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PERSPECTIVE

Highly active metallocene catalysts for olefin polymerization

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The fascinating story of the discovery of the metallocene–methylaluminoxane catalysts for olefin polymerization is reviewed from its conception up until the first commercial production of polymers. A great number of different titanocenes and zirconocenes have been synthesized that give tailored polymers of totally different structures, and allows control of polymer tacticity, molecular weight and molecular weight distribution to be more efficient. New kinds of copolymers and elastomers can be synthesized.

1 Introduction

The discovery of metallocene catalysts for the polymerization of olefins has opened a frontier in the area of organometallic chemistry, polymer synthesis, and processing. What is the cause for this surge in interest? The classical polymers like polyethylene, polypropylene, and polystyrene are not only the most extensively used polymers, but the production of different polyolefin types also records above-average growth rates. New tailor-made polymers can be synthesized by metallocene catalysts. Some recent reviews give detailed information on metallocene catalysis.[1–4]

Professor Dr. Walter Kaminsky was born in 1941 in Hamburg. Since 1979 he has been a Full Professor of Technical and Macromolecular Chemistry, was Director of the Institute of Technical and Macromolecular Chemistry and Dean of the Department of Chemistry at the University of Hamburg. He has published more than 200 papers/books, and holds 20 patents. His research interests include metallocene catalysis for olefin polymerization and the pyrolysis of plastic wastes, scrap tyres, and oil shale/oil sand for recycling. He received several awards for his investigations and in 1997 was awarded an Honorary Fellowship from the Royal Society of Chemistry.

Table 1 Worldwide production of polyolefins* (source: Parpinelli Tecnon) (×10^6 tons)

	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

* LDPE = low density polyethylene, HDPE = high density polyethylene, LLDPE = linear low density polyethylene

In 1995, 53.6 × 10^6 tons 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 the production of individual types such as LLDPE (linear low density polyethylene) or PP doubled in a period of about 5 to 7 years; which 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 polyolefines 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 (hence the expression ‘sliceable mineral oil’). Being thermoplastics they can be easily processed; used 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 crack process 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 (1 bar = 10^5 Pa), polyolefins are synthesized at far lower pressures using catalysts.

The discovery of the catalyst based on titanium tetrachloride and diethylaluminium 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. 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. Both Zeigler and Natta were awarded the Nobel Prize for chemistry in 1963 for these discoveries.

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.

Currently, the Ziegler–Natta catalysts most often applied are

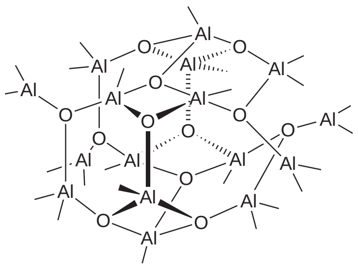


Fig. 1 Suggestion of a structure for methylaluminoxane clusters by Sinn[9]

heterogeneous. They are comprised of titanium tetrachloride supported on magnesium chloride with triethylaluminium as cocatalyst.[1] Lewis bases, such as ethylbenzoate or silanes, are added in the polymerization of propene in order to improve the stereocontrol of the polymerization. As these heterogeneous catalysts are complex systems with different active sites, the polymer structure can be influenced only to a limited degree.

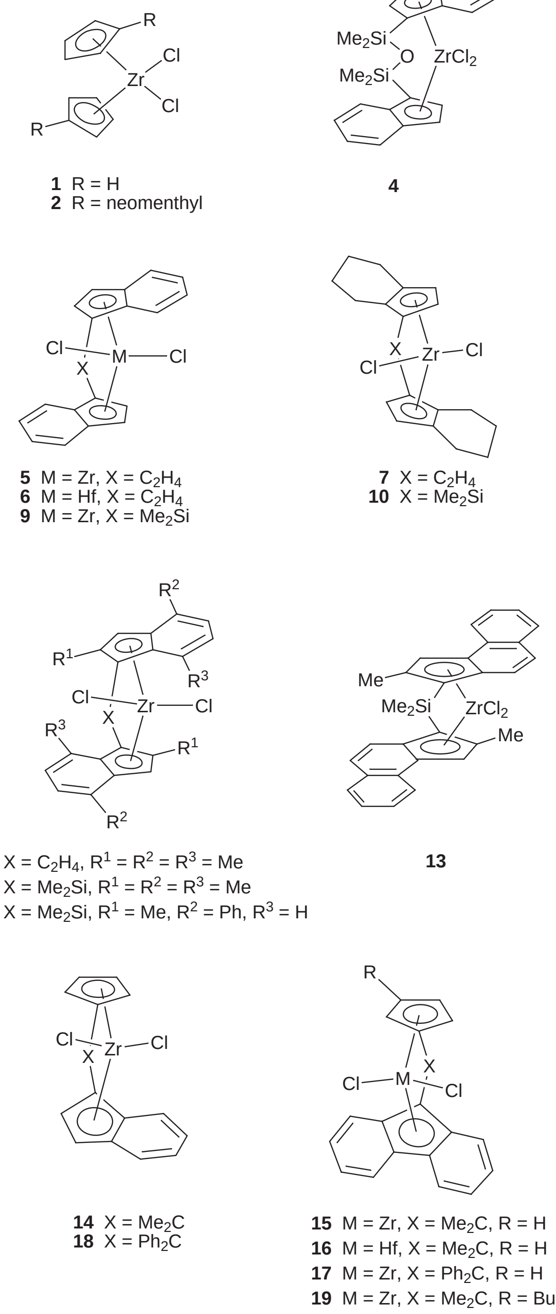
2 Metallocene Catalysts

In comparison, metallocene catalysts represent a great development: they are soluble in hydrocarbons, show only one type of active site and their chemical structure 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 classic Zeigler–Natta systems. The structure of metallocenes, so called ‘sandwich compounds’ in which a π-bonded metal atom is situated between two aromatic ring systems, was uncovered by Ernst O. Fischer and Geoffrey Wilkinson in 1952.[5,6] They were both awarded the Nobel Prize in 1973 for this achievement. This compound class initiated a more resourceful organometallic chemistry that did not play a role in larger industrial processes in the past.

Metallocenes, in combination with the conventional aluminium alkyl cocatalysts used in Ziegler systems, are indeed capable of polymerizing ethane, but only at a very low activity. Only with the discovery and application of methylaluminoxane (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 catalysis with metallocenes. Methylaluminoxane is a compound in which aluminium and oxygen atoms are arranged alternately and free valences are saturated by methyl substituents. It is gained by careful partial hydrolysis of trimethylaluminium and, according to investigations by Sinn[9] and Barron,[10] it consists mainly of units of the basic structure [$Al_4O_3Me_6$], which contains four aluminium, three oxygen atoms and six methyl groups. As the aluminium atoms in this structure are co-ordinatively unsaturated, the basic units (mostly four) join together forming clusters and cages (Fig. 1). These have molecular weights 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 tons of ethene per g 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. A comparison with enzymes is not far-fetched.

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 aluminium compounds (Fig. 3). In a further step, either Cl^- or CH_3^- is abstracted from the metallocene compound by an



1 R = H
2 R = neomenthyl

4

5 M = Zr, X = C_2H_4
6 M = Hf, X = C_2H_4
9 M = Zr, X = Me_2Si

7 X = C_2H_4
10 X = Me_2Si

8 X = C_2H_4, $R^1 = R^2 = R^3$ = Me
11 X = Me_2Si, $R^1 = R^2 = R^3$ = Me
12 X = Me_2Si, R^1 = Me, R^2 = Ph, R^3 = H

13

14 X = Me_2C
18 X = Ph_2C

15 M = Zr, X = Me_2C, R = H
16 M = Hf, X = Me_2C, R = H
17 M = Zr, X = Ph_2C, R = H
19 M = Zr, X = Me_2C, R = Bu^t

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

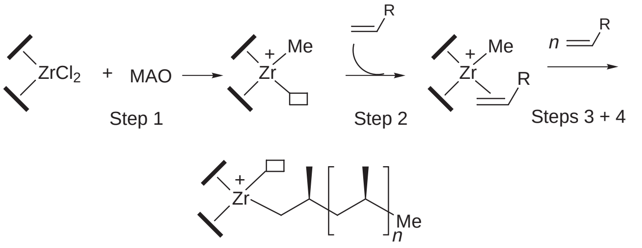


Fig. 3 Mechanism of the polymerization of olefins by zirconocenes. Step 1: the cocatalyst MAO converts the zirconocene after complexation into the active species which has a free co-ordination position for the monomer and stabilizes the latter. Step 2: the monomer (olefin) is allocated to the complex. Step 3: insertion of the olefin into the zirconium–alkyl bond and provision of a new free co-ordination position. Step 4: repetition of step 3, in a very short period of time (about 2000 propene molecules per catalyst molecule per s), thus rendering a polymer chain

Al-centre in MAO, thus forming a metallocene cation and a MAO anion.[11–13] The alkylated metallocene cation represents the active centre. Meanwhile, other weakly co-ordinating cocatalysts, such as tetra(perfluorophenyl)borate anions $[(C_6F_5)_4B]^-$, have been successfully applied to the activation of metallocenes.[14–17]

A further milestone was reached when Brintzinger[18] synthesized chiral bridged metallocenes in 1982 at the University of Konstanz and in 1984, when Ewen,[19] at the Exxon Company (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, up 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 (COC) with high catalytic activity,[32] optically active oligomers[33] and composite materials of biomass, powdered metals with polyolefines.[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]

3 Ethene and Propene Polymerization

The catalysts allow polymerizations to be controlled precisely. The building blocks are joined together in a linear fashion (see Fig. 3) at only one type of active centre ('single site'). The polymerization of ethene and propene with selected metallocenes under the same conditions is summarized in Table 2.[36] It is evident that the unsubstituted zirconocene Cp_2ZrCl_2 has a remarkable activity in the polymerization of ethene. Hafnocenes are less active than the analogous zirconocenes. Metallocenes containing tetrahydroindenyl rings which are bridged by C_2H_4 or Me_2Si groups afford polymers with especially high molecular weights. Surprisingly, the sterically congested and highly substituted metallocene **11** displays the highest activity in the polymerization of ethene amongst the compounds listed in Table 2. This leads to the conclusion that electronic effects are particularly important for the insertion reaction.[37] The molecular weight of polyethylene as well as of polypropylene can be adjusted to lower values by raising the polymerization temperature, the addition of small amounts of hydrogen or decreasing the monomer concentration. Using blends of metallocenes that render polymers with different molecular weights makes the tuning of molecular weight distributions to values of $M_w/M_n = 5–10$ possible.

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 polypropylene can be synthesized by complexes containing fluorenyl and cyclopentadienyl ligands bridged by X (compounds **15**–**17**, Table 2).[29] The block lengths of equal tacticity in isoblock PP (in which the position of the methyl groups are in one direction) can be varied in a broad range (4–100) on the 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]

Table 2 Homopolymerization of ethene and propene at 30 °C, 2.5 bar monomer pressure, 6.25×10^{-6} mol l^{-1} metallocene concentration, molar MAO–metallocene ratio = 250 : 1

	Ethene		Propene		
Catalyst	Activity[a]	10^3 M	Activity[a]	10^3 M	Isotacticity[b] (%)
1	60 900	620	140	2	7
2	12 200	1000	170	3	59
3 $(C_5Me_4Et)_2ZrCl_2$	18 800	800	290	0.2	7
4	57 800	930	230	0.3	24
5	41 100	140	1 690	323	95
6	2 900	480	610	446	94
7	22 200	1000	1 220	24	98
8	78 000	190	750	418	>99
9	36 900	260	1 940	79	97
10	30 200	900	7 700	44	95
11	111 900	250	3 800	192	94
12	16 600	730	15 000	650	99
13	7 600	450	6 100	380	98
14	1 550	25	180	3	49
15	2 000	500	1 550	159	0.6
16	890	560	130	750	0.7
17	2 890	630	1 980	729	0.4

[a] Measured in kg polyolefin per mol metallocene per h per concentration of metallocene. [b] mmmm (*meso*) Pentads as determined by ^{13}C NMR spectroscopy.

Table 3 Comparison of some properties of polypropylene made by Ziegler–Natta and metallocene catalysts[18]

	PP from metallocene catalyst	PP from Ziegler–Natta catalyst
Melting point/°C	161	162
M_w/M_n	2.5	5.8
Stress tensile/N mm^{-2}	1620	1190
Hardness/N mm^{-2}	86	76
Extractable fraction (%)	0.1	2–4

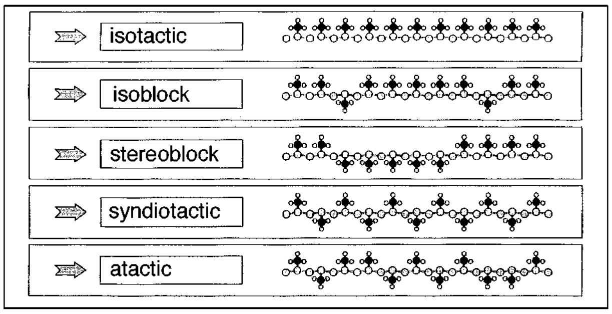
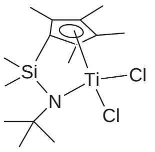


Fig. 4 Microstructures of polypropylene

By inserting a silyl bridge and substituting the indenyl ligands in zirconocene **1**, the metallocene work-group at Hoechst AG in Frankfurt was able to enhance the activity and stereoselectivity of the isotactic functioning catalyst considerably (compounds **9**–**13**). These catalysts afford isotactic PP of high molecular weights with a melting point of 161 °C.[39] Polypropylenes made by metallocenes exhibit distinct differences to conventionally produced polypropylenes, such as narrow molecular weight distributions, higher stiffness and greater tensile strength (Table 3). This is caused not only by the more uniform structure but also by the extremely low fractions of oligomeric products of low molecular weight. These fractions amount to less than 0.1%, compared to 2–4% in Ziegler–Natta PP. Copolymers of ethene and oct-1-ene produced by analogous 'single site' catalysts **20** of the Exxon and Dow companies in the USA have already captured a market in the packaging industry and in the field of medicinal applications.[40] High contents of octene of more than 20 mol % afford polyolefin elastomers (POE).



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4 Elastomers

One of the biggest impacts of metallocene catalysts will be in the manufacture of elastomers with elastic properties similar to rubber. The copolymers of ethene and propene with a molar ratio of 1 : 0.5 up to 1 : 2 are of great industrial interest. These ethene–propene (EP) polymers show elastic properties and, together with 2–5 wt. % of dienes as third monomers they are used as elastomers (EPDM).[41,42] Since there are no double bonds in the backbone of the polymer, it is less sensitive to oxidation and degradation reaction by daylight. The dienes 5-ethylidene-2-norbornene (ENB) (norbornene = bicyclo[2.2.1]-hept-2-ene), hexa-1,4-diene and dicyclopentadiene are used. Up until today, in most technical processes for the production of EP and EPDM rubber, soluble or highly dispersed vanadium components are used. Similar elastomers which are less coloured, can be obtained with the same metallocene–MAO catalysts used for the homopolymerization of ethene or propene at a much higher activity.

The regiospecificity of the metallocene catalysts towards propene leads exclusively to the formation of head-to-tail enchainments. 5-Ethylidene-2-norbornene polymerizes *via* vinyl polymerization of the cyclic double bond and the tendency to branch is low. The molecular weight distribution of about 2 is narrow.

At low temperatures the polymerization time to form one polymer chain is long enough to consume one monomer and then to add another one. So, it becomes possible to synthesize block copolymers if the polymerization, catalyzed specifically by hafnocenes, starts with propene and, after the propene is nearly consumed, continues with ethene.

High branching, which is caused by the incorporation of long chain olefins into the growing polymer chain, is obtained with a new class of silyl bridged amido(cyclopentadienyl)-titanium compound **20**.[43,44] This catalyst, used by Dow and Exxon in combination with MAO or borates, 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.[45]

5 Cycloolefin Copolymers (COC)

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 rendered, that have extremely high melting points of at least 380 °C, sometimes being higher than the decomposition temperature.[46]

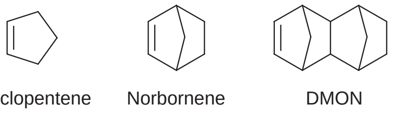

Fig. 5 Cycloolefins used for polymerization by metallocenes

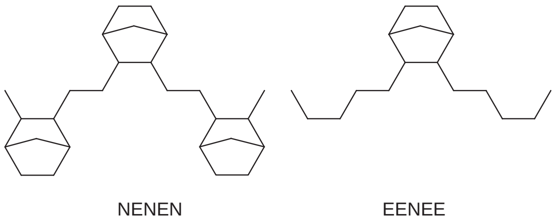

Fig. 6 Structures of norbornene (N)–ethene (E) copolymers. Alternating blocks can also occur

Table 4 Copolymerization of norbornene (N) and ethene by different metallocene–MAO catalysts at 30 °C *

Catalyst	Time/min	Activity/kg mol^{-1} h^{-1}	Incorporation of N (%)
1	30	1200	21.4
5	10	9120	26.1
9	15	2320	28.4
7	40	480	28.1
15	10	7200	28.9
17	10	6000	27.3
18	15	2950	33.3

* Conditions: MAO–Zr = 200, [metallocene] = 5×10^{-6} mol l^{-1}; ethene pressure = 2 bar, [N] = 0.05 mol l^{-1}.

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, for example (Fig. 6).[47–49]

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. For the copolymerisation of ethene and propene r_1 is between 3 and 6. Table 4 compares activities and incorporation of norbornene for different catalysts.

The metallocene **19** shows not only high activities for the copolymerization of ethene with norbornene, but gives an alternating structure, too.[50] 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. From cycloolefin insertion rates of 10 mol % upwards, these cycloolefin copolymers (COC) are no longer crystalline but amorphous. They are very resistant towards solvents and chemicals, they exhibit high softening temperatures (glass temperatures of up to 200 °C) and can be processed on a thermoplastic basis. A further peculiarity of these materials is their tendency to absorb little light, which makes them suitable for optoelectronic applications. Norbornene–ethene copolymers are most interesting for technical uses because of their readily available monomers. Currently, such COC polymers are already being used for the production of compact discs in Japan within the framework of a joint venture between the Hoechst and Mitsui companies. Applications for optoelectronic data transfer and storage as well as for other areas of high technology have been provided for.

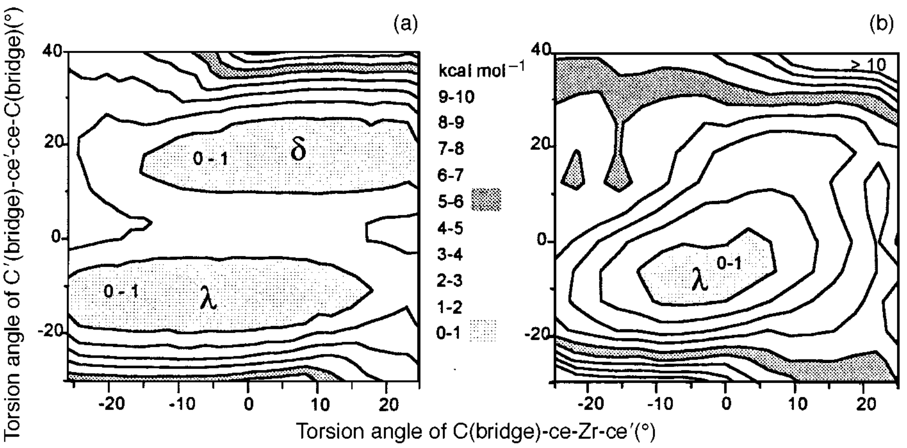

Fig. 7 Contour diagrams of (a) zirconocene **5** and (b) zirconocene **8**. Complete conformational analysis of the angle of torsion in 5° steps. ce is the centroid of the five-membered ring of the indenyl and ce′ that of the second indenyl. C(bridge)–ce–Zr–ce′ is a measurement of the orientation of the indenyl group relative to the $ZrCl_2$ fragment, while C′(bridge)–ce′–ce–C(bridge) describes the orientation of the indenyl rings with respect to one another. The lines represent isoenergetic areas. Energies are scaled to the energy minimum 11.3 kcal mol^{-1} ($E_{min} = 0$ at λ for **5**) and 15.8 kcal mol^{-1} (at λ for **8**)

6 Supporting of Metallocene Catalysts

Metallocene catalysts in dissolved forms are unsuitable for the production of polyethylene or isotactic polypropylene on an industrial scale. In order to use them in existing technical processes (drop-in technology) by exchanging them for the conventional Ziegler–Natta catalysts, the metallocenes have to be applied to a powdery, insoluble substrate. One way to do so is to support them on silica, alumina, magnesium dichloride or other supports. Different methods are possible.[51] Two of them are: (1) initial absorption of MAO on the support with subsequent addition of metallocenes in a second step which is mostly used. These washed catalysts are used in combination with additional MAO or other aluminium alkyls in the polymerization. (2) Another way is either absorption and immobilization of the metallocene first or direct bonding by a spacer to the support surface. Then after addition of MAO, this catalytic system is used in the polymerization process. Both procedures afford different catalysts and these in turn produce polyolefins with different properties.[52,53]

The polymers obtained by method (1) are very similar to those obtained by the homogeneous system. Each metallocene on the support forms an active center and the starting point for the growth of a polymer chain. As the active sites on the surface of each catalyst grain are identical, all chains grow uniformly resulting in polymers with narrow molecular weight distributions.

If the metallocene is linked to the support first, different absorptions occur. A large part of the metallocene is also destroyed by acid centers. This different bonding leads to different active sites. Therefore, the activity is much lower than in the case of the homogeneous system and the molecular weight distribution of the produced polymer is much broader.

7 Syndiotactic Polystyrene

Idemitsu was able to demonstrate that titanium compounds combined with MAO are capable of polymerizing styrene in a syndiotactical manner.[30] 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 (Table 5).

Previously, it was already possible to produce isotactic polystyrene with classical Ziegler–Natta catalysts with very low polymerization activities. However, it crystallized so slowly that technical usages were unthinkable. Furthermore, the polymerization activity of $CpTiCl_3$–MAO catalysts was also unsatisfactory for technical usage. If fluorinated complexes are employed such as trifluoro(pentamethylcyclopentadienyl)titanium, the activity can then be improved by a factor of 30 (Table 6).[55] At the same time the molecular weight rises from 169 000 to 660 000.

Table 5 Properties of atactic, isotactic and syndiotactic polystyrene (PS)

	Atactic PS	Isotactic PS	Syndiotactic PS
Structure	Amorphous	Crystalline	Crystalline
Crystallization rate	—	Slow	Fast
Glass temperature/°C	100	99	100
Melting point/°C	—	240	275

Table 6 Synthesis of syndiotactic polystyrene

Catalyst	Temperature/°C	Activity*	M.p./°C	M_n	M_w/M_n
$CpTiCl_3$	50	1 100	258	140 000	1.9
$CpTiF_3$	50	3 000	265	100 000	2.0
Cp^*ZrCl_3	30	0.01	249	20 000	2.2
Cp^*TiCl_3	50	15	275	169 000	3.6
Cp^*TiF_3	50	690	275	660 000	2.0

* Measured in kg PS per mol metallocene per h.

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

8 Modeling of Metallocene Catalysis

Explanations for the strong temperature dependency of particular zirconocenes that function isotactically were sought using force-field calculations in order to enable the optimization of metallocenes that are as stereorigid as possible.

Ethylidene bridged zirconocenes are possibly less rigid than assumed so far. Potential flexibility of the molecular structure could coincide with loss of stereospecifity for polymerisations at ‘high’ temperatures. Substituents in the 2- and 7-positions of the indenyl structure should restrict the mobility of the molecule, especially the bridge ‘twist’, because of their interaction with the ethylidene bridge. For this reason, the mobility of ethylidenebis[(2,4,7-trimethyl)indenyl]zirconium dichloride **8** was compared to that of ethylidenebis(indenyl)zirconium dichloride **5** (Fig. 7).[57]

The contour diagram of the energy hypersurface proves that, considering the same energy, **5** in comparison to **8** can occupy an area on the energy hypersurface that is four times larger. Furthermore, the modeling shows that **5** exists in two conformers, the δ- and λ-form, that are only separated by a small barrier of 1.5 kcal mol^{-1} (cal = 4.184 J). This is supplemented by NMR spectroscopic investigations which show that a conversion of the δ-form into the λ-form is feasible at room temperature. In contrast, substituted **8** exists only in the λ-form.

Silyl bridged zirconocenes also exhibit only one energy minimum, by which its higher stereospecifity can be explained. Force-field calculations demonstrate, thereby, why some metallocenes exhibit such a high temperature dependency of the isotacticity.[58] The reason can be found, for example, in the coexistence of two conformers, that are only separated by a low barrier and that are, therefore, more unstable affording polypropylene with a lower isotacticity.

9 Outlook

Meanwhile, the first products synthesized by metallocene catalysts, such as LLDPE, POE, EPDM elastomers or certain types of isotactic polypropylene, are already commercially available. The COC polymers and syndiotactic polystyrene are to follow. The application of metallocenes beyond the synthesis of polymers is discernable as in the enantioselective preparation of fine chemicals of low molecular weight.

A racemic mixture of chiral metallocenes can be separated into its enantiomers. Using optically active catalysts, oligomerization leads to optically active branched olefins.

The development of metallocene catalysts has not yet been concluded and for certain processes, such as the isotactic polymerization of propene, only temporary optimum values have been reached. The future will certainly yield further custom-made structures and a whole string of new polymers and oligomers; the catalysts involved will have metallocenes as their main component.

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