New Polymers by Copolymerization of Ethylene and Norbornene with Metallocene Catalysts

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Summary: To increase the thermal stability of metallocene-methylaluminoxane catalysts. pentalene bridged zirconocenes and a constrained geometry catalyst were used for the copolymerisation of ethene and norbornene. The constrained geometry catalyst is stable in solution up to 90 °C. Surprisingly the molecular weight of the copolymers increases with higher incorporation rates of norbornene. Glass transition temperatures of 120 °C are reached. The microstructure of the cyclic olefin copolymers material is more alternating.

Keywords: COC; ethene-norbornene copolymers; metallocene catalysts; olefin polymerization; pentalene-zirconocene complexes

Introduction

Cyclic olefin copolymers (COC) are a new class of polyolefins which can be produced in an easy way by metallocene/methylaluminoxane (MAO) and other single-site catalysts.[1-9] These catalysts are able to copolymerize ethylene and strained cyclic olefins such as cyclopentene, norbornene, and substituted norbornenes. While polymerisation of cyclic olefins by Ziegler-Natta catalysts is accompanied by ring opening,[10] homogeneous metallocene and palladium catalysts achieve exclusive double bond opening polymerisation.[11-15] The obtained copolymers have special properties and a high potential as engineering plastics.

COCs are characterized by excellent transparency and very high long-life service temperatures. They are soluble, chemically resistant and can be melt-processed. Due to their high carbon/hydrogen ratios, these polymers feature a high refractive index, e.g. 1.53 for ethylene-norbornene copolymer at 50 mol% norbornene incorporation. 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

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films.[16,17] Ticona GmbH runs a commercial COC plant with a capacity of 30,000 tons a year since 2000 in Oberhausen, Germany.

The first metallocene-based COC material was synthesized from ethylene and cyclopentene.[18] While homopolymerisation of cyclopentene results in 1,3-enchainment of the monomer units,[19] isolated cyclopentene units are incorporated into the ethylene-cyclopentene copolymer chain by 1,2-insertion. Ethylene is able to compensate the steric hindrance at the α-carbon of the growing chain after and before the insertion of cyclopentene.[20]

The microstructure of ethene norbornene polymers can be tailored in a wide range by different zirconium and titanium complexes. Chiral C_2-symmetric zirconocenes produce random copolymers while C_s-symmetric complexes produce more alternating structures (Table 1).

Table 1. Copolymerization of ethylene/norbornene by different metallocene/MAO catalysts by 30 °C. Norbornene ratio in feed:= 80 mol%, Al:Zr = 4000

Catalyst	Activity (kg/mol m·h)	r_E	$r_E \cdot r_N$	X_N (polymer) (mol%)	M_w (g/mol)
$[C_2H_4(Ind)_2]ZrCl_2$	9 080	3.6	0.9	28	220 000
$[Me_2Si(Flu)(Cp)]ZrCl_2$	25 000	4.4	0.1	32	1 010 000
$[Me_2C(Flu)(t\text{-}BuCp)]ZrCl_2$	430	6.0	0	30	80 000
$[Me_2Si(t\text{-}BuCpo)(N\text{-}t\text{-}Bu)]TiCl_2$	1 500	15.1	>0.1	19	270 000

Most active is the complex $[Me_2Si(Flu)(Cp)]ZrCl_2$ which gives also a copolymer with the highest molecular weight and a more alternating structure. Due to different incorporation values of the cyclic olefin in the copolymer, the glass transition temperature can vary over a wide range for a random copolymer 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 $[Me_2C(t\text{-}BuCp)(Flu)]ZrCl_2$ shows not only high activities for the copolymerisation of ethylene with norbornene, and gives alternating structure, too. The melting points and the glass transition temperatures of the alternating copolymer depend on the molar ratio of norbornene in the polymer, the microstructure, and the catalyst. A maximum melting point of 320 °C can be reached.

Palladium diimine complexes also show high norbornene incorporation and give more alternating microstructures.[21]

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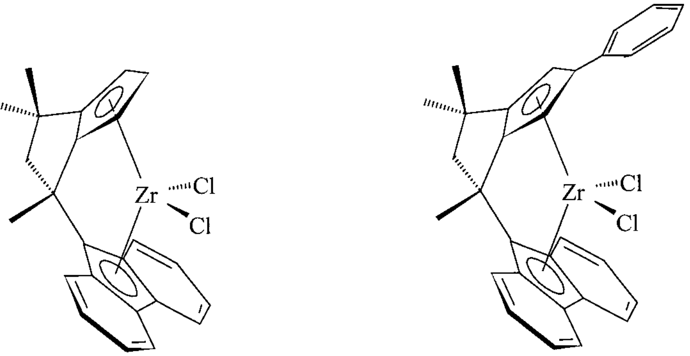
Results and Discussion

Most metallocene/MAO catalysts are instable at temperatures higher than 60 °C and the activity decreases drastically. We synthesized new zirconocenes (Figure 1) with pentalene ligands to stabilize the bridge in ansa metallocenes.



I [1-(Fluorenyl)-1,3,3-trimethyl tetrahydro-trimethyl-pentalenyl]zirconiumdichloride

II [1-(Fluorenyl)-1,3,3-5-phenyl-tetrahydro-pentalenyl]-zirconiumdichloride

Figure 1. Structures of used zirconocenes

Zirconocenes I and II were prior used to polymerise propene and tailor the microstructure.[22] Because of their open wedge, the catalysts 1 and 2 are also very active in ethylene/norbornene copolymerisation (Figure 2).

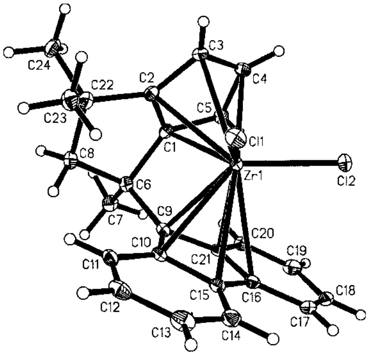


Figure 2. X-ray structure of I

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The activities for the two catalysts are shown in Table 2.

Table 2. Copolymerization of ethylene and norbornene by 30 °C in 200 ml toluene. Ethylene pressure = 2 bar, zirconocene concentration : 10^{-7} - $5\cdot10^{-6}$ mol/L, MAO: 500 mg, reaction time 15 – 60 min, activity: kg Polymer(Ethylene)/mol $Zr\cdot h\cdot C_E$. M_v: viscosity average of molecular weight, M_w : molecular weight, measured by GPC

Zirconocene	x_N Norb. (in feed)	Activity (in copo)	X_N Norb. (kg/mol)	M_v (kg/mol)	M_w
I	0	2 700	0	490	520
I	0.19	3 700	0.07	360	400
I	0.39	3 800	0.16	230	340
I	0.59	3 500	0.23	160	330
I	0.80	3 000	0.34	190	390
I	0.90	600	0.42	120	370
II	0	3 700	0	630	660
II	0.20	5 780	0.05	660	-
II	0.40	7 600	0.09	540	670
II	0.59	6 700	0.18	470	690
II	0.80	2 500	0.29	280	830
II	0.90	100	0.36	300	830

For both catalysts we can see an increase of the activity if norbornene is present in the starting reaction mixture (feed). Up to 59 mol% of norbornene the activity is still high but decreases by higher norbornene ratios. Zirconocene II is more active for the ethylene homopolymerisation and the ethylene/norbornene copolymerisation at low norbornene concentration but incorporates less amounts of norbornene in the copolymer. The phenyl substitution of the ligands causes steric hindrance to the cycloolefin incorporation. The calculation of the copolymerisation parameter r_1 by a first order Markov-model gives a value of:

$r_1 = 3.24$ for I/MAO

$r_1 = 5.52$ for II/MAO

$r_1 = 4.43$ for $[Me_2C(PhCp)(Flu)]ZrCl_2$/MAO.

For comparison also the r_1 value is given of another C_1-symmetric catalyst. The values of the copolymerisation parameters r_1 show that both catalysts can incorporate norbornene in a relatively good way. For I the norbornene incorporation is only slower by the factor 3.2 than the ethene incorporation. With both catalysts the molecular weights of the obtained copolymers are high and reach values of 800 000 (see Table 2). While in most

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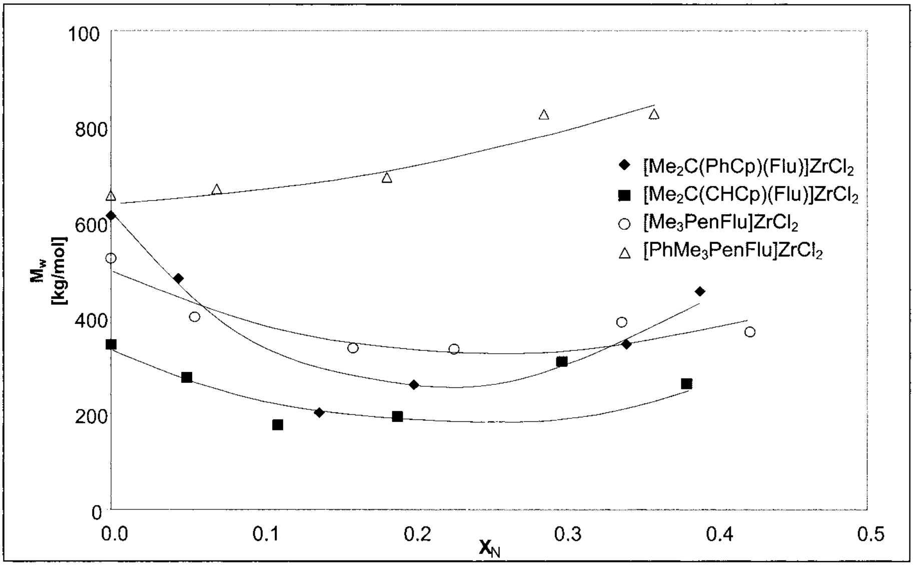

Figure 3. Molecular weights of ethylene/norbornene copolymers in dependence of the molar fraction X_N of norbornene in the polymer

copolymerisation cases the molecular weight decreases with increasing norbornene incorporation in opposite with zirconocene II/MAO the molecular weights increase (Figure 3). This is an unusual observation. The high molar masses obtained with II seem to be due to the fact that the phenyl substitution hinders β-hydrogen transfers in ethene polymerisation.

In the presence of norbornene they are further reduced. Even after an incorporation of 36 mol% of norbornene, the molecular weight of the copolymer is at the highest point of 830,000 g/mol. The microstructure is a more alternating one (Figure 4).

The calculation (lines) was made by a chain retention mechanism after each insertion step. The alternating structure is not perfect and near 70 %. Glass transition and melting temperatures are shown in Table 3.

Copolymers with norbornene parts of less than 10 % are partially crystalline and the others are amorph. The alternating structure is not high enough to form crystalline parts again. Copolymers with an incorporation of only 4 or 5 mol% of the cyclic olefin decrease the melting point to less than 100 °C. We have carried out also copolymerizations of ethylene and

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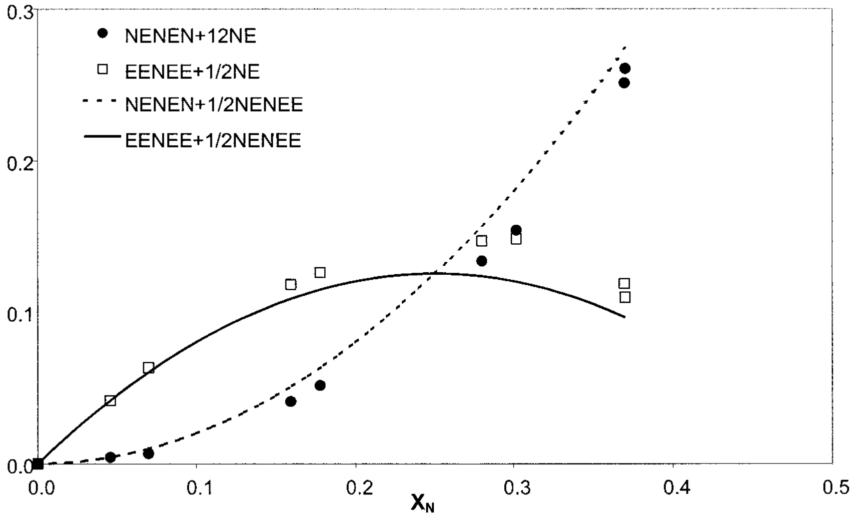

Figure 4. Part of the norbornene centralyzed pentads as a function of the incorporation rate

Table 3. Glass transition temperatures (Tg), melting points (Tm), melting entropies (ΔHm) and crystallinity (α) of ethylene/norbornene copolymers obtained by zirconocene I and II/MAO catalysts; conditions see Table 2; n.d. = not detectable

Catalyst	x_N (copo)	Tg (°C)	Tm (°C)	ΔHm	α
I	0	n.d.	134.5	152.1	54
I	0.04	n.d.	79.0	45.1	16
I	0.16	4.6	n.d.	n.d.	0
I	0.23	35.6	n.d.	n.d.	0
I	0.34	82.6	n.d.	n.d.	0
I	0.42	115.1	n.d.	n.d.	0
II	0	n.d.	135.4	149.7	53
II	0. 05	n.d.	98.0	56.3	20
II	0.09	n.d.	57.2	41.0	15
II	0.18	16.7	n.d.	n.d.	0
II	0.29	59.3	n.d.	n.d.	0
II	0.36	90.1	n.d.	n.d.	0

norbornene using the constrained geometry complex $[Me_2Si(3-^{tert}Bu)]TiCl_2$ and MAO as cocatalyst. This catalyst is known to be stable at higher temperatures. The activities of the copolymerisation at reaction temperatures of 30, 60, and 90 °C are shown in Table 4.

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Table 4. Copolymerization of ethylene and norbornene with [$Me_2Si(3\text{-}^{tert}BuCp)(N^{tert}Bu)]TiCl_2$/MAO in 200 ml toluene with polymerisation temperature; Ti-complex: $1.3 \cdot 10^{-5}$-$2.5 \cdot 10^{-7}$ mol/L; MAO: 500 mg; ethylene pressure: 2 bar, norbornene 0-1.13 mol/L

x_N [a]	Activities in kg Copolymer / mol Ti · h		
	30°C [b]	60°C [b]	90°C [b]
0	800	2 500	12 000
0.20	1 000	5 000	20 000
0.40	2 100	9 800	27 000
0.60	2 500	10 100	29 000
0.80	1 500	5 100	18 000
0.90	1 000	2 200	13 000
0.95	300	1 300	3 500

a) Molar fraction of Norbornene in feed;

b) Polymerization temperature

As assumed, the activities rise with increasing temperature and the differences between the activities at different temperatures decrease for $x_N \rightarrow 0$ and $x_N \rightarrow 1$. The data show that the activities at 60 °C are approximately 5 times and at 90 °C about 15 times higher than at 30 °C depending on the norbornene molar fraction in the feed x_N. The maximum of activities lies between $x_N = 0.4$ and $x_N = 0.6$. That maximum of activity is known in the literature as the positive comonomer effect and with 29 000 kg copolymer/mol Ti · h by 90 °C quite high. The molar masses of the copolymers are summarized in Table 5.

Table 5. Ethylene/norbornene copolymerizations by [$Me_2Si(3\text{-}^{tert}BuCp)(N^{tert}Bu)]TiCl_2$/MAO at 30, 60, and 90 °C, respectively. Molar masses determined by viscosimetry and molar fraction norbornene in the feed x_N

x_N	30 °C $M\eta$ (g/mol)	60 °C $M\eta$ (g/mol)	90 °C $M\eta$ (g/mol)
0.2	200 000	81 000	45 000
0.4	230 000	85 000	48 000
0.6	321 000	95 000	46 000
0.8	259 000	62 000	37 000
0.9	100 000	33 000	22 000
0.95	83 000	23 000	20 000
0.99	76 000	28 000	20 000

The molar masses increase with increasing norbornene fraction in the feed until $x_N = 0.6$. At higher norbornene fractions the molar masses decrease. For COCs prepared at 30 °C, the

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molar masses increase from 200 000 to 320 000, and then decrease to 76 000 g/mol. They are much lower than the COCs prepared by the zirconocenes I and II with pentalene ligands. The incorporation of norbornene into the polymer chain is lower for the constrained geometry catalyst compared with the zirconocenes. At 30 °C and $x_N = 0.6$, the molar fraction of norbornene in the copolymer is 0.09 and by $x_N = 0.9$ it is 0.22.

Conclusions

It could be shown that there are metallocene catalysts which can produce ethylene norbornene copolymers even at temperatures up to 90 °C. High molecular weights of the copolymers are obtained by tailored zirconocenes even at high norbornene concentrations in the feed. The norbornene incorporation, copolymerisation parameters, microstructures, and glass transition temperatures are barely influenced by the temperature. C_1-symmetric catalysts give copolymers with more alternating structures and the maximum norbornene incorporation is near 50 mol%.

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