Defined Synthesis of Copolymers Using Metallocene Catalysis

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Summary: The copolymerization of propene with small amounts of ethene, catalyzed by tetrahydroindenyl zirconocenes such as $[En(H_4Ind)_2]ZrCl_2$ or $[Me_2Si(H_4Ind)_2]ZrCl_2$ and MAO in liquid propene produces polymers with much higher activities and molecular weights than the homopolymerization of propene. The normal bisindenyl complexes doesn't present such differences. The investigation of the microstructure shows for the tetrahydroindenyl catalyst that after a 2,1-insertion of a propene unit the system is in a sleeping state and can be activated when an ethene unit is inserted. In this case these catalysts become faster than the *ansa* bis-indenyl catalysts. An active catalyst for the copolymerization of ethene and norbornene is the more temperature stable $[Me_3PhPen(Flu)]ZrCl_2$. This catalyst produces atactic copolymers with high molecular weights of over 900 000 g/mol at 30 °C and 38 mol % of norbornene content.

Introduction

Metallocenes are highly active catalysts for the production of precisely designed polyolefins and copolymers. Especially zirconocene methylalumoxane (MAO) catalysts, half-sandwich amido titanium complexes in a 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[1-3].

Important are ethylene-1-octene and ethylene-styrene copolymers. These polymers show increased impact strength and toughness, better melt characteristics or elasticity, and improved clarity 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

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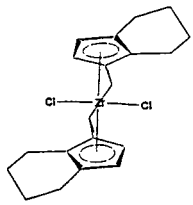
independenly from the used catalysts. A copolymer with 50 mol % of norbornene yields a material with a glass transition point of 145 °C. A Tg of 205 °C can be achieved at higher incorporation rates. The metallocene $[Me_2C(tert\text{-}BuCp)(Flu)]ZrCl_2$ shows not only high activities for the copolymerization of ethene with propene or norbornene, and gives alternating structure, too[9]. 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 about 22 % for copolymers containing 49 mol% of the cycloolefin. Block structures can be prepared also[10].

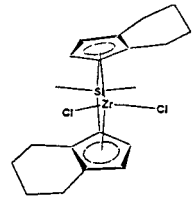
Ethene can be copolymerized with propene, dienes and other olefins to give EP or EPDM elastomers. It was shown in the past that with some ansa zirconocenes the activities of the copolymerization of ethene with propene increase. Investigations by Busico et al. have shown that sleeping active centers, formed by 2,1-insertion of propene, could be activated by hydrogen or ethylene[11-13].

Experimental Part

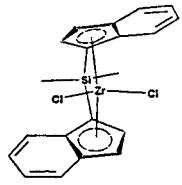
Different C_1- and C_2-symmetric zirconocenes were used for the copolymerization of the olefins (Fig. 1)



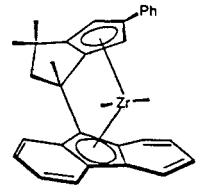
$Et(H_4Ind)_2ZrCl_2$



$Me_2Si(H_4Ind)_2ZrCl_2$



$Me_2Si(Ind)_2ZrCl_2$



$Me_3PhPen(Flu)ZrCl_2$

Fig. 1. Molecular structures of the used zirconocenes and their terms

The zirconocenes were prepared as described in the literature[14,15]. 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 COC experiments, the reactor was evacuated at 95 °C for 1 h and charged subsequently with 200 ml toluene, 500 mg MAO(purchased by Witco), norbornene, and ethene at different pressures. Norbornene was dried over triiso-butylaluminum and subsequently distilled. Gaseous monomers (ethene, propene) were purified by passing through columns with a copper-catalyst (BASF R3-11) and molecular sieve of 3-4 Å. Copolymerizations of propene with ethene were carried out in 375 ml of liquid propene. The polymerization was started by injection of a toluenic solution of the metallocene. The polymerization was quenched by addition of 5 ml of ethanol. Work-up proceeded by stirring over night in diluted hydrochloric acid followed by neutralization with aqueous $NaHCO_3$ and washing with water. After phase separation, the polymer was precipitated, if possible. Otherwise the organic solvent was removed under reduced pressure and the obtained polymer was dried in vacuo.

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-d_2. Molar masses 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 an Ubbelohde viscosimeter at 30 °C (Kapillare Oa, K = 0,005).

Results and Discussion

Copolymerization of Propene with Ethene

We were the first to show that small amounts of ethene added to propene increase the activity of the polymerization when using tetrahydroindenyl zirconocenes (see Fig. 1)[16]. With these catalysts up to 2 mol% in a 2,1-insertion of propene is observed (Fig. 2).

After a rare 2,1-insertion of propene into the active site, the zirconium-$CH(CH_3)$-bond is sterically so hindered that a next propene insertion is much slower [sleeping state (a)]. But it is easy to incorporate an ethene unit into this bond (b). After this step it is possible again to insert a propene unit in the normal 1,2-position (c) high rate.

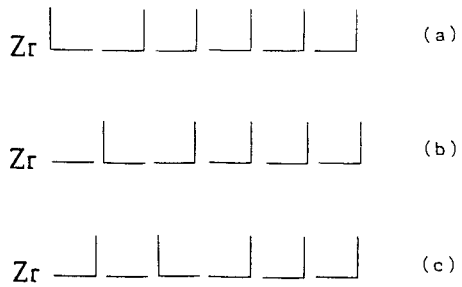


Fig. 2. 2,1 Insertion of propene in a Zr-polymer bond (a) followed by an ethene insertion (b) and a 1,2-propene insertion (c)

The activity of the copolymerization of propene with small amounts of ethene can be up to fivetimes higher than the homopolymerization (Tab. 1).

Table 1. Propene/ethene copolymerization with different zirconocene/MAO catalysts in liquid propene at different temperatures; MAO=500 mg, 375 ml liquid propene, ethene flow =1,7 l/h, a): the activity of homopolypropene, produced under same conditions for comparison.

Catalyst	Polymerizations-temperature (°C)	Zircono-cene ($x10^6$ mol)	Activity copolymer kg_{Pol}/mol_{Zr}	Activity a) homopolymer kg_{Pol}/mol_{Zr}
$[Me_2Si(H_4Ind)_2]ZrCl_2$	0	8,05	650	21
	30	2,00	16 200	
	30	0,43	20 330	4 290
	60	0,09	149 200	71 700
$[Et(H_4Ind)_2]ZrCl_2$	0	3,00	1 200	750
$[Me_2Si(Ind)_2]ZrCl_2$	0	6,13	520	320
	30	0,62	9 900	8 000
	60	0,07	55 960	51 200

Astonishingly, the increase of the activity is only given for tetrahydroindenyl complexes. The bisindenyl metallocene $[Me_2Si(Ind)_2]ZrCl_2$ shows nearly no 2,1-insertion and by addition of small amounts of ethene only a very small increase of the activity. To explain the increase of

the activity by a factor of two it could be calculated that for the homopolymerization of propene about half of all active centers are "sleeping".

The 2,1-insertion of propene blocks not only the following insertion but favours β-hydrogen transfer reactions and therefore chain terminations. By this means the molecular weight of the obtained homo polypropene is low. The copolymer obtained with 2-6 mol% of ethene units has a significant higher molecular weight. Because of the higher activity for the copolymerization and the same rate for the chain termination, the chain length of the polymer is longer (Tab. 2).

Table 2. Molecular weights of propene/ethene copolymers with 2-6 mol% of ethene prepared by different catalysts. Polymerization conditions are the same as in Tab. 1. M_w homopolymer: molecular weight of polypropene without ethene addition.

Catalyst	Temp. (°C)	M_w (kg/mol)	M_n (kg/mol)	M_w/M_n	M_w homo polymer
$[Me_2Si(H_4Ind)_2]ZrCl_2$	0	239	79	3,0	155
	30	71	31	2,3	45
	30	109	43	2,5	
	60	26	12	2,2	18
$[Et(H_4Ind)_2]ZrCl_2$	0	257	65	2,7	
$[Me_2Si(Ind)_2ZrCl_2$	0	113	45	2,6	122
	30	88	37	2,2	75
	60	48	20	2,4	48

The catalyst $[Me_2Si(Ind)_2]ZrCl_2$/MAO gives nearly the same molecular weights for the homo- and copolymerization. Fig. 3 shows that the GPC curves become more narrow with increasing polymerization temperatures.

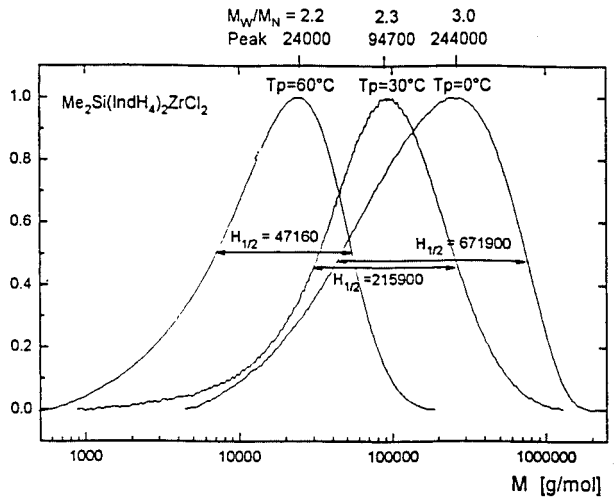


Fig. 3. GPC curves of propene/ethene copolymers with 2 mol% of ethene catalyzed by $[Me_2Si(H_4Ind)_2]ZrCl_2$/MAO

The microstructures of the propen/ethene copolymers were determined by ^{13}C NMR measurements using the calculation of Cheng and Benett[17]. Table 3 presents the calculated and measured chemical shifts for the 2,1-insertion followed by an ethene insertion in a propene/ethene copolymer.

Table 3. ^{13}C-NMR chemical shifts (ppm) of propene/ethene copolymers for the ethene insertion after 1,2- and followed by 1,2-insertion of propene (e-i), for the 2,1-insertion of propone followed by an ethene insertion (2,1–e-i-), for the meso 2,1-insertion followed by a 1,2-insertion of propene (2,1-i); (P) = primary carbon atom, (S) = secondary carbon atom, (T) = tertiary carbon atom.

Sequency (e-i)	1(S)	2(T)	3(P)	4(S)	5(S)	6(S)	7(T)
calculated	45,9	31,0	20,9	37,7	24,5	37,7	31,0
experimental	45,9	30,7	20,8	37,6	24,3	37,6	30,7
Sequency (2,1-e-i)	1(S)	2(T)	3(P)	4(S)	5(S)	6(T)	7(P)
calculated	45,7	31,3	21	34,8	34,5	34	20,3
experimental	45,5	31,0	21	34,6	34,3	33,8	20,1
Sequency (2.1-i)	1(S)	2(T)	3(P)	4(T)	5(P)	6(S)	7(T)
calculated	41,9	35,9	17,8	38,4	17,1	30,2	31,4
experimental	41,9	35,6	17,4	38,3	17,8	30.1	31,2

The NMR-measurements show that after a 2,1-insertion of propene selectively ethene is inserted. 2,1-inserted propene units surrounded by 1,2-inserted units are no longer detectible (Tab. 4).

Unexpected is the fact that for copolymers with $[Me_2Si(H_4Ind)_2]ZrCl_2$/MAO at high temperatures the amount of 2,1- and 1,3-insertions of propene are reduced significantly. This shows that in the presence of ethene as a comonomer misinsertions are reduced.

Table 4. ^{13}C-NMR spectroscopic determination of the microstructures of propene/ethene copolymers compared to homo polypropene. Explanations for the symbols see Tab. 3. 1,3-i: 1,3-insertion of propene, I: isotacticity mmmm pentads, incorporations in mol%.

Catalyst	Temp. (°C)	Copolymers I mmmm	e-i	2,1-e-i	2,1-i	Ethen		Homopolypropene I	2,1-i	1,3-i mmmm
$[Me_2Si(H_4Ind)_2]$-	0	95	1,6	0,5	0	2,1		94	0,6	0
$ZrCl_2$	30	91	2,3	0,3	0	2,4		96	0,3	0,2
		60	85	3,0	0	0	3,0		91	0
0,5										
$[Me_2Si(Ind)_2]ZrCl_2$	0	92	2,7	0	0	2,6		96	0,3	0
	30	93	5,1	0,3	0	5,4		93	0,4	0
	60	83	5,8	0,8	0	5,6		91	0,5	0

Ethene-Norbornene Copolymers

To increase the thermostability and the molecular weight of cycloolefin copolymers, a new metallocene with a more stable bridge was used[15]. For the propene polymerization we have received good results with the pentalene-fluorenyl zirconium complex ($Me_3PhPen(Flu)ZrCl_2$) showed in Fig. 1. Ethene and norbornene were polymerized with this complex in combination with MAO under different conditions. Table 5 shows composition and properties of the copolymers produced at variable norbornene concentrations.

Table 5. Copolymerization of ethene with norbornene by [$Me_3PhPen(Flu)ZrCl_2$]/MAO at 30 °C. x_N : norbornene mol part in the starting solution; X_N: norbornene mol part in the copolymer; c_E: ethene concentration: 0,237 mol/l; Zr-concentration: $5 \cdot 10^{-6}$ mol/l; MAO: 2,5 g/l; Tg: glass transition temperature, Tm: melting point; M_w: molecular weight; n.d.: not detected.

x_N	X_N	Tg (°C)	Tm (°C)	M_w (g/mol)	Activity (kg $_{Copo}$/mol $_{Zr}$·h·c_E)	
0	0		135	660 000	3	700
0,20	0,046		98	658 000	5	780
0,37	0,094		66	538 000	7	600
0,54	0,159	2	atactic	593 000	6	700
0,79	0,280	65	atactic	758 000	2	500
0,91	0,380	93	atactic	930 000	n.d.	

Copolymers with a norbornene content of over 15 mol% are amorphous as also measured for metallocene catalysts[18].

Copolymers with lower norbornene contents are partial crystalline with melting points between 66 and 135 °C. Due to different incorporation rates of the cyclic olefin into the copolymer, the glass transition temperature varies over a wide range. A copolymer containing 38 mol% of norbornene yields a material with a glass transition point of 93 °C.

The molecular weights are unusually high and increase with the norbornene concentration in the starting solution. Normally the molecular weight decreases with a higher norbornene concentration. Even at an incorporation of 38 mol% of norbornene the copolymer has a molecular weight of 930 000 g/mol. A minimum molecular weight is given at about 10 mol% of norbornene. The activity reaches 7 600 kg $_{copo}$/mol $_{Zr}$·h by 30 °C and can be increased at higher temperatures.

The high molecular weight is very useful for the physical properties and industrial applications. These COC materials present excellent transparency and very high service temperatures. They are soluble, chemically resistant and can be melt-processed. Their stability against hydrolysis and chemical degradation in combination with their stiffness let them

become desirable materials for optical applications, e.g. for compact discs, lenses, optical fibers and films. The first commercial COC plant runs at TICONA with a capacity of 30 000 tons a year.

This shows that it is possible to find metallocene/MAO catalysts which can produce copolymers with high molecular weights even by high temperatures and norbornene concentrations.

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