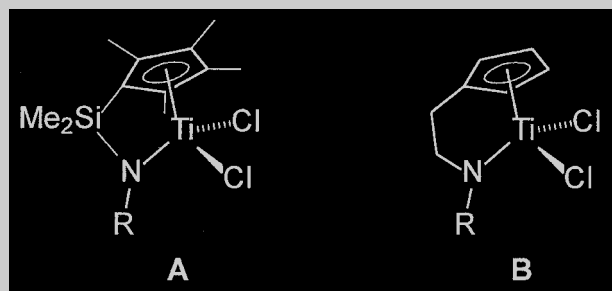


**Communication:** In the homopolymerisation of propene by the cyclopentadienyl-amide titanium catalyst systems  $[\eta^5, \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{TiCl}_2/\text{MAO}$  and  $[\eta^5, \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{Ti}(\text{CH}_2\text{Ph})_2/\text{B}(\text{C}_6\text{F}_5)_3$  ( $\text{R} = \text{'Bu}, \text{'Pr}, \text{Me}$ ), the catalyst with the smallest substituent ( $\text{Me}$ ) on the amido moiety consistently gives the highest polymer molecular weight. This differs from the trend usually observed in related catalysts with tetramethylcyclopentadienyl-amide ancillary ligands, where larger amide substituents result in higher molecular weights. Based on the present information a hypothesis is formulated in which an increased cation-anion interaction for the less sterically hindered catalyst is responsible for disfavoured chain transfer relative to chain growth.



## The effect of the amido substituent on polymer molecular weight in propene homopolymerisation by titanium cyclopentadienyl-amide catalysts<sup>a</sup>

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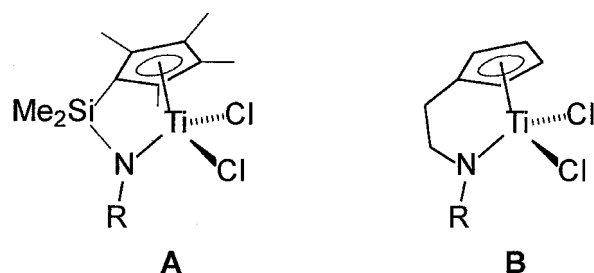
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### Introduction

Titanium complexes with linked dianionic cyclopentadienyl-amide ancillary ligands form a class of important catalysts for olefin polymerisation, especially for copolymerisation of ethene with a range of  $\alpha$ -olefins (including 1-octene, styrene and even isobutene)<sup>1–3</sup>. The ligands in which the cyclopentadienyl moiety has four methyl substituents have been most extensively studied, as these tend to give catalysts with much higher activities than those with unsubstituted cyclopentadienyl moieties do<sup>1,2</sup>. For the case of the ‘archetypal’ catalysts with the  $\eta^5, \eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NR}$  ancillary ligand<sup>4</sup> (**A**,  $\text{R} = \text{alkyl, aryl}$ ), the catalyst activity and polymer molecular weight were found to be the highest with a sterically demanding  $\text{R}$ -group (e. g.  $\text{'Bu}$ ).

As with the well-known metallocene catalysts<sup>5</sup>, the active species in these catalyst systems are cationic metal alkyls. We are investigating the effects of the interactions of these active centres with the complementary anion and the reaction medium on polymerisation behavior. The species with unsubstituted cyclopentadienyl ligands seem



particularly suitable, to study these effects because of their limited steric requirements, which should enhance the effects of these interactions.

Previously we described the synthesis of the dichloride complexes  $[\eta^5, \eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{TiCl}_2$  (**B**,  $\text{R} = \text{'Bu}, \text{'Pr}, \text{Me}$ ) and, for  $\text{R} = \text{'Bu}$ , the generation of a cationic benzyl complex by reaction of the dibenzyl derivative with the Lewis acid  $\text{B}(\text{C}_6\text{F}_5)_3$ <sup>6</sup>. Here we describe the homopolymerisation of propene with the corresponding Ti-dichloride/methylaluminoxane (MAO) and Ti-dibenzyl/ $\text{B}(\text{C}_6\text{F}_5)_3$  catalyst systems. Within this group of catalysts, the molecular weight of the obtained polypropene was found to vary strongly with the substituent  $\text{R}$ , the *smallest* substituent

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ent (Me) giving by far the highest molecular weight. In addition, it was found that in the  $R = {}^i\text{Pr}$  system the activator used strongly affects the nature of the polymer obtained.

## Experimental part

### General procedures and materials

All manipulations were performed under nitrogen atmosphere using standard Schlenk or dry-box techniques unless mentioned otherwise. Solvents used for the synthesis and characterisation of the catalysts and catalyst precursors were pre-dried on sodium wire and distilled under nitrogen from sodium or sodium-potassium alloy before use. A toluene solution of MAO (1.5 M, Akzo Nobel) was used as received,  $\text{B}(\text{C}_6\text{F}_5)_3$ <sup>7)</sup> and  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{TiX}_2$  ( $R = \text{Me}, {}^i\text{Pr}, {}^t\text{Bu}; X = \text{Cl}, \text{CH}_2\text{Ph}$ )<sup>6,8)</sup> were prepared according to literature procedures. Ethene, propene (AGA, polymer grade) and toluene (Aldrich 99.8%, anhydrous) for the polymerisation experiments were passed over columns of a supported copper oxygen scavenger (BASF R 3–11) and mol. sieves (3 Å) before being passed to the reactor.

### Polymerisation experiments

Polymerisations of ethene and propene were carried out in thermostated (electrical heating, water cooling) stainless steel autoclaves (Medimex, reactor volume 1 l for MAO-activated polymerisations, 0.5 l for  $\text{B}(\text{C}_6\text{F}_5)_3$ -activated polymerisations), equipped with solvent and catalyst injection systems. A typical MAO-activated propene polymerisation proceeds as follows. The autoclave is pre-dried by heating in vacuo at 120 °C for 1 h. After cooling to the desired reaction temperature 250 ml of toluene is added, followed by injection of 13.5 ml of a 1.5 M MAO/toluene solution and 10 ml of toluene. Propene ( $4.7 \times 10^5$  Pa) is admitted and the system is allowed to equilibrate for 15 min. A solution of the  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{TiCl}_2$  catalyst precursor in 10 ml of toluene is then injected to start the reaction, followed by another 20 ml of toluene (total volume 300 ml). The propene pressure is kept constant within  $0.2 \times 10^5$  Pa during the reaction. After 30 min the reaction is stopped by the injection of 10 ml of methanol. After venting, the reactor is opened to ambient for product work-up. The solvent is removed from the mixture in vacuo and the resultant material dried at 100 °C for 1 h. The product is then dissolved in chloroform and filtered. Removal of the solvent in vacuo and drying for several hours at 100 °C yields the polymer. For borane-activated polymerisations a total of 200 ml of toluene was used, and the titanium dibenzyl complexes were used as catalyst precursor. In the ethene polymerisation experiments, the product was slurried for several hours in acidified methanol, repeatedly rinsed with ethanol and petroleum ether and dried in vacuo at 70 °C overnight.

### Polymer characterisation

The molecular weight distributions of the polyethenes were analysed by GPC (Polymer Laboratories PL-GPC210) at

150 °C using 1,2,4-trichlorobenzene solvent. For the polypropenes the molecular weight distributions were determined by GPC (Spectra Physics LC-1000 system) at 30 °C using chloroform solvent. Molecular weight data were calculated from universal calibration curves of polystyrene. Carbon NMR spectra of the polypropenes were recorded at 100 °C in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> on a Varian Unity 500 spectrometer at 125.7 MHz.

## Results

To obtain a first indication of catalyst performance, the polymerisation of ethene was performed using the catalysts  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{TiCl}_2$  ( $R = {}^t\text{Bu}, {}^i\text{Pr}, \text{Me}$ )<sup>6)</sup> activated by MAO in toluene solvent. With both metallocene and cyclopentadienyl-amide catalysts it is usual to contact the dichloride precursor with MAO in the solvent, prior to the introduction of this mixture into the reactor. We observed that with the present catalysts (where  $R = \text{Me}, {}^i\text{Pr}$ ) within several minutes of the reaction start, reduction of the metal centre and concomitant loss of activity resulted. This was seen by a colour change from yellow to blue-green and in the ESR spectra a signal at  $g = 1.975$ , indicative of the formation of Ti(III). Only for  $R = {}^t\text{Bu}$  were solutions of dichloride/MAO in toluene obtained that were stable and retained activity for longer periods (1–2 days). Precharging the reactor with toluene and MAO, followed by saturation with the monomer and subsequent addition of a toluene solution of the dichloride catalyst precursor did lead to consistent catalyst activity for all three catalysts. Therefore this procedure was adopted in the catalysis experiments.

The results of the ethene homopolymerisation experiments with the  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{TiCl}_2$  and MAO catalytic system (toluene, 50 °C,  $2 \times 10^5$  Pa ethene) are shown in Tab. 1. The trend in catalyst productivity observed for  $R$  ( ${}^t\text{Bu} > {}^i\text{Pr} > \text{Me}$ ) is as expected when compared to the trends observed in the  $[\text{C}_5\text{Me}_4\text{SiMe}_2\text{NR}]\text{Ti}$  catalysts, although the overall productivity is considerably lower. Remarkably, it was found that the trend in the polymer

Tab. 1. Ethene homopolymerisation with the  $[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{TiCl}_2$  and MAO catalytic system<sup>a)</sup>

Run	R	Productivity in $\text{kg} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
1	Me	840	777	211	3.7
2	Me	840	732	191	3.8
3	<sup>i</sup> Pr	1470	123	52	2.4
4	<sup>i</sup> Pr	1460	113	49	2.3
5	<sup>t</sup> Bu	1850	58	31	1.9
6	<sup>t</sup> Bu	1750	73	30	2.4

<sup>a)</sup> Polymerisation conditions: toluene = 300 ml,  $[\text{Ti}] = 7 \cdot 10^{-5}$  M, Al/Ti = 520 (mol/mol), temp. = 50 °C, ethene pressure =  $2 \times 10^5$  Pa, polymerisation time = 30 min.

Tab. 2. Propene homopolymerisation with the  $[C_5H_4(CH_2)_2NR]TiCl_2$  and MAO catalytic system<sup>a)</sup>

Run	R	Productivity in $kg \cdot mol^{-1} \cdot h^{-1}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
7	Me	295	720	344	2.1
8	Me	287	722	344	2.1
9	<sup>i</sup> Pr	114	16.3	8.4	1.9
10	<sup>i</sup> Pr	106	15.7	8.7	1.8
11	<sup>t</sup> Bu	224	11.4	6.5	1.8
12	<sup>t</sup> Bu	243	18.1	8.0	2.3

<sup>a)</sup> Polymerisation conditions: toluene = 300 ml,  $[Ti] = 2.10^{-4}$  M, Al/Ti = 520 (mol/mol), temp.: = 30°C, propene pressure =  $4.7 \times 10^5$  Pa, polymerisation time = 30 min.

molecular weight is the opposite (Me > <sup>i</sup>Pr > <sup>t</sup>Bu), and also, opposite to that known from experience for  $C_5Me_4$ -based catalysts. The polydispersity of the high molecular weight polyethene, obtained with the catalyst with R = Me, is relatively high, which may be associated with polymer precipitation and/or mass transfer problems. Therefore it was deemed more suitable to study the effects of the substituent R on polymer formation on propene, rather than ethene polymerisation. Polypropene produced with cyclopentadienyl-amido catalysts is usually atactic or slightly syndiotactically enriched<sup>1a,9,10</sup>, and soluble in toluene up to high molecular weights. Also, the polymer microstructure can give additional information on the processes taking place at the active centre.

The results of the propene homopolymerisation experiments with the  $[C_5H_4(CH_2)_2NR]TiCl_2$  and MAO catalytic system (toluene solvent, 30°C,  $4.7 \times 10^5$  Pa propene) are shown in Tab. 2. In contrast to the ethene polymerisation experiments, there seems to be no clear trend in catalyst productivity. The R = <sup>i</sup>Pr catalyst is consistently found to be least active. After the completion of the runs, all reaction mixtures were homogeneous solutions of varying viscosity. Polydispersities of all polypropenes are in reasonable agreement with the assumption that a single type of active species is operative. There is a striking difference in polymer molecular weight between the polypropene prepared with the R = Me catalyst and the others, the former being more than 40 times higher. Molecular weights of the polypropene prepared by the R = <sup>i</sup>Pr and R = <sup>t</sup>Bu catalysts do not differ significantly.

In order to see if the observed effects are in any way influenced by the anion that is complementary to the cationic active centre, propene polymerisation experiments were performed in which titanium dibenzyl catalyst precursors  $[C_5H_4(CH_2)_2NR]Ti(CH_2Ph)_2$  were activated by the Lewis acid  $B(C_6F_5)_3$ , thus producing the  $PhCH_2B(C_6F_5)_3$ -anion as counterion to the active catalyst species. As in these experiments an excess of aluminium

Tab. 3. Propene homopolymerisation with the  $[C_5H_4(CH_2)_2NR]Ti(CH_2Ph)_2$  and  $B(C_6F_5)_3$  catalytic system<sup>a)</sup>

Run	R	Productivity in $kg \cdot mol^{-1} \cdot h^{-1}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
13	Me	782	1064	544	2.0
14	Me	662	1047	411	2.5
15	<sup>i</sup> Pr	1110	138	63	2.2
16	<sup>i</sup> Pr	1085	132	60	2.2
17	<sup>t</sup> Bu	492	33	10	3.3
18	<sup>t</sup> Bu	750	30	14	2.1

<sup>a)</sup> Polymerisation conditions: toluene = 200 ml,  $[Ti] = 4.10^{-4}$  M, B/Ti = 1.5 (mol/mol), temp.: = 30°C, propene pressure =  $4.7 \times 10^5$  Pa, polymerisation time = 30 min.

alkyl (and thus a means to scavenge impurities) is absent, the polymerisations had to be carried out at a higher titanium concentration (double that of the MAO-activated experiments) to obtain consistent catalyst productivities. The results of these propene homopolymerisations are shown in Tab. 3.

Despite the absence of an impurity scavenger, the experiments are quite reproducible (with only run 17 being somewhat anomalous with a relatively low productivity and a relatively high polydispersity). The overall productivity is higher than in the MAO-activated systems (an observation that has been made for many other systems as well), and now the R = <sup>i</sup>Pr catalyst is found to have the highest productivity. The R = Me catalyst again gives by far the highest polymer molecular weight. This is about 8 times higher than that obtained with the R = <sup>i</sup>Pr catalyst, which in turn is about 4 times higher than that obtained with the R = <sup>t</sup>Bu catalyst. In these experiments all polymer molecular weights are higher than those found in the analogous systems with the MAO cocatalyst. <sup>i</sup>Pr end-groups can be observed in the latter using <sup>13</sup>C NMR, indicating a certain degree of chain transfer to aluminium (as is usual with alkylaluminium cocatalysts). It is remarkable, however, that for the R = <sup>i</sup>Pr system the  $\bar{M}_w$  of the polymer obtained with the borane activator is more than 8 times higher than that with the MAO activator, whereas for the others this is only 1.4–2 times higher.

<sup>13</sup>C NMR analysis of the polypropenes obtained indicates that they are predominantly atactic, with 3–5% regioirregularities and with a combination of vinylidene and linear olefinic end-groups (indicative of  $\beta$ -H transfer after 1,2- and 2,1-propene insertion respectively). Certain samples show a modest, but significant syndiotactic enrichment. The triad distributions for representative samples are shown in Tab. 4. It may be noted that for all products with relatively high molecular weights (R = Me with MAO or borane activator, R = <sup>i</sup>Pr with borane activator) a syndiotactic enrichment is observed. This is especially remarkable for R = <sup>i</sup>Pr, where the switch from the

Tab. 4. Triad sequence distributions of the polypropenes as determined by  $^{13}\text{C}$  NMR ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $100^\circ\text{C}$ ).

Run	R	Activator <sup>a)</sup>	%mm	%mr	%rr
7	Me	A	17.2	48.4	34.4
13	Me	B	14.3	48.8	36.9
9	<sup>i</sup> Pr	A	21.4	54.5	24.2
15	<sup>i</sup> Pr	B	14.8	49.3	35.9
11	<sup>t</sup> Bu	A	23.8	53.5	22.7
18	<sup>t</sup> Bu	B	24.5	51.8	24.0

<sup>a)</sup> A = MAO; B =  $\text{B}(\text{C}_6\text{F}_5)_3$ .

MAO activator to the borane activator is accompanied by both an 8-fold increase in polymer molecular weight as well as a syndiotactic enrichment. As the microstructure reflects the stereochemistry of the processes taking place at the metal during catalysis, the latter suggests that in this system the change of activator also effects a modification of the environment of the active centre. Care has to be taken with the interpretation of the microstructure data, however, as stereoregularities and contributions from the chain ends in low molecular weight polymers can be of influence<sup>a</sup>.

## Discussion

For the tetramethylcyclopentadienyl-amide titanium catalysts it was observed that a reduction in steric bulk of the amido substituent generally leads to reduced polymer molecular weight (e.g. in ethene polymerisation by  $[\text{C}_5\text{Me}_4\text{SiMe}_2\text{NR}]\text{TiCl}_2/\text{MAO}$  the  $\text{R} = \text{CH}_2\text{Ph}$  catalyst gives a polymer with a much higher melt-flow index than the  $\text{R} = \text{}^t\text{Bu}$  catalyst<sup>1)</sup>). Indeed, high molecular weight atactic polypropene is obtained by catalysts with particularly large amide substituents ( $\text{R} = \text{adamantyl}$ , cyclododecyl)<sup>10)</sup>. In the less sterically hindered  $[\text{C}_3\text{H}_4(\text{CH}_2)_2\text{NR}]\text{Ti}$ -system this trend is reversed. The observation that for  $\text{R} = \text{}^i\text{Pr}$  a change in activator leads to an anomalously large change in polymer molecular weight as well as a change in polymer microstructure suggests that interaction between the active centre and the counterion may be responsible. Several reports have shown that the more electron-deficient cationic cyclopentadienyl-amide complexes are more prone to give observable cation-anion interactions than *bis*-cyclopentadienyl complexes, but that these are sensitive to the steric environment of the cation<sup>12)</sup>. For the ionic Ti-benzyl compound  $\{[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{NR}]\text{Ti}(\text{CH}_2\text{Ph})\}[\text{PhCH}_2\text{B}(\text{C}_6\text{F}_5)_3]$  we obser-

<sup>a</sup> See for example ref.<sup>11)</sup> As the difference in microstructure between the samples of runs 9 and 15 ( $\text{R} = \text{}^i\text{Pr}$ ) is also reflected in the ratio between the *mmmm* and *rrrr* pentads (1:1 in run 9, 1:3 in run 15), it is unlikely that superposition of end-group related resonances is the only source of the observed differences.

ved by NMR that for  $\text{R} = \text{}^t\text{Bu}$  this complex exists in  $d_5$ -bromobenzene solution as a solvent-separated ion pair from  $-35^\circ\text{C}$  to  $+65^\circ\text{C}$ . For  $\text{R} = \text{Me}$ , cooling such a solution leads to broadening of the  $^{19}\text{F}$  and  $^1\text{H}$ -NMR resonances of the anion, suggesting a rapid equilibrium with a contact ion pair<sup>6, 12)</sup>. For the cationic Ti-alkyl species present during catalysis the latter is expected to be much more favoured than for the Ti-benzyl species (in which the benzyl group can impart extra electron density to the metal centre by  $\eta^2$ -coordination<sup>12, 13)</sup>). For the  $\text{Me}_2\text{Si}(\text{Flu})(\text{N}t\text{-Bu})\text{Zr}$ -based catalyst system the effect of the counterion was held responsible for the observed switch in stereoregularity of the produced polypropene depending on the cocatalyst used (syndiotactic with MAO, isotactic with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  cocatalyst). In the latter case a substantially lower activity was found, and the effect on the molecular weight is somewhat ambiguous (broad MWD)<sup>14)</sup>.

Recent *ab initio* calculations on the cyclopentadienyl-amido titanium catalyst with a methyltriaryborate counterion have shown that even with a noticeable cation-anion interaction olefin insertion can take place with a reasonable activation barrier<sup>15)</sup>. Other calculations have shown that the transition state for hydrogen transfer to monomer (the dominant chain transfer mechanism in these catalysts) occupies more space in the coordination sphere of the metal than that the transition state for olefin insertion does<sup>16)</sup>. Thus it is possible that cation-anion interaction, by crowding the metal centre, can disfavour chain transfer relative to chain growth. In this way increased cation-anion interaction in a catalyst with a sterically less demanding ancillary ligand can lead to formation of a polymer with a higher molecular weight. We are presently studying ways to test this hypothesis. If this were correct, it would provide a means to increase polymer molecular weight in sterically unhindered catalyst systems through tuning of the complementary anion. It may be noted that in the sterically and electronically more encumbered metallocene catalysts an increased cation-anion interaction usually leads to a decrease in polymer molecular weight<sup>17)</sup>.

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