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Polymerization of Ethene and Longer Chained Olefins by Metallocene Catalysis

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Summary: Copolymers of ethene and longer chained 1-olefins such as 1-octene, 1-decene, 1-dodecene, 1-octadecene and 1-hexacosene with 8 to 28 carbon atoms were carried out using $[Ph_2C(2,7)\text{-di}^{tert}BuFlu)(Cp)]ZrCl_2/MAO$ as catalyst. Precisely designed microstructures and activities up to 168 000 $kg_{copolymer}/(mol_{zirconocene}\cdot h\cdot mol/l_{monomer})$ can be obtained. There is a remarkable polymerization activity left even after a time of 4 hours. The incorporation of the longer chained 1-olefins reaches 19 wt% and depends on the chain length and the concentration of the comonomer in the feed, the LLDPE materials prepared show melting points of 129 – 112 °C.

Keywords: copolymerization; LLDPE; long chained olefins; metallocene; polyolefins

Introduction

Polyethenes show a high growth rate compared to other plastics and materials. Especially linear low density polyethene (LLDPE) is one of the most growing plastics. A remarkable part of the 15 million tons of the worldwide produced LLDPE is made by metallocene catalysts. The ligand structure of the metallocene complex has a large influence on the polymerization activities, on the molar masses, on the microstructure and comonomer incorporation [1-5]. LLDPE, POE, EP and EPDM are obtained by copolymerization of ethene with propene or longer chained 1-olefins. These polymers show increased impact strength and toughness, better melt characteristics or elasticity and improved clarity.

Ethene/1-octene copolymerizations were carried out with different single-site catalysts under the same conditions for comparison (Table 1) [6].

The complexes $[Me_2C(PhCp)(Flu)]ZrCl_2$ (2) and *meso*-$[Me_2Si(2\text{-Me-}4,6\text{-}^iPr_2Ind)_2]ZrCl_2$ (7) are the most active catalysts. The CGC systems (4-6) show only a low activity at 30 °C but they incorporate 1-octene in a high amount. This can be seen at the low copolymerization parameter r_E. They are much more active at higher polymerization temperatures. The *meso*-complex 7 and complex 3 with a *tert*-butyl substitution are slow

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in the incorporation of 1-octene. Complexes 1, 3-7 form random copolymers while complex 2 forms a more alternating copolymer.

Table 1. Copolymerization of ethene and 1-octene with different catalysts.

#	Catalyst / MAO	activity[1]	r_E
1	$[(H_4\text{-}Me_3\text{-}Pen)(Flu)]ZrCl_2$	2400	5.1
2	$[Me_2C(PhCp)(Flu)]ZrCl_2$	55000	5.5
3	$[Me_2C(^{tert}BuCp)(Flu)]ZrCl_2$	12000	20.0
4	$[Me_2Si(Ind)(N^{tert}Bu)]TiCl_2$	610	3.2
5	$[Me_2Si(Me_4Cp)(N^{tert}Bu)]TiCl_2$	1900	3.1
6	$[Me_2Si(PhCp)(N^{tert}Bu)]TiCl_2$	100	2.1
7	*meso*-$[Me_2Si(2\text{-}Me\text{-}4,6\text{-}^iPr_2Ind)_2]ZrCl_2$	41000	25.0

Temperature: 30°C.
solvent: 200 ml toluene, 200 mg MAO, mol fraction 1-octene: 0.9.
[1] $[kg_{polymer}/(mol_{Zr} \cdot h \cdot mol/l_{monomer})]$

Due to the high activity of zirconocene 2 for the copolymerization we synthesized a diphenyl-carbon bridged complex 8, $[Ph_2C(2,7\text{-}di^{tert}BuFlu)(Cp)]ZrCl_2$ because we know that there is again an increase in activity by changing the dimethyl carbon against a diphenyl carbon bridge [8]. The copolymerization was carried out at 30 and 60 °C. Activities of up to 58 000 $kg_{copolymer}/(mol_{Zr} \cdot h \cdot mol/l_{monomer})$ are obtained.

The molecular weights of the copolymers synthesized with this catalyst are unusually high. Even with 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 incorporated. The melting points decrease linearly with higher 1-octene contents in the polymer.

Not only short chain branches but also a very small amount of long-chain branches (LCB) along the polymer backbone leads to totally different properties of the polyethene which makes this material very interesting for industrial processing. The tandem copolymerization with two different catalysts makes the synthesis of long-chained, comb-structured polyethene with side-chain lengths up to 250 carbons and branching contents up to 0.9 mol% (Figure 1) possible. Such long-chain branched polyethene, even at very low concentration of branches in the PE-backbone, shows a large increase in viscosity and in shear flow. The macromers used as comonomers for the polymerization with ethene were synthesized by the $[Me_2C(Cp)_2]ZrCl_2$ / MAO-catalyst at different oligomerization temperatures and ethene pressures [7].

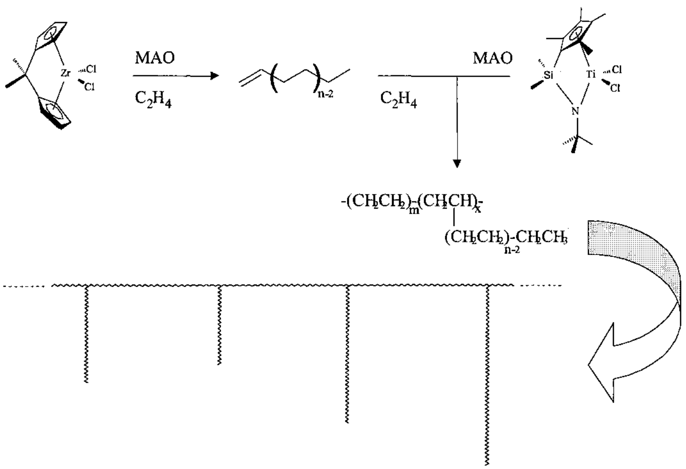

Figure 1. Schematic representation of a tandem copolymerization with the catalysts $[Me_2C(Cp)_2]ZrCl_2$ / MAO and $[Me_2Si(N^{tert}Bu)(Me_4Cp)]TiCl_2$ / MAO to yield LCB-PE.

The branch length was varied between C70 and C250 and the PE-backbone length was varied between C7000 and C25000. With these settings up to 0.9 mol% of the oligomeric material was inserted into the PE-backbone during the copolymerization.

The copolymers LCB-PE with branching percentages in this dimension have a lower melting point T_m and crystallinity α as compared to the equivalent linear polyethene. First rheological measurements show the formation of reduced polymer sphere sizes and a more intensive entanglement compared to the equivalent linear HDPE.

To obtain the catalyst activities and the polymer properties of copolymers with side chain length between the short chain and long chain branches, we synthesized copolymers of ethene and 1-olefins with chain length of C_8 to C_{28}.

Experimental

All procedures were performed under argon using Schlenk techniques. 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 and stored as a solid. Freshly prepared solutions in dry toluene were used for polymerizations. Ethene (Messer Griesheim) and toluene (Merck) were purified by passing through columns with Cu catalyst (BASF R3-11) and molecular sieve 3Å. 1-Octene, 1-decene, 1-dodecene and 1-octadecene were purchased from Merck, hydrogen (Linde) was employed without further purification. The comonomer further on named 1-hexacosene is a commercial available α-olefin wax fraction (mainly C_{26} to C_{28} olefins, Chevron Phillips Chemical Company LP, USA). Synthesis of complex 8 (Fig. 2) was performed according to the general procedure reported in literature [9]. The catalyst was stored under argon atmosphere and freshly prepared solutions in dry toluene were used for polymerizations.

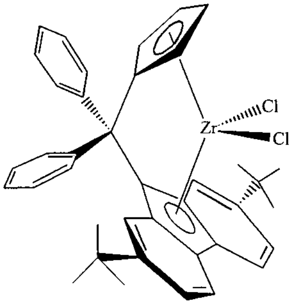

Figure 2. Structure of $[Ph_2C(2,7\text{-di-}^{tert}\text{-BuFlu})(Cp)]ZrCl_2$.

Polymerizations were carried out in a 3 l Büchi glass reactor equipped with a magnetical stirrer. For the standard experiment, the reactor was evacuated at 95 °C for 1 h, flushed several times with argon and charged subsequently with 2000 ml toluene, 1000 mg of MAO and a defined amount of 1-octene or the other longer chained 1-olefins. After reaching 60°C polymerization temperature, 0.5 bar hydrogen pressure was set. Ethene was added so that the total monomer concentration was 0.5 mol/l. Polymerization was started by addition of toluenic metallocene solution (8×10^{-8} mol). During the reaction, the total pressure was kept constant by supplying ethene and the ethene flow was recorded by a Brooks Mass Flow Controller constantly. The polymerization was quenched after 4 hours by injection of 1 ml of ethanol. The polymer solution was stirred over night in an ethanol / HCl / water solution, filtered, washed with plenty of ethanol followed by evaporation of the solvents and drying of the polymer in vacuo at 60 °C over night.

^{13}C NMR spectra were measured with a Bruker Ultrashield 400 spectrometer. Polymer samples were measured at 100.62 MHz and 100 °C using 200 – 300 mg of polymer in 2.5 ml of 1,2,4-Trichlorobenzene and 0.5 ml of 1,1,2,2-tetrachloroethane-d_2 (IGATED, 4k scans, 10 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.

Gel permeation chromatography was carried out with a Waters GPC 2000 Alliance system equipped with a refractive index detector, viscosimetric detector and a set of three columns, Styragel type. The particle size for each column was 10 µm, and the pore sizes were 10^3 Å (HT3), 10^4 Å (HT4), and 10^6 Å (HT6). 1,2,4-Trichlorobenzene was used as solvent. The analyse were performed at 140 °C and 1.0 mL/min. The columns were calibrated with narrow molar mass distribution polystyrene standards. The sample concentration was 1 mg/mL and the injection volume 215 µL, 2,6-Di-^{tert}butyl-4-methylphenol was used as thermostabilizer.

Results and Discussion

For the copolymerization of ethene with the longer chained 1-olefins 1-decene, 1-dodecene, 1-octadecene, and 1-hexacosene (waxy mixture of C_{26} - C_{28}) were used. The polymerization results are shown in Table 2. For comparison also two runs with 1-octene and pure PE were added.

Table 2. Copolymerization of ethene with longer chained 1-olefins by [Ph_2C(2,7-di^{tert}-BuFlu)(Cp)]$ZrCl_2$ at 60 °C and 0.5 bar H_2.

run	comonomer	feed$_{Com.}$ [mol%]	acti-vity[1]	$X_{Com.}$ [mol%]	$W_{Com.}$ [wt.%]	T_c [°C]	T_m [°C]	crist. [%]	M_w [g/mol]	MWD
1	-	0	45400	0	0	111	140	60	146000	2.48
2	octene	10	90100	0.98	4.0	100	120	34	252000	1.77
3	octene	15	127000	1.47	5.6	96	116	38	204000	1.99
4	octene	20	100000	2.24	8.4	88	112	28	165000	2.08
5	decene	10	74000	0.87	4.2	102	120	45	183000	2.14
6	decene	15	77000	1.35	6.4	97	116	32	177000	2.08
7	dodecene	10	38000	0.53	3.1	101	120	34	191000	1.99
8	dodecene	15	90000	1.56	8.7	96	116	46	169000	2.04
9	octadecene[2]	5	129000	0.40	3.5	103	123	41	551000	1.68
10	octadecene	5	90800	0.32	2.8	108	128	45	211000	2.24
11	octadecene	10	123000	0.78	6.6	100	122	42	185000	1.98
12	octadecene	15	109000	1.19	9.8	98	117	38	194000	1.97
13	octadecene	20	107000	1.88	14.7	87	116	34	182000	1.98
14	hexacosene	5	117000	0.22	2.9	106	129	47	216000	1.97
15	hexacosene	10	168000	0.82	10.1	99	125	40	218000	1.96
16	hexacosene	15	96000	1.19	14	98	116	33	184000	2.19
17	hexacosene	20	52000	1.72	19.3	91	113	26	209000	1.90

[1] [$kg_{polymer}/mol_{Zr} \cdot h \cdot mol/l_{monomer}$]
[2] polymerization without hydrogen

In all experiments the activities were very high and reached 168 000 $kg_{polymer}/mol_{Zr} \cdot h \cdot mol/l_{monomer}$. The differences in the activities depend mainly on the purity of the comonomers. Surprisingly, the copolymerization with the waxy hexacosene gives the highest activity of all. Under these conditions, the content of hexacosene in the feed is 10 %. In other copolymerizations, this comonomer effect is also observed [10].

The molecular weight of the copolymer was controlled by the addition of hydrogen to be between 150 000 and 250 000 g/mol. When no hydrogen was added, the molecular weight of the ethene/octadecene copolymer (run 9) was more than 550 000 g/mol. The molecular weight of the synthesized copolymers is slightly dependent on the ethene concentration. As expected for metallocene catalysis, the polydispersity is narrow and about 2. Fig. 3 shows the activity in dependence of the polymerization time for run number 10, 11 and 13 (table 2).

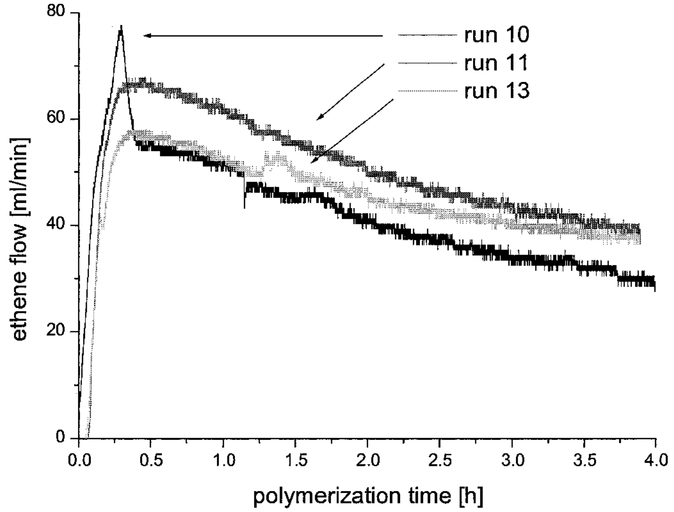

Figure 3. Activity of the ethene/octadecene copolymerization in dependence of the polymerization time and different feed ratios.

After 10 – 20 minutes, the maximum of the polymerization activity is reached, then a slow decrease can be observed. The activity course is the same for all comparable copolymerization runs, depending on the feed ratio of the monomers. Even after a polymerization time of 4 hours, there is still a remarkable activity. The higher 1-olefins are well incorporated into the polymer chain (Figure 4).

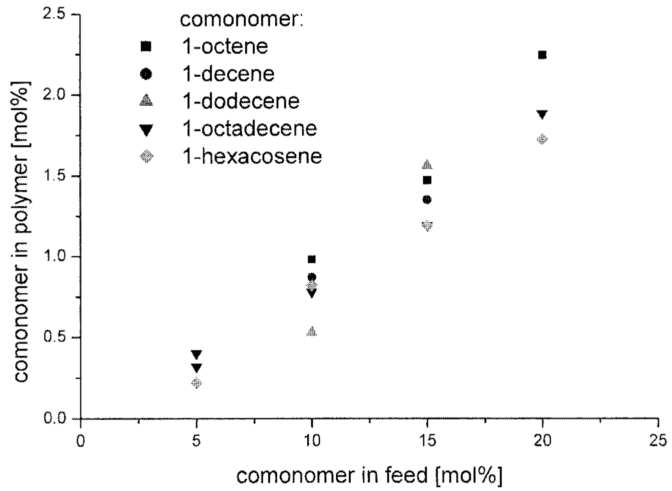

Figure 4. Content of longer chained 1-olefins in the copolymer in dependence of their content in the feed.

Using the catalyst [$Ph_2C(2,7\text{-di}^{tert}BuFlu)(Cp)]ZrCl_2/MAO$, the content of the 1-olefin in the polymer is nearly a tenth of that in the starting feed for all different olefins. Also the hexacosene with 26 carbon atoms is inserted in a similar way. That means, that in weight % (Figure 5) much more of the hexacosene then of the 1-octene is inserted.

A copolymer with 1 mol% of hexacosene contains 12 weight% of the olefin in the polymer, with 1-octene it is only 4 weight%. However, no effect of the side chain length on the melting temperature is measured (Figure 6).

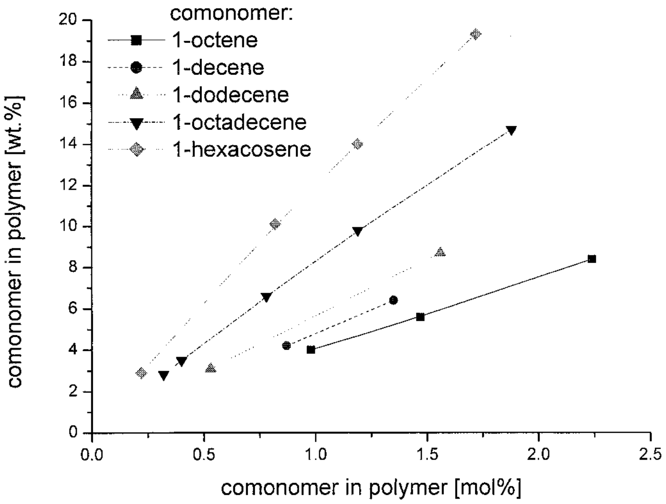

Figure 5. Weight % of longer chained 1-olefins in the copolymer in dependence of their mol%.

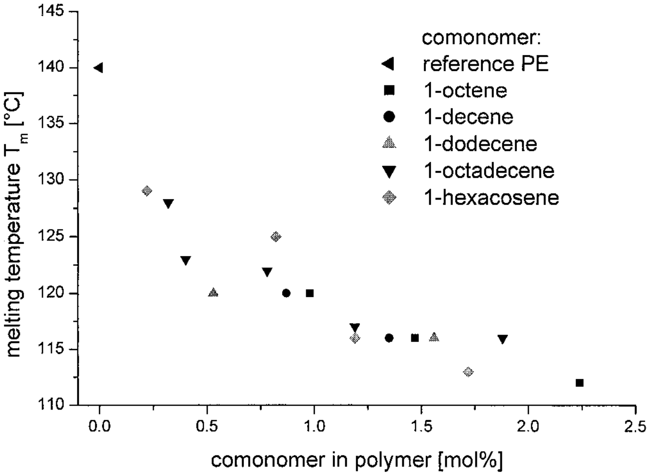

Figure 6. Influence of the incorporated amount of 1-olefin on the melting temperature of the copolymer.

There is a strong dependence of the melting temperature on the molar ratio of the longer chained olefin in the copolymer. The temperature decreases from 130 °C to 112 °C at a comonomer content of 2.3 mol% for all copolymers. These are melting temperatures as they are known of common LLDPE materials.

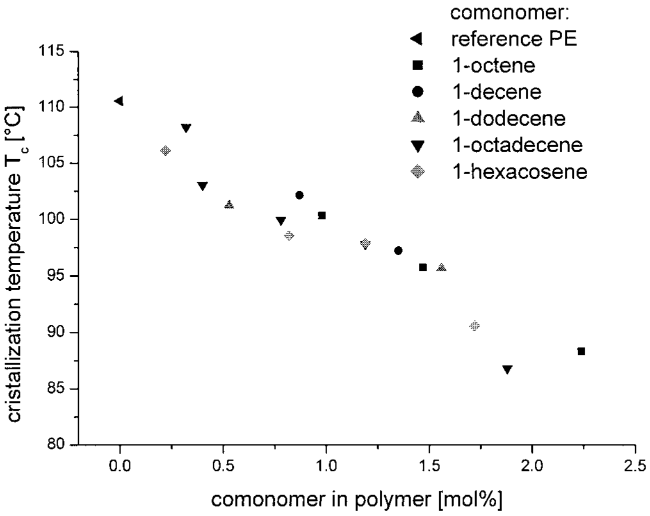

Figure 7. Cristallization temperatures of ethene/1-olefins in dependence of their incorporation in the copolymer.

The cristallization behavior of the copolymers is also not effected by the length of the short side chains. The cristallization temperature is decreasing linearly with increasing comonomer content but independent of the comonomer type (Figure 7).

Conclusions

It could be shown that special metallocene/MAO catalysts are able to incorporate longer chained 1-olefins up to a chain length of 26 carbon atoms in high amounts (16 wt%). the molecular weights can be reduced from 551 kg/mol to 211 kg/mol by the addition of hydrogen. The melting temperatures of the obtained LLDPE materials can be varied from 130 to 112 °C.

Acknowledgements

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