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New Materials by Polymerisation of Olefins and Styrene with Metallocene Catalysts

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SUMMARY: 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. The materials obtained show different microstructures, tacticities and properties compared with conventional polymers. Alternating ethene/propene polymers show lower glass transition temperatures than random copolymers. Constrained geometry catalysts are useful for the synthesis of norbornene/ethene copolymers.

Introduction

The polymerisation of olefins by organometallic catalysts has grown to one of the largest industrial applications in the field of chemistry. Almost 100 million tons of polyethylene, polypropylene, copolymers and polydienes are produced worldwide.[1] Metallocene catalysts give the possibility to tailor the structure of polymers in a way, which has not been achieved before.[2-4] Additionally, they offer a detailed understanding of the mechanism and the stereochemistry of the polymerisation of olefins. Classical Ziegler catalysts are heterogeneous, with the polymerisation taking place on dislocations and edges of the surface of $TiCl_3$ or crystal mixtures of $MgCl_2/TiCl_4$. Consequently there are many different types of active sites, and the resulting polymer has a typically broad molecular weight distribution.[5]

Metallocene catalysts 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[6], such properties include temperature resistance, hardness, impact strength and transparency. Propylene and long chain olefins can be built up stereoregularly, with the building blocks in the chain having a defined and constantly repetitive configuration. This configuration has considerable influence on the service properties of the material. There is a variety of materials which, for the first time, can be produced with metallocene catalysts, such as:

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- long-chain branched polyethylene;
- polypropylenes 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;
- elastomers made of ethene, propene and dienes (EPDM);
- syndiotactic polystyrene with a high melting point;
- homo- and copolymers of cyclo-olefins;
- cyclo-polymers of 1,5-hexadienes, and
- polymers prepared in emulsions or in the presence of fillers (nano particles).

Some of the new polymers are transparent. Cyclo-olefin copolymers (COC) have special properties and may be very useful as engineering plastics. Ethene/norbornene copolymers are potentially very useful because the monomers are readily available.[7,8] Due to different incorporation values of the cyclic olefin in the copolymer, the glass transition temperature can vary over a wide range, independent of the catalysts used. A copolymer with 50 mol% 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 $[Me_2C(3\text{-}^{tert}Bu Cp)(Flu)]ZrCl_2$ shows not only high activities for the copolymerisation of ethene with propene or norbornene, it also gives an alternating structure.[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 thereof. A maximum melting point of 320 °C was reached. Supporting the zirconocenes on silica decreases the necessity for an excess of MAO, which can influence the tacticity.

Fluorinated half-sandwich titanium complexes $(R\text{-}Cp)TiF_3$ in combination with MAO are very active catalysts for the polymerisation of styrene and butadiene.[10,11] The obtained syndiotactic polystyrene has a molecular weight of over 400 000 g/mol and a melting point of 275 °C. Metallocene-based polybutadiene has a special microstructure with 80 % *cis* 1,4-, 1 % *trans* 1,4- and 19 % 1,2-vinyl units.

Experimental

The zirconocenes and constrained geometry catalysts were prepared as described in the literature.[12-14] Polymerisations were carried out under an argon atmosphere using a 1 l Büchi

A6 Type 1 autoclave equipped with an additional external cooling system. For COC experiments, the reactor was evacuated at 95 °C for 1 h and subsequently charged with 200 ml toluene, 500 mg MAO (Witco), norbornene, and ethene at different pressures. Norbornene was dried over triisobutylaluminum and subsequently distilled. The gaseous monomers (ethene, propene) were 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 solution of the metallocene in toluene. The polymerisation was quenched by addition of 5 ml ethanol. Work-up proceeded by stirring overnight in dilute hydrochloric acid, followed by neutralisation with aqueous $NaHCO_3$ and washing with water. After phase separation and reduction of the volume of the organic solvent the polymer was precipitated. If this was not possible, the organic solvent was removed completely 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 determinations were conducted by viscosimetry, using an Ubbelohde viscometer at 135 °C (Capillary Oa, K = 0,005).

Results and Discussion

Alternating Ethene/Propene Copolymers

There are some C_1-symmetric zirconocene catalysts such as $[Me_2C(3\text{-}PhCp)(Flu)ZrCl_2]$ or $[Me_3Pen(Flu)]ZrCl_2$ which copolymerise ethene and propene to partial alternating structures.[15] High amounts of alternating structures are obtained when $[Me_2Si(Ind)(Flu)]ZrCl_2$/MAO in toluene at 30 °C is used.

The most general progression of such a copolymerisation (when neglecting regio- and stereo-errors) involves consecutive insertions from one site (retention mechanism of insertion) as well as insertions by chain migratory insertion (alternating mechanism). Taking into account effects of the terminal unit on insertion as well as on the mechanism of insertion 12 parameters are needed to describe the copolymerisation. In order to keep the number of parameters low for this first approach to the problem we investigated the two limiting cases of a retention mechanism which will lead to a description by the terminal or penultimate model and the strictly alternating mechanism where chemoselectivity of both sites is taken into account in an alternating fashion.

While the terminal model (Markov 1) considers only the last insertion step of either ethene or propene, the penultimate model (Markov 2) also considers the second last insertion. The new TSAM model is based on the assumption of a strictly alternating mechanism of insertion, in which one of the two different sites of the catalyst (Re or Si enantio face) follows a first-order Markovian statistic, as for the terminal model, while on the other site only ethene may insert.

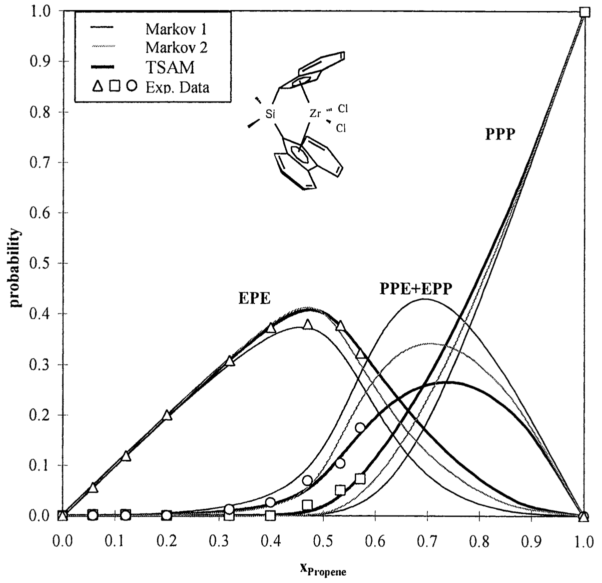


Fig. 1: Distribution of the propene-centered triads as determined from the copolymers and the calculated data (Markov 1, Markov 2, and TSAM model).

In Fig. 1 the experimental data for the copolymerisation of ethene and propene by $[Me_2Si(Ind)(Flu)]ZrCl_2$ are compared with calculations according to Markov 1, Markov 2 and the TSAM model.[15]

This copolymerisation is best described by the TSAM calculation, especially at higher propene concentrations. Four copolymerisation parameters are necessary for the calculation (Table 1).

Table 1 Copolymerisation parameters for the different Markov and TSAM models for the ethene(E)/propene(P) copolymerisation with [$Me_2Si(Ind)(Flu)]ZrCl_2$/MAO in toluene at 30°C. A and B are the different sites of the catalyst

Model	Parameter			
Markov1	r_E		r_P	
	4,52		0,003	
Markov 2	r_{EE}	r_{PE}	r_{EP}	r_{PP}
	5,37	3,30	0,003	0,009
TSAM	r_E^A	r_P^A	r_E^B	r_P^B
	2,40	0,044	43,5	0,002

A copolymer with a propene content of 51,6 mol% shows only four signals in the ^{13}C-NMR spectrum while a random copolymer gives rise to 20 and more signals (Fig. 2).

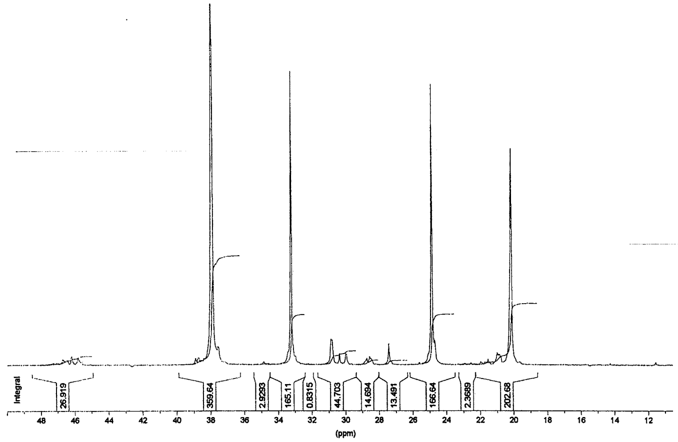


Fig. 2 ^{13}C-NMR spectra of an ethene/propene copolymer with 85 % alternating triads

The copolymer has 85 % alternating sequences of EPE and PEP triads. Such copolymers with high amounts of alternating sequences have special properties. The 15 % non-alternating sequences formed by EEP, EPP, PPP, and EEE are distributed randomly over the polymer chain. No long ethene blocks can be formed and crystallise.

Such a highly alternating copolymer shows a lower glass transition temperature than the random copolymer (Fig. 3). The Tg is about 6 °C lower than for the random copolymer with the same composition. This is an advantage of EP or EPDM elastomers.

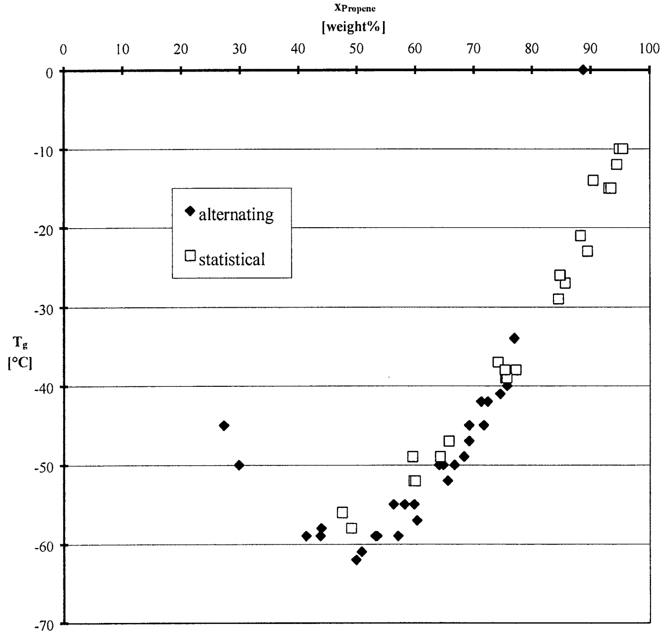
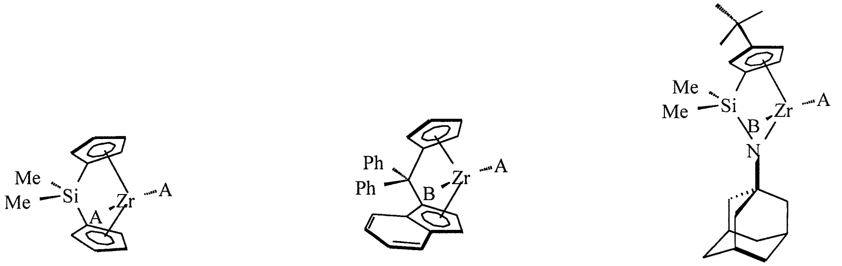


Fig. 3 Glass transition temperature of ethene/propene copolymers-influence of the microstructure

Ethene/Norbornene Copolymers

Three metallocene/MAO catalysts were used to copolymerise ethene and norbornene (Fig. 4). In all zirconium components one ligand was a cyclopentadienyl ring, which gave less steric hindrance. The polymerisations were carried out at different temperatures and with different ethene/norbornene monomer ratios. Table 2 compares the activities of the different catalysts.



$[Me_2Si(Cp)_2]ZrCl_2$ I

$[Ph_2C(Cp)(Ind)]ZrCl_2$ II

$[Me_2Si(3\text{-}^{tert}BuCp)(NAdam)]ZrCl_2$ III

Fig. 4 Metallocene catalysts used for the copolymerisation of ethene and norbornene

Table 2 Activities of different metallocene/MAO catalysts at 30 °C used in the copolymerisation of ethene/norbornene

Catalyst	X_N (feed)	x_N (polymer)	activity [kg $_{Pol}$/(mol $_{Zr}$·h)]	M_η [g/mol]
I	0	0	19 600	59 200
	0,2	0,09	6 900	29 600
	0,45	0,17	3 800	28 000
	0,6	0,28	1 930	26 100
	0,8	0,44	460	13 800
	0,95	0,64	80	n.d.
II	0	0	1 560	14 700
	0,3	0,17	2 560	14 500
	0,5	0,33	1 250	16 100
	0,66	0,38	1 040	21 000
	0,8	0,40	770	33 200
	0,95	0,56	240	n.d.
III	0	0	150	n.d.
	0,4	0,11	24	n.d.

n.d.: not detected

Catalysts I and III show higher activities for the homopolymerisation of ethene than for the copolymerisation. For catalyst II a higher activity was observed for an ethene/norbornene molar ratio of 0,3 than for the homopolymerisation. The lowest activities were found for the constrained zirconium complex III. Fig. 5 shows the polymerisation activity of the catalyst [$Ph_2C(Cp)(Ind)]ZrCl_2$/MAO at different polymerisation temperatures and ethene/norbornene molar ratios.

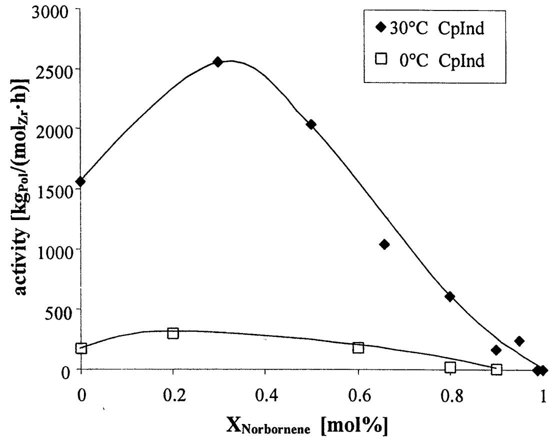


Fig. 5: Activity of [$Ph_2C(Cp)(Ind)]ZrCl_2$/MAO in the copolymerisation of ethene/norbornene at 0°C and 30°C

To increase the activity of catalyst III, the temperature was raised to 90 °C. Results are tabulated in Table 3.

Table 3 Copolymerisation of ethene/norbornene by $[Me_2Si(3^{tert}BuCp)(NAdam)]ZrCl_2/MAO$ at 90 °C

X_N (feed)	x_N (polymer)	activity [kg $_{Pol}$/(mol $_{Zr}$·h)]	$M\eta$ [g/mol]	Tg [°C]
0	0	280	17600	n.d.
0,2	0,11	330	n.d.	-9
0,4	0,22	580	5900	n.d.
0,6	0,32	580	5 300	38
0,8	0,39	420	13 800	51
0,9	0,45	770	2 900	91
0,95	0,50	360	4 400	106

(n.d. = not detected)

For the metallocene $[Me_2Si(Cp)_2]ZrCl_2$ (I) the copolymerisation was found to be best described by the penultimate Markov 2 model (Fig. 6):

As was seen in Table 2, catalyst I incorporates high amounts of norbornene in the copolymer; up to 70 mol% can be incorporated.

The copolymerisation parameters at 30°C were:

$r_{EE} = 2,9$ $\qquad$ $r_{NN} = 0,006$

r_{NE} = 3,5 r_{EN} = 0,208

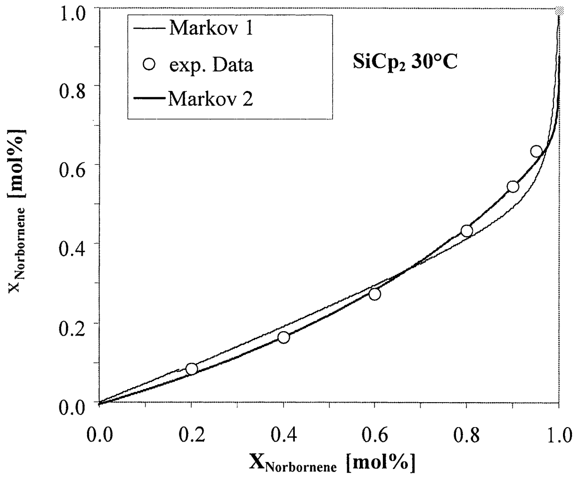


Fig. 6 Copolymerisation diagram of the copolymerisation of ethene/norbornene, catalysed with $[Me_2Si(Cp)_2]ZrCl_2$-/MAO at 30°C. Lines represent the fits of the appropiate models

The catalyst $Ph_2C[Cp)(Ind)]ZrCl_2$ (II) also gives high incorporation and is best described by the Markov 1 model. The copolymerisation parameters at 30 °C were:

r_E = 1,6 r_N = 0,010

The TSAM model was used to describe the incorporation in $[Me_2Si(3-{}^{tert}BuCp)(NAdam)]ZrCl_2$ (III)-catalysed reactions.

r_E^A = 0,95 r_E^B = 1000

r_N = 0,045 r_N^B = 0,004

If the norbornene content in the feed was higher than 60 mol%, a slow increase in the comonomer incorporation was observed for catalyst III. Only isolated and alternating norbornene units were found in the polymer chain.

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