Macromol. Symp. ***183****, 89–94 (2002)*

Tuning the Ligand Structure in Metallocene Polymerization Catalysts

Walter Kaminsky, Frank Freidanck*

Institute for Technical and Macromolecular Chemistry, University of Hamburg,
Bundesstr. 45, D-20146 Hamburg, Germany

Summary: Meso-[$Me_2Si(2\text{-}Me\text{-}4,6\text{-}{}^iPr_2Ind)_2ZrCl_2$] was synthesized in a pure form and used as catalyst for the copolymerization of ethene and α-olefins. The results are compared with polymers obtained by C_1-symmetric metallocenes and constrained geometry catalysts. The activity of the meso form is remarkable high and reaches more than 100 000 kg polymer/mol Zr · h. The ligand structure has large influence on the incorporation of 1-octene forming thermoplastics (LLDPE) and thermoplastic elastomers (POE).

Introduction

Metallocene catalysts offer the possibility to produce new types of copolymers of ethene, α-olefins, cycloolefins, and styrene. Especially zirconocene methylalumoxane (MAO) catalysts and half-sandwich amidotitanium complexes in combination with perfluorophenylborate have opened a frontier in the area of new copolymer synthesis and processing. The copolymers obtained show different microstructures, tacticities and properties in dependence of the ligand structure of the catalyst [1-3].

Important are ethene-1-octene and ethene-styrene copolymers. These polymers show increased impact strength and toughness, better melt characteristics or elasticity, and improved claritiy in films[4]. Supporting of the zirconocenes on silica decreases the necessary surplus of MAO and can change the tacticity[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 plastics[6-8]. Ethene/norbornene copolymers are the 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

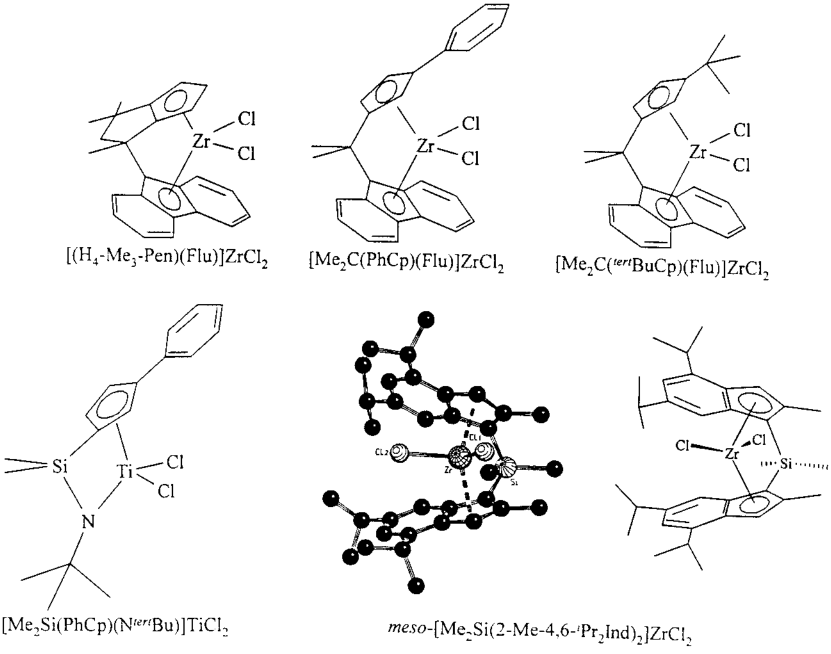
CCC 1022-1360/00/$ 17.50+.50/0

activities for the copolymerisation of ethene with propene or norbornene, and gives alternating structure, too9). The melting point of the alternating copolymer depends on the molar ratio of norbornene in the polymer while the glass transition temperature is almost independent. A maximum melting point of 320 °C was reached. Crystallinity of these copolymers is detected using wide angle X-ray scattering of films. The degree of crystallinity is aobut 22 % for copolymers containing 49 mol% of the cycloolefin. Block structures can be prepared also10).

Ethene can be copolymerised with propene, dienes and other olefins to give EP or EPDM elastomers. It was shown in the past that with some ansa zirconocenes the activities of the copolymerisation of ethene with propene increase.

Experimental Part

Different C_1- and C_2-symmetric zirconocenes and methylaluminoxane (MAO) were used for the copolymerisation of the olefins (Fig. 1).



$[(H_4\text{-}Me_3\text{-}Pen)(Flu)]ZrCl_2$ $[Me_2C(PhCp)(Flu)]ZrCl_2$ $[Me_2C(^{tert}BuCp)(Flu)]ZrCl_2$

$[Me_2Si(PhCp)(N^{tert}Bu)]TiCl_2$ *meso*-$[Me_2Si(2\text{-}Me\text{-}4,6\text{-}^iPr_2Ind)_2]ZrCl_2$

Fig. 1 X-ray structure and transition metal compounds for ethene/1-octene copolymerisation

The zirconocenes and constrained geometry catalysts were prepared as described in the literature$^{11-13)}$. The meso-[$Me_2Si(2\text{-}Me\text{-}4,6\text{-}{}^iPr_2Ind)_2]ZrCl_2$ was obtained from the racemic form when dissolved and then exposed to day light $^{14)}$. This irradiation leads to the side of the meso-diastereomer.

Polymerizations were carried out under an argon atmosphere using a 1 l Büchi A6 Type I autoclave equipped with an additional external cooling system. For the experiments, the reactor was evacuated at 95 °C for 1 h and charged subsequently with 200 ml toluene, 500 mg MAO (purchased by Witco), ethene, and 1-octene at different concentrations. Ethene was purified by passing through columns with a copper-catalyst (BASF R3-11) and molecular sieve of 3-4 Å. The polymerisation was started by injection of a toluenic solution of the metallocene. The polymerisation was quenched by addition of 5 ml of ethanol.

All ^{13}C NMR spectra of the polymers were recorded on a Bruker MSL 300 spectrometer operating at 75.47 MHz and 100 °C. Polymer samples were dissolved in perchlorobutadiene and tetrachloroethane-de_2. Molar mases and molar mass distributions were determined by size exclusion chromatography on a Waters 150-C instrument (1,2,4-trichlorobenzene at 135 °C) employing a PL-EMD-960 evaporation light scattering detector. Additional molar mass determination was conducted by viscosimetry using a Ubbelohde viscosimeter at 30 °C (Kapillare Oa, K = 0,005).

Results and Discussion

The polymerisation activities differ with different ligand structure (Table 1). Among the catalysts investigated meso-[$Me_2Si(2\text{-}Me\text{-}4,6\text{-}{}^iPr_2Ind)_2]ZrCl_2$/MAO and [$Me_2C(PhCp)(Flu)]ZrCl_2$/MAO feature the highest activities at 30 °C of more than 100.000 kg $_{Pol}/(mol_M*h*mol_{E+O}/l)$.

[$Me_2Si(Me_4Cp)(N^{tert}Bu)]TiCl_2$ was investigated too for comparison and shows a moderate activity.

The three zirconocene dichlorides used bearing a fluorenyl ligand can be derivated from the same basic system [$Me_2C(Cp)(Flu)]ZrCl_2$ by just one alteration. Despite their structural similarity they show a great variety in copolymerisations of ethene and 1-octene at 30 °C with

Table 1

Copolymerization of ethane (E) and 1-octene (O) by 30 °C in toluene. MAO = 500 mg, Zr-concentration = 0,05 – 2,5 µmol/l, Ti-concentration = 1 – 20 µmol/l

Catalyst	C(E) (mol/l)	C(O) (mol/l)	Activity (kg Pol/mol Zr·h·mol$_{E+O}$/l)	Molecular weight (kg/mol)
[H$_4$-Me$_3$-Pen)(Flu)]ZrCl$_2$	0,50	0	3 500	101
	0,40	0,10	4 800	910
	0,24	0,26	4 500	640
	0,10	0,40	4 100	570
[Me$_2$C(PhCp)(Flu)]ZrCl$_2$	0,50	0	42 000	430
	0,40	0,10	110 000	180
	0,24	0,20	110 000	130
	0,10	0,40	64 000	86
[Me$_2$C(^{tert}BuCp)(Flu)]ZrCl$_2$	0,50	0	230 000	360
	0,42	0,08	170 000	310
	0,24	0,26	130 000	210
	0,12	0,38	35 000	150
meso[Me$_2$Si(2-Me-4,6-^{i}Pr$_2$Ind)$_2$]ZrCl$_2$	0,50	0	440 000	500
	0,40	0,10	360 000	320
	0,25	0,25	300 000	570
	0,13	0,37	120 000	620
[Me$_2$Si(PhCp)(N^{tert}Bu)]TiCl$_2$	0,50	0	570	500
	0,40	0,10	1 400	240
	...0,25	0,25	130	84
	0,12	0,38	240	200
[Me$_2$Si(Me$_4$Cp)(N^{tert}Bu)]TiCl$_2$	0,50	0	7 700	1600
	0,25	0,25	7 900	2150

respect to monomer incorporation into the polymer chain (Tab. 2): Thus products with predominantly blocky ([Me$_2$C(^{tert}BuCp)(Flu)]ZrCl$_2$, statistic ([(H$_4$-Me$_3$-Pen)(Flu)]ZrCl$_2$) or prevailingly alternating monomer sequence distributions were obtained. Me$_2$C(^{tert}BuCp)(Flu)] ZrCl$_2$/MAO represents an example of a catalyst connecting ethene and 1-octene to a polymer with preponderant block structure.

Analysing the polymer microstructure reveals that [(H$_4$-Me$_3$-Pen)(Flu)]ZrCl$_2$/MAO inserts monomers at high 1-octene incorporation rates mostly by chain migration. Poly-1-octene syndiotacticity (rrrr = 0,48) is disturbed by isolated meso-diads (m), caused by every sixth polymerisation step being a stationary insertion, but not by triad errors (mm).

Table 2
Parameters of the copolymerisation of ethene/1-octene at 30 °C

Catalyst	r_E	r_O	r_E*r_O
$[(H_4\text{-}Me_3\text{-}Pen)(Flu)]ZrCl_2$	5,1	0,14	0,72
$[Me_2C(PhCp)(Flu)]ZrCl_2$	5,5	0,028	0,15
$[Me_2C(^{tert}BuCp)(Flu)]ZrCl_2$	20	0,079	1,6
meso-$[Me_2Si(2\text{-}Me\text{-}4,6\text{-}^{i}Pr_2Ind)_2]ZrCl_2$	44	0,018	0,77
$[Me_2Si(PhCp)(N^{tert}Bu)]TiCl_2$	3,1	0,28	0,85
$[Me_2Si(PhCp)(N^{tert}Bu)]TiCl_2$	2,1	0,24	0,50

The polymerisation behaviour of $[Me_2C(^{tert}BuCp)(Flu)]ZrCl_2$/MAO can be regulated by the reaction temperature. At 0 °C insertion mostly takes place by chain migration, leading to a prevailingly alternating polymer structure. Whereas at 30 °C and, even more so, at 60 °C the retention mechanism dominates and the formation of monomer blocks if favoured. The monomer concentration exerts no influence on the copolymerisation statistics The poly-1-octenes formed at all three polymerisation temperatures are high isotactic. The PO obtained by $[Me_2C(PhCp)(Flu)]ZrCl_2$/MAO at 30 °C has an isoblock structure. Concerning its tacticity (mmmm = 0,53) it lies between ideally isotactic and ideally hemiisotactic polymers.

It is remarkable that the insertion mechanism of meso-$[Me_2Si(2\text{-}Me\text{-}4,6\text{-}^{i}Pr_2Ind)_2]ZrCl_2$/MAO depends on the mol fraction of 1-octene in the reaction mixture. Bridged Cp-amido complexes of titanium have the most suitable copolymerisation parameters for the insertion of 1-octene. $[Me_2Si(PhCp)(N^{tert}Bu)]TiCl_2$ shows the smallest, i.e. for a technical application best, $r_E(T_{Pol} = 30\ °C)$ compared to all other complexes.

While the four zirconocene/MAO catalysts used in this work insert 1-alkenes exclusively in a regioregular (1,2) manner, the titanium complexes also execute 2,1-incorporations. When using $[Me_2Si(Me_4Cp)(N^{tert}Bu)]TiCl_2$/MAO every 20th and when using $[Me_2Si(PhCp)(N^{tert}Bu)]TiCl_2$/MAO every ninth 1-octene is 2,1-connected. Increasing the polymerisation temperature to 90 °C extends the number of misinsertions. The presence of ethene in the reaction mixture prevents the 1-octene units from being connected head-to-head. Because of their cyclopentadienyl rings being substituted in α-position to the bridge $[(H_4\text{-}Me_3\text{-}Pen)(Flu)]ZrCl_2$/MAO, meso-$[Me_2Si(2\text{-}Me\text{-}4,6\text{-}^{i}Pr_2Ind)_2]ZrCl_2$/MAO and $[Me_2Si(Me_4Cp)(N^{tert}Bu)]TiCl_2$/MAO produce copolymers of ethane and 1-octene at 30 °C with high molecular masses up to more than 1,000,000 g/mol (see Tab. 1).

With one exception, all catalysts used show a stable acvtivity over time in copolymerisations of ethene and 1-octene at 30 °C. For [$Me_2C(^{tert}BuCp)(Flu)]ZrCl_2$/MAO first order deactivation was found. The half-life periods amount to about 140 min in the homopolymerisation of ethene and about 20 min in copolymerisations. They are shortened to 18 min or 7 to 2 min, respectively, by increasing the reaction temperature to 60 °C. At T_{Pol} = 0 °C however no deactivation could be detected.

The comparison of two catalysts at the high polymerisation temperature of 90 °C reveals considerable differences in the stability of the activity over time. While the zirconium dichloride [$Me_2C(PhCp)(Flu)]ZrCl_2$ shows half-lives of below 2 min, the Cp-amido titanium complex [$Me_2Si(Me_4Cp)(N^{tert}Bu)]TiCl_2$ exhibits no measurable deactivation. Except for meso-[$Me_2Si(2\text{-}Me\text{-}4,6\text{-}^iPr_2Ind)_2]ZrCl_2$/MAO the catalysts used show in the copolymerisations of ethene and 1-octene at 30 °C the higher activities in the presence of 1-octene. All activity maxima lie at the same 1-octene incorporation rate. Ethene and 1-octene can be polymerised with high activities not only by constrained geometry catalysts but also by metallocene compounds. Meso-complexes show very high activity but low insertion of 1-octene. The insertion of 1-octene is better by [$Me_2C(PhCp)(Flu)]ZrCl_2$.

References

[1] W. Kaminsky, J. Chem. Soc. Dalton Trans. 1998, p. 1413

[2] J. Scheirs, W. Kaminsky (eds.) Metallocene-Based Polyolefins sVol. I + II, Wiley 2000, Chichester

[3] R. Blom, A. Follestad, E. Rytter, M. Tilsel, M. Ystenes (eds.), Organometallic Catalyst and Olefin Polymerisation, Springer 2001, Berlin

[4] A. Torres, K. Swogger, C. Kao, S. Chum, in Ref. 2, p. 143

[5] W. Kaminsky, F. Renner, Makromol. Chem. Rapid Commun. 1993

[6] W. Kaminsky. A. Bark, M. Arndt, Makromol. Chem., Macromol. Sym. 1991, 47, 8

[7] H. Cherdron, M.-J. Brekner, F. Osan, Angew. Makromol. Chem. 1994, 223, 121

[8] D. Ruchatz, G. Fink, Macromolecules 1998, 31, 4669

[9] W. Kaminsky, M. Arndt, I. Beulich, Polym. Mater. Sci. Eng. 1997, 76, 18

[10] M. Arndt, I. Beulich, Macromol. Chem. Phys. 1998, 199, 1221

[11] F. Amor, J. Okuda, J. Organomet. Chem. 1996, 520, 245

[12] W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E.F. Paulus, Organometallics 1994, 13, 954

[13] F. Freidanck, Dissertation, University of Hamburg, p. 1-314

[14] W. Kaminsky, A.-M. Schauwienold, F. Freidanck, J. Molecul. Cat. A: Chemical 1996, 112, 37