

Stereospecific Olefin Polymerization with Chiral Metallocene Catalysts

Hans H. Brintzinger,* David Fischer, Rolf Mülhaupt, Bernhard Rieger,
and Robert M. Waymouth

Dedicated to all those excellent graduate students who are the true heroes of this story

Current studies on novel, metallocene-based catalysts for the polymerization of α -olefins have far-reaching implications for the development of new materials as well as for the understanding of basic reaction mechanisms responsible for the growth of a polymer chain at a catalyst center and the control of its stereoregularity. In contrast to heterogeneous Ziegler–Natta catalysts, polymerization by a homogeneous, metallocene-based catalyst occurs principally at a single

type of metal center with a defined coordination environment. This makes it possible to correlate metallocene structures with polymer properties such as molecular weight, stereochemical microstructure, crystallization behavior, and mechanical properties. Homogeneous catalyst systems now afford efficient control of regio- and stereoregularities, molecular weights and molecular weight distributions, and comonomer incorporation. By providing a means for

the homo- and copolymerization of cyclic olefins, the cyclopolymerization of dienes, and access even to functionalized polyolefins, these catalysts greatly expand the range and versatility of technically feasible types of polyolefin materials.

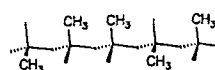
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1. Introduction

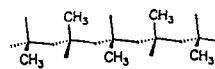
Forty years after Karl Ziegler's invention of transition metal catalyzed polyinsertion and Giulio Natta's discovery of the stereoselective polymerization of α -olefins,^[1–4] we are witnessing the evolution of new generations of catalysts and polyolefin materials, which originate from studies on homogeneous, metallocene-based polymerization catalysts. In the following, we will attempt to review some of these recent developments.^[5–7]

Research on metallocene-catalyzed olefin polymerization has derived much of its impetus from the desire to model the reaction mechanisms of heterogeneous polymerization catalysts. In the evolution of Ziegler–Natta catalysis, an empirical approach has proven highly successful. Modern MgCl_2 -supported catalysts have tremendous activities for the production of polypropylene and other polyolefins; at the same time, they are

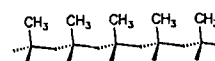
Sawhorse projection:



atactic

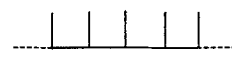
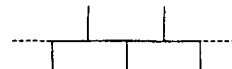


syndiotactic

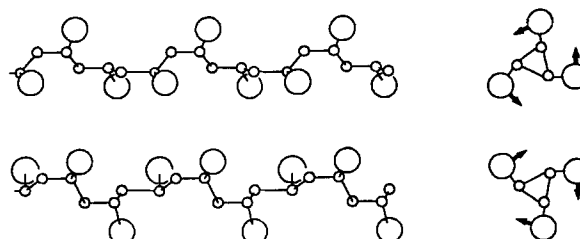


isotactic

Modified Fischer projection:



Conformation of chains in crystalline isotactic polypropylene:



Scheme 1. Structure of isotactic, syndiotactic, and atactic polypropylene in sawhorse and modified Fischer projections [107] (top), and conformation of the chains in crystalline isotactic polypropylene, determined by Natta and Corradini [2] (bottom).

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highly stereoselective, forming practically only the isotactic, most useful stereoisomer of the polymer^[8] (Scheme 1). Still unsatisfactory, however, is our understanding of the reaction mechanisms that are the basis of this advanced catalyst technology. Plausible hypotheses concerning these mechanisms have certainly been advanced, most notably Cossee's model of polymer chain growth by *cis*-insertion of α -olefins into a Ti-C bond on the surface of crystalline TiCl_3 .^[9,10] Based on Natta's early ideas about the role of chiral surface sites in the formation of isotactic polyolefins,^[6,11] very adequate models were proposed to explain the induction of stereoregular polymer growth by the chiral environment of the catalyst centers^[9b,12] (Scheme 2).

The relationship between the properties of a particular catalyst and the coordination geometry of its reaction centers, however, leaves many questions open,^[8g,h] due to the notorious nonuniformity of active sites in these heterogeneous catalysts and the limited experimental access to their structural details. In a review written in 1980, Pino and Mülhaupt summarized this shortcoming:^[4b] "Up to now, there is no direct proof for the structures proposed; most of them are the result of speculations or derived from indirect experimental indications."

In this situation, related developments in other fields of catalysis nourished the hope that homogeneous organometallic catalysts capable of stereoselective olefin polymerization might eventually allow more direct observations on the catalyst species



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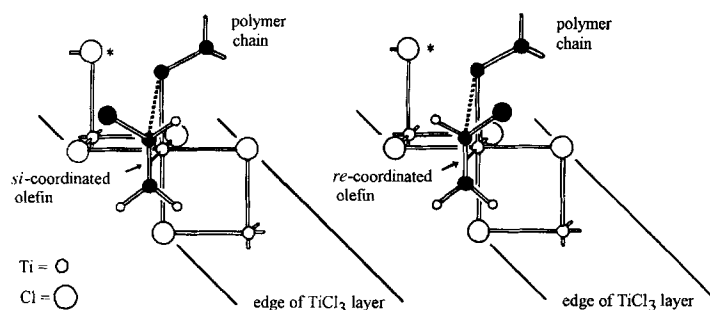
Hans-Herbert Brintzinger, born in Jena, Germany, in 1935, studied chemistry in Basel, where he received his Ph.D. in 1960 with Hans Erlenmeyer and his Habilitation in 1964. After teaching chemistry at the University of Michigan for several years, he moved to the University of Constance in 1972, where he holds a professorship for General Chemistry and Coordination Chemistry. His fields of interest are organometallic chemistry and reaction mechanisms in homogeneous catalysis.

David Fischer, born 1963 in Cologne, Germany, studied chemistry at the University of Cologne. After earning his diploma in physical chemistry, he joined Rolf Mülhaupt's group at the University of Freiburg as a graduate student. He received his Ph.D. in 1992 for studies on propene polymerization with homogeneous zirconocene catalysts. After a postdoctoral period with Robert Waymouth at Stanford, he joined the plastics laboratory of BASF AG in 1993, where he is still working on stereospecific propene polymerization with metallocene catalysts.

Rolf Mülhaupt was born in Waldshut-Tiengen, Germany, in 1954. From 1973 to 1978 he studied chemistry in Freiburg; he received his Ph.D. in 1981 with Professor Pino at the Laboratory for Technical Chemistry at the ETH in Zürich. Following industrial research positions at the Central Research and Development Experimental Station of Dupont in Wilmington, Delaware, from 1981 to 1985 and at Ciba-Geigy AG in Marly, Switzerland, from 1985 to 1989, he was appointed professor of Macromolecular Chemistry at the University of Freiburg in 1989. Since 1992 he has been director of the Material Research Center in Freiburg. His research interests include, besides transition metal catalyzed polymerization, new polymer structural materials, material compounds, dispersions and specialty polymers.

Bernhard Rieger was born in Augsburg, Germany, in 1959. He studied chemistry at the University of Munich and received his Ph.D. in 1988 for studies on enantioselective hydrogenations with rhodium-phosphane catalysts. After research appointments at the Institute for Polymer Science and Engineering of the University of Massachusetts at Amherst and in the plastics laboratory of BASF AG, he received his Habilitation in 1995 at the University of Tübingen, where he presently holds a faculty position in chemistry.

Robert M. Waymouth was born in Warner Robins, Georgia (USA), in 1960. He received bachelor's degrees in mathematics and chemistry at Washington and Lee University and his Ph.D. from California Institute of Technology in 1987, where he worked with Professor R. Grubbs. Following a year's postdoctoral appointment at the ETH in Switzerland with Professor Pino, he joined the faculty at Stanford in 1988, where he is now an Associate Professor of Chemistry. His research interests are in stereoselective catalysis.



Scheme 2. Model for the stereospecific polymerization of propene at a chiral Ti center on the edge of a TiCl_3 crystal, as proposed by Corradini and co-workers [12b]. The growing polymer chain occupies the open sector of the chiral coordination sphere: the olefin adopts that enantiofacial orientation which places the olefin substituent *trans* to the polymer chain at the incipient C–C bond (left); a *cis* orientation of olefin substituent and polymer chain is disfavored (right).

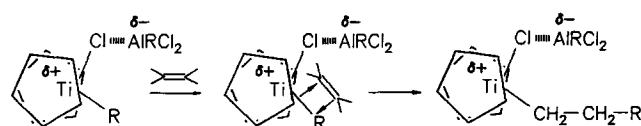
involved and, hence, on the mechanisms of polymer growth and its stereochemical control.^[13] This sentiment was expressed, for example, by Boor in the concluding chapter of his book on Ziegler–Natta catalysts.^[3c]

Particularly attractive as model systems of this kind appeared alkylaluminum-activated metallocene complexes of the Group 4 transition metals, which have been known since 1955 to catalyze the polymerization of ethene^[14, 15] and have since been the topic of many studies. The simple coordination geometry of Group 4 metallocene complexes—only two reactive, *cis*-positioned ligand sites—promised opportunities for identifying and characterizing essential intermediates of homogeneous polymerization catalysts and providing more direct experimental verification for some of the hypotheses in the field of Ziegler–Natta catalysis.

2. Activation of Metallocene Halides for α -Olefin Polymerization

In 1957, patents and publications by Breslow and Newburg^[14] at the Hercules Research Center and by Natta, Pino, and their co-workers^[15] reported that homogeneous reaction mixtures of dicyclopentadienyltitanium dichloride (Cp_2TiCl_2) and diethylaluminum chloride (Et_2AlCl) catalyze the formation of polyethene under conditions similar to those used with heterogeneous Ziegler catalysts. Numerous subsequent studies were aimed at the identification of reaction intermediates and reaction mechanisms of this homogeneous catalysis. The results obtained have been summarized previously;^[4a, b, 16] some are particularly noteworthy in the context of the following discussion.

Formation of (alkyl)titanocene complexes Cp_2TiRCl ($\text{R} = \text{Me}$ or Et) by ligand exchange with the alkylaluminum cocatalyst, polarization of the $\text{Cp}_2\text{Ti}–\text{Cl}$ bond by Lewis-acidic aluminum centers in an adduct of the type $\text{Cp}_2\text{Ti}(\text{R})–\text{Cl} \cdot \text{AlRCl}_2$, and insertion of the olefin into the $\text{Cp}_2\text{Ti}–\text{R}$ bond of this (or some closely related) electron-deficient species, had been deduced by 1960 from spectroscopic, kinetic, and isotope labeling studies done at the Hercules laboratories by Breslow, Newburg, and Long and by Chien^[17, 18] (Scheme 3). These ear-



Scheme 3. Polymerization of ethene by *cis*-insertion into the Ti–C bond of an alkylaluminum halide activated titanocene complex, as proposed by Breslow, Newburg, and Long [17].

ly metallocene studies contributed to the ideas put forth by Cossee^[9a] with regard to the mechanisms of heterogeneous Ziegler–Natta catalysis.

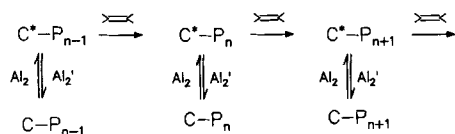
2.1. Metallocene Cations in the Polymerization of Ethene

An interesting question remained unresolved by this early research: does olefin insertion occur in a bimetallic species, in which an alkyl group or a halogen bridges the titanium and aluminum centers, as advocated by Natta and his group,^[19] by Patat and Sinn,^[20] by Reichert and co-workers,^[21] and by Henrici-Olivé and Olivé?^[22] Or does it require the formation of a truly ionic species $[\text{Cp}_2\text{TiR}]^+$ by abstraction of a halide anion and its incorporation into an anion $\text{R}_x\text{Cl}_{4-x}\text{Al}^-$, as proposed by Shilov, Dyachkovskii, and Shilova?^[23]

Crystal structures of complexes that were occasionally isolated from reaction mixtures containing Cp_2TiCl_2 and an alkylaluminum chloride^[24, 25] were not conclusive in this regard, as they represented degradation products, which require either reoxidation^[17] or renewed alkyl exchange with alkylaluminum cocatalysts^[4a] for reactivation. In 1986, however, Jordan and co-workers isolated the tetraphenylborate salts of cations such as $[\text{Cp}_2\text{ZrCH}_3 \cdot \text{THF}]^+$ and $[\text{Cp}_2\text{ZrCH}_2\text{Ph} \cdot \text{THF}]^+$ and demonstrated their capability to polymerize ethene without addition of any activator.^[26] These and related findings in the groups of Bochmann,^[27] Teuben,^[28] and Taube^[29] and by Hlatky and Turner at Exxon^[30] lent general credence to the proposal that (alkyl)metallocene cations are crucial intermediates in homogeneous polymerization catalysis.

A useful concept for the description of alkylaluminum-activated metallocene catalyst systems goes back to kinetic studies in Reichert's group.^[21] During the growth of a polymer chain, each metal–polymer species appears to alternate between a “dormant” state and a state in which it actively grows. This “intermittent-growth” model was further elaborated by Fink^[31] and by Eisch^[32] and their co-workers in extensive kinetic and reactivity studies. Consecutive equilibria appear to convert alkylaluminum and (alkyl)metallocene halides first into Lewis acid–base adducts equivalent to inner (or contact) ion pairs and then into dissociated (or separated) ion pairs. In these highly dynamic equilibria, only the cation of a separated ion pair appears to be capable of interacting with an olefin substrate and, hence, of contributing to polymer growth.^[33] Contact ion pairs, which appear to dominate in these equilibria, can then be termed “dormant” in this regard^[34, 35] (Scheme 4).

This model would explain the inability of metallocenes activated by alkylaluminum halides to catalyze the polymerization of propene and higher olefins^[4a, 36] by the insufficient capability of the more weakly coordinating, substituted α -olefins to form



Scheme 4. "Intermittent-growth" model involving equilibria between polymer-bearing, but inactive primary complexes ($C-P_n$) and active catalyst species (C^*-P_n), generated by excess alkylaluminum halide, as proposed by Fink and co-workers [31]. $Al_2 = (AlEtCl_2)_2$, $Al_2^1 =$ unknown. P_n = polymer chain with n monomer units; $C-P_n$ here $Cp_2TiP_nCl \cdots AlCl_2Et$.

reactive, olefin-separated ion pairs by displacement of an aluminate anion from the metal center. At any rate, the limitation of homogeneous catalyst systems to the polymerization of only ethene was a crucial obstacle for progress in this field for many years. Fortunately, this impediment was overcome by a series of serendipitous observations,^[37–39] which led, around 1980, to the discovery by Kaminsky, Sinn, and co-workers that metallocenes are activated for the catalytic polymerization of propene and higher olefins by methyl aluminoxanes.^[4a, 39]

2.2. Polymerization of Propene and Higher Olefins

Water, which had long been considered to be a "poison" for Ziegler–Natta catalysts, was first reported by Reichert and Meyer to cause a surprising increase in the rate of ethene polymerization by the catalyst system $Cp_2TiEtCl/AlEtCl_2$.^[37] Subsequent studies by Long and Breslow on the effects of water in the otherwise inactive system Cp_2TiCl_2/Me_2AlCl led to the notion that formation of a dimeric aluminoxane, $ClMeAl-O-AlClMe$, by partial hydrolysis of Me_2AlCl might generate an exceptionally strong Lewis acid and, hence, a potent activator for $Cp_2TiMeCl$ toward ethene polymerization.^[38]

While studying halogen-free systems such as $Cp_2ZrMe_2/AlMe_3$, Sinn and Kaminsky noticed that addition of water imparts to this otherwise inactive reaction system a surprisingly high activity for ethene polymerization which was, furthermore, unprecedentedly constant over extended reaction times.^[39a, b] Sinn and Kaminsky observed that an interaction between Cp_2ZrMe_2 and $AlMe_3$ occurred only when water had been added. The suspected formation of methyl aluminoxane (MAO) by partial hydrolysis of $AlMe_3$ was subsequently supported by its direct synthesis and characterization as a mixture of oligomers of approximate composition $(MeAlO)_n$. Activation of Cp_2ZrMe_2 and Cp_2ZrCl_2 with preformed MAO did indeed yield exceedingly active catalysts for the polymerization of ethene.^[39b] Similar activities were obtained with MAO-activated Cp_2TiCl_2 ; however, at temperatures above 0 °C this catalyst system is rapidly deactivated, most likely by reduction to the Ti^{III} stage.^[40]

Sinn, Kaminsky, and co-workers noticed furthermore that MAO-activated homogeneous metallocene catalysts were—in contrast to previously studied metallocene catalysts activated by aluminum halides—capable of polymerizing propene and higher olefins.^[4a, 39c–g] Although the achiral metallocene catalysts were still lacking the stereoselectivity of heterogeneous Ziegler–Natta systems, aluminoxane-activated metallocene catalysts now came to be most promising as model systems.

While oligomeric alkyl aluminoxanes have been known for more than 30 years, for example as initiators for the polymerization of oxiranes,^[41] their exact composition and structure are still not entirely clear. When the hydrolysis of $AlMe_3$, which is highly exothermic (and indeed potentially dangerous^[39j, 42b]), is conducted under controlled conditions, it appears to generate mostly oligomers $Me_2Al-[O-AlMe]_n-OAlMe_2$ with $n \approx 5–20$.^[39j]

Investigations in quite a number of research groups by cryoscopy, UV, vibrational and NMR spectroscopy, chromatography, and other means^[38, 39j, 42–50c] yield the following picture for aluminoxane solutions. Residual $AlMe_3$ in MAO solutions^[42b, 43] seems to participate in equilibria that interconvert different MAO oligomers^[42b, 43–46] and possibly also cyclic and branched oligomers.^[39e–j, 46] Cross-linking by methyl-free oxoaluminum centers has been proposed to generate a microphase with an Al_2O_3 core.^[47] Aluminoxane clusters $[RAl(\mu_3-O)]_n$, with $R = \textit{tert}$ -butyl and $n = 4, 6$, or 9 , have been isolated and structurally characterized by Barron and his group.^[48a] Complexes with four-coordinate Al centers seem to predominate in MAO solutions^[48a, 49] and might contain intramolecular $Al_2O \rightarrow Al$ or $Al-CH_3 \rightarrow Al$ bridges.^[42b] The presence of three-coordinate Al centers in MAO solutions has been deduced by Siedle and co-workers from ^{27}Al NMR data.^[50b, c] While species of exceptional Lewis acidity are certainly present in MAO solutions, their exact composition and structure is still not adequately understood.^[51]

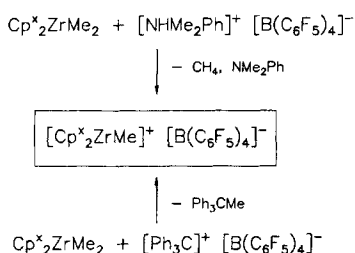
When toluene solutions of Cp_2ZrCl_2 are treated with MAO, a fast, initial ligand exchange reaction generates primarily the monomethyl complex $Cp_2ZrMeCl$.^[39i, 44b] excess MAO leads to Cp_2ZrMe_2 .^[39i] These systems become catalytically active when the concentration of excess MAO is raised to Al:Zr ratios of about 200:1 or higher.^[39] The ways in which excess MAO induces this activity have been investigated largely by spectroscopic methods.^[39i, 50–52, 53a] It is generally assumed that some of the Al centers in MAO have an exceptionally high propensity to abstract a CH_3^- ion from Cp_2ZrMe_2 and to sequester it in a weakly coordinating ion CH_3-MAO^- . A fast, reversible transfer of $^{13}CH_3$ groups from Cp_2ZrMe_2 to the Al centers of a MAO activator was observed by Siedle et al.^[50b, c] Barron and co-workers^[48b] obtained NMR spectroscopic evidence that Cp_2ZrMe_2 and aluminoxane clusters like $(\mu_3-O)_6Al_6tBu_6$ form complexes of the type $[Cp_2ZrMe^+ \cdots (\mu_3-O)_6Al_6(tBu)_6Me^-]$ in $[D_8]$ toluene solution, which polymerize ethene. The tendency of four-coordinate Al centers in these aluminoxane clusters to abstract a methyl anion is ascribed by these authors to the relief of ring strain upon formation of the methyl complex.

^{91}Zr and ^{13}C NMR spectra of Cp_2ZrMe_2/MAO solutions^[50b, c] and solid-state XPS^[52] and ^{13}C NMR^[53a] studies indicate formation of a cation $[Cp_2ZrR]^+$, which is most likely stabilized by coordinative contact with its CH_3-MAO^- counterion, for example through bonding like that in $Al_2O \rightarrow Zr$ or $Al-CH_3 \rightarrow Zr$. These contacts appear to give way, in the presence even of substituted olefins, to olefin-separated ion pairs $[Cp_2ZrR(olefin)]^+ CH_3-MAO^-$, the presumed prerequisite for olefin insertion into the $Zr-R$ bond. This hypothesis—that the unusually low coordinating capability of the anion A^- in the ion pair $[Cp_2ZrMe]^+ A^-$ is crucial for catalytic activity^[50e]—led to the discovery of a series of highly active cationic metallocene

catalysts for the polymerization of propene and higher α -olefins.

Even for large, weakly coordinating anions such as $(C_6H_5)_4B^-$ and $C_2B_9H_{12}^-$ fairly strong interactions have been observed with cationic (alkyl)zirconocene species.^[30, 53b, 58a] Reaction systems containing $[Cp_2ZrMe]^+$ together with $(C_6H_5)_4B^-$, $C_2B_9H_{12}^-$, or other carborane anions thus polymerize propene only at low rates, if at all.^[26f, g, j, 27–30]

A breakthrough in this regard was the introduction of perfluorinated tetraphenylborate as a counterion by Hlatky and Turner^[54] and by Marks and co-workers.^[53b] An ion pair $[Cp^*_2ZrMe]^+ [B(C_6F_5)_4]^-$ (where Cp^* is some substituted Cp or indenyl ligand) is formed by reaction of $Cp^*_2ZrMe_2$ with dimethylanilinium tetrakis(perfluorophenyl)borate or by abstraction of CH_3^- from a (dimethyl)zirconocene complex by trityl tetrakis(perfluorophenyl)borate^[55, 56] (Scheme 5). These



Scheme 5. Alternative ways to generate a propene-polymerizing (alkyl)zirconocene cation (associated with the weakly coordinating $B(C_6F_5)_4^-$ anion) as reported by Hlatky, Upton, and Turner [54], by Marks and co-workers [53b], by Ewen and Elder [55], and by Chien and co-workers [56]. Cp^* represents a variety of substituted and/or bridged cyclopentadienyl and indenyl ligands (see Section 3.1).

were the first well-defined zirconocene catalysts capable of polymerizing propene and higher olefins at high rates without addition of a further activator. Similar activities for propene polymerization were subsequently observed also with other base-free or weakly stabilized^[53, 57, 58] (alkyl)metallocene cations. Cations obtained by abstraction of CH_3^- from a (dimethyl)zirconocene complex by the powerful Lewis acid $B(C_6F_5)_3$

were likewise found to be highly active catalysts for α -olefin polymerization.^[59, 60]

Crystal structures obtained by Marks and co-workers,^[60] for example that of $[(Me_2C_5H_3)_2ZrCH_3^+ \cdots H_3C-B(C_6F_5)_3]^-$, reveal residual coordinative contacts between the cationic Zr center and its counterion (Fig. 1). This contact appears to resemble those yet unidentified interactions that stabilize an (alkyl)metallocene cation in contact with a H_3C-MAO^- counterion.

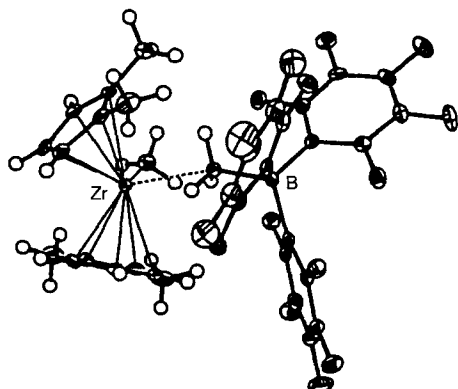


Fig. 1. Crystal structure of the zirconocene catalyst $[(Me_2C_5H_3)_2ZrCH_3^+ \cdots H_3C-B(C_6F_5)_3]^-$, as determined by Marks and co-workers [60]. The bridging $Zr \cdots CH_3B$ bond is substantially longer (255 pm) than the terminal $Zr-CH_3$ bond (225 pm).

In both cases, a fast methyl exchange occurs between the cationic and anionic complex moieties;^[50, 60] most importantly, both types of contacts appear to be weak enough to allow an α -olefin to displace the anion from its coordination site at the Zr center.

Cationic metallocene complexes, particularly those that arise by in situ activation of a stable zirconocene precursor,^[56] yield catalysts with very high activities. They are easily deactivated, however, probably by minute traces of impurities. Addition of $AlMe_3$ or $AlEt_3$ has been shown to stabilize these cationic metallocene catalysts^[55, 56b] by formation of AlR_3 adducts.^[57d]

Of even greater simplicity, at least conceptionally, are catalysts based on an (alkyl)metallocene complex containing a Sc^{III} , Y^{III} , or a trivalent lanthanide center. As shown by Ballard et al.^[61] and by Watson et al.,^[62] neutral complexes of the type $Cp_2M^{III}R$ act as single-component catalysts for the oligomerization of α -olefins.^[63, 64] While generally more difficult to prepare and to handle than the Group 4 metallocene catalyst systems described above, catalysts such as $(C_5Me_5)_2ScR$ ($R = Me, Et$) provided Bercaw and his co-workers detailed information on the rates and mechanisms of individual olefin insertion steps.^[63] The results of these studies lent additional support to the concept that an analogous olefin insertion into the isoelectronic species $[Cp_2ZrR]^+$ is responsible for the growth of polymer chains in zirconocene-based catalyst systems.

2.3. Kinetics and Mechanisms of α -Olefin Polymerization

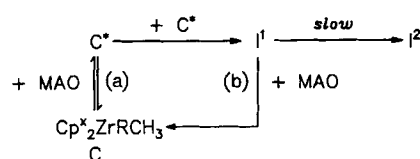
Because of many practical advantages, activation of zirconocene dichloride derivatives by methyl aluminoxane still appears to be the generally favored route to homogeneous polymerization catalysts. Substantial efforts have been made, therefore, to identify intermediates arising in the resulting, relatively complex reaction systems and to clarify the kinetics of the polymer chain growth they induce.

At propene pressures of 1–2 bar and ambient temperatures these reaction systems produce roughly 100–1000 kg polypropene per hour and mol of Cp_2ZrCl_2 . This corresponds to about 2000–10000 olefin insertions per hour at each Zr center. T is equivalent to the production of 500–5000 polymer chains with average molecular weights on the order of $M_n = 200$ –2000. Ethene is polymerized by these catalyst systems with still higher turnover numbers of 10–100 insertions per second, which approach those of C–C bond forming enzymes.^[39b, c, g]

Attempts to identify the species involved in the rate-determining step of the polymerization process by kinetic methods (i.e. by determining the rate of polymer formation as a function of the concentrations of zirconocene, MAO, and olefin reagents) have been hampered by the complex time-dependence of the catalytic reaction. Relatively high initial values, reached shortly after the components are mixed, decrease to much lower steady-state values.^[65–69] This decrease occurs within minutes at temperatures of 40–60 °C; at lower temperatures, it can take hours until the steady-state rate is reached.

In kinetic studies, Fischer and Mülhaupt^[69a, b] describe the steady-state activity of a Cp_2ZrCl_2/MAO catalyst system as a sequence of reversible and irreversible processes. A reactive species C^* appears to be generated in a fast equilibrium reaction

involving excess MAO and an (alkyl)zirconocene complex C (Scheme 6).^[170] Another, slower reaction, which shows a second-order dependence on the concentration of the active species C*, converts C* to some inactive species I¹. This inactive species I¹ is constantly reconverted to the catalyst species C and C* by reaction with excess MAO; this was demonstrated by the effects of MAO additions on the catalytic activity of a system that had already reached steady-state conditions.^[69c] A further, still slower reaction converts I¹ to another inactive species I² from which C* is not regenerated in these reaction systems. Since the transformation of C* to I¹ is bimolecular, the steady-state fraction of the inactive species I¹ decreases at low concentrations of C*. Accordingly, specific activities are observed to increase at lower zirconocene concentrations.^[39, 69]



Scheme 6. Dual effect of MAO on the steady-state activity of a zirconocene-based polymerization catalyst, derived from kinetic studies by Mülhaupt and Fischer [69a, b]. (a) Generation of active species C* in a fast equilibrium with a (di-alkyl)zirconocene complex and (b) reactivation of an inactive intermediate I¹ arising from a second-order deactivation reaction of C*; I¹ slowly decays to another inactive species I², from which the active catalyst is not regenerated.

The reaction that converts C* to I¹ is undoubtedly connected with the known propensity of (methyl)zirconocene cations to react with a wide variety of C–H units by means of σ -bond metathesis and release of CH₄.^[26d–f, 28, 30, 50, 71] Kaminsky and co-workers have indeed observed a steady liberation of CH₄ from MAO-activated zirconocene catalysts, which reached up to 50 molecules of CH₄ per Zr center.^[39i] The inactive, dominant steady-state species is proposed to be a binuclear complex with CH₂ bridges between a Zr and an Al center. Binuclear species with C₂H₄ bridges between two Zr centers were isolated by the same authors from ethene-polymerizing catalyst systems.^[4a, 39] Regeneration of active polymerization catalysts from these binuclear, C₂H₂-bridged deactivation products by MAO is proposed to occur by alkyl exchange reactions, for instance between a Zr–CH₂–Al species and the alkylaluminum activator;^[72] the latter will thus be consumed gradually under formation of Al–CH₂–Al units. Evidence for the formation of binuclear cations of the type [Cp₂ZrMe(μ -CH₃)MeZrCp₂]⁺ is now firmly established.^[53a, 57d, 60a, 73, 120e, 132b] Further insights with regard to their identity and their involvement in deactivation processes^[74] can be expected from studies on MAO-free, cationic zirconocene catalysts.

The question of why such a huge excess of MAO is required to induce catalytic activity for α -olefin polymerization is still unanswered. Catalytic activities are found to decline dramatically for MAO concentrations below an Al:Zr ratio of roughly 200–300:1. Even at Al:Zr ratios greater than 1000:1, steady-state activities increase with rising MAO concentrations,^[75] approximately as the cube root of the MAO concentration.^[39d, 69b] MAO appears to be involved in a fast equilibrium $C + MAO \rightleftharpoons C^* + CH_3-MAO^-$ as well as in the slower re-

activation process $I^1 + MAO \rightarrow C^*$. The concentration of the most Lewis-acidic Al centers must be related, furthermore, to the total MAO concentration through complicated equilibria. To date, it has not been possible to model the overall effects of MAO concentrations on catalytic reaction rates by a plausible, comprehensive system of kinetic equations.

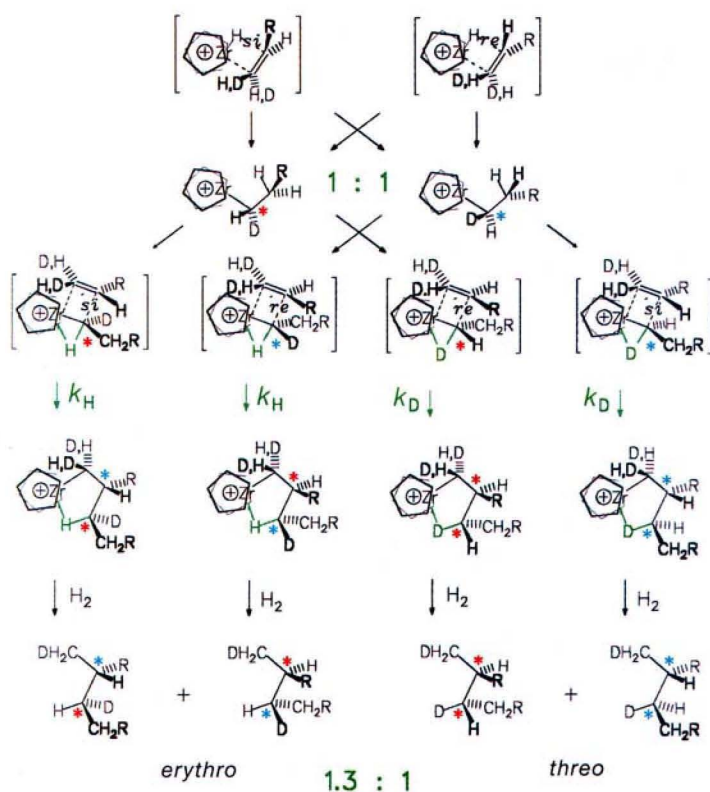
The effect of olefin concentration on the reaction rates is likewise complicated by catalyst deactivation. Since the reactive species appears to be stabilized by excess olefin, rates of polymer production under steady-state conditions are not proportional to propene concentrations, but approximately to $c(\text{olefin})^{1.3}$.^[69b] Related observations (see for example refs. [50b, c]) that polymerization rates depend on olefin concentration to a fractional order between 1 and 2 have led to the proposal that two olefin molecules are involved in the insertion transition state.^[76] While initial rates of polymer production, determined before the onset of catalyst deactivation, have been reported in two instances to increase in proportion to ethene^[65c] or propene concentration^[69b] (i.e. as $c(\text{olefin})^{1.0}$), this point requires further clarification (see Section 3.3).

For the present we will assume, in accord with general opinion, that the productive reaction complex in MAO-activated zirconocene catalysts is a cationic alkyl(olefin)zirconocene complex of the type [Cp₂ZrR(olefin)]⁺H₃C–MAO[–], which is generated by displacement of an anion H₃C–MAO[–] from its [Cp₂ZrR]⁺ counterion by an olefin molecule.

The reaction step by which such an alkyl(olefin)zirconocene cation is finally converted to the olefin-insertion product has been further characterized by kinetic isotope effects. Laverty and Rooney,^[77] and Brookhart and Green^[78] had proposed that an agostic interaction of one of the α -H atoms of the metal-bound alkyl chain with the metal center of a Ziegler–Natta catalyst^[79] facilitates the insertion of an olefin into the metal–alkyl bond. To test this hypothesis, Krauledat and Brintzinger^[80] investigated the catalytic hydrodimerization of α -deuterated hexenes to the *threo* and *erythro* diastereomers of 5-CH₂D-6-[D]-undecane by MAO-activated Cp₂ZrCl₂. Diastereomer ratios in accord with a value of $k_H/k_D \approx 1.3$ were observed with *cis* and *trans* α -deuterated 1-hexene. This indicates—along a line of reasoning developed earlier by Grubbs and co-workers^[81]—that the transition state for the insertion of hexene into the Zr–C bond of the initially formed Zr–CHD–(CH₂)₄CH₃ unit involves considerable weakening either of its α -C–H or of its α -C–D bond. In other reaction systems agostic interactions with H atoms have been shown to be preferred over those with D atoms by a factor of about 1.2–1.5.^[79a] The stereokinetic isotope effect $k_H/k_D \approx 1.3$ associated with the insertion of an α -olefin into the metal–CHD–R unit of a MAO-activated zirconocene catalyst can thus be regarded as evidence that this reaction requires the agostic interaction of one of the α -H atoms with the metal center (Scheme 7).

Similar results were obtained by Piers and Bercaw^[82] in studies on hydrocyclizations and hydrodimerizations induced by single-component scandocene catalysts. It remains to be tested whether this notion can be generalized or whether olefin insertions into metal–alkyl species might occasionally occur without agostic assistance.^[83]

Olefin insertion into the metal–alkyl bond of a cationic metallocene complex of the type [Cp₂MMe(olefin)]⁺ (M = Ti,



Scheme 7. Stereokinetic isotope effects in the $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2/\text{MAO}$ -catalyzed hydrodimerization of (E) - and (Z) -1-[D]-1-hexene ($\text{R} = n\text{-C}_4\text{H}_9$) favor the *erythro* over the *threo* products in a ratio of 1.3:1 [80]. While the achiral starting compounds must give the $\text{Zr-CHD-CH}_2\text{R}$ enantiomers in a 1:1 ratio, the second olefin insertion is influenced by α -agostic interactions. A $\text{H-C}(\alpha)$ bond is weakened in the formation of the *erythro* isomers, a $\text{D-C}(\alpha)$ bond in the formation of the *threo* isomers of the hydrodimer product.

Zr) has been the subject of numerous theoretical studies.^[84–89] Calculations with *ab initio* and density functional methods depict the transition state as a planar^[84e, g, 85, 87, 88] or slightly puckered^[84f, 86] four-membered ring with Ti-C and Zr-C distances of 2.1–2.3 and 2.3–2.5 Å, respectively, an incipient alkyl–olefin $\text{C}\cdots\text{C}$ distance of 2.1–2.3 Å, and a slightly increased olefin $\text{C}=\text{C}$ bond length of roughly 1.4 Å^[84e–g, 85–88] (Fig. 2).

Most of these studies concur with the view that in the insertion transition state one α -H atom of the migrating $\text{Zr-CH}_2\text{-R}$

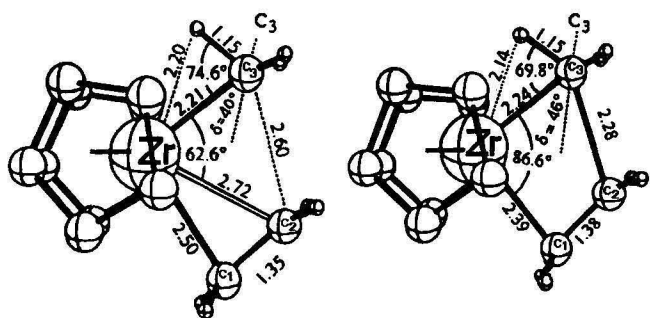


Fig. 2. Structures of a cation $[(\text{C}_5\text{H}_5)_2\text{ZrMe}(\text{C}_2\text{H}_4)]^+$ (left) and of the transition state for insertion of the ethene ligand into the Zr-Me bond (right), as determined by Ziegler and co-workers by density functional methods [87]. A shortening of the agostic $\text{Zr-H}(\alpha)$ contact helps align the C_3 axis of the CH_3 group for interaction with the ethene π^* orbital.

group is in close proximity to the metal center and that this Zr-H interaction is due to an α -agostic bond.^[86–88] An Extended-Hückel MO study^[89] indicates that the α -agostic interaction of a $\text{Zr-CH}_2\text{-R}$ unit with the Zr center is linked to the increasing electron deficiency of the reaction complex as it progresses along the olefin-insertion coordinate from a 16-electron to a 14-electron species. The size of the contribution of the agostic interaction to the stabilization of the olefin-insertion transition state is still a matter of debate.^[89]

These studies also indicate that the $\text{Zr-}n$ -propyl unit at the end of the insertion path is stabilized by the agostic interaction of one of its $\gamma\text{-C-H}$ bonds with the Zr center.^[84g, 85–89] A yet more stable structure appears to be a product in which one of the $\beta\text{-C-H}$ bonds of the $\text{Zr-}n$ -propyl unit interacts with the electron-deficient Zr center.^[85–88] The γ -agostic species initially arising from the insertion process is thus likely to rearrange into a structure with a β -agostic bond;^[79] the latter probably represents something like a resting state for a $[\text{Cp}_2\text{Zr-alkyl}]^+$ ion (see ref. [63]). Theoretical studies indicate that the $\gamma \rightarrow \beta$ rearrangement might be relatively slow.^[85b, 87b]

Effects of the solvent and counterions, neglected so far in these theoretical studies, might be of more than peripheral concern. In an ion-cyclotron resonance study, Richardson and co-workers^[74] showed that $[\text{Cp}_2\text{TiCH}_3]^+$ and C_2H_4 react in vacuo to form the allyl complex $[\text{Cp}_2\text{TiC}_3\text{H}_5]^+$ and H_2 , rather than the insertion product $[\text{Cp}_2\text{TiC}_3\text{H}_7]^+$. It remains to be clarified which interactions induce the more useful course to polymers in the analogous condensed-phase reaction systems.

2.4. Molecular Weights and Chain Termination Reactions

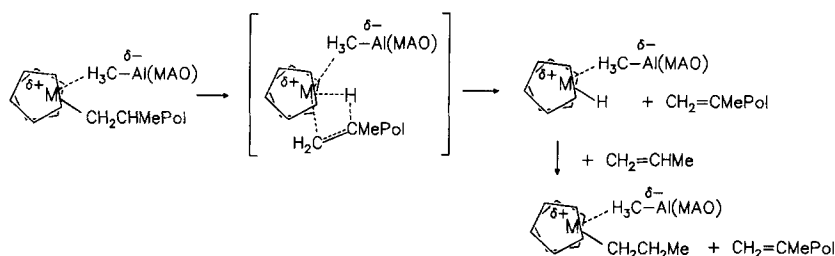
An important aspect in which homogeneous olefin polymerization by metallocene catalysts differs from heterogeneous Ziegler–Natta catalysis is the narrow molecular weight distribution of homogeneously produced polymers. While polyolefins obtained with heterogeneous catalysts have broad molecular weight distributions with large polydispersities of $M_w/M_n \approx 5\text{--}10$,^[8] homogeneous catalysts produce polymers with polydispersities M_w/M_n close to 2.^[39f] A polydispersity of 2 is predicted by Schulz–Flory statistics^[90] for polymers arising from identical catalyst centers with fixed rates of chain propagation and chain termination, v_p and v_t . A polydispersity of 2 is thus regarded as evidence that only a single catalyst species contributes to polymer growth in a homogeneous catalyst system. Even though the deactivation and reactivation reactions discussed above are likely to generate a diversity of complex species in these catalyst systems under steady-state conditions, only one of these species, presumably the cation $[\text{Cp}_2\text{Zr-alkyl(olefin)}]^+$, appears to contribute to polymer growth.

While ethene is polymerized by MAO-activated or cation-type Cp_2Zr -based catalysts to give polymers with high molecular weights in the range of 100 000 to 1 000 000,^[39i] propene polymers obtained at room temperature with these catalysts have rather low degrees of polymerization, with molecular weights in the range of 200–1000.^[39e, g, 69b] The relatively low molecular weights of the polymer products must be due either to an increased rate of chain termination or to a decreased rate of olefin insertion (or both), since the average degree of polymerization

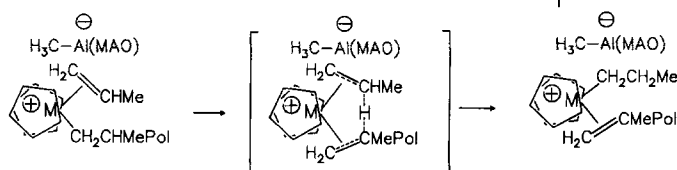
P_N is determined by the ratio of the rates of chain propagation and chain termination, $P_N \approx v_p/v_T$.^[90]

^1H and ^{13}C NMR analyses show that polypropene chains produced with zirconocene-based catalysts bear *n*-propyl and 2-propenyl end groups.^[91] The 2-propenyl end groups could arise by transfer of a β -H atom from the polymer chain to the metal center (Scheme 8). The Zr-H unit generated by this process can then react with propene to form a Zr-*n*-propyl unit, from which a new polymer chain can start to grow.^[96] Another conceivable chain termination mechanism is the transfer of a β -H atom from the Zr-bound polymer chain directly to the β -C atom of a coordinated olefin molecule. In this case, the 2-propenyl-terminated polymer chain and a new Zr-*n*-propyl unit are generated without the intermediacy of a Zr-H species (Scheme 8).

β -H transfer to metal:



β -H transfer to olefin:



Scheme 8. Chain termination by β -H transfer to the metal (top) and to a coordinated olefin (bottom). A polymer chain with a 2-propenyl end and a metallocene complex with a *n*-propyl chain result from both of these processes, but the rate of the latter increases with olefin concentration in parallel to that of olefin insertion, while the rate of the former is olefin-independent. Molecular weights of the polymers will thus increase with olefin concentration in the case of β -H transfer to the metal, while molecular weights independent of olefin concentration indicate β -H transfer to an olefin ligand.

Evidence for direct β -H transfer to a coordinated olefin was obtained by Kashiwa and co-workers^[97] from studies on ethene-propene copolymers. A Zr-H intermediate would be expected to react at least as fast with ethene to give a Zr-ethyl unit as with propene to give a Zr-propyl unit; ethyl end groups should thus be found at the head of a polymer chain with the same frequency as *n*-propyl ends. In fact, very few ethyl ends were formed at comparable concentrations of ethene and propene. The most plausible explanation for this observation is that β -H transfer to a coordinated propene molecule occurs more often than that to a coordinated ethene molecule, since the rate of insertion of propene into a Zr-polymer bond is lower than that of ethene.^[97]

This mechanism does not appear compatible, on the other hand, with observations that polymer molecular weights increase linearly with ethene^[65c] or propene^[69b] concentrations. For chain termination by β -H transfer to a coordinated monomer one would expect v_T like v_p to depend linearly on monomer concentration. In this case, the mean degree of polymerization, $P_N \approx v_p/v_T$, is expected to be independent of the

monomer concentration. This discrepancy obviously needs to be readdressed; we will return to it in the discussion of stereoselective polymerization catalysis in Section 3.3.

Molecular weights of polyolefins obtained with MAO-activated zirconocene systems generally increase with the concentration of the MAO cocatalyst,^[39, 69b, 98] in parallel with increased rates of chain growth. Effects of zirconocene concentrations on polymer molecular weights again parallel those on catalytic activities: molecular weights increase substantially as zirconocene concentrations are decreased.^[39, 69b, 98] This might be due to dilution effects favoring the dissociated or olefin-separated ion pairs C^* relative to their associated precursors C , and hence the rate of chain propagation over that of chain termination.^[99] As an alternative, Kaminsky and co-workers^[39, 98] advocate that a bimolecular reaction of the active complex with a second zirconocene species terminates growth of the polymer chain in a manner possibly related to the second-order deactivation process discussed in Section 2.3. Further clarification of these questions can be expected from future studies on MAO-free, cationic metallocene polymerization catalysts.

3. Stereoregular Polymers from Chiral Metallocene Catalysts

The discovery of homogeneous catalysts capable of polymerizing propene and higher α -olefins around 1980 revived a long-standing question:^[13] Would it be possible to induce these homogeneous polymerizations in a stereoregular fashion, so as to produce isotactic polymers, by using suitably designed chiral metallocenes as catalysts?

Chiral metallocenes suitable for this purpose^[100] became available, not quite accidentally^[101] just at that time. Using ethylene-bridged ligands,^[102] Wild and Brintzinger^[103] obtained ethylenebis(indenyl)- and ethylenebis(tetrahydroindenyl)titanium complexes, *rac*-(en)(ind)₂TiCl₂ and *rac*-(en)(thind)₂TiCl₂, and their zirconium analogues. The conformationally constrained indenyl and tetrahydroindenyl ligands give these complexes chiral structures (Fig. 3) which

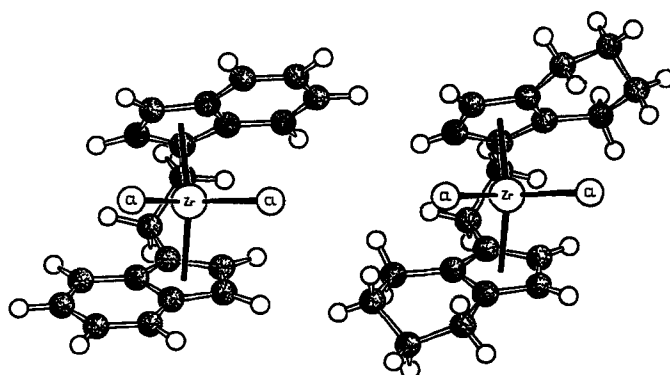


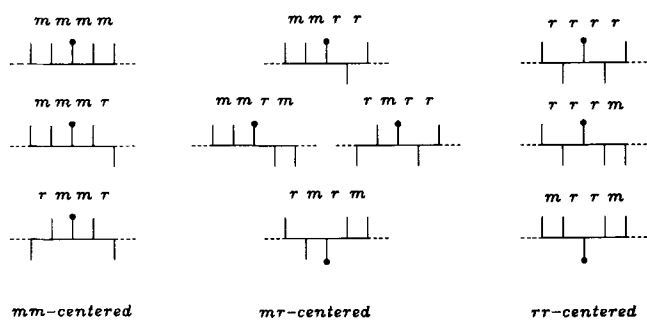
Fig. 3. Prototypical *ansa*-zirconocene complexes prepared by Wild et al. [103]: *rac*-(en)(ind)₂ZrCl₂ (left) and *rac*-(en)(thind)₂ZrCl₂ (right).

could be expected to be retained even under catalysis conditions. When activated with MAO in the manner described above, these *ansa*-metallocenes^[104] were indeed found, in independent studies by Ewen with (en)(thind)₂TiCl₂/MAO^[105] and by Kaminsky and Külper with *rac*-(en)(thind)₂ZrCl₂/MAO,^[106] to polymerize propene and other α -olefins to give highly isotactic polymers. These findings led to extensive exploration of the mechanisms by which these catalysts control the stereochemistry of polymer growth and the effects of different metallocene structures on the tacticities and other properties of the polymers produced.

3.1. Catalyst Structures and Stereoselectivities

Polypropylene produced by MAO-activated chiral *ansa*-zirconocenes such as *rac*-(en)(ind)₂ZrCl₂ or *rac*-(en)(thind)₂ZrCl₂ has similar isotacticity to polymers produced with heterogeneous Ziegler–Natta catalysts. For a more quantitative discussion of these relations, we consider briefly the ¹³C NMR spectroscopic methods^[107] currently used to characterize the stereoregularity of poly(α -olefins).

The ¹³C NMR signals of a polymer are most conveniently related to its microstructure by a stereochemical notation developed by Bovey.^[1107a] Relative configurations of neighboring units (or “dyads”) are designated as *m* (*meso*) for equally and *r* (*racemo*) for unequally positioned substituents in a Fischer-type projection of the polymer chain. In polypropylene, the ¹³C NMR shift of each CH₃ group is determined by the configurations of two neighboring repeat units on either side;^[108] each CH₃ signal is thus assignable to a particular “pentad” pattern, represented by the four consecutive *m* or *r* designators framing the CH₃ group under consideration (Scheme 9). All ten possible



Scheme 9. The ten possible stereochemical pentads of a polyolefin [107].

pentad signals (*mmmm*, *mmmr*, *rmmr*, *mmrr*, *mmrm*, *rmrr*, *rmrm*, *rrrr*, *rrrm*, and *mrrm*)^[109] are observed for the randomly configured repeat units of atactic polypropylene^[110] (Fig. 4). Isotactic polypropylene, on the other hand, is ideally characterized by a single ¹³C NMR signal for *mmmm* pentads, since its repeat units have identical configuration over long segments of the polymer chain.

The degree of isotacticity of such a polymer is usually expressed as the ratio of the *mmmm* pentad integral to the integral sum of all pentad signals observed; it will be designated in the following as *[mmmm]*.^[111] Isotactic polypropylene produced by modern heterogeneous Ziegler–Natta catalysts^[8] is highly

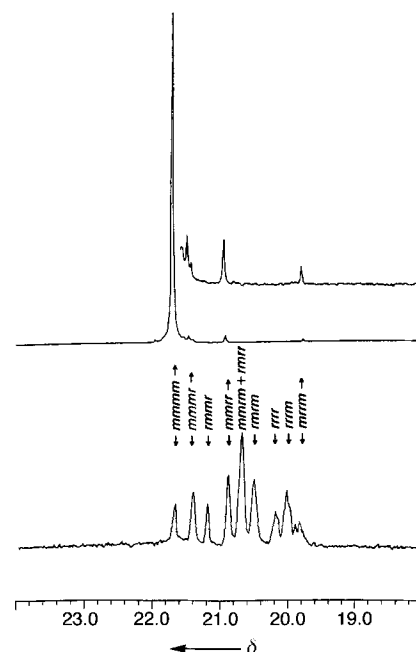


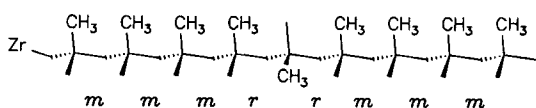
Fig. 4. ¹³C NMR spectra of isotactic polypropylene (CH₃ region) with *[mmmm]* > 90% obtained with *rac*-Me₂Si(1-benz[e]indenyl)₂ZrCl₂/MAO [117h, 120d] (top), and of atactic polypropylene with random pentad distribution obtained with the *meso* isomer of the same catalyst (bottom).

stereoregular with *[mmmm]* > 0.95. At ambient temperatures, typical MAO-activated chiral *ansa*-metallocene catalysts yield polypropylene with stereoregularities of *[mmmm]* \approx 0.8–0.9.^[106, 112, 113] At increased polymerization temperatures, however, most of these homogeneous catalysts are distinctly less stereoselective than typical heterogeneous Ziegler–Natta catalysts.^[114a]

The ¹³C NMR signals associated with occasional stereoerrors in the isotactic polymers produced by metallocene catalysts indicate that stereoregularity is controlled by the chirality of the metallocene catalyst and not by the asymmetry of the last inserted unit: Such “chain-end” control would give rise to the single-inversion pentad *mmrm* as a main error signal, since an occasionally inverted chain-end configuration would generally be followed by units of the same configuration. For this chain-end control one would expect an error pentad ratio close to *mmmr*:*mmrr*:*mmrm*:*mrrm* = 1:0:1:0. In fact, an error pentad distribution close to *mmmr*:*mmrr*:*mmrm*:*mrrm* = 2:2:0:1 is observed for these polymers (Scheme 10). As previously established for heterogeneous catalysts,^[12] this pentad pattern is expected when olefin insertion is indeed under “catalytic-site” control.^[105, 115] In this case, *r* dyads due to stereoinversions will occur in pairs, since a catalyst center of fixed chirality forces the enantiofacial orientation of subsequent olefin insertions to return to the previous preference immediately after an occasional mistake (Scheme 10).

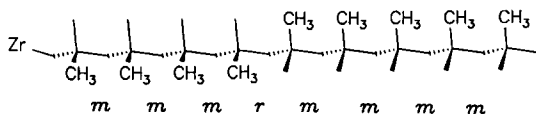
How the stereoselectivities of chiral catalysts depend on the structure of the complex, in particular on different bridging units and substituent patterns, has been the subject of comparative studies in several research groups.^[116–120] In investigations of this kind, it is crucial to take into account the polymerization temperature *T_p*.^[121] Even an unbridged metallocene catalyst with unsubstituted ring ligands, Cp₂TiPh₂/MAO, has been

Catalytic-site control



$$mmmr : \underline{mmrr} : mmrm : \underline{mrrm} = 2 : 2 : 0 : 1$$

Chain-end control



$$mmmr : mmrr : \underline{mmrm} : \underline{mrrm} = 1 : 0 : 1 : 0$$

Scheme 10. Pentad distributions of stereoregions in isotactic polypropylene characteristic for catalytic-site stereocontrol (top; see also insert in Fig. 4) and for chain-end stereocontrol (bottom).

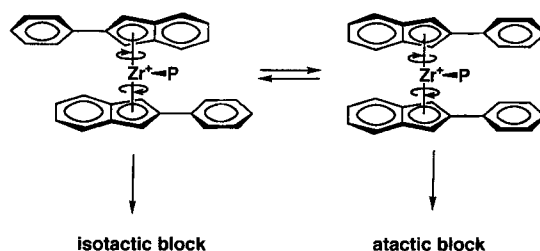
shown by Ewen^[105] to yield partially isotactic polypropylene with $[mmmm] \approx 0.5$ at temperatures below -40°C . In this case, the nearly equal intensities of the $mmmr$ and $mmrm$ pentad signals indicate a chain-end control mechanism.^[105, 122]

Similar observations were reported by Erker and co-workers^[123] for unbridged zirconocenes with substituents containing an asymmetric C atom; these were found to give isotactic polymers with $[mmmm] \approx 0.4\text{--}0.8$ at polymerization temperatures of -50°C or lower. This partial control by the configuration of the last inserted unit over the stereochemistry of the next olefin insertion is almost completely lost at ambient temperatures. Apparently, insufficiently restricted rotations of the C_5 ring ligands and their substituents and the increasing conformational mobility of the growing polymer chain abolish this stereocontrol mechanism at ambient temperatures.

An unbridged, chiral zirconocene that produces an isotactic polymer even at $T_p = 60^\circ\text{C}$ was described by Razavi and Atwood.^[124] MAO-activated (1-methylfluorenyl) $_2\text{ZrCl}_2$ generates polypropylene with $[mmmm] = 0.83$ and a catalytic site controlled pentad distribution. The fluorenyl ligands of this complex are chirally disposed, due to their methyl substituents, and apparently so strongly hindered in their mutual rotation that the enantiomers of this complex are not interconverted during the growth of a polymer chain.

Waymouth and co-workers recently reported on an unbridged metallocene catalyst, (2-phenylindenyl) $_2\text{ZrCl}_2$ /MAO, which appears to isomerize, by restricted rotation of its indenyl ligands, between chiral and achiral coordination geometries during chain growth; this catalyst yields a highly stretchable atactic-isotactic stereoblock polypropylene with elastomeric properties (Scheme 11).^[125]

A short interannular bridge will necessarily restrict rotation of the C_5 ring ligands. Accordingly, high stereoselectivities are found for all chirally substituted *ansa*-metallocene catalysts with one-atom or two-atom bridges,^[116–120] at least at lower polymerization temperatures. At temperatures of $50\text{--}70^\circ\text{C}$, typical for technical polymerizations, stereoselectivities are of-



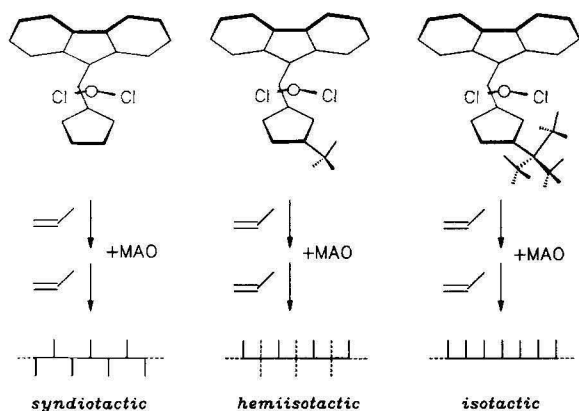
Scheme 11. Reversible isomerization of an unbridged zirconocene catalyst between chiral and achiral geometries found by Waymouth and co-workers [125] to yield isotactic and atactic blocks alternating along each polymer chain. The resulting polypropylene is an elastomer.

ten substantially decreased. Incorporation of the ethylene bridge of (en)(ind) $_2\text{ZrCl}_2$ (which can fluctuate between δ and λ chelate ring conformers^[126a]) into a carbocyclic system^[127] or its replacement by a one-atom silanediyl or germanediyl bridge^[114b, 116c, 117b] increases stereoselectivities, but only to a limited extent.^[117g] Even in metallocenes with a short Me_2Si bridge, the ZrX_2 and ligand framework moieties appear to retain substantial degrees of mobility.^[126b] Molecular mechanics studies indicate that much of this mobility is restricted by substituents placed in α -position to the bridgehead atom.^[126b] Chirally substituted *ansa*-zirconocene catalysts with $\alpha\text{-CH}_3$ groups at each C_5 ring do indeed show increased stereoselectivities.^[118–120]

Most interesting with respect to their effects on polymer stereoregularities, however, are the substituents in β -position to the bridgehead atom of an *ansa*-zirconocene. These β -substituents are in close proximity to the coordination sites at which the growing polymer chain and the α -olefin substrate are bound. In the chiral complexes (en)(ind) $_2\text{ZrCl}_2$, (en)(thind) $_2\text{ZrCl}_2$, and $\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2$, CH or CH_2 groups of the annelated C_6 ring function as β -substituents and flank each of the adjacent coordination sites. If the β -substituents are very bulky, as in $\text{Me}_2\text{Si}(2\text{-Me-4-}i\text{Bu-C}_5\text{H}_2)_2\text{ZrCl}_2$ ^[120a, b] or in Bercaw's $[\text{Me}_2\text{Si}(2\text{-SiMe}_3\text{-4-}i\text{tert-butyl-C}_5\text{H}_2)_2\text{YH}]_2$,^[144] or particularly protruding, as in Spaleck's $\text{Me}_2\text{Si}(2\text{-methyl-4-aryl-1-indenyl})_2\text{ZrCl}_2$,^[117b] polypropylenes with stereoregularities of $[mmmm] > 0.95$ are generated even at polymerization temperatures of $70\text{--}80^\circ\text{C}$.

Chiral *ansa*-zirconocene complexes with two identical ligand moieties have C_2 symmetry. Both coordination sites of such a C_2 -symmetric complex are thus equivalent; each is framed by the β -substituents in such a manner that olefin insertions at the Zr center occur with equal enantiofacial preference at both sites. *Unilateral* coverage of each coordination site is essential for this stereoselectivity; this is documented by the observation that atactic polypropylene is produced if both coordination sites are flanked by *two* β -substituents, as in $\text{C}_2\text{H}_4(3\text{-methyl-1-indenyl})_2\text{ZrCl}_2$ /MAO or in its silyl-bridged analogue $\text{Me}_2\text{Si}(3\text{-methyl-1-indenyl})_2\text{ZrCl}_2$ /MAO.^[116c, 117h] The bilateral coverage of each coordination site in these complexes, by a CH and a CH_3 group, appears to render them indifferent with respect to the enantiofacial orientation of an entering olefin. The same result, production of essentially atactic polymers, was also observed for the *meso* isomers of each *ansa*-metallocene catalyst.^[105]

The relationship between the stereoselectivity of *ansa*-metallocene catalysts and the spatial disposition of their β -sub-



Scheme 12. Relationship between catalyst structure and stereoselectivity discovered by Ewen and co-workers [116d–h]. Syndiotactic polypropylene is produced by $\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(9\text{-fluorenyl})\text{ZrCl}_2/\text{MAO}$; introduction of a $\beta\text{-CH}_3$ group on the C_5 ring results in formation of hemiisotactic polymer in which every other repeat unit is randomly configured; introduction of a $\beta\text{-tert-butyl}$ group gives highly isotactic polypropylene.

stituents has been most elegantly utilized by Ewen and co-workers in a series of studies on Me_2C -bridged fluorenyl complexes (Scheme 12).^[116d–h] The complex $\text{Me}_2\text{C}(\text{Cp})(9\text{-fluorenyl})\text{-ZrCl}_2$, for example, is not a C_2 -symmetric but a C_s -symmetric structure with one unsubstituted C_5 ring ligand and, in its fluorenyl ligand, one C_5 ring ligand with two β -substituents.^[124b, c] In the presence of MAO or cationic activators this complex produces highly syndiotactic polypropylene.^[116d–g, 117d]

Syndiotactic polypropylene is ideally characterized by a ^{13}C NMR spectrum with a single *rrrr* pentad signal, as configurations alternate here from one repeat unit to the next.^[128] Ewen's syndiospecific catalyst provided this polypropylene isomer for the first time in substantial quantities, with stereoregularities of $[rrrr] > 0.9$ and with a pentad intensity distribution in accord with catalytic-site control.^[116d] The alternating enantiofacial orientation of subsequent olefin insertions, which gives rise to this particular tacticity, is undoubtedly due to the fact that the two coordination sites in this C_s -symmetric complex are no longer homotopic, as in a complex with C_2 symmetry, but enantiotopic.^[129c]

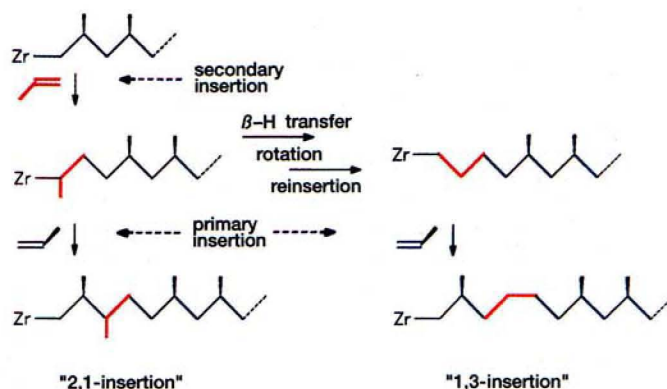
The correlation between the substituent pattern of a metallocene and the stereoregularity of its polymer products is further extended by Ewen's finding that still another polypropylene stereoisomer is formed with MAO-activated $\text{Me}_2\text{C}(3\text{-MeC}_5\text{H}_3)(9\text{-fluorenyl})\text{ZrCl}_2$.^[116e–g, 117d] This catalyst, with one coordination site framed by one β -substituent and one by two β -substituents (Scheme 12), produces hemiisotactic polypropylene^[129] in which every other repeat unit is of identical configuration while the remaining units are randomly configured. By totally blocking one of the coordination sites in the catalyst $\text{Me}_2\text{C}(3\text{-}t\text{BuC}_5\text{H}_3)(9\text{-fluorenyl})\text{ZrCl}_2/\text{MAO}$ with a *tert*-butyl group and a fluorenyl C_6 ring, while keeping the other site unilaterally framed by the other fluorenyl C_6 ring, Ewen and Elder finally obtained isotactic polypropylene again.^[116h]

The stereoselectivity of a C_2 -symmetric isotactic polymerization catalyst such as $\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2$ is practically independent of zirconocene and MAO concentrations^[131] and essentially unaffected even by the replacement of MAO by a borane or borate activator.^[116f, g, 132a, b] The C_s -symmetric syndiospecific catalyst $\text{Me}_2\text{C}(\text{Cp})(9\text{-fluorenyl})\text{ZrCl}_2/\text{MAO}$, how-

ever, behaves differently in this regard: its syndiotactic polymers show more frequent *rmrr* errors when either MAO or olefin concentrations are decreased.^[116e, f, 132a]

Ewen et al.^[116f] and Herfert and Fink^[132a] showed that this dependence must indeed result from a crucial requirement for syndiotactic polymerization: each olefin insertion has to occur at the coordination site opposite to the previous one. This requirement can only be met when the polymer chain remains at the coordination site of the previous olefin unit until the next olefin insertion occurs. Stereoerrors with single-*m* dyads must result whenever the polymer chain moves to the opposite coordination site before the next olefin inserts. Such an event^[133] will become more likely when the rate of olefin insertion is decreased by low olefin or MAO concentrations. Similar changes in the stereoregularity of hemiisotactic polypropylene, recently reported by Herfert and Fink^[132c] and by Farina and co-workers,^[129b] and of partly isotactic polypropylene obtained with several asymmetric catalysts,^[130] underscore the importance of the relative rates of olefin insertion and chain migration between coordination sites for these non- C_2 -symmetric metallocene catalysts.

While olefin insertion in metallocene-based homogeneous catalysts, as in heterogeneous Ziegler–Natta systems,^[10, 12] generally occurs with 1,2-regioselectivity so as to generate primary Zr–alkyl units, polyolefins produced with metallocene-based catalysts contain varying fractions of regioinverted units.^[114a, 135, 136] Depending on the polymerization temperature and on the metallocene catalyst used, one finds either head-to-head concatenations resulting from primary olefin insertion into regioinverted secondary Zr–alkyl units, or tetramethylene units (1,3-insertions). The latter arise from an isomerization of a secondary Zr–alkyl unit to one with a terminal Zr–alkyl bond prior to insertion of the next olefin^[114a, 136] (Scheme 13).



Scheme 13. Alternative sequences arising from a secondary olefin insertion [114a, 136]. A (relatively slow) primary insertion gives the tail-to-tail and head-to-head pattern typical of a 2,1-insertion; rearrangement of the secondary Zr–alkyl unit into its terminal isomer, followed by a primary insertion, yields a tetramethylene or 1,3-insertion unit.

Different zirconocene catalysts produce the regioirregularities in different ratios:^[69b] only 1,3-misinsertions (ca. 1%) are found in polymers made with $(\text{en})(\text{thind})_2\text{ZrCl}_2/\text{MAO}$; with $(\text{en})(\text{ind})_2\text{ZrCl}_2/\text{MAO}$ both types of misinsertions are present; and $\text{Me}_2\text{Si}(\text{ind})_2\text{ZrCl}_2/\text{MAO}$ forms polymers with only 2,1-misinsertions (ca. 0.6%) at 40 °C. With “fast” catalysts, misin-

sections are generally of the 2,1-type; slower catalysts produce mainly 1,3-misinsertions.^[117h, 120d] Effects of these misinsertions on catalyst activities will be considered in Section 3.3.

The irregularities introduced into a polypropene chain by 2,1- or 1,3-misinsertions decrease its melting point considerably (see Section 3.4); these misinsertions are thus of practical concern. Their frequency seems to depend mainly on the steric demands of the substituents on the C_5 ring. Rather frequent misinsertions are found for metallocenes with bulky β -substituents, while α -methyl substituents appear to suppress these regioirregularities.^[120a-c]

Steric relationships in a metallocene complex can be described by its "coordination-gap aperture", the largest possible angle spanned by two planes through the metal center which touch the van der Waals surfaces of the β -substituents at the C_5 ring ligands, and by its "lateral extension angle", which is limited by the two α -substituents protruding into the coordination gap (Fig. 5).^[137a]

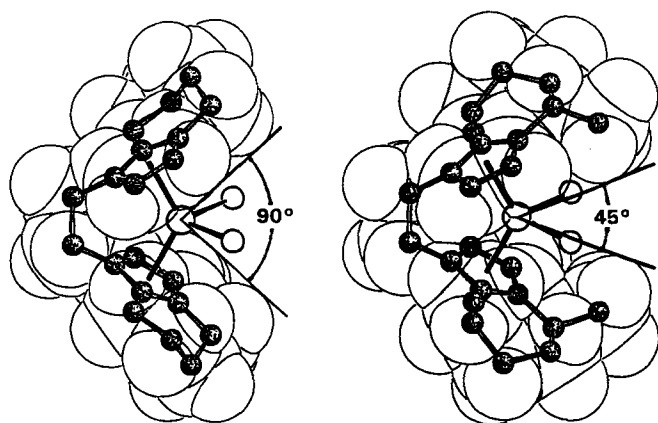


Fig. 5. Right: Narrow coordination gap aperture [137] of $rac\text{-}C_2H_4(4,7\text{-dimethyl-tetrahydroindenyl})_2ZrCl_2$ was found by Spaleck and co-workers [117i] to produce unusually large fractions (ca. 24%) of 1,3-misinsertions (molecular model). Left: Crystal structure of unsubstituted $rac\text{-}C_2H_4(tetrahydroindenyl)_2ZrCl_2$ [103] for comparison (see Fig. 3).

A secondary olefin insertion (2,1-insertion) is expected—due to the lateral orientation of the olefin substituent—to require less space in the aperture direction but more space in the lateral direction than a regular 1,2-insertion. Regioversions are thus favored by those zirconocene catalysts whose β -substituents strongly limit the gap aperture, provided that the lateral extension angle is not restricted also by α -substituents protruding into the coordination gap.^[137b,c] Polypropene with an unusually high fraction of 1,3-misinsertions has been reported by Spaleck and co-workers^[117i] to arise from the catalyst $C_2H_4(4,7\text{-dimethyl-thind})_2ZrCl_2/MAO$, whose *endo*-oriented 4-methyl groups severely restrict the coordination gap aperture (Fig. 5).

3.2. Mechanisms of Stereochemical Control

The mechanisms by which chiral *ansa*-metallocenes control the stereochemistry of polymer growth are reasonably well-understood today. As usual, stereochemical analysis affords more reliable information on a reaction mechanism than most other

methods. This analysis is simplified, furthermore, by the observation that the stereoregularity of isotactic polymers is rather insensitive to MAO or zirconocene concentrations^[120c, 132a] (see, however, ref. [131]) and even to the type of activator used to generate the reactive cationic species.^[116f, g, 132b, 151b]

First important clues as to the factors governing the stereoselectivity of C_2 -symmetric, chiral metallocene catalysts came from ^{13}C NMR studies of Zambelli and co-workers. These authors followed the course of propene and 1-butene insertions into ^{13}C -enriched CH_3 and CH_2CH_3 end groups, which were introduced into a MAO-activated $(en)(ind)_2TiMe_2$ catalyst by alkyl exchange with $Al(^{13}CH_3)_3$ or $Al(^{13}CH_2CH_3)_3$.^[138] The results of these studies can be summarized as follows:

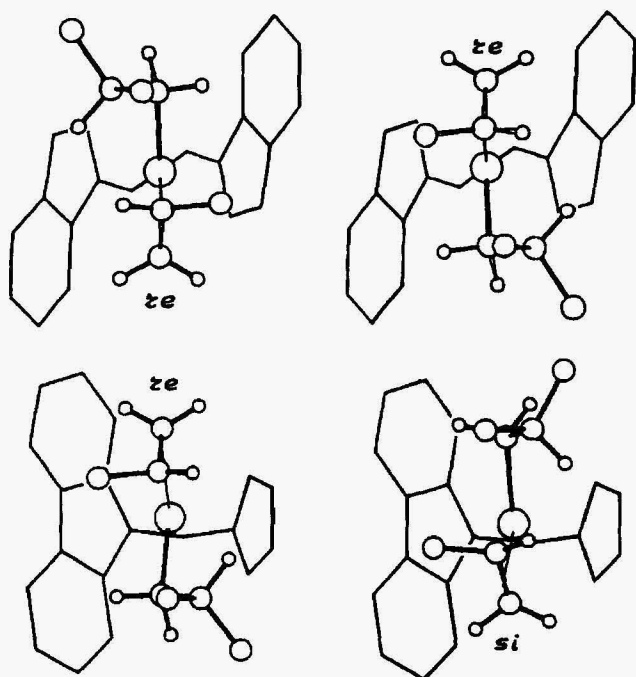
1. Propene inserts into $(en)(ind)_2Ti\text{-}^{13}CH_3$ bonds without significant stereoselectivity, as shown by signals of diastereomeric end groups with almost equal intensity.
2. Butene insertion into $(en)(ind)_2Ti\text{-}^{13}CH_3$ bonds occurs with slight (2:1) selectivity.
3. Complete stereoselectivity prevails when either propene or butene inserts into $(en)(ind)_2Ti\text{-}^{13}CH_2CH_3$ bonds.
4. All these results resemble those obtained before with analogously activated heterogeneous polymerization catalyst systems.^[112]

Efficient control of the chiral catalyst over the enantiofacial orientation of the entering olefin is thus clearly contingent on the presence of a metal-alkyl segment with at least two C atoms. This segment appears to act as a sort of lever in transmitting the effects of the β -substituents on the orientation of the prochiral α -olefin.

The nature of this stereocontrol mechanism was clarified by molecular mechanics calculations by Corradini, Guerra, and co-workers.^[139] As previously proposed for heterogeneous Ziegler-Natta catalysis,^[12b] repulsive interactions were shown to force an olefin into that enantiofacial approach to the metal-alkyl unit which places the olefin substituent *trans* to (i.e. away from) the β -C atom of the metal-bound alkyl chain. The metal-alkyl chain, in turn, was proposed to favor an orientation in which its $C(\alpha)\text{-}C(\beta)$ segment is in the most open sector of the chiral *ansa*-metallocene ligand framework (Scheme 14). Subsequent model studies in other groups by means of more elaborate force field and ab initio methods^[85, 86] support this proposal.

Analogous considerations hold for stereocontrol mechanisms for *ansa*-metallocene derivatives that produce syndiotactic and hemiisotactic polymers.^[116e-g, 139e, g-i, 140] In each case, the $C(\alpha)\text{-}C(\beta)$ segment of the polymer chain appears to orient itself so as to avoid interaction with the C_5 ring substituents in β -position adjacent to its coordination site (Scheme 15); an entering olefin is then forced into that orientation in which the two alkyl substituents at the incipient $C\cdots C$ bond are *trans* to each other.^[141]

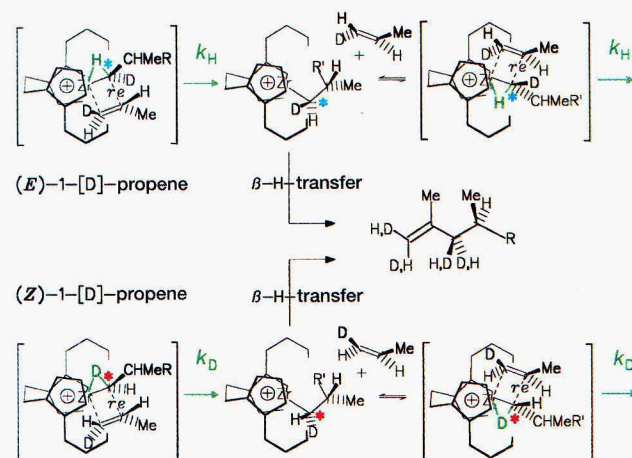
Experimental proof for this catalytic-site control by means of chain-segment orientation was provided by Pino and co-workers.^[142] Chiral hydrotrimers and hydrotetramers with the predicted absolute configurations were obtained when propene was hydrooligomerized^[143a] with enantiomerically pure^[103, 125] $(en)(thind)_2ZrMe_2$ activated by MAO in the presence of H_2 . Formation of asymmetric oligomers with olefinic end groups in similar reaction systems without H_2 were studied by Kaminsky and co-workers^[143b] and found to follow the same rules.



Scheme 14. Models for the stereocontrol of olefin insertions in *ansa*-zirconocene catalysts, proposed by Corradini, Guerra, and co-workers [139]. The growing alkyl chain occupies an open sector of the ligand framework; the olefin enters the reaction complex with its substituent *trans* to the C(α)–C(β) chain segment. For C_2 -symmetric complexes identical enantiofacial olefin orientation at both coordination sites results in isotactic polymer formation (top); for C_s -symmetric complexes the enantiofacial orientation alternates between coordination sites and leads to syndiotactic polymers (bottom).

The origin of stereoselectivity in *ansa*-metallocene catalysts was further examined by use of α -deuterated olefins. In studies similar to those previously reported for achiral zirconocene and scandocene catalyst systems,^[80, 82] stereokinetic isotope effects of $k_H/k_D \approx 1.4$ were observed for hydrodimerization of (*E*)- and (*Z*)-1-[D₁]-1-hexene by chiral *ansa*-zirconocene and scandocene catalyst systems.^[144–146] This indicates that the insertion reaction favors a transition state in which the α -H and not the α -D atom of initially formed Zr–CHD–R unit is in a position suitable for α -agostic interaction with the metal center. Recently stereokinetic isotope effects of $k_H/k_D \approx 1.3$ were determined directly for isotactic propene polymerizations catalyzed by (en)(thind)₂ZrCl₂/MAO and other chiral *ansa*-zirconocene catalysts from the mean chain lengths of polymers produced from either (*E*)- or (*Z*)-1-[D₁]-propene (Scheme 15).^[145b] These results indicate that α -agostic interactions control the stability of alternative transition states for the insertion of an olefin into a metal–alkyl bond.

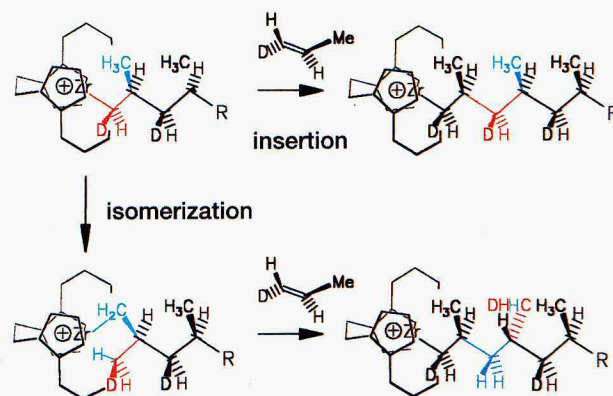
These α -agostic interactions can thus be considered to be the origin of the stereoselectivity of chiral *ansa*-metallocene catalysts. Of the two alternative Zr–C(α)–C(β) orientations resulting from binding one of the α -H atoms to the metal center, one orientation is sterically inaccessible since it would cause the growing chain to collide with a β -substituent of the chiral ligand framework; the other one is sterically unencumbered and in fact practically indistinguishable from that proposed by Corradini and co-workers^[139] on the basis of nonbonding van der Waals repulsions alone (see Scheme 14). The α -agostic model would thus describe the *re* or *si* orientation of an inserting olefin as



Scheme 15. Stereokinetic isotope effects in isotactic polypropene formation indicate α -agostic interactions in the olefin insertion transition state [145]. Chain growth with (*E*)-1-[D]-propene proceeds faster, due to its Zr \leftarrow H–C(α)-stabilized transition state, than that with (*Z*)-1-[D]-propene, which proceeds via a transition state with a Zr \leftarrow D–C(α) interaction; this is manifested in polymer chain lengths that are ca. 1.3 times longer for (*E*)- than for (*Z*)-1-[D]-propene.

being controlled by the required placement of the β -C atom of the growing chain in the more open of the two possible positions at a rigid three-membered Zr–H(α)–C(α) ring.

The exclusion of one of the possible Zr–H(α) interactions implied by this model raises questions as to the origin of the stereoerrors produced by homogeneous catalysts especially at higher reaction temperatures. Increased stereoerror frequencies at decreased olefin concentrations, recently observed by Cipullo and Busico, and by Resconi and co-workers,^[131] were ascribed to an epimerization of the last inserted unit, which competes with olefin insertion. Direct evidence for stereoerror formation by chain-end isomerization was obtained by Leclerc and Brintzinger from a study of D-label distributions in isotactic polypropene obtained from (*E*)- or (*Z*)-[D₁]-propene with chiral *ansa*-zirconocene catalysts.^[145b] The appearance of CH₂D instead of CH₃ groups in the *mrrm* stereoerror positions indicates that most of these errors arise from the isomerization represented in Scheme 16. *ansa*-Zirconocene catalysts with par-



Scheme 16. Formation of stereoerrors by chain-end isomerization [145]. Isolated (*mrrm*-framed) stereoerrors are associated with CH₂D instead of CH₃ groups in isotactic polypropene made from (*E*)- or (*Z*)-1-[D]-propene with (en)(thind)ZrCl₂/MAO. The stereoinverted CH₂D groups must originate from the α -CHD olefin terminus by an isomerization process, the exact mechanism of which is still being debated [131 a, b].

ticularly high stereoselectivity^[117h, i, 120b, d] thus appear to owe this property to their suppression of chain-end isomerization relative to olefin insertion.

3.3. Activities of *ansa*-Zirconocene Catalysts

The rate of a reaction is normally expected to decrease when it is made stereoselective by imposing steric restrictions on some of its possible reaction modes. Yet even the first studies on propene polymerization with the chiral *ansa*-zirconocene catalyst *rac*-(*en*)(*thin*)₂ZrCl₂/MAO showed its catalytic activity to be substantially higher than that of the stereochemically unselective, unsubstituted catalyst Cp₂ZrCl₂/MAO.^[106, 107g] Even the sterically strongly congested chiral catalyst *rac*-Me₂Si(2-Me-4-*t*Bu-C₅H₂)₂ZrCl₂/MAO produces polypropene at higher rates than Cp₂ZrCl₂/MAO system.^[120c]

Apparently, some favorable effects compensate for the steric congestion of a β -substituted *ansa*-metallocene. β -Substituents might favor formation of active, olefin-separated ion pairs at the expense of the presumably dormant contact ion pairs or, alternatively, facilitate access to an α -agostic insertion transition state by destabilizing the β -agostic interactions that otherwise compete.

With regard to the effects of different bridging units linking the C₅ ring ligands, one finds that zirconocenes with the one-atom bridge Me₂Si yield somewhat more active catalysts than otherwise comparable complexes with the two-atom bridge C₂H₄.^[116f, 117g] most likely because such a short bridge widens the coordination-gap aperture.^[137] Zirconocenes with three-atom or four-atom bridges have so far all been found to be practically inactive for propene polymerization in the presence of MAO.^[117b, 148–150a] The same is true for chiral zirconocenes containing two Me₂Si bridges.^[150b] Structural studies on these inactive complexes reveal that the geometrical constraints of their interannular bridges place at least one and, in some cases, two of the substituents on the C₅ ring in a central position close to the meridional centroid–Zr–centroid plane (Fig. 6). Substituents in this position appear to interfere with the course of the otherwise facile insertion of an α -olefin into the Zr-bound alkyl chain, most probably by colliding with the alkyl substituent of the olefin substrate, which has to be close to this meridional position in the insertion transition state. In accord with this view, these propene-inactive catalysts are generally found to be active in the polymerization of ethene, which is unobstructed by a substituent.^[117b, 150, 151a]

Different ring substituents also affect catalyst activities to a substantial degree. Low activities in MAO-activated propene polymerization are obtained with the *tert*-alkyl-substituted *ansa*-zirconocenes Me₂Si(2-Me-4-R-C₅H₂)₂ZrCl₂ with R = *tert*-butyl or 1-methyl-cyclohexyl.^[120c] A kinetic study by Fischer and Mülhaupt revealed, however, that these catalyst systems show even higher initial activities than some of the most productive bis(benzindenyl) catalysts, but differ from these by a very fast deactivation to rather low levels of residual steady-state activity.^[69d]

Annulation of further six-membered rings as in Me₂Si(benz[*e*]indenyl)₂ZrCl₂ results in three- to fourfold increases in productivity.^[117h, i, 120d] These high activities are likely to stem

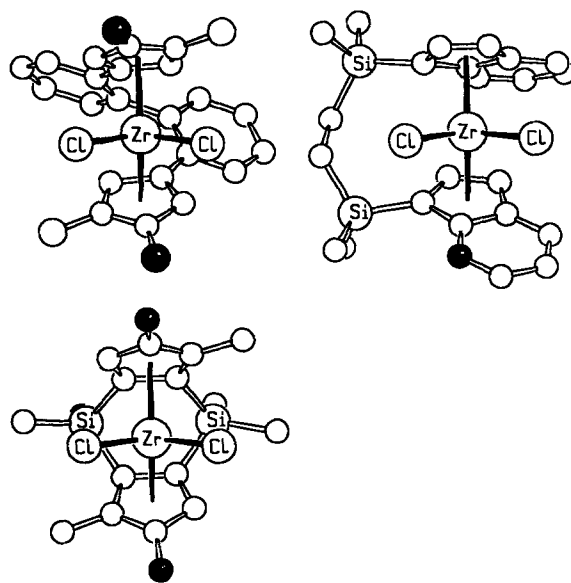


Fig. 6. Crystal structures of *ansa*-zirconocene complexes that are inactive for propene polymerization in the presence of MAO [117b, 150]. A substituent on the C₅ ring close to the meridional centroid–Zr–centroid plane appears to block the insertion of propene (but not that of ethene).

from steric or electronic shielding of the cationic reaction center against coordination of MAO-bound anions or other metallocene units by the extended annelated ring systems. Overall, little is known about the effects of electronic factors on catalyst activities.^[119b, 152]

Isospecific metallocene catalysts usually polymerize propene at rates four to five times slower than those for ethene.^[132a] This preference for ethene is less pronounced, however, than that observed with the unsubstituted system Cp₂ZrCl₂/MAO.^[39e, f] Ewen's C_s-symmetric, syndiospecific catalyst is unique in that it polymerizes propene with higher activity than ethene.^[132a] Higher α -olefins such as 1-butene^[106] and 1-hexene,^[50c] and even α -olefins branched at their 4-position such as 4-methyl-1-hexene^[152] are polymerized by *ansa*-metallocene catalysts at rates only moderately lower than those for propene. The rather low degree of chemoselectivity of these catalysts is essential for their properties as copolymerization catalysts (cf. Section 4.1).

Studies with chiral olefins such as 4-methyl-1-hexene have shown that an enantiomeric catalyst center—both in homogeneous^[152] and in heterogeneous catalyst systems^[153a]—tends to incorporate preferentially one of the olefin enantiomers into the growing polymer chain.^[153b, c]

With α -olefins branched in 3-position such as 3-methyl-1-pentene, *ansa*-zirconocene catalysts generally have negligible activities.^[154] Styrene, formally also an olefin branched in 3-position, has not yet been polymerized at any worthwhile rate by MAO-activated metallocene catalysts.^[36] The CpTiR₃/MAO systems that catalyze this reaction^[7b] appear to polymerize styrene through a 2,1-concatenation, that is, by formation of secondary insertion products.^[138b, 155] Apparently, the regioselectivity of *ansa*-zirconocene-based polymerization catalysts for 1,2-insertions is incompatible with the preference of styrene for 2,1-insertion.

Occasional regioerrors appear to inhibit the polymerization of normal α -olefins by MAO-activated metallocene catalysts

significantly.^[114, 120, 136, 156, 157] Kashiwa, Tsutsui, and co-workers^[156] found that the rates of propene and butene polymerization by (en)(ind)₂ZrCl₂/MAO increase in the presence of H₂ roughly 10- and 60-fold, respectively. These polymers were found to be free of misinserted units; hydrogenolysis apparently eliminates the slowly inserting 2,1-units and allows the start of a new, fast-growing polymer chain.

Busico, Cipullo, and Corradini^[157] determined the frequency with which oligomers having primary and secondary end groups are liberated from zirconocene centers by hydrogenolysis in propene hydrooligomerization catalyzed by (en)(ind)₂ZrCl₂/MAO. Their data indicate that insertion of propene into a secondary Zr-alkyl unit is about 100 times slower than into a primary one.^[158] As a consequence, 2,1-insertions with an incidence frequency of only 1 % are sufficient to tie up about 90 % of the catalyst in secondary Zr-alkyl units when polymerizations are conducted in the absence of H₂. Based on Busico's estimate, substantially increased activities can be expected for a catalyst that would be unimpeded by occasional 2,1-misinsertions.

Activities of chiral zirconocene catalysts are also affected by MAO concentrations. Increasing activation occurs at Al:Zr ratios of up to roughly 1–5000:1, while inhibition is observed at still higher Al:Zr ratios.^[75, 132a] For propene polymerization with (en)(thind)₂ZrCl₂/MAO,^[106, 116b] Me₂Si(ind)₂ZrCl₂/MAO,^[116c, 117c] or Me₂C(Cp)(9-fluorenyl)ZrCl₂/MAO activity maxima are found at Al:Zr ratios between about 1000:1 and 10000:1.^[116d–f] Apparently, yet unknown types of equilibria interconnect a diversity of species in these reaction systems.

Puzzling is also the dependence of catalyst activities on the monomer concentration. In several recent studies^[69e, 120d, 132c] polymerization rates have been observed to increase more than linearly with olefin concentrations, for example, as [olefin]^{1.4–1.7}. Whether these observations indicate the participation of more than one olefin molecule in the insertion transition state^[76]—a notion diverging from most of the current thinking about this reaction—or whether they arise from the participation of a second olefin in another reaction step that augments the overall activity of the catalyst, such as reactivation following a 2,1-insertion,^[156, 157] remains to be clarified.

3.4. Polymer Chain Lengths and Crystallinity

Molecular weight is another property of polyolefins that is strongly influenced by the metallocene catalyst employed. Initial studies with (en)(ind)₂ZrCl₂/MAO and (en)(thind)₂ZrCl₂/MAO yielded polypropene with molecular weights ranging from $M_w \approx 50\,000 \text{ g mol}^{-1}$ at ambient polymerization temperatures down to $M_w \approx 10\,000 \text{ g mol}^{-1}$ at 60–70 °C.^[106, 112, 114, 116c, 117g] These molecular weights are almost two orders of magnitude higher than those of the atactic polypropene obtained under otherwise identical conditions with Cp₂ZrCl₂/MAO. This effect is probably due, at least in part, to an increased rate of chain propagation v_p for *ansa*-metallocene catalysts.^[117g] In addition to an increased v_p , β -substituents in these complexes might also cause a decreased rate of chain termination v_t , for example by sterically hindering the tertiary β -CH group of the growing chain in its approach to the Zr center. Bulky β -*tert*-butyl sub-

stituents as in Me₂Si(2-Me-4-*i*Bu-C₅H₂)₂ZrCl₂/MAO lead to rather low molecular weights at elevated temperatures.^[69b, 120a–c] A relatively high fraction of isopropyl end groups indicates that chain growth is frequently terminated here by transfer of the polymer chain to an Al center, presumably of the trimethylaluminum component of the MAO cocatalyst.^[120c]

The molecular weights initially accessible with metallocene-based catalysts were far lower than those obtained with heterogeneous Ziegler–Natta catalysts. Higher molecular weight polymers were obtained with the analogous hafnium complexes (en)(ind)₂HfCl₂/MAO and (en)(thind)₂HfCl₂/MAO, albeit at the expense of substantially decreased catalytic activities.^[116b, c, 135] Further studies revealed that additional α -methyl substituents at each C₅ ring ligand increase molecular weights of the polymers produced by factors of 3 to 5.^[118, 120a–c] With α -methylated complexes such as Me₂Si(2-Me-ind)₂ZrCl₂ and Me₂Si(2-Me-benzind)₂ZrCl₂, polypropene can be obtained at $T_p = 50^\circ\text{C}$ with molecular weights of $M_w = 100\,000\text{--}400\,000 \text{ g mol}^{-1}$.^[117f, h, 120d] Polypropene with M_w close to $1\,000\,000 \text{ g mol}^{-1}$ is accessible with the catalyst Me₂Si(2-methyl-4-naphthyl-1-indenyl)₂ZrCl₂/MAO developed by Spaleck and co-workers.^[117h]

β -Hydride transfer from the growing polymer chain directly to a coordinated olefin (see Scheme 8) has been implied as a dominant chain termination process by studies on end-group distributions in ethene–propene copolymers^[97] and on hydrooligomer distributions at different olefin concentrations.^[157c] In *ansa*-zirconocene catalysts without α -methyl substituents, direct β -H transfer from the growing polymer chain to a coordinated olefin does indeed appear to predominate, as indicated by a near-constancy of molecular weights with increasing olefin concentration.^[120d, 157c] For *ansa*-metallocene catalysts with α -methyl substituents, however, a strong increase of molecular weight almost proportional to olefin concentration^[117h, 120d] indicates that the remaining chain termination arises almost exclusively from β -H transfer to the metal. α -Methyl substituents thus appear to block a relatively large fraction of chain terminations that would otherwise arise from β -H transfer directly to a coordinated olefin.

Narrow molecular weight distributions, as measured by polydispersity ratios of $M_w/M_n \approx 2$,^[105, 106, 112, 114, 117g, 118, 120] are as typical for these stereoregular polyolefins as for the atactic polymers produced with MAO-activated Cp₂ZrCl₂.^[39e, g] Substituted *ansa*-zirconocene catalysts thus also appear to induce the growth of their respective polymer products at a single type of active center.

A polydispersity of $M_w/M_n \approx 1$, which indicates a “living” polymerization system (i.e. polymer chains permanently attached to the metal centers on which they simultaneously start to grow),^[90] are typically observed for ring-opening metathesis^[159, 160] and group-transfer polymerization catalysts,^[161a, b] but so far not with either heterogeneous Ziegler–Natta catalysts or with zirconocene-based catalysts for normal α -olefin polymerization. Polymerization systems with a finite life span have been obtained with scandium-based metallocene catalysts.^[162] Their utilization for the formation of ethene–methacrylate block copolymers as well as partially living polymerizations of cycloolefins with zirconocene-based catalysts will be discussed

in Sections 4.1 and 4.2, respectively. Development of truly living α -olefin polymerization systems remains a challenge.^[162]

Stereoregularity, regioregularity, and chain length of a polypropylene all appear to influence its crystallinity as well as its melting behavior and mechanical properties. Heterogeneously produced isotactic polypropylenes normally crystallize in a regular packing of parallel helices, the classical α -modification.^[163] In contrast, isotactic polypropylenes produced by homogeneous, C_2 -symmetric *ansa*-zirconocene catalysts often crystallize from their melts with sizeable fractions of a heretofore infrequently observed^[164] γ -modification,^[114, 165–167b] which was found by Brückner and co-workers to contain alternate layers of helices oriented at an angle of 81° to each other.^[166] For a given polypropylene sample, the fraction of this γ -modification, as measured by wide-angle X-ray diffraction (WAXD), appears to be inversely related to the average length of isotactic chain segments, n_{iso} , if one takes into account that stereoerrors as well as regioinversions and chain ends limit the length of the isotactic segments.^[69b, d, 168]

Statistical factor analysis has been used to correlate the melting points of isotactic polypropylenes with the substituent patterns of the *ansa*-zirconocene catalysts used, without differentiating between effects of regio- and stereoerrors and chain lengths variation.^[169a] Melting points and total crystallinity both appear to be directly correlated with the average length of isotactic chain segments in these polyolefins.^[69d] A finite fraction of noncrystalline segments within each polypropylene chain appears to augment the toughness of the polymer materials.^[117c, 169b] These segments apparently function as flexible links between the crystalline polymer domains (Fig. 7).

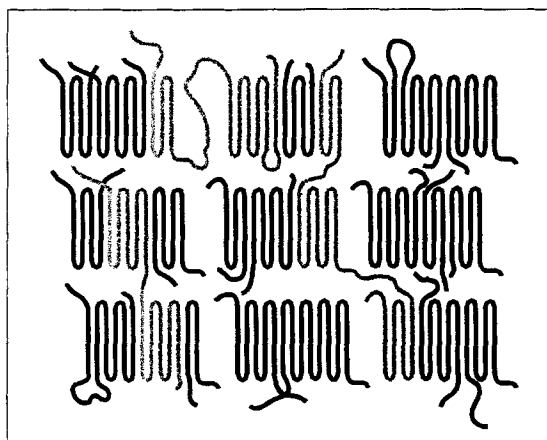


Fig. 7. Noncrystalline segments within longer polymer chains act as flexible links; they connect the crystalline polymer domains and render the polymer tougher (less brittle).

Several crystal modifications have now also been characterized for the syndiotactic polypropylenes formed with C_2 -symmetric metallocene catalysts.^[167c, 170–173] Their crystallinity appears to correlate again with the length of uninterrupted syndiotactic chain segments.^[174] A large proportion of an amorphous phase, together with a small crystallite size, appears to cause the high transparency of this material.^[169b] Syndiotactic polypropylene can slowly form highly crystalline solids with a melting point of about 160°C when kept just slightly below the

melting temperature.^[171b] Correlations between the structures of polyolefin materials produced with different homogeneous catalysts and their respective thermal, mechanical, and optical properties are presently being studied in more detail than can be accounted for within the limits of this review.^[167, 175]

4. Olefin Copolymerization and New Polyolefin Materials

While the development of homogeneous, chiral metallocene catalysts can be seen mainly as an opportunity for in-depth studies on the fundamental principles of stereoselective α -olefin polymerizations, two examples of homogeneously produced polymers encountered already, syndiotactic and hemiisotactic polyolefins, are inaccessible with heterogeneous Ziegler–Natta catalysts. In the following chapter, we summarize additional examples for the formation of polyolefin materials by homogeneous metallocene catalysts which extend beyond the capabilities of classical heterogeneous polymerization catalysts.

4.1. Copolymers from Ethene and Higher Olefins

Olefin copolymers, especially those of ethene with propene and/or another α -olefin, are of great practical interest; their total production volume is comparable to that of the homopolymers. New possibilities for controlling the properties of olefin copolymers with metallocene-based catalysts have recently caught the interest of industrial chemists and will thus be summarized here.

Linear polyethene with short-chain branches, which has low crystallinity and, hence, low density (linear low-density polyethene, LLDPE) is obtained by copolymerization of ethene with 1-butene, 1-hexene, and/or 1-octene.^[176] Its mechanical properties, which differ from those of the long-chain branched LDPE (low-density polyethene) produced by high-pressure radical polymerization, make LLDPE one of the largest volume polyolefin products. Copolymerization of propene with small amounts of ethene gives copolymers of lower crystallinity;^[177] increased fractions of ethene lead to amorphous materials with rubber-like elasticity (EP-rubbers). Blending of these EP-rubbers with the stiffer but brittle polypropylene yields heterophase materials with balanced toughness–stiffness properties which have opened new ranges of practical applications for these polyolefin blends.^[178, 179]

Mechanical, thermal, and optical properties of these copolymers obviously depend on their comonomer content; however, to a significant degree they also depend on the distribution of the comonomers between and within individual polymer chains. If a catalyst distributes the comonomers randomly along each chain, an amorphous polymer is to be expected, whereas partially crystalline polymers are likely to result when the monomers are collected into separate blocks.

The comonomer selectivity of a given catalyst, in other words its tendency to insert one of two competing monomers into each type of metal–chain-end bonds, is expressed by its copolymerization parameters r_1 and r_2 (the subscripts specify the monomer).^[176a, 180] These are defined as $r_i = k_{ii}/k_{ij}$, the ratio of

the rate constant for a homopolymerization step (k_{ii}) over that for a copolymerization step (k_{ij}).^[181, 182] The product $r_1 r_2$ is an indicator for the distribution of two monomers along each chain.^[176] Values of $r_1 r_2 > 1$ indicate that a catalyst tends to collect at least one of the comonomers into separate blocks, while a catalyst with $r_1 r_2 < 1$ tends to alternate isolated comonomer units along each chain.^[183]

Values of $r_1 r_2 > 1$ are typical for ethene-propene copolymers made with heterogeneous polymerization catalysts^[177b, 184b] (Table 1) and indicate that these catalysts tend to collect each

Table 1. Copolymerization parameters r_1 and r_2 for ethene and a second α -olefin. For heterogeneous catalysts (entries 1–3) values of $r_1 r_2 > 1$ indicate that the monomers are incorporated in blocks; for metallocene-based catalyst systems (entries 4–9), random or alternating monomer sequences are indicated by values of $r_1 r_2 \leq 1$.

Entry	Catalyst	r_1	r_2	$r_1 r_2$
1	δ -TiCl ₃ /AlEt ₃ [176c]	7.3	0.76 [a]	5.5
2	MgCl ₂ /TiCl ₄ /AlEt ₃ [184a]	–	– [a]	4
3	SiO ₂ /MgCl ₂ /TiCl ₄ /AlEt ₃ [184a]	5–10	0.2–0.34 [a]	1.9
4	(C ₅ H ₅) ₂ ZrCl ₂ /MAO [190]	48	0.015 [a]	0.72
5	C ₂ H ₄ (ind) ₂ ZrCl ₂ /MAO [194a]	2.57	0.39 [a]	1.0
6	C ₂ H ₄ (thind) ₂ ZrCl ₂ /MAO [194a]	2.90	0.28 [a]	0.81
7	Me ₂ C(Cp)(flu)ZrCl ₂ /MAO [197]	1.3	0.20 [a]	0.26
8	C ₂ H ₄ (thind) ₂ ZrCl ₂ /MAO [193]	59	0.012 [b]	0.71
9	Me ₂ Si(ind) ₂ ZrCl ₂ /MAO [193]	25	0.016 [b]	0.4

[a] Ethene/propene. [b] Ethene/1-hexene.

type of monomer into separate blocks. In addition, the nonuniform centers of heterogeneous polymerization catalysts have in general different copolymerization characteristics.^[6, 176b, 185] Analysis of the copolymer products by temperature-rising elution/fractionation (TREF) and cross-fractionation^[186] (Fig. 8) shows that the higher α -olefin is preferentially incorporated at the centers that produce shorter chains; higher olefins are thus enriched in the low molecular weight fractions of these copolymers.^[187] This increases the content of extractables and tends to make these materials sticky, two generally undesirable properties.

In their early studies on chiral, metallocene-based catalysts such as (en)(thind)₂ZrCl₂/MAO, Kaminsky and co-workers had noticed that these catalysts polymerize propene or 1-butene with only modestly lower rates than ethene.^[39c–h, 188] Accordingly, copolymers obtained with these catalysts contain larger fractions of higher olefins than those obtained with heterogeneous catalysts under comparable conditions.^[176, 177] These and additional studies,^[189–193] particularly by the groups of Zambelli,^[122, 136b] Chien,^[194] Soga,^[195] and Kashiwa,^[66, 97] showed that copolymers produced by metallocene-based catalysts consist of uniform chains with narrow molecular weight distributions typical of single-site catalysts. The copolymer chains contain the comonomers in nearly random placement,^[196] as indicated by copolymerization-factor products of $r_1 r_2 \approx 1$ (Table 1); their TREF characteristics (Fig. 8) show that comonomer distributions are essentially independent of chain lengths, an important aspect for applications of these copolymers, for instance in films or sealant layers.

The copolymerization characteristics of metallocene-based catalysts vary with the metallocene complex used.^[197] Higher

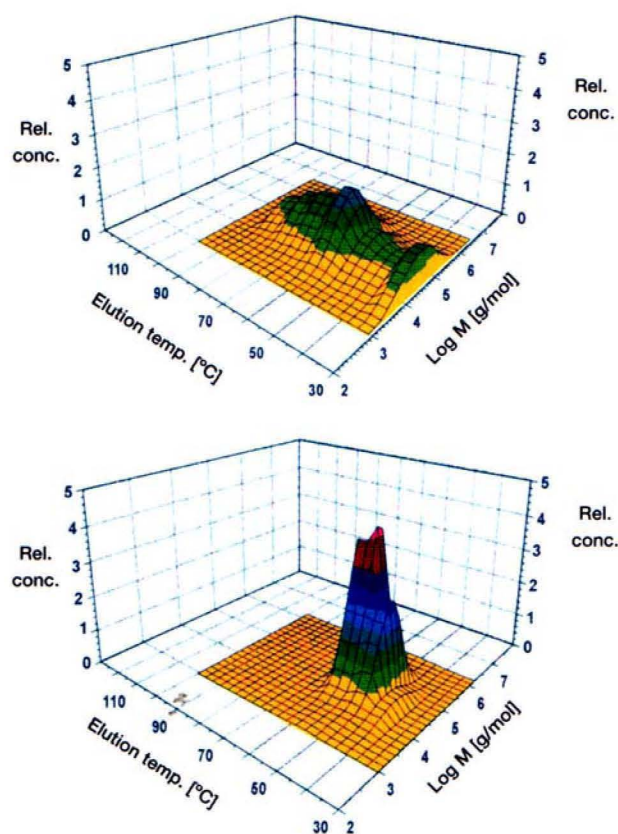


Fig. 8. Holtrup cross-fractionation of a conventional (top) and a metallocene-derived (bottom) ethene-butene random copolymer (LLDPE). Whereas LLDPE produced by classical heterogeneous catalysts contains a mixture of polymer chains with different composition and chain lengths, LLDPE produced by metallocene catalysts shows chemical uniformity and a very narrow molecular weight distribution.

α -olefins are taken up more readily by isospecific, chiral *ansa*-metallocenes than by unbridged complexes. An even greater tendency for the incorporation of higher α -olefins is evident for the syndiospecific catalyst Me₂C(Cp)(fluorenyl)ZrCl₂/MAO. This trend reflects the rising activities in this series of catalysts for the homopolymerization of higher α -olefins as compared to that of ethene.^[132a] But even monomers that are not homopolymerized by metallocene catalysts, for example isobutene,^[188f] styrene, and 1,3-dienes,^[188e, 191] are incorporated, albeit in minor amounts, into various copolymers.^[39c, 188, 189d, 191, 194d]

Even less restricted than the metallocene-based catalysts with regard to comonomer selection are monocyclopentadienyl complexes such as MAO-activated dimethylsilyl-bridged amidocyclopentadienyltitanium complexes.^[7a, 189c, 198] These catalysts (Fig. 9) incorporate into their polymer products even the vinylic end groups of polymer chains terminated by β -hydrogen transfer; they can thus generate copolymers with long-chain branches, in contrast to the strictly linear LLDPE copolymers produced by metallocene-based catalysts.^[189c, 198a] These catalysts can also copolymerize styrene with ethene;^[7a] styrene units in these copolymers are mostly isolated and of low regioregularity. Whether styrene-ethene and styrene-1,3-diene copolymers can be obtained also with the unbridged titanium system CpTiCl₃/MAO,^[199–201] which catalyzes the syndiotactic homopolymerization of styrene,^[7b] needs further clarification.^[202]

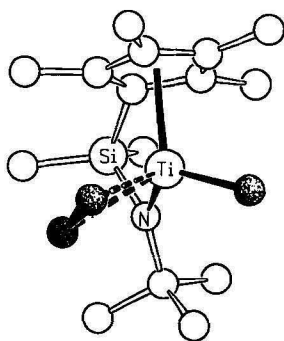
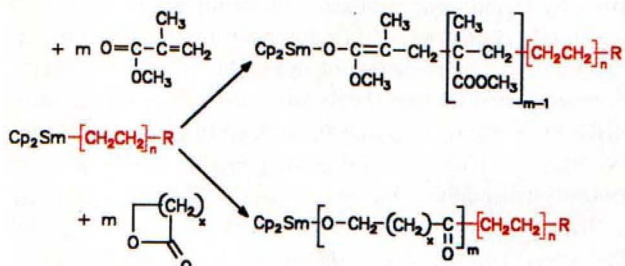


Fig. 9. Monocyclopentadienyltitanium complex with an Me_2Si -bridged alkyl-amido ligand framework [7a] which catalyzes, in the presence of MAO, formation of long-chain branched copolymers [198] (ab initio model for the C_2H_4 complex of $\text{Me}_2\text{Si}(\text{Me}_2\text{C}_3)(t\text{BuN})\text{Ti}-\text{CH}_3^+$ [87b, 88b]).

A long-standing goal in olefin polymerization catalysis is the copolymerization of ethene or propene with olefins bearing polar functional groups such as acrylate esters or vinyl ethers. Copolymers of this type might endow polyolefins with some of the useful properties of polyvinyl esters or ethers such as their adhesiveness. While most metallocene-based polymerization catalysts appear to be as sensitive to oxygen-containing functional groups as their heterogeneous predecessors, advances toward the goal of incorporating olefins with polar functional groups into Ziegler–Natta polymerization systems have recently been made and will be discussed in Section 4.3.

Living polymerizations, briefly mentioned in Section 3.4, would allow the formation of block copolymers, with polar olefins as well as with other alkenes. Advances in this regard—catalyst systems with polymer chains bound to the central metal atom for at least some minutes—have recently been reported. Ethene–propene block copolymers, prepared by Turner and Hlatky with cationic hafnocene catalysts at lower temperatures, indicate that Hf–polymer bonds have a finite lifetime at these temperatures.^[203] Yasuda and co-workers^[204] utilized the persistence of lanthanide–alkyl bonds^[62] to prepare ethene copolymers with polar polyacrylate or polyester blocks. They first polymerized ethene with a samarocene catalyst and used this system then to initiate the polymerization of the polar monomer by group-transfer polymerization or by ring-opening polymerization of a lactone (Scheme 17).



Scheme 17. Block copolymers from ethene and polar monomers obtained by Yasuda and co-workers [204] with a samarocene catalyst. A living Sm–polyethene system is utilized to initiate group-transfer or ring-opening polymerizations of unsaturated or cyclic esters.

Studies on ^{13}C NMR characteristics of ethene–propene copolymers have led to rather complete assignments of their repeat patterns and end group signals.^[97, 205] Isospecific *ansa*-zirconocene catalysts generate copolymers with mainly *m*-oriented side chains, as expected from their stereoselectivity.^[197] Studies

by Zambelli and co-workers on propene copolymers with ^{13}C -labeled ethene showed furthermore that the stereoselectivity of the catalyst system is undiminished by incorporation of ethene, thus proving that this stereoselectivity is indeed caused by the chirality of the metallocene centers and not by that of the last inserted monomer unit.^[122]

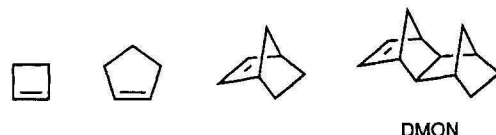
End group distributions in ethene–propene copolymers were studied by Kashiwa and co-workers by ^{13}C NMR spectroscopy.^[97] The strong prevalence of *n*-propyl ends and the near-absence of ethyl end groups were taken as evidence that chain termination occurs mainly by β -H transfer directly to a coordinated propene molecule rather than to the metal followed by monomer insertion into the Zr–H bond, as discussed in Section 2.4.

As with heterogeneous Ziegler–Natta catalysts,^[176b] a distinct comonomer effect is generally observed with MAO-activated zirconocenes.^[66, 182, 188, 206] Under otherwise identical conditions, the rate of copolymerization of ethene with higher α -olefins often exceeds that of the homopolymerization of ethene. This effect is difficult to reconcile with the fact that homopolymerization rates are higher for ethene than for other α -olefins and that ethene is always preferentially incorporated into the copolymer. It remains to be clarified whether these comonomer effects are due to increased rates of ethene insertion into a Zr– CH_2 –CHR- rather than into a Zr– CH_2 – CH_2 –polymer bond (e.g. by destabilization of a β -agostic resting state of the former^[26i, 63, 89, 120a]), to cooperative effects of both olefins (e.g. in insertion transition states involving two olefins^[76]), or simply to a higher solubility of a copolymer in the reaction medium^[206b] (which might allow for higher rates of diffusion of the monomers to the catalyst centers).

4.2. Cycloolefin Polymerization and Diolefin Cyclopolymerization

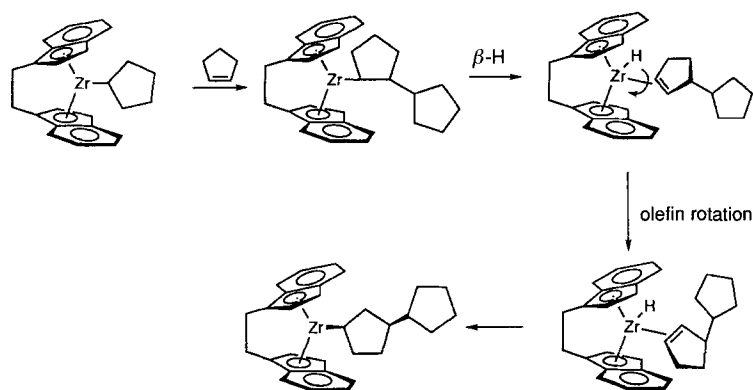
A distinctive property of homogeneous, metallocene-based polymerization catalysts is their capability to induce the polymerization of cyclic olefins without inducing ring-opening metathesis, which is characteristic of those heterogeneous Ziegler–Natta catalyst systems that polymerize cycloolefins.^[4a] As noted by Kaminsky and co-workers,^[207a] cyclobutene, cyclopentene, norbornene, and dimethanooctahydronaphthalene but not cyclohexene (Scheme 18) are polymerized with remarkably high activities by chiral *ansa*-zirconocene catalysts such as $(\text{en})(\text{ind})_2\text{ZrCl}_2/\text{MAO}$ and its Me_2Si -bridged analogue.

The homopolymers obtained from these reactions are highly crystalline with melting points around or above 400°C ,^[207] close to their respective decomposition temperatures. Structural assignments for these polymers are rendered difficult by their



Scheme 18. Cyclic olefins used by Kaminsky and co-workers [207] in ring-preserving polymerization reactions with $\text{rac}(\text{en})(\text{ind})_2\text{ZrCl}_2/\text{MAO}$ or $\text{rac}\text{-Me}_2\text{Si}(\text{ind})_2\text{-ZrCl}_2/\text{MAO}$.

insolubility in all common solvents. Instead of a 1,2-enchainment as originally proposed by Kaminsky and co-workers for polymers of cyclopentene,^[207b] a 1,3-enchainment was revealed in a recent study by Collins and Kelly^[208a] on the corresponding zirconocene/MAO-catalyzed hydrooligomerization. The mechanism proposed for this enchainment—1,2-insertion followed by β -H elimination, olefin rotation, and reinsertion—is analogous to that assumed to lead to the minor fraction of 1,3-inserted propene units in propene polymerization with these catalysts.^[114, 136a, b, 208b] Apparently, the intermediate derived from 1,2-insertion of cyclopentene is sterically too demanding to permit insertion of another cyclopentene and has to isomerize before another olefin inserts (Scheme 19). This system is an interesting example for an insertion–isomerization type of polymerization with metallocene-based catalysts.^[209]

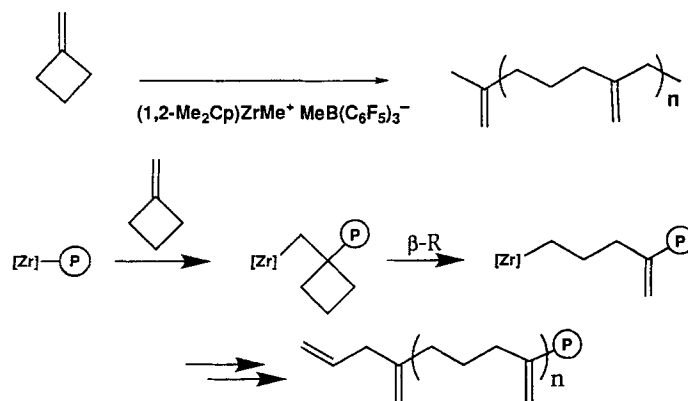


Scheme 19. Mechanism for the formation of 1,3-linked polycyclopentene proposed by Collins and co-workers [208].

The cycloolefin polymers prepared with chiral (en)(ind)₂-ZrCl₂/MAO as catalyst are undoubtedly stereoregular;^[208, 209] whether they have an isotactic structure like that of the other olefin polymers produced by this catalyst could not yet be established unequivocally.

Studies on the copolymerization of cyclic monomers with ethene or propene^[207, 210] showed that all of the cycloolefins mentioned above, as well as cycloheptene and cyclooctene, are incorporated into copolymers. While ethene is vastly more reactive than cyclopentene in the catalyst system (en)(ind)₂-ZrCl₂/MAO, with a comonomer selectivity factor of $r_1 = 80$ –300, norbornene is quite readily incorporated, with $r_1 = 1.5$ –3.2, such that a broad range of ethene/norbornene copolymers can be obtained with this system.^[207] The cycloolefin copolymers are mostly amorphous (rather than crystalline like the respective homopolymers) and have a relatively high glass transition temperature. A 1,2-enchainment, rather than a 1,3-enchainment has been determined for the copolymers of cyclopentene and ethene.^[207] Apparently, insertion of ethene is faster than isomerization of the cyclopentyl group at the zirconium center. In contrast to cyclopentene homopolymers, these copolymers are mostly amorphous; however, they often have relatively high glass transition temperatures.

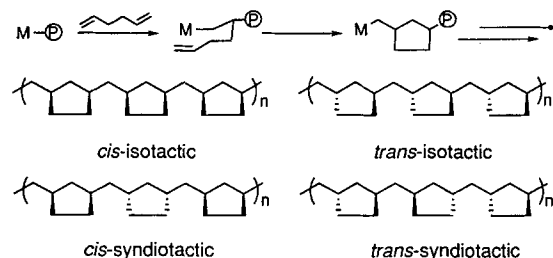
An interesting ring-opening polymerization, which contrasts the ring-preserving polymerizations of internal cycloolefins dis-



Scheme 20. Ring-opening polymerization of methylenecyclobutane reported by Marks and co-workers [211]. Ring-opening β -alkyl transfer appears to be faster than insertion of methylenecyclobutane into the sterically hindered cyclobutylmethyl–Zr bond.

cussed above, was recently reported by Marks and co-workers,^[211] who observed that polymerization of exomethylenecyclobutane by [(1,2-Me₂C₃H₃)₂-ZrMe⁺...MeB(C₆F₅)₃[–]] yields a polymer with mainly ring-opened 2-methylene-1-buten-4-yl rather than the expected 1-methylenecyclobutan-1-yl units (Scheme 20). Apparently, insertion of the disubstituted olefin into a Zr–alkyl unit with a quaternary β -C atom is so slow that rearrangement of the latter by β -alkyl transfer to give a secondary Zr–alkyl unit is the preferred process. Kinetic data indicate that insertion of the disubstituted olefin into the latter—rather than the β -alkyl transfer—still limits the overall rate of this process, which has turnover numbers of about 400 h^{–1} at 25 °C.

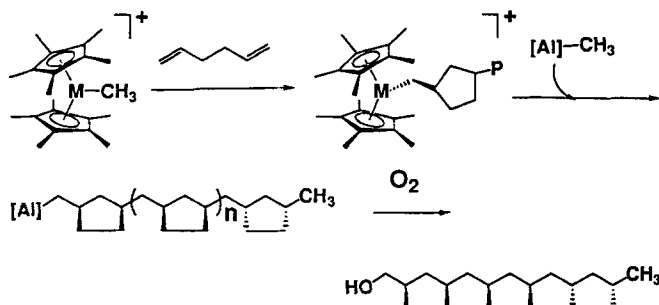
Another polymerization process that leads to 1,3-cycloalkanediyl units, connected this time by methylene groups, is the cyclopolymerization of nonconjugated dienes.^[93, 95b, 212–217] It involves 1,2-insertion of one of the vinyl functions into a metal–carbon bond followed by an intramolecular cyclization (Scheme 21). The microstructure of the resulting polymers concerns the *cis/trans* stereochemistry of the rings and the relative stereochemistry between rings. The latter, i.e. the tacticity of the polymer, is determined by the enantiofacial selectivity of the metallocene catalyst in the first insertion step; the *cis/trans* stereochemistry of the rings, on the other hand, arises from the diastereoselectivity of the cyclization step.



Scheme 21. Cyclopolymerization of nonconjugated dienes studied by Waymouth and co-workers [93, 95, 213–217]. The *trans*-isotactic form represents an effectively chiral polymer; polymers with substantial molar optical rotations are obtained with *R*- or *S*-(en)(thind)₂-ZrCl₂/MAO.

While the *cis/trans* diastereoselectivity can hardly be controlled with heterogeneous catalysts,^[212] it is strongly influenced by substituents at the cyclopentadienyl ligands in metallocene-based catalysts.^[93] Cyclopolymerization of 1,5-hexadiene by MAO-activated $(C_5H_5)_2MX_2$ ($M = Ti, Zr, Hf$; $X = Cl, CH_3$) leads to polymers containing predominantly *trans* rings, while cyclopolymerization with the more hindered catalyst $(C_5Me_5)_2MX_2/MAO$ yields predominantly *cis* rings.

The melting points of the resulting polymers proved to be quite sensitive to the *cis/trans* ratio of the carbocycles.^[213] *trans* Polymers are waxes with melting points $\leq 70^\circ C$; polymers containing $> 90\%$ *cis* rings are crystalline and melt at $189^\circ C$. Cyclopolymerization of unsymmetrical dienes such as 2-methyl-1,5-hexadiene with catalysts such as $Cp_2^*ZrMe_2/MAO$ or with $[Cp_2^*ZrMe^+ \cdots X^-]$ ($X = B(C_6F_5)_4$ or $H_3CB(C_6F_5)_3$) affords highly regioregular cyclopolymers.^[215] The perfectly alternating head-to-tail microstructure must arise from the regioselective insertion of the less hindered terminus of the diene into the metal–polymer bond, which is sterically encumbered by its quarternary β -C atom. Cyclization of the disubstituted olefin yields a methylene-1-methylcyclopentan-3-yl intermediate (Scheme 22). This insertion appears to be greatly facilitated by its intramolecular nature; intermolecular insertions of disubstituted olefins into Zr–alkyl bonds are at best quite sluggish.



Scheme 22. Hydroxy-terminated cyclopolymers formed by alkyl exchange with a methylaluminum activator [95b].

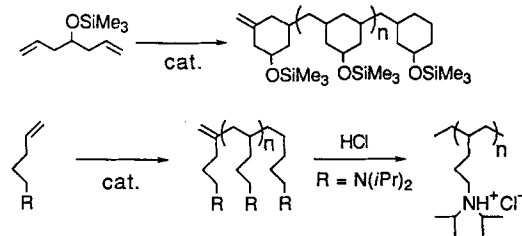
Cyclopolymerization of 1,5-hexadiene generates polymers with substantially higher molecular weights than polymerization of 1-hexene with the same catalysts,^[93] undoubtedly due to some hindrance of the β -H transfer that normally terminates growth of a polymer chain. For the cyclopolymerization of 1,5-hexadiene with a $Cp_2^*ZrCl_2/MAO$ catalyst at $-25^\circ C$, chain transfer to aluminum was found to be the only chain termination process.^[95b] The resulting poly(methylene–cyclopentane) was shown to bear an alkylaluminum end group, which could be oxidized with O_2 to give hydroxy-terminated polymers (Scheme 22). Cyclopolymerization of 2-methyl-1,5-hexadiene with the catalysts $[Cp_2^*ZrMe^+ \cdots X^-]$ ($X = B(C_6F_5)_4$ or $H_3CB(C_6F_5)_3$), for which neither β -H transfer nor chain transfer to aluminum are feasible, gave a polymer with end groups derived from a β - CH_3 transfer process.^[95b]

Although optically active olefin oligomers of low molecular weight can be obtained with enantiomerically pure *ansa*-metallocene catalysts,^[140, 141b, 143b] stereoregular polyolefins of high molecular weight contain an effective mirror plane perpendicu-

lar to the molecular axis in the middle of the molecule and are thus achiral.^[107c] Chiral polymers have now become available by metallocene-catalyzed cyclopolymerization of 1,5-hexadiene. Coates and Waymouth recognized that the *trans*-isotactic form of poly(methylene-1,3-cyclopentane) is chiral.^[213, 217] Using MAO-activated, resolved (1*R*)-(en)(thind)₂Zr–binaphtholate as a catalyst, they obtained optically active poly(methylene-1,3-cyclopentane) with a molar optical rotation of $[\Phi]_D^{20} = +51.0$ ($c = 0.8$ in $CHCl_3$). Cyclopolymerization with the (1*S*) enantiomer of the catalyst gave the enantiomeric polymer. Cyclopolymers of 1,5-hexadiene obtained with (en)(thind)₂Zr-derived catalysts contain a mixture of *cis* and *trans* rings. Despite the presence of roughly 32% *cis* rings, the molar optical rotation of the polymer ($[\Phi]_D^{20} = +22.8$) is considerably higher than that of the model compound *trans*-(1*R*,3*R*)-1,3-dimethylcyclopentane ($[\Phi]_D^{20} = +3.1$), presumably due to the presence of helical polymer conformations in solution. Interesting insights in this regard might come from X-ray diffraction studies on these chiral polymers. A ^{13}C NMR analysis of the microstructure of the polymer at tetrad resolution provided an estimate of 91% for the enantiofacial selectivity of this cyclopolymerization reaction.^[217]

4.3. Functionalized Polyolefins

Advances toward the goal of polymerizing polar monomers by Ziegler–Natta catalysis have recently been made with cationic metallocene catalysts. Waymouth and co-workers found that these catalysts are considerably more tolerant of functional groups than either conventional heterogeneous catalysts or homogeneous catalysts activated by MAO. Catalysts of the type $[Cp_2^*ZrMe^+ \cdots X^-]$ ($X^- = B(C_6F_5)_4^-$ or $H_3CB(C_6F_5)_3^-$) are indeed capable of polymerizing a variety of functionalized α -olefins and dienes such as 4-*tert*-butyldimethylsiloxy-1-pentene, 5-*N,N*-diisopropylamino-1-pentene, and 4-trimethylsiloxy-1,6-heptadiene^[218] (Scheme 23).



Scheme 23. Formation of polymers with O- or N-functional groups by use of borane-activated zirconocene catalysts reported by Waymouth and co-workers [218, 219]. $R = N(iPr)_2$, OTBDMS; cat = $[Cp_2^*ZrMe^+ MeB(C_6F_5)_3^-]$.

Activities for the polymerization of 4-*tert*-butyldimethylsiloxy- and 5-*N,N*-diisopropylamino-1-pentene by the catalyst $[(C_5Me_5)_2ZrMe^+ \cdots X^-]$ were lower than for 1-hexene, with average turnover numbers (at ca. 40–50% conversion) ranging from $2700\ h^{-1}$ for 1-hexene to $190\ h^{-1}$ for 4-*tert*-butyldimethylsiloxy-1-pentene and $130\ h^{-1}$ for 5-*N,N*-diisopropylamino-1-pentene. Chiral $[rac\text{-(en)(thind)}_2ZrMe^+ \cdots X^-]$ catalysts are active for the polymerization of 5-*N,N*-diisopropylamino-1-pentene, but not for that of 4-*tert*-butyldimethyl-

siloxo-1-pentene. Preliminary ^{13}C NMR analysis of poly-(5-*N,N*-diisopropylamino-1-pentene) obtained in this manner indicates an isotactic microstructure.^[219]

Another approach toward functionalized polyolefins is the generation of α -olefin polymers capped by polar end groups. Polymers of this kind are principally accessible through living polymerizations. Living polymers of α -olefins have been obtained so far only in rare instances, at low temperatures^[220, 221] (see Section 4.1). Complete transfer of polymer chains to aluminum centers of the cocatalyst, also useful for this purpose, has been observed in only one special case, again at temperatures below ambient.^[95b]

In contrast to heterogeneous polymerization catalysts, which afford shorter propene oligomers only in the presence of H_2 , that is, only with saturated chain ends, metallocene catalysts give easy access to propene oligomers with olefinic end groups, which can be converted to various other functional groups.^[222, 223] Thiol-terminated oligopropenes have been used as chain transfer reagents in methacrylate polymerization to form poly(propene-*block*-methylmethacrylate). A new class of polymers containing pendant polypropylene chains such as polymethylmethacrylate-*graft*-polypropylene is derived from methacrylate-terminated oligopropene macromonomers, which are copolymerized with various acrylic esters, acrylonitrile, or styrene.^[224a]

These polypropylene block and graft copolymers are efficient blend compatibilizers. By enhancing the dispersion of otherwise incompatible polymers and improving their interfacial adhesion, these copolymers allow the formation of "alloys" of isotactic polypropylene, for example, with styrene-acrylonitrile or polyamides.^[224b, c] Polymer blends of this type afford property synergisms such as improved stiffness combined with improved toughness. They are obtained by way of the short isotactic polypropylene chains with unsaturated end groups formed by the *ansa*-metallocene catalyst $\text{Me}_2\text{Si}(2\text{-Me-4-}i\text{Bu-C}_5\text{H}_2)_2\text{ZrCl}_2/\text{MAO}$.

5. Perspectives

The most remarkable aspect of metallocene-based catalysts appears to be that they can produce an unprecedented variety of polyolefins. The range of stereo- and regioregularities, molecular weights, and polydispersities of copolymers and cyclopolymer available with these catalysts exceeds that accessible with classical heterogeneous Ziegler–Natta catalysts and opens new possibilities for producing tailored polyolefin materials.

Much of our knowledge in this area has been acquired by application of rational conceptional models to the design of new metallocene structures and catalyst activators. Some traits of these catalysts, in particular their stereoselectivity, are now close to being predictable, based on our understanding of the essential elementary reaction steps in these homogeneous reaction systems. Other traits such as the formation of cyclic or functionalized polyolefins have been and continue to be discovered by testing our understanding of the basic reaction mechanisms of these catalysts against increasingly demanding tasks. This approach derives substantial support from the rapidly advancing methods for modeling even large metallocene reaction systems

by ab initio and density functional methods.^[84–88] These methods can also provide a calibration for useful molecular mechanics models for these catalysts,^[86, 139, 225] which may eventually allow estimates of steric effects on the course of essential reaction steps, for example on competing insertion and chain termination reactions.

The evolution of advanced catalysts and catalytic processes based on rational model hypotheses is now beginning to carry over to heterogeneous Ziegler–Natta catalysis as well. Practical application of metallocene catalysts requires their preadsorption on solid supports such as alumina or silica gels.^[189c, 200, 226–228] Instead of the polymer dust produced by a homogeneously dissolved metallocene catalyst, the solid catalyst particles generate coherent polymer grains.^[117e, 229] As with classical heterogeneous catalysts, these grains appear to be enlarged replicas of the catalyst particles^[117e, 228] (Fig. 10). Metallocene catalysts that are heterogenized, for example on a silica gel support, can thus be readily used in existing Ziegler–Natta production facilities, for instance in solvent-free slurry or gas-phase reaction systems.^[227, 228]

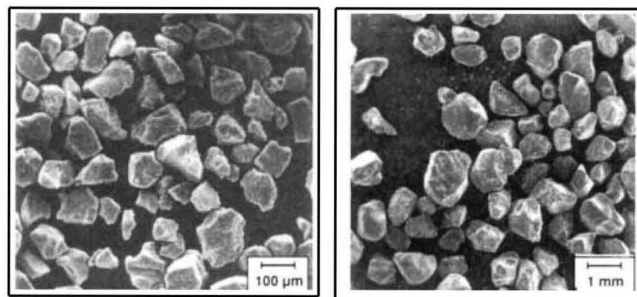


Fig. 10. Catalyst grains containing $\text{Me}_2\text{Si}(2\text{-Me-benz[e]indenyl})_2\text{ZrCl}_2/\text{MAO}$ on a silica gel support (left) and polymer grains grown on these in a gas-phase reactor at 70 °C (right, note different scale) [228].

Detailed guidelines have been developed for the selection of supports with optimal composition, particle size, pore size distribution, and surface OH group density, and for their treatment with various alkyl aluminum and aluminoxane activators^[227, 228] prior or subsequent to adsorption of the metallocene complex. The more advanced of these protocols require only limited excess ratios of alkylaluminum activators per zirconocene unit; Al:Zr ratios of roughly 100–400:1, much below those used for homogeneous catalyst systems, appear to give entirely satisfactory activities for these surface-supported metallocene catalysts.^[228, 230] In contrast to modern MgCl_2 -supported heterogeneous Ziegler–Natta catalysts, silica gel supported metallocene catalysts are practically free of chlorine. This could be an advantage from an ecological standpoint when the chemical or thermal recycling of polymer products reaches a larger scale.^[231]

Despite the practical advantages of supported catalysts, interactions between support materials and catalyst complexes are only partly understood on a molecular level. Based on the generally close resemblance of the polymer microstructures produced by a metallocene catalyst in homogeneous solutions and on solid supports, even in solvent-free gas phase systems,^[228, 232] it appears likely that the active catalysts are quite

similar, in other words that the (presumably cationic) metallocene catalyst is only physisorbed on the alkylaluminum-pre-treated (possibly anionic) catalyst surface. Based on this model, "microreactors" might be fabricated by immobilizing different types of single-site metallocene catalysts—or even catalyst cascades^[193]—on suitable supports for in situ production of novel polyolefin blends and other environmentally friendly polyolefin materials.

Polymers with properties distinctly different from those produced in homogeneous solution—with unusually high molecular weights—have recently been obtained by fixing a metallocene catalyst on unpretreated supports^[233] and by synthesizing covalently linked *ansa*-metallocenes directly on a SiO₂ support.^[234] These observations are probably connected with the site-isolation effects, that is, with the strict suppression of all binuclear reaction intermediates, known to arise from linking catalyst centers covalently to a solid support.^[235] If methods become available for a controlled synthesis of such covalently supported metallocenes and for their structural characterization, one could imagine another round of developments toward novel metallocene-based Ziegler–Natta catalysts that are heterogeneous, like their predecessors discovered forty years ago, yet endowed with wider process and product variability and with superior environmental properties.

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- [34] These "dormant" species might still be quite reactive, however, with regard to other important transformations, such as chain termination or catalyst deactivation reactions.
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