

Stereospecific propylene polymerization using half-sandwich metallocene/MAO systems: a mechanistic insight

R. Kleinschmidt, Y. Griebenow, G. Fink *

Max-Planck Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, Mülheim an der Ruhr 45470, Germany

Received 15 September 1999; received in revised form 5 December 1999; accepted 24 December 1999

Abstract

The propylene polymerizations with different half-sandwich metallocene complexes of the general formula, $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNR}]\text{TiCl}_2$, result in the formation of polymers with increased isotacticity as compared to atactic polypropylene. This was observed if a sterically demanding aromatic system at the amido-ligand coordinates with the polymerization active metal center. In this case, the metal center is partly shielded and the steric demand of the ligand is similar to an ansa-metallocene. The monomer partly coordinates stereospecifically at the metal center. Additionally, the solvent polarity has a great influence on the microstructure of the produced polymers. Using the complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{-naphthyl}]\text{TiCl}_2$ in toluene, *ortho*-dichlorobenzene and hexane polypropylenes of similar microstructures were formed (mmmm \approx 45%) whereas in methylene chloride as solvent, the isotacticity of the polypropylene was decreased by 50%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Polymerization; Half-sandwich; Metallocene/MAO system

1. Introduction

With respect to the recently developed constrained geometry catalysts [1] of the IV subgroup, a new class of substances has been generated, which, together with MAO as the cocatalyst, turns into highly active polymerization catalysts [2,3]. In the late 1980s, Shapiro et al. [4,5] synthesized the first complexes with linked amido-cyclopentadienyl ligands. These complexes contained scandium as central atom and were found to be adequate for catalyzing

the polymerization of α -olefins. Following thereafter, Okuda [6,7] synthesized iron and titanium complexes with linked amido-cyclopentadienyl ligands. Based on these results, companies such as DOW Chemical and Exxon Chemical developed such numerous constrained geometry catalysts to be used for the α -olefin homo- and copolymerization. The polymerization behavior of these catalysts is mainly described in the patent literature [8–15].

Polymerization catalysts with linked amido-cyclopentadienyl ligands usually produce atactic polymers. In the patent literature, there are only a few examples which describe the stereospecific propylene polymerization with these types of catalysts. Shiomura et al. [16] used the cata-

* Corresponding author. Tel.: +49-208-306-2240; fax: +49-208-306-2980.

E-mail address: fink@mpi-muelheim.mpg.de (G. Fink).

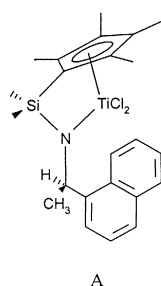


Fig. 1. $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A).

lyst system, $\text{Me}_2\text{Si}[\text{FluN}^t\text{Bu}]\text{ZrX}_2$ ($\text{X} = \text{Cl}$ or NMe_2) and obtained, with MAO as the cocatalyst, a syndiotactic polypropylene and with $\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ as the cocatalyst, an isotactic polypropylene.

In this paper, we discuss what kind of influence the substituent at the amido-ligand has on the stereospecific behavior of the constrained geometry catalysts during propylene polymerization. Therefore, numerous complexes were synthesized and propylene polymerizations were carried out under similar reaction conditions with MAO as the cocatalyst.

We further investigated the influence of solvent polarity on the propylene polymerization reaction catalyzed by $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A) and MAO as the cocatalyst.

2. Results and discussion

We have synthesized complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A) (Fig. 1) and carried out propylene polymerizations at variable

Table 1

Results of the propylene polymerization with the complex, $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A)
 Polymerization conditions: $p = 2$ bar, $[\text{Al}]/[\text{Ti}] = 3000/1$, $[\text{Ti}] = 1.25 \times 10^{-4}$ mol/l, solvent = toluene.

Catalyst	T_p [°C]	Activity [kg PP/mol Ti h]	T_m [°C]	M_w	M_w/M_n
A	7	1201	92	87.000	1.8
A	15	1381	91	60.400	1.8
A	28	1269	83	42.300	2.0
A	35	804	70	34.200	1.4

Table 2

Results of the microstructure analysis for the polypropylenes produced with the complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A)

Polymerization conditions: $p = 2$ bar, $[\text{Al}]/[\text{Ti}] = 3000/1$, $[\text{Ti}] = 1.25 \times 10^{-4}$ mol/l, solvent = toluene.

Pentad	$T_p = 7^\circ\text{C}$	$T_p = 15^\circ\text{C}$	$T_p = 28^\circ\text{C}$	$T_p = 35^\circ\text{C}$
mmmm	56.1	54.5	51.7	47.6
mmmr	13.9	14.8	16.3	16.2
rmmr	0.9	1.4	1.0	1.3
mmrr	13.0	13.5	14.8	16.2
mrmm/rmmr	5.5	4.5	4.5	5.8
mrmr	2.2	2.1	1.7	1.3
rrrr	1.1	1.4	1.5	1.8
rrrm	2.1	2.1	2.0	2.7
mrrm	5.3	5.9	6.6	7.3

temperatures. This catalyst is, with MAO being the cocatalyst, the first complex with a linked amido-cyclopentadienyl ligand, which produces polypropylene along with an increased amount of isotactic units. As can be seen, this complex contains an asymmetrically substituted carbon atom at the amido-ligand.

Table 1 presents the results of propylene polymerizations using catalyst A.

Table 2 depicts the results of the microstructure analysis of the produced polypropylenes.

It is apparent that the polymers have isotacticities reaching 56%. One possible explanation for the stereospecific behavior of this complex might be chiral induction of the asymmetrically substituted carbon atom at the amido-ligand. Another explanation might be the stabilization and shielding of the polymerization active metal cation through a coordination of the naphthyl group at the metal center analogous to the known complexes applied by Jordan et al. [17] (Fig. 2).

In order to determine which of the two explanations might be the correct one in the formation of a polymer with an increased isotacticity, the following complexes were synthesized (Fig. 3).

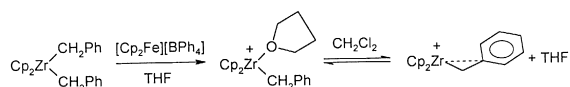


Fig. 2. Cationic benzyl complex according to Jordan et al. [17].

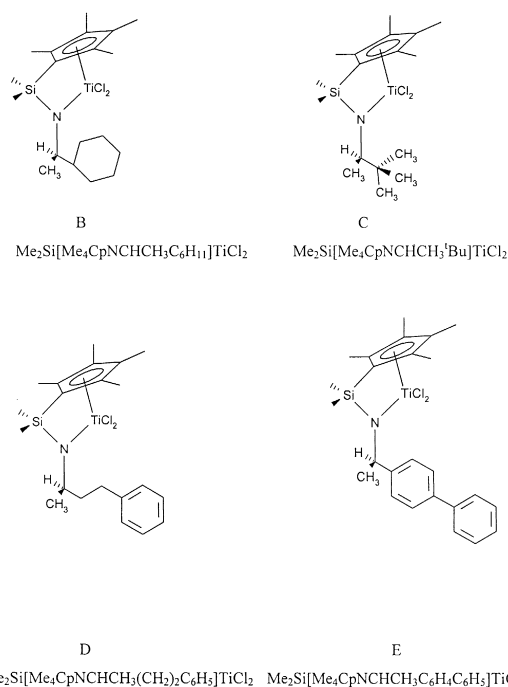


Fig. 3. $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_{11}]\text{TiCl}_2$ (B), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3^t\text{Bu}]\text{TiCl}_2$ (C), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3(\text{CH}_2)_2\text{C}_6\text{H}_5]\text{TiCl}_2$ (D), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_5]\text{TiCl}_2$ (E).

Table 3 summarizes the polymerization results obtained using the complexes B–E. The results of the analytical investigations of the polypropylenes are also listed in Table 3.

All complexes showed a high polymerization activity during propylene polymerization. Applying any of the catalysts, sticky, amorphous polymers were produced. The molecular weight distribution of all polymers was narrow, as has been expected. The results of the microstructure

analysis are listed in Table 4. The pentad values as calculated for atactic and hemiisotactic polypropylene are recorded in Table 4.

As can be seen by comparing the values of the 10 pentads with the values calculated for an atactic polypropylene, the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_{11}]\text{TiCl}_2$ (B), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3^t\text{Bu}]\text{TiCl}_2$ (C) and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3(\text{CH}_2)_2\text{C}_6\text{H}_5]\text{TiCl}_2$ (D) produced atactic polymers.

Only the polymerization behavior of the catalyst, $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_5]\text{TiCl}_2$ (E), was different. The polypropylene produced with this particular complex has an isotacticity reaching 14.0%.

Two additional catalysts, namely $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_5]\text{TiCl}_2$ (F) [18,31] and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCH}_2\text{C}_6\text{H}_5]\text{TiCl}_2$ (G) (Fig. 4), were synthesized and their polymerization behavior was also investigated.

The polymerization results obtained with these catalysts are summarized in Table 5. The results of the microstructure analysis are listed in Table 6.

In both cases, a polypropylene with an increased amount of isotactic units as compared to atactic polypropylene was obtained at a polymerization temperature reaching 30°C. The half-sandwich complex F produced a polypropylene with an isotacticity of 14.9%. A polypropylene, which was formed using the G complex, showed an isotacticity reaching 11.8%. These isotacticities are in the same order of magnitude as the isotacticities of the polypropylene which

Table 3

Results of the propylene polymerization obtained with the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_{11}]\text{TiCl}_2$ (B), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3^t\text{Bu}]\text{TiCl}_2$ (C), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3(\text{CH}_2)_2\text{C}_6\text{H}_5]\text{TiCl}_2$ (D) and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_5]\text{TiCl}_2$ (E). Polymerization conditions: (B) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 3.5 \times 10^{-4}$ mol/l; (C) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 4.9 \times 10^{-5}$ mol/l; (D) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 1.3 \times 10^{-4}$ mol/l; (E) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 6.3 \times 10^{-5}$ mol/l.

Catalyst	$v_p \times 10^3$ [mol/l s]	Activity [kg PP/mol Ti h]	T_g [°C]	M_w	M_w/M_n
B	3.44	819	−2.63	76.240	1.7
C	6.69	6626	−2.33	269.100	1.8
D	0.95	670	−7.46	63.100	1.3
E	3.79	3907	−4.47	179.200	1.4

Table 4

Results of the pentad analysis of the polypropylenes produced with the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_{11}]\text{TiCl}_2$ (B), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}^t\text{Bu}]\text{TiCl}_2$ (C), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3(\text{CH}_2)_2\text{C}_6\text{H}_5]\text{TiCl}_2$ (D) and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_5]\text{TiCl}_2$ (E). Polymerization conditions: (B) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 3.5 \times 10^{-4}$ mol/l; (C) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 4.9 \times 10^{-5}$ mol/l; (D) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 1.3 \times 10^{-4}$ mol/l; (E) $T_p = 30^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 6.3 \times 10^{-5}$ mol/l.

Pentad	Ideal atactic polypropene	Ideal hemiisotactic polypropene	B	C	D	E
mmmm	6.25	18.75	4.0	6.5	3.4	14.0
mmmr	12.50	12.50	10.2	13.0	8.2	13.2
rmmr	6.25	6.25	7.1	5.4	6.2	5.0
mmrr	12.50	25.00	11.9	16.3	11.3	14.2
mrmm/rmrr	25.00	0.00	23.3	20.5	25.0	19.0
mrmm	12.50	0.00	16.8	15.2	13.0	10.0
rrrr	6.25	18.75	6.3	4.6	8.5	5.5
rrrm	12.50	12.50	10.6	8.5	15.6	10.7
mrrm	6.25	6.25	9.8	10.0	8.8	8.4

was formed with the complex, $\text{Me}_2\text{Si}[\text{Me}_4\text{-CpNCHCH}_3\text{C}_6\text{H}_4\text{C}_6\text{H}_5]\text{TiCl}_2$ (E). Noticeable in this comparison is the fact that the half-sandwich G complex produced a polypropylene with increasing amounts of isotactic units although the carbon atom next to the nitrogen atom in the amido-ligand is not asymmetrically substituted. In contrast, the polypropylenes obtained in applying the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_{11}]\text{TiCl}_2$ (B), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}^t\text{Bu}]\text{TiCl}_2$ (C) and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3(\text{CH}_2)_2\text{C}_6\text{H}_5]\text{TiCl}_2$ (D) were totally atactic although the nitrogen atom next to the carbon atom in the amido-ligand is asymmetrically substituted. These results show that the formation of a polypropylene with an increased amount of isotactic units is not due to the presence of a chiral component as is the

case with respect to complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A) (mmmm = 51.7% at polymerization temperatures reaching 28°C). The presence of an asymmetrically substituted carbon atom in the amido-ligand and concurrently, of a sterically demanding substituent in the amido-ligand is also not enough to raise the stereospecificity of a half-sandwich metallocene complex. Otherwise, the complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}^t\text{Bu}]\text{TiCl}_2$ (C), would also produce a polypropylene with an increased amount of isotactic units.

While comparing the polymerization behavior of the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_{11}]\text{TiCl}_2$ (B) and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{Ph}]\text{TiCl}_2$ (F), it becomes noticeable that complex B forms a completely atactic polypropylene (mmmm = 4.0%), whereas complex F produced a polypropylene with isotactic units amounting to 11.8%. In both cases, the ligand is

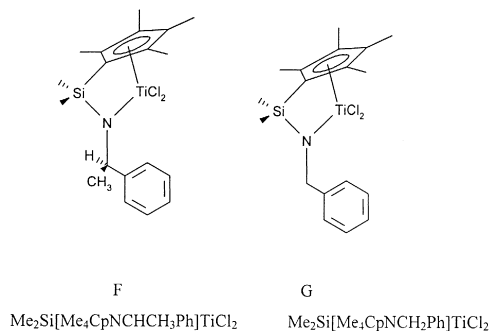


Fig. 4. $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{Ph}]\text{TiCl}_2$ (F), $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCH}_2\text{Ph}]\text{TiCl}_2$ (G).

Table 5

Results of the propylene polymerization with the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{Ph}]\text{TiCl}_2$ (F) and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCH}_2\text{Ph}]\text{TiCl}_2$ (G)

Polymerization conditions: (F) $p = 2$ bar, $T_p = 35^\circ\text{C}$, $[\text{Al}]/[\text{Ti}] = 2400/1$, $[\text{Ti}] = 1.7 \times 10^{-4}$ mol/l; (G) $T_p = 35^\circ\text{C}$, $p = 2$ bar, $[\text{Al}]/[\text{Ti}] = 2400/1$, $[\text{Ti}] = 1.7 \times 10^{-4}$ mol/l.

Catalyst	Activity [kg PP/mol Ti h]	T_g [$^\circ\text{C}$]	M_w	M_w/M_n
F	1025	-6	63.200	1.8
G	235	-5	69.900	1.5

Table 6

Results of the microstructure analysis for the polypropylenes produced with the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{Ph}]\text{TiCl}_2$ (F) and $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCH}_2\text{Ph}]\text{TiCl}_2$ (G)

Polymerization conditions: (F) $T_p = 35^\circ\text{C}$, $p = 2$ bar, $[\text{Al}]/[\text{Ti}] = 2400/1$, $[\text{Ti}] = 1.7 \times 10^{-4}$ mol/l; (G) $T_p = 35^\circ\text{C}$, $p = 2$ bar, $[\text{Al}]/[\text{Ti}] = 2400/1$, $[\text{Ti}] = 1.7 \times 10^{-4}$ mol/l.

Pentad	Ideal atactic polypropylene	Ideal hemiisotactic polypropylene	F	G
mmmm	6.25	18.75	14.9	11.8
mmmr	12.50	12.50	15.2	14.7
rmmr	6.25	6.25	5.2	5.4
mmrr	12.50	25.00	15.9	15.6
mrmm/rmrr	25.00	0.00	19.0	19.5
mrmr	12.50	0.00	9.0	9.4
rrrr	6.25	18.75	5.3	6.3
rrrm	12.50	12.50	8.9	10.1
mrrm	6.25	6.25	6.6	7.3

nearly the same. The only difference being the existence of a cyclohexyl ring at the asymmetrically substituted carbon atom in the case of catalyst B and a phenyl ring in the case of catalyst F. The different polymerization behavior is incomprehensible from the first point of view. If the polymerization active metal cation is stabilized through a complexation of the phenyl group at the amido-ligand (complex F), there are, in principle, the same requirements as for an ansa-metallocene and the formation of a polypropylene with higher amounts of isotactic units is, from this point of view, explainable.

This would also explain the fact that complex, $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{C}_6\text{H}_{11}]\text{TiCl}_2$ (B) catalyzed the formation of an atactic polypropylene because of the missing aromatic substituent at the amido-ligand. The increased isotacticity of the polypropylenes, which were obtained using complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A), is explainable now, too. Due to the sterically more demanding aromatic group at the amido-ligand, the polymerization active metal center becomes more shielded.

An investigation concerning the behavior of the half-sandwich complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3(\text{CH}_2)_2\text{C}_6\text{H}_5]\text{TiCl}_2$ (D) during the process of propylene polymerization resulted into yet another interesting aspect. Although this complex contains an aromatic system at the amido-ligand, a totally atactic polypropylene was

formed. Obviously, the two methyl groups relating to the phenyl ring prevent a possible interaction between the aromatic system and the metal cation.

Altogether, it can be concluded that polypropylenes with increased stereospecificity are only formed if the half-sandwich metallocene complexes contain a sterically demanding aromatic system at the amido-ligand which can interact with the polymerization active metal cation (Fig. 5). Only in this case the active center is shielded and the steric demand of the ligand similar to an ansa-metallocene.

Using the half-sandwich complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A), in which these conditions have mostly been fulfilled, propylene polymerizations were carried out in hexane, *ortho*-dichlorobenzene, methylene chloride, and toluene under identical polymerization conditions. All polymerization results are sum-

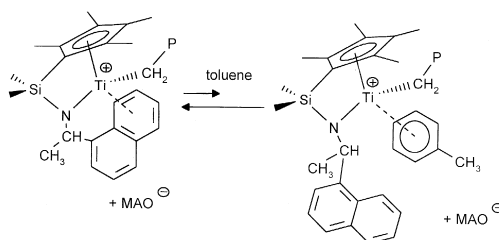


Fig. 5. Interaction of an aromatic system with a half-sandwich metallocene cation in toluene as solvent (schematic).

Table 7

Results of the propylene polymerization with the complex $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A)
 Polymerization conditions: $p_{\text{propene}} = 2.0$ bar, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 4.6 \times 10^{-5}$ mol/l and $T_p = 25^\circ\text{C}$.

Solvent	ϵ^T [$^\circ\text{C}$]	$v_p/[\text{M}] \times 10^4$ [1/s] ^a	Activity [kg PP/mol Ti h]	T_m [$^\circ\text{C}$]	M_w	M_w/M_n
<i>ortho</i> -Dichloro benzene	9.93 ²⁵	8.70	746	83.5	108.010	3.9
Methylene chloride	9.08 ²⁰	1.70	637	79.8	18.800	5.0
Toluene	2.38 ²⁵	3.88	544	84.2	66.810	2.1
<i>n</i> -Hexane	1.89 ²⁰	0.95	311	85.9	114.900	4.8

^aFor comparison, the polymerization rate v_p is standardized to the propylene concentration.

marized in Table 7 together with the dielectric constants of the solvents [19] and the analytical results of the polymers.

With an increasing polarity of the solvent, the polymerization activity also increases — the reason being a separation of the contact ion pair between the polymerization active metal cation and the MAO anion with an increasing polarity of the solvent. The formation of a solvent-separated ion pair results inevitably into an increased activity [20–23]. The low polymerization activity of the half-sandwich complex in hexane is partly due to the small solubility of the MAO in this solvent. The dependency of the molecular weights and the molecular weight distribution of the formed polypropylenes on the polarity of the solvents is not clear at this point.

Table 8 shows the results of the microstructure analysis of the obtained polymers.

The polypropylenes, which were formed in *ortho*-dichlorobenzene, toluene, and hexane,

have nearly the same microstructure. The isotacticities of the polymers are between 45.0% (hexane) and 46.3% (toluene). The similar microstructures of the polypropylenes, which were formed in hexane and toluene, are conceivable because these solvents have a small difference in polarity. Surprising is the fact that in the much more polar solvent *ortho*-dichlorobenzene, the formed polypropylene has a similar isotacticity of 46.2% too. The equilibration between contact ion pair and solvent-separated ion pair should be in the polar solvent on the side of the separated ion pair and, as a consequence, the stereospecificity of the complex should decrease in a more polar solvent. It has been known that metallocene cations coordinate η^6 with six-membered aromatic rings [17,24–30]. Fig. 6 shows an example of a half-sandwich metallocene complex.

Compared to the propylene polymerization in various solvents using the catalyst Me_2Si -

Table 8

Results of the pentad analysis of the polypropylenes produced with the complexes $\text{Me}_2\text{Si}[\text{Me}_4\text{CpNCHCH}_3\text{naphthyl}]\text{TiCl}_2$ (A) in different solvents

Polymerization conditions: $p_{\text{propene}} = 2.0$ bar, $[\text{Al}]/[\text{Ti}] = 2000/1$, $[\text{Ti}] = 4.6 \times 10^{-5}$ mol/l and $T_p = 25^\circ\text{C}$.

Pentad	<i>n</i> -Hexane ($\epsilon = 1.89$)	Toluene ($\epsilon = 2.38$)	Methylenechlorid ($\epsilon = 9.08$)	<i>ortho</i> -Dichloro benzene ($\epsilon = 9.93$)
mmmm	45.0	46.3	24.8	46.2
mmmr	15.6	15.7	13.7	14.8
rmmr	2.3	2.3	4.8	2.7
mmrr	13.8	14.1	14.0	13.6
mrmm/rmr	7.3	7.1	13.7	7.3
rrmr	2.8	2.8	8.1	2.5
rrrr	2.2	2.0	4.3	2.2
rrrm	3.6	2.8	8.8	3.0
mrrm	7.4	6.9	7.7	7.7

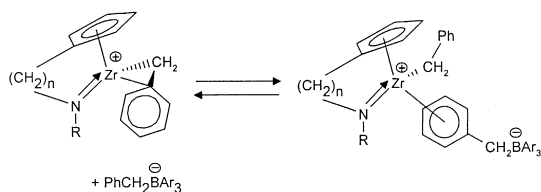


Fig. 6. Interaction of an aromatic system with a half-sandwich metallocene cation [30].

[Me₄CpNCHCH₃naphthyl]TiCl₂ (A), the group PhCH₂BAR₃ conforms to the solvent and the CH₂Ph group conforms to the substituent at the amido-ligand (CHCH₃naphthyl). On one hand of this comparison, the equilibrium now makes an explanation of the observed results possible. In hexane, the equilibrium lies partly on the left side and the naphthyl group coordinates at the metal cation. During a polymerization in toluene and *ortho*-dichlorobenzene, the naphthyl group coordinates also at the metal center. This results in the formation of polypropylenes with similar microstructures in any of these solvents. A polymerization in methylene chloride results in the formation of a polypropylene with a decreased isotacticity. In this case, a solvent molecule coordinates at the active metal center, resulting into a reduced shielding of the active center (Fig. 7).

Due to the small steric demand of the solvent molecule, the isotacticity of the resulting polymer is nearly decreased by 50%.

3. Experimental

3.1. Materials

All half-sandwich complexes were synthesized by following the general route described in literature [2,15,31] and characterized by nuclear magnetic resonance (NMR) and mass spectroscopy.

All solvents and air-sensitive compounds were handled under argon using standard Schlenk technique.

The propylene gas was purified by being passed through a series of columns filled with

NaAl(Et)₄ to remove residual traces of moisture and oxygen.

The toluene used for polymerization was purified by distillation under argon over NaAl(Et)₄. MAO (10 wt.% solution in toluene) was obtained from Witco.

3.2. Polymerizations

All polymerizations were carried out in a 0.25 dm³ glass autoclave at 2.0 bar propylene pressure. The glass autoclave was filled with solvent and MAO, thermostated, and saturated with propylene gas. A stirrer was used at 1200 rpm to stir the mixture. The preactivated metallocene was injected in the reactor with an argon pressure of 4.0 bar. In all experiments, the total volume of the liquid phase was 110 ml. The monomer consumption was detected by mass flow meters. The reaction was stopped through addition of methanol. The precipitated polymer was stirred in a mixture of methanol and hydrochloric acid. The polymer was filtered, washed with methanol, and dried via vacuum.

3.3. ¹³C NMR spectroscopy

The ¹³C NMR spectra of the polymers were measured on Bruker AMX300 spectrometer at 75.5 MHz at a temperature of 120°C.

Therefore, 300 mg of the polymer was solved in 3 ml of a 1:3 mixture of 1,1,2,2-tetrachloroethane-*d*₂ and 1,2,4-trichlorobenzene. The measurements were taken in 10 mm NMR tubes for normally 90 min.

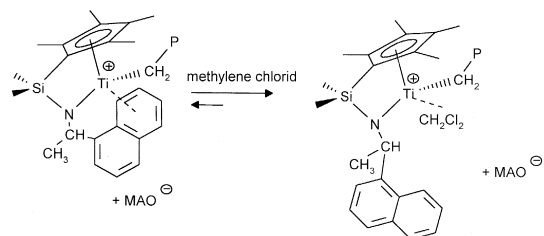


Fig. 7. Interaction of an aromatic system with a half-sandwich metallocene cation in methylene chloride as solvent (schematic).

References

- [1] J.C. Stevens, *Stud. Surf. Sci. Catal.* 89 (1994) 277.
- [2] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nicklas, R.K. Rosen, G.W. Knight, S. Lai, European Patent Application 416815, 1990.
- [3] J.A.M. Canich, European Patent Application 420436, 1990.
- [4] P.J. Shapiro, E.E. Bunel, W.P. Schaefer, J.E. Bercaw, *Organometallics* 9 (1990) 867.
- [5] P.J. Shapiro, W.D. Cotter, W.P. Schaefer, J.A. Labinger, J.E. Bercaw, *J. Am. Chem. Soc.* 116 (1994) 4623.
- [6] J. Okuda, *Top. Curr. Chem.* 160 (1991) 97.
- [7] J. Okuda, *Chem. Ber.* 123 (1990) 1649.
- [8] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nicklas, R.K. Rosen, G.W. Knight, S. Lai, European Patent Application 416815, 1990.
- [9] J.A.M. Canich, European Patent Application 420436, 1990.
- [10] J.A.M. Canich, United States Patent 5026798, 1991.
- [11] J.A.M. Canich, United States Patent 5055438, 1991.
- [12] J.A.M. Canich, United States Patent 5168111, 1992.
- [13] United States Patent 5096867, 1991.
- [14] S. Lai, D.R. Wilson, G.W. Knight, J.C. Stevens, P.W.S. Chum, United States Patent 5272236, 1993.
- [15] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.W. Rosen, G.W. Knight, S.Y. Lai, European Patent Application 416815 A2, 1991.
- [16] T. Shiomura, T. Asanuma, T. Sunaga, *Macromol. Rapid Commun.* 18 (1997) 169.
- [17] R.F. Jordan, R.E. LaPointe, C.S. Bajgur, S.F. Echols, R. Willet, *J. Am. Chem. Soc.* 109 (1987) 4111.
- [18] J. Okuda, S. Verch, S.P. Spaniol, R. Stürmer, *Chem. Ber.* 129 (1996) 1429.
- [19] R.C. Weast, *Handbook of Chemistry and Physics*, CRC Press, 1980.
- [20] N. Herfert, G. Fink, *Makromol. Chem.* 193 (1992) 773.
- [21] P. Longo, L. Olivia, A. Grassi, C. Pellicchia, *Makromol. Chem.* 190 (1989) 2357.
- [22] S.W. Ewart, M.J. Sarsfield, D. Jeremic, T.L. Tremblay, E.F. Williams, M.C. Baird, *Organometallics* 17 (1998) 1502.
- [23] N. Herfert, Thesis Heinrich-Heine, Universität Düsseldorf, 1992.
- [24] D.J. Gillis, M.J. Tudoret, M.C. Baird, *J. Am. Chem. Soc.* 115 (1993) 2543.
- [25] D.J. Gillis, R. Quyoum, M.J. Tudoret, Q. Wang, D. Jeremic, A.W. Roszak, M.C. Baird, *Organometallics* 15 (1996) 3600.
- [26] C. Pellicchia, A. Immirzi, A. Grassi, A. Zambelli, *Organometallics* 12 (1993) 4473.
- [27] C. Pellicchia, A. Grassi, A. Immirzi, *J. Am. Chem. Soc.* 115 (1993) 1160.
- [28] A.D. Horten, J. deWith, A.J. van der Linden, H. van de Weg, *Organometallics* 15 (1996) 2672.
- [29] A.D. Horten, J. deWith, *J. Chem. Soc., Chem. Commun.* (1996) 1160.
- [30] P.J. Sinnema, K. Liekelema, O.K.B. Stahl, B. Hessen, J.H. Teuben, *J. Mol. Catal. A: Chem.* 128 (1998) 143.
- [31] A.L. McKnight, M.A. Massod, R.M. Waymouth, *Organometallics* 16 (1997) 2879.