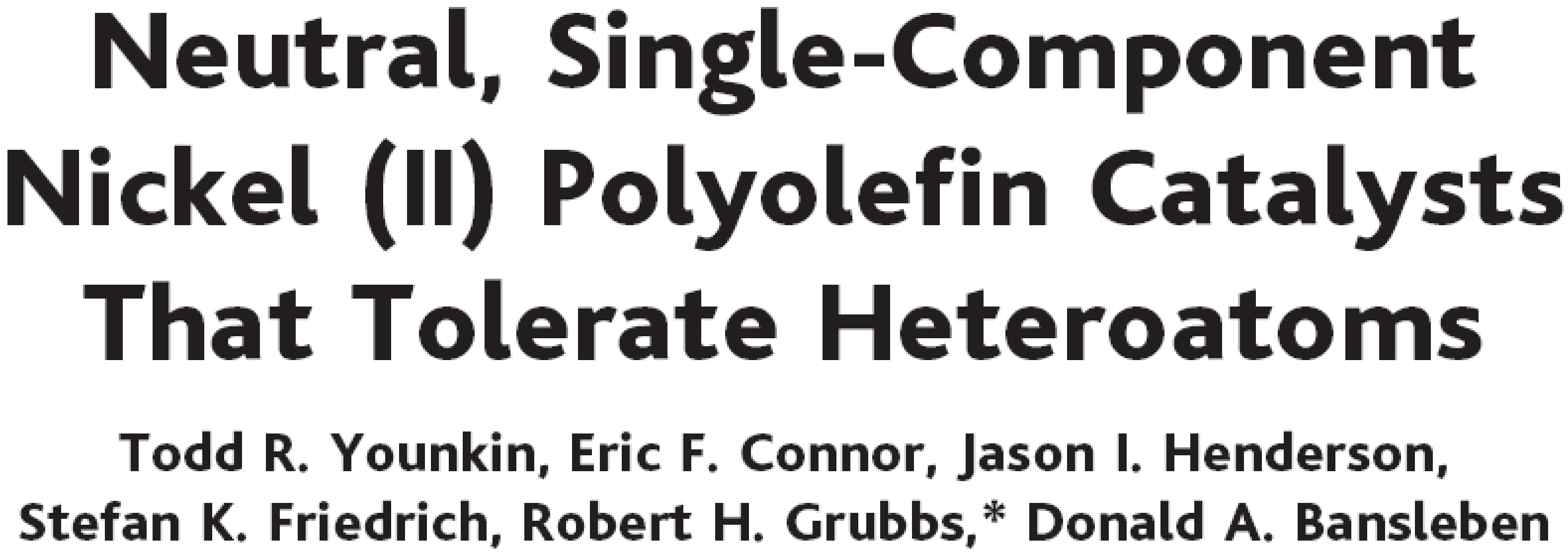
FROM OLIGOMERIZATION TO POLYMERIZATION CATALYSTS

Highly Lewis acidic, cationic metal centers are easily poisoned by Lewis bases like CO_2, O_2, and S, O or N containing molecules. Is there a chance to polymerize polar monomers and/or to avoid such a high sensitivity towards Lewis bases?



Because of the less oxophilic nature of nickel, catalysts used in SHOP are tolerant towards alcohols, or esters.

See Science 2000, 287, p.437



Neutral, Single-Component Nickel (II) Polyolefin Catalysts That Tolerate Heteroatoms

Todd R. Younkin, Eric F. Connor, Jason I. Henderson,
Stefan K. Friedrich, Robert H. Grubbs,* Donald A. Bansleben

More than half of the 170 million metric tons of polymers produced each year are polyolefins. Current technology uses highly active cationic catalysts, which suffer from an inability to tolerate heteroatoms such as oxygen, nitrogen, and sulfur.

These systems require scrupulously clean starting materials and activating cocatalysts. A family of catalysts has been developed whose members are tolerant of both heteroatoms and less pure starting materials. These heteroatom-tolerant neutral late transition metal complexes are in fact highly active systems that produce high-molecular-weight polyethylene, polymerize functionalized oleÞns, and require no cocatalyst.

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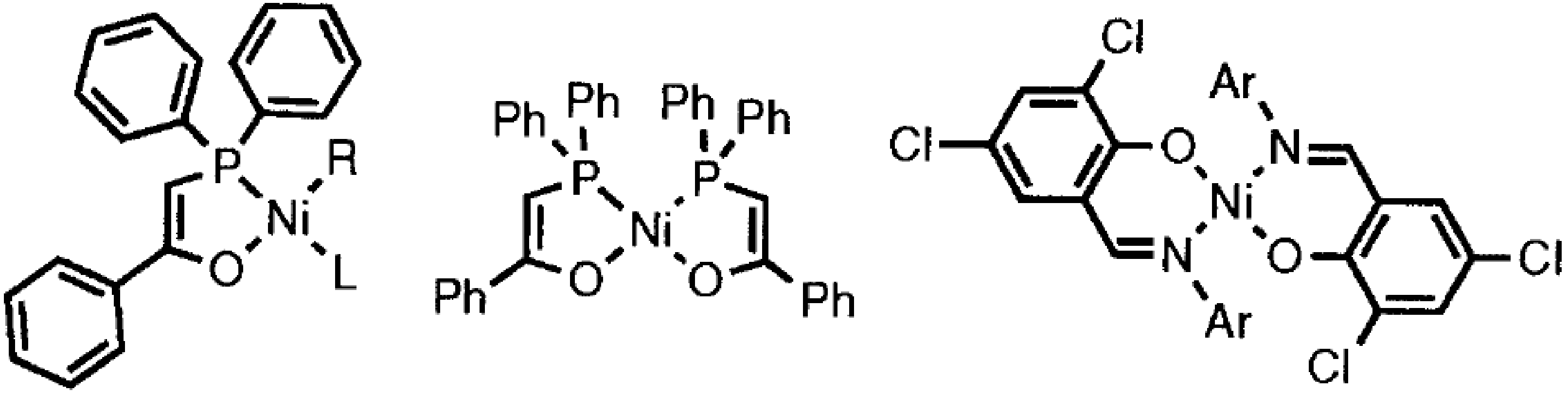
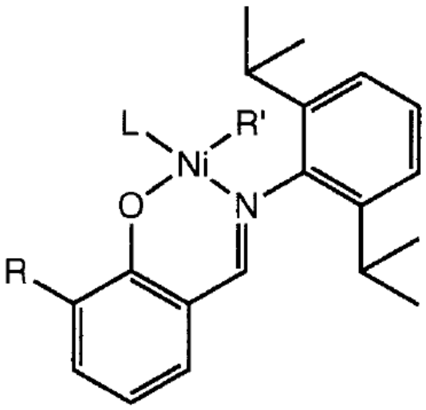
FROM OLIGOMERIZATION TO POLYMERIZATION CATALYSTS



3 **4** **5**

Fig. 2. 3, Classical SHOP complex. **4**, deactivated SHOP complex or bis ligand complex. **5**, bis ligand analog of salicylaldimine systems, which is inactive for ethylene polymerization under standard conditions.

FROM OLIGOMERIZATION TO POLYMERIZATION CATALYSTS



6 - 13

	R	R'	L
6	H	Ph	Ph_3P
7	^tBu	Ph	Ph_3P
8	Ph	Ph	Ph_3P
9	Phen	Ph	Ph_3P
10	Anth	Ph	Ph_3P
11	Anth	CH_3	CH_3CN
12	Trityl	CH_3	CH_3CN
13	TPhen	CH_3	CH_3CN

Fig. 3. Ni(II) salicylaldimine complexes. Compounds **6** and **7** require cocatalyst activation. Compounds **8** through **13** are neutral, single-component polymerization catalysts. Abbreviations: ^{t}Bu, tert-butyl; Ph, phenyl; Phen, 9-phenanthroline; Anth, 9-anthracene; Trityl, triphenylmethyl; TPhen, *meta*-terphenyl.

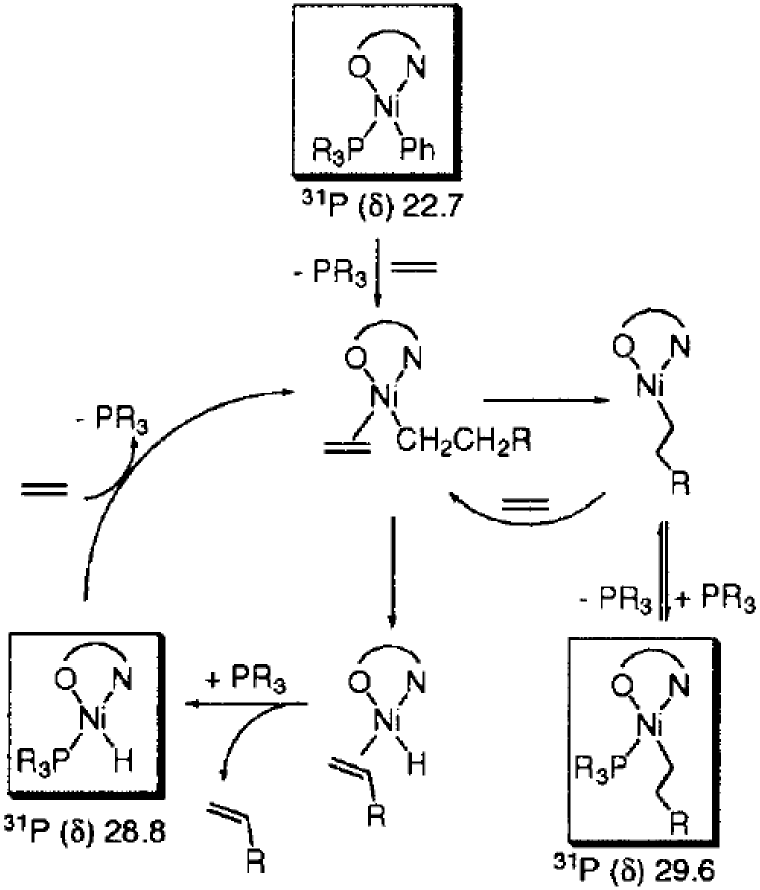
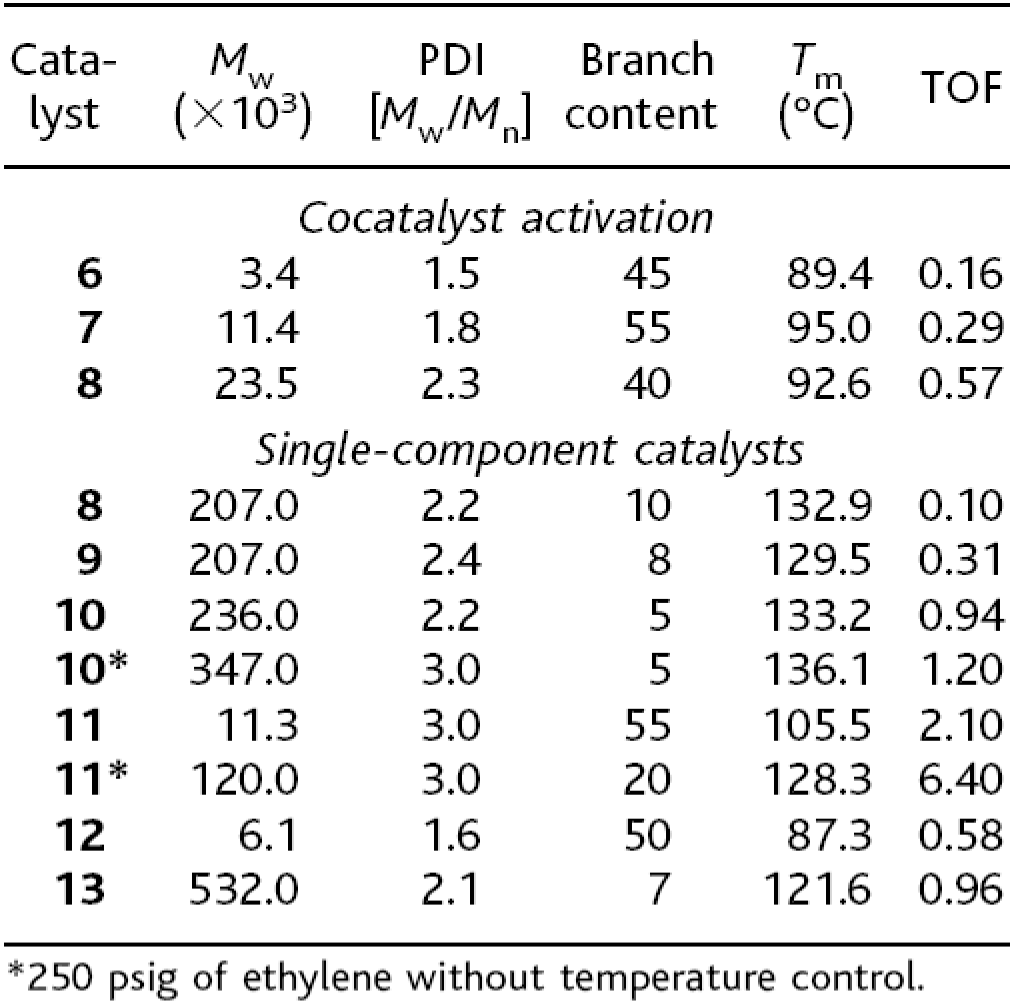


Fig. 4. Possible catalytic cycle based on ^{31}P NMR spectroscopic studies. Boxed structures are tentatively assigned on the basis of observed species.

FROM OLIGOMERIZATION TO POLYMERIZATION CATALYSTS



Catalyst	M_w ($\times 10^3$)	PDI [M_w/M_n]	Branch content	T_m (°C)	TOF
		Cocatalyst activation			
6	3.4	1.5	45	89.4	0.16
7	11.4	1.8	55	95.0	0.29
8	23.5	2.3	40	92.6	0.57
		Single-component catalysts			
8	207.0	2.2	10	132.9	0.10
9	207.0	2.4	8	129.5	0.31
10	236.0	2.2	5	133.2	0.94
10*	347.0	3.0	5	136.1	1.20
11	11.3	3.0	55	105.5	2.10
11*	120.0	3.0	20	128.3	6.40
12	6.1	1.6	50	87.3	0.58
13	532.0	2.1	7	121.6	0.96

*250 psig of ethylene without temperature control.

(250 psig = 17 bars)

FROM OLIGOMERIZATION TO POLYMERIZATION CATALYSTS

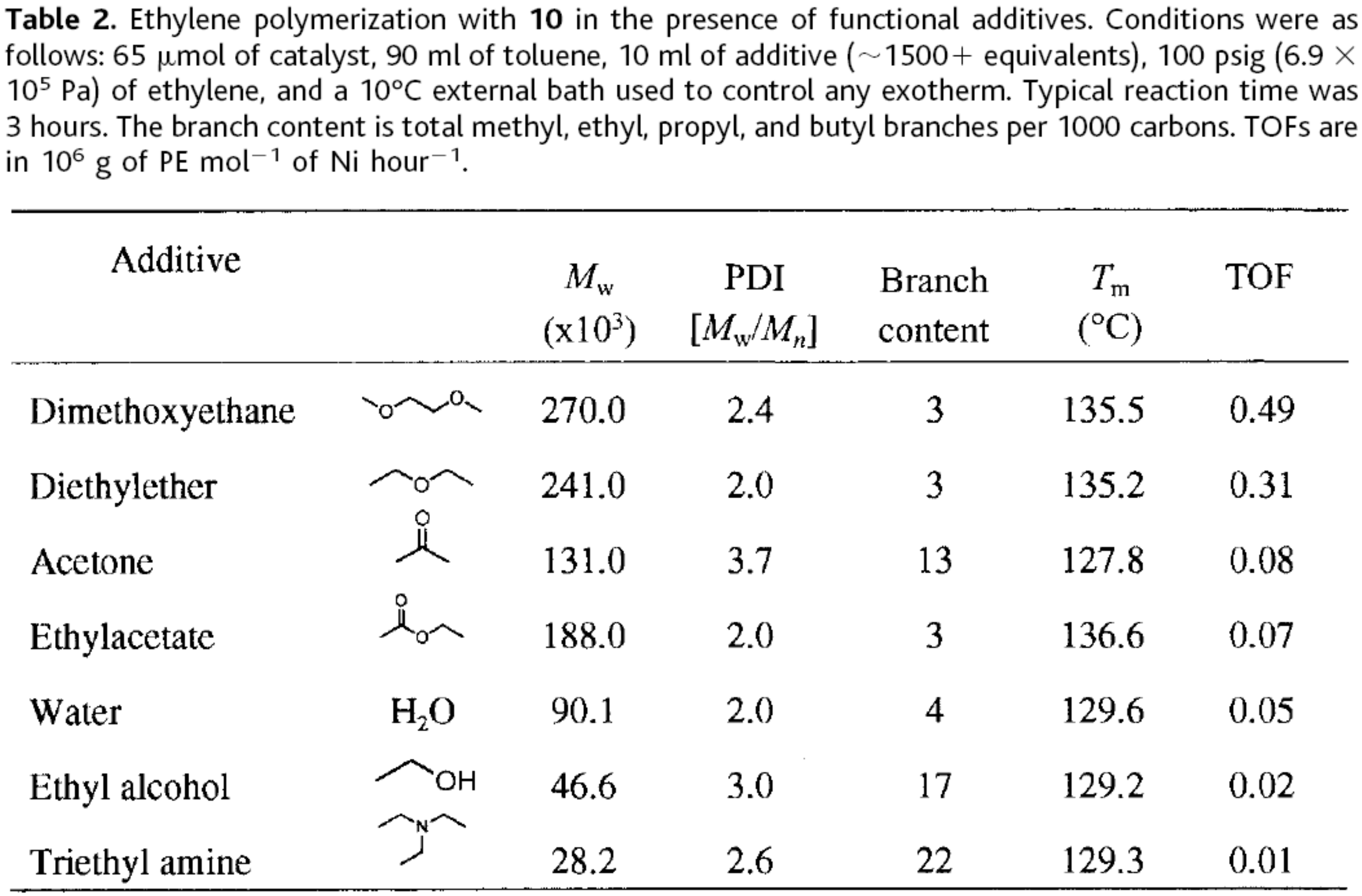


Table 2. Ethylene polymerization with **10** in the presence of functional additives. Conditions were as follows: 65 μmol of catalyst, 90 ml of toluene, 10 ml of additive (~1500+ equivalents), 100 psig (6.9×10^5 Pa) of ethylene, and a 10°C external bath used to control any exotherm. Typical reaction time was 3 hours. The branch content is total methyl, ethyl, propyl, and butyl branches per 1000 carbons. TOFs are in 10^6 g of PE mol^{-1} of Ni $hour^{-1}$.

Additive		M_w ($x10^3$)	PDI [M_w/M_n]	Branch content	T_m (°C)	TOF
Dimethoxyethane		270.0	2.4	3	135.5	0.49
Diethylether		241.0	2.0	3	135.2	0.31
Acetone		131.0	3.7	13	127.8	0.08
Ethylacetate		188.0	2.0	3	136.6	0.07
Water	H_2O	90.1	2.0	4	129.6	0.05
Ethyl alcohol	OH	46.6	3.0	17	129.2	0.02
Triethyl amine	N	28.2	2.6	22	129.3	0.01