

Hafnocene-Based Olefin Polymerizations

T. Diesner, C. Troll, and B. Rieger

Abstract Zirconocenes have been used for a long time in the field of olefin polymerization using MAO as cocatalyst. The equivalent hafnocenes were seldom used due to a lack of productivity while using MAO activation. In the last few years borane and borate activation has come into the focus of research for olefin polymerization. A variety of different hafnocenes were used to investigate the polymerization mechanism and the different cocatalysts.

Differences in the polymer microstructures prepared with MAO and borate as cocatalysts are especially noted. While using TIBA/borate for building the active species, activities increase dramatically. Activities exceeded those of comparable Zr/MAO systems, obtaining high and ultrahigh molecular weight polypropylenes with molecular weights of up to 5,000,000 g mol⁻¹ and tacticities of 10–80% depending on the structure of the catalyst.

Keywords Borate activation, Hafnocene catalysts, Olefin polymerization, Ultrahigh M_w polyolefins

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1 Introduction

Propylene, a light olefin, is like ethylene one of the most important feedstocks for the petrochemical industry. In recent years the main way to obtain propylene and ethylene has been via cracking of naphtha. For this reason the cost of the corresponding polymers, mainly polypropylene and polyethylene, depends on the international oil price. One big challenge for modern chemistry is to look for an alternative production of feedstocks that is independent of the oil-industry.

Much research has been done, and in the last few years the production process of propene out of natural gas or coal via methanol (methanol-to-propylene, MTP) has become more important and is already commercially used. The following transformation of cheap, easily available propene into high molecular weight polypropylene with unique, tailor-made material properties is a research field with an enormous potential. The key to tailoring polymer properties such as stiffness, mechanical strength, or transparency is to control the molecular architecture. For the polymerization of olefins, the development of metallocene catalysts gave access to new polymer microstructures. One significant advantage in metallocene polymerization catalysis [1, 2] is that the polymer microstructures and the corresponding material properties can be easily designed by variation of the catalyst. This enables the production of metallocene-catalyzed polypropylene with various types and degrees of stereoregularity [1–4], from highly stereoregular isotactic or syndiotactic polypropylenes to amorphous or low crystalline ones.

An important step in the field of investigation of metallocenes was the design of zirconocene catalysts. These made it possible to produce polypropylenes with a great variation in tacticity [5]. Although the ligands of the catalysts were varied, the molecular weights mostly did not exceed $300,000 \text{ g mol}^{-1}$.

To reach high and ultrahigh molecular weight polypropylenes, investigation took place by exchanging zirconium by hafnium in isostructural complexes. Literature provides a few examples showing that this exchange of the central metal leads to up to a threefold increase in molecular weight. Unfortunately, the activity of the hafnium complexes was reported to be negligible compared to the zirconium analogs while using standard MAO (methylaluminoxane) activation [6]. Research work by Rieger et al. showed the same low activity for HfCl_2 complexes after MAO activation. The situation changed the first time that Rieger et al. activated a hafnium-dimethyl complex with trityl-tetrakis(pentafluorophenyl) borate. The activity increased to be equivalent to the zirconium complexes and even higher. For the first time it was possible to obtain polypropylenes with molecular weights up to $5,000,000 \text{ g mol}^{-1}$ and tacticities of 10–80%. Investigations during the following years showed that polypropylenes can be produced through hafnocene catalysts with high activities by using borate instead of MAO activation [5, 7].

In a time when prices for oil are continuously rising, hafnocene catalysts enable production of “high-tech” materials in a relatively cheap way. Hafnocenes are the key to a family of high and ultrahigh molecular weight polypropylenes whose material properties can be individually and simply varied. To help comprehend the importance

and the development of hafnocene catalysts in recent years, the following chapters show the function, polymerization mechanism, and the resulting polypropylenes of representative hafnocenes.

2 Catalyst Characterization

2.1 Overview

Collins et al. reported in 1995 that catalysts based on hafnium are desirable for the production of elastomeric polypropylene in that they polymerize propylene to a high molecular weight polymer and are indefinitely stable under typical polymerization conditions [8]. Based on the theory that hafnium as a catalytic center leads to a significant increase of molecular weight in propene polymerization compared with the zirconium-based catalyst, Rieger et al. searched for hafnocene systems to obtain polymers with new properties.

The exchange of zirconium in isostructural complexes leads to a new family of asymmetric metallocenes (Fig. 1) bearing a 2-methyl substituent and varied substituents in positions 5, 6, and 7 of the indenyl moiety. After borate activation all catalysts show an unexpected high and constant activity toward the polymerization of propylene and lead to significantly increased molecular weight products compared to the zirconocene species [9–11].

The explanation is based on the ability of these “dual-side” complexes to combine an isoselective side with one side leading predominantly to single stereoerrors within one particular species. This nonselective side can be exposed to migratory insertion reactions depending on the monomer concentration. This provides a new tool to control the amount and the distribution of single stereoerrors along an isotactic chain [5]. With catalyst **1**, depending on the reaction parameters, polypropylenes with tacticities of $17\% \leq [\text{mmmm}] \leq 34\%$ can be obtained with molecular weights up to $4.9 \times 10^6 \text{ g mol}^{-1}$.

To find more information about the influence of steric effects on the polymerization performance, catalyst **2** (5,6 triptycene indenyl hafnocene dichloride) was developed.

Besides the investigations into polymerization mechanisms and steric effects, a matter of particular interest was to extend the portfolio of material properties toward isotactic plastomers (higher stiffness materials). Therefore, hafnocene catalyst **3** (2-methyl-benzo-indeno [6,7] thiophen) bearing a substituted indenyl fragment derived from dibenzothiophene was synthesized. It was intended to look for other structural motifs that maintained the excellent performance of the asymmetric catalyst **1** but might afford higher tacticity values. Rigid substituents in the 6,7-positions of the 2-methylinden-1-yl fragment created a situation with a similar enantiofacial discrimination of the prochiral propylene monomer on either complex side in the migratory polyinsertion reaction [5, 10]. With the help of catalyst **3**, flexible

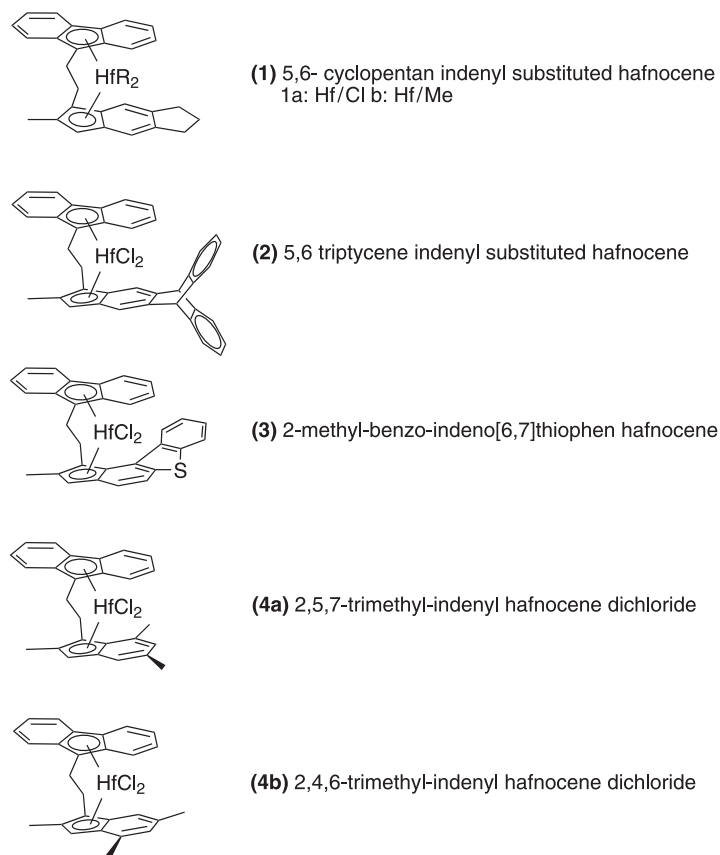


Fig. 1 Catalysts overview

polypropene plastomers with isotacticities in the range 65–85% and again ultrahigh molecular weights (up to $1.5 \times 10^6 \text{ g mol}^{-1}$) could be achieved [5, 10]. This nicely fills the gap between “soft” elastomers and stiffer polypropene plastomers.

Since plastomeric polypropylenes were insufficiently investigated, further improvement of catalyst activity correlated with an easy synthetic approach was required. Therefore, the two asymmetric hafnocene dichloride complexes, each bearing a 2,5,7- and 2,4,6-trimethyl substituted indenyl moiety (**4a**, **4b**) were developed.

2.2 Mechanism

In the early stages of the metallocene-catalyzed olefin polymerizations the focus of research lay on C_2 - and C_s -symmetric complexes [3, 12, 13]. Since the beginning of the 1990s C_1 -symmetric catalysts have had more and more impact. The reason is

based on the different substituted coordination sides of these systems, which allow creation of new and auspicious polymer structures.

By using the asymmetric titanocene $[\text{MeHC}(\text{Me}_4\text{-Cp})(\text{Ind})]\text{TiCl}_2$ (Fig. 2), Chien obtained the first elastic polypropene with a narrow molecular weight distribution [14–17].

Based on Chien's research results, Collins et al. modified the basic structure of the catalysts and also achieved elastic material [8, 18, 19]. In both cases the elastic properties of the polymers are justified in a block structure with isotactic and atactic sequences. In 1999 Rieger et al. presented a couple of asymmetric, highly active metallocene catalysts, e.g., the “dual-side” catalyst *rac*-[1-(9- η^5 -fluorenyl)-2-(5,6-cyclo-penta-2-methyl-1- η^5 -indenyl)ethane]zirconium dichloride (Fig. 3). These catalysts allowed building of isolated stereoregularities in the polymer chain to control the tacticity and therefore the material properties of the polymers [9].

2.2.1 C_2 Polymerization Mechanism

Looking at C_2 -symmetric catalysts, there exist in principle two different metallocene–olefin complexes (Fig. 4). Structure **a** is energetically favored because the methyl group of the propene is in *trans*-position relative to the β -methyl structure of the polymer chain. Both methyl groups in structure **b** are in *cis* position to each

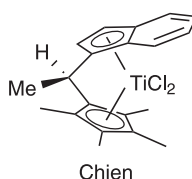


Fig. 2 C_1 -symmetric complex for synthesis of elastic polypropene

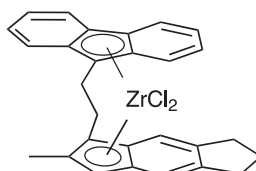


Fig. 3 “Dual-side” catalyst for variable material properties

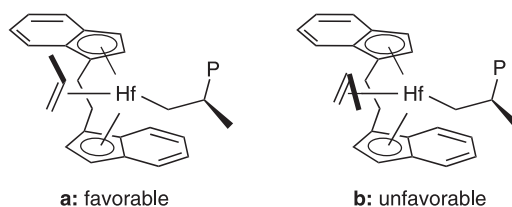


Fig. 4 Possible C_2 -symmetric metallocene complexes

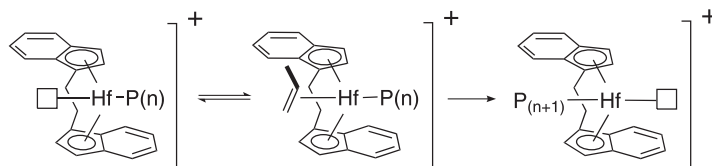


Fig. 5 Coordination cycle by C_2 -symmetric complexes

other, which is energetically unfavorable [1, 3, 20]. The coordinated monomer is therefore geometrically fixed. After the polymer changes place, a new monomer will find the same steric surrounding for insertion due to the C_2 symmetry of the complex. By repeating this coordination–insertion cycle an isotactic polymer structure will be achieved (Fig. 5).

2.2.2 “Chain Back” Polymerization Mechanism

The polymerization mechanism for the “dual-side” catalysts is totally different from the C_2 -symmetric complexes. Due to their geometry, the “dual-side” complexes show different stereoselectivities for monomer coordination and insertion. It was shown that the introduction of the stereoerror formation by the 5-substituted asymmetric catalysts originates predominately from the kinetic competition between chain back-skip and monomer coordination at the aspecific side of the catalyst [9].

As a consequence of the dependence of the polymer stereoregularity on monomer concentration and polymerization temperature, the mechanism shown in Fig. 6 was established.

Chien already postulated that C_1 -symmetric *ansa*-bridged complexes exist in two isomeric states, which interconvert during the course of the polymerization reaction [14, 15, 21, 22]. Different stereoselectivities for monomer coordination and insertion are found for the two coordination sites of the asymmetric metallocene catalysts (Fig. 6, **I** and **IV**). The migration of the polymer chain to the monomer, coordinated at the isoselective site (**I**→**II**), followed by a consecutive chain back-skip (at higher temperatures) to the sterically less hindered side (**II**→**III**) leads to isotactic [mmmm] sequences [11].

By the time the concentration of monomer is low, the back-skip of the polymer chain to the less-hindered site is faster than the formation of the high-energy alkene coordinated intermediate (**IV**). For this reason, at low propene concentrations and elevated temperatures isotactic sequences are formed. The probability of monomer coordination at the aspecific site (**IV**) is enhanced when the propene concentration increases. The consequence is that single stereoerrors [mrrm] are introduced in the isotactic polymer chain. ^{13}C -NMR was able to prove the mechanism because a

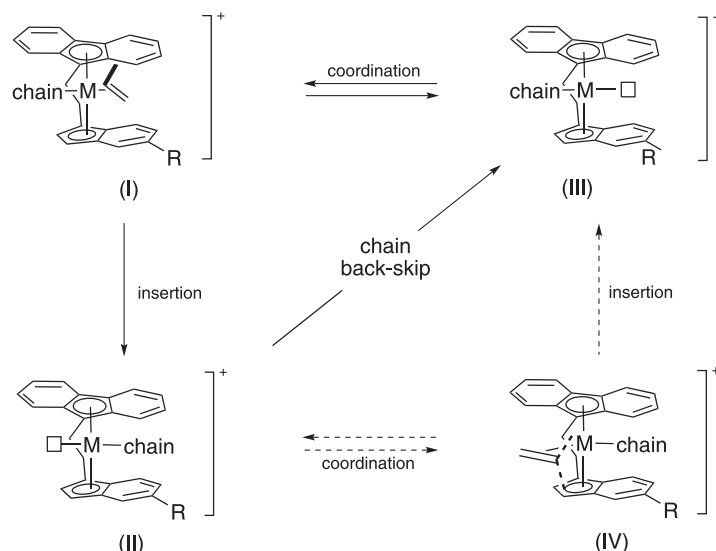


Fig. 6 Proposed mechanisms for the formation of isotactic polypropylenes **I-IV** with isolated stereoerrors obtained from C_1 -symmetric catalysts [9]

[mrmr] pentade would be observable from two consecutive misinsertions and is missing in the spectra derived from the latter polymers.

2.2.3 “ C_2 -Symmetric-Like” Polymerization Mechanism

A special case of the “chain back skip polymerization mechanism” and therefore an entirely different polymerization behavior was observed for differently substituted asymmetric complexes (for example catalyst **3**). Although asymmetric in structure, these catalysts follow the trend observed for C_2 -symmetric metallocenes [20]. Chien et al. [23] reported a similar behavior for *rac*-[1-(9- η^5 -fluorenyl)-2-(2,4,7-trimethyl-1- η^5 -indenyl)ethane]zirconium dichloride and attributed this difference in the stereoerror formation to the fact that both sides of the catalyst are stereoselective; thus isotactic polypropylene is obtained in the same manner as in the case of C_2 -symmetric metallocene catalysts.

In the case of catalyst **3**, the thiophene substitution in the 6,7 position controls the gap aperture between fluorenyl and indenyl ligands by repulsing steric interactions at the complex backside [10, 11]. This leads to increased stereoselectivities [9] and is responsible for a “ C_2 -symmetric-like” polymerization mechanism, characterized by increasing isotacticities when the polymerization temperature is reduced [5, 11] (Fig. 7).

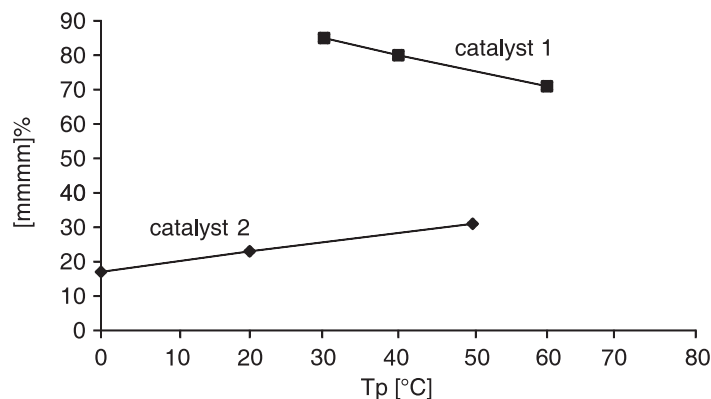


Fig. 7 Polypropylene stereoregularity versus polymerization temperature (catalyst **1**: chain back-skip mechanism, catalyst **2**: C_2 -symmetric-like mechanism) [11]

3 Cocatalysts

The key to highly active metallocene catalysts is the use of cocatalysts. In an activation step, the cocatalyst creates out of the metallocene a polymerization-active species. At first, methylaluminoxane (MAO) was usually used to activate metallocenes. Nowadays an alternative activation via borane and borate is becoming more and more important [20, 24, 25].

3.1 Methylaluminoxane (MAO)

Alkylaluminoxanes, oligomeric compounds consisting of $-Al(R)-O-$ subunits, have been known to be active for polymerization of monomers such as oxiranes since the early 1960s [26]. Methylaluminoxane $[-Al(Me)-O-]_n$ (MAO) prepared by controlled hydrolysis of $AlMe_3$ and typically having $n \approx 5-20$, affords highly active catalysts for polymerizing ethylene, propylene, and higher α -olefins when combined with group 4 metallocenes.

Although the structure of MAO was analyzed by different methods, such as IR and NMR spectroscopy, mass spectroscopy and lots more, the exact composition and structure of MAO are still not entirely clear or well-understood [27, 28]. It is assumed that the structures of MAO include one-dimensional linear chains, cyclic rings that contain trisubstituted Al centers, and three-dimensional clusters with tetracoordinated aluminum [24] (Fig. 8).

In metallocene-catalyzed polymerization reactions the active species is built through the reaction of a metallocene dichloride with the Lewis acid MAO. In the first step, a monomethyl-monochloro complex is formed and with an excess of MAO a dimethyl complex is created. In a fast equilibrium reaction through an

abstraction of a methyl group, the polymerization-active 14-valence electron cationic species $\text{Cp}_2\text{M}(\text{CH}_3)^+$ ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) is generated. $(\text{MAO}-\text{CH}_3)^-$ acts as soft coordinated counterion (Fig. 9).

In another slow balance reaction the active cation changes to an inactive dimeric species. This species is converted with the help of surplus MAO continuously back [29]. The transformation is connected with the property of alkylmetallocene cations, to react with a lot of CH-groups by elimination of CH_4 [30, 31].

As inactive species, a binuclear complex with a CH_3 bridge between the metal and Al center is existent (Fig. 10) [20]. For the regeneration of the binuclear inactive products to the active hafnocene cations, alkyl-exchange reactions are assumed between the $\text{M}-\text{CH}_2-\text{Al}$ - unit and MAO.

Therefore, the cocatalyst is expended by the building of $\text{Hf}-\text{CH}_3$ - and $\text{Al}-\text{CH}_2-\text{Al}$ - units and has to be used in a big overage to assure a high polymerization activity.

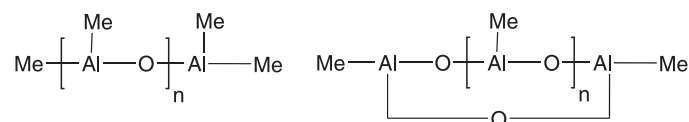


Fig. 8 Oligomer structures of MAO with $n = 5-20$ (linear/cyclic)

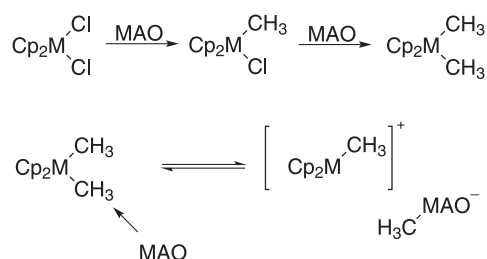


Fig. 9 Creation of the active species by MAO activation

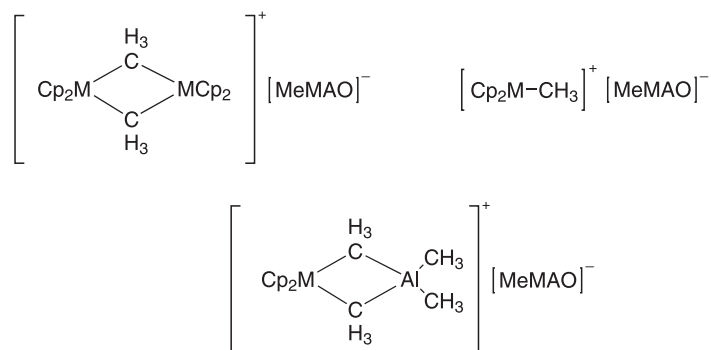


Fig. 10 Hypothetical products of the reaction between MAO and metallocene

3.2 Borane and Borate

An alternative to MAO activation is the formation of the active species via introduction of borate counterions by using borane or borate cocatalysts [32–34]. Relatively strong Lewis acidic organoboranes, such as $\text{B}(\text{C}_6\text{F}_5)_3$, or organoborates, such as $[\text{PhNMe}_2\text{H}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[\text{PH}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (Fig. 11) could be used. With the help of the activation with borate it was possible for the first time to isolate alkylzirconocene cations (e.g., $\{[(\text{CH}_3)_2\text{C}_5\text{H}_3]\text{ZrCH}_3\}^+ [\text{H}_3\text{CB}(\text{C}_6\text{F}_5)_3]^-$) and investigate them with single-crystal X-ray analysis [35, 36].

An advantage of borate activation is that the boron-containing substances are used in a 1:1 proportion, in contrast to MAO, which is used in overage. Landis was able to show with the help of kinetic research that all centers are activated in the case of borate activation, whereas in activation with MAO only a fraction exists in the active form [36].

A considerably higher polymerization activity is reached by using borate and borane. Furthermore, molecular weights increase because the chain termination (compared to MAO activation) via transfer to aluminum is not possible.

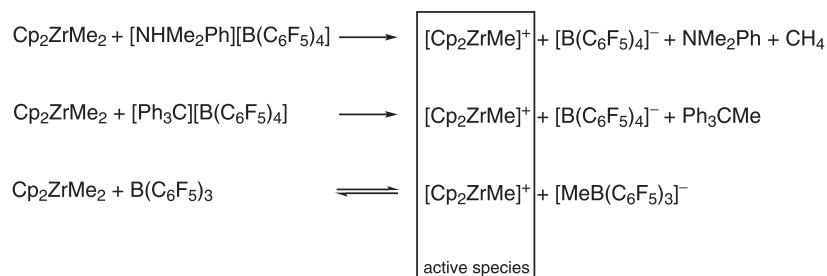


Fig. 11 Borate/borane activation

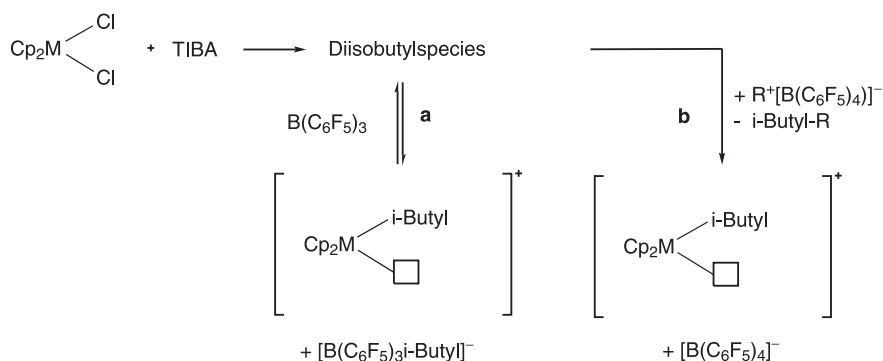


Fig. 12 “In situ” activation with borane (*a*) or borate (*b*)

A disadvantage of borane and borate systems is that the alkylmetallocene cations are more instable and more sensitive to impurities and water. To overcome this higher sensitivity, a dialkyl species can be build by an “in situ” reaction with triisobutylaluminum (TIBA). TIBA acts as alkylation reagent and as a scavenger and stabilizes the dialkyl species in solution; it is used as stock solution for the polymerization experiments (Fig. 12).

4 Polymerization Experiments

The synthesis of the catalysts **1**, **2**, **3** and **4** have ben reported previously [9–11, 25, 37].

4.1 Polymerization Procedure

The polymerization reactions were performed in a 0.5- or 1-L Büchi steel autoclave at constant pressure and temperature. The steel reactor was charged with 200–300 mL of toluene and with the desired amount of cocatalyst and hafnocene (MAO activation, entries 1 and 2, Table 1) or with the desired amount of preactivated catalyst solution (borate activation, entries 12–16, 19–21; Table 1). Subsequently, the polymerization temperature was adjusted and the reactor was charged with propene up to the desired pressure. For borate activation the cocatalyst solution was injected into the autoclave via a pressure burette. The monomer consumption was followed using a calibrated gas flow meter (Bronkhorst F111C-HA-33P) and the pressure was kept constantly during the entire polymerization period (Bronkhorst pressure controller F-111C-HAP-602C-EA-33P). Pressure, temperature, and monomer consumption were monitored and recorded online [38].

Some experiments (entries 3–10, 17, 18, 22–25; Table 1) were performed in liquid propene, which was condensed at $-10\text{ }^{\circ}\text{C}$ up to the desired volume in the autoclave. Using liquid propene, the catalyst and cocatalyst solutions were both injected into the autoclave via a pressure burette.

Both in liquid propene or in toluene the polymerization reactions were quenched with MeOH, and the polymer products were precipitated by pouring the toluene solution into an excess of MeOH. The product was filtered, washed with acidified methanol, and dried in vacuum at $60\text{ }^{\circ}\text{C}$ overnight [39].

4.2 Activities, Molecular Weights, and Stereoselectivity

The experimental data of the polymerization reactions of propylene performed with the hafnocene compounds **1–4** after MAO or $[(\text{C}_6\text{H}_5)_3\text{C}^+][(\text{C}_6\text{F}_5)_4\text{B}^-]$ activation are summarized in Table 1.

Table 1 Selected polymerization results obtained with the catalysts 1–4 after MAO or borate activation

Entry	Catalyst	Activator	T_p (°C)	$[C_3]$ (mol L ⁻¹)	Activity ^a (kg mol ⁻¹ h ⁻¹)	M_w (g mol ⁻¹)	M_w/M_n	[mmmm] (%)
1	1a	MAO	30	3.1	150	55,000	2	31
2		MAO	50	2.2	320	27,000	2.1	40
3	1b	Borate	0	C ₃ H ₆ (l)	6000	4,900,000	6.9	17
4		Borate	20	C ₃ H ₆ (l)	23,000	1,600,000	2.6	24
5		Borate	50	C ₃ H ₆ (l)	50,000	700,000	3.5	34
6	1a	TIBA (RT)/ borate	30	C ₃ H ₆ (l)	100,000	1,000,000	2.7	25
7		TIBA (60 °C)/ borate	30	C ₃ H ₆ (l)	350,000	1,300,000	2.6	27
8	2	Borate	30	C ₃ H ₆ (l)	1300	260,000	2.2	20
9		Borate	30	C ₃ H ₆ (l)	2400	300,000	2.5	19
10	3	Borate	30	C ₃ H ₆ (l)	15,900	254,000	2.6	77.7
11		Borate	0	C ₃ H ₆ (l)	5300	1,524,000	3.8	75.4
12	4a	Borate	30	2.1	80,000	200,000	2.8	76
13		Borate	30	2.9	138,000	350,000	2.4	74
14		Borate	30	3.9	166,000	380,000	2.9	72
15		Borate	40	2.4	151,000	130,000	2.5	78
16		Borate	50	1.9	214,000	50,000	2.6	82
17		Borate	10	C ₃ H ₆ (l)	39,000	960,000	3.3	63
18		Borate	40	C ₃ H ₆ (l)	321,000	300,000	3.2	72
19		Borate	20	4.2	50,000	360,000	2.9	60
20	4b	Borate	30	2.9	45,000	160,000	2.6	60
21		Borate	40	2.4	25,000	70,000	2.4	60
22		Borate	10	C ₃ H ₆ (l)	1500	600,000	2.6	48
23		Borate	20	C ₃ H ₆ (l)	21,500	500,000	3.8	47
24		Borate	30	C ₃ H ₆ (l)	6400	300,000	3.7	46
25		Borate	40	C ₃ H ₆ (l)	100	300,000	3	58

^akg PP per mmol Hf [C₃] per h

The asymmetric 5,6-cyclopentyl-substituted metallocene **1a**/MAO shows a very low activity in toluene solution (around 150–320 kg PP mol⁻¹ Hf h⁻¹). In addition, the molecular weight is quite low (entry 1, M_w 5.5 × 10⁴ g mol⁻¹). By increasing the temperature to 50 °C the activity more than doubled, but on the other hand the molecular weight decreased to 2.7 × 10⁴ g mol⁻¹ [5, 7, 11].

Compared to the previously studied complex **1a**/MAO, the catalyst **1b**/borate proved to be highly active (up to 50,000 kg PP mol⁻¹ Hf h⁻¹). The excellent catalytic performance of **1b**/borate is complemented by the high molecular weight of the polymer products. At 0 °C polymer chains with ultrahigh molecular weight (entry 3, M_w 4.9 × 10⁶ g mol⁻¹) are accessible. The broad molecular weight distribution results most likely from the insolubility of the ultrahigh molecular weight products in liquid propene at 0 °C [7].

Increasing the temperature leads to a decline of the molecular weight (e.g., entry 3, 20 °C, M_w 1.6×10^6 g mol⁻¹). However, even at technical process temperatures elastic homopolypropylenes with very high molecular weights (entry 9, 50 °C, M_w 7×10^5 g mol⁻¹) are produced. According to the data from Table 1, there was a strong influence of the polymerization temperature on the substituted catalyst **1b**, for which the isotacticity is increased from 17% (at 0 °C) to 34% (50 °C).

Incredibly increased activities could be observed using the in situ activation method for the catalyst **1a** (up to 350,000 kg PP mol⁻¹ Hf h⁻¹). The resulting polypropylenes have ultrahigh molecular weight (entries 6 and 7, M_w 1,000,000 g mol⁻¹) and tacticities round 25% (30 °C).

For further investigations on the influence of steric effects on the polymerization performance of dual-side catalysts, Rieger et al. examined the incorporation of the sterically demanding triptycene ligand in several bridged hafnocenes **2** (Table 1.) [25]. In comparison to the sterically less demanding 5,6-cyclopentyl substitution, the triptycene unit leads to significantly lower activities (up to 2400 kg PP mol⁻¹ Hf h⁻¹) and molecular weights (M_w 150,000–300,000 g mol⁻¹) whereas tacticities stayed within the range of catalyst **1**.

In the case of **3/borate** the highest activity was obtained at T_p 30 °C (1.59×10^4 kg PP mol⁻¹ Hf h⁻¹, entry 9). As shown by different investigations, a sufficiently high molecular weight and isotacticities above 60% are a prerequisite for the appearance of plastomeric properties. In polymerization experiments with the 6,7-substituted complex **3**, isotactic polypropylenes with [mmmm] pentad concentrations ranging around 75–78% were obtained, with molecular weights up to 1.5×10^6 g mol⁻¹ (entry 10), properties that fall into the expected range for plastomers. The polymerization experiments in liquid propene show that the molecular weight could be highly increased. This is in accordance with recent observations that significantly higher molecular masses could be obtained for borate-activated dimethyl complexes due to the absence of the chain transfer to aluminum [5].

Compared to the previously studied complex **3**, the catalyst **4a/borate** shows much higher activity (Table 1, 12–18). Increasing the polymerization temperature affords the highest productivity at 50 °C in toluene solution (up to 2.14×10^5 kg PP mol⁻¹ Hf h⁻¹). The activity of catalyst **4a** even reaches values up to 3.21×10^5 kg PP mol⁻¹ Hf h⁻¹ in liquid monomer. Evidently, the catalytically active species has not been deactivated by the sulfur function **3** via an intramolecular mechanism, but might take part in intermolecular coordination processes that facilitate chain growth. This assumption could explain the activities (up to 14 times higher) achieved with each of the catalysts mentioned. So far the trend for asymmetric metallocene catalyst is that higher molecular weights of the polypropylenes could be reached at lower polymerization temperatures [9–11, 20]. Following the same trend, ultrahigh molecular weight plastomeric polypropylenes (M_w 9.6×10^5 g mol⁻¹) were obtained with **4a/borate** at low polymerization temperature (20 °C). One explanation could be that the backward oriented 5,7-dialkyl substitution effectively suppress the chain-end isomerization process [11] (source of

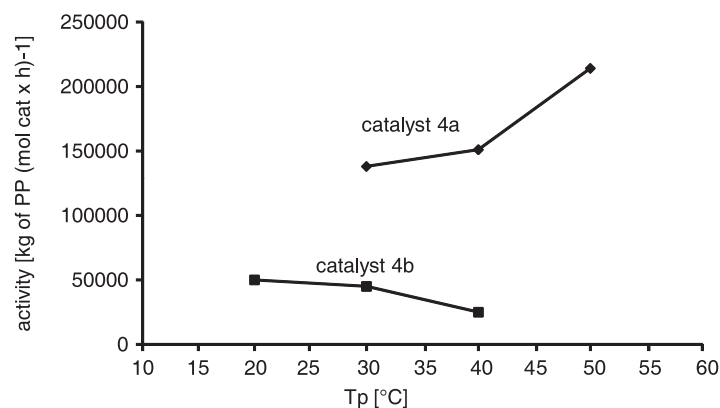


Fig. 13 Polypropylene activity vs. polymerization temperature (catalyst **4a**: chain back-skip mechanism, catalyst **4b**: C_2 -symmetric-like mechanism)

stereoerrors in C_2 -symmetric catalysts) and hinders at the same time a subsequent chain termination reaction, leading to higher molecular weight products (C_2 -symmetric-like polymerization mechanism).

The catalyst **4b/borate** was tested under similar conditions as in the case of **4a** (toluene solution and liquid propylene) in propylene polymerization experiments after preactivation with TIBA (Table 1). According to the data from Table 1, the catalytic properties of **4b** are inferior to those of **4a**. The behavior of **4b** is similar to that of asymmetric catalysts with a forward orientation of the 4-substituted indene unit [10]. The effect of the substitution position is remarkable. While the 5,7-substituted hafnocene **4a** shows higher activities (up to 3.2×10^5 kg PP mol⁻¹ Hf h⁻¹ at 40 °C) with increasing temperatures, substantially lower or almost no activities were found for the 4,6-substituted hafnocene **4b** at the same temperature (Fig. 13).

Tacticities of the polypropylenes above 60% [mmmm] highlights the tendency of the backward oriented substitution (**4a**) to produce plastomeric materials. During experiments in liquid propylene, no similarity is observed between the two isomeric catalysts. Catalyst **4b/borate** does not follow the same trend in the catalytic performance as previously mentioned, but leads to polypropylenes with sufficient amount of isotactic sequences and relatively high molecular weight for the design of plastomeric polypropylenes.

5 Conclusion

The combination of structural studies and polymerization experiments of a series of hafnocene catalysts has provided greater insight into the polymerization mechanism and the possibilities of tailoring polymer microstructures.

Depending on the hafnocene catalyst, it is possible to obtain polypropylenes with different tacticities in a range from 10 to 80%. Taking into consideration the

correlation between polymer tacticity and material properties it was demonstrated that hafnocene catalysts possess a high potential for tailoring the polymer microstructures, leading to new materials with properties ranging from thermoplastic elastomers to highly isotactic plastomers with ultrahigh molecular weights.

Independent of the ligand system, two different activation methods have been used in performing the propylene polymerization experiments. In both cases, the catalytic activities and molecular weights of the polymers are a sensitive function of the aluminum content provided by the activators. This dependence suggested an additional reversible chain transfer to aluminum when activating with MAO. As lower contents of Al are provided in the polymerization system in the case of in situ activation with TIBA/borate, the only mechanism occurring is the chain back-skip. Furthermore, the differences in the polymer microstructures prepared with MAO and borate as cocatalysts are reflected. They sustain the proposed reversible chain transfer.

The long-existing theory that the activity of hafnocene catalysts is negligible compared to the zirconium analogs can now be abandoned. The deciding point is not hafnium; it is more the way of activation! While using TIBA/borate for building the active species, activities increase dramatically and exceed those of comparable Zr/MAO systems, obtaining high and ultrahigh molecular weight polypropylenes.

Based on the current situation that oil prices are continuously rising and the industrial process of natural gas to methanol, methanol to propylene, propylene to polypropylene becomes more important, it will be interesting to see what importance hafnocene-catalyzed polypropylenes will have in future daily life.

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