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Polymerization catalysis

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Abstract

Organometallic catalysts play an important role in the polymerization of olefins, dienes and styrene. A great part of the chemical industry is using these catalysts to produce increasing amounts of plastic materials. Catalysts such as metallocenes, half-sandwich, nickel and iron complexes, are able to tailor the microstructure of the polymer chain. New properties are obtained. Metallocenes in combination with methylalumoxane or perfluorinated borates as cocatalyst form extremely active catalysts for the polymerization of olefins and are now used in industrial processes. Meanwhile a great number of symmetric and chiral zirconocenes have been synthesized that give totally different structures of isotactic, syndiotactic, stereoblock, or isoblock polymers. The isotactic sequence length of polypropylene is influenced by the nature of the ligands of the metallocenes. It has become possible to polymerize cyclic olefins, like cyclopentene or norbornene, with different zirconocenes or nickel and palladium catalysts without any ring opening reaction. The crystalline polycycloalkenes show extremely high melting points which are between 400 and 600°C. Copolymers of cycloalkenes with ethene are amorphous and transparent with a glass transition temperature between 120 and 160°C and they can be used as materials for optical discs and fibers. Half-sandwich titanocenes are able to catalyze the formation of syndiotactic polystyrene. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polymerization; Organometallic catalysts; Metallocenes; Single site catalysts; Polyolefins

1. Introduction

Classical polymers such as polyethylene, polypropylene, and polystyrene are again of great interest for science and industry. These polymers are not only the most extensively used plastics but they show an above-average growth rate as materials. This increase is caused largely by new catalysts which are able to tailor the polymer structure and, by this, the physical properties. Some recent reviews give detailed information on olefin catalysis, now one of the largest fields in chemistry [1–4,64].

In 1995, 53.6×10^6 t of polyolefins were produced worldwide. This amount makes up 47% of the entire production of plastics (Table 1).

Furthermore, in the past the extent of production of individual types such as LLDPE (linear low density polyethylene) or PP doubled in a period of about 5–7 years; this is an outstanding growth rate when compared to that of other materials. Estimates show that this development will continue. In the year 2005, the proportion of polyolefins will climb to 55%, taking into account a simultaneous increase in the entire production of plastics. In turn, this means that polyolefins will displace some of the commercial plastics of today that are less easy to manufacture or pose more problems for recycling or waste disposal. Polyolefins are composed solely of carbon and hydrogen. Being thermoplastics, they can be easily processed; used

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Table 1
Worldwide production of polyolefins (source: Parpinelli Tecnon) ($\times 10^6$ t)[a]

	Polyethylene, LDPE	Polyethylene, HDPE/LLDPE	Polypropylene (PP)	Fraction of plastics production (%)
1983	11.3	7.9	6.4	–
1990	14.0	16.1	12.6	43
1995	14.4	22.1	17.1	47
2005	15.8	36.1	27.7	55

[a] LDPE: low density polyethylene; HDPE: high density polyethylene; LLDPE: linear low density polyethylene.

polyolefin materials can be recycled or combusted with a gain in energy, the only products being merely carbon dioxide and water. The basic units ethene and propene are easily obtained from the cracking of mineral oil. Apart from LDPE discovered by ICI, which has a highly branched structure and is produced radically at ethene pressures of 1000–3000 bar, polyolefins are synthesized at far lower pressures using catalysts.

The discovery of the catalyst based on titanium tetrachloride and diethylaluminum chloride as cocatalyst was made by Karl Ziegler, who succeeded in polymerizing ethene into HDPE (high density polyethylene) at standard pressure and room temperature in 1953 at the Max-Planck-Institute in Mülheim [5]. A little later, Giulio Natta, at the Polytechnical Institute of Milan, was able to demonstrate that an appropriate catalyst system was capable of polymerizing propene into semi-crystalline polypropylene [6]. Ziegler and Natta shared a Nobel Prize for Chemistry in 1963 for their work. The modern Ziegler–Natta catalysts are mixtures of solid and liquid compounds, often containing $MgCl_2/TiCl_4/Al(C_2H_5)_3$ and, for propene polymerization, different internal and external donors such as ethylbenzoate, silanes or ethers to increase the tacticity.

Important for ethylene polymerization is the Phillips catalyst prepared by chromium trioxide on silica and reduced by hydrogen. This catalyst is very stable and useful in gas-phase polymerization but unable to polymerize propene to isotactic polymers.

Natta perceived that propene and long-chain olefins can be assembled in a stereoregular manner, the building blocks of the resulting chain having a defined and recurring arrangement. This alignment has a considerable influence on the functional properties of the material. A statistical arrangement leads to amorphous polypropylene which flows at room temperature, whereas stereoregular polypropylene is crystalline having a melting point of 165°C.

As Ziegler–Natta catalysts are heterogeneous and complex systems with different active sites, the polymer structure can be influenced only to a limited degree.

2. Metallocene catalysts

In comparison, metallocene catalysts are soluble in hydrocarbons, show only one type of active site and their chemical structures can be easily changed. These properties allow one to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molecular weight and distribution, comonomer content and tacticity by careful selection of the appropriate reactor conditions. In addition, their catalytic activity is 10–100 times higher than that of the classical Ziegler–Natta systems.

Metallocenes, in combination with the conventional aluminum alkyl cocatalysts used in Ziegler systems, are indeed capable of polymerizing ethene, but only at a very low activity. Only with the discovery and application of methylalumoxane (MAO) in our institute in Hamburg in 1977 was it possible to enhance the activity, surprisingly, by a factor of 10 000 [7,8]. Therefore, MAO plays a crucial part in the catalysis with metallocenes. Methylaluminoxane is a compound in which aluminum and oxygen atoms are arranged alternately and free valences are saturated by methyl substituents. It is gained by careful partial hydrolysis of trimethylaluminum and, according to investigations by Sinn [9] and Barron and coworkers [10], it consists mainly of units of the basic structure $[Al_4O_3Me_6]$ which contain four aluminum, three oxygen atoms and six methyl groups. As the aluminum

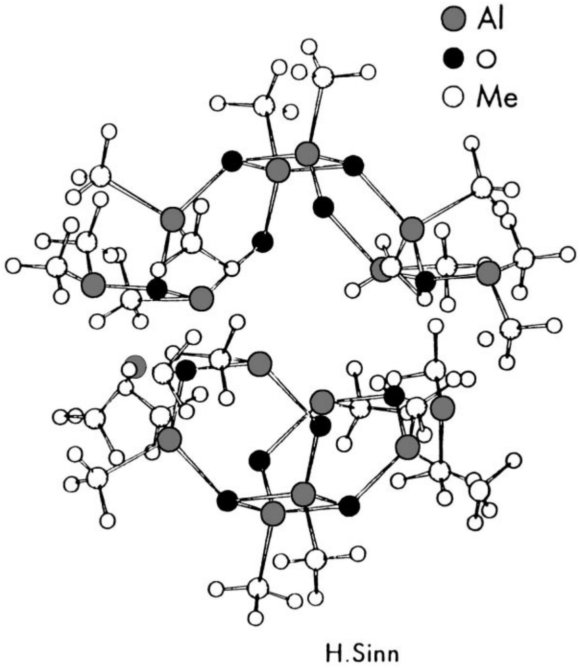


Fig. 1. The structure of methylaluminoxane clusters suggested by Sinn [9].

atoms in this structure are coordinatively unsaturated, the basic units (mostly four) join together, forming clusters and cages (Fig. 1). These have molecular weights ranging from 1200 to 1600 and are soluble in hydrocarbons.

If metallocenes, especially zirconocenes (Fig. 2), are treated with MAO, then catalysts are acquired that allow the polymerization of up to 100 t of ethene per gram of zirconium. At such high activities, the catalyst can remain in the product. The insertion time (for the insertion of one molecule of ethene into the growing chain) amounts to some 10^{-5} s only. In some respects, a comparison with bio-catalysts is appropriate.

It is generally assumed that the function of MAO is firstly to undergo a fast ligand exchange reaction with the metallocene dichloride, thus rendering the metallocene methyl and dimethyl compounds (Fig. 3). In the further step, either Cl^- or $CH_3{}^-$ is abstracted from the metallocene compound by an Al-center in MAO, thus forming a metallocene cation and a MAO anion [11–13]. The alkylated metallocene cation represents the active center. Meanwhile, other weakly coordinating cocatalysts, such as tetra(perfluorophenyl)borate anions $[(C_6F_5)_4B]^-$, have been successfully applied to the activation of metallocenes [14–17].

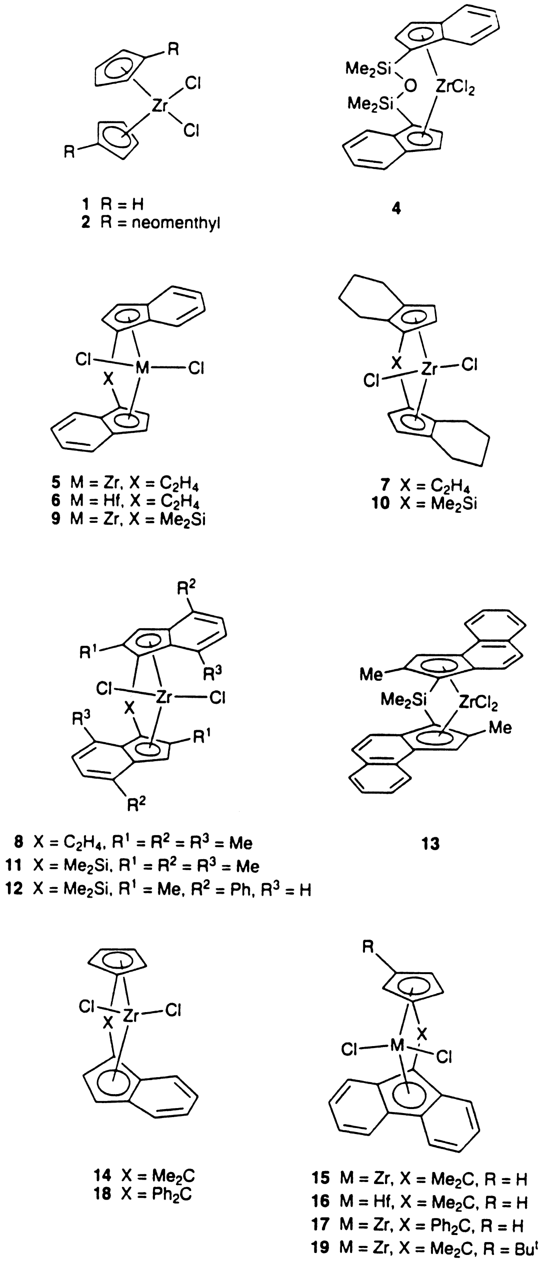


Fig. 2. Structures of metallocenes that are used in the polymerization of olefins.

A further milestone was reached when Brintzinger and coworkers [18] synthesized chiral bridged metallocenes in 1982 at the University of Konstanz and

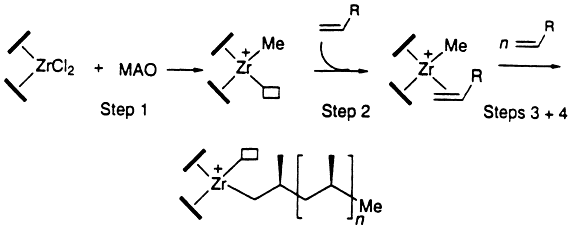


Fig. 3. Mechanism of the polymerization of olefins by zirconocenes. Step 1: The cocatalyst (MAO: methylalumoxane) converts the catalyst after complexation into the active species that has a free coordination position for the monomer and stabilizes the latter. Step 2: The monomer (alkene) is allocated to the complex. Step 3: Insertion of the alkene into the zirconium alkyl bond and provision of a new free coordination position. Step 4: Repetition of Step 3, in a very short period of time (about 2000 propene molecules per catalyst molecule per second), thus rendering a polymer chain.

in 1984, when Ewen [19], at the Exxon (USA), was able to demonstrate that appropriate titanocenes render partially isotactic polypropylene. A little later, highly isotactic material was obtained with analogous zirconocenes in our institute [20]. After this discovery, a fervent development of industrial and scientific research in the metallocene sector commenced and, until today, it has not been concluded.

Polyolefins, with different microstructures and characteristics, can be custom-made just by varying the ligands on the metallocene (Fig. 2) [21–27]. By combining different olefins and cycloolefins with one another, the range of characteristics can be further broadened. The production of polyolefins with narrow molecular weight distributions ($M_W/M_n = 2$), of syndiotactic polymers and of chemically uniform copolymers has not yet been achieved by conventional heterogeneous catalysts.

Using metallocene catalysts, it was possible for the first time to produce polyethylenes, polypropylenes and copolymers with narrow molecular weight distributions [28], syndiotactic polypropylene (in technical scale amounts) [29], syndiotactic polystyrene [30], cyclopolymerisates of 1,5-hexadiene [31], cycloolefin copolymers (COCs) with high catalytic activity [32], optically active oligomers [33,65] and composite materials of biomass, powdered metals with polyolefins [34]. Organic or inorganic particles (starch, cellulose, quartz sand or powdered metal) can be coated with a hydrocarbon-soluble metallocene catalyst and in turn, after polymerization, with a polyolefin film of variable thickness [35].

The polymerizations can be controlled precisely by metallocene catalysts. The polymerization activity differs over a wide range [36,37]. Apart from isotactic and atactic polypropylene, the syndiotactic as well as the isoblock and stereoblock materials can be achieved for the first time in large quantities and in high purity (Fig. 4).

Syndiotactic polypropene can be synthesized by complexes containing fluorenyl and cyclopentadienyl ligands bridged by X (compounds 15–17, Fig. 2). The block lengths of equal tacticity in isoblock PP (in which the position of the methyl groups in one direction) can be varied over a broad range on a nanoscale (4–100 units). This leads to microcrystalline PP which is suitable for making transparent foils. The development of applications for elastic stereoblock PP has just begun [38].

By inserting a silyl bridge and substituting the indenyl ligands (compounds 9–13), these catalysts afford isotactic PP of high molecular weight with a melting point of 161°C [39].

Metallocene catalysts are particularly important for the polymerization of cycloolefins (cyclopentene, norbornene and their substituted compounds) (Fig. 5). In this process, only the double bond is opened and not the ring. Crystalline polycycloolefins are produced, that have extremely high melting points of at least 380°C, sometimes even higher than the decomposition temperature [40].

While homopolymerization of cyclopentene results in 1,3-enchainment of the monomer units, norbornene is inserted in 1,2-enchainment as usual for olefin polymerization. The problems of processing that arise from the high melting temperatures of the homopolymers can be solved by copolymerizing cycloolefins with ethene [41–43].

The insertion of norbornene units into the growing polymer chain is very easy. As seen by the copolymerization parameter r_1, which is between 2.0 and 3.4 and shows how much faster ethene is inserted than norbornene when the previous insertion was ethene, it is easy to incorporate this huge monomer (Table 2).

The r_1 parameter increases with the temperature, as does, in some other cases, the rate for the copolymerization with norbornene. A ratio of norbornene/ethylene = 0.6 gives the highest activity of 3780 kg

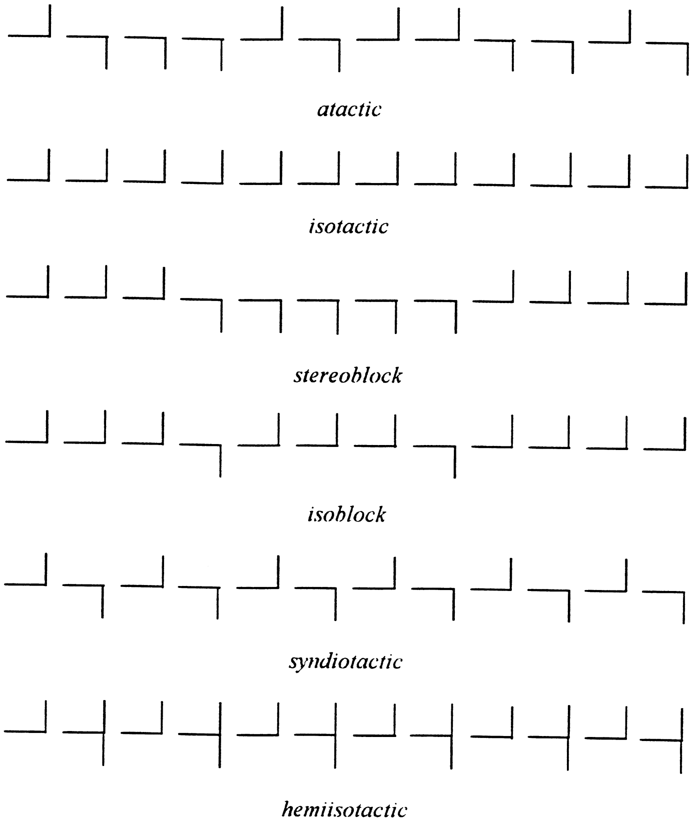


Fig. 4. Microstructures of polypropylene.

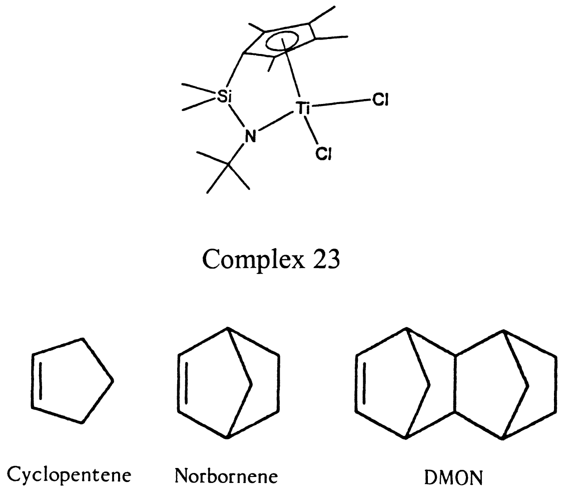


Fig. 5. Cycloolefins used for the polymerization by metallocenes.

polymer, which is about 5–6 times higher than that of the homopolymerization of ethylene by catalyst 17 in Fig. 2.

The metallocene 19 shows not only high activities for the copolymerization of ethene with norbornene but also gives an alternating structure [44]. Most metallocenes produce polymers with a statistical structure.

It is impossible to achieve copolymers with more than 50 mol% of norbornene. The melting point of the alternating copolymer depends on the molar ratio of norbornene units in the polymer while the glass transition temperature is nearly independent of this. A maximum melting point of 320°C was reached.

Such materials characteristically have an excellent transparency and a very high continuous service temperature. Having cycloolefin insertion rates of 10 mol% upwards, these COCs are no longer crystalline but amorphous.

Table 2
Copolymerization parameters r_1 and r_2 of ethylene/cycloolefin copolymerizations with different metallocene/MAO catalysts

Cycloolefin	Catalyst	Temperature (°C)	r_1	r_2	r_1r_2
Cyclopentene	$[En(IndH_4)_2]ZrCl_2$	0	1.9	<1	~1
Cyclopentene	$[En(IndH_4)_2]ZrCl_2$	25	2.2	<1	~1
Norbornene	$[Me_2Si(Ind)_2]ZrCl_2$	30	2.6	<2	~1
Norbornene	$[Me_2C(Fluo)(Cp)]ZrCl_2$	30	3.4	0.06	0.2
Norbornene	$[Ph_2C(Fluo)(Cp)]ZrCl_2$	0	2.0	0.05	0.1
Norbornene	$[Ph_2C(Fluo)(Cp)]ZrCl_2$	30	3.0	0.05	0.15
Norbornene	$[Me_2C(Fluo)(t\text{-}BuCp)]ZrCl_2$	30	3.1	0	0
DMON	$[Ph_2C(Fluo)(Cp)]ZrCl_2$	50	7.0	0.02	0.14
DMON	$[Ph_2C(Ind)(Cp)]ZrCl_2$	50	6.4	0.10	0.64
DMON	$[Ph_2C(Fluo)(Cp)]HfCl_2$	50	7.1	0.04	0.28

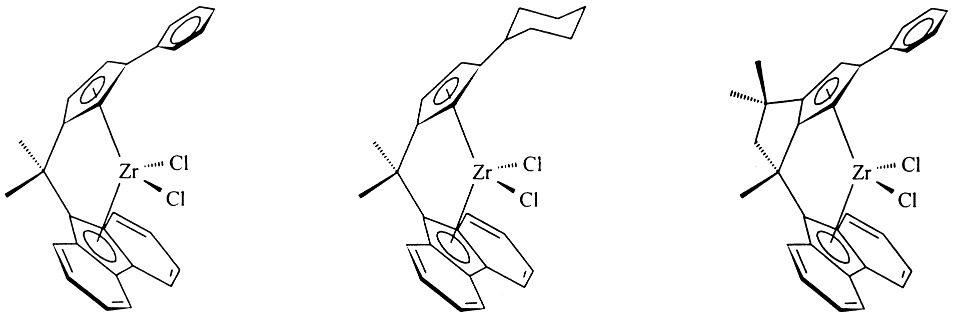
3. New C_1-symmetric metallocenes

C_1-symmetric zirconocenes with an isopropylidene bridge and substituted cyclopentadienyl and fluorenyl ligands are of large interest as catalysts for the polymerization of propene, leading to syndiotactic and hemiisotactic polymers [45]. They are stable and can be synthesized without achiral side products. For industrial use, some disadvantages have to be solved. The polymers often have low molecular mass and the catalysts are not very stable at higher temperatures and deactivate rapidly. In many cases, these catalysts are not active enough and give only low stereoselectivities.

Therefore there is an interest to increase the activity and to make the metallocenes more stable at higher temperatures. It is known from the bisindenylzirconocenes that substitution by phenyl groups increases the activity [46]. A stronger bridge should increase the thermal stability.

Three C_1-symmetric metallocenes have been synthesized and compared with phenyl or cyclohexyl substitution at the cyclopentadienyl ligand (Fig. 6) [47]. For comparison of activity and stereoselectivity, the polymerization with these catalysts has to be carried out under the same conditions. The experiments were carried out in a 1-l autoclave at 30°C using MAO as cocatalyst.

Table 3 summarizes the activities of the three zirconocenes with dependence on the temperature. The phenyl substituted zirconocene I gives the highest activities at low temperatures. This activity is up to 9 times higher than that of the unsubstituted compound. Whereas metallocenes 20 and 21 show a fast thermal



20 $[Me_2C(PhCp)(Flu)]ZrCl_2$

21 $[Me_2C(cHCp)(Flu)]ZrCl_2$

22 $[PhMe_3PenFlu)]ZrCl_2$

Fig. 6. C_1-symmetric zirconocenes for the polymerization of ethene and propene.

Table 3
Polymerization activity as a function of temperature

T (°C)	$[Me_2C(PhCp)(Fl)]ZrCl_2$ (20) (kg PP/(mol Zr h))	$[Me_2C(CHCp)(Flu)]ZrCl_2$ (21) (kg PP/(mol Zr h))	$[PhMe_3PenFlu]ZrCl_2$ (22) (kg PP/(mol Zr h))
15	6630	1880	100
30	8400	3600	890
30	11400	4060	1200
45	4950	4460	1700
60	1300	1100	7600

deactivation at higher polymerization temperatures, an increase in activity was found for complex 22 by raising the temperature; this may be an effect of the very rigid structure of this compound. The cyclohexyl substitution gives a lower activity than the phenyl substitution at all temperatures.

There is a great difference in the dependence of the activities on the propene concentration. Fig. 7 compares the polymerization activities of the metallocenes as a function of the monomer concentration. For all metallocenes, an increase of the activity is observed at higher monomer concentrations. Catalyst 20 shows the strongest increase, compound 22 the lowest. The reaction order for propene in all cases is 1.4–1.5. While the polymerization activity is very important for the technical process, the molecular mass and the microstructures are relevant for the properties of the polymer.

Catalyst 22 gives a polymer with a very high molecular mass of up to 480 000. This is 16 times higher than that of the isotactically working system, rac-$[En(Ind)_2]ZrCl_2$ [36]. Compared to the other complexes, a factor of 3 is given. There could be a dependence of the high molecular mass of the polypropylene produced and the unusual geometry of the pentalene structure of zirconocene 22. The

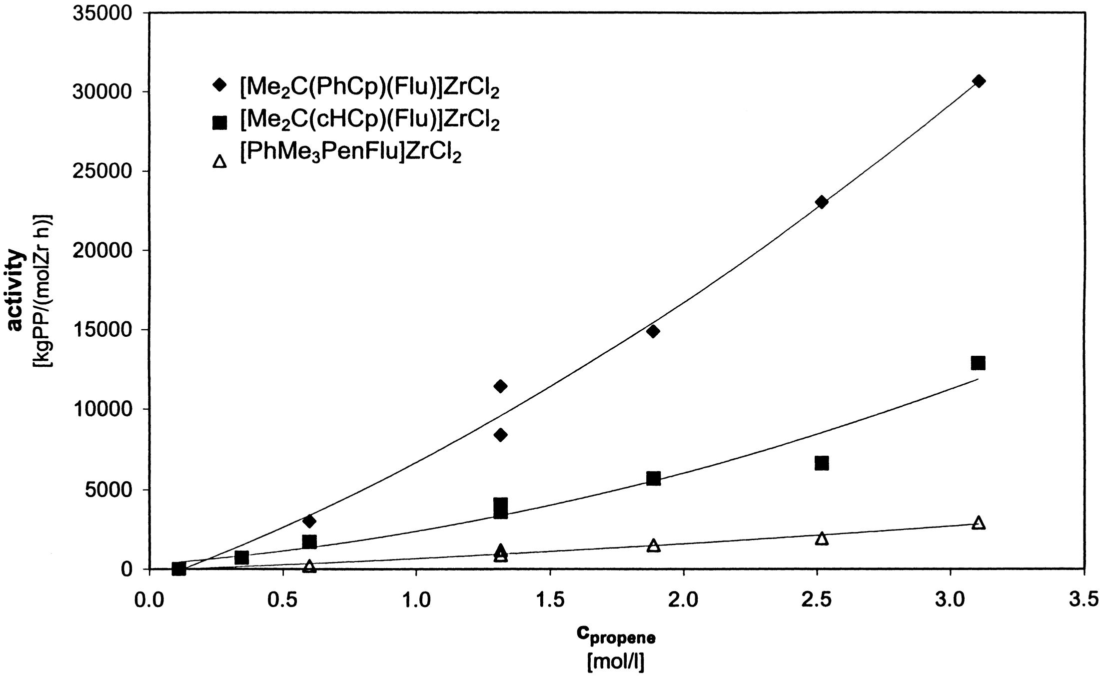


Fig. 7. Activity as a function of the monomer concentration.

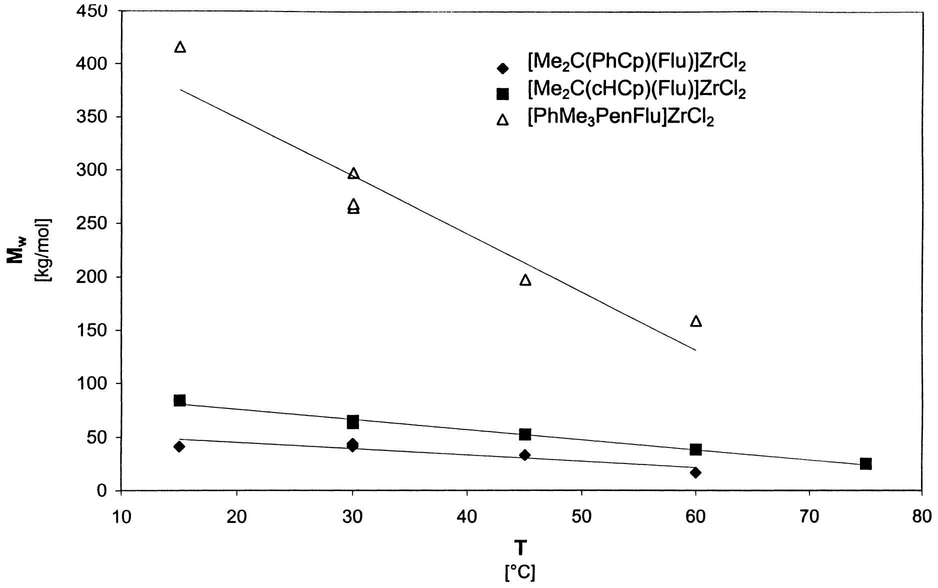


Fig. 8. Molecular weight as a function of the polymerization temperature.

stereorigid structure poses the polymer chain in such a position that β-agostic interaction with the metal center is hindered. This decreases chain termination and leads to a higher molecular mass.

The molecular masses show a strong dependence on the polymerization temperature (Fig. 8). Between 15 and 60°C, the molecular mass decreases by a factor of 3. On the other hand, the molecular mass can be decreased with the propene concentration. Especially, the more stereorigid complex 22 gives much higher molecular masses with increasing propene concentration while those of the other catalysts are more independent. Above a propene concentration of 3 mol/l, in all cases, the molecular mass becomes independent. While the propagation step is always bimolecular and depends strongly on the monomer concentration, the chain transfer reaction is monomolecular. At a limiting propene concentration, there is no increase in the molecular mass.

The microstructure of the polypropylene has a significant influence on the polymer properties. There are some mechanistic and theoretical models to interpret the microstructure of the polymer in dependence on the structure of the catalyst [48]. Catalysts 20 and 21 produce polypropylenes with high amounts of syndiotactic pentads (Table 4). Both metallocenes have two different half sides which are the background for the rrrr-pentads. On the other hand, the concentration of mrmr-pentads is low. A practically isotactic polymer is yielded by zirconocene 22. The mmmm-pentads reaches a value of 58% which means that the isotactic sequence length is about 10.

An explanation can be given if the polymer chain is located on the pentalenyl side while the coordination of the propene takes place at the phenyl substituted side of the metallocene. The phenyl group interacts

Table 4
Parts of ^{13}C NMR measured pentades (%) of polypropylenes synthesized with the catalysts I–III at 30°C

	Catalyst		
	I	II	III
mmmm	9.6	11.8	57.5
mmmr	8.8	9.7	11.4
rmmr	8.1	5.7	1.9
mmrr	22.7	21.2	15.7
mrmm + rmrr	2.3	3.8	0.4
mrmr	0	0	0.3
rrr	32.7	33.5	2.8
rrrm	11.8	11.5	3.4
mrrm	4.2	2.9	6.6

with the monomer and leads to a preferred orientation of the propene. By this, an isotactic polymer is formed. No regio-errors such as 2.1 or 3.1 insertion can be found.

There is almost no influence of the temperature or monomer concentration on the microstructure of the polypropylene prepared with catalyst 22. In contrast to this, the cyclohexyl-substituted catalyst 21 shows a strong dependence of the microstructure with increasing polymerization temperature.

At low polymerization temperatures, a polymer with more syndiotactic structures is formed, while at temperatures over 50°C, more isotactic structures are given. There are different steric arrangements of the hexyl group in dependence on the temperature so that there is a higher steric-hindrance of the cyclohexyl group that brings the incoming propene into an isotactic position.

4. Half-sandwich titanocenes

Half-sandwich titanocenes such as silyl bridged amido(cyclo-pentadienyltitaniumtrichloride) (compound 23), unsubstituted and substituted cyclopentadienyltitanium trichlorides or trifluorides play important roles in the copolymerization of ethene and 1-octene or in the styrene homo- and copolymerization [49–51].

High branching which is caused by the incorporation of long chain olefins into the growing polymer chain is obtained with titanium complex 23 [52]. This catalyst, used by Dow and Exxon in combination with MAO or perfluorophenylborates, incorporates oligomers with vinyl end-groups which are formed during polymerization by β-hydrogen transfer, resulting in long-chain branched polyolefins. In contrast, structurally linear polymers are obtained when catalyzed by other metallocenes. Long branched copolymers of ethene with oct-1-ene show elastic properties as long as the comonomer content is more than 20%. Other elastomers with different microstructures can be synthesized from dienes [53].

Ishihara et al. [30] were able to demonstrate that titanium compounds combined with MAO are capable of polymerizing styrene in a syndiotactical manner. Moreover, trichloro(cyclopentadienyl)titanium ($CpTiCl_3$) has been proved to be remarkably active [54]. Syndiotactic polystyrene is crystalline and shows a melting point of 275°C, which nearly makes it a high performance plastic.

Previously, it was already possible to produce isotactic polystyrene with classical Ziegler–Natta catalysts with very low polymerization activities. However, this polymer crystallized so slowly that technical usage was unthinkable. Furthermore, the polymerization activity of $CpTiCl_3$–MAO catalysts was also unsatisfactory for technical usage. If fluorinated complexes such as trifluoro(pentamethylcyclopentadienyl)titanium are employed, the activity can be improved by a factor of 30 (Table 5) [55]. At the same time the molecular weight rises from 169 000 to 660 000. The highest activity is reached by using methylcyclopentadienyltitanium trifluoride $(MeCp)TiF_3$ in combination with MAO (Table 5).

At a low Al:Ti ratio of 300, activities of up to 14 000 kg of syndiotactic polystyrene in 1 h can be achieved. These are values very close to the activities obtained with metallocene catalysts in the polymerization of olefins. Up to 50°C, the activity is very stable over time. An influence on the melting points of the obtained polystyrenes can also be observed. On average, the melting points of the polymers are 7°C higher than those of the polymers obtained with $CpTiF_3$. This shows that the substitution of methyl not only has an influence on the activity caused by electronic effects but also has an effect on the syndiotacticity and the molecular mass.

Therefore, the influence of other higher substituted cyclopentadienyltitanium trichlorides and trifluorides such as $(EtMe_4)TiCl_3$, $(PrMe_4Cp)TiCl_3$, $(BuMe_4Cp)TiCl_3$, $(EtMe_4Cp)TiF_3$, and $(BuMe_4Cp)TiF_3$ was investigated (Table 6). Table 6 compares the activities of

Table 5
Synthesis of syndiotactic polystyrene

Catalyst	Temperature (°C)	Activity[a]	M.m. (°C)	M_n	M_W/M_n
$CpTiCl_3$	50	1100	258	140000	1.9
$CpTiF_3$	50	3000	265	100000	2.0
Cp^*ZrCl_3	30	0.01	249	20000	2.2
Cp^*TiCl_3	50	15	275	169000	3.6
Cp^*TiF_3	50	690	275	660000	2.0
$MeCpTiF_3$	10	450	272	1420000	2.1
$MeCpTiF_3$	30	2750	271	520000	2.0
$MeCpTiF_3$	50	14000	269	140000	1.9

[a] Measured in kilogram PS per mole of metallocene per hour.

Table 6
Comparison of the activities (kg PS)/(mol Ti h) of chlorinated and fluorinated $(RMe_4Cp)TiX_3$ of the syndiospecific polymerization of styrene at 30°C[a]

Catalyst	X = Cl	X = F
$(Me_5Cp)TiX_3$/MAO	6.0	480
$(EtMe_4Cp)X_3$/MAO	3.1	160
(*n*-$PrMe_4Cp)X_3$/MAO	2.6	160
(*n*-$BuMe_4Cp)X_3$/MAO	2.8	180

[a] Ti concentration $= 6.25 \times 10^{-5}$ mol/l, Al : Ti = 500, styrene concentration = 4.3 mol/l.

pentamethyl-, ethyltetramethyl-, propyltetramethyl-, and butyltetramethylcyclopentadienyltitanium trichlorides and trifluorides at a polymerization temperature of 30°C.

It is apparent that the influence of the substitution from ethyl to butyl is not very strong. Only the pentamethylcyclopentadienyl compound has a significantly higher activity. In all cases, the fluorinated catalysts are about 40 times more active than the chlorinated ones.

The copolymerization of styrene with ethene, as examined by Mülhaupt et al. [56] expands the property domains and employment areas beyond that. Syndiotactic polystyrene has already been produced in technical amounts by Idemitsu and Dow.

5. Late-transition metal catalysts

Since the early 1990s, the field of olefin polymerization catalysis has witnessed a small revolution. Brookhart et al. [57,58] described square planar nickel and palladium–diimine systems (Fig. 9) which are capable of polymerizing ethylene to high molecular weight polymers with activities comparable to the metallocene catalyst systems when activated with methylaluminoxane.Important for the polymerization activity is the substituent R1 which has to be a bulky aryl group. The task of this substituent is to fill up the coordination spheres below and above the square plane of the complex and thus enable the growing polymer chain to stay coordinated to the metal center. This is one of the main differences to the well-known SHOP catalysts invented by Keim et al. [59] and Ostoja-Starzewski and Witte [60] which produces mainly ethene oligomers.

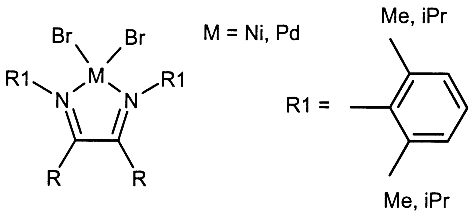


Fig. 9. Nickel/palladium–diimine catalysts.

A very interesting feature of this new catalyst generation is that chain isomerization processes can take place during the polymerization cycles. This results in more or less branched polymers with varying product properties depending on polymerization conditions and catalyst type. The number of isomerization cycles which are carried out directly one after another determines the nature of the branching formed. Branches ranging from methyl to hexyl and longer can be formed.

The extent of branching can be tailored precisely by tuning the polymerization conditions and products, from highly crystalline HDPE to completely amorphous polymers with glass transition temperatures of about −50°C. These products are different to all known conventionally produced copolymers due to their content and distribution pattern of short chain branching [61].

Another new catalyst generation based on iron and cobalt is the result of a consequent development of the “diimine idea”: the direct iron analogs of the nickel–diimine catalysts derived from Fig. 9 did not seem to be very active in olefin polymerization at all. The electronic and steric structure analysis shows why: the nickel d^8-system favors a square planar coordination sphere but the iron d^6-system favors a tetrahedral one. It is very likely that these tetrahedral coordination sites are not available for olefin insertion, and hence no polymerization can take place.

The next logical step was the employment of another electron donating atom in the ligand structure in order to obtain a trigonal-bipyramidal coordination sphere. Gibson and Brookhart both succeeded with a catalyst system based on an iron–bisiminopyridyl complex. Fig. 10 illustrates the three types of catalysts [62,63].

The ethene polymerization activity of these new family of catalysts is comparable with the one obtained

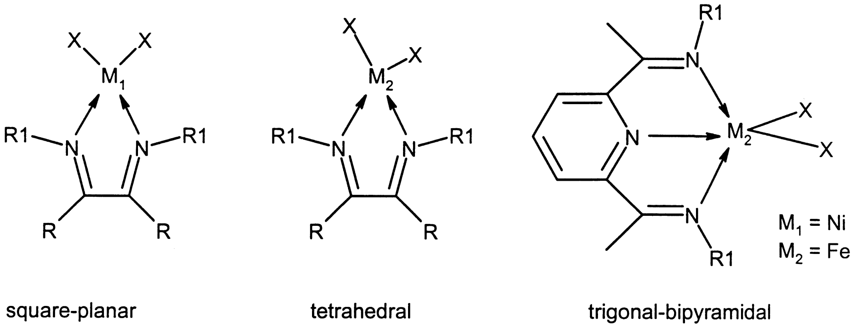


Fig. 10. Coordination spheres of different types of catalysts.

with the most productive metallocenes under similar conditions if activated with methylaluminoxane. Again, the nature of the aryl substituents R1 plays a major role in controlling the molecular weight of the polymers.

In contrast to the nickel–diimine catalysts no chain isomerization take place and thus only linear HDPE is formed.

These two new families of catalytic systems mark another milestone in olefin polymerization chemistry "beyond metallocenes". The understanding of electronic and steric structures will result in new ligand systems which correspond with other metal centers. Much research work can be carried out in this interesting field of polymerization catalysis.

6. Conclusions

Catalytic olefin polymerization has made a great steps forward over last few years. New metallocene or late-transition complexes have contributed enormous increase in catalytic activity accompanying the formation of new polymers with tailored microstructures. Even iron complexes have become active polymerization catalysts. There are a lot of other organometallic complexes with special properties possible for the catalysis of new homo- and copolymers. The copolymerization of olefins with polar monomers is just beginning and has great potential.

It could be estimated that a great number of polyolefin producers will use metallocene and other single-site catalysts in their processes over the next decade.

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