

Tailoring polyolefins by metallocene catalysis: kinetic and mechanistic aspects

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Abstract

The C_s -symmetric complex $[\text{Ph}_2\text{C}(2,7\text{-di}^{tert}\text{BuFlu})(\text{Cp})\text{ZrCl}_2]$ is beside the constrained geometry compounds a very active catalyst for the copolymerisation of ethene and 1-octene. Activities up to $200,000 \text{ kg}_{\text{polymer}}/(\text{mol}_{\text{Zr}} \text{ h } c_{\text{monomer}})$ were reached at 60°C . The activity shows a maximum at 10 mol% 1-octene in the feed and decreases with higher amounts of comonomer. The molecular weights of the obtained copolymers are between 670 and 900 kg/mol. The melting points can be varied between 140 and 60°C . There are no octene-diblocks observed in the microstructure. The insertion mechanism can be described by a second-order Markov model. The activity decreases with time because of β -H-transfer reaction and elimination of methane.

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1. Introduction

Metallocenes are highly active catalysts for the production of precisely designed polyolefins and engineering plastics [1–4]. Especially zirconocene/methylaluminoxane (MAO) catalysts and half-sandwich titanium complexes have opened a frontier in the area of new polymer synthesis and processing. The materials obtained show different microstructure, tacticities and properties compared with conventional polymers.

By molecular modelling the optimal substitutions of the zirconocenes can be calculated. The synthesised catalysts polymerise propene to highly isotactic or syndiotactic polymers [5]. The ligand structure has a great influence on the polymerisation activities, the melting points and the molecular weights of the obtained polypropylenes. The analogous hafnium complexes produce polymers with very high molecular weights. Hydrogen transfer reactions are responsible for molecular weight regulation and deactivation. The formation of methane and $\text{Zr-CH}_2\text{-Al}$ structures leads to dead catalyst structures [6].

The substitution pattern influences also the microstructure and comonomer incorporation of ethene–1-olefin-copoly-

mers such as LLDPE, POE, EP, EPDM and ethene–styrene copolymers. These polymers show increased impact strength and toughness, better melting characteristics or elasticity and improved clarity at films [7].

Alternating copolymers can be obtained by blocking one of the two insertion positions of the active site for the longer chained olefin. These copolymers have different properties compared to those with a random structure.

Metallocenes are useful catalysts for the production of cycloolefin copolymers (COC), materials with special properties and a high potential as engineering plastic [8–10]. Ethene/norbornene copolymers are interesting 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 catalyst. A copolymer with 50 mol% of norbornene yields material with a glass transition point of 145°C . The catalyst $[\text{Me}_2\text{C}(^{tert}\text{BuCp})(\text{Flu})\text{ZrCl}_2/\text{MAO}]$ shows not only high activities for the copolymerisation of ethene with propene or norbornene, but gives also an alternating structure [11]. The melting point of the alternating copolymer depends on the molar ratio of norbornene in the polymer. A maximum melting point of 320°C was reached [12].

Today ethene/1-octene copolymers are the most produced polyolefins in industries by metallocene catalysts, mainly obtained by constrained geometry catalysts (CGC) [13]. We

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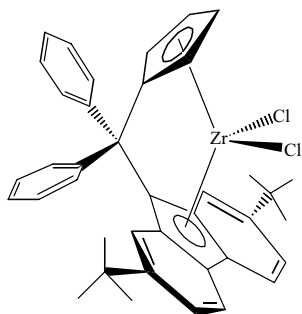


Fig. 1. Structure of $[\text{Ph}_2\text{C}(2,7\text{-di-}^{\text{tert}}\text{BuFlu})(\text{Cp})]\text{ZrCl}_2$ (**8**).

have shown that there are also other very active zirconocenes for the synthesis of these copolymers [14].

2. Experimental

All procedures were performed under argon using Schlenk techniques.

2.1. Materials

Argon was purchased from Linde and purified by passing through a Messer Griesheim Oxisorb cartridge. Methylaluminoxane (10 wt.% toluene solution) was purchased from Crompton. After filtration of the commercial solution MAO was obtained by removal of toluene and residual TMA under vacuum. Ethene (Messer Griesheim) and toluene (Merck) were purified by passing through columns with Cu catalyst (BASF R3-11) and molecular sieve 3 Å. 1-Octene was purchased from Merck and distilled after drying over CaH_2 for at least 24 h, hydrogen (Linde) was employed without further purification. Synthesis of complex **8** (Fig. 1) was performed according to the general procedure reported in literature.

2.2. Polymerisation reactions

Polymerisations were carried out in a 1 l Büchi AG laboratory autoclave with type I glass pressure vessel equipped with an additional internal cooling system. Monomer feed of the gaseous monomer was maintained with a Peteric 3002

pressflow controller. The reaction was monitored by a Büchi Data System bds 488. For the standard experiment, the reactor was evacuated at 95 °C for 1 h, flushed several times with argon and charged subsequently with 200 ml toluene, 200 mg of MAO and 1-octene, 0.5 bar hydrogen pressure was set. Ethene was added so that the total monomer concentration was 0.5 mol/l. Polymerisation was started by addition of toluenic metallocene solution (30 °C: 5×10^{-7} mol, 60 °C: 5×10^{-8} mol). During the reaction the total pressure was kept constant by supplying ethene. Polymerisation was quenched by injection of 5 ml of ethanol. The content of the reactor was stirred overnight with dilute hydrochloric acid followed by neutralisation with NaHCO_3 , washing with water, filtered off and dried under vacuum at 60 °C until the weight remained constant.

2.3. Analytical procedures

^{13}C NMR spectra were measured with a Bruker Ultra-shield 400 spectrometer. Polymer samples were measured at 100.62 MHz and 100 °C using 200–300 mg of polymer in 2.7 ml of hexachloro-1,3-butadiene and 0.3 ml of 1,1,2,2-tetrachloroethane- d_2 (1200 scans, 5 s delay time). Differential scanning calorimetry curves were recorded on a Mettler Toledo DSC 821^e instrument calibrated with *n*-heptane, mercury, gallium, indium and zinc. Results of the second thermal cycle are presented exclusively. Viscometric measurements were performed in decahydronaphthalene at 135 °C using an Ubbelohde viscosimeter (0a capillary, $K = 0.005 \text{ mm}^2/\text{s}^2$). Mark–Houwink constants were taken from literature.

3. Ethene/1-octene copolymers

The ethene/1-octene copolymerisations were carried out with different single-site catalysts under the same conditions for comparison (Table 1).

The complexes ($[\text{Me}_2\text{C}(\text{PhCp})(\text{Flu})]\text{ZrCl}_2$) (**2**) and (*meso*- $[\text{Me}_2\text{Si}(2\text{-Me-4,6-}^i\text{Pr}_2\text{Ind})_2]\text{ZrCl}_2$) (**7**) are the most active catalysts in this study. The CGC systems (**4–6**) show at 30 °C only a low activity but they incorporate high amounts of 1-octene. This can be seen by the low copolymerisation

Table 1
Copolymerisation of ethene and 1-octene by different catalysts

Catalyst/MAO	Activity ($\text{kg}_{\text{polymer}}/(\text{mol}_{\text{Zr}} \text{ h } C_{\text{monomer}})$)	r_{E}	r_{O}	$r_{\text{E}r_{\text{O}}}$	X_{O}^{a}
$[(\text{H}_4\text{-Me}_3\text{-Pen})(\text{Flu})]\text{ZrCl}_2$ (1)	2,400	5.1	0.14	0.72	0.56
$[\text{Me}_2\text{C}(\text{PhCp})(\text{Flu})]\text{ZrCl}_2$ (2)	55,000	5.5	0.03	0.15	0.44
$[\text{Me}_2\text{C}(^{\text{tert}}\text{BuCp})(\text{Flu})]\text{ZrCl}_2$ (3)	12,000	20.0	0.08	1.60	0.40
$[\text{Me}_2\text{Si}(\text{Ind})(\text{N}^{\text{tert}}\text{Bu})]\text{TiCl}_2$ (4)	610	3.2	0.20	0.65	0.75
$[\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{N}^{\text{tert}}\text{Bu})]\text{TiCl}_2$ (5)	1,900	3.1	0.28	0.85	0.73
$[\text{Me}_2\text{Si}(\text{PhCp})(\text{N}^{\text{tert}}\text{Bu})]\text{TiCl}_2$ (6)	100	2.1	0.24	0.50	0.74
<i>meso</i> - $[\text{Me}_2\text{Si}(2\text{-Me-4,6-}^i\text{Pr}_2\text{Ind})_2]\text{ZrCl}_2$ (7)	41,000	25.0	0.05	1.25	0.16

Temperature: 30 °C, solvent: 200 ml toluene, 200 mg MAO, mol fraction 1-octene in feed: 0.9.

^a 1-Octene in polymer.

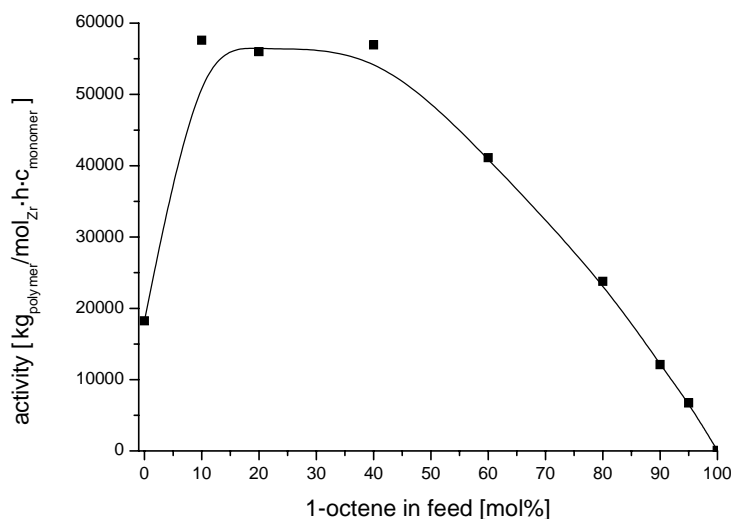


Fig. 2. Copolymerisation of ethene/1-octene with $[\text{Ph}_2\text{C}(2,7\text{-di}^{tert}\text{BuFlu})(\text{Cp})]\text{ZrCl}_2/\text{MAO}$ at 30°C in toluene.

parameter r_E . The complex **7** and complex **2** with a *tert*-butyl substitution are slow in the incorporation of 1-octene. Complexes **1**, **3–6** and **7** form random copolymers and complex **2** forms a more alternating copolymer.

Because of the high polymerization activity and good copolymerization properties of zirconocene **2** we have synthesised a diphenyl-carbon bridged and fluorenyl substituted complex **8** (Fig. 1).

This catalyst is a syndiospecific working system and gives high syndiotactic polypropylene [5]. The copolymerisation was carried out at 30 and 60°C . Fig. 2 shows the activities of the copolymerisation of ethene and 1-octene at 30°C with zirconocene **8**.

The activity reaches a maximum at 10 mol% of 1-octene in the starting feed. A high activity of $58,000 \text{ kg}_{\text{polymer}}/(\text{mol}_{\text{Zr}} \text{ h } c_{\text{monomer}})$ is obtained. The activity decreases with higher 1-octene concentrations. This comonomer effect can be seen in many copolymerisations by metallocene catalysts. The comonomer influence the structure of the active site because the copolymer is soluble and diffusion control cannot take a place. The different solubility of ethene in a mixture of toluene and 1-octene cannot explain an increase of the activity by the factor of 3 and more. The molecular weights, melting points and crystallinities of the copolymers are presented in Table 2.

The molecular weights of the copolymers with this catalyst **8** are unusual high. Even by 1-octene incorporation of 70 mol% 900 kg/mol are obtained. There is a minimum of the molecular weight at about 30–50 mol% of 1-octene. The melting points decrease linear with higher 1-octene contents. A minimum in the glass transition temperature of the copolymers can be obtained (Fig. 3).

The minimum is observed at 30–50 mol% of 1-octene similar to the molecular weights of the copolymers. The copolymers show at 30 mol% of octene a glass transition temperature of -65°C , which is useful for applications of

Table 2

Polymer properties (molecular weights, melting points, crystallinities) of ethene/1-octene copolymers obtained by catalyst **8**/MAO at 30°C in dependence of the mol% of 1-octene in the copolymers

1-Octene in polymer (mol%)	Molecular weight M_n (kg/mol)	Melting point ($^\circ\text{C}$)	Crystallinity (%)
0.0	890	139	40
2.3	830	135	37
4.1	590	133	28
9.3	630	125	24
17.3	540	a ^a	–
29.0	420	a	–
48.6	530	a	–
69.8	905	a	–

^a a, amorphous.

polyolefin elastomers. From ^{13}C NMR the triad fraction was used to calculate the copolymerisation diagram. The different triad fractions are summarised in Table 3.

There are no octene-diblocks up to an 1-octene incorporation of 49 mol% in the polymers observed. This means that we have a more or less good alternating copolymerisation. Only by insertions more than 50 mol% also di- and triblocks

Table 3

Microstructure of ethene/1-octene copolymers obtained by complex **8** at 30°C , triads in dependence of the 1-octene molar fraction in the feed

x_0^a	X_0^b	EEE	EEO	OEO	EOE	EOO
0.1	0.022	93.62	4.13	0.00	2.25	0
0.2	0.041	86.98	8.71	0.23	4.08	0
0.4	0.093	75.07	14.16	1.50	9.27	0
0.6	0.175	54.86	23.12	4.52	17.50	0
0.8	0.290	27.74	27.28	15.93	29.05	0
0.9	0.486	15.07	n.d.	31.36	63.80	0
0.95	0.698	n.d.	2.74	30.97	19.32	n.d.

^a 1-Octene in feed.

^b 1-Octene in polymer.

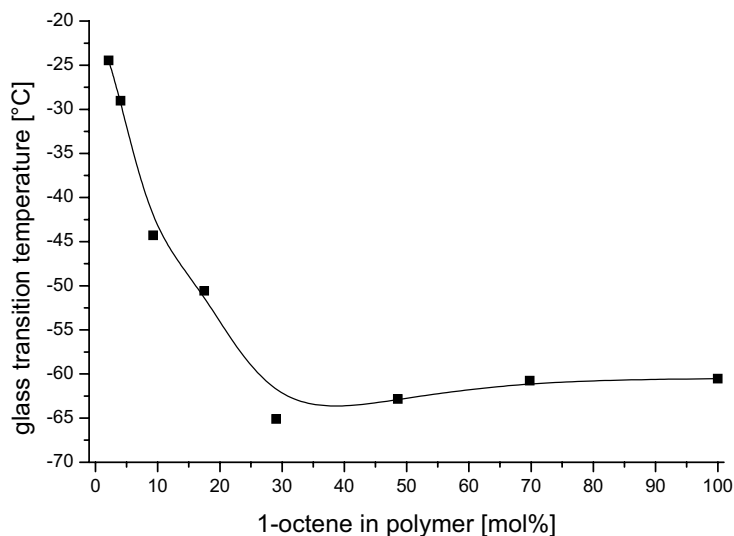


Fig. 3. Glass transition temperatures of ethene/1-octene copolymers synthesised by complex **8** at 30 °C.

are observed. The copolymerisation diagram is shown in Fig. 4.

The copolymerisation of ethene and 1-octene can be described by the second-order Markov model. Fink has used this model in ethene/1-hexene copolymerisation [15]. For industrial applications lower molecular weights are needed. Therefore, we carried out the experiments also at polymerisation temperature of 60 °C and by addition of 0.5 bar hydrogen to decrease the molecular weights. Table 4 shows the results using the higher polymerisation temperature of 60 °C.

The activities are extremely high with more than 200,000 kg_{polymer}/(mol_{Zr} h c_{monomer}). But still the molecular

Table 4
Polymerisation of ethene/1-octene with **8** at 60 °C

x_O in feed	Activity ^a	M_η (kg/mol)	T_m (°C)	T_g (°C)	X_O in polymer
0.05	200,000	535	118	-33	0.0058
0.10	170,000	446	113		0.0104

^a Activity: kg_{polymer}/(mol_{Zr} h c_{monomer}).

weights are more than 400 kg/mol. The activity in dependence of small amounts of 1-octene in the copolymer is shown in Fig. 5. Again, there is a comonomer effect and a strong decrease of the activity with increasing amounts

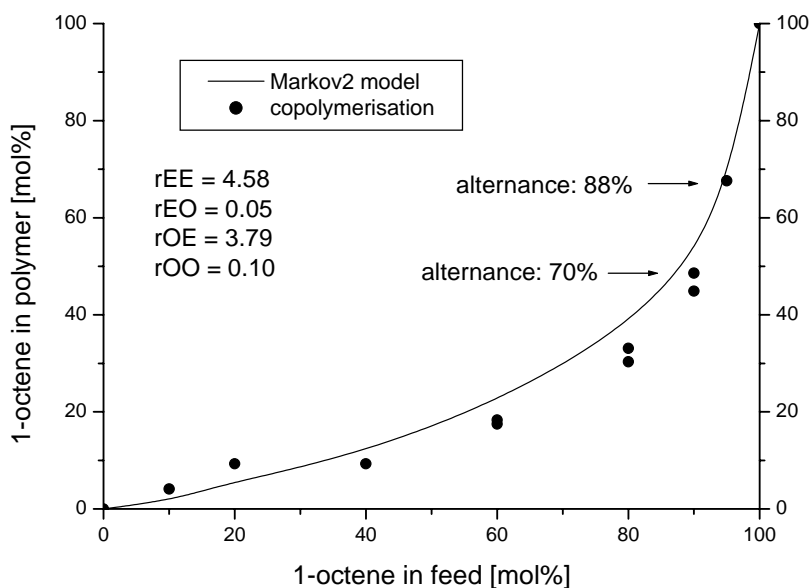


Fig. 4. Copolymerisation diagram of ethene/1-octene with [Ph₂C(2,7-di-^{tert}BuCp)(Cp)]ZrCl₂/MAO at 30 °C.

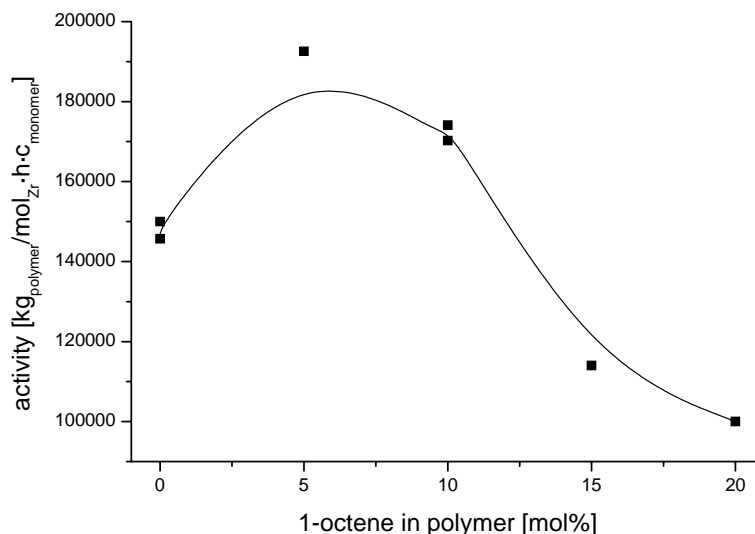


Fig. 5. Activity in dependence of the 1-octene content in the copolymer obtained by complex **8** at 60 °C and 0.5 bar hydrogen pressure.

Table 5
Molecular weights and crystallinities of ethene/1-octene copolymers obtained by catalyst **8**/MAO, 60 °C and 0.5 bar hydrogen pressure

1-Octene in polymer (mol%)	Molecular weights (kg/mol)	Crystallinity (%)	Triads EEO (%)	EEO (%)
0.0	140	54		
0.2	170	37	0.37	0.23
1.0	180	36	1.28	0.95
1.5	140	37	1.72	1.46
2.1	130	32	3.22	2.13

of 1-octene in the copolymer. As expected, the molecular weights of the synthesised copolymers decrease (Table 5). The melting temperatures are decreasing from 140 to 116 °C.

4. Conclusion

The metallocene catalyst $[\text{Ph}_2\text{C}(2,7\text{-di}^{tert}\text{BuFlu})(\text{Cp})\text{Zr-Cl}_2/\text{MAO}]$ is found to be a very active catalyst was found for the copolymerisation of ethene and 1-octene. Up to 200,000 kg of copolymer can be produced by 1 mol of catalyst in 1 h. The obtained copolymers show a more alternating microstructure. At low 1-octene incorporation, no octene-diblocks are observed. It could be shown that beside

constrained geometry catalysts, also zirconocene/MAO catalysts are able to produce polyolefin elastomers in a good yield.

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