C_s-symmetric hafnocene complexes for synthesis of syndiotactic polypropene

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Received 10 April 2003; accepted 17 July 2003

Dedicated to Professor Ernst Otto Fischer on the occasion of his 85th birthday

Abstract

Three new C_s-symmetric *ansa*-hafnocene complexes such as dichloro[η^{10}-2,4-cyclopentadienyl-1-ylidenebis(4-methyldiphenyl-methylen)[2,7-bis(1,1-di-methylethyl)-9H-fluorene-9-ylidene]]hafnium (2) were synthesized which produce partiell syndiotactic polypropylenes with very high molecular weights. The influence of the methyl and methoxy substitution in the bridge was studied on the activity, tacticity, and molar mass. The hafnocene–MAO catalysts (1–4) were active up to polymerisation temperatures of 90 °C and produces 55 000 kg polymer in 1 h by 1 mol of hafnocene. The molecular weight of the obtained elastic polypropylene reaches 2.2 million g mol^{-1}.

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Keywords: Hafnocene complexes; Metallocene catalysts; Propene polymerisation; Syndiotactic polypropylene

1. Introduction

Metallocene complexes are in combination with methylaluminoxane (MAO) highly active catalysts for the synthesis of precisely designed polyolefins [1–4]. They show only one active site and produce polymers with a narrow molecular weight distribution, different microstructures and tacticities and new physical and mechanical properties. Depending on the ligand structure, highly isotactic or syndiotactic polypropenes can be obtained as well as iso- and stereoblock materials.

C_s-symmetric Group-4 metallocene complexes catalyse the stereospecific polymerisation to syndiotactic polypropene [5]. The first successful synthesis of syndiotactic polypropene was carried out with the catalysts

[Me$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)]MCl$_2$–MAO and [Ph$_2$C(C$_5$H$_4$)-(C$_{13}$H$_8$)]MCl$_2$–MAO (M = Zr, Hf). The Ph$_2$C-bridged catalyst showed a higher stereoselectivity, higher activities and higher molar masses than the isopropylidene bridged catalyst [6–9]. The mechanism for the synthesis of syndiotactic polypropene involves an alternating enchainment of monomer with inverse relative configuration and the formation of a syndiotactic chain. This 'enantiomorphic site control mechanism' implies that the chiral catalytic centres are capable of discriminating between the two prochiral enantiofaces of a propene molecule [10].

Theoretically studies and molecular modelling showed that a suitable substitution of the fluorenyl ligand of the complexes [Ph$_2$C(C$_5$H$_4$)(C$_{13}$H$_8$)]MCl$_2$ (M = Zr, Hf) should lead to an increase in the stereoselectivity and therefore to higher racemic pentads measured by ^{13}C-NMR spectroscopy as rrrr-values [11,12]. The most successful positions for a substitution of the fluorene are the position 3/6 and 2/7. A substitu-

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tion of the positions 3 and 6 with a methyl group should result in very high tacticities as well as a substitution at the positions 2 and 7 with bulky *tert*-butyl groups [12]. Substitution of the phenyl groups in the bridge with electron drawing or pushing groups should increase this effect. Such substituted zirconocenes and hafnocenes were synthesized and tested in the propene polymerisation. The polypropylenes obtained by these zirconocene complexes show highest syndiotacticities and melting points, published [13]. Generally, the zirconocenes are more syndiospecific than the hafnocenes but the hafnocenes produce polymers with higher molar masses. For a lot of applications, high molar masses are very useful especially if the tacticities are low and more or less elastic polymers are formed [14]. It was goal of this study to synthesize hafnocenes which produce polypropenes with high molecular masses and syndiotactic microstructures.

2. Results and discussion

2.1. General synthesis

The bridged fluorenyl-cyclopentadienyl ligand is prepared in three steps. The reaction of fluorene by Friedel–Crafts alkylation leeds to substitution of the fluorene in 2 and 7 position [15]. The synthesis of 2,7-*tert*-butylfluorene is possible by electrophile substitution of 2,6-*tert*-butyl cresole in the presence of $AlCl_3$ in nitromethane [16].

The synthesis of the substituted fulvenes goes over the condensation of cyclopentadiene with substituted benzophenons in methanol–THF and sodium metal for reduction analogue to literature [17] (Scheme 1). The substituted fluorene is then deprotonised by *n*-butyl lithium and reacted with the fulvene (Scheme 2). The ligand is crystallized from diethylether solution and received as white solids.

After this, the ligand is treated with two equivalents of *n*-butyl lithium in diethylether and reacted with the

equivalent amount of hafniumtetrachloride [18]. The yield of the hafnocene complexes reaches after crystallisation 40–60%.

2.2. Polymerisation activities

Four C_s-symmetric hafnocene complexes (Fig. 1) were synthesized and used for the polymerisation of propene in toluene solution.

MAO was added as cocatalyst into a 1 l Büchi glass reactor. The function of MAO is complexing of poisons such as traces of CO_2, alcohol, mercaptanes and other compounds in the toluene and propene, methylation of the hafnocene complexes and formation of the active site, a hafnocene cation.
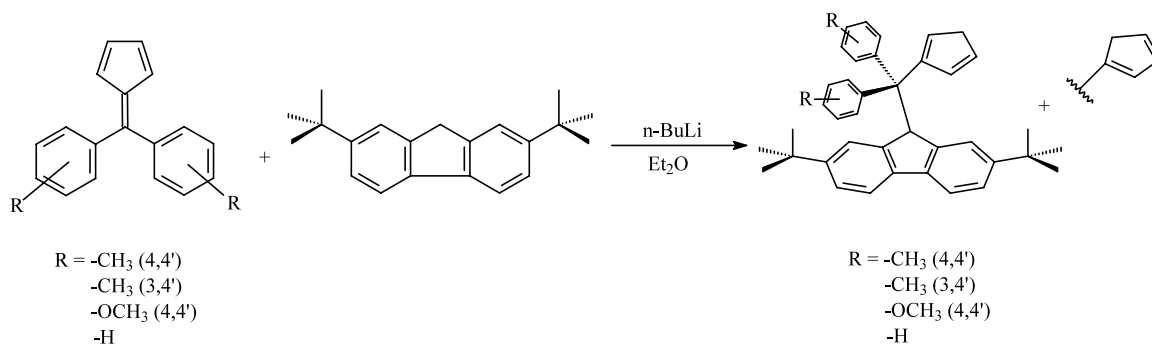
The polymerisation rate depends on the polymerisation temperature and the catalyst concentration (Fig. 2). The activities increase with the temperature for the hafnocene complexes **1**, **2** and **4**. Catalyst **3** shows only a slight increase of activity by higher temperature. Compared to the analogue zirconocene, the activities are by the factor of 6 slower at 30 °C and of only 1.3 at 60 °C. Most active is catalyst **4** with methyl substitutions in *para* and *meta* positions at the phenyl groups in the bridge. With this catalyst, 12 900 kg polypropene is produced with 1 mol complex in 1 h and a propene concentration of 1 mol l^{-1} at 60°C. The methyl substitution is far away from the cationic active center but even than electronic effects influence the formation of the cation. The greater steric hinderence decreases the syndiotacticity. The hafnocene complexes are more stable by higher polymerisation temperatures than the zirconocene complexes. At 90 °C an activity of 55 000 kg $PP/(mol_{Hf}$ h $c_{propene})$ is obtained, while the zirconocene complex is decomposed at this temperature.

2.3. Melting points and tacticity

Only low melting temperatures are observed for the synthesized polypropylene samples, corresponding to low syndiotacticities. There is a great influence of the

R = -CH$_3$ (4,4')
-CH$_3$ (3,4')
-OCH$_3$
-H
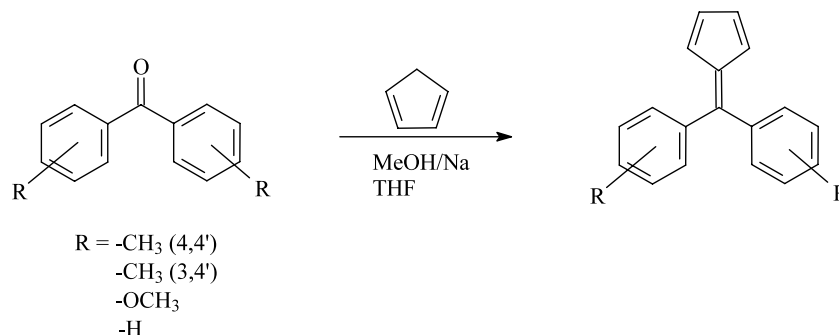
Scheme 1. Synthesis of the substituted fulvenes.

Scheme 2. Synthesis of the ligands.

polymerisation temperature (Table 1). For comparison, the analogue zirconocene complex (**2a**) is also presented in Table 1 [13].

Only the polymers produced at 30 °C are partial crystalline. There are observed no melting points at higher polymerisation temperatures (Fig. 3).

These elastic polymers show only glass transition temperatures. Polypropylene produced by the zirconium complex **2a** has a 50 °C higher melting point.

The polymers obtained by the hafnocene complexes are characterized by relative low syndiotacticities (Fig. 4). The meso rrrr-pentads measured by ^{13}C-NMR spectroscopy are between 68 and 78% at 30 °C poly-
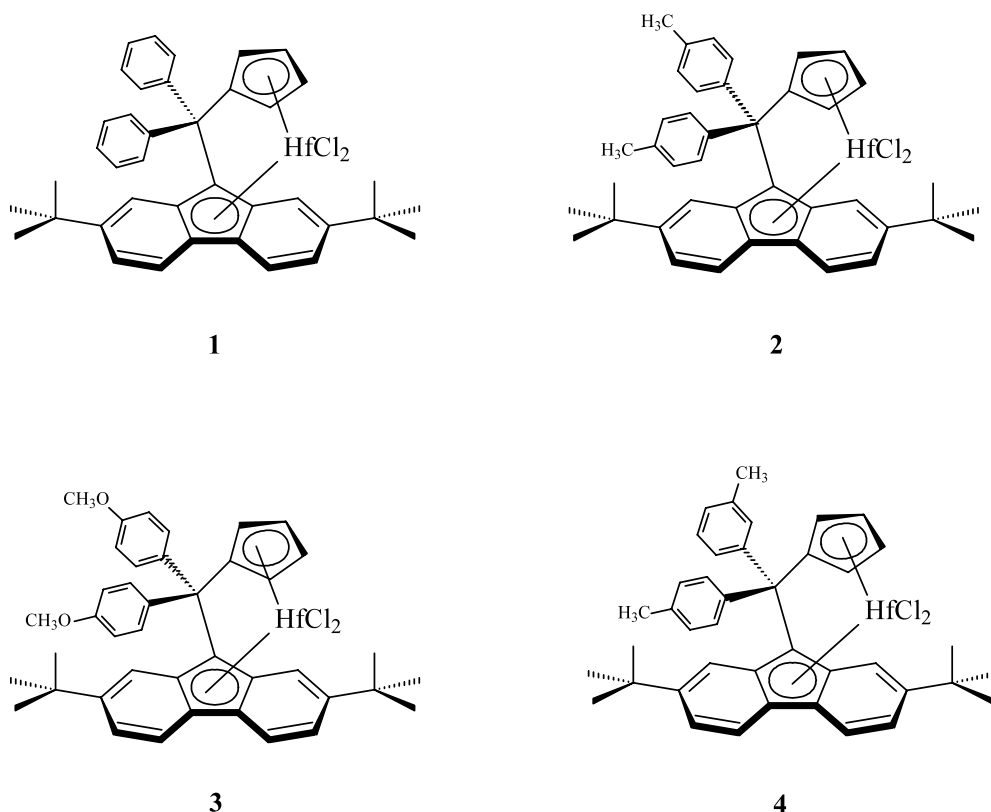
merisation temperature while the polymer of the zirconocene complex **2a** has a rrrr value of 93%.

At higher polymerisation temperatures, the rrrr values decreases to 55% (60 °C) and to 30% (90 °C).

2.4. Molecular weights

Of interest are the molecular weights obtained by the hafnium complexes (Fig. 5).

At polymerisation temperatures up to 60 °C they reach very high values of 1 million g/mol and more. 2.2 million g/mol can be measured by using hafnocene complexes **2** and **4**. Only polymers synthesized by

Fig. 1. New synthesized hafnocene complexes **2**–**4** and **1** for comparison.
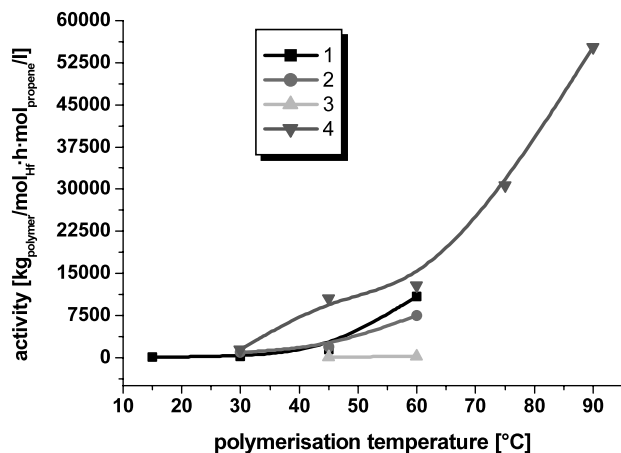
Fig. 2. Activities of the hafnocene complexes **1**–**4** for the polymerisation of propene in dependence of the polymerisation temperature.

Fig. 4. ^{13}C-NMR spectroscopy measured rrrr pentads of polypropylenes synthesized by hafnocene complexes **1**–**4** in dependence of the polymerisation temperature.

catalyst **3** show values which are between 550 000 and 650 000 g mol^{-1}. The zirconocene complex **2a** gives a molecular weight of the polymer of only 210 000 g mol^{-1} at 60 °C. The influence of the methyl substitution in the bridge increased the molecular weight of the polypropylene at least by 20%. Polypropylenes with a syndiotacticity of 30–70% and molecular weights of more than one million are useful elastomers for coating and blending.
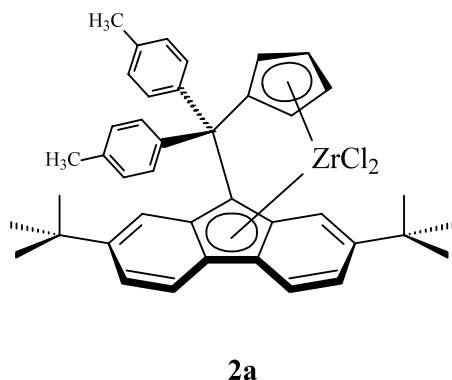
3. Experimental

3.1. General comments

The C_s-symmetric hafnocene complexes **2**–**4**, Fig. 1, were synthesized analogue as described for **1**′ in the literature [19,20]. Synthesis products were verified with ^{1}H-NMR and ^{13}C-NMR on a Bruker 400 MHz spectrometer in CDCl$_3$ and TMS under argon atmosphere at 25 °C.

3.2. Synthesis

3.2.1. Ligand synthesis

2,7-bis-*tert*-Butylfluorene (5 g, 18 mmol) was dissolved in 80 ml diethylether and 11.25 ml of a 1.6 M butyllithium in hexane solution was added slowly. The solution was stirred until gas evolution was finished and then 4.14 g of the methyl substituted 6,6-diphenyl fulvene was added. After 10–12 h, a small amount of water was added, the organic layer separated and dried over Na$_2$SO$_4$. The solution was reduced and crystallized at −25 °C to yield colorless crystals (yield 65–70%).

2a

Fig. 3. Dichloro[η^{10}-2,4-cyclopentadien-1-ylidenbis(4-methyldiphenylmethylen)[2,7-bis(1,1-di-methylethyl)-9H-fluoren-9-yliden]]zirkonium (**2a**).

Table 1
Melting points (T_m) and glass transition temperatures (T_g) of polypropylenes obtained by the hafnocene complexes **1**, **2**, **4** in dependence of the polymerisation temperature

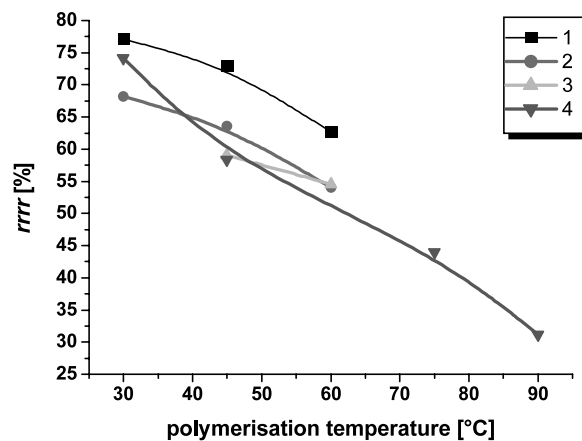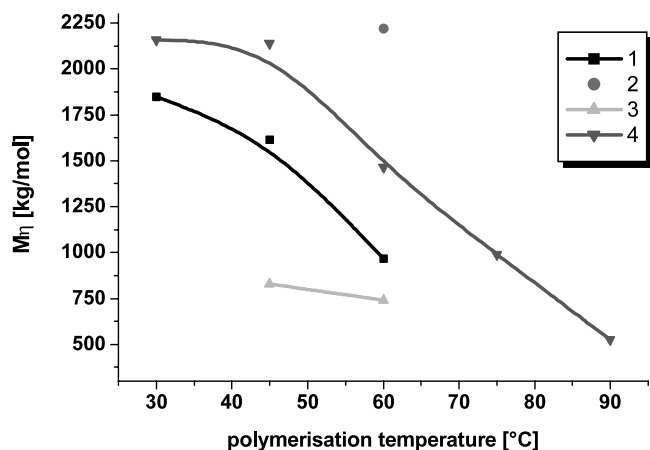| Polymerisation temperature (°C)	Hf compounds			Zr compound
	1	**2**	**4**	**2a**
	T_m (T_g) (°C)	T_m (T_g) (°C)	T_m (T_g) (°C)	T_m (°C)
30	99 (3)	96 (−1)	96 (2,6)	141
45	– (1)	– (−01)	– (1.7)	131
60	– (0.7)	– (−0,5)	– (0.4)	122

Fig. 5. Molecular masses of polypropylene samples synthesized by hafnocenes **1**–**4** in dependence of the polymerisation temperature.

3.2.1.1. 9-[1,3-Cyclopentadien-yl-bis(4-methylphenyl)methyl]-2,7-bis(1,1-dimethylethyl)-9H-fluorene and isomers (2′).

^{1}H-NMR δ [ppm] = 1.12–1.16 (s, 18 H, *tert*-butyl), 2.24 (s, 6H, CH$_3$), 2.82–2.95 (m, 2H), 5.37–5.38 (s, 1H$_{Cp}$), 6.27–6.45 (m br, 3H$_{Cp}$), 6.93 (m br, 4H$_{Ar}$), 7.16–7.37 (m, 10 H$_{Ar}$). ^{13}C-NMR δ [ppm] = 20.84 (CH$_3$), 20.86 (CH$_3$), 31.29 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 40.6, 43.1, 54.0, 54.5, 58.1, 59.1, 117.96, 118.08, 123.29, 123.36, 124.5, 127.8, 129.7, 129.8, 131.4, 132.2, 135.09, 135.25, 135.68, 139.4, 144.6, 144.9, 148.2, 148.3. MSEI [M$^{+\bullet}$] = 536.

3.2.1.2. 9-[1,3-Cyclopentadien-1-yl-bis(4-methoxyphenyl)methyl]-2,7-bis(1,1-dimethyl-ethyl)-9H-fluorene and isomers (3′).

Analogous to the preparation of **2′**. ^{1}H-NMR δ [ppm] = 1.15–1.18 (s, 18H, *tert*-butyl), 2.87–3.00 (m br, 2H), 3.70 (s, 6H, OCH$_3$), 5.31–5.34 (s, 1H$_{Cp}$), 6.26–6.46 (s, 3H$_{Cp}$), 6.62 (m br, 3H$_{Ar}$), 6.9–7.5 (m br, 11H$_{Ar}$). ^{13}C-NMR δ [ppm] = 31.4 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 40.7, 42.9, 54.1, 54.6, 55.1, 57.5, 58.5, 65.8, 112.3 (br), 118.1, 118.2, 123.36, 123.43, 124.2, 124.4, 126.0, 126.8, 128.8, 130.8, 130.9, 132.3, 135.6, 139.35, 139.40, 142.0, 144.5, 144.8, 148.26, 148.35, 157.31, 157.45. MSEI [M$^{+\bullet}$] = 568.

3.2.1.3. 9-[1,3-Cyclopentadien-1-yl-bis(3,4-methylphenyl)methyl)-2,7-bis(1,1-dimethyl-ethyl)-9H-fluorene and isomers (4′).

Analogous to the preparation of **2′**. ^{1}H-NMR δ [ppm] = 1.12–1.14 (s, 18H, *tert*-butyl), 2.15–2.26 (m br, 6H, CH$_3$), 2.86–2.98 (m br, 2H), 5.39–5.42 (s, 1H$_{Cp}$), 6.22–6.41 (m br, 3H$_{Cp}$), 6.92–6.98 (m, 6H$_{Ar}$), 7.17 (m, 5H$_{Ar}$), 7.34 (m, 3H$_{Ar}$). ^{13}C-NMR δ [ppm] = 20.88 (CH$_3$), 21.56 (CH$_3$), 31.3 (C(CH$_3$)$_3$), 34.6 (C(CH$_3$)$_3$), 40.6, 51.9, 53.8, 58.5, 117.9, 118.1, 123.3, 124.5, 126.5, 127.1, 129.7, 130.5, 135.3, 135.6, 139.4, 139.5, 144.9, 148.24, 148.26. MSEI [M$^{+\bullet}$] = 536.

3.2.2. Hafnocene complex synthesis

The ligands **2′**, **3′** and **4′** were dissolved in diethylether, *n*-butyl lithium added and after gas evolution the hafniumtetrachloride added. After filtering, the solution was reduced and crystallized. Orange–red crystals were obtained, yield 40–50%.

3.2.2.1. Dichloro[η^{10}-2,4-cyclopentadien-1-ylidenbis(4-methyldiphenylmethylen)[2,7-bis(1,1-di-methylethyl)-9H-fluoren-9-yliden]]hafnium (2).

^{1}H-NMR δ [ppm] = 1,04 (s, 18H, *tert*-butyl), 2.33 (s, 6H, CH$_3$), 5.6 (m, 2H$_{Cp}$), 6.27 (m, 2H$_{Cp}$), 6.37 (m, 2H), 7.15 (dd, 2H, J_{HH} = 8.08 Hz, 7.84 Hz), 7.2–7.4 (br, 4H$_{Ar}$), 7.56 (dd, 2H, J_{HH} = 8.84 Hz, 9.08 Hz), 7.74 (dd, 2H, J_{HH} = 8.08 Hz), 7.78 (dd, 2H, J_{HH} = 8.08 Hz), 8.01 (d, 2H, J_{HH} = 8.84 Hz). ^{13}C-NMR δ [ppm] = 20.8 (CH$_3$), 30.53 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 57.8 (PhCPh), 102.8, 110.6, 118.4, 118.8, 120.2, 120.7, 121.6, 123.9, 124.0, 126.3, 129.2, 129.4, 129.8, 136.7, 141.9, 150.2. FABMS [M$^{+\bullet}$] = 784.

3.2.2.2. Dichloro[η^{10}-2,4-cyclopentadien-1-ylidenbis(4-methoxydiphenylmethylen)[2,7-bis(1,1-di-methylethyl)-9H-fluoren-9-yliden]]hafnium (3).

^{1}H-NMR δ [ppm] = 1.07 (s, 18H, *tert*-butyl), 3.80 (s, 6H, CH$_3$), 5.62 (m, 2H$_{Cp}$), 6.3 (m, 3H$_{Cp}$), 6.4 (m, 2H), 6.90 (dd, 2H, $^3J_{HH}$ = 8.84 Hz.), 6.97 (dd, 2H, J_{HH} = 8.6 Hz), 7.2–7.4 (br, 4H), 7.58 (dd, 2H, $^3J_{HH}$ = 8.84 Hz), 7.74 (dd, 2H, J_{HH} = 8.84 Hz, 8.6 Hz), 7.83 (dd, 2H, J_{HH} = 8.6 Hz), 8.01 (d, 2H, $^3J_{HH}$ = 8.84 Hz). ^{13}C-NMR δ [ppm] = 31.4 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 55.2 (OCH$_3$), 65.8 (PhCPh), 100.3, 112.3, 113.8, 114.8, 118.2, 118.4, 119.2, 119.4, 120.4, 123.8, 124.0, 124.2, 130.4, 132.0, 137.6, 139.2, 143.9, 148.5, 150.2, 157.8, 158.0, 158.4. FABMS [M$^{+\bullet}$] = 817.

3.2.2.3. Dichloro[η^{10}-2,4-cyclopentadien-1-ylidenbis(3,4-methyldiphenylmethylen)[2,7-bis(1,1-di-methylethyl)-9H-fluoren-9-yliden]]hafnium and stereo isomer (4).

^{1}H-NMR δ [ppm] = 1.05 (s, 18H, *tert*-butyl), 2.25 (s, 2H, CH$_3$), 2.34 (s, 3H, CH$_3$), 2.41 (s, 1H), 5.62 (m, 2H$_{Cp}$), 6.27 (m, 2H$_{Cp}$), 6.36 (br, 1H), 6.41 (br, 1H), 7.09 (d, 1H, J_{HH} = 732 Hz), 7.14–7.35 (br, 4H), 7.56 (d, 2H, $^3J_{HH}$ = 8.84 Hz), 7.67 (br, 1H), 7.76 (m, 2H), 7.84 (m, 1H), 8.01 (d, 2H, $^3J_{HH}$ = 8.84 Hz). ^{13}C-NMR δ [ppm] = 21.0 (CH$_3$), 21.6 (CH$_3$), 30.52 (C(CH$_3$)$_3$), 31.4 (C(CH$_3$)$_3$), 34.7 (C(CH$_3$)$_3$), 35.0 (C(CH$_3$)$_3$), 57.6 (PhCPh), 100.3, 113.2, 113.4, 117.2, 117.3, 117.4, 119.2, 119.6, 120.5, 123.4, 123.7, 123.8, 124.1, 124.2, 126.3, 126.4, 126.5, 127.1, 127.6, 127.8, 128.7, 128.8, 129.2, 129.4, 129.5, 129.7, 129.8, 136.7, 138.4, 142.0, 144.8, 145.0, 150.1. FABMS [M$^{+\bullet}$] = 784.

3.3. Polymerisations

3.3.1. Polymerisation conditions

All operations were performed under a dry argon atmosphere using standard Schlenk techniques. The solvents used were purified passing through two columns with a 4-Å molecular sieve and BASF copper catalyst R3-11. MAO solution from Crompton GmbH was filtered, the toluene was removed in vacuo and used as a solid.

Polymerisations were carried out in 200 ml toluene, as a good solvent for MAO, in a 1 l Büchi glass reactor equipped with a magnetic stirrer. The concentration of propene for every run was 1.38 mol l^{-1} and the pressure was kept constant during the polymerisation. The polymerisations were started through injection of the metallocene complex in toluene to the propene saturated toluene–MAO solution. After 1 h the reaction was stopped by addition of 2 ml methanol. The polymer solution was stirred over night in a methanol–HCl–water solution, filtered followed by evaporation of the solvents and drying of the polymer under vacuo at 60 °C over night.

3.3.2. Polymer analysis

^{13}C-NMR was used to verify the syndiotacticity of the polymers. The NMR samples were prepared by the dissolution of the polymers (10 mass%) in a mixture of hexachloro-1,3-butadiene and 1,1,2,2-tetrachloro-1,2-dideuteroethane and were measured at 100 °C on a Bruker 400-MHz NMR spectrometer and referenced against $C_2D_2Cl_4$ at 100 °C, pulse angle 30 °C, delay time 5 s, 1024 scans. DSC was performed on a Mettler-Toledo DSC 821e.

The molecular weights (M_η) were determined with an Ubbelohde viscometer (530 01/0a capillary, $K = 0.005$ mm^2 s^{-2}). The samples were prepared by the dissolution of 50 mg of the polymer in 50 ml of decahydronaphthaline (stabilized with 1 g l^{-1} 2,6-di-*tert*-butyl-4-methyl-phenol) and were measured at 135 °C. All molecular weights were calculated with the Mark-Houwink constants for polypropylene which were taken from the literature [21].

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