

Progress of Olefin Polymerization by Metallocene Catalysts

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SUMMARY: New C_1 -symmetric metallocenes such as $[\text{Me}_2\text{C}(\text{PhCp})(\text{Flu})\text{ZrCl}_2]$, $[\text{Me}_3\text{Pen}(\text{Flu})]\text{ZrCl}_2$, $[\text{PhMe}_3\text{Pen}(\text{Flu})]\text{ZrCl}_2$ were synthesized and used for the polymerization of propene by higher polymerization temperatures. Different polypropylene micro structures were obtained. Important for industrial processes are the high molecular weights of the polymers produced by the pentalenelike catalysts, which are very stable by higher temperatures. For synthesis of syndiotactic polystyrene and new substituted half-sandwich titanocenes are used such as 1,3- $\text{Me}_2\text{-CpTiCl}_3$, $\text{Me}_5\text{CpTiCl}_3$, PhCpTiCl_3 , cyclohexyl- CpTiCl_3 . If they are fluorinated, the activity for the production of syndiotactic polystyrene can be increased 10 times. The synthesized polymer shows a high melting point of 275 °C.

Introduction

Metallocene and half sandwich complexes are in combination with methylaluminoxane (MAO) active catalysts for the production of precisely designed polyolefins and engineering plastics ^{1–3}. Especially C_s or C_1 symmetric zirconocenes with an isopropylidene bridge and substituted cyclopentadienyl and fluorenyl ligands are of great interest as catalysts for the polymerization of propene, which leads to syndiotactic and hemiisotactic polymers ^{4–7}. They can be synthesized without achiral side products. They are also very active for the polymerization of ethene and copolymers by ethene and other 1-olefins (Tab. 1).

Table 1 Ethene Homopolymerization by Different $[\text{Me}_2\text{C}(3\text{-RCp})(\text{Flu})]\text{ZrCl}_2/\text{MAO}$ Catalysts at 30 °C in Toluene; $[\text{Zr}] = 5 \times 10^{-6}$ mol/l, $\text{Al}:\text{Zr} = 7800$

[Ethene]	Activity (kg PE/mol Zr x h)		
	R = Me	iPr	tBu
0,118	640	640	21 000
0,236	1 700	1 400	87 000
0,472	2 900	6 600	124 000
0,708	4 700	9 500	210 000

Only by changing the substitution at the Cp-ring, the activity can be increased by the factor of 20 from i-propyl to t-butyl. For an industrial use some disadvantages have to be solved. The polymers often show a low molecular mass, and the catalysts are not very stable at higher temperatures and deactivate fast. In other cases these catalysts are not active enough and give only low stereoselectivities.

Therefore there is an interest to increase the activity and to make the metallocenes more stable for higher temperatures ⁷⁾. It is known from the bisindenylzirconocenes that substitution by phenyl groups increases the activity ⁸⁾. A stronger bridge should increase the thermal stability. X-ray structures and calculations showed that the angle between the rings of the zirconocene can be influenced (Fig. 1).

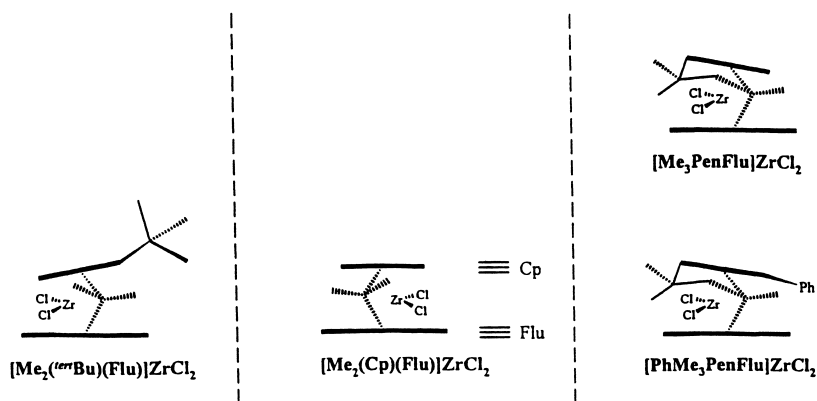


Fig. 1 Angle between the rings of different C_s and C_1 symmetric metallocenes

The pentalenelike compounds give more space for the insertion of longer chained 1-olefins, or cyclic olefins and should be useful for copolymerization.

Substitution of the cyclopentadienyl ring in $[\text{Me}_2\text{C}(\text{tert-Bu Cp})(\text{Flu})]\text{ZrCl}_2$ yields ethene/norbornene copolymers with an alternating structure, because the rigid norbornene can only be inserted from the open side of the metallocene. By variation of the polymerization parameters, copolymers with glass transition temperatures above 180 °C and molecular weights >100 000 are synthesized. Other substitutions lead to block micro-structures of the copolymers.

Results and Discussions

Propene Polymerization

Four new ansa zirconocenes (1-4) were synthesized to increase the activity and the thermal stability of the metallocenes for the polymerization of ethene and propene (Fig. 2)

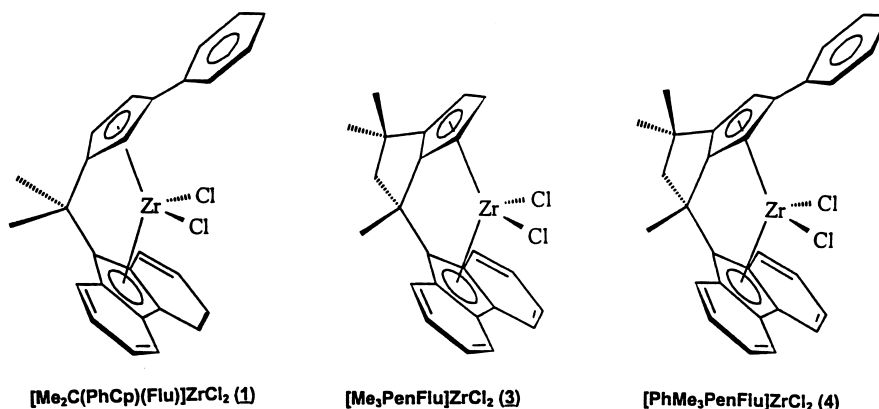


Fig. 2 Structures of C_1 -symmetric zirconocenes

The compounds [1-(Fluorenyl)-1,3,3-trimethyl-tetrahydropentalenyl]zirconium dichloride ($[\text{Me}_3\text{PenFlu}]\text{ZrCl}_2$, **3**) and [1-(Fluorenyl)-1,3,3-trimethyl-5-phenyl-tetrahydropentalenyl]zirconium dichloride ($[\text{PhMe}_3\text{PenFlu}]\text{ZrCl}_2$, **4**) show a more stereorigid bridge than the zirconocenes 1 and 2, which have an isopropyl bridge.

The zirconocenes activated by MAO are used for the polymerization of propene under the same conditions and compared with some other known complexes (Tab. 2).

The characteristics of the polymerization of propene with the four new catalysts were investigated with reference to the influence of temperature and monomer concentration. The significance of these effects was rated by means of design of experiments. Particular reference was paid to the effects on the activity of the catalysts and on the molecular weight and microstructure of the polymers prepared.

Table 2 Results of Polymerizations under Standardized Conditions

Catalyst	Activity ^a	M_v^b	T_g^c	T_m^d	n_{iso}^e	n_{syn}^f
1 $[Me_2C(PhCp)(Flu)]ZrCl_2$	7 500	60	-2.7	-	3.1	4.9
2 $[Me_2C(cHCp)(Flu)]ZrCl_2$	2 900	70	-2.9	-	3.2	4.8
3 $[Me_3PenFlu]ZrCl_2$	4 000	480	8.9	133.8	1.5	14.9
4 $[PhMe_3PenFlu]ZrCl_2$	790	260	-4.0	82,0	9.6	2.6
for comparison:						
5 $[Me_2C(^{tert}BuCp)(Flu)]ZrCl_2$	1 100	50	n.d.	133.5	n.d.	n.d.
6 $[Me_2C(Cp)(Flu)]ZrCl_2$	1 600	160	5.1	143.1	1.6	46.0
7 $rac-[En(Ind)_2]ZrCl_2$	1 700	30	n.d.	136.5	48.5	1.5
8 $rac-[Me_2Si(Ind)_2]ZrCl_2$	1 900	80	n.d.	148.9	99.0	1.0

Conditions: Temperature: 30 °C; monomer concentration: 1.31 mol/l (propene); volume: 200 ml toluene; cocatalyst: MAO; ^a) [kgPP/(molZr · h · $c_{propene}$)]; ^b) average viscosity molecular weight [kg/mol]; ^c) glass transition temperature [°C]; ^d) melting point [°C]; ^e) average isotactic chain length; ^f) average syndiotactic chain length; n.d.: not detected

The phenyl substituted **1** revealed an activity of up to nine times higher than the rest of the systems to which it was compared. Whereas metallocenes **1** and **2** show a fast thermal deactivation at higher polymerization temperatures, an increase in activity of complexes **3** and **4** was found by raising the temperature; this may be an effect of the very rigid structure of these compounds.

One of the most important results of the work presented is the high molecularweight of the polymers produced by the pentalenelike catalysts **3** and **4**: That are up to nine times the value the isopropylidene bridged zirconocenes reach.

The microstructure of the polymers prepared at 30 °C by catalysts **1** and **2** is, in general, the same (rrrr = 33 %). At high temperatures or low monomer concentrations, however, the product polymerized by metallocene **2** is isotactic. The steric hindrance can explain this unusual phenomenon. While complex **3** produces polymers with a syndiotactic microstructure, metallocene **4** yields an isotactic product. Another remarkable result of this work is the lack of effects of variation in temperature and monomer concentration on the polymer structure produced by catalyst **4** ⁷⁾.

Of great interest is the activity by higher polymerization temperatures. Fig. 3 compares the activity of the complexes 1 - 4 for the polymerization of propene by different temperatures.

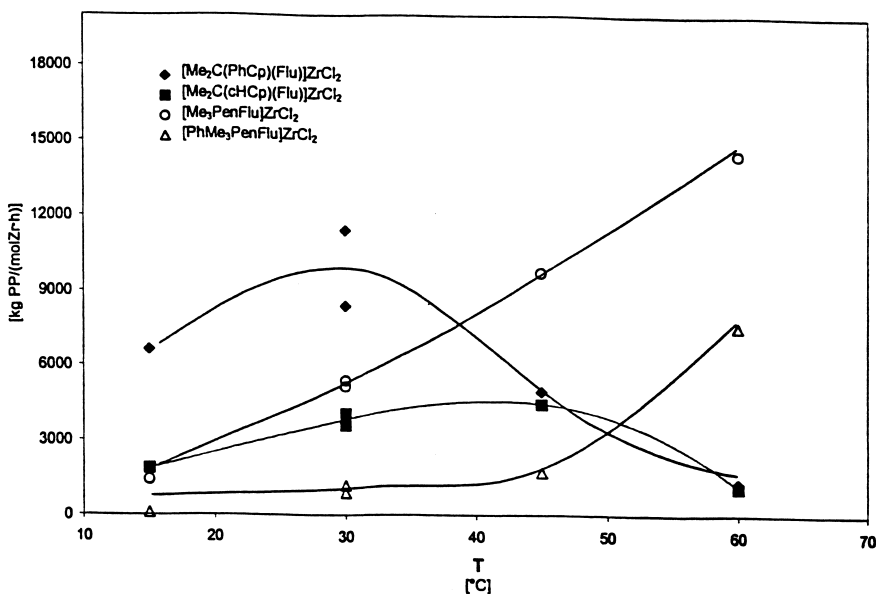


Fig. 3 Polymerization activity of propene in dependence of temperature for different zirconocenes

It can be seen that by low polymerization temperatures (30 °C) the activity of zirconocene 1 with a phenyl substitution at the Cp-ring shows a maximum but by increasing the temperature (60 °C) the pentalene like complex 3 is much active and produces the polypropylene with the higher molecular weight.

Syndiotactic polystyrene

As found by Ishihara, syndiotactic polystyrene can be synthesized by titanium/MAO catalysts⁹⁾. Half sandwich complexes such as CpTiCl₃, Cp*TiCl₃, or tetra-alkoxy complexes in combination with MAO polymerize styrene affording a highly syndiotactic polymer with a melting point of 275 °C in contrast to the commercial atactic polystyrene with a glass transition point of 100 °C¹⁰⁻¹³⁾.

The activity however is much less compared with olefin polymerization so that catalyst costs become important for industrial production. Therefore, it is necessary to enhance the activity of the catalyst.

New substituted half-sandwich titanocenes ($1,3\text{-Me}_2\text{-CpTiCl}_3$, $\text{Me}_4\text{CpTiCl}_3$, PhCpTiCl_3 , $\text{C}_6\text{H}_{11}\text{CpTiCl}_3$) were synthesized and used for comparison with other substituted compounds for the polymerization of styrene (Fig. 4)

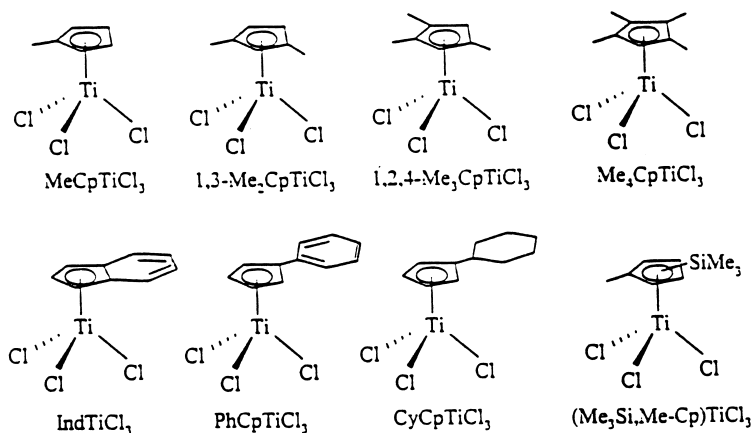


Fig. 4 Half-sandwich titanocenes used as catalysts for the polymerization of styrene

Fluorinated half-sandwich metallocenes show an increase in activity, compared to chlorinated compounds ¹⁴⁾. The polymerization was carried out within a temperature range of 10 to 70 °C.

Fig. 5 shows the polymerization rate of styrene by some selected half-sandwich titanocenes.

After about 10 minutes, the catalysts reach the maximum on activity. The differences between the average activities between chlorinated and fluorinated compounds can be seen in Table 3.

Under the used conditions, PhCpTiCl_3 is the most active catalyst. The fluorinated complexes are about three times more active than the chlorinated ones. The fluorine atom stabilizes the active site and by this increases the number of active centers.

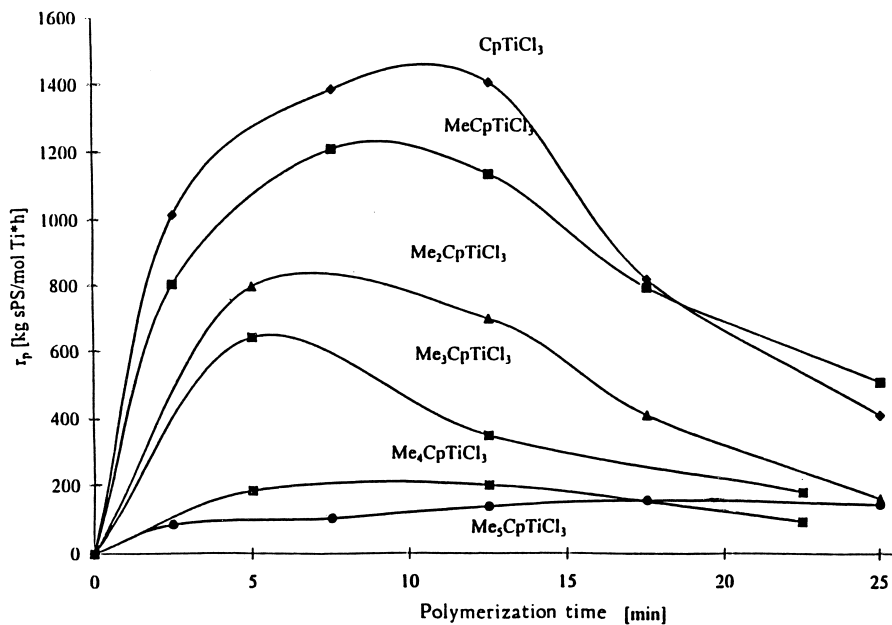


Fig. 5 Styrene polymerization rate in dependence of polymerization time for different catalysts, conditions see Tab. 3

There is another advantage of the fluorinated catalysts. They are more active by low aluminoxane/titanium ratios (Fig. 6).

The activity maximum for CpTiF_3 is obtained by an Al/Ti ratio of 200 while for CpTiCl_3 it has to be more than 1000. Using a low Al/Ti ratio, the costs especially for MAO can be decreased drastically. The activity of all investigated catalysts increases lineary by the styrene concentration.

In Table 3 the molecular weights and the melting points can be found of the obtained syndiotactic polystyrenes. The molecular weights are independent on the polymerization time.

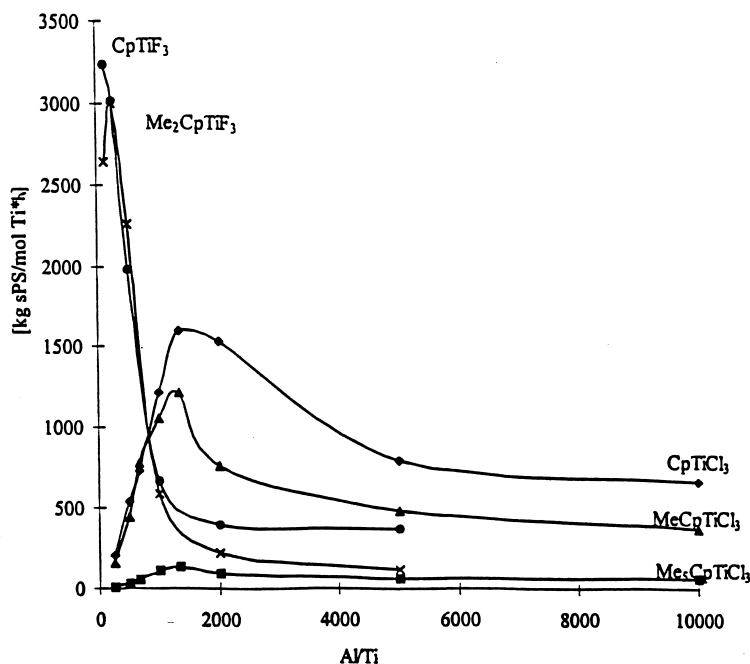


Fig. 6 Influence of the Al/Ti molar ratio for the styrene polymerization by different half-sandwich titanocenes; reaction time = 20 min.; further conditions see Tab. 3

Table 3 Activities (kg sPS/mol Ti · h, molecular weights and melting points (°C) of different half-sandwich titanocenes for the syndiospecific polymerization of styrene by 30 °C, molecular weights and melting points for the obtained syndiotactic polystyrenes. Polymerization time 10 min.; 25 ml toluene, 25 ml styrene, Al/TiCl = 1000, Al/TiF = 500, [Ti] = $5 \cdot 10^{-5}$ mol/l; 0,145 g MAO

Catalyst	Activities	Molecular weight	Melting point
CpTiCl ₃	1 200	224 000	259
MeCpTiCl ₃	950	190 000	266
Me ₂ CpTiCl ₃	780	257 000	271
Me ₃ CpTiCl ₃	550	335 000	269
Me ₄ CpTiCl ₃	200	387 000	270
Me ₅ CpTiCl ₃	110	469 000	270
PhCpTiCl ₃	3 200	280 000	266
(Me ₃ Si,MeCp)TiCl ₃	260		
CpTiF ₃	3 100	186 000	264
MeCpTiF ₃	3 050	258 000	270
Me ₂ CpTiF ₃	2 700	321 000	273
Me ₃ CpTiF ₃	830	397 000	272
Me ₄ CpTiF ₃	460	421 000	272
Me ₅ CpTiF ₃	350	388 000	273
Cp*TiF ₂ (OCOCF ₃)	270	-	273
Cp*TiF ₂ (OCOC ₆ F ₅)	340	-	273

With an increasing substitution of the Cp-rings of the catalyst the molecular weight of the produced polystyrene increased. The molecular weight distribution M_w/M_n is around 2 and indicates that there is only a single active site. The melting points of the polystyrenes differ between 259 and 273 °C. Higher substituted catalysts increase the syndiotacticity and give polymers with higher melting points. The maximum is almost reached by the dimethyl substituted complex.

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