

METALLOCENE CATALYSTS

The term “metallocene” refers to compounds that have a metal atom bound to two cyclopentadienide anions in a π - or pentahapto/ η^5 -mode. The cyclopentadienyl rings can coordinate in a coplanar (parallel) or bent fashion to the metal center. Besides the two cyclopentadienyl rings, the metal can have additional ligands depending on its valence state (Fig. 1).

The cyclopentadienyl ring can be modified in many ways by substituting the hydrogen atoms through alkyl or aryl groups or anellated rings (or a combination thereof). Furthermore, a C–H group can be replaced by an isoelectronic nitrogen or phosphorus atom. The unspecified term *cyclopentadienyl ligands* (Cp) or *cyclopentadienylmetal complexes* is meant here to include substituted derivatives of the C_5H_5 parent ligand, such as C_5R_5 and also the indenyl (Ind) and fluorenyl (Flu) system, respectively, the complexes thereof. If *the* parent cyclopentadienyl ligand or its metal compound is meant exclusively, it is specifically stated by giving the formula C_5H_5 or $(C_5H_5)_mML_n$, respectively.

The term “metallocene catalyst” typically refers to the bent metallocenes of Group 4 (IVB) transition metals titanium, zirconium, and hafnium. In particular, “metallocene catalysts” refer to zirconocene complexes that are in the center of academic and industrial attention. The titanocene catalysts are unstable at conventional polymerization temperatures, the hafnium systems are too expensive. From the beginning of the 1990s, these bis(cyclopentadienyl) Group 4 IVB metal complexes (single-site catalysts) were introduced in industry as a new generation of Ziegler-Natta catalysts for the polymerization of olefins. Ziegler-Natta catalysis means the rapid polymerization of ethene and α -olefins with the aid and in the coordination sphere of a metal-containing catalyst, operating at low pressures (up to 30 bar) and low temperatures ($<120^\circ\text{C}$).

A noteworthy other metallocene compound used in industrial olefin polymerization is chromocene, $(\eta^5-C_5H_5)_2Cr$. This catalyst does not need any cocatalysts. The nature of the active species is not fully known but at least one cyclopentadienyl ring is lost to give a surface bound cyclopentadienylchromium fragment (so-called half-sandwich complex).

Also included under the term “metallocene catalysts,” albeit not adhering to the definition of a metallocene, are complexes with the cyclopentadienylsilylamido ligand.

The novelty of Group 4 (IVB) metallocene versus classical Ziegler-Natta catalysis is best summarized in the word “single-site catalyst.” This means that the active catalytic sites in the molecular zirconocene species are almost identical, whereas classical Ziegler-Natta catalysts are heterogeneous not just by the phase (as solid-state catalysts) but also by their composition in having active sites with different environments at corners and edges on the solid surface. Metallocene catalysts are sometimes also termed “homogeneous” referring both to their solubility and to their single-site character. In terms of their solubility, such a description may be slightly misleading, however, since for industrial applications in slurry or gas-phase processes and to gain control over the polymer morphology, the metallocene systems have to be heterogenized on support materials. Other descriptive names found in the literature for the zirconocene catalysts are “molecular defined” or after the names of the founders and long-time principal investigators “*Kaminsky-Brintzinger*” systems. The impact of “metallocene catalysts” extends beyond simple olefin polymerization. It has opened the doors to new classes of polyolefins inaccessible by classical Ziegler-Natta polymerization. It has advanced the development of chiral metallocenes. It is promoting the interest to explore further possible applications of metallocenes in general and it is encouraging the search for other single-site catalysts in place of heterogeneous industrial systems.

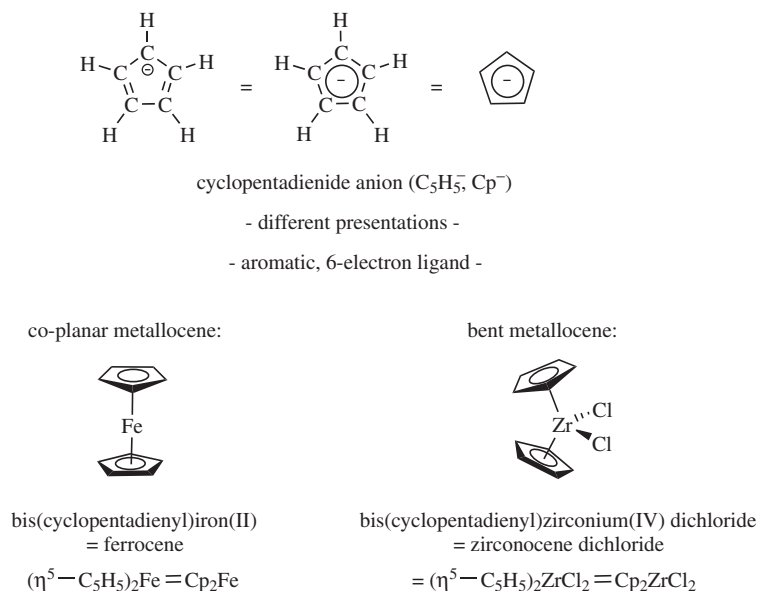


Figure 1. Introduction to metallocenes and their nomenclature.

INDUSTRIAL PERSPECTIVES

Differences between Classical Ziegler-Natta Catalysts and Metallocene Catalysts

Classical Ziegler-Natta catalysts have several chemically different active metal sites. This leads to less uniform polymers, ie, a higher molar mass, composition, and tacticity distribution.

Metallocene catalysts have essentially a single type of active metal site. This gives a “single,” more uniform type of polymer chain, ie, lower molar mass, more uniform composition (eg, branching, comonomer content), and tacticity distribution. Allow for a high versatility with countless variations through the ligand system.

Advantages–Disadvantages of Metallocene Catalysts

Advantages are

- A single type of catalytic site producing a polymer with narrow molar mass, composition (comonomer), and tacticity distribution.
- The versatility of the metallocene structure to allow for a greater range of polyolefin types.
- The precise control over the molecular architecture of the catalyst for highly tailored polymers (Fig. 2).
- Polyolefin products with new and favorable properties.
- High activity.

Disadvantages are

- The high amount of MAO cocatalyst.

The major disadvantage of metallocene catalysts are the extremely high molar Al-to-transition-metal ratios (Al/M) of between 1000 and 15,000:1 that are required to achieve the high activities.

Polyolefin Improvements with Metallocene Catalysts

Metallocene catalysts allow to produce consistent, controllable molecular polymer structures that can be designed to improved toughness, provide excellent impact resistance, reduced haze, better clarity, etc. A key feature of metallocene-catalyzed polymers that differs from conventional polyolefins is structural uniformity. This feature (a) eliminates very low and very high molar mass polymer fractions present with classical Ziegler-Natta catalysts, (b) leads to uniform amounts of comonomers and their statistical distribution, and (c) results in a narrow tacticity distribution.

- (a) Narrow molar mass distribution (MMD). MMD refers to the breadth of variation in chain lengths in a polymer.
- (b) Narrow composition distribution. Metallocene catalysts yield polymer chains with uniform amounts of comonomer and a statistical comonomer distribution. Classical Ziegler-Natta catalysts give

polymers where the comonomer content is concentrated in shorter chains.

- (c) Narrow tacticity distribution. Isotactic polypropene made with classical Ziegler-Natta catalysts still has some atactic fractions. The presence of atactic PP fractions reduces stiffness, heat distortion temperature, and cleanliness. The absence of atactic PP in metallocene isotactic polypropene means higher stiffness, higher use temperature, and lower extractable content.

Control of Polypropene Microstructure

Changes in the steric ligand situation allow for an unprecedented control of the polymer microstructure. Besides the iso- and atactic mode, other polypropene microstructures, such as isotactic with varying degree of stereoerrors, isotactic–atactic–stereoblock, isotactic–syndiotactic stereoblock, hemiisotactic and especially syndiotactic PP can be obtained as well, with appropriate ligand modification. The microstructure can also be greatly affected by temperature.

The different forms of homopolypropenes have different mechanical properties (without the addition of comonomer) ranging from plastic to elastic PP with decreasing stereoselectivity. The mechanical properties of different polypropenes and other poly- α -olefins strongly depend on their microstructure, which is determined by the regio- and stereoselectivity of the catalyst. Metallocene catalysts opened up the way to influence the polypropene properties in an understood and controlled way by altering the ligand system of the metal complexes.

Heterogenization of Metallocene Catalysts

Current polymerization technology is based on gas-phase and slurry processes. The established Ziegler-Natta catalysts are all heterogeneous, hence, it is necessary to also heterogenize metallocene catalysts for industrial applications. Thus, metallocene catalysts have to be fixed on a carrier or support to be used as “drop-in” catalysts in existing plants. The carrier functions as a template for the polymer morphology so that free flowing powders are obtained, thereby preventing wall deposits of the polymer. The obtained polymer particles represent a replica of the shape of the support with an increase in size. Fragmentation of the support is a prerequisite for the particle growth and the simultaneous conservation of morphology. Carriers can be inorganic support materials as (wet) silica (gel), alumina, or zeolites or organic support materials as cyclodextrins or polymers such as cross-linked polystyrene, or poly(organosiloxanes).

Common methods of immobilizing the catalyst involve first heterogenization of the cocatalyst. The support can be treated either with methylalumoxane (or methylaluminumoxane) MAO or with trimethylaluminum. The latter may be followed by addition of water to generate MAO if the carrier, such as wet silica does not already contain water.

Metallocene complexes that contain α -olefinic side groups on the ligand can be simultaneously incorporated into a growing polyethylene chain as a comonomer upon activation in an ethene solution polymerization process. As a

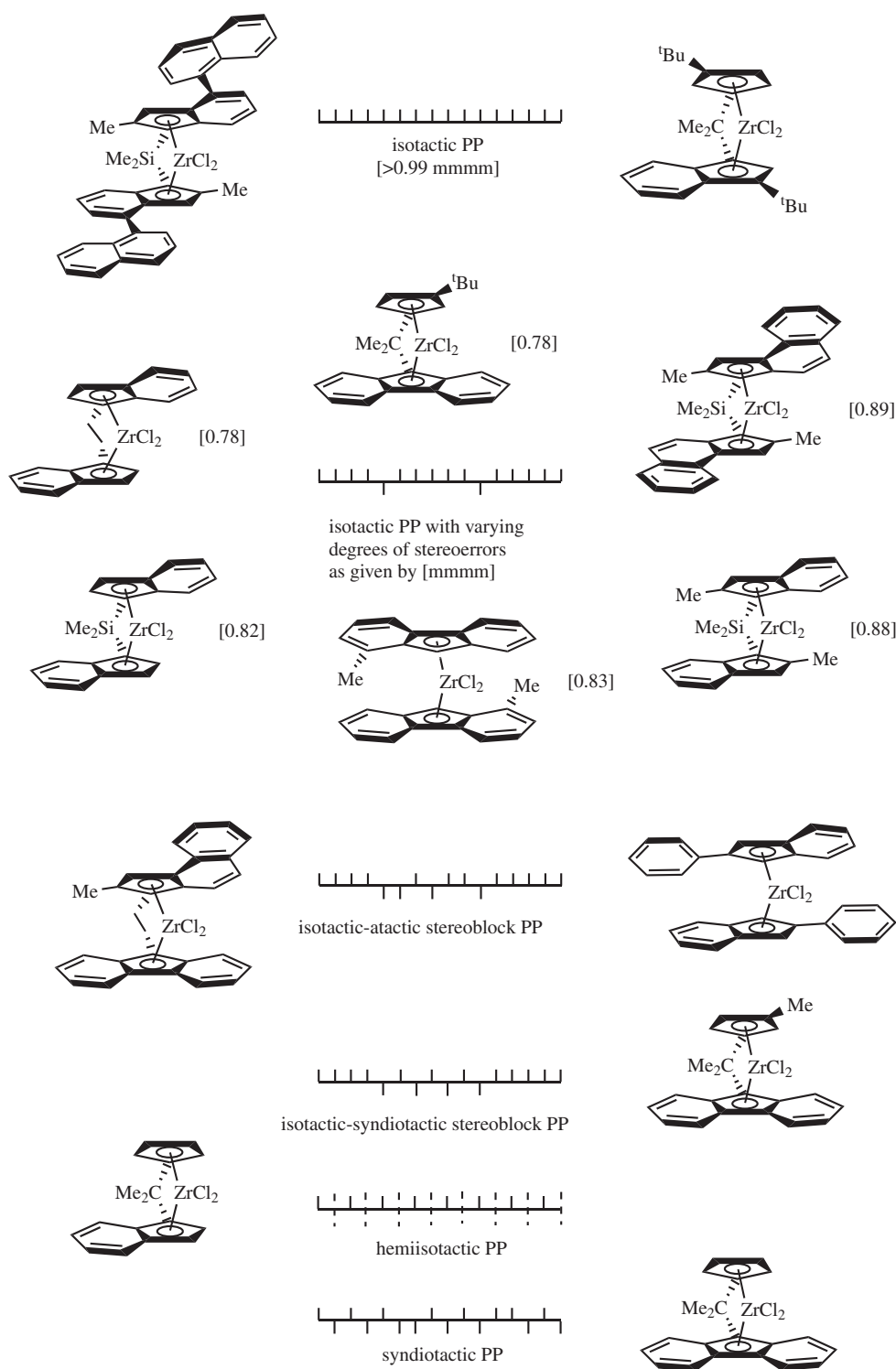


Figure 2. Examples for a correlation between the metallocene precatalyst and the PP microstructure (comb notation) to illustrate the control over the different degrees of PP stereochemistry.

consequence the active, homogeneous metallocene/MAO moiety is transferred to the heterogeneous polymer precipitate where it is available for further use. The formation of its own support by the metallocene catalyst in a polymerization process is also termed “self-immobilization”.

A clear advantage of heterogenized metallocene/MAO catalysts is the significant decrease in the necessary excess of MAO that leads to a strong decrease in catalyst costs. As a disadvantage of the catalyst immobilization or heterogenization, a marked drop in activity when compared to the

solution behavior can be noted, as the metal centers may become less accessible for the monomer approach. Also, a metallocene catalyst may change its stereoselectivity.

COCATALYSTS

The zirconocene complexes are not catalytically active by themselves but require the action of a cocatalyst. The cocatalyst directly associated with their application oriented development is MAO.

Methylalumoxane—Characteristics and Function

The development of metallocene catalysis for olefin polymerization is closely tied to the discovery and use of the cocatalyst MAO (104). Alumoxanes, in general, are understood as species containing an oxygen bridge between two aluminum atoms, $-Al-O-Al-$. Any alkyl, aryl, halide, alkoxy or other group can then be the other ligand(s) bonded to the aluminum atoms. Alumoxanes are obtained from the controlled hydrolysis of organoaluminum compounds. Technically MAO is made from the direct reaction of water/ice with TMA.

The full cocatalytic functionality of MAO toward zirconocenes is not known. The following functions of MAO in metallocene catalysis can be assumed:

- MAO methylates the metallocene dihalide (Cp_2ZrCl_2) to give the species $Cp_2ZrMeCl$ and Cp_2ZrMe_2 .
- MAO abstracts a chloride or methide anion with the formation of a $[Cp_2ZrMe]^+$ cation and a weakly coordinating $[Cl-MAO]^-$ or $[Me-MAO]^-$ anion.
- MAO establishes a stabilizing environment for the metallocene cation or cation–anion pair in the form of a host–guest or “crown-alumoxane” complex.
- MAO is a scavenger for deactivating impurities in the monomer or solvent.

MAO is a better alkylating agent and has a greater capacity for producing and stabilizing cation-like complexes, than TMA. Zirconocene dichloride and TMA alone were found to be either inactive or to exhibit very low polymerization activity.

It has been found that very high ratios of MAO to metallocene are required to achieve a good polymerization activity. Many zirconocene systems described in the literature require Al/Zr ratios on the order of 1000:1–10 000:1 to achieve a reasonable activity in solution. This is a serious shortcoming of the MAO cocatalyst.

The Borane Activators or Cationic Catalysts

Highly Lewis-acidic perfluorinated arylboranes can be used for the generation of polymerization active zirconocenium cations. The zirconocenium cations are then stabilized by weakly or *noncoordinating* perfluorinated arylborate anions, so-called “BArF” anions.

The metallocenium–BArF–borate cation–anion contacts are weak enough so that the *noncoordinating* anion can easily be displaced by the olefin. Quantitative

thermodynamic and kinetic parameters for ion pair formation, dissociation and reorganization in $[Cp_2MMe]^+ - [MeB(C_6F_5)_3]_3^-$ complexes ($M = Zr, Hf$) and other metallocenium ions in various solvents are available. The activity of these ionic, base-free catalysts is comparable to or even surpasses those of zirconocene–MAO systems. Yet, in the absence of scavenging agents, the cationic catalyst is not very long lived. Thus, in applications of the zirconocenium–borate catalysts, higher aluminum alkyls are favorably added to act as purifying agents and thereby enhance the observed activity.

GENERAL MECHANISM OF CHAIN GROWTH AND CHAIN TRANSFER

Mechanism of Chain Growth

Olefin insertion into a transition-metal alkyl bond at a metallocene is believed to occur via a combination of the Cossee–Arlman and modified Green–Rooney mechanism. The direct insertion mechanism, proposed by Cossee and Arlman, involves a loosely coordinated four-center transition state. The modified Green–Rooney mechanism proposed an α -agostic C–H interaction in the transition state to assist the insertion of an olefin. Such an α -agostic interaction in metal-catalyzed olefin polymerizations is supported by experimental evidence and theoretical considerations. The α -agostic interaction stabilizes (lowers the energy of) the transition state by relieving part of the electron deficiency of the 14-valence electron $[Cp_2ZrR]^+$ species.

Regioselectivity in α -Olefin Insertion. Regioselectivity concerns which end of the α -olefinic double bond is linked to the metal atom of the catalyst and which end to the growing chain. Consecutive regio-regular insertions result in a head-to-tail enchainment. When position 2 of the olefin is linked to the metal center a “2-1” (also 2,1- or secondary) insertion follows. Regio-irregularities such as a 2-1-addition in a series of 1-2 insertion (and vice versa) than leads head-to-head and tail-to-tail structures. The secondary alkyl ligand can also isomerize to a primary ligand before the next insertion to give a 1-3 insertion. At higher temperature, isomerization or 1-3 insertion becomes more dominant and can replace all original 2-1 insertions. A 2-1 insertion represents a steric hindrance to further chain growth, often leads to a β -hydride elimination or via isomerization to a 1-3 insertion. Ethene as a comonomer also activates catalyst sites blocked by a 2-1 insertion.

Stereoselectivity in α -Olefin Insertion. Stereoregulation in the polymerization of α -olefins can either be achieved through interaction between the entering monomer and the growing chain (chain-end control) or through an interaction between the monomer and the metal center and its environment (enantiomorphic-site control) or both. The polymerization of propene to an isotactic polymer remains a unique example of stereoselectivity in organic, non-enzymatic reactions.

Chain Transfer Processes

The two main chain-transfer processes observed with metallocene catalysts are

- Chain transfer by β -H elimination to the metal center. This leads to an olefinic end group and a metal hydrido species.
- Chain transfer to the aluminum cocatalyst. This gives a saturated end group after hydrolytic workup. Additional important chain transfer processes are
- β -H transfer to monomer.
- Hydrogenolysis by added H_2 .

ETHENE HOMOPOLYMERIZATION

In comparison to high-density polyethylene (HDPE) from classical Ziegler-Natta catalysts, the so-called metallocene HDPEs are characterized by their low polydispersity and the total absence of branching, which in turn leads to a different rheological behavior. The polyethylene molar mass from metallocene catalysis can be controlled by the metallocene type and concentration, the reaction temperature or by addition of hydrogen through the hydrogenolysis reaction.

Ethene polymerization studies are often used to investigate basic effects like the influence of catalyst concentration, cocatalyst characteristics and other aluminum alkyls, Al/Zr ratio, temperature, steric effects, catalyst formulation with support materials, etc, on the catalyst activity and the polymer parameters such as molar mass and molar mass distribution. When comparing different metallocenes, ethene may in some cases be better suited as a monomer, since with propene or other α -olefins the stereoselectivity of the metallocene strongly affects the activity. One has to be aware that in an ethene solution polymerization, the C–C bond forming reaction is truly homogeneous only at the very beginning.

Activity data for related metallocene complexes is often taken from the sources of other workers. Such a comparison should be judged with care because of the unavoidably different polymerization conditions. The large number of obvious and less obvious parameters often renders such comparisons rather dubious. Obvious activity parameters are, eg, temperature, Al/Zr concentration, pressure, and solvent; less obvious are zirconocene concentration, quality of MAO (degree of oligomerization, age, TMA content), monomer purity, pre-activation times between the zirconocene and MAO, reactor preparation, stirrer frequency, etc. The custom to collect activity data from the literature for comparison may be the source of many of the conflicting ideas in metallocene catalysis.

PROPENE HOMOPOLYMERIZATION

Generally, five different catalyst symmetries may be distinguished for the stereoselective propene polymerization:

- (1) Achiral, C_{2v} -symmetric metallocenes
- (2) Chiral, C_2 -symmetric (dissymmetric) bridged and unbridged metallocenes
- (3) Chiral, C_1 -symmetric (asymmetric) bridged metallocenes
- (4) Oscillating unbridged metallocenes
- (5) C_s -symmetric bridged metallocenes

Achiral, C_{2v} -Symmetric Unbridged Metallocenes

Such metallocenes mostly give atactic and low molar mass polypropene at conventional polymerization temperatures ($>50^\circ\text{C}$). Atactic polypropene almost always has a low molar mass and is an oily or waxy material. At low enough temperatures, eg, -45°C for $(C_5H_5)_2TiPh_2$, achiral catalysts are, however, capable of polymerizing propene with chain-end stereocontrol.

Chiral, C_2 -Symmetric Bridged Metallocenes

These metallocene–MAO catalysts afford isotactic polypropene. The chiral, C_2 -symmetric metallocenes are typically based on the bis(indenyl)ligand with the two indenyl rings connected by a bridge. However, chiral, C_2 -symmetric unbridged metallocenes and chiral C_1 -symmetric (asymmetric) metallocenes including modifications of C_s -symmetric metallocenes can also yield isotactic polypropene.

Chiral, C_2 -Symmetric Unbridged Metallocenes

Metallocenes of this type could, eg, be prepared with the help of chiral auxiliaries, such as cholestanyl, neoisopinocampyl, neomenthyl, and neoisomenthyl that were attached to unbridged indenyl and tetrahydroindenyl ligands. Only at low temperature did the resulting zirconocene complexes (activated by MAO) produce high molecular weight polypropene with enantiomorphic-site control.

With the appropriate ligands unbridged, C_2 -symmetric metallocene catalysts could, however, polymerize propene to crystalline isotactic polypropene even at conventional polymerization temperatures. It is noteworthy that a bridged bis(fluorenyl)zirconium complex gave predominantly atactic polypropene, albeit of high molecular mass.

Chiral, C_1 -Symmetric (Asymmetric) Bridged Metallocenes

Metallocene complexes with the *ansa*-cyclopentadienyl-indenyl backbone produce homopolypropenes with excellent thermoplastic elastomeric properties attributable to isotactic-atactic stereoblock or hemiisotactic microstructures. The term hemiisotactic means that the insertion of every second (even) propene unit is sterically controlled while the intermediate (odd) insertions occur statistically. The microstructure of the elastomeric polypropenes produced with these unsymmetrical catalysts is (as expected) sensitive to changes in catalyst structure and temperature but also to changes in pressure. With the appropriate bulky substitution, the polymerization of propene was found to afford highly isotactic polymers of medium to

high molecular weight. Chiral C_1 -symmetric catalysts are also derived from C_s -symmetric $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{Flu}')\text{ZrCl}_2$ metallocenes, eg, through substitution on the Cp ring.

Oscillating Unbridged Catalysts

In unbridged metallocenes, ring rotation may be sufficiently hindered to only an oscillatory movement about the metal-ring bonds.

C_s -Symmetric Bridged Metallocenes

C_s -Symmetric catalysts, such as $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{Flu}')\text{ZrCl}_2/\text{MAO}$, where the metal carries a bridged cyclopentadienyl and fluorenyl ligand typically yield syndiospecific polypropene with some isotactic triads (*mm*) as defects.

HOMOPOLYMERIZATION OF OTHER α -OLEFINS

In catalytic alkene polymerization with metallocene catalysts, the molar mass of polyalkenes and the reaction rates decrease in the order ethene > propene > 1-butene > 1-pentene > 1 hexene.

OLEFIN OLIGOMERIZATION

Initially, the finding of low molar mass products from propene polymerization with zirconocene catalysts was generally regarded as unfortunate. Now, it is recognized that metallocene catalysts may be used effectively for the directed oligomerization of α -olefins to give oligomers with double-bond end groups, predominantly of the vinylidene type. The use of olefin oligomers as intermediates for specialty chemicals drives the interest in the catalytic oligomerization.

Olefin oligomerization is also used to study mechanistic aspects of metallocene catalysis because of the homogeneity of the system (no heterogenization through polymer precipitation) and because the oligomeric products are easier to analyze than high molar mass polymers.

COPOLYMERIZATION

Comonomer insertion into the polymer chain is solely statistical for polymers obtained with metallocene catalysts (proven by nmr), contrary to conventional Ziegler-Natta catalysis where the comonomer is mainly incorporated into the low molar mass fraction.

Small amounts of ethene comonomer content in propene (homo)polymerization lead to polymers with two times higher molecular weights and only slightly lower melting points. The increase in chain length is due to an activation of the catalytic sites by ethene insertion that were blocked by a preceding 2-1 insertion, which normally leads to β -hydride elimination and chain growth termination.

POLYMERIZATION AND COPOLYMERIZATION OF CYCLIC OLEFINS

The metallocene-MAO catalyst systems allow polymerization of cyclic olefins with no ring opening taking place. With chiral metallocenes, cycloolefins like cyclobutene, cyclopentene, and norbornene can be polymerized to give isotactic polymers. For polycyclopentene, contrary to the initial formulation as a 1-2 insertion product, it was later proven that incorporation proceeded in a *cis*- and *trans*-1-3 manner to give poly(1,3-cyclopentene).

In general, the polycycloalkenes show extremely high melting points that lie above their decomposition temperatures (in air). Such high melting points make the homopolymers difficult to process. To lower the melting points, the cycloolefin can be copolymerized with ethene or propene. Now, it was possible with metallocene catalysts to solve a decade old problem, viz, the technical synthesis of cycloolefin-copolymers (COCs).

The norbornene-ethene copolymer features a high glass transition temperature, excellent transparency, thermal stability, and chemical resistance. It is suggested that these materials could be used for optical disks and fibers.

POLYMERIZATION OF POLAR MONOMERS

The use of Group 4 (IVB) metallocenes as initiating systems for the synthesis of polar or functional monomers has also been reported. Although, here in some cases it is more reasonable to assume not a Ziegler-Natta type insertion but a cationic polymerization reaction. The polymerization of polar monomers such as alkyl acrylates can also be initiated by Group 3 (IIIB) and lanthanoid metallocenes to give high molecular weight polymers with extremely narrow molecular mass distributions.

- G. M. Benedikt, ed., *Metallocene Technology in Commercial Applications*, William Andrew Publishing, Norwich, N.Y. 2000. <http://www.williamandrew.com/titles/766.html>
- R. Blom, A. Follestad, E. Rytter, M. Tilset, and M. Ystenes, eds., *Organometallic Catalysts and Olefin Polymerization—Catalysts for a New Millennium*, Springer Verlag, Berlin (2001).
- C. Elschenbroich and A. Salzer, *Organometallics*, 2nd ed., Wiley-VCH, Weinheim, 1992.
- N. J. Long, *Metallocenes*, Blackwell Science, Oxford, 1998.
- A. Togni and R. L. Halterman, eds., *Metallocenes*, Vols. 1 and 2, Wiley-VCH, Weinheim, 1998.

CHRISTOPH JANIÁK
Universität Freiburg,
Institut für Anorganische
und Analytische Chemie