

# Propene polymerization with *rac*-Me<sub>2</sub>Si(2-Me-Benz[*e*]Ind)<sub>2</sub>ZrX<sub>2</sub> [X = Cl, Me] using different cation-generating reagents

Stefan Beck<sup>1</sup>, H. H. Brintzinger<sup>1</sup>, Jürgen Suhm<sup>2</sup>, Rolf Mülhaupt\*<sup>2</sup>

<sup>1</sup> Fakultät für Chemie der Universität Konstanz, D-78434 Konstanz, Germany

<sup>2</sup> Freiburger Materialforschungszentrum und Institut für Makromolekulare Chemie der Albert-Ludwigs-Universität Freiburg, Stefan-Meier-Str. 21, D-79104 Freiburg i. Br., Germany

**SUMMARY:** Propene was polymerized with methylaluminoxane (MAO) and cationic activated *rac*-dimethylsilylene-2-methylbenz[*e*]indenylzirconocene [MBI-Cl<sub>2</sub>] and [MBI-Me<sub>2</sub>]. For cationic activation of the MBI-Me<sub>2</sub> system tris(pentafluorophenyl)borane [I], *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate [II] or trityl tetra(pentafluorophenyl)borate [III] were used. The MAO-activated dimethyl complex showed higher activity with respect to the dichloride system using high catalyst concentrations and [Al]/[Zr] ratios. Most effective cationic activator for MBI-Me<sub>2</sub> was *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate [II] in combination with Al(*i*-Bu<sub>3</sub>). Using tris(pentafluorophenyl)borane [I] at different polymerization conditions or *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate [II] in combination with Al(Et)<sub>3</sub> no propene polymerization was observed due to the occurrence of reduction of the catalytically active site.

## Introduction

In 1994 the benzannelated zirconocene *rac*-Me<sub>2</sub>Si(2-Me-Benz[*e*]Ind)<sub>2</sub>ZrCl<sub>2</sub> (MBI) was discovered leading to highly active homogeneous Ziegler-Natta catalysts capable of producing isotactic polypropene with high molar masses and melting temperatures<sup>1,2</sup>. Uniform catalytically active sites produced polypropene polymers with narrow molar mass distribution and controlled stereo- and regio-regularities. Changes of propene concentration, temperature, [Al]/[Zr] ratios, addition of comonomer and hydrogen as well as heterogenization of the MBI catalyst on support materials with respect to the propene polymerization kinetic and polypropene polymers were recently investigated<sup>3,4</sup>. Cationic metallocene polymerization catalysts using effective counter anion starting mostly from the dimethylmetallocenes were initially introduced by Jordan<sup>5</sup>. The interaction of the metallocene cation and counteranion was suggested to influence polymerization properties such as activity and stereospecificity of the metallocene<sup>6</sup>. Kaminsky found the Cp<sub>2</sub>ZrMe<sub>2</sub>/MAO system at low catalyst concentration less active in ethylene polymerization with respect to the dichloride system<sup>7</sup> and Fischer confirmed the higher activity in propene polymerization<sup>8</sup>. Therefore the effect of cationic activation reagent and metallocene precursor (dimethyl or dichloride) is still not well understood, because experimental difficulties strongly influence reproducibility of polymerization results due to the low stability of the cationic activated metallocene catalysts<sup>9</sup>.

Objective of this work was to study the influences of different cationic activators such as methylaluminoxane (MAO), tris(pentafluorophenyl)borane [I], *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate [II] or trityl te-

tra(pentafluorophenyl)borate [III] on polymerization activity and polymer properties, using alkylated dimethyl MBI-Me<sub>2</sub> as a catalyst source. The role of alkylaluminum, used as a scavenger, in cationic propene polymerization was elucidated. The results of the propene polymerizations with MBI-Me<sub>2</sub> were compared to MAO activated MBI-Cl<sub>2</sub>.

## Experimental part

The zirconocene complexes were synthesized as described elsewhere<sup>1,10</sup>. Tris(pentafluorophenyl)borane [I] was synthesized according to ref.<sup>11</sup> *N,N*-Dimethylanilinium tetra(pentafluorophenyl)borate [II] and trityl tetra(pentafluorophenyl)borate [III] were obtained from BASF AG. Al(*i*-Bu)<sub>3</sub> (25 wt.-% toluene solution) and AlEt<sub>3</sub> (2 mol/L toluene solution) were obtained from Aldrich. Propene (polymerization grade) was obtained from BASF AG. MAO (10 wt.-% in toluene,  $\bar{M}_n = 1000$  g/mol) from Witco Germany, toluene from Roth GmbH. Toluene solvent was rectified over LiAlH<sub>4</sub>, refluxed and distilled over Na/K alloy prior to use. All catalyst components, including toluene solvent and monomers, were handled and stored under dry argon atmosphere.

### Polymerization

Polymerization reactions were performed in a glass reactor rinsed with 150 mL of a 0.03 mol/L Al(*i*Bu)<sub>3</sub> solution in toluene prior to use. After evacuation of the glass reactor toluene was pumped in. If a scavenger was applied, it was syringed in before the system was saturated with propene. After complete saturation and thermal equilibration of the system the polymerizations were started by adding the prepared catalyst solutions to the reactor. In the case of the MAO activated polymerizations the catalysts were preacti-

Tab. 1. Propene polymerization of *rac*-Me<sub>2</sub>Si(2-Me-Benz[e]Ind)<sub>2</sub>ZrX<sub>2</sub> at 40 °C and 2bar propene pressure using MAO as activator

Metalocene Run No.	MBI-Cl <sub>2</sub> 1	MBI-Me <sub>2</sub> 2	MBI-Cl <sub>2</sub> 3	MBI-Me <sub>2</sub> 4
[MBI-X <sub>2</sub> ] <sup>a)</sup>	5	5	20	20
[Al]/[Zr]	1000/1	1000/1	5000/1	5000/1
<i>p</i> /bar	2	2	2	2
<i>c</i> <sub>Propene</sub> /(mol/l) <sup>b)</sup>	1.5	1.5	1.5	1.5
activity in g/(mol[Zr] · mol/L[ <i>c</i> <sub>Pr</sub> ] · h)	19500	12700	116000	393800
$\bar{M}_n$ /(kg/mol) <sup>c)</sup>	218	218	127	112
$\bar{M}_w/\bar{M}_n$ <sup>c)</sup>	1.8	1.8	1.7	1.9
<i>T</i> <sub>m</sub> /°C <sup>d)</sup>	152.0	151.4	151.6	151.1
<i>mmmm</i> in % <sup>e)</sup>	97.3	98.1	96.4	97.1

a) Concentration of *rac*-Me<sub>2</sub>Si(2-Me-Benz[e]Ind)<sub>2</sub>ZrX<sub>2</sub> in μmol/L.

b) Calculated to experimental data by BASF AG.

c) Determined by GPC using polypropene standards.

d) Determined by DSC, heating rate 20 K/min.

e) Determined via <sup>13</sup>C NMR spectroscopy.

vated for 15 min and in the case of the cationic activated polymerizations the catalyst solutions were pumped in the reactor within 5 min. The total volume of the reaction mixtures were 100 mL at all polymerizations. Propene was continuously added by a mass-flow meter (F-111C, Bronkhorst, NI-7261 AK Ruurlo, Netherlands)<sup>12)</sup>. The pressure of propene was kept constant during the polymerization and propene consumption was monitored. Typically, after 60 min the polymerization was quenched by adding 10 mL 2-propanol. The polypropene produced was precipitated in 300 mL methanol acidified with 10 ml 10 wt.-% aq. HCl, filtered, washed and dried at 60 °C under vacuum.

### Characterization

<sup>1</sup>H NMR polypropene spectra were recorded from solutions of 40 to 100 mg of polymer in 0.5 ml C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 400 K by a Bruker ARX 300 at 300 MHz; <sup>13</sup>C NMR polypropene spectra at 75.4 MHz, with a 30° pulse angle, 2s delay and at least 5000 scans. The signals were referenced to the signal of the solvent ( $\delta = 74.06$  ppm). Size exclusion chromatographic (GPC, SEC) analyses and viscosity measurements of molar mass and molar mass distribution were performed at BASF AG. Melting temperatures were determined by means of differential scanning calorimetry (DSC) with a Perkin Elmer Series 7 from the heating curve at a heating rate of 20 K/min after twice previous heating to 180 °C with 20 K/min and cooling to 50 °C with 20 K/min.

## Results and discussion

### Propene polymerization using MAO-activated MBI-Cl<sub>2</sub> and MBI-Me<sub>2</sub>

Propene polymerization was performed in a reactor at 2bar propene pressure in toluene using MAO and cationic activated MBI-X<sub>2</sub>. Tab. 1 shows the experimental results comparing MAO-activated MBI-Cl<sub>2</sub> and MBI-Me<sub>2</sub> using different Al/Zr ratios and catalyst concentrations.

The MBI-Me<sub>2</sub> showed substantially lower activity 127000 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h) at low catalyst concentration compared to 19500 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h) and low Al/Zr ratio with respect to the MBI-Cl<sub>2</sub> system. In contrast, when using higher catalyst concentration (cf. run 3 and 4, Tab. 1) and high Al/Zr ratio MBI-Me<sub>2</sub> gave higher activity (393800 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h)) with respect to MBI-Cl<sub>2</sub> (116000 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h)). Molar masses increased using low amounts of MBI-X<sub>2</sub> catalyst and did not be influenced whether the MBI system precursor was the dimethyl or the dichloride species.

Poly(propene)s obtained with the MBI-Me<sub>2</sub> and MBI-Cl<sub>2</sub> catalyst showed no significant difference concerning melting points *T*<sub>m</sub> and isotacticity, as displayed in Tab. 1. For the investigation of effects on propene polymerization and propene polymers obtained with cationic activated MBI-Me<sub>2</sub> it must be considered the oxygen and moisture sensitivity of the system. Therefore we increased MBI-Me<sub>2</sub> catalyst concentration significantly up to 100 or 200 μmol/L to reduce catalysts deactivation due to impurity effects (cf. Tab. 2). In fact, MBI-Me<sub>2</sub> is the more active catalyst precursor. Due to the high sensitivity of the MBI-Me<sub>2</sub> catalyst, at low concentrations the MBI-Me<sub>2</sub> catalysts seems to be less active. In contrast to results in literature at low catalyst concentration<sup>7,8)</sup> when using high catalyst concentrations the zirconocene dimethyl is more effective compared to the dichloride.

### Propene polymerization using tris(pentafluorophenyl)borane [I] and *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate [II] activated MBI-Me<sub>2</sub>

The MBI-Me<sub>2</sub> system was inactive for propene polymerization when using tris(pentafluorophenyl)borane [I] as an activator under conditions of [B]/[Zr] = 1.2 to 1, *p* = 2, 3, 4 bar despite using high catalyst concentration [Zr] = 200 μmol/L. Adversely, using the same polymerization condi-

Tab. 2. Propene polymerization of *rac*-Me<sub>2</sub>Si(2-Me-Benz[*e*]Ind)<sub>2</sub>ZrMe<sub>2</sub> at 40 °C and 3bar propene pressure using *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate [II] and trityltetra(pentafluorophenyl)borate [III] as activators and Al(*i*-Bu)<sub>3</sub> or Al(Et)<sub>3</sub> as scavenger

Metalocene Run No.	MBI-Me <sub>2</sub> 5	MBI-Me <sub>2</sub> 6	MBI-Me <sub>2</sub> 7	MBI-Me <sub>2</sub> 8	MBI-Me <sub>2</sub> 9	MBI-Me <sub>2</sub> 10
[MBI-Me <sub>2</sub> ] <sup>a)</sup>	100	100	200	200	100	200
activator	(II)	(II)	(II)	(III)	(II)	(II)
trialkylaluminium	Al( <i>i</i> -Bu) <sub>3</sub>	Al(Et) <sub>3</sub>	Al(Et) <sub>3</sub>			
[Al]/[Zr]	100/1	100/1	100/1	100/1	100/1	100/1
[B]/[Zr]	1.3/1	2.9/1	1/2	1/2	2.7/1	1.9/1
<i>p</i> /bar	3	3	3	3	3	3
<i>c</i> <sub>propene</sub> /(mol/l) <sup>b)</sup>	2.3	2.3	2.3	2.3	2.3	2.3
activity in g/(mol[Zr] · mol/L[ <i>c</i> <sub>Pr</sub> ] · h)	8300	19200	34000	32300	0	0
$\bar{M}_n$ /(kg/mol) <sup>c)</sup>	239	218	175	154	–	–
$\bar{M}_w/\bar{M}_n$ <sup>c)</sup>	1.9	1.8	1.8	1.8	–	–
<i>T</i> <sub>m</sub> /°C <sup>d)</sup>	152.6	153.2	152.0	153.1	–	–
<i>mmmm</i> in % <sup>e)</sup>	96.4	96.1	96.9	96.2	–	–

a) Concentration of *rac*-Me<sub>2</sub>Si(2-Me-Benz[*e*]Ind)<sub>2</sub>ZrX<sub>2</sub> in μmol/L.

b) Calculated to experimental data by BASF AG.

c) Determined by GPC using polypropene standards.

d) Determined by DSC, heating rate 20 K/min.

e) Determined via <sup>13</sup>C NMR spectroscopy.

tions the *N,N*-dimethylanilinium tetra(pentafluorophenyl)borate [II] activated **MBI-Me<sub>2</sub>** gave low polymerization activities (16800 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h)) at [Zr] = 200 μmol/L, [B]/[Zr] = 1.2 to 1 and *p* = 4 bar comparable to those obtained with MAO activated **MBI-Cl<sub>2</sub>** at the expense of high amounts of **MBI-Me<sub>2</sub>** catalyst. The polypropene showed similar properties as those obtained with MAO-activated **MBI-Me<sub>2</sub>**. For further investigation of the efficiency of cationic activators on **MBI-Me<sub>2</sub>**, a scavenger was used to avoid significant impurities on the cationic system.

*Propene polymerization using N,N-dimethylanilinium tetra(pentafluorophenyl)borate [II] and trityl tetra(pentafluorophenyl)borate [III] activated MBI-Me<sub>2</sub> and Al(i-Bu)<sub>3</sub> or Al(Et)<sub>3</sub>*

Propene polymerizations using **MBI-Me<sub>2</sub>** and the cationic activators (II) and (III) were investigated using different alkylaluminium scavengers to evaluate the role of Zr/B ratio on polymerization activity and polypropene properties. Experimental results and reaction conditions are displayed in Tab. 2.

The polymerizations using Al(*i*Bu)<sub>3</sub> as a scavenger at constant cationic zirconocene concentration (run 5 to 8) gave polypropenes with comparable degree of isotacticity and melting points. Polymerization with excess of **MBI-Me<sub>2</sub>** (cf. run 7 and 8) showed highest activity of about 34000 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h), polymerization with excess of borate gave reduced activity 19200 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h) (cf. run 10) and polymerization using only

a slight excess of borate (cf. run 9) gave poorest activities of 8300 g/(mol[Zr] · mol/L[*c*<sub>Pr</sub>] · h), respectively.

The use of AlEt<sub>3</sub> as a scavenger for the polymerizations (cf. run 9 and 10) did not succeed, no polypropene was obtained. Despite the fact that aluminiumtrialkyls are reported to be useful scavengers<sup>9)</sup>, AlEt<sub>3</sub> seems to reduce the activity of the **MBI-Me<sub>2</sub>** catalyst drastically, when comparing propene polymerization with no scavenger with the polymerizations using AlEt<sub>3</sub> (cf. run 9 and 10, Tab. 2). The enhanced reduction of the transition metal center with AlEt<sub>3</sub> compared to Al(*i*-Bu)<sub>3</sub> possibly accounts for the observed deactivation behaviour<sup>13,14)</sup>. As shown for the side reaction of zirconocene dichloride with AlR<sub>3</sub> by Sinn and Kaminsky et al.<sup>15)</sup>, this could be confirmed with <sup>1</sup>H NMR investigations using Cp<sub>2</sub>ZrMe<sub>2</sub> and AlR<sub>3</sub>.

When treating Cp<sub>2</sub>ZrMe<sub>2</sub> with AlEt<sub>3</sub> (Zr:Al = 1:2) no Cp<sub>2</sub>ZrMe<sub>2</sub> could be detected in the NMR spectra. Adversely, when using Al(*i*-Bu)<sub>3</sub> about 75% of Cp<sub>2</sub>ZrMe<sub>2</sub> remained unchanged (cf. Fig. 1). As displayed in Fig. 2, in the case of the activated cationic species Cp<sub>2</sub>ZrMe(μ-Me)B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub><sup>6)</sup> AlR<sub>3</sub> (with R = Et and *i*-Bu) showed the same influence with regard to stability of the zirconocene as Cp<sub>2</sub>ZrMe<sub>2</sub>. In similar <sup>1</sup>H NMR experiments with **MBI-Me<sub>2</sub>** and cationic borane activated **MBI-Me<sub>2</sub>** higher excesses of AlR<sub>3</sub> were needed to destroy the zirconocene complexes. As in the Cp<sub>2</sub>ZrMe<sub>2</sub> case AlEt<sub>3</sub> was more effective in decomposing the zirconocenes than Al(*i*-Bu)<sub>3</sub>.

By increasing the excess of borate to zirconium from 1.3 to 2.9 at constant **MBI-Me<sub>2</sub>** concentration of 100 μmol/l the activity was increased from 8300 g/(mol[Zr] ·

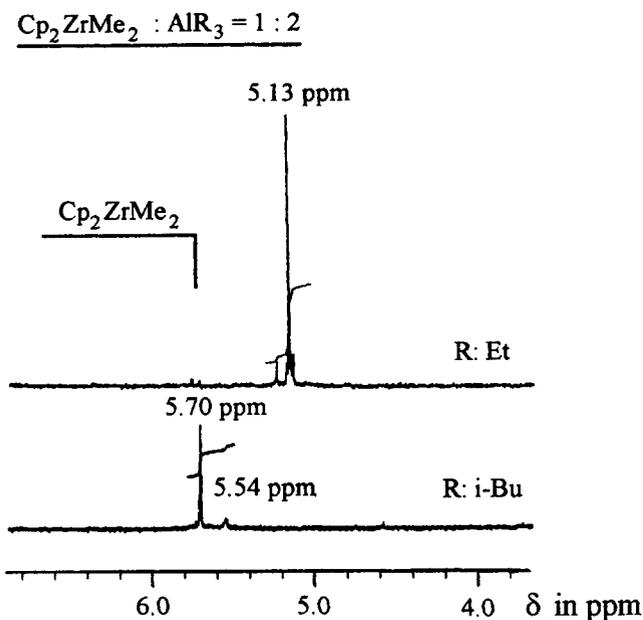


Fig. 1.  $^1\text{H}$  NMR spectra of the Cp-region of  $\text{Cp}_2\text{ZrMe}_2$ :  $\text{AlR}_3 = 1 : 2$  with  $\text{R} = \text{Et}, \text{i-Bu}$ ,  $[\text{Zr}] = 10 \text{ mmol/L}$  (Bruker WM 250, in  $\text{C}_6\text{D}_6$  7.15 ppm at 300 K).  $\text{Cp}_2\text{ZrMe}_2$ :  $\delta$  5.70 (s, Cp-H)

$\text{mol/L}[\text{Cp}] \cdot \text{h}$ ) to 19200  $\text{g}/(\text{mol}[\text{Zr}] \cdot \text{mol/L}[\text{Cp}] \cdot \text{h})$ . At 200  $\mu\text{mol/l}$  **MBI-Me<sub>2</sub>** concentration the activity was best in terms of activator [II] at constant twofold excess of zirconium.

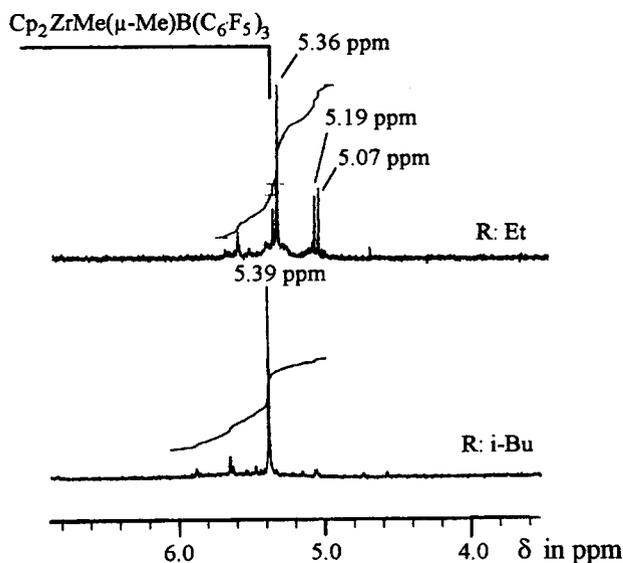


Fig. 2.  $^1\text{H}$  NMR spectra of the Cp-region of  $\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ :  $\text{AlR}_3 = 1 : 2$  with  $\text{R} = \text{Et}, \text{i-Bu}$ ,  $[\text{Zr}] = 10 \text{ mmol/L}$  (Bruker WM 250, in  $\text{C}_6\text{D}_6$  7.15 ppm at 300 K).  $\text{Cp}_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ :  $\delta$  5.39 (s, Cp-H)

## Conclusions

Polypropene melting temperatures and isotacticities are independent of the catalyst source (**MBI-Me<sub>2</sub>** or **MBI-Cl<sub>2</sub>**) and the cocatalyst (MAO or cationic activators II and III). Only the tris(pentafluorophenyl)borane (I) did not succeed as an activating agent when using **MBI-Me<sub>2</sub>** catalyst. The **MBI-Me<sub>2</sub>** is more efficient for propene polymerization at high catalyst concentration compared to **MBI-Cl<sub>2</sub>**. For achieving same activities with the cationic activators (II and III) compared to MAO higher amount of catalyst is necessary. The use of  $\text{Al}(\text{i-Bu})_3$  as a scavenger retained the catalytically active site as demonstrated by  $^1\text{H}$  NMR investigations. In contrast,  $\text{AlEt}_3$  is more an inhibitor than an activator and changes the active center. Therefore polymerization activity decreased drastically. The ratio of borate to zirconium influences polymerization activities, but polypropene microstructure and properties remained unchanged. As a result of NMR investigations conversion of the zirconocenedimethyl by a borate to a zirconocene cation showed a complete turnover at a slight excess of borate activator. A high excess of the borate on other zirconocene catalyst systems (e.g. *rac*- $\text{Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}_2/\text{n-Bu}_3\text{NH}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ ) lowers the polymerization activity by protonolysis of the second Zr-Me-group<sup>10</sup>. With the steric demanding ligand of the MBI system such a compositional attack is not possible<sup>16</sup> and the higher excess of the borate can help to reactivate dormant sites. In the case of the MBI system, the positive effect on the polymerization activity of a zirconocene excess can not be explained with the formation of binuclear cationic zirconocenes<sup>17</sup>, as the MBI systems are not able to form stable binuclear structures<sup>10</sup>. The increase in activity might be explained by activation of the total zirconocene catalyst by second order activation processes.

*Acknowledgement:* This work was supported by the *Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie* (project No. 03D0055) and by *BASF AG, Ludwigshafen*. We are grateful for providing the metallocene catalysts, cationic activators and analytical assistance. Also we want to thank *Witco Germany* for supplying samples of MAO.

- 1) U. Stehling, J. Diebold, R. Kirsten, W. Röhl, H. H. Brintzinger, S. Jüngling, R. Mühlhaupt, F. Langhauser, *Organometallics* **13**, 964 (1994)
- 2) W. Spaleck, F. Küber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E. F. Pauls, *Organometallics* **13**, 954 (1994)
- 3) S. Jüngling, R. Mühlhaupt, U. Stehling, H.H. Brintzinger, D. Fischer, F. Langhauser, *Macromol. Symp.* **97**, 205 (1995)
- 4) S. Jüngling, R. Mühlhaupt, *J. Organomet. Chem.* **497**, 27 (1995)
- 5) R. F. Jordan, W. E. Dasher, S. F. Echols, *J. Am. Chem. Soc.* **108**, 1718 (1986)

- <sup>6)</sup> X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **113**, 3623 (1991)
- <sup>7)</sup> a) W. Kaminsky, M. Schlobohm, *Makromol. Chem., Macromol. Symp.* **4**, 103 (1986); b) W. Kaminsky, *Macromol. Chem. Phys.* **197**, 3907 (1996)
- <sup>8)</sup> D. Fischer, *Dissertation*, Universität Freiburg i. Br. (1993)
- <sup>9)</sup> a) J. C. W. Chien, W. Song, M. D. Rausch, *Macromolecules* **26**, 3229 (1993); b) J. C. W. Chien, W. M. Tsai, *Makromol. Chem., Macromol. Symp.* **66**, 141 (1993)
- <sup>10)</sup> S. Beck, M. H. Prosenc, H. H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, *J. Mol. Catal. A: Chemical* **111**, 67 (1996)
- <sup>11)</sup> a) J. L. W. Pohlmann, F. E. Brinckman, G. Tesi, R. E. Donadio, *Z. Naturforsch.* **20b**, 1 (1965); b) J. L. W. Pohlmann, F. E. Brinckman, *Z. Naturforsch.* **20b**, 5 (1965)
- <sup>12)</sup> M. J. Schneider, R. Mülhaupt, *J. Mol. Catal. A: Chemical* **101**, 11 (1995)
- <sup>13)</sup> E. I. Negishi, D. Y. Kondakov, D. Choueiry, K. Kasai, T. Takahashi, *J. Am. Chem. Soc.* **118**, 9577 (1996), references cited therein
- <sup>14)</sup> S. Beck, H. H. Brintzinger, *Inorg. Chim. Acta*, in press
- <sup>15)</sup> a) W. Kaminsky, H. J. Vollmer, E. Heins, H. Sinn, *Makromol. Chem.* **175**, 443 (1974); b) W. Kaminsky, H. Sinn, *Liebigs Ann. Chem.* 428 (1975), 438 (1975)
- <sup>16)</sup> S. Beck, H. H. Brintzinger, in preparation
- <sup>17)</sup> S. Hahn, G. Fink, *Macromol. Rapid Commun.* **18**, 117 (1997)