Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 7271–7278

polymer

www.elsevier.com/locate/polymer

# Copolymerization of propylene and norbornene with different metallocene catalysts

Walter Kaminsky*, Stefanie Derlin, Matthias Hoff

*Institute of Technical and Macromolecular Chemistry, University of Hamburg, Bundesstrasse 45, 20146 Hamburg, Germany*

Received 22 June 2007; received in revised form 5 October 2007; accepted 11 October 2007
Available online 22 October 2007

## Abstract

Propylene and norbornene were copolymerized by metallocene/MAO catalysts. The organometallic compounds *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**1**) and [$Me_2C(Cp)(Flu)$]$ZrCl_2$ (**2**), [$Ph_2C(Cp)(2,7\text{-di}^t\text{BuFlu})$]$ZrCl_2$ (**3**) and [$Me_2Si(3\text{-}^t\text{BuCp})(N^t\text{Bu})$]$TiCl_2$ (**4**) were used to catalyze polymerization series, in which the influence of the molar fraction of norbornene in the feed and of the polymerization temperature were investigated in detail. The obtained polymers, which exhibit a wide range of properties with glass transition temperatures above 200 °C, were characterized by $^{13}$C NMR spectroscopy, differential scanning calorimetry and gel permeation chromatography techniques.

In this article, the emphasis is placed on the copolymerization behaviour of the catalysts and the properties of the obtained polymers, while other articles concentrate on NMR investigations of propylene/norbornene copolymers.

*Keywords:* Propylene/norbornene copolymers; Metallocenes; High glass transition temperatures

## 1. Introduction

Cyclic olefin copolymers (COCs) are attractive materials, which exhibit high transparency and glass transition temperatures, good chemical and heat resistance and a good processability. With some metallocenes, such as [$Ph_2C(Cp)(Flu)$]$ZrCl_2$, glass transition temperatures of amorphous ethylene/norbornene polymers reached up to 220 °C [1].

Preparation and properties of the COCs with regard to improvements concerning the manufacturing found large interest [2–4], especially in the case of ethylene/norbornene copolymers, whose glass transition temperatures are variable over a wide range and are therefore accessible to most processing techniques, such as injection moulding, extrusion, coextrusion, extrusion blow and spray blow. Although already in the middle of the 20th century cycloolefin copolymers were synthesized [5], only in the beginning of the 1990s, with the use of metallocenes in combination with MAO [6,7], ethylene/norbornene copolymers became producible in an economical way with high quality. After the breakthrough of ethylene/norbornene copolymers, the next step became the investigation on propylene/norbornene copolymers, which were expected to have higher glass transition temperatures than the copolymers of ethylene because of the higher glass transition temperature of propylene in comparison to ethylene. With the system [$Me_2Si(Ind)_2$]$ZrCl_2$/MAO Arnold produced amorphous copolymers with a norbornene incorporation up to 98 mol% [8]. Several publications followed, putting the emphasis on NMR experimental details, i.e., signal assignment and determination of the comonomer incorporation [9–15]. Besides, the copolymerization of the norbornene derivative 5-vinyl-2-norbornene by metallocene catalysis has been studied [16].

Nevertheless, the copolymerization of propylene and norbornene in detail has been scarcely studied because of comparatively low activities. In this paper, we report detailed information about the copolymerization of propylene and norbornene with the sufficiently active systems *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**1**) and [$Me_2C(Cp)(Flu)$]$ZrCl_2$ (**2**),

---

* Corresponding author. Tel.: +49 40 42838 3162; fax: +49 40 42838 6008.
*E-mail address:* kaminsky@chemie.uni-hamburg.de (W. Kaminsky).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.10.013

$[Ph_2C(Cp)(2,7\text{-di}^tBuFlu)]ZrCl_2$ (**3**) and the half-sandwich complex $[Me_2Si(3\text{-}^tBuCp)(N^tBu)]TiCl_2$ (**4**) in combination with dried MAO.

## 2. Experimental part

### 2.1. General remarks

All manipulations were performed using standard Schlenk, drybox and syringe techniques.

Propylene was purchased by the firm Messer in a purity >99.8% and purified by passage through two columns, from which the first one was filled with BASF R3-11 catalyst and the second one with 3 Å molecular sieve. Toluene, used for the polymerizations as solvent and for the preparation of the metallocene solutions, was purified in the same manner, using molecular sieve 4 Å.

Norbornene (Fluka) was stirred for two days with triisobutylaluminium in toluene at 50 °C and afterwards distilled off. A solution of 6−7 mol $L^{-1}$ norbornene in toluene was used for polymerizations.

The metallocenes *rac*-$[Me_2C(Ind)_2]ZrCl_2$ (**1**) [17] and $[Me_2C(Cp)(Flu)]ZrCl_2$ (**2**) [18] $[Ph_2C(Cp)(2,7\text{-di}^tBuFlu)]ZrCl_2$ (**3**) [19] and $[Me_2Si(3\text{-}^tBuCp)(N^tBu)]TiCl_2$ (**4**) [20−22] were synthesized in our workgroup according to the literature procedures. MAO was purchased from Crompton as a 10% solution in toluene. It was filtrated over a D4 frit. The toluene and residual trimethylaluminium were removed at 40 °C in vacuo. After drying in oil pump vacuo, the MAO was used as a white solid for the polymerizations. The reason, why MAO was used as a solid, is that this assures exactly defined, reproducible reaction parameters. The experience has shown that commercially available solutions of MAO in toluene afford various shares of solid MAO despite a given specification. The influence of trimethylaluminium on the activation process is not clarified, but the addition of further alkylaluminum compounds than MAO has an influence on the catalytic activities and this should be quantitatively taken into account if MAO was used in a purchased solution.

### 2.2. General polymerization procedure

The polymerizations were performed in a 1 L Büchi glass autoclave, which allows monomer pressures up to 6 bar. The pressure during a polymerization run was kept constant by using a pressure control. The gas flow was recorded with a Brooks 5850 TR mass flow meter and an Ahlborn Almemo 2390-5 data logger. Temperature was adjusted with a heat jacket which allowed to keep the temperature constant by approximation during a polymerization run. For a typical polymerization procedure, the reactor was heated in vacuo for 1 h and afterwards tempered to the desired temperature. The reactor was charged with 200 mg of MAO and the desired volume of the norbornene/toluene solution and toluene up to a volume of 200 mL. After saturation with propylene up to the desired feed composition, the polymerization was started by injecting the metallocene solution. The reaction was quenched with 5 mL of ethanol after an adequate reaction time.

The polymer solution was stirred overnight in a solution of diluted hydrochloric acid in ethanol (1 volume part of concentrated hydrochloric acid, 2 volume parts of ethanol and 7 volume parts of distilled water).

After phase separation the organic phase was washed with sodium hydrogencarbonate solution and three times with water. In the case of toluene soluble polymers, the solvent was removed in vacuo by means of a rotary evaporator. Toluene insoluble polymers were filtered off and washed with ethanol. The polymers were dried in vacuo at 40 °C until the weight remained constant.

### 2.3. Polymer analysis

The samples for $^{13}C$ NMR spectroscopy were prepared by dissolving approximately 200 mg of polymer in 2.5 mL of hexachloro-1,3-butadiene and 0.5 mL 1,1,2,2-tetrachloroethane-$d_2$ in a 10 mm NMR tube. For $^1H$ NMR spectra, at least 20 mg of the polymer was dissolved in pure 1,1,2,2-tetrachloroethane-$d_2$ in a 5 mm NMR tube. The samples were measured at 100 °C with a Bruker 400 MHz spectrometer.

The $^1H$ NMR spectra were recorded at 400.15 MHz, while $^{13}C$ broadband decoupled and DEPT spectra were recorded at 100.62 MHz.

For the determination of the thermal behaviour of the products, a Mettler Toledo differential scanning calorimetry $821^e$ device was used, which had been calibrated with five standards: *n*-heptane (−90.6 °C), mercury (−38.8 °C), gallium (29.8 °C), indium (156.6 °C), and zinc (419.5 °C). The heating rate was 20 °C $min^{-1}$. Only the second heating cycle was used for the interpretation of the DSC curves. In the case of the products obtained with $[Me_2C(Cp)(Flu)]ZrCl_2$ (**2**), the polymers were also heated with a lower heating rate (10 °C $min^{-1}$).

The molar masses were determined via viscometry with an Ubbelohde viscosimeter (capillary 0a, $K = 0.005$). The running time was detected by a Viscoboy 2 from Lauda. For sample preparation, appropriate amounts of the polymers were dissolved in 50 mL decahydronaphthalene at 135 °C overnight. For thermal stabilization, 2,6-di-*tert*-butyl-4-methylphenol (1 g $L^{-1}$) was added. The evaluation of the molar masses was made with the constants of polypropylene, which are under the given conditions: $K = 0.0234\ mL\ g^{-1}$ and $a = 0.725$. It has to be pointed out, that this, especially in the case of the products obtained with metallocene **2**, where the incorporations rates are high, must lead to noteworthy variations, so that the obtained values should not be seen as absolute values but in regard to their ratios.

## 3. Results and discussion

The following results concerning the copolymerization of norbornene and propylene with the four metallocenes, whose structures are displayed in Fig. 1, shall show first coherences between experimental parameters and polymer properties.

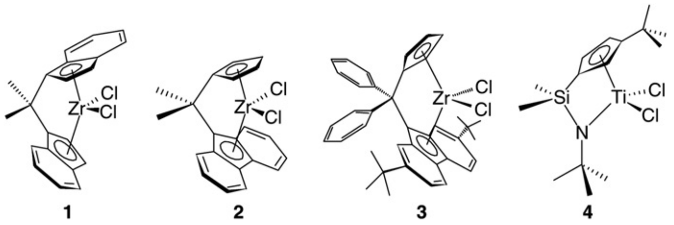

Fig. 1. Catalyst precursors used in this work for the copolymerization of propylene and norbornene.

Catalyst precursor **1** is a $C_2$-symmetric metallocene, while compound **2** and the optimized, highly substituted *ansa*-metallocene **3** with their cyclopentadienyl and their fluorenyl ligands are $C_s$-symmetric metallocenes, the systems therefore show a different stereospecific polymerization behaviour in the polymerization of propylene. Compound **4** is a constrained geometry catalyst. This group of catalysts usually exhibits no steric control and allows high incorporation rates even in the case of sterically hindered monomers. Hence, the chosen metallocenes were expected to show remarkable differences in the copolymerization process of propylene with the bulky monomer norbornene.

### *3.1. Copolymerization at different monomer ratios*

While propylene was continuously supplied via a pressure control, the amount of norbornene with which the reactor was charged in the beginning, was consumed during the course of the reaction.

Strictly observed, the comonomer consumption has to be kept low in order to keep the reaction conditions constant by approximation. Usually, it is not difficult to fulfil this condition. In the present case, however, it became quite difficult because of high incorporation levels already at low norbornene contents in the feed. The chosen reaction conditions in this article therefore are a compromise between yielding sufficient for full analytical investigations on the polymers and as low as possible norbornene conversion.

Nevertheless, conversion rates at lower molar fractions of norbornene in the feed were quite high. Hence, the polymerizations with variation of the monomer composition were repeated with shorter polymerization times, in order to determine the difference in the obtained copolymer in dependence on lower comonomer conversions.

The polymerization conditions and results for metallocenes **1** and **2** are given in Tables 1 and 2.

#### *3.1.1. Comonomer incorporation*

The amount of incorporated comonomer into the polymer chain is very decisive for the macroscopic properties of a polymer. The most powerful method for determination of the monomer incorporation is $^{13}C$ NMR spectroscopy. The spectra of propylene/norbornene copolymers exhibit a high complexity because of different monomer sequences in the polymer chain, comprising norbornene blocks of variable length and a variable stereochemical orientation of norbornene in microblocks and alternating structures. Already ethylene/norbornene spectra are quite complex, but the analysis of propylene/norbornene spectra becomes even more difficult compared to ethylene because of the methyl group of the propylene, which brings further stereochemical information into the polymer chain.

In the case of the copolymers synthesized with the $C_2$-symmetric catalyst precursor **1**, a signal assignment according to

Table 1
Results of the copolymerizations of propylene and norbornene at different comonomer ratios in the feed using metallocene **1** at a polymerization temperature of 30 °C

| $X_N$[a] | $t_{poly}$[b] [h] | Activity[c] | $x_N$[d] | $T_g$[e] [°C] | $M_\eta$[f] [g mol$^{-1}$] |
|---|---|---|---|---|---|
| 0.00 | 4.0 | 4100 | 0.00 | $T_m$: 137.0 | 9700 |
| 0.20 | 4.0 | 186 | 0.28 | 37.9 | 5000 |
| 0.40 | 4.0 | 61 | 0.44 | 123.5 | 5300 |
| 0.60 | 4.0 | 32 | 0.67 | 159.3 | 4200 |
| 0.80 | 4.0 | 31 | 0.80 | 206.6 | 3600 |
| 1.00 | 4.0 | 5 | 1.00 | [g] | [h] |
| 0.00 | 0.5 | 4550 | 0.00 | $T_m$: 133.2 | 10,800 |
| 0.20 | 0.5 | 380 | 0.40 | 82.5 | 6400 |
| 0.40 | 1.0 | 182 | 0.61 | 107.7 | 6500 |
| 0.60 | 1.0 | 55 | 0.76 | 135.7 | 4000 |
| 0.80 | 1.0 | 41 | 0.92 | 167.3 | 4500 |

[a] Molar fraction of norbornene in the feed.
[b] Polymerization time. Further polymerization conditions: polymerization temperature: 30 °C; 0.7 bar propylene pressure; total volume (norbornene and toluene): 200 mL; 200 mg of MAO; $n_{cat} = 1 \times 10^{-2}$ mmol.
[c] Activity in $kg_{pol}\,mol_{cat}^{-1}\,h^{-1}\,(mol\,L^{-1})_{mon}^{-1}$.
[d] Molar fraction of norbornene in the polymer determined by $^{13}C$ NMR spectroscopy.
[e] Glass transition temperatures determined by DSC.
[f] Viscosity molecular weight.
[g] Not detected.
[h] Not detected because of insolubility.

Table 2
Results of the copolymerizations of propylene and norbornene at different comonomer ratios in the feed using metallocene **2** at a polymerization temperature of 30 °C

| $X_N$[a] | $t_{poly}$[b] [h] | Activity[c] | $x_N$[d] | $T_g$[e] [°C] | $M_\eta$[f] [g mol$^{-1}$] |
|---|---|---|---|---|---|
| 0.00 | 4.0 | 706 | 0.00 | 122.2/133.3 | 61,500 |
| 0.20 | 4.0 | 97 | 0.36 | [g] | 990 |
| 0.40 | 4.0 | 94 | 0.57 | [g] | 730 |
| 0.60 | 4.0 | 68 | 0.71 | [g] | 820 |
| 0.80 | 4.0 | 48 | 0.81 | [g] | [h] |
| 1.00 | 4.0 | 5 | 1.00 | [g] | [h] |
| 0.00 | 0.5 | 2950 | 0.00 | 123.2/133.8 | 117,800 |
| 0.20 | 0.5 | 384 | 0.42 | [g] | 5190 |
| 0.40 | 0.75 | 300 | 0.56 | [g] | 630 |
| 0.60 | 1.0 | 196 | 0.73 | [g] | 140 |

[a] Molar fraction of norbornene in the feed.
[b] Polymerization time. Further polymerization conditions: polymerization temperature: 30 °C; 0.7 bar propylene pressure; total volume (norbornene and toluene): 200 mL; 200 mg of MAO; $n_{cat} = 1 \times 10^{-2}$ mmol.
[c] Activity in $kg_{pol}\,mol_{cat}^{-1}\,h^{-1}\,(mol\,L^{-1})_{mon}^{-1}$.
[d] Molar fraction of norbornene in the polymer determined by $^{13}C$ NMR spectroscopy.
[e] Glass transition temperatures determined by DSC.
[f] Viscosity molecular weight.
[g] Not detected.
[h] Not detected because of insolubility.

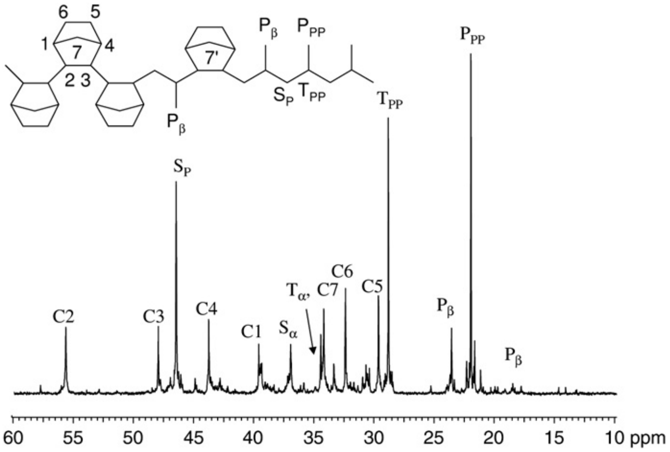

Fig. 2. Signal assignment of the carbon atoms in the $^{13}C$ NMR spectrum of a propylene/norbornene copolymer. The copolymer was obtained by using *rac*-$[Me_2C(Ind)_2]ZrCl_2$ (**1**)/MAO as catalyst system at $X_N = 0.20$ and $T_{poly} = 30\ °C$.

the literature mentioned before, especially according to the article of Tritto [13], is proposed for the obtained polymers in Fig. 2. DEPT experiments were made for confirmation.

The molar fraction of norbornene in the polymer was calculated from the peak area of the signals via Eq. (1) according to the literature [11].

$$\frac{F_P}{F_N} = \frac{I_{CH_3}}{(I_{tot} - 3I_{CH_3})/7} \tag{1}$$

where $F_P$ is the molar fraction of propylene and $F_N$ is the molar fraction of norbornene in the polymer, $I_{CH_3}$ is the peak area of the methyl carbon atoms and $I_{tot}$ is the sum of the areas of all peaks. This means that the area of the methyl carbon atom of the propylene share was correlated with the total peak area for the indirect determination of the norbornene incorporation.

The determination of the incorporation rates of the polymers obtained with $[Me_2C(Cp)(Flu)]ZrCl_2$ (**2**) is problematic, because of the low molecular masses. Chain end groups become visible in the spectra in the regions between 10–28 and 32–40 ppm, which are not taken into account for the determination of the incorporation rate. At present, it is impossible to determine the exact incorporation rate because of the enormous complexity of the spectra for the polymers obtained with this metallocene, which is shown in Fig. 3. Therefore, the incorporation rates given for the polymers, which were produced with this metallocene should just be seen as tendencies, but never as absolute values. Consequently, comonomer reactivity ratios are not given in this publication and no quantitative conclusion about the share of propene 1,3-misinsertions can be drawn. In Fig. 3 the increase in complexity of the $^{13}C$ NMR spectra with increasing incorporation rate of norbornene is also shown.

In other publications, a determination of the norbornene content in the polymers via the signals of the norbornene units was presented, which is impractible in the case of the obtained spectra because of the complexity of the spectra, which show a multitude of overlapping signals.

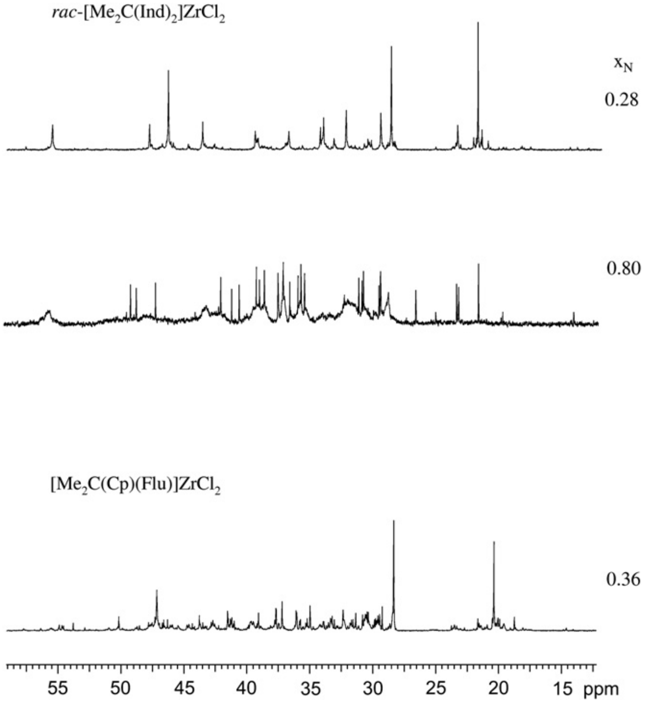

Fig. 3. The complexity of different $^{13}C$ NMR spectra of the obtained propylene/norbornene copolymers. The incorporation rate of norbornene is given. In the case of the metallocene $[Me_2C(Cp)(Flu)]ZrCl_2$ (**2**) the given incorporation rate of the obtained polymer is significantly error afflicted, for chain end groups remain unaccounted because of the complexity of the spectrum.

What remains safe to say is that the incorporation of norbornene in comparison to that one of propylene is clearly favoured in the case of both metallocenes.

Shorter polymerization times afforded copolymers with even higher norbornene incorporation rates, which is due to the high norbornene conversion rates in the case of a polymerization time of 4 h (up to a maximum value of 55% for $X_N = 0.20$ and $t_{poly} = 4$ h) and the associated decreasing availability of the comonomer in the feed.

The comonomer incorporation rates are remarkably high. With both catalysts at a molar fraction of norbornene in the feed of 0.80, an incorporation rate of approximately 80 mol% is achieved. Already at 20 mol% of norbornene in the feed, incorporation rates of 28 mol% with metallocene **1** and 36 mol% with metallocene **2** over a polymerization time of 4 h are obtained.

The question comes up, why the incorporation of the bulky monomer norbornene is favoured against that of propylene. To explain it with energetic reasons, the assumption might be made that the released energy due to the opening of the double bond to a single bond reduced hoop stress overweights the influence of the insertion barrier due to the bulkiness of the norbornene.

$^1H$ NMR spectra showed with resonances at 5.7 and 4.9 ppm a high share of vinyl end groups of the polymers obtained with $[Me_2C(Cp)(Flu)]ZrCl_2$ (**2**), which are the dominating end groups by far. β-Methyl elimination is the dominating termination reaction. With a from $X_N = 0.20$ to

$X_N = 0.80$ increasing molar fraction of norbornene in the feed one can registrate a further increase of those signal intensities. Also trisubstituted, internal olefin and vinylidene end groups were found.

### *3.1.2. Catalytic activities*

Because of the bulky form of the comonomer norbornene, the activities were expected to be comparatively low. An insertion of a monomer unit into a metal–tertiary carbon bond formed after norbornene insertion is sterically more hindered than it is after a regio-irregular (2,1)-insertion of propylene, whose strongly reducing influence on polymer activities is well known [23]. The influence of the comonomer on polymerization activities was even higher than expected because of astonishingly high norbornene incorporation rates. It is obvious that such a sterically hindered monomer such as norbornene, incorporated into the growing polymer chain, should aggravate the next insertion step. This is expressed in the fact that already at a molar fraction of 0.20 of norbornene in the feed, the activities decrease in a multiple in comparison to the homopolymerization of propylene, in the case of $[Me_2C(Cp)(Flu)]ZrCl_2$ (**2**) about factor 7 from approximately 700 to 100 $kg_{pol}\,mol_{cat}^{-1}\,h^{-1}\,(mol\,L^{-1})_{mon}^{-1}$ and in the case of *rac*-$[Me_2C(Ind)_2]ZrCl_2$ (**1**) even about factor 22 from 4100 to 186 $kg_{pol}\,mol_{cat}^{-1}\,h^{-1}\,(mol\,L^{-1})_{mon}^{-1}$. The homopolymerization of norbornene with an activity of 5 $kg_{pol}\,mol_{cat}^{-1}\,h^{-1}\,(mol\,L^{-1})_{mon}^{-1}$ yielded only small amounts of polynorbornene. Shorter polymerization times led to an increased activity because in case of a comparison of polymerizations with a polymerization time of 4 h and one with half an hour the deactivation of the catalyst over the reaction time becomes important.

### *3.1.3. Molecular weights*

The molecular weight for each of the obtained polymers was determined via viscometry. Therefore the obtained values express the viscosity molecular weight.

The molecular weights of the propylene/norbornene copolymers are low, especially in the case of the ones produced with metallocene **2**, where the molecular weight of the polypropylene is comparatively high with a value of 61,500, respectively, 120,000 $g\,mol^{-1}$, dependent on the polymerization time. The molecular weights of the copolymers obtained with this catalyst in the case of a polymerization time of 4 h are below a value of 1000 $g\,mol^{-1}$. The oligomeric structure can be seen as one explanation for the complexity of the NMR spectra. A shorter polymerization time led to the polymerization at $X_N = 0.20$ to an increased molecular weight of approximately 5200 $g\,mol^{-1}$. Molecular weights for the copolymers produced with metallocene **1** with values around 5000 $g\,mol^{-1}$ were slightly higher, whereas the molecular weight decreases with increasing norbornene incorporation rates. The polymer with an incorporation rate of 80 mol% norbornene has a viscosity molecular weight of 3600 $g\,mol^{-1}$. Shorter polymerization times led to polymers with higher molecular weights despite higher incorporation rates of norbornene into the polymer chain. This is astonishing, since in general the coherence of lower molecular weights with higher norbornene incorporation is observed, which is explicable with the increased insertion barrier after insertion of a norbornene unit.

### *3.1.4. Thermal behaviour*

For the copolymers obtained with metallocene **2**, the thermal behaviour was complex. Despite several attempts with variation of the measurement parameters with the DSC device, it was not possible to detect any exact glass transition temperature. There was an irregular development of the heating curves with small, stretched, and not analyzable steps. This and the consideration of the high conversion rates, which is connected with probably a little changing incorporation rates over the long polymerization time and therefore also in a certain rate changing molecular weights, may indicate that multimodal polymers are present.

In the case of metallocene **1**, however, the norbornene content of the polymer shows a large influence on the glass transition temperatures. With increasing incorporation rate of norbornene into the polymer chain, a remarkable, almost linear increase in glass transition temperatures is observed. It has to be pointed out that at shorter polymerization times glass transition temperatures were lower despite higher incorporation rates and higher molecular weights. The reason must lie in the microstructure of the polymers, which cannot be elucidated at present because of a limited solving of the NMR spectra.

Based on the polymerization series with a polymerization time of 4 h, in the case of the lowest achieved incorporation rate of 28 mol%, a glass transition temperature close to room temperature of 38 °C was determined while the polypropylene shows a melting temperature of 137 °C. Incorporation of 80 mol% leads to a remarkably high glass transition temperature of 207 °C, a good parallel between the present work and that one of Arnold [8], in which the system $[Me_2Si(Ind)_2]ZrCl_2$/MAO was investigated and a polymer was obtained with a comparable molecular weight, incorporation rate and glass transition temperature ($X_N = 81$ mol%, $T_g = 204$ °C).

## *3.2. Copolymerization at different polymerization temperatures*

The influence of the polymerization temperature on the catalytic activity of the two catalyst systems and the resulting copolymers was investigated. For this purpose, polymerizations were performed at a fixed molar fraction of norbornene in the feed of 0.80 at 15, 30, 45 and 60 °C (Tables 3 and 4). The reaction conditions ensured a low conversion of norbornene (<15%).

### *3.2.1. Catalytic activities*

Comparison of the activities for both metallocenes in dependence on the polymerization temperature shows a behaviour which is vice versa. While the activities for metallocene **1** increase from 9 $kg_{pol}\,mol_{cat}^{-1}\,h^{-1}\,(mol\,L^{-1})_{mon}^{-1}$ at a polymerization temperature of 15 °C about factor 7.5 to 67 $kg_{pol}\,mol_{cat}^{-1}\,h^{-1}\,(mol\,L^{-1})_{mon}^{-1}$ at 60 °C, the activities for

Table 3
Results of the copolymerizations of propylene and norbornene at different polymerization temperatures using metallocene **1** at $X_N = 0.80$

| $T_{poly}$[a] [°C] | Activity[b] | $x_N$[c] | $T_g$[d] [°C] | $M_\eta$[e] [g mol$^{-1}$] |
|---|---|---|---|---|
| 15 | 9 | 0.85 | 191.9 | 2600 |
| 30 | 20 | 0.81 | 200.4 | 3000 |
| 45 | 37 | 0.76 | 204.1 | 3300 |
| 60 | 67 | 0.69 | 205.8 | 3600 |

[a] Polymerization temperature. Further polymerization conditions: 0.3 bar propylene pressure; total volume (norbornene and toluene): 200 mL; 200 mg of MAO; $n_{cat} = 1 \times 10^{-2}$ mmol; polymerization time: 4 h.

[b] Activity in $kg_{pol}\, mol_{cat}^{-1}\, h^{-1}\, (mol\, L^{-1})_{mon}^{-1}$.

[c] Molar fraction of norbornene in the polymer determined by $^{13}$C NMR spectroscopy.

[d] Glass transition temperature determined by DSC.

[e] Viscosity molecular weight.

the $C_s$-symmetric metallocene **2** decrease by half within the investigated polymerization temperature range from 48 to 25 $kg_{pol}\, mol_{cat}^{-1}\, h^{-1}\, (mol\, L^{-1})_{mon}^{-1}$. An increase in activity is explainable via the law of Arrhenius according to which the activity exponentially depends on the polymerization temperature. Besides, it might be tentatively estimated that possibly isomerization processes of the *rac*-bis-indenyl system lead to an active species with one less sterically hindered site, so that the incorporation of the bulky norbornene is facilitated. The loss in activity with increasing polymerization temperature in the case of metallocene **2** seems not to be explainable only with a decomposition of the catalyst, because previous polymerization experiments have shown the highest catalytic activities not at 15 °C, but at higher polymerization temperatures [24–26].

### *3.2.2. Comonomer incorporation*

Concerning the norbornene incorporation in dependence on the polymerization temperature, no effect in the case of metallocene **2** is given. In the range of measuring accuracy, the incorporation rate of norbornene at different polymerization temperatures with a value of 84 mol% is constant. For the $C_2$-symmetric metallocene **1**, however, incorporation rates significantly decrease from 85 mol% at $T_{poly} = 15$ °C to 69 mol% at 60 °C. Without awareness of the available literature and the other results of the present article, this could be a surprising development, because one might expect that the incorporation of the bulky norbornene is disadvantaged in comparison to propylene and that a higher polymerization temperature would help this bulky cyclic olefin to overcome the insertion barrier, but in fact norbornene has shown to be the more reactive monomer. Hence, the present result is not due to a less preferred incorporation of norbornene, but to an eased incorporation of propylene.

Table 4
Results of the copolymerizations of propylene and norbornene at different polymerization temperatures using metallocene **2** at $X_N = 0.80$

| $T_{poly}$[a] [°C] | Activity[b] | $x_N$[c] | $T_g$[d] [°C] | $M_\eta$[e] [g mol$^{-1}$] |
|---|---|---|---|---|
| 15 | 48 | 0.85 | [f] | 550 |
| 30 | 47 | 0.83 | [f] | 450 |
| 45 | 41 | 0.84 | [f] | 870 |
| 60 | 25 | 0.84 | [f] | 2120 |

[a] Polymerization temperature. Further polymerization conditions: polymerization temperature: 0.3 bar propylene pressure; total volume (norbornene and toluene): 200 mL; 200 mg of MAO; $n_{cat} = 1 \times 10^{-2}$ mmol; polymerization time: 4 h.

[b] Activity in $kg_{pol}\, mol_{cat}^{-1}\, h^{-1}\, (mol\, L^{-1})_{mon}^{-1}$.

[c] Molar fraction of norbornene in the polymer determined by $^{13}$C NMR spectroscopy.

[d] The thermal behaviour was complex. No exact glass transition temperatures were detectable because of only very small, long drawn-out steps in the DSC thermograms.

[e] Viscosity molecular weight.

[f] Not detected.

### *3.2.3. Molecular weights*

The molecular weights of the copolymers obtained with *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**1**) are in accordance with the incorporation rates: the molecular weights decrease with decreasing polymerization temperature, thus with increasing norbornene content of the polymers. The polymer which was obtained at 15 °C has a viscosity molecular weight of 2600 g mol$^{-1}$, while that one produced at 60 °C exhibits a molecular weight of 3600 g mol$^{-1}$. The next insertion after incorporation of a norbornene unit is energetically seen less favoured in comparison to that one after a propylene unit, which does, under consideration of the other present results, not mean that the reactivity of norbornene compared to that one of propylene is lower.

The highest molecular weight of the synthesized polymers in the case of [$Me_2C(Cp)(Flu)$]$ZrCl_2$ (**2**) was achieved at 60 °C with a value of about 2100 g mol$^{-1}$, while the ones of copolymers produced at lower polymerization temperatures were remarkably lower with values under 1000 g mol$^{-1}$, which is surprising.

### *3.2.4. Thermal behaviour*

As mentioned before, the thermal behaviour of the copolymers obtained with metallocene **2** cannot be expressed in values, while for the ones obtained with compound **1** the glass transition temperatures increase with higher polymerization temperature, which is opposed to the series investigating the influence of the feed composition, where the results have shown that an increased incorporation of norbornene leads to higher glass transition temperatures. The increasing glass transition temperatures of the at increasing polymerization temperatures obtained polymers are probably due to the higher molecular weights, which would be the predominant factor in that case.

## *3.3. Further polymerization results*

Further investigations were made on propylene/norbornene copolymerizations with the metallocene [$Ph_2C(Cp)$-(2,7-di$^t$BuFlu)]$ZrCl_2$ (**3**) and the half-sandwich complex [$Me_2Si(3\text{-}^tBuCp)(N^tBu)$]$TiCl_2$ (**4**) with MAO as co-catalyst. The results are presented in Table 5. In contrast to the copolymers produced with the $C_s$-symmetric metallocene **2**, the copolymers obtained with the metallocene **3** show clear

Table 5
Results of the copolymerizations of propylene and norbornene at different comonomer ratios using metallocenes **3** and **4** at a polymerization temperature of 30 °C

| Catalyst | $X_N$[a] | $n_{cat}$[b] [$10^{-3}$ mmol] | $t_{poly}$[c] [min] | Activity[d] | $x_N$[e] | $T_g$[f] [°C] |
|---|---|---|---|---|---|---|
| 3 | 0.00 | 2 | 17 | 3213 | 0 | 3.0[g] |
| 3 | 0.10 | 2 | 18 | 1337 | 0.16 | 22.6 |
| 3 | 0.20 | 2 | 24 | 992 | 0.29 | 40.0 |
| 3 | 0.30 | 2 | 31 | 714 | 0.37 | 48.7 |
| 3 | 0.50 | 2 | 54 | 398 | 0.50 | 52.1 |
| 3 | 0.70 | 2 | 75 | 235 | 0.61 | 59.2 |
| 3 | 0.80 | 2 | 98 | 143 | 0.68 | 79.9 |
| 3 | 0.90 | 2 | 107 | 68 | 0.72 | 82.4 |
| 3 | 0.95 | 2 | 247 | 17 | 0.84 | 101.4 |
| 4 | 0.00 | 1 | 43 | 399 | 0 | −12.1 |
| 4 | 0.10 | 2 | 135 | 51 | 0.20 | 36.7 |
| 4 | 0.20 | 2 | 200 | 35 | 0.29 | 56.1 |
| 4 | 0.40 | 2 | 240 | 22 | 0.35 | 72.2 |
| 4 | 0.60 | 2 | 243 | 17 | 0.39 | 83.8 |
| 4 | 0.80 | 2 | 263 | 6 | 0.54 | 94.4 |
| 4 | 0.90 | 3 | 247 | 4 | 0.64 | 107.5 |
| 4 | 0.95 | 4 | 241 | 2 | 0.77 | 104.9 |

[a] Molar fraction of norbornene in the feed.
[b] Amount of catalyst.
[c] Polymerization time. Further polymerization conditions: polymerization temperature: 30 °C; total concentration: 3 mol $L^{-1}$; total volume (norbornene and toluene): 200 mL; 200 mg of MAO.
[d] Activity in $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}\ (mol\ L^{-1})_{mon}^{-1}$.
[e] Molar fraction of norbornene in the polymer determined by $^{13}C$ NMR spectroscopy.
[f] Glass transition temperature determined by DSC.
[g] Melting temperature: 140.3 °C.

glass transition temperatures, which linearly increase from 23 °C for a polymer with 16 mol% incorporated norbornene to 101 °C for a copolymer with 84 mol% norbornene content. In the case of the polymers obtained with catalyst precursor **4**, the development of the glass transition temperatures in dependence on the norbornene content differs from that one which was detected for the copolymers obtained with the compounds **1–3**. To an incorporation rate of approximately 60 mol%, glass transition temperatures increase up to about 105 °C, but then a plateau of the glass transition temperatures of the copolymers is reached. In comparison to the metallocenes **1** and **2**, the incorporation behaviour of the compounds **3** and **4** results as a clear shaped S-curve for the norbornene content of the polymer in dependence on the norbornene content in the feed, while with the catalysts **1** and **2**, the reactivity of norbornene in comparison to the one of propylene is significantly higher, and only a weak S-curve is given, for only at $X_N = 0.80$ the norbornene content in the polymer is approximately equivalent to the molar fraction of norbornene in the feed. In the middle range of the molar fraction of norbornene in the feed, incorporation rates are comparatively low for the catalysts **3** and **4**. For example, at $X_N = 0.60$ and under use of [$Me_2Si(3\text{-}^tBuCp)(N^tBu)]TiCl_2$ (**4**), an incorporation of 39 mol% norbornene into the polymer chain was determined, compared to a value of approximately 70 mol% of incorporated norbornene for the metallocenes **1** and **2**. This might be due to a steric hindrance resulting from the *tert*-butyl group of the cyclopentadienyl ligand, which should particularly hinder the bulky norbornene in its approach to the active site. Concerning the activities, in the case of metallocene **3**, the decrease in activity is not that abrupt as it is in the case of catalysts **1** and **2** even at low norbornene shares in the feed. The activity decreases to about one third for the polymerization at a molar fraction of norbornene in the feed of 0.20 with a value of approximately 1000 $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}\ (mol\ L^{-1})_{mon}^{-1}$ from about 3200 $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}\ (mol\ L^{-1})_{mon}^{-1}$ for the pure propylene polymerization. With catalyst **4**, however, activities are far lower. Already at a norbornene content in the feed of 10 mol%, the activity with a value of about 50 $kg_{pol}\ mol_{cat}^{-1}\ h^{-1}\ (mol\ L^{-1})_{mon}^{-1}$ is very low.

## 4. Conclusions

The present study shows that with the $C_2$-symmetric metallocene *rac*-[$Me_2C(Ind)_2$]$ZrCl_2$ (**1**) and MAO, as with the systems [$Me_2C(Cp)(Flu)$]$ZrCl_2$/MAO (**2**) and [$Ph_2C(Cp)(2,7\text{-}di^tBuFlu)$]$ZrCl_2$ (**3**) copolymers with a wide range of glass transition temperatures respectively oligomers are producible with satisfying activities, while the activities for the constrained-geometry catalyst **4** are much lower. Because of the high reactivity of the cyclic monomer despite its bulky form, copolymers with high incorporation rates of norbornene are easily accessible in contrast to ethylene/norbornene copolymers. Nevertheless it is not astonishing that the number of publications until present is limited, because the analytical characterization raises several questions for which answers and solutions are unsatisfyingly hard to find.

## References

[1] Kaminsky W, Noll A. Polym Bull 1993;31:175–82.
[2] Alt FP, Heitz W. Acta Polym 1998;49:477–81.
[3] Ruchatz D, Fink G. Macromolecules 1998;31:4681–3.
[4] Kaminsky W. Catal Today 1994;20:257–72.
[5] Natta G, Dall'Asta G, Mazzanti G, Pasquon I, Valvassori A, Zambelli A. (Montecatini) BE-Patent 619877; 1962; Chem Abstr 1963;58:53817.
[6] Kaminsky W, Bark A, Arndt M. Makromol Chem Macromol Symp 1991; 47:83–93.
[7] Kaminsky W, Arndt M, Bark A. Polym Prepr 1991;32:467–8.
[8] Henschke O, Köller F, Arnold M. Macromol Rapid Commun 1997;18: 617–23.
[9] Boggioni L, Tritto I, Ragazzi M, Carbone P, Ferro DR. Macromol Symp 2004;218:39–50.
[10] Boggioni L, Bertini F, Zannoni G, Tritto I, Carbone P, Ragazzi M, et al. Macromolecules 2003;36:882–90.
[11] Hasan T, Ikeda T, Shiono T. Macromolecules 2005;38:1071–4.
[12] Carbone P, Ragazzi M, Tritto I, Boggioni L, Ferro DR. Macromolecules 2003;36:891–9.
[13] Tritto I, Boggioni L, Ferro DR. Coord Chem Rev 2006;250:212–41.
[14] Cai Z, Nakayama Y, Shiono T. Macromolecules 2006;39:2031–3.
[15] Naga N, Imanishi Y. J Polym Sci Part A Polym Chem 2003;41:441–8.
[16] Sarazin Y, Fink G, Hauschild K, Bochmann M. Macromol Rapid Commun 2005;26:1208–13.
[17] Spaleck W, Antberg M, Dolle V, Klein R, Rohrmann J, Winter A. New J Chem 1990;14:499–503.

[18] Ewen JA, Jones RL, Razavi A. J Am Chem Soc 1988;110:6255–6.

[19] Hopf A, Kaminsky W. Catal Commun 2002;3:459–64.

[20] Okuda J. Chem Ber 1990;123:1649–51.

[21] McKnight AL, Waymouth R. Macromolecules 1999;32:2816–25.

[22] Kaminsky W, Tran PD, Werner R. Macromol Symp 2004;213: 101–8.

[23] Carvill A, Tritto I, Locatelli P, Sacchi MC. Macromolecules 1997;30: 7056–62.

[24] Derlin S, Kaminsky W. Macromolecules 2007;40:4130–7.

[25] Weingarten U. Dissertation, University of Hamburg; 1999.

[26] Arndt M, Kaminsky W, Schauwienold AM, Weingarten U. Macromol Chem Phys 1998;199:1135–52.