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Copolymerization of norbornene and ethene with homogenous zirconocenes/methylaluminoxane catalysts

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Abstract

The norbornene/ethene copolymerization was investigated by using two *Cs*-symmetric ([$Me_2C(Fluo)(Cp)]ZrCl_2$ **III**, [$Ph_2C(Fluo)(Cp)]ZrCl_2$ **IV**) and two *C2*-symmetric ([$Me_2Si(Ind)_2]ZrCl_2$ **I**, [$Ph_2Si(Ind)_2]ZrCl_2$ **II**) catalysts with methylaluminoxane (MAO) as cocatalyst. This investigation focussed not only on the different polymerization behavior, like catalyst activity, but also considers the material properties of the synthesized copolymers. It was found, that the *Cs*-symmetric catalysts are very well suitable to yield amorphous copolymers with glass transition temperatures above 180°C and molecular weights > 100.000 g/mol. These copolymers could be used as potential starting materials for optical discs and fibers.

Introduction

During the past ten years intensive research in the field of homogenous ZN-catalysis (1-3) led to highly isospecific catalysts. These systems consist for example of ethylene-bis-(1-indenyl)-zirconiumdichloride/methylaluminoxane ([$En(Ind)_2]ZrCl_2$/MAO) and are able to polymerize propene and other α-olefins to result isotactic polymers (4). Furthermore it is possible to polymerize cycloalkenes like cyclopentene, norbornene and dimethano-octahydronaphthalene, without ring opening (5-7). Exchanging the ethylene-bridge between the indenyl-rings for a disubstituted silyl-group gives even higher activities, molecular weights and longer isotactic sequence lengths (8,9). Ewen (10) developed the fluorenyl-cyclopentadienyl system [$Me_2C(Fluo)(Cp)]ZrCl_2$ **III**, and Spaleck (11) the [$Ph_2C(Fluo)(Cp)]ZrCl_2$ **IV** catalyst, which produce syndiotactic polypropylene with relatively low activities, but very high molecular weights (8,9).

This work was intended to prove the possibility to combine the properties of the different catalysts, regarding activity and molecular weights, with the copolmerization of cycloolefines/α-olefines. To obtain these data, experiments with constant reaction parameters but varying norbornene/ethene monomer ratio were conducted. According to the standard [$En(Ind)_2]ZrCl_2$ catalyst system (6) information of the difference in the material properties were provided.

Experimental part

All operations were performed under argon atmosphere using standard Schlenck techniques. Toluene was refluxed and freshly destilled under argon from an Na/K alloy. Norbornene (from Aldrich and Janssen) dissolved in toluene was dried over trimethylaluminium, followed by condensation. Polymerization-grade ethene was deoxygenated, dried by passage through

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columns of BASF R3-11 catalyst and 10 Å molecular sieves and was condensed into a 500 mL lecture bottle.

The metallocenes used and methylaluminoxane (MAO) (12) were prepared as published already, **I**, **II** (8), **III** (10) and **IV** (11).

The polymerizations were carried out in a 1 L glass autoclave equipped with a thermometer tube, magnetic stirrer and several valves for argon and the monomer.

38 mL of norbornene solution in toluene, 62 mL toluene (for example) and 300 mg MAO were added to the autoclave. The mixture was stirred at 30 °C and saturated with ethene at a pressure of 2 bar. Meanwhile 20 mg of MAO was dissolved in 2 mL of a solution of the metallocene in toluene ($5*10^{-7}$ mol metallocene). After a 15 min preactivation this mixture was added via a syringe to the reactor. For kinetic investigations the weight of the ethene suppling bottle was determined by repeated weighting.

The copolymerization runs have been carried out only a short reaction time to minimize the consumption of comonomer, so that the monomer ratio in the polymerization runs were nearly constant during a run. After quenching by blowing off the monomer and adding a few drops of ethanol, the obtained polymer was stirred in a 20 vol.-% ethanolic hydrochloric acid solution overnight and washed with water. The polymer material was separated, washed in a Büchner tunnel and dried at 70 °C to constant weight.

The viscosity-average molecular weights M_η for all polymers obtained were measured in decalin (decahydronaphthalene) at 135 °C. Gel-permeation chromatography measurements (GPC) of the polymers were obtained at 135°C by using a Waters Model 150-C ALC/GPC.

The phase transition temperatures were determined with a Perkin Elmer DSC 4 system at a heating rate of 20 °C/min. The results of the second scan are reported.

^{13}C-NMR measurements were performed on a Bruker MSL 300 spectrometer operating at 75 MHz. The samples were dissolved in 1,1,2,2,-tetrachloroethane-d_2.

The wide angle X-ray scattering (WAXS) patterns were scanned by using a Siemens D 500 diffractometer with monochromatic radiation at a wavelength of 1,54 Å. Scanning was performed from $2\ \Theta = 4° - 40°$ for the polymers in form of powders.

Results and discussion

Norbornene/ethene copolymers possess rather interesting material properties. Not only they are highly resistant to chemicals and heat, but they also show very high glass transition temperatures and desirable elastic modules. These properties make them suitable as potential materials for polymer optical fibers (POF).

Copolymerization of norbornene and ethene

The polymer properties depend only on the polymerization conditions, which can be fitted to requirements of the polymer. This is demonstrated by the following data. Table 1 shows the activity of the copolymerization with four different catalysts **I** - **IV** as a function of the norbornene/ethene ratio.

Figure 1 illustrates that there are large differences in reaction rate between the two kinds of catalysts. The C_2-symmetric catalysts **I**, **II** are highly active in ethene polymerization. But with an increasing norbornene/ethene ratio the activity decreases rapidly. In this case the diphenylsilyl-bridged catalyst **II**, as found in ethene polymerization, possess a lower activity as the responding dimethylsilyl-system **I**. The $[En(IndH_4)_2]ZrCl_2$ system shows a similiar behavior like the other C_2-symmetric catalysts, but the activity is at a low norbornene concentration more than 10 times less (6).

Surprisingly, the C_s-symmetric catalysts **III**, **IV** reveal a completely different copolymerization behavior. For both components **III**, **IV** the activity curve reaches a maximum (figure 1). This maximum lies in the case of [$Me_2C(Fluo)(Cp)]ZrCl_2$ **III**, at a monomer ratio of 3 and for [$Ph_2C(Fluo)(Cp)]ZrCl_2$ **IV** at 0,6. Even at a high norbornene concentration the activity values approach a constant level of 2200 and 2400 kg copolymer per mol Zr, bar ethene and hour, respectively. This means, that the copolymerization with bulky cyclic olefins is 4 - 5 times faster than ethene homopolymerization. The polymerization activity behavior verify, that the C_s-symmetric catalysts have better steric conditions for insertion of bulky olefines than the C_2-symmetric ones, attributed to the greater coordination space, which results from the shorter dimethylcarbyl-bridge.

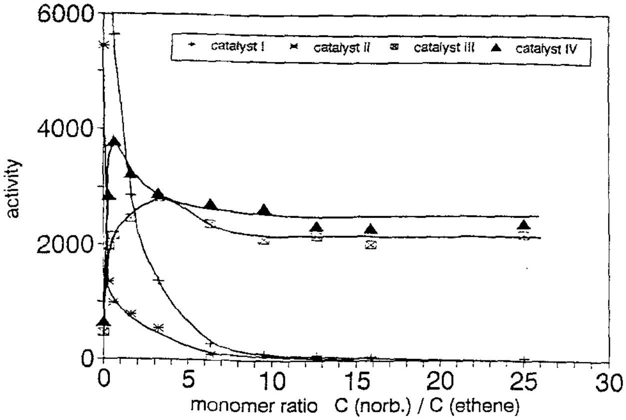

Figure 1: Polymerization activity [$kg_{copolymer}/mol_{Zr}*bar_{ethene}*h$] as function of the monomer ratio C_N/C_E (**I** = [$Me_2Si(Ind)_2]ZrCl_2$, **II** = [$Ph_2Si(Ind)_2]ZrCl_2$, **III** = [$Me_2C(Fluo)(Cp)]ZrCl_2$, **IV** = [$Ph_2C(Fluo)(Cp)_2]ZrCl_2$)

Table 1 shows the rate of incorporation of norbornene, which was determined by means of ^{13}C-NMR spectroscopy. From Figure 2 it is evident that there

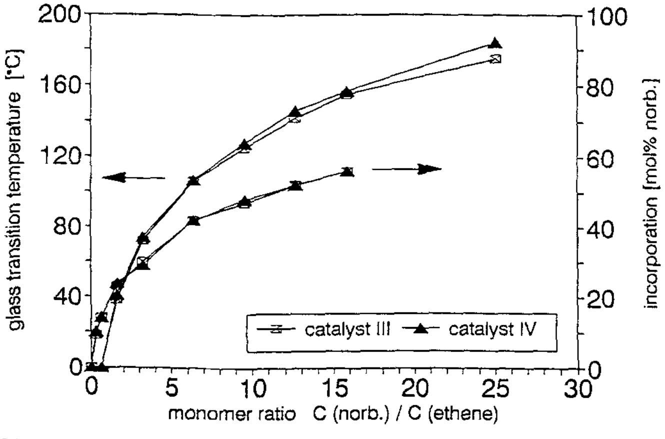

Figure 2: Glass transition temperatures of copolymers type **B** and norbornene incorporation into the copolymer as function of norbornene/ethene ratio in the reaction mixture (**III** = [$Me_2C(Fluo)(Cp)]ZrCl_2$, **IV** = [$Ph_2C(Fluo)(Cp)]ZrCl_2$)

Table 1: Activity (* : in $kg_{copolymer}/mol_{Zr} * bar_{ethene} * h$) of catalysts I–IV in norbornene/ethene copolymerization and norbornene incorporation, phase transition temperatures (Tg, Tm) viscosity-average molecular weight Mμ and ratio of weight- to number-average molecular weights Mw/Mn of norbornene/ethene copolymers obtained as function of the monomer ratio C_N/C_E in the reaction mixture

C (norb.)/ C (ethene)	catalyst	activity*	incorp. mol%	Tg / Tm °C	Mμ*10³ [g/mol]	Mw/Mn
0,000	I	9700	0	/ 136	234	
	II	5440	0	/ 135	310	
	III	470	0	/ 132	484	
	IV	660	0	/ 138	620	
0,322	I	8250	10	/ 67	unsol.	
	II	1360	8	/ 75	231	
	III	1980	9			
	IV	2860	10	/ 68	unsol.	
0,637	I	5640	13	-1 / 107	165	
	II	990	13	-1 / 124	208	
	III	2160	14	-2 / 40		
	IV	3780	14	0 / 42	322	
1,608	I	2860	29	38 / 123	126	
	II	785	24	46 / 134	204	
	III	2460	23	38		
	IV	2940	24	41	280	
3,215	I	1370	35	82	188	
	II	540	34	86 / 134	147	
	III	2810	30	72		
	IV	2810	29	74	191	
6,370	I	290	42	/ 124	198	
	II	90	39	/ 133	93	10,74
	III	2380	42	106	158	2,08
	IV	2840	42	107	146	
9,524	I	110	47	/ 124	184	17,42
	II	60	48	/ 134	72	
	III	2120	47	125	71	2,60
	IV	2760	48	128	132	4,59
12,658	I	95	51		86	
	II	40	54	/ 128	56	10,10
	III	2180	52	142	146	4,84
	IV	2370	52	146	95	5,45
15,873	I	55	55	/ 133	74	8,22
	II	30	56	/ 134	71	9,02
	III	2040	56	155	157	1,71
	IV	2335	56	157	97	4,89
25,050	I	30				
	III	2210		175	127	4,88
	IV	2410		184	140	2,20

are only small differences in the ability of the four catalysts to incoporate norbornene. It is necessary to mention, that there are uncertainties with the evaluation of the ^{13}C-NMR spectra of copolymers which contain more than 50 mol% norbornene.

From the determined rates of incorporation, dependent on the reaction temperature, the copolymerization parameter r_1 could be calculated according to the Fineman-Ross method.

All catalysts show extremely low r_1 values:

r_1 = 2,66 (30 °C) for $[Me_2Si(Ind)_2]ZrCl_2$ **I**
r_1 = 3,44 (30 °C) for $[Ph_2Si(Ind)_2]ZrCl_2$ **II**
r_1 = 2,93 (30 °C) for $[Me_2C(Fluo)(Cp)]ZrCl_2$ **III**
r_1 = 2,61 (30 °C) ; r_1 = 1,85 (0 °C) for $[Ph_2C(Fluo)(Cp)]ZrCl_2$ **IV**

These values are in the order of the already investigated systems ($[En(IndH_4)_2]ZrCl_2$: r_1 = 2,2, $[En(Ind)_2]ZrCl_2$: r_1 = 6,6, T = 25 °C) (6).

Figures 3.1 and 3.2 show the ^{13}C-NMR spectra of two copolymers **A** and **B**, which were synthesized with the same monomer ratio but using the two different kinds of catalysts (copolymer of type **A** was produced by C_2-symmetric catalyst **I**, and **B** by C_s-symmetric catalyst **IV**).

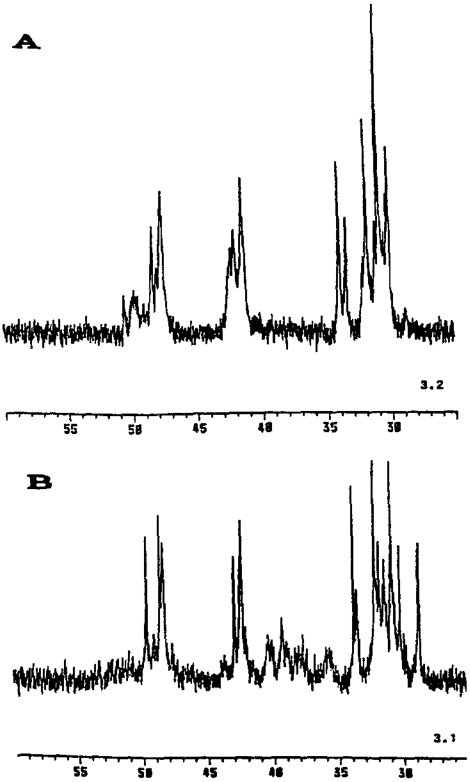

Figure 3: ^{13}C-NMR spectrum of norbornene/ethene
3.1: copolymer **A**, prepared with $[Me_2Si(Ind)_2]ZrCl_2$ **I**,
3.2: copolymer **B**, prepared with $[Ph_2C(Fluo)(Cp)]ZrCl_2$ **IV**,
with the same monomer ratio of C_N/C_E = 25,05

As a result of the high content of norbornene in both copolymers, a splitting of each norbornene-^{13}C-signal can be observed. This is due to the formation of short blocks. For the copolymer **A** additional peaks in the range of 36 - 40 ppm are observed. Based on the ^{13}C-NMR results of norbornene-dimeres and -trimeres it can be shown that these additional signals are a consequence of the formation of longer norbornene blocks.

Investigations by means of WAXS and differential scanning calorimetry (DSC) prove this assumption.

The copolymer **B**, as synthesized, has to be regarded as amorphous; it shows only a glass transition temperature and the WAXS pattern of an amorphous halo (figure 4.1). In contrast, the WAXS diagram of the copolymer **A** can be related to the norbornene homopolymer (figures 4.2 and 4.3). Moreover, the DSC curves show two endothermal peaks at 124 °C and 225 °C in the second heating scan.

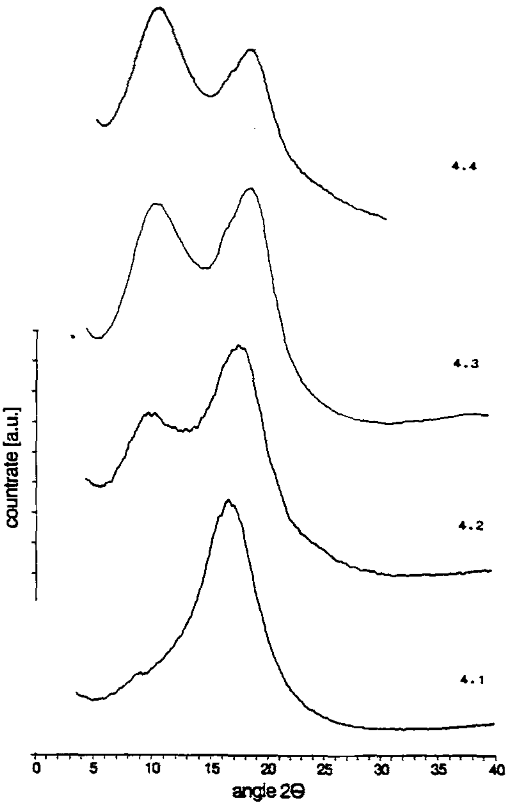

Figure 4: WAXS diagrams of
4.1: norbornene/ethene copolymer type **B**
4.2: norbornene/ethene copolymer type **A**
4.3: polynorbornene prepared with $[Me_2Si(Ind)_2]ZrCl_2$ **I**
4.4: polynorbornene prepared with $[Me_2C(Fluo)(Cp)]ZrCl_2$ **III**

In the case of copolymers of type **A** with lower norbornene incorporation rates the results from WAXS and DSC experiments can also be interpreted as a formation of blocks. In table 1 the influence of the norbornene content on the phase transition temperatures is given. In the case of low incorporation rates of norbornene (10 - 35 mol%) a glass transition temperature can be observed, which is attributed to the existence of amorphous regions beside semicrystalline PE-regions.

Copolymers of type **B** with a content greater than 14 mol% norbornene are fully amorphous. It is nearly possible to incorporate as much norbornene as wanted. A continuous increase of the norbornene content produces a corresponding increase of the glass transition temperature. At a monomer ratio of C_N/C_E = 25 these copolymers have a glass transition temperature of approx. 180 °C (see figure 2). Starting from such a material it is possible to use it as optical fibers at elevated temperatures.

Molecular weights and polydispersities Mw/Mn as determined by viscosimetry and GPC are listed in table 1. Depending on the catalysts, viscosimetry-average molecular weight Mμ decreases with increasing norbornene content of the copolymer.

As can be seen from figure 5 at high norbornene incorporation rates the C_s-symmetric catalyst produces copolymers with higher molecular weights. The average value of the difference to the C_2-symmetric catalyst is about 50.000 g/mol. Possible ß-H-elimination as the most important chain termination reaction (13) is geometrically less favoured in syndiotactic than in isotactic polymerization (8).

The two catalyst systems show a rather different behavior regarding the molecular weight distribution of the copolymers. The GPC-diagrams of type **A** copolymers provide bimodal and therefore broad molecular weight distribution. This behavior has to be attributed to the occurence of two fractions the copolymer consists of: A lower molecular weight fraction (6 - 8 %) and one of higher molecular weight; both show polydispersities < 2.

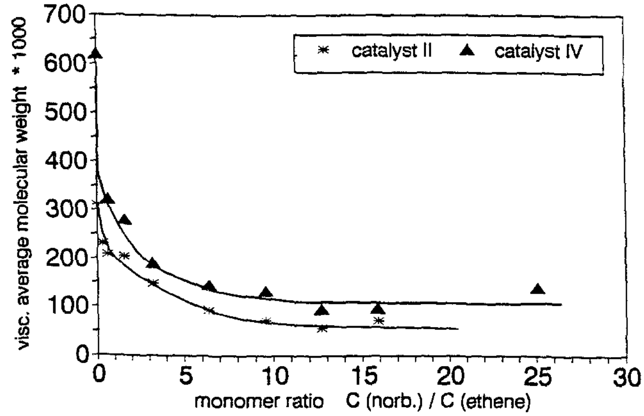

Figure 5: Viscosimetry-average molecular weight Mμ as function of the monomer ratio C_N/C_E (II = $[Ph_2Si(Ind)_2]ZrCl_2$, IV = $[Ph_2C(Fluo)(Cp)]ZrCl_2$)

These two fractions can be separated by extracting with different solvents. ^{13}C-NMR spectra of these fractions show a remarkable difference in the norbornene content.

In contrast the GPC-diagrams of the type **B** copolymers only show a monomodal distribution with Mw/Mn in the range of 2 - 5.

From thermogravimetric measurements under nitrogen atmosphere it can be concluded that the polymers are stable up to 400 °C ($T_{5\%}$ = 435 °C). Copolymers of type **B** with high norbornene incorporation possess birefringence index of 1,53 and an elastic module of 3,5 GPa.

Norbornene homopolymerization

Norbornene was homopolymerized under the same reaction conditions. Table 2 compares the activity in dependence of the different catalysts **I - IV**.

Table 2: Activity of homopolymerization of norbornene with different catalyst **I-IV** ($n = 2{,}75 * 10^{-6}$ mol), [Al]/[Zr] = 1100, for a period of 8 days with $n = 0{,}817$ mol norbornene in toluene at 23 °C

catalyst	yield [g]	activity [$kg_{polymer}$ / mol_{Zr} * $mol_{norb.}$]
I	0,39	172
II	0,23	102
III	1,03	458
IV	0,91	405

The catalysts show nearly the same behavior in polymerization activity for co- and homopolymerization. The C_s-symmetric catalysts feature four times higher activity than C_2-symmetric ones.
It is uncertain, if the stereospecific polymerization behavior can be transferable to the homopolymerization of cycloalkenes. Among the ^{13}C-CPMAS-NMR spectra of the polynorbornenes listed in table 2 no significant differences of chemical shifts could be detected, whereas the WAXS diagrams only differ in the relative intensity (see figures 4.3 and 4.4).

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