Macromol. Symp. **2003**, *201*, 301—307

Efficient and Tailored Polymerization of Olefins and Styrene by Metallocene Catalysts

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Summary: Different optimised new c_s-symmetric ansa zirconocenes were used for the homopolymerization of propene – activated by methylaluminoxane (MAO) with an Al : Zr molar ratio of 2000. In a series of experiments, the polymerisation temperature was varied in a range from 0 to 60 °C. The obtained syndiotactic polypropenes show highly isotacticities up to rrrr pentads of 98 % and melting points of 150 °C. Stereoselectivities are sensitive to the monomer concentration, showing decreasing syndiotacticities with decreasing propene concentration due to increasing amount of skipped insertion which is demonstrated for the zirconium catalyst.

Keywords: homopolymerization, methylaluminoxane (MAO), propene, syndiotactic polypropenes, zirconium catalyst

Introduction

Metallocenes are highly active catalysts for the production of precisely designed polyolefins and engineering plastics. Especially zirconocene methylalumoxane (MAO) catalysts and half-sandwich titanium complexes have opened a frontier in the area of new polymer synthesis and processing.[1-3] They show only one active site and produce polymers with a narrow molecular weight distribution and new properties. With the aid of metallocenes, plastics can be made for the first time with a property profile that is precisely controllable within wide limits, comprising temperature resistance, hardness, impact strength and transparency.

There is a variety of materials which can be produced with high activity by metallocene catalysts such as:

- Long chain branched polyethene;
- Polypropenes with low amounts of oligomers and different tacticities (atactic, isotactic, isoblock, stereoblock, syndiotactic);
- Copolymers with a high proportion (up to 60 mol%) of longer chain α-olefins such as LLDPE, POE, EP, and ethene/styrene copolymers;

DOI: 10.1002/masy.200351133

- Elastomers made of ethene, propene, and dienes (EPDM);
- Syndiotactic polystyrene with a high melting point;
- Homo- and copolymerisation of cycloolefins;
- Homo- and copolymers of butadiene with special microstructures;
- Polymerisation in emulsions or in the presence of fillers (nano particles).

Important are ethene-1-octene and ethene-styrene copolymers. These polymers show increased impact strength and toughness, better melt characteristics or elasticity, and improved clarity in films.[4,5]

Metallocenes are useful catalysts for the production of cycloolefin copolymers (COC) and α-olefin copolymers – new types of polymers with special properties and a high potential as engineering plastics6-8). Ethene/norbornene copolymers are most interesting for technical uses because of the easily available monomers. Due to different incorporation values of the cyclic olefin in the copolymer, the glass transition temperature can vary over a wide range independently from the used catalysts. A copolymer with 50 mol% of norbornene yields a material with a glass transition point of 145 °C. A Tg of 205 °C can be achieved at higher incorporation rates. The metallocene $[Me_2C(tert\text{-}BuCp)(Flu)]ZrCl_2$ shows not only high activities for the copolymerisation of ethene with propene or norbornene, and gives alternating structure, too.[9,10]

Fluorinated half-sandwich titanium complexes $(R\text{-}Cp)TiF_3$ are in combination with MAO very active catalysts for the polymerisation of styrene and butadiene. The obtained syndiotactic polystyrene shows a molecular weight of over 400 000 g/mol and a melting point of 275 °C. Metallocen-based polybutadiene has a special microstructure with 80 % cis 1,4-, 1 % trans 1,4- and 19 % 1,2-vinyl units. The activity is mainly influenced by the ligand structure while the microstructure is nearly untouched.[11]

C_s-symmetric group 4 ansa metallocenes were introduced first for the syndiotactic polymerisation of propene by Ewen and Razavi.[12] 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 so-called enantiomorphic-site control mechanism implies that the chiral catalytic centres are capable of discriminating between the two prochiral enantiofaces of a propene molecule.[13]

So far there are no studies dealing with a theoretical calculation of the influence of different substituents on catalysts of the type $Ph_2C(Flu)(Cp)MCl_2$ on stereoselectivity whereas many publications are known demonstrating the possibilities of variations on the ligand system.[14]

Experimental Part

The c_s-symmetric zirconocenes (Catalyst 1-4, Fig. 1) were synthesized analogue as described in the literature.[14,15] 5 g (18 mmol) 2,7-bis-t-buthylfluorene were dissolved in 80 ml ether and 11,25 ml of a solution of 1,6 molar butyllithium in hexane were slowly added. The solution was stirred until gas evolution was finished and then 4,14 g of the methyl substituted 6,6-diphenyl fulvene were added. After 10 – 12 hours, a small amount of water is added, the organic layer separated and dried over Na_2SO_4. The solution was reduced and crystallized at – 25 °C to yield colorless crystals (yield 65 – 70 %). This ligand was dissolved in ether, butyllithium added and after gas evolution the zirconiumtetrachlorid added. After filtering, the solution was reduced and crystallyzed. Orange-red crystals were obtained yield (40 – 50 %).

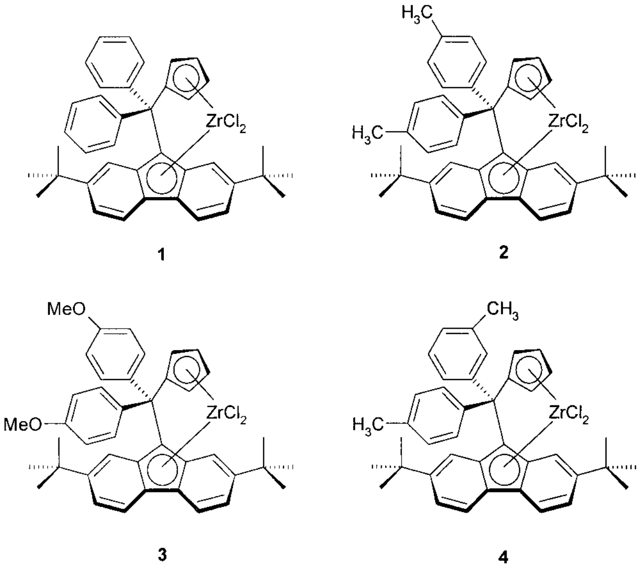

Fig. 1. New synthesized zirconocene complexes 2-4 and 1 for comparison.

Polymerizations were carried out in 200 ml toluene in a 1 l Büchi glass reactor equipped with a magnetical stirrer. The concentration of propene for every run was 1,38 mol/l and the pressure was kept constant during the polymerisation. The polymerisations were started through injection of the metallocene 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 overnight in a methanol/HCl solution, filtered followed by evaporation of the solvents and drying of the polymer under vacuo at 60 °C over night.

Toluene was purified through passing through two columns (molecular sieves and BASF copper catalyst), propene was passed through two columns packed with molecular sieves and Basf copper catalyst).

Polymer samples were recorded using a Bruker avance 400 spectrometer and referenced against $C_2D_2Cl_4$ at 100 °C, pulse angle 30 °, delay time 5 s, 1200 scans.

Results and Discussion

Syndiotactic Polypropene

By molecular modelling using a modified Biosym program analog to the calculation of the stereorigidity of ansa-bis-indenylzirconium complexes[16)], the syndiotactic rrrr pentads in molar ratio were calculated. Starting from the unsubstituted $[Me^2C(Cp,Flu]ZrCl_2$ (Fig. 2), different substitutions at the fluorenyl ring and different bridges were investigated (Table 1 and 2 show the results of the calculations). The program makes it possible to calculate the rrrr pentads by different polymerisation temperatures starting from –30 °C up to 90 °C.

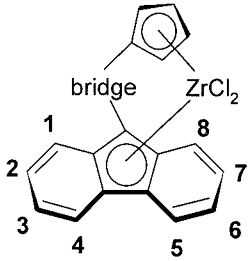

Fig. 2. Unsubstituted $[Me^2C(Cp,Flu]ZrCl_2$.

Table 1. Calculation of the syndiotactic rrrr pentads in molar ratio of polypropylenes produced by different fluorenyl substituted $[Me_2C(Cp,Flu)]ZrCl_2$/MAO catalysts.

Polymerization temperature	-30°C	0 °C	30 °C	60 °C	90 °C
Substitution					
all H	0.9584	0.9451	0.9314	0.9178	0.9044
2,7-Me_2	0.9616	0.9488	0.9356	0.9223	0.9091
2,7-tBu_2	0.9644	0.9520	0.9391	0.9260	0.9130
4,5-Me_2	0.8242	0.8060	0.7904	0.7769	0.7648
4,5-Benzo	0.9083	0.8904	0.8738	0.8587	0.8447

It can be seen that from the calculated rrrr pentads, the zirconocene with the 2,7-t-Bu_2 substitution gives the highest values not only at –30 °C, but also at a polymerisation temperature of 90 °C.

Table 2. Calculation of the syndiotactic rrrr pentads in molar ratio of polypropylenes produced by different bridged c_s-symmetric [bridge(Cp,Flu)]$ZrCl_2$/MAO catalysts.

Polymerization Temperature	-30 °C	0°C	30 °C	60 °C	90 °C
Bridge					
Me_2C	0.9584	0.9451	0.9314	0.9178	0.9044
Me_2Si	0.9517	0.9370	0.9224	0.9082	0.8945
Ph_2C	0.9748	0.9643	0.9529	0.9410	0.9289
Ph_2Si	0.9402	0.9310	0.9252	0.9128	0.9007
C_5	0.9652	0.9527	0.9397	0.9265	0.9132
C_6	0.9561	0.9415	0.9265	0.9114	0.8965

If complexes with different bridges such as dimethylsilyl, diphenylcarbon, 1,1-cyclopentane, 1,1-cyclohexane, are calculated, the complex with a diphenylcarbon bridge gives the highest value of rrrr pentads of 97,48 % calculated for –30 °C and 92,89 % at 90 °C. Based on this theoretical studies, we optimized a zirconocene with a diphenylcarbon bridge and a 2,7-di-tert.butyl substitution at the fluorenyl ring. As the bridge shows the greatest effect, a fine tuning was carried out which was not possible to be calculated, the phenyl groups of the bridge were substituted by methyl groups (electron pressing) and by methoxy groups (electron drawing). The zirconocenes 1-4, Fig. 1 were synthesized and used for the polymerisation of propene together with MAO as cocatalyst over a wide range of polymerisation temperatures.
A maximum activity of 10 000 kg PP/mol Zr x h is given at 45 °C for the methyl substituted catalyst 2. Zirconocene 1 shows at 45 °C an activity of 6000 kg/mol Zr x h. Electron drawing substituents decrease the polymerisation activity (4500 kg PP/mol Zr x h, catalyst 4).
The picture is different when the melting points of the obtained syndiotactic polypropylenes are studied (Fig. 3). At low polymerisation temperatures, the melting points for complex 4 reaches 152 °C. This is a very high melting point for an unfractionated original sample of syndiotactic polypropylene. For all samples, the melting points decrease with increasing polymerisation temperature. Polymers produced at 60 °C show only melting points between 122 and 130 °C.

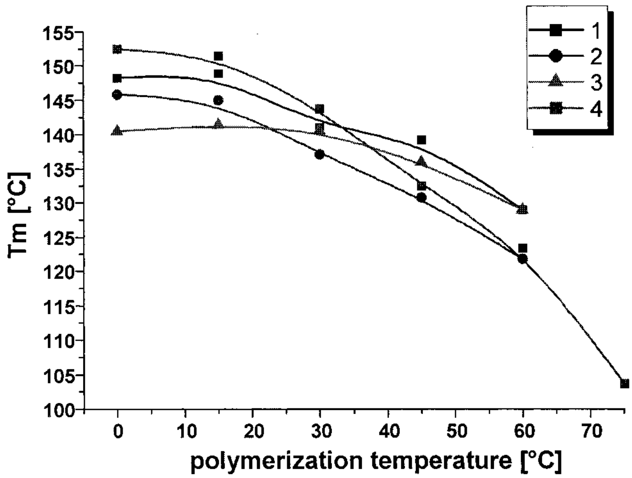

Fig. 3. Melting points of syndiotactic propene samples prepared by catalysts 1-4 and different polymerisation temperatures in toluene as solvent.

Unusual high are the molecular masses of the obtained polypropylenes. If catalyst 2 used, the synthesized polypropylene shows a molecular mass of 750 000 g/mol (0 °C), 600 000 (15 °C), 450 000 (30 °C), 300 000 (45 °C), and 170 000 (60 °C). The ^{13}C-NMR measured syndiotactic rrrr pentade reaches a molar ratio of 0,97 at 0 °C and 0,94 at 30 °C.

Even higher are the values if the polymerisation is carried out in liquid propene (bulk polymerisation). Table 3 shows for the complex 1 some data on activities and polymer properties.

Table 3. Bulk polymerisation of propene with $[Ph_2C(Cp)(2,7\text{-}t\text{-}Bu_2Flu)]ZrCl_2/MAO$ (cata-lyst 1) at different temperatures.

T_{pol} (°C)	Activity kg PP/mol Zr x h x Cp	Tm (°C)	Mη (kg/mol)	rrrr (%)
-20	350	146	1 200	93
-10	400	150	1 100	93
0	600	147	1 300	98
30	1 200	140	720	90
60	3 200	133	460	92

For the bulk polymerisation, the activities are always increasing with the polymerisation temperature. Molecular masses of more than 1 million can be reached. The value of the rrrr pentade is the highest for samples prepared at 0 °C and is in agreement with the calculation for the catalyst.

Conclusion

Molecular modelling leads to optimised c_s-symmetric zirconocenes which show in combination with MAO very high activities for the syndiotactic propene polymerisation. The produced polymers have extremely high molecular masses and melting points. The ^{13}C-NMR measured racemic pentads reaches values of more than 98 %.

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