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Review

Pentalene substituted metallocene complexes for olefin polymerization

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Contents

Abstract

Pentalene bridged zirconocene/methylaluminoxane catalysts are described as useful for the polymerization of ethene, propene, and copolymerizations with norbornene. They show a high thermostability up to polymerization temperatures of 105 °C. Polyethylenes with molecular masses of 4 million g/mol are obtained at 30 °C and 500,000 g/mol at more than 90 °C. The molecular mass distribution varies between 2 and 15 because of the steric isomers of the pentalene ligand. Some of the complexes are active for the polymerization of propene. Similar to ansa cyclopentadienyl–fluorenyl complexes, the tacticity of the produced polypropylenes can be changed from syndiotactic to isotactic by substitution of the cyclopentadienyl ring.

Keywords: Metallocene catalysts; Olefin polymerization; Polypropylene; Pentalene–zirconium complexes

1. Introduction

The production of polyolefins has increased rapidly in the last 20 years to make polyolefins the major tonnage plastics material wordwide. This production, using Ziegler–Natta or Phillips catalysts, the high pressure process, and also more and more metallocene and other single site catalysts, has increased from 25 million tons/year (1980) to 90 million tons in 2003 [1,2]. In 2003, 51 million tons of polyethylene and 38 million tons of polypropylene were produced. The metallocene/methylaluminoxane (MAO) catalysts for olefin polymerization were discovered about 25 years ago in our laboratory in Hamburg [3,4].

These catalyst systems have only one kind of active metal center (single site catalysts) and were the start-up for the introduction of a new family of transition metal complexes for olefin, diene, and styrene polymerization. A method was presented to chemists, material scientists, and engineers to tailor the microstructure, that is, co-monomer distribution, stereo-, and regioregularity of polymers, which was not possible before.

Metallocene catalysts are soluble in hydrocarbons and their chemical structure can be easily changed. That allows us to predict accurately the properties of the resulting polyolefins by knowing the structure of the catalyst used during their manufacture and to control the resulting molecular weight and distribution, branching and tacticity by careful selection of the appropriate reactor conditions. In addition, their catalytic activity is 10–100

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times higher than that of the classical Ziegler–Natta systems.

Metallocenes, in combination with the conventional aluminumalkyl co-catalysts used in Ziegler systems, are indeed capable of polymerizing ethene, but only at a very low activity. Only with the application of methylalumoxane (MAO) it was possible to enhance the activity, surprisingly, by a factor of 10,000 or more [5]. Therefore, MAO plays a crucial part in the catalysis with metallocenes.

Methylaluminoxane is a compound in which aluminum and oxygen atoms are arranged alternately and free valences are saturated by methyl substituents. It is gained by careful partial hydrolysis of trimethylaluminum and, according to investigations by Sinn [6], Barron [7], Rytter [8], and Ziegler [9] it consists mainly of units of the basic structure $[Al_4O_3(CH_3)_6]$, which contains four aluminum, three oxygen atoms and six methyl groups. As the aluminum atoms in this structure are coordinatively unsaturated, the basic units join together forming clusters and cages. These have molecular weights from 1200 to 1600 and are soluble in hydrocarbons.

If metallocenes, especially zironocenes, are treated with MAO, then catalysts are acquired that allow the polymerization of up to 100 tons of ethene per gram of zirconium. At such high activities, the catalyst can remain in the products. The insertion time (for the insertion of one molecule of ethene into the growing chain) amounts only to some 10^{-5} s.

It is generally assumed that the function of MAO is first to undergo a fast ligand exchange reaction with the metallocene dichloride, thus rendering the metallocene methyl and dimethylaluminum compounds. In a further step, either Cl^- or CH_3^- is abstracted from the metallocene compound by an Al-centre in MAO, thus forming a metallocene cation and a MAO anion [10–12]. The alkylated metallocene cation represents the active centre. Meanwhile, other weakly coordinating co-catalysts such as tetra(per-fluorophenyl)borate anions $[(C_6F_5)_4B]^-$, and other aluminoxanes have been successfully applied for the activation of metallocenes [13–16].

A further milestone was reached when Brintzinger [17] synthesized chiral bridged metallocenes in 1982 at the University of Konstanz and in 1984, when Ewen [18] at the Exxon Company (USA) was able to demonstrate that appropriate titanocenes render partially isotactic polypropylene. A little later, highly isotactic material was obtained with analogous zirconocenes in our institute [19]. After this discovery, a fervent development of industrial and scientific research in the metallocene sector commenced and, until today, it has not ceased.

Polyolefins with different microstructures and characteristics can be custom-made just by varying the ligands of the metallocene [20–22]. By combining different olefins and cycloolefins with one another, the range of characteristics can be further broadened. The production of polyolefins with narrow molecular weight distributions ($M_w/M_n = 2$), of syndiotactic polymers and of chemically uniform copolymers has not yet been achieved by conventional heterogeneous catalysts. Using metallocene catalyst, it was possible for the first time to produce:

- polyethylenes, polypropylenes and copolymers with narrow molecular weight distributions [23],
- syndiotactic polypropylene (in technical scale amounts) [24],
- syndiotactic polystyrene [25],
- elastomeric polypropylenes [26],
- long chain branched polyethylenes [27],
- cycloolefin copolymers (COC) with high catalytic activity [28],
- optically active oligomers [29],
- composite materials of biomass, solid oxides, and powdered metals with polyolefins [30].

Most metallocene/MAO catalysts are not stable at temperatures above 50 °C which is necessary for an industrial use [31]. There are different deactivation steps discussed [32,33]. Impurities play a stronger role at higher temperatures. More important are hydrogen transfer reactions between alkylated zirconocenes or MAO [34]. Inactive $Zr–CH_2–Zr$ or $-Al$ complexes are formed. These polymerization inactive structures can be reactivated by an excess of MAO and an alkyl exchange. Irreversible are reactions by which the whole cyclopentadienyl ring is split off. This happens more easily in unbridged metallocenes than in ansa-metallocenes. The thermo stability of ansa metallocenes can even increase if the bridge contains a pentalene ring and by this a part of a double handle [35]. We therefore have synthesized a series of zirconocenes with pentalene-bridged cyclopentadienyl/indenyl or fluorenyl ligands.

2. Polymerization of propene by $[RMe_3Pen(Flu)]ZrCl_2$

To obtain 1,3,3-trimethyl-5-phenyl-2,3-dihydropentalene, a mixture of acetone and pyrrolidine in methanol was stirred at room temperature for one hour at least; then phenylcyclopentadiene was added and allowed to react for 40 h, and the product was dried in vacuum. The formation of the dehydropentalene is a multistep condensation reaction between the cyclopentadiene and two moles of acetone[36].

The combination of the fulvene together with the fluorenyl was carried out as described in the literature [37]. For example, the 1-fluorenyl-1,3,3-trimethy-5-phenyl-1,2,3,4-tetrahydro-pentalen was produced by reaction of the fluorene with butyl lithium in THF and at −50 °C. Then the 1,3,3-trimethyl-5-phenyl-2,3-dihydropentalene in THF was added and reacted over night. After extraction with ether and recrystallization, the solid product was obtained in 20% yield. In the last step, the obtained ligand was treated with butyl lithium and reacted with zirconium tetrachloride in hexane after which a crystalline red compound precipitated in a yield of 31%.

Fig. 1 shows the X-ray structure of the [1-fluorenyl-1,3,3-trimethyl-5-phenyl - tetra - hydropentalenyl]zirconium

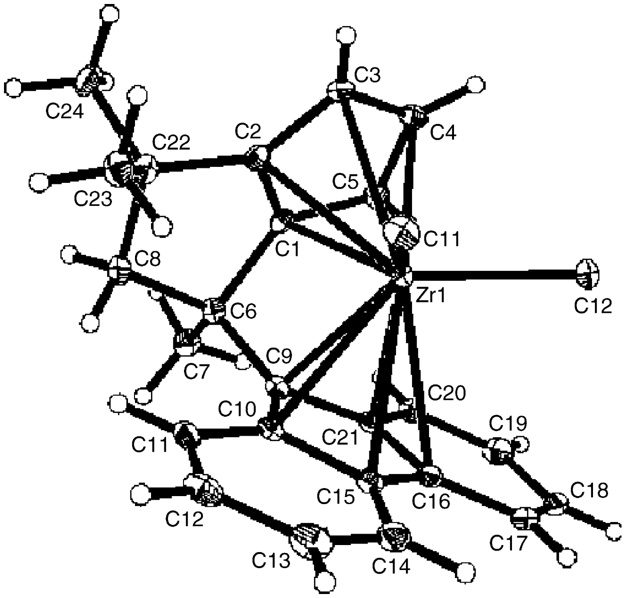


Fig. 1. X-ray structure of [Me$_3$PenFlu]ZrCl$_2$. Distances and angles of complex **2**.

Table 1
Polymerization under standard conditions

Experimental parameters	
Volume	200 ml
Solvent	Toluene
Monomer	Propene
Monomer concentration	1.29 mol/l
Temperature	30 °C
Co-catalyst	MAO
Al:Zr ratio	4000–5500

dichloride

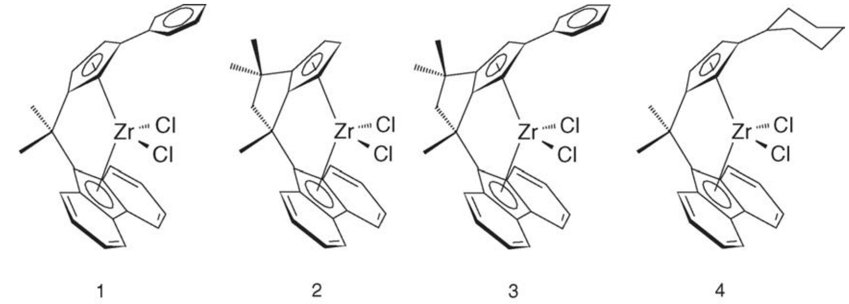
Distance	(Å)		(Å)	Angle	(°C)	Torsion angle	(°C)
Zr–Cl(1)	2.4306(9)	C(6)–C(7)	1.528(4)	Mp–Zr–Mp	117.72(3)	Zr-C(1)-C(6)-C(9)	−14.4(2)
Zr–Cl(2)	2.4353(9)	C(6)–C(8)	1.567(4)	Cl–Zr–Cl	99.26(4)	–	–
Zr–Mp$_{Cp}$	2.1773(14)	C(6)–C(9)	1.543(4)	C(1)–C(6)–C(9)	99.4(2)	–	–
Zr–Mp$_{Flu}$	2.2818(14)	C(9)–C(10)	1.461(4)	C(23)–C(22)–C(24)	108.2(3)	–	–
C(1)–C(2)	1.419(4)	C(10)–C(15)	1.442(4)	C(7)–C(6)–C(8)	110.0(2)	–	–
C(2)–C(3)	1.417(4)	C(15)–C(16)	1.440(4)	C(1)–Zr–C(9)	57.98(10)	–	–
C(3)–C(4)	1.413(4)	C(16)–C(21)	1.430(4)	Mp$_{Cp}$–Zr–Cl(1)	111.62(4)	–	–
C(4)–C(5)	1.422(4)	C(9)–C(21)	1.455(4)	Mp$_{Cp}$–Zr–Cl(2)	108.71(4)	–	–
C(1)–C(5)	1.427(4)	C(8)–C(22)	1.580(4)	–	–	–	–
C(1)–C(6)	1.539(4)	C(22)–C(23)	1.544(4)	–	–	–	–
C(2)–C(22)	1.515(4)	C(22)–C(24)	1.537(4)	–	–	–	–

Angle between the ring planes	(°C)	Ring-slippage	(Å)
Cp-Pen	11.38(17)	Mp$_{Cp}$–Zr	0.142
Cp-Flu	73.66(17)	Mp$_{Flu}$–Zr	0.329

The centroids form a similar open angle (118°) to the other C_1- and C_s-symmetric zirconocenes. The activity and stereoselect-ivity of the propene polymerization by [RMe$_3$Pen(Flu)]ZrCl$_2$ (R = H **2** or phenyl **3**) were compared with that of [Me$_2$C(PhCp)(Flu)]ZrCl$_2$ **1** (Fig. 2) under the same conditions (Table 1). In every case, methylaluminoxane (MAO) was used as co-catalyst. The experiments were carried out in a 1 l autoclave. The catalyst concentration was varied from 2×10^{-5} to 2×10^{-6} mol/l.

Table 2 summarizes the activities of the three zirconocenes as a function of the temperature. The phenyl substituted zirconocene **1** gives the highest activities at 30 °C. This activity is higher than that of the other complexes. While metallocene **1** shows a fast thermal deactivation at higher polymerization temperatures, an increase in activity up to 10 times was found for complexes **2** and **3** by raising the temperature; this may be an effect of the very rigid structure of this compound.

For all metallocenes, an increase of the activity at higher monomer concentrations is observed. Catalyst **1** shows the



1
[Me$_2$C(PhCp)(Flu)]ZrCl$_2$

2
[Me$_3$PenFlu]ZrCl$_2$

3
[PhMe$_3$PenFlu]ZrCl$_2$

4
[Me$_2$C(cHCp)(Flu)]ZrCl$_2$

Fig. 2. Structures of zirconocenes with pentalene bridges and [Me$_2$C(PhCp)Flu)]ZrCl$_2$ for comparison.

Table 2
Polymerization activity as a function of the temperature

T (°C)	[Me $_2$C(PhCp)(Flu)]ZrCl$_2$ (kg PP/mol Zr h) **1**	[Me$_3$PenFlu]ZrCl$_2$ (kg PP/mol Zr h) **2**	[PhMe$_3$PenFlu]ZrCl$_2$ (kg PP/mol Zr h) **3**
15	6630	1430	100
30	11,400	5400	1200
45	4950	9750	1700
60	1300	14,480	7600

strongest increase, compound **3** the lowest. The reaction order for propene is in all cases 1.4–1.5. While the polymerization activity is very important for the technical process, the molecular mass and the microstructures are relevant for the properties of the polymer.

Fig. 3 shows the molecular masses of the polypropylenes obtained as a function of the polymerization temperature. To show the similarity of an aromatic (phenyl) substitution of the cyclopentadienyl ring in Figs. 3 and 4, the dependence on the aliphatic (cyclohexyl) substitution is also added (complex [Me$_2$C(cHCp)(Flu)]ZrCl$_2$ **4**). Catalyst **3** gives a polymer with a molecular mass of more than 400,000 g/mol at 15 °C. This is 9 times higher than that prepared by catalyst **2**.

There is a connection between the high molecular mass of the polypropylene produced and the unusual geometry of the pentalene structure of zirconocene **3**. The stereorigid structure fixes the polymer chain in such a position that β-agostic interaction with the metal center is hindered. This decreases chain termination and leads to a higher molecular mass. As known, molecular masses show a strong dependence on the polymerization temperature. Between 15 and 60 °C, the molecular mass decreases by a factor of 3. On the other hand, the molecular mass can be decreases with the propene concentration (Fig. 4). Especially the more stereorigid complex **3** gives much higher molecular masses with increasing propene concentration while those of the other catalysts are more independent. At propene concentrations higher than 3 mol/l, the molecular mass becomes independent in all other cases. While the propagation step is always bimolecular and depends strongly on the monomer concentration, the chain transfer reaction is monomolecular. At a limit propene concentration there is no increase in the molecular mass.

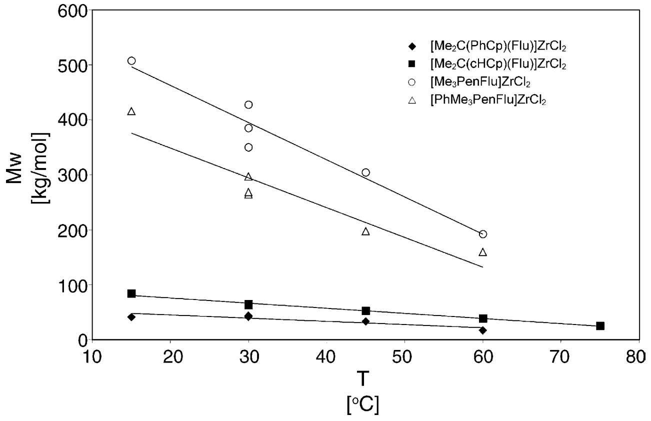


Fig. 3. Molecular masses of polypropenes synthesized by different metallocenes as a function of the polymerization temperature.

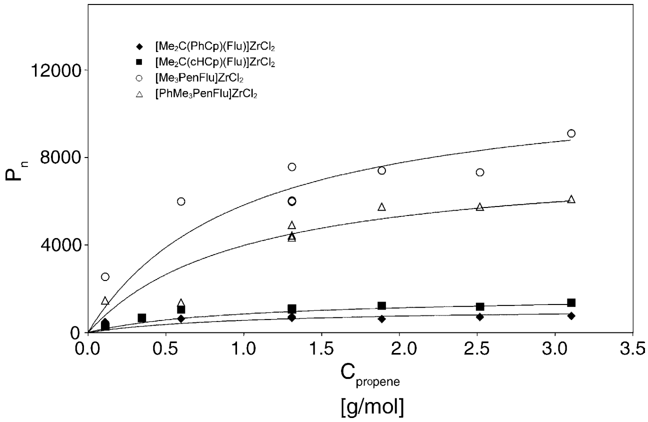


Fig. 4. Average polymerization grade of polypropenes synthesized by different metallocenes as a function of the monomer concentration.

The microstructure of the polypropylene has a significant influence on the polymer properties. There are some mechanistic and computational models to interpret the microstructure of the polymer as a function of the structure of the catalyst [38–42]. Catalysts **1** and **2** produce polypropylenes with high amounts of syndiotactic pentads (Table 3). The pentalene–zirconocene **2** gives surprisingly high syndiotacticity of more than 80%. Both metallocenes have two different half sides which are the background for the rrrr-pentads. On the other side the concentration of mrmr-pentads is low. A partially isotactic polymer is yielded by zirconocene **3**. The mmmm-pentads reach values of 58% which means that the isotactic sequence length is about 10. It results an elastomeric polypropylene.

An explanation can be given if the polymer chain is located on the pentalenyl side while the coordination of the propene

Table 3
Parts of ^{13}C-NMR measured pentads (in%) of polypropylenes synthesized with the catalysts **1**–**3** at 30 °C

Catalyst	1	2	3
mmmm	9.6	0.0	57.5
mmmr	8.8	0.1	11.4
rmmr	8.1	3.1	1.9
mmrr	22.7	5.0	15.7
mrmm + rmrr	2.3	3.1	0.4
mrmr	0	4.1	0.3
rrrr	32.7	81.9	2.8
rrrm	11.8	2.6	3.4
mrrm	4.2	0.1	6.6

Table 4
Polymerization of ethene and norbornene at 30 °C with the catalyst $[Me_2C(PhCp)(Flu)]ZrCl_2$ **1**, $[Me_3PenFlu]ZrCl_2$ **2**, and $[PhMe_3PenFlu]ZrCl_2$ **3** in toluene, MAO co-catalyst

Catalyst	x_N	X_N	Activity (kg Copo/mol Zr h C_E)	T_g (T_m) (°C)	M_w (kg/mol)
1	0	0	47,700	(137.9)	610
	0.19	0.06	41,400	(85.8)	480
	0.39	0.14	18,900	−1.5	200
	0.59	0.20	7500	30.3	260
	0.80	0.34	2100	90.4	340
	0.90	0.39	1400	105.2	460
2	0	0	2700	(134.5)	520
	0.19	0.07	3700	(79)	400
	0.39	0.16	3800	4.6	340
	0.59	0.23	3500	35.9	330
	0.80	0.34	3000	82.6	390
	0.90	0.42	600	115.1	370
3	0	0	3700	(135.4)	660
	0.20	0.05	5780	(98.0)	–
	0.40	0.09	7600	(57.2)	670
	0.59	0.18	6700	16.7	690
	0.80	0.29	2500	59.3	830
	0.90	0.36	100	90.1	830

x_N, molar ratio norbornene in starting solution; X_N, molar ratio of norbornene in copolymer.

takes place at the phenyl substituted side of the metallocene. The phenyl group interacts with the monomer and leads to a preferred orientation of the propene. By this an isotactic polymer is formed. No regio-errors such as 2.1 or 3.1 insertion can be found by ^{13}C NMR measurements (2000 scans).

3. Ethene–norbornene copolymerization

The catalysts **1**–**3** were used for the copolymerization of ethene and norbornene. The open angle between the aromatic rings of the pentalene–zirconocenes open up the possibility to incorporate the bulky norbornene in an easy way as well as to be stable at higher temperatures. Table 4 shows the copolymerization results for the three catalysts.

While the C_s-symmetric zirconocene **1** gives decreasing activities with increasing norbornene concentrations, the other pentalene containing complexes show increasing activities up to 50 mol% of norbornene in the feed. Only at very high norbornene mol% (90), are the activities low. Most surprising is the influence of the norbornene concentration on the molecular mass of the copolymer obtained (Fig. 5). For comparison are shown again the results using a cyclohexyl-substituted cyclopentadienyl–zirconocene $[Me_2C(cHCp)(Flu)]ZrCl_2$ **4**. While in most cases the molecular masses of copolymers decrease with increasing co-monomer content, the copolymers obtained by catalyst **3** show the opposite. The molecular masses started at a high value of 660,000 g/mol and increased to 830,000 g/mol at the highest norbornene content. This means that the steric hindrance of the phenyl-substituted pentalene ligand is less relevant for the chain termination than for the chain propagation.

From the kinetic data and the copolymer composition by ^{13}C-NMR it was possible to calculate the copolymerization parameter r_1, representing how much faster ethene is inserted in the growing polymer chain than norbornene (Table 5).

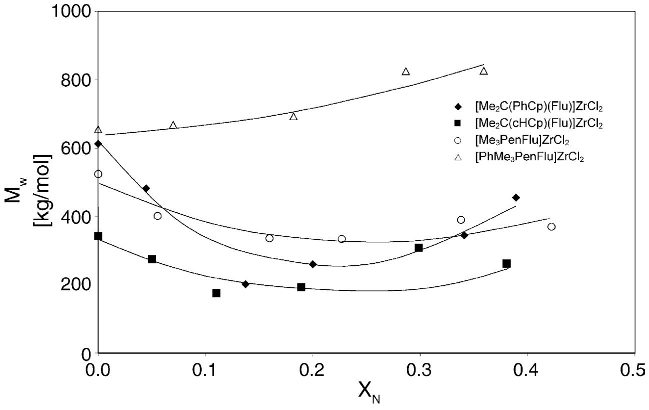


Fig. 5. Molecular masses of ethene/norbornene copolymers synthesized by different metallocenes as a function of norbornene insertion (molar ratio).

Table 5
Copolymerization parameters of the ethene/norbornene polymerization at 30 °C by different catalysts

$[Me_2C(PhCp)(Flu)]ZrCl_2$	**1**	4.43
$[Me_3PenFlu]ZrCl_2$	**2**	3.24
$[PhMe_3PenFlu]ZrCl_2$	**3**	5.52

These data show that it is easy to incorporate norbornene by the pentalene-zirconocene **2**. Norbornene is only incorporated three times more slowly than ethene.

4. Ethene polymerization

For the ethene polymerization, the pentalene bridged zirconocenes **5**–**11** were synthesized (Fig. 6).

The synthesis of the fulvene ligands was carried out analogous as described in the literature by Griesbeck [43], Erker

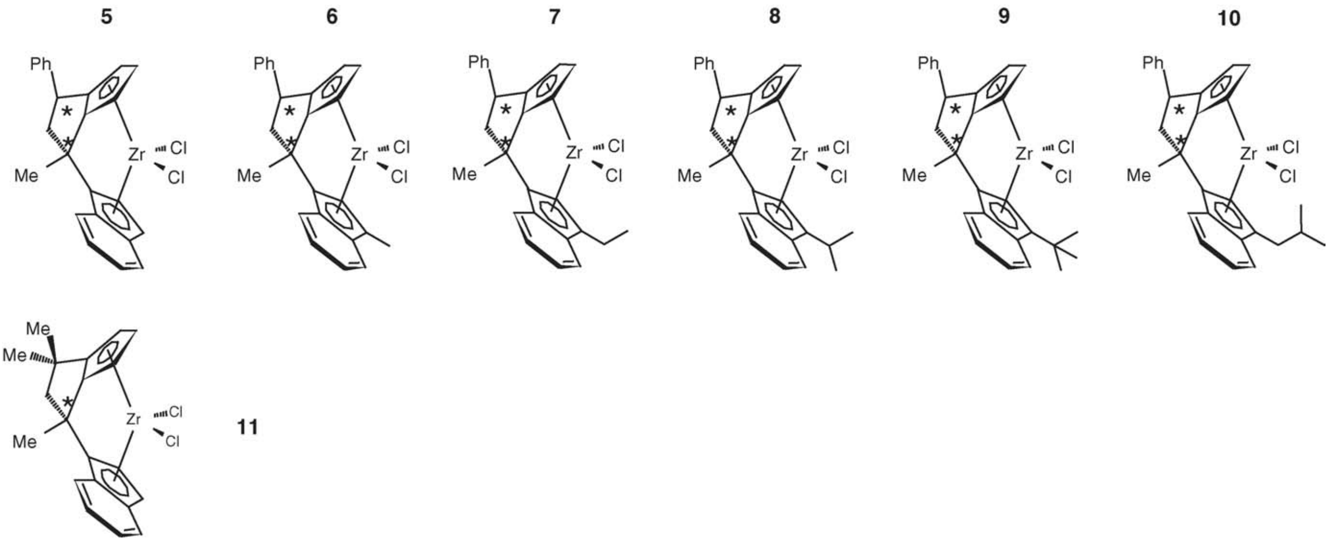


Fig. 6. Structures of the pentalene bridged zirconocenes [MePhPenInd]ZrCl$_2$(5), [MePhPenMeInd]ZrCl$_2$(6), [MePhPenEtInd]ZrCl$_2$(7), [MePhPen^{iso}-PrInd]ZrCl$_2$(8),[MePhPen^{tert}BuInd]ZrCl$_2$(9), [MePhPen^{iso}BuInd]ZrCl$_2$(10), [Me$_3$PenInd]ZrCl$_2$(11).

[44], Collins [45], and Grimmer [46]. In a first step, indene is metallated by butyl-lithium and then reacted with the wanted alkyl bromide. The substituted indenyl is metallated again and treated with the pentalene compound (Fig. 7). By this reaction, a new chiral center is formed and therefore different stereo isomers. The last step is after a new metallization the reaction with ZrCl$_4$ and the synthesis of the zirconocene complexes. A racemic mixture of the zirconocenes is obtained.

All pentalene bridged zirconocenes are active for ethene polymerization (Table 6).

Complex **11** gives the highest activities with 31,000 kg PE/mol Zr h cE followed by complex **6**. Compared with other zirconocene catalysts, the activities are only an average but as desired, the thermal stability is excellent. The catalysts reach their highest activities at 90 or 105 °C and not at 30 or 50 °C. The pentalene bridge leads to a much better stability than only a C(CH$_3$)$_2$-, Si(CH$_3$)$_2$-, or CH$_2$–CH$_2$-bridge.

As shown in Fig. 8, the catalyst 6/MAO has the highest activity after 10 min. The activity decreases then slowly but is

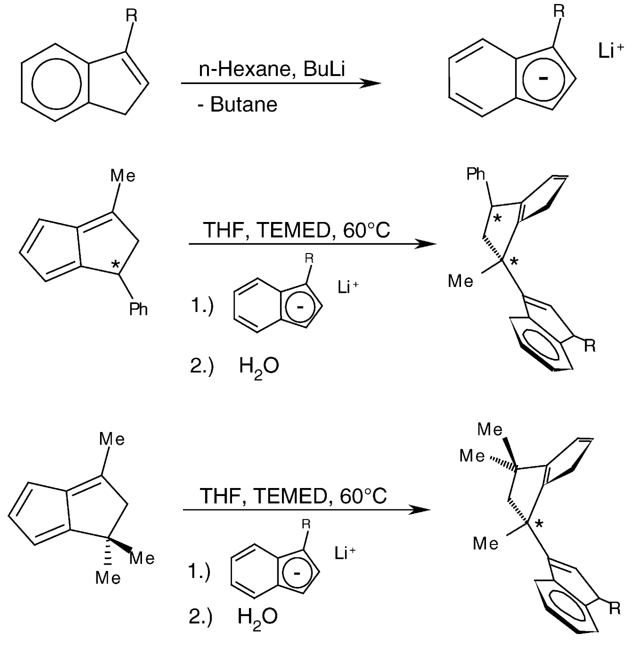


Fig. 7. Synthesis of substituted indenyl and pentalene ligands and ansa zirconocenes with pentalene bridges.

Table 6
Polymerization of ethene by the zirconocene complexes **5**–**11** and MAO as co-catalyst in 200 ml toluene at different temperatures

Complex	T_p (°C)	Activity	M_w (kg/mol)	D	T_m (°C)	E_a (kg/mol)
5	30	340	3087	8.7	136	54
	45	740	1988	6.1	136	–
	60	210	438	4.6	133	–
	75	3290	350	5.2	133	–
	90	5350	178	5.7	130	–
	105	5700	147	4.7	130	–
6	30	500	3927	4.7	136	46
	45	860	3105	9.5	135	–
	60	1890	2556	15.5	134	–
	75	3110	1510	11.5	137	–
	90	4580	689	7.0	134	–
	105	9500	440	3.9	132	–
7	90	8150	885	6.4	137	55
8	90	2770	542	8.8	135	45
9	90	4920	354	4.6	137	49
10	90	4200	55	2.7	137	35
11	30	2370	302	2.3	135	53
	45	4920	186	2.0	135	–
	60	11,550	114	2.2	133	–
	75	16,320	89	2.1	133	–
	90	31,370	70	2.1	131	–
	105	25,500	45	2.2	131	–

Zr concentration, 5×10^{-6} mol; Al:Zr, 680; ethene concentration (CE), 0.239 mol/L; T_p, polymerization temperature; Activity in kg PE/mol Zr h cE; M_w, molecular weight (mass average); D, dispersity M_w/M_n; T_m, melting point of PE; E_a, activation energy of the polymerisation.

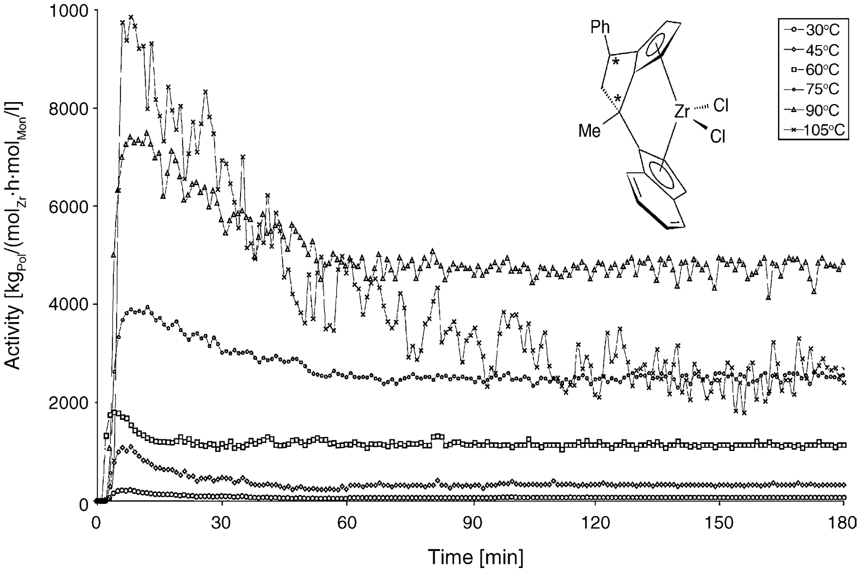


Fig. 8. Mass flow measured consumption of ethene by zirconocene **5** at different temperatures, activities vs. polymerization time.

still remarkable after 60 min reaction time. The same dependence was found for the other catalysts.

Very high molecular masses are obtained which is very surprising. With complex **6** as catalyst component, a polyethylene with a molecular mass of 4 million g/mol was reached at a polymerization temperature of 30 °C.

As usual, the molecular masses of the obtained produced polyethylenes decrease with increasing temperature as presented in Table 6 for complexes **5**, **6**, and **11**. The most active complex **11** gives the lowest molecular mass at a polymerization temperature of 105 °C with only 45,000 g/mol. The other complexes produce even at high temperatures molecular masses useful for most commercial applications. All polyethylenes produced by zirconocene complexes **5**–**10** show a multimodal mass distribution up to 15 which can be explained with the stereometric character of the ligands. Each stereoisomer synthesizes a polyethylene with a different molecular mass. The differences are surprisingly high. Only the enantiomers of complex **11** give polyethylenes with nearly the same molecular mass resulting in a polydispersity of M_w/M_n around 2, and monomodal distribution. The melting points of all polyethylenes are in the range of 130–137 °C. Only few ethyl branches are observed. The activation energies differ between 35 and 54 kJ/mol. Complexes **5**–**10** are in combination with MAO not able to polymerize propene or longer chained α-olefins. The only exception is the sterically less hindered, symmetric bridged metallocene 11 which produces polypropylene with a low molecular mass of 13,700 g/mol and an activity of 269 kg PP/mol Zr h at 60 °C. The polypropylene shows a melting point of 113 °C.

5. Conclusions

The more stereorigid bridge in the ansa metallocenes increases their thermal stability and makes them useful for polymers with higher molecular masses. Different substitution patterns of the zirconocene ligand structure not only result in different activities but also different microstructures of polypropylenes are obtained. Some pentalene–zirconocenes (**2** and **3**) are very useful for the copolymerization of ethene and norbornene. The pentalene catalyst $[Me_3PhPenEtInd]ZrCl_2$/MAO shows excellent thermostability. Even at an ethylene polymerization temperature of 105 °C, the half life period of the activity is 3 h. Under these conditions, it produces a polyethylene with an average molecular mass of 500,000 g/mol. The polyethylene samples have a multimodal mass distribution which can be explained by the stereometric character of the pentalene ligands. The combination of the ring components cyclopentadiene and indene together with the symmetric 1-phenyl-3-methylpentalene-bridge was, however, not ideal for the polymerization of higher 1-olefins such as propene. Here the only exception is the sterically less hindered, symmetric bridged metallocene 11 which is a complex that produces polyolefins with a monomodal mass distribution and is active in the polymerization of propene.

References

[1] H.S. Ko, Proceedings of the IUPAC Congress-Macro 2004, vol. 7.1, Paris, July 4–9, 2004.

[2] P. Galli, G. Vecellio, J. Polym. Sci. A 42 (2004) 396.

[3] H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99.

[4] H. Sinn, W. Kaminsky, H.J. Vollmer, Angew. Chem. Int. Ed. Engl. 19 (1980) 390.

[5] W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907.

[6] H. Sinn, Macomol. Symp. 97 (1995) 27.

[7] Y. Koide, S.G. Bott, A.R. Barron, Organometallics 15 (1996) 2213.

[8] M. Ystenes, J.L. Eilertsen, J. Liu, M. Ott, E. Rytter, J.A. Stoveng, J. Polym. Sci. 38 (2000) 3106.

[9] E. Zurek, T.K. Woo, T.K. Fiurman, T. Ziegler, in: R. Blom, A. Follestad, E. Rytter, M. Tilset, M. Ystenes (Eds.), Organometallic Catalysts and Olefin Polymerization, Springer Press, Heidelberg, 2001, p. 109.
[10] J.J. Eisch, S.I. Bombrick, G.X. Zheng, Organometallics 12 (1993) 3856.
[11] P. Tait, in: W. Kaminsky, H. Sinn (Eds.), Transition Metals and Organometallics as Catalysts for Olefin Polymerization, Springer Press, Berlin, 1988.
[12] R.F. Jordan, W.E. Dasher, S.F. Echols, J. Am. Chem. Soc. 108 (1986) 1718.
[13] C. Sishta, R.M. Hathorn, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 114.
[14] V.C. Gibson, K.S. Spitzmesser, Chem. Rev. 103 (2003) 283.
[15] R. Duchatean, S.J. Lancaster, M. Thornton-Pett, M. Bochmann, Organometallics 16 (1997) 4995.
[16] J.K.G. Erker, R. Fröhlich, J. Am. Chem. Soc. 119 (1998) 11165.
[17] F.R.W.P. Wild, L. Zsolnai, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 232 (1982) 233.
[18] J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355.
[19] W. Kaminsky, K. Külper, H.H. Brintzinger, F.R.W.P. Wild, Angew. Chem. Int. Ed. Engl. 24 (1985) 507.
[20] W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E.F. Raulus, Organometallics 13 (1994) 954.
[21] H.G. Alt, J.S. Han, U. Thewalt, J. Organomet. Chem. 456 (1993) 89.
[22] V. Busico, R. Cipullo, G. Monaco, M. Vacatello, Macromolecules 30 (1997) 6251.
[23] M. Arndt, W. Kaminsky, A.-M. Schauwienold, U. Weingarten, Macromol. Chem. Phys. 199 (1998) 1135.
[24] J.A. Ewen, R.L. Jones, A. Razavi, J.P. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255;
A. Razavi, V. Bellina, Y. de Brauwer, K. Hortmann, L. Peters, S. Sirole, S. van Belle, U. Thewalt, Macromol. Chem. Phys. 205 (2004) 347.
[25] N. Ishihara, M. Kuromoto, M. Uol, Macromolecules 21 (1988) 3356.
[26] G.W. Coates, R.M. Waymouth, J. Am. Chem. Soc. 113 (1991) 6270.
[27] Z.J. Komon, G.M. Diamond, M.K. Leclerc, V. Murphy, M. Okazaki, G.C. Bazan, J. Am. Chem. Soc. 124 (2002) 15280.
[28] W. Kaminsky, R. Spiehl, Makromol. Chem. 190 (1989) 515.
[29] W. Kaminsky, A. Ahlers, N. Möller-Lindenhof, Angew. Chem. 101 (1989) 1304;
W. Kaminsky, A. Ahlers, N. Möller-Lindenhof, Angew. Chem. Int. Ed. Engl. 28 (1989) 1216.
[30] J. Dutschke, W. Kaminsky, H. Lüker, in: K.H. Reichert, W. Geiseler (Eds.), Polymer Reaction Engineering, Hanser Publisher, Munich, 1983, p. 207.
[31] M. Hoff, W. Kaminsky, Macromol. Chem. Phys. 205 (2004) 1167.
[32] W. Kaminsky, A. Laban, Appl. Catal. A: Gen. 222 (2001) 47.
[33] Y.V. Kissin, Macromolecules 36 (2003) 7413–7421.
[34] W. Kaminsky, R. Steiger, Polyhedron 7 (1988) 2375.
[35] W. Kaminsky, R. Werner, in: W. Kaminsky (Ed.), Metalorganic Catalysts for Synthesis and Polymerization, Springer, Heidelberg, 1999, p. 170.
[36] G. Erker, C. Psiorz, C. Krüger, M. Nolte, Chem. Ber. 127 (1994) 1551.
[37] A.G. Griesbeck, Chem. Ber. 124 (1991) 403.
[38] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1283.
[39] M. Farina, G. di Silvestro, P. Sozzoni, Macromolecules 15 (1982) 1451.
[40] B. Rieger, C. Troll, J. Preuschen, Macromolecules 35 (2002) 5742.
[41] W. Fan, R.M. Waymouth, Macromolecules 36 (2003) 3010.
[42] V. Busico, R. Cipullo, P. Corradini, Makromol. Chem. Rapid Commun. 14 (1993) 97.
[43] A.G. Griesbeck, J. Org. Chem. 54 (1989) 4981.
[44] G. Erker, C. Psiorz, R. Fröhlich, M. Grehl, C. Krüger, R. Noe, M. Nolte, Tetrahedron 51 (1995) 4347.
[45] S. Collins, Y. Hong, N.J. Taylor, Organometallics 9 (1990) 2695.
[46] N.E. Grimmer, N.J. Coville, C.V. de Koning, J.M. Smith, L.M. Cook, J. Orgnomet. Chem. 616 (2000) 112.