

New polyolefins by metallocene catalysts

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Abstract : New zirconocenes and half-sandwich titanium compounds have been synthesized, that give tailored polymers of different structures. They are useful for obtaining highly isotactic polypropylene with melting points near 170°C, alternating ethene/propene and cycloolefin polymers with melting points upto 320°C. These new types of polymers have special properties and a high potential as engineering plastics. Molecular modeling shows that one explanation for the different regio- and stereospecificity of metallocene catalysts is attributed to the flexibility of the ligand.

RESULTS AND DISCUSSION

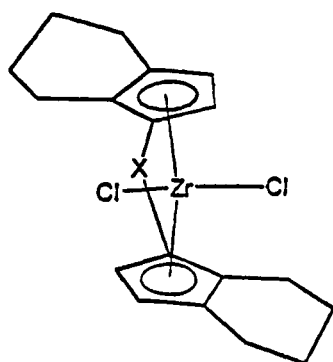
Metallocenes are a new generation of catalysts for the production of precisely designed polyolefins and engineering plastics. The discovery of metallocene methylalumoxane catalysts has opened a frontier in the areas of organometallic chemistry, polymer synthesis, and processing (ref.1,2). Based on transition metals such as titanium and zirconium atoms sandwiched between ring structures they have well defined single catalytic sites and well understood molecular structures (ref. 3-5). Stereoselective catalytic sites can polymerize almost any olefin in an exact manner to new materials. A great number of symmetric and chiral zirconocenes have been synthesized to give isotactic, syndiotactic, or stereoblock polypropylenes with increased impact strength and toughness, better melt characteristics or elasticity. Figure 1 shows metallocenes that are mainly used in our Institute .Hafnocenes are less active but produces polymers with a higher molecular weight as zirconocenes. Table 1 compares some zirconocenes for the polymerization of propene

TABLE 1 Polymerization of propene with different metallocenes in toluene under the same conditions; temp.: 30°C; 2,5 bar propene pressure; $6,25 \cdot 10^{-6}$ mol/l metallocene concentration; MAO/ metallocene ratio = 250

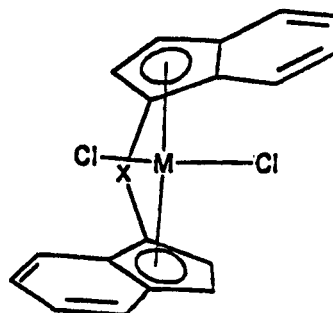
No	Catalyst	Activity in kg PP/mol M · h · c _a	M η · 10 ⁻³	Isotacticity mmmm in %
1	Cp ₂ ZrCl ₂	140	2	7
2	[En(Ind) ₂]ZrCl ₂	1690	32	91
3	[En(Ind) ₂]HfCl ₂	610	446	85
4	[En(2,4,7Me ₃ Ind) ₂]ZrCl ₂	750	418	> 99
5	[Me ₂ Si(Ind) ₂]ZrCl ₂	2160	90	96
6	[Me ₂ Si(2Me-4PhInd) ₂]ZrCl ₂	15000	650	99
7	[Me ₂ Si(2Me-4,5BenzInd) ₂]ZrCl ₂	6100	380	98
8	[MeC(Flu)(Cp)]ZrCl ₂	1550	159	0,6
9	[Me(Flu)(3-t-BuCp)]ZrCl ₂	1045	52	89

Especially the catalyst No. 4 gives polymers with a very high isotacticity. By a polymerization temperature of -30°C the melting point of the resulting polypropylene is about 170°C, the highest ever measured (ref. 6) Molecular modelling shows that one explanation for the different regio- and stereospecificity of metallocene catalysts is attributed to the flexibility of the ligand. Catalyst No. 4 is very stereorigid.

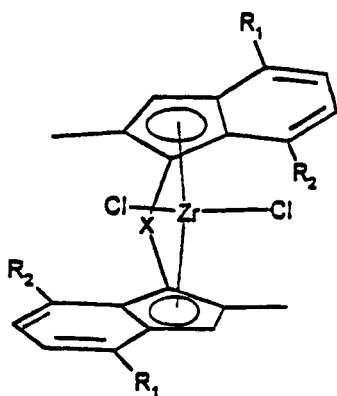
Supporting of the zirconocenes on silica are shown in Fig. 2.



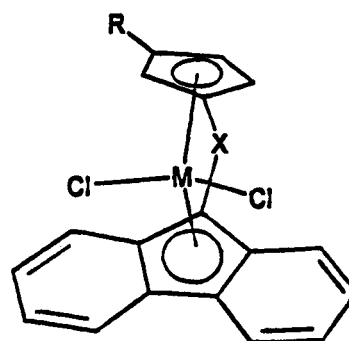
$X = C_2H_4, Me_2Si$



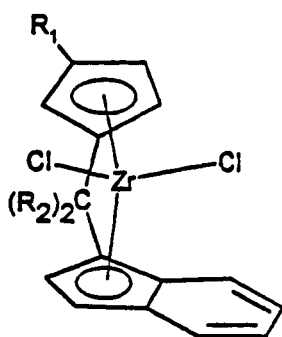
$M = Zr, Hf$
 $X = C_2H_4, Me_2Si$



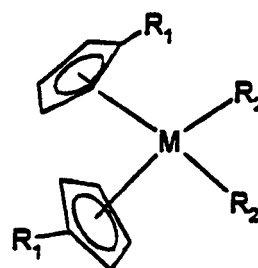
$X = C_2H_4, Me_2Si$
 $R_1 = Me, Ph, Naph$
 $R_2 = H, Me$



$M = Zr, Hf$
 $X = Me_2C, Ph_2C$
 $R = H, Me, t-Bu$



$R_1 = H, Me$
 $R_2 = Me, Ph$



$M = Ti, Zr, Hf$
 $R_1 = H, 5-Me, neomenthyl$
 $R_2 = Cl, Me$

Fig. 1: Structures of metallocenes that are used in the polymerization of olefins

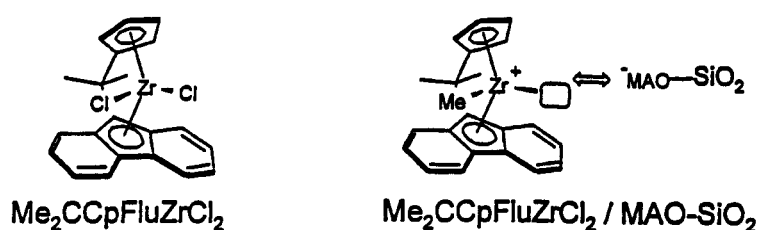


Fig. 2

To use the bridged -Flu-Cp-Zirconocene opens up the possibility to observe a change of the tacticity in the resulting polymer. Both the unsupported and the supported catalysts give syndiotactic polypropylene. The filtrate of the supported catalyst is inactive for the propene polymerization if TIBA is used as scavenger. But if the supported catalyst is washed with MAO, a lot of activity is given in the filtrate (ref. 7)

Supported and unsupported zirconocene catalysts decrease the necessary surplus of MAO (Table 2). There is a good activity given by a ratio of Al (MAO) :Zr = 300. If triisobutyl aluminum (TIBA) is used as scavenger, the optimum (TIBA:Zr) is about 500. The supported catalyst shows an increase of the isotacticity with a growing propene concentration while the homogeneous catalyst is more independent. Similar results are found for the molecular weight of the resulting polypropylene.

TABLE 2 Polymerization of propene with silica supported zirconocene catalysts in dependence of the amount of cocatalyst

$\text{Me}_2\text{CCpFluZrCl}_2/\text{MAO-SiO}_2$		$\text{Me}_2\text{CCpFluZrCl}_2/\text{MAO-SiO}_2$	
Al(MAO):Zr	Activity	[TIBA]:[Zr]	Activity
[]	[kg sPP/(mol Zr*h*c _{mon})]	[]	[kg sPP/(mol Zr*h*c _{mon})]
30	47	1000	470
100	352	500	708
300	708	100	331
1000	1034	10	94

Metallocenes are also useful for obtaining cycloolefin copolymers (COC) and syndiotactic polystyrene - new types of polymers with special properties and a high potential as engineering plastics (ref. 8-10).

The copolymers of ethylene and norbornene are amorphous if more than 15 mol% of the cycloolefin is incorporated. They also feature glass transition temperatures exceeding 200°C, have high mechanical strength, a low density which is 20% lower than that of its competitor polycarbonate, and are well suited for optoelectronic applications.

The comonomer distribution may be varied from statistical to alternating. Statistical copolymers are amorphous and show a glass transition temperature in dependence of the comonomer content. Copolymerization of ethene and norbornene with $[\text{Me}_2\text{C}(\text{Flu})(\text{tBuCp})]\text{ZrCl}_2$ leads to a strong alternating structure. It is impossible to receive copolymers with more than 50 mol % of norbornene.

An alternating structure with high amounts of ENEN-pentads is given if the starting monomer mixture there is a low ethene and a high norbornene concentration. Because of the low copolymerization parameter r_1 of 3 norbornene inserts always in the more open side feature of the catalyst. In the blocked side only ethene can insert even when its concentration is low. The alternating copolymer of ethene and norbornene is partially crystalline and shows melting points up to 320°C (Fig. 3).

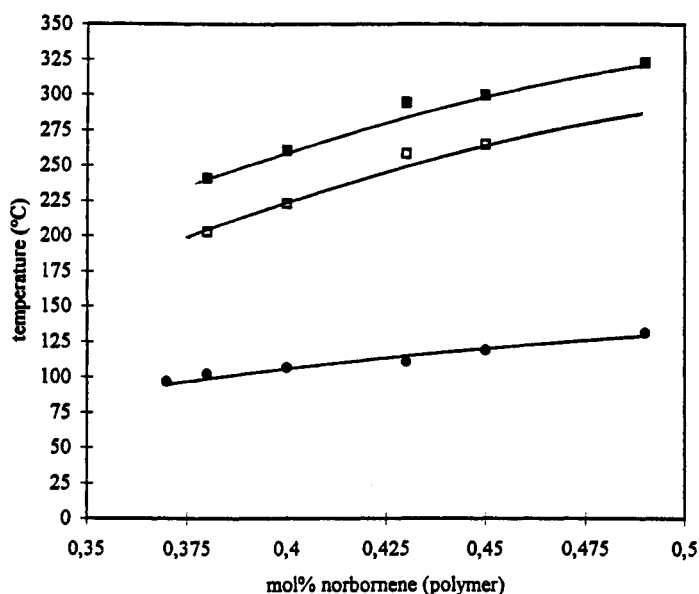


Fig. 3 Melting points (■) and crystallization temperature (□) and glass transition temperature (●) of ethene/norbornene copolymers containing alternating sequences

The melting point depends on the molar ratio of norbornene units in the polymer while the glass transition temperature is nearly independent of that. Crystallinity of these copolymers is detected using wide angle X-ray scattering of films. The degree of crystallinity is about 22 % for copolymers containing 49 mol % of the cycloolefin. The polymers show a good heat resistance and resistance against unpolar solvents.

For synthesis of syndiotactic polystyrene (ref. 11, 12), fluorinated half-sandwich titanocenes are used. Table 3 shows the results of the polymerisation of styrene (ref. 13, 14).

TABLE 3 Synthesis of syndiotactic polystyrene with half-sandwich metallocenes

Catalyst	Temp. (°C)	Activity (kg PS/mol M·h)	Mp (°C)	M_w	M_w/M_n
CpTiCl ₃	50	1100	258	140,000	1,9
CpTiF ₃	50	3000	265	100,000	2,0
Cp*TiCl ₃	30	3,5	277	186,000	2,3
Cp*TiCl ₃	50	15	275	169,000	3,6
Cp*TiCl ₃	70	30	274		
Cp*TiF ₃	30	300	277	700,000	1,8
Cp*TiF ₃	50	690	275	660,000	2,0
Cp*TiF ₃	70	1200	275		

The fluorinated catalysts are 5 to 50 times more active than the chlorinated compounds. The synthesized syndiotactic polystyrene shows a high melting point of 275°C. The highest melting point (277°C) can be obtained with pentamethylcyclopentadienyltitanium compounds. The fluorinated complex gives a significantly higher molecular weight, 660 000 at 50°C, than the chlorinated one, 169 000, and is more stable up to a polymerization temperature of 70°C.

The following structure of the active site is proposed.

Coordination Center

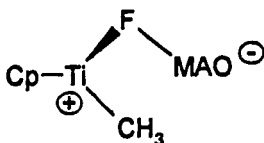


Fig. 4 Proposed active site for the fluorinated titanium compounds to produce syndiotactic polystyrene

There is a back coordination of the fluor atom that activates the titanium center.

Some of the plastics made by metallocene catalysts are already on the market, and it is expected that there will be a rapid increase in the next few years.

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