Synthesis and olefin polymerization using supported and non-supported geometry constrained titanium complexes

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Abstract

The synthesis of a constrained geometry titanium complex and its immobilization on different supports have been studied for the catalytic polymerization of ethylene, propylene and styrene. The formation of higher molecular weight polymers was found in the heterogeneous system as compared to the homogenous parent for polyethylene and polypropylene. Polymerization of propylene yielded atactic products with elastomeric properties due to long polymer chains. However, syndiotactic polymers were formed in the polymerization of styrene. Catalytic activity was found to be dependent on MAO and titanium concentration; the higher the metal concentration the lower the activity of the catalyst. The activity of the heterogeneous system was determined as a function of time, and a first-order deactivation pathway was found at room temperature. The type of solvent (toluene or CH_2Cl_2) also played an important role in the polymerization of ethylene and styrene, although different tendencies were found for either monomers. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

A new era in the Ziegler–Natta polymerization of α-olefins has been uncovered by the discovery of the metallocene-type catalysts. Special attention has been devoted to *rac*-isomers of *ansa*-metallocene complexes with C_2 symmetry for producing stereospecific isotactic polymers and to C_s-symmetric complexes for producing syndiotactic polymers [1]. As far as the unique performance of the metallocene complexes for the polymerization of α-olefins is concerned, from the results published in the literature, a common behavior of the metallocenes is observed, and general conclusions can be made: (i) metallocenes show the highest polymerization activities, higher than those obtained with the MgCl_2 supported titanium catalysts; (ii) metallocenes produce polymers with much higher stereospecificity than the conventional Ziegler–Natta catalysts; (iii) as single-site catalysts, metallocenes have the ability to polymerize propylene to polypropylene chains with the same structure, and almost equal length, i.e. with very narrow molecular weight distribution (MWD). In addition, they have the ability to copolymerize various monomers, including polar monomers, with homogeneous distribution of the comonomers [2].

Attachment of these metallocene complexes to either organic or inorganic supports either by absorption or coordination is an area of increasing interest [1,3–10]. It exhibits the advantages of homogeneous systems mentioned before, allows the synthesis of polymers with higher molecular weight and melting points compared to the corresponding homogeneous complexes, and permits their use in the gas-phase and slurry polymerization reactions without reactor-fouling problems [1].

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Three main routes are known for the immobilization of metallocene complexes: (i) direct application of the metallocene to the support (modified by previous treatment) [3,4]. (ii) Immobilization of the cocatalyst methylalumoxane (MAO) or an aluminum alkyl on the support and reaction with the metallocene complex [6]. (iii) Modification of the inorganic support by addition of compounds such as $SiCl_4$, $C_2H_2Br_2$, $SOCl_2$, or Me_2SiCl_2, then addition of the metallated cyclopentadienyl ligand, metallation of the bound ligand and addition of the metal salt [7]. The main inorganic supports are silica, alumina and magnesium compounds. Other materials such as cyclodextrin [8], polystyrene [9a], polysiloxane derivatives [9b] and zeolites have been investigated.

In addition to the *rac*-metallocenes, new asymmetric homogeneous complexes have also attracted considerable attention. These complexes are formed by replacing the two linked or unlinked cyclopentadienyl rings with the dianionic chelating ligand $[(C_5Me_4)SiMe_2(N-t-Bu)]$ [2–11]. In these constrained geometry catalysts, weaker π-donating character and the lower steric requirements of the pendant amido moiety enhance the metal's Lewis acidity by lowering the formal electron count and the steric bulkiness at the metal center [11–19]. Constrained geometry catalysts are currently of great scientific and technological interest as a new generation of Ziegler–Natta-type catalysts, due to the apparent lower tendency of the bulk polymer chain to undergo chain transfer, which allows the production of high molecular weight copolymers (ethylene-α-olefins) [11]. In general, the open nature of the catalytic site does not permit steric control of the polymerization of α-olefins and generally leads to atactic polymers [12–14], although it has been reported that by using the appropriate cocatalyst, syndiotactic and isotactic polymers might be obtained [15].

Bercaw and Shapiro have prepared a series of neutral scandium complexes, which are the first examples of homogeneous single-component living α-olefin polymerization catalysts [16,17]. The ethylene polymerization rates of these scandium-based catalysts were relatively slow. Based on constrained geometry catalysts with Group IV metals [18–27], Dow and Exxon have developed high polyethylene elastomers (LLDPE) with enhanced processability as a result of long-chain branching [21–23,25]. It seems that the less crowded and more electron-deficient d^0 metal center enhances the ability of the active catalysts to promote migratory olefin insertion into the metal–carbon bond of the growing polymer chain [18,19]. The long-chain branches are postulated to be the result of the incorporation of vinyl-terminated polymer molecules on the catalytically active site [11].

Constrained geometry Group IV catalysts, like the other polymerization catalysts, require a large excess of the cocatalyst (MAO) to become active and reach satisfactory activities (Al:M = 500–1000). The catalytic efficiency of these complexes with MAO is relatively low for commercial application (10^4–10^5 g polymer/g Ti), however, the addition of $B(C_6F_5)_3$ as a cocatalyst is very useful for solution polymerization, and the cationic catalyst shows higher activity, exceeding 10^7 g polymer/g Ti [11].

Research on the immobilization of constrained geometry catalysts has been collected only in the patent literature [20–27]. The catalysts are supported on different materials (Al_2O_3, SiO_2), modified by treating the surface with the cocatalysts [21–27]. Dow Chemical has developed a new group of constrained geometry supported catalysts. The preparation consists basically of fixing MAO to the support followed by the addition of the transition metal compound [21]. This type of complex has shown high activity, good resistance to poisoning and long life for the polymerization of ethylene and other α-olefins [21,22]. Mitsuibishi Petrochemical has developed a similar type of catalyst, in which trialkyl aluminum compounds were added to the reaction mixture [20–24]. Exxon Chemicals used of *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)-boron in the presence of $(CH_3CH_2)_3Al$, to activate a titanium complex on silica [23]. Supported metallocene catalysts based on borate derivatives have also been prepared to avoid the use of expensive MAO [20,25,27].

In view of the technological importance of these constrained geometry complexes and the interest in the corresponding heterogeneous dialkyl complexes as catalytic precursors, we report here an efficient synthetic approach to heterogeneous constrained geometry complexes which are *covalently* bound to an inorganic surface through a pendant amido group. The catalytic activity of the heterogeneous and homogeneous parent complexes was compared for a number of α-olefins.

Interestingly, the molecular weight of the polyethylene prepared with the heterogeneous complex is in the range of $M_w = 281\,000$ whereas for polypropylene a high molecular weight of $M_w = 905\,100$ was obtained but with very low activities. For polystyrene, a low molecular weight is obtained in toluene ($M_n = 73\,850$), whereas in CH_2Cl_2 higher molecular weights and broader molecular weight distributions are observed ($M_w = 723\,480$ and $\rho = 11.2$).

2. Results

2.1. Synthesis of the homogeneous ligand and complex

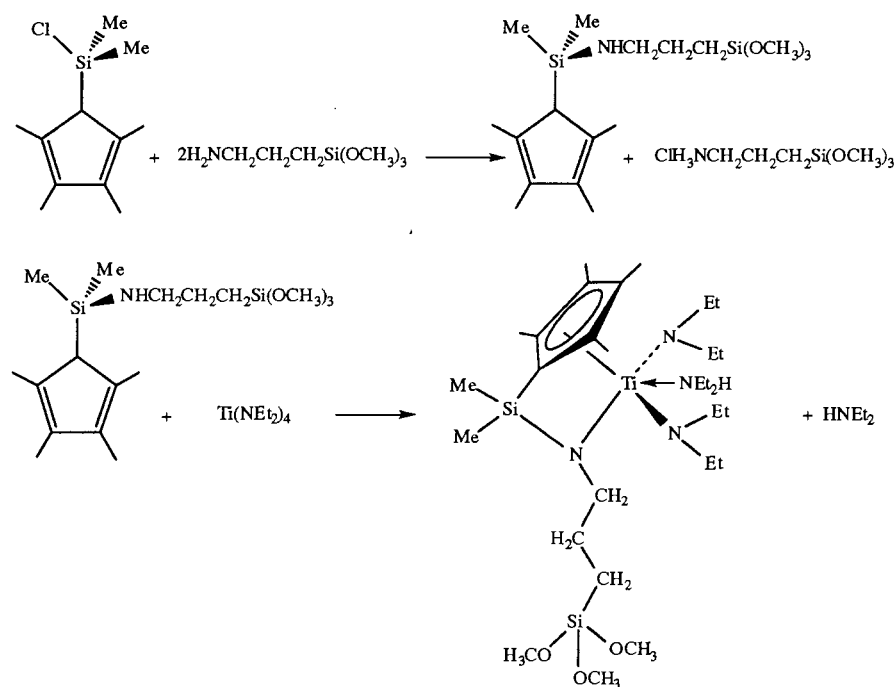The ancillary ligand was synthesized on a large scale

Fig. 1. Synthesis of complex **1**.

by the reaction of tetramethylchlorodimethylsilylcyclopentadiene [28a,29,30] with two equivalents of 3-aminopropyl(trimethoxy)silane to give equimolar amounts of HCp′SiMe$_2$NHR (Cp′ = C$_5$Me$_4$; R = CH$_2$CH$_2$CH$_2$Si(OCH$_3$)$_3$) and the corresponding ammonium chloride salt RNH$_3$Cl (Fig. 1). The reactivity of the trimethoxysilyl moiety thwarted our attempts to produce the corresponding alkali metal derivative for reaction with the metal chloride salts. Hence, the constrained geometry complex (Cp′SiMe$_2$NR)–Ti–(NEt$_2$)$_2$·NHEt$_2$ was synthesized by the reaction of titanium tetrakis(diethylamide) with one equivalent of HCp′SiMe$_2$NHR in toluene, as a brown moisture-sensitive oil [28a].

The metal complex **1** was characterized by ^{1}H-, ^{13}C-NMR, JMOD, DEPT and COSY spectroscopy and elemental analysis. In the ^{1}H-NMR spectrum, the diethylamido group of the starting titanium tetrakis(diethylamido) complex gives a triplet and a quartet at 1.04 and 3.53 ppm for the methyl and methylene groups, respectively. In the constrained geometry titanium complex **1**, the signals are shifted upfield relative to the parent complex. Additional signals are obtained for the coordinated amine. The upfield shift is associated with the difference in Lewis acidity between complex **1** and the starting material. Interestingly, the signals for the methylene groups of the amido groups exhibit a small splitting ($J = 8$ Hz). This splitting is characteristic of non-equivalent protons as CH$_A$H$_B$CH$_3$ in molecules with a mirror plane [28a].

2.2. Synthesis of the supported catalysts

Complex **1** was anchored to either silica or alumina, pretreated under vacuum at 300°C for 3 h, by impregnating the solid support with a solution of **1** in refluxing toluene and drying the solids under high vacuum (10^{-6} mm Hg), to give the heterogeneous precatalysts **2** and **3**, respectively (0.025 g Ti/g catalyst). The OH groups of the surface react with the Si–(OCH$_3$)$_3$ moiety of the Ti complex as indicated in Fig. 2, with elimination of methanol. Under these conditions, only traces of the free ligand were observed indicating that methanol does not protonate the ancillary ligand.

2.3. Polymerization activity studies

The activity of the unsupported and supported Cp catalysts was measured in the polymerization of ethylene, propylene, and styrene. The catalytic precursors were activated to the corresponding cationic species by using an 800-fold excess of MAO as cocatalyst in CH$_2$Cl$_2$ or toluene as the solvent. The activity data for the polymerization of the different α-olefins is shown in Table 1.

The activity of the homogeneous and the supported catalysts in the polymerization of ethylene are very similar but are lower than those of simple homogeneous constrained geometry complexes containing a *tert*-butyl-amido group [11]. Nevertheless, the anchoring of complex **1** to an inorganic surface provides stable catalysts in which the ligand is firmly fixed to the metal under
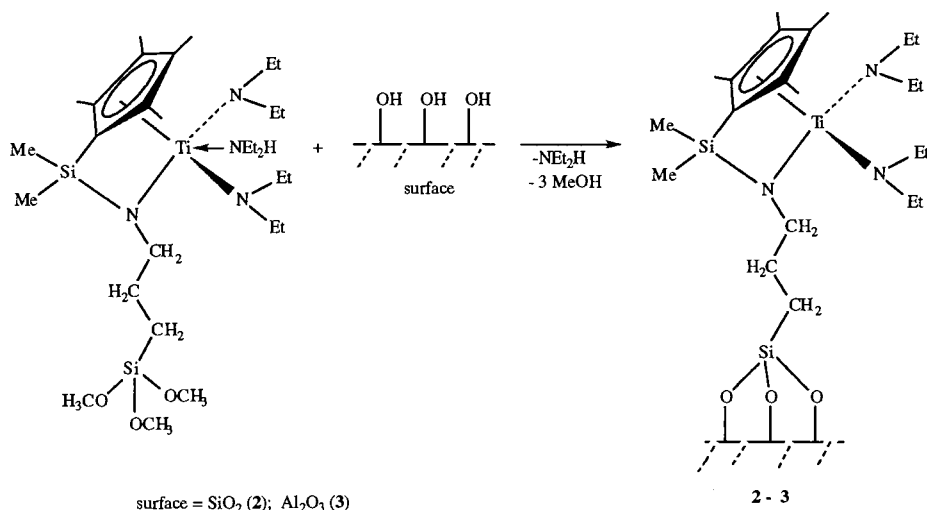
surface = SiO$_2$ (**2**); Al$_2$O$_3$ (**3**)

Fig. 2. Synthesis of supported catalysts: complex **2**, **3**.

the catalytic conditions. However, to determine the stability of the complex and whether it is released from the support, the supported catalyst was washed several times with hot toluene, filtered, dried and its catalytic activity measured under the same conditions showed no major change (entries 2 and 4). Refluxing the heterogeneous catalysts with toluene in the presence of MAO, washing, filtering and drying led to a decrease in activity (entries 4 and 5). This indicates that MAO is able to release at least part of the complex from the support. Further washing did not cause any further decrease in activity revealing that the titanium complex is still fixed to the support.

The ethylene polymerization activity of **1** was measured as a function of the concentration of MAO (Fig. 3, Table 2). Different amounts of cocatalyst were used in order to understand the effect of MAO on the catalytic activity [31–34]. Maximum polymerization activity was reached at a catalyst:cocatalyst ratio of 1:2400. Higher MAO concentrations did not enhance the productivity of polyethylene as found for other systems, and in contrast to metallocene complexes [34]. The effect of the concentration of the metal complex on the polymerization was investigated by measuring the polymerization activity at constant catalysts:cocatalyst ratio (Table 2, entries 7, 8). Remarkably, the lower the concentration of the metal center, the higher the catalytic activity.

The activity of the supported catalyst **3** was measured as a function of the reaction time, in order to optimize the polymerization conditions. The maximum activities were obtained in the first 30 min of the reaction. Longer reaction times, beyond 3 h, led to a decrease in the calculated rate of polymerization. Interestingly, the deactivation follows first-order kinetics (Fig. 4), which is similar to the behavior found in homogeneous metallocenes [32].

The product obtained from the polymerization of propylene is highly dependent on pressure. At low pressure, atactic polypropylene oil was obtained with complex **1**. The polymer was characterized by ^{13}C- and ^{1}H-NMR spectroscopy and, as expected, showed no vinylidene or vinyl chain end groups (4.25–5.50 ppm region in ^{1}H-NMR) which would indicate an aluminum chain transfer termination mechanism [35]. At higher pressure and in liquid propylene (20°C, 7.2 atm), both the homogeneous and heterogeneous complexes produced an *elastomeric* atactic polypropylene of very high molecular weight. In general, complexes **1–3** exhibit higher activity towards ethylene than propylene, for the former the solvent plays an important role [36,37] (compare entries 2 and 3, Table 1).

For styrene, polymerization with the homogeneous complex **1** was studied under different conditions. In toluene at room temperature (r.t.), no product was observed, but at 60°C syndiotactic polystyrene was obtained (m.p. = 267.6°C). Note that although the NMR spectrum of the polystyrene indicates very high stereoregularity, the DSC melting and crystallization curves show two polymer regimes in agreement with the GPC measurements, which also showed two major signals. On the other hand, yellow cross-linked polystyrene with a T_g of 110°C was obtained when CH$_2$Cl$_2$ was used as the solvent. The insolubility of this product in organic solvents makes its characterization difficult.

The molecular weights of the polyolefins obtained within the different catalytic systems are summarized in Table 3. As a general trend, the heterogeneous constrained geometry catalyst shows a bimodal molecular weight distribution (Table 3 and Fig. 5). This type of distribution is characteristic of multi-site catalytic systems, which are expected on the surface of most common heterogeneous catalysts. In the polymerization of

Table 1
Polymerization activities for olefin polymerization by homogeneous and heterogeneous constrained geometry titanium complex

Entry	Precursor	Olefin	Solvent	T (°C)	Activity $\times 10^{-4}$ (g mol^{-1} h^{-1})	M.p.
1	**1**	Ethylene	Toluene	20	1.93	132.6
2	**2**	Ethylene	Toluene	20	2.06	128.1
3	**2**	Ethylene	CH$_2$Cl$_2$	20	0.47	132.8
4	**2**[a]	Ethylene	Toluene	20	1.81	130.7
5	**2**[b]	Ethylene	Toluene	20	0.6	132.8
6	**3**	Ethylene	Toluene	20	1.3	133.4
7	**1**	Propylene	Toluene	20[d]	0.5	Atactic oil
8	**1**	Propylene	Toluene	20[e]	0.37	Elastomer
9	**2**	Propylene	Toluene	20[e]	0.35	Elastomer
10	**1**	Styrene	Toluene	20	–	–
11	**1**[c]	Styrene	Toluene	60	0.95	267.6
12	–	Styrene	CH$_2$Cl$_2$	20	0.2	110[f]
13	**1**	Styrene	CH$_2$Cl$_2$	20	7.6	110[f]
14	**2**	Styrene	CH$_2$Cl$_2$	20	8.87	110[f]

[a] Washed with toluene.
[b] MAO pretreated.
[c] Ti:MAO 1:1600.
[d] 1.5 atm. of propylene.
[e] Liquid propylene, 7.2 atm.
[f] T_g.

propylene in toluene with the homogeneous or the heterogeneous catalyst system, a small fraction of low molecular weight oligomers (ca. 38 monomers) were produced (entries 4 and 5, Table 3). For ethylene and propylene the molecular weights of the heterogeneous-based polymers are higher than those for the homogeneous-based polymers, as already shown for other homogeneous and heterogeneous metallocene systems [38,39]. Interestingly, for polystyrene different behaviors are found. With the homogeneous catalyst in toluene a syndiotactic polymer was obtained with a small polydispersity ($\rho = 2.2$) whereas in dichloromethane a cross-linked polystyrene was obtained with a very broad molecular weight distribution ($\rho = 11.2$).
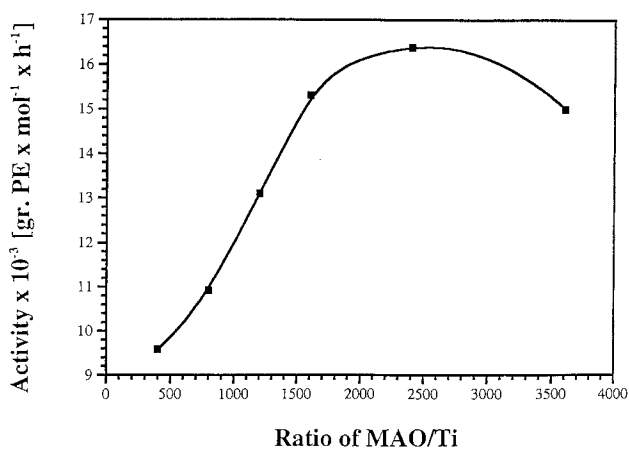
3. Discussion

The aim of this study was the synthesis of a constrained geometry titanium complex with a pendant amido group, bearing a functionalized anchoring arm for covalent attachment to inorganic supports. In addition, to study and to compare the homogeneous and heterogeneous complexes in the polymerization of α-olefins under a variety of conditions.

The synthesis of the ligand and the homogeneous titanium complex is straightforward if the homoleptic titanium amido complex and the neutral ligand are used as the starting materials. Attempts to prepare the lithiated version of the ligand were thwarted by the reaction of the methoxy groups with the strong base. Due to the high Lewis acidity of the titanium center,

Fig. 3. Ethylene polymerization of complex **1** as a function of the Ti/MAO ratio.

Table 2
Activity in the polymerization of ethylene for the homogeneous **1**/MAO system

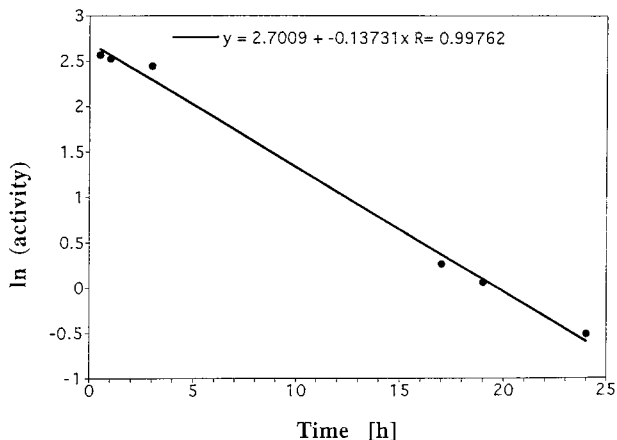| Entry	Ti:MAO	Activity $\times 10^{-3}$ (g mol^{-1} h^{-1})	Ti $\times 10^{-3}$ (mol)
1	1:400	9.50	0.01
2	1:800	10.90	0.01
3	1:1200	13.66	0.01
4	1:1600	15.37	0.01
5	1:2400	16.38	0.01
6	1:3600	15.01	0.01
7	1:800	4.90	0.024
8	1:800	10.92	0.007

Fig. 4. Polymerization activity for ethylene using complex **3** as a function of time.

the homogeneous complex was obtained as the Et_2NH adduct. The use of Group 4 $M(NR_2)_4$ complexes as starting materials in the synthesis of metallocene complexes was originally developed by Lappert et al. for unbridged metallocenes [40], widely used by others in the synthesis of *ansa*-cyclopentadienyl and indenyl complexes, and provides a more efficient preparation route than the salt elimination pathway [19,28a,41]. However, it is reported to be unsuitable for the preparation of $(C_5Me_4)Me_2Si('BuN)Ti(NMe_2)_2$, yielding a myriad of undesired products [19]. For the analogous complexes $(C_5H_4)Me_2Si('BuN)M(NMe_2)_2$ (M = Ti, Zr), the amine elimination route provides the best synthetic pathway although their conversion to the corresponding dichloride compounds was obtained as the dimethyl-amine adduct. For $(C_5Me_4)Me_2Si('BuN)Ti-(NMe_2)_2$ it seems that the bulky cyclopentadienyl and *t*-Bu moieties preclude the clean formation of the Ti complex whereas for complex **1**, the lower steric hindrance of the alkyl group attached to the nitrogen atom seems to compensate for the bulkiness of the tetramethylcyclopentadienyl moiety allowing the formation of the constrained geometry titanium complex. In a similar manner to $(C_5H_4)Me_2Si('BuN)M(NMe_2)_2$ (M = Ti, Zr), complex **1** is obtained as the amine adduct.

Anchoring the homogeneous complex **1** to partially dehydroxylated silica or alumina is achieved by the elimination of methanol and presumably the coordinate amine. Noteworthy is the fact that homogeneous Group 4 *ansa*-metallocene complexes react with equimolar amounts of alcohol with removal of one of the cyclopentadienyl rings [10]. For complex **1**, the reaction with methanol does not remove either of the Cp ligands and allows attachment to the surface through the silyloxy groups. Possibly, the open coordination at the metal center and the more coordinatively unsaturated complex causes stronger amido- and cyclopentadienyl-bonds to the Lewis acid titanium center. Due to the

reactivity of the inorganic surfaces, it can be also expected, in principle, that Et_2NH could be released from the complex forming a metal silyloxide bond with the surface (Fig. 6) or combination of Si–O– (Fig. 2) and Ti–O– (Fig. 6).

This pathway (Fig. 6) was believed to be a competing route in anchoring the complex to the surface, although no significant difference in the catalytic activity was observed between the homogeneous and heterogeneous complexes without special treatment (vide infra). This type of attachment could be responsible for the elimination of the homogeneous catalyst and the concomitant reduction in reactivity, as found when the heterogeneous catalytic system was treated and washed with MAO solution prior to reaction.

The activation of the homogeneous and heterogeneous precursors to the corresponding cationic methyl complexes was performed with an excess of MAO. At this stage of the discussion, it is important to point out that the requirement to transform the bisamido complex into the dimethyl complex, sometimes through the dichloro complex [19], is exclusively essential when cocatalysts such as perfluoroaryl boranes are in demand [13]. On the contrary, we have recently shown, for many homogeneous catalytic systems containing the starting bis (cyclopentadienyl) bisamido [41b,c], bisphosphido or bisarsenido [41d,e] early transition metal complexes, that the corresponding active cationic methyl complexes are obtained by using the cocatalyts MAO, avoiding the synthesis of the corresponding dimethyl or dichloro complexes. Thus, we have precluded our research, in this study, only to those complexes that are activated by MAO.

The catalytic activity in ethylene, propylene, and styrene polymerization of the supported and unsupported catalysts was rather similar in all cases. On the other hand, the use of different solvents had a strong influence on the polymerization reaction.

The activity of the catalysts for ethylene polymerization was higher in toluene than in CH_2Cl_2. Methylene chloride is a weakly coordinating solvent with a larger dielectric constant than toluene and should enhance ionic dissociation. For example, Dyachkovskii et al. found a higher activity for the polymerization of ethylene in CH_2Cl_2 than in aromatic solvents and suggested an increase in ionic dissociation [36,37a]. The increased polymerization activity in toluene may be due to η^6 coordination of the aromatic solvent to the cationic active species (Fig. 7). Although greater dissociation might be expected in CH_2Cl_2, the open coordination environment of this constrained geometry catalyst may allow cationic active species to react with the solvent to give the non-active form of the complex. Recently, we have shown that chiral benzamidinate titanium and zirconium methyl complexes react with CH_2Cl_2 to give the corresponding chloro complexes [37b].

Table 3
Molecular weight and molecular weight distribution for polyethylene, polypropylene and polystyrene prepared with homogeneous and heterogeneous constrained geometry catalysts

Entry	Catalyst	Olefin	Solvent	M_n	M_w	ρ
1	**1**	Ethylene	Toluene	3730	29120	7.8
2	**2**	Ethylene	Toluene	1120	1590	1.4
				84000	280990	3.3
3	**2**	Ethylene	CH_2Cl_2	73440	151740	2.1
4[a]	**1**	Propylene	Toluene	1180	1370	1.1
				56550	331480	5.9
5[a]	**2**	Propylene	Toluene	1500	1770	1.1
				27480	44370	1.6
				672210	905100	1.3
6[b]	**1**	Styrene	Toluene	33060	73850	2.2
7	**1**	Styrene	CH_2Cl_2	14200	723480	11.2
8	**2**	Styrene	CH_2Cl_2	21320	166400	7.8

[a] Performed at liquid propylene, 7.2 atm.
[b] 60°C.

The dependence of the activity on reaction time is shown in Fig. 4. It is known that MAO is involved in a fast equilibrium to generate the active species that are responsible for the higher activity in the initial state [32,33]. As a result, the olefin is able to coordinate to the cationic center initiating the polymerization process. Decay in activity with time has been found for other homogeneous systems [32–34], and several possible deactivation mechanisms have been postulated [18,31–33]. Once the polyethylene has reached a certain molecular weight, chain elimination normally occurs via β-H elimination to give a metal hydride, which has lower propensity for monomer insertion [32]. However, the presence of polymer molecules already generated in the reaction mixture may hamper the access of the monomer to the active site, and thus may also be responsible for such a drop in activity after the first hour [34]. Since the polymerization activity is propor-

tional to the number of active sites, and no bimolecular pathways are possible for the heterogeneous catalyst, first order deactivation is expected as observed in Fig. 4.

The variation in the concentration of Ti or MAO has an important influence on the activity of the reaction for the homogeneous catalyst, as indicated in Table 2. A decrease in the Ti concentration at a constant Ti/Al ratio results in an increase in the catalytic activity. It has been postulated that MAO, besides its role as a catalyst activator, can coordinate to the transition metal, stabilizing the active sites and preventing their deactivation [32,33]. The MAO reacts with the catalyst to give the cationic species, but rapid deactivation occurs in the case of low Al:Ti ratio. However, a slower deactivation process takes place at higher MAO concentration [33]. On the other hand, extremely high concentrations of MAO would hamper the access of the monomer to the catalytic center, or the use of low monomer pressure which will lead to diffusion-control process leading to a decrease in activity [33,42]. Based on these results it seems that above certain concentrations of MAO, the activity is not improved. For complex **1**, higher activities were found at lower Ti concentrations, probably due to better accessibility of the monomers to the active site. At higher concentrations of metal, a deactivation process occurs, presumably by dimer formation [18,32], and an increased precipitation of polyethylene takes place during polymerization, leading to a heterogeneous phase with a diffusion-control reaction [42].

Molecular weights of the resulting polymers are collected in Table 3. Heterogeneous catalysts showed a multimodal distribution of polymer weights (entries 2 and 5) characteristic of catalysts with different active centers. The heterogeneous catalysts also gave longer polymer chains than the homogeneous catalysts. The
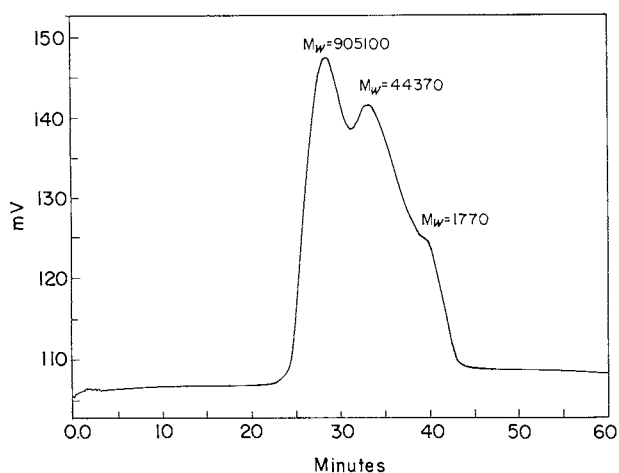
Fig. 5. Molecular weight and molecular weight distribution of heterogeneous based polypropylene (GPC chromatogram eluted with 1,2,4-trichlorobenzene at 140°C).
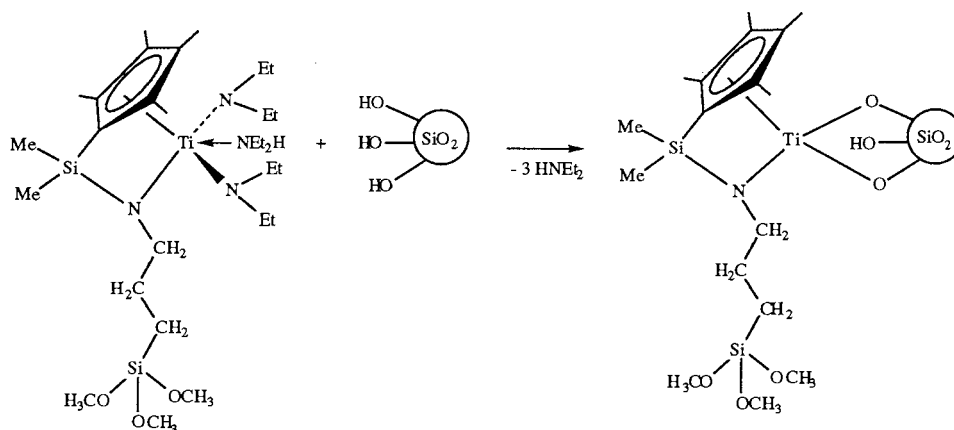
Fig. 6. Attachment of the complex **1** through the metal center.

immobilization of a metallocene complex on an inorganic carrier provides polymers with an increased molecular weight; the main reason for this is that β-hydrogen transfer cannot be catalyzed by a second titanocene center [39].

The polymerization of propylene yields an atactic polypropylene, as expected for a constrained geometry cyclopentadienyl catalyst [8–10], as the more open coordination site of the catalyst does not allow for much stereocontrol of the polymerization reaction. Nevertheless, it was recently reported that in homogeneous fluorenyl-constrained catalysts an inversion in the stereoselectivity of polypropylene is obtained from syndiotactic to isotactic polymers, on replacing MAO by a borane cocatalyst [14].

The principal mechanism found for the insertion of propylene was the 1,2-head-to-tail addition, although the presence of signals in the ^{13}C-NMR spectrum at 15–18, 30 and 35 ppm, characteristic of isolated 2,1

propylene units indicated that the insertion was not highly regular [35]. The known ability of the constrained geometry catalyst to reincorporate vinyl-terminated polymer molecules results in long-chain branch formation, the unsaturated ending being neglected [11,18]. The aluminum-transfer pathway can be excluded as the chain termination mechanism since the expected isobutyl signals in the ^{13}C-NMR are either not observed or extremely weak [35]. Molecular weight distributions for polypropylene are listed in Table 3. The extremely high molecular weight polymers obtained with the heterogeneous system corroborate the long-chain branches found by ^{1}H-NMR spectroscopy. The different polypropylene properties found in the homogeneous and heterogeneous systems show that although part of the complex may be released into the solution, the supported complex is able to yield polypropylene chains with higher molecular weight (M_w ca. 905 100) [34] than the homogeneous system.

The polymerization of styrene was achieved only on raising the temperature to 60°C in toluene. Syndiotactic polystyrene was formed under these conditions. The DSC curve and the ^{13}C-NMR spectrum are shown in Fig. 8. Two clear crystallization regimes of highly syndiotactic polystyrene are observed by DSC (the ^{13}C-NMR spectrum shows only one type of polymer), as corroborated by GPC measurements, which also showed signals for two different molecular weights. When the reaction was performed in dichloromethane, a cross-linked polystyrene was obtained. Surprisingly, the same type of polymer was obtained when the reaction was carried out without the catalyst. In fact, MAO is able to catalyze the polymerization of polystyrene with incorporation of the solvent into the polymer chain to give a cross-linked polymer, however the addition of the catalysts enhances this process by an order of magnitude. Polymers obtained with homogeneous and heterogeneous catalysts have different
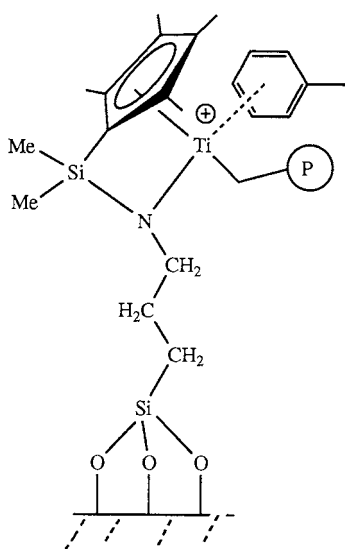

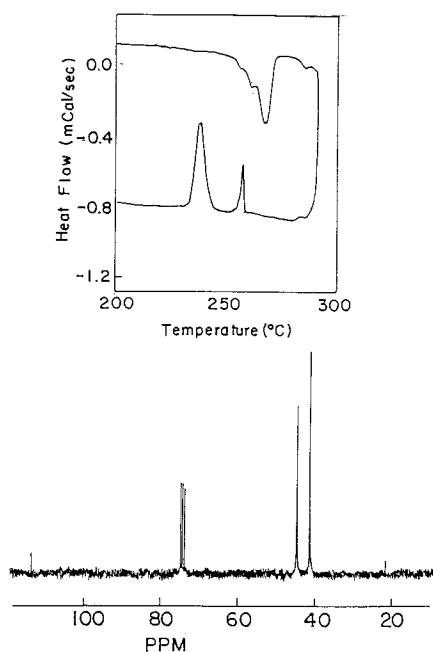Fig. 7. Arene coordination of the complex with the solvent.

Fig. 8. DSC curve and ^{13}C-NMR spectrum of polystyrene at 120°C on 1,3,4-trichlorobenzene and CDCl$_3$.

molecular weight distributions. The homogeneous-based polymers prepared in CH$_2$Cl$_2$ have higher polydispersity and M_w values than the corresponding heterogeneous-based polymers (entries 7 and 8; Table 3), whereas the values of M_n of the homogeneous-based polymers in toluene are much lower and have narrower molecular weight distributions than the homogeneous-based polymers obtained in CH$_2$Cl$_2$.

4. Conclusions

The main goal of this work was to develop an efficient synthetic route for *covalently* attaching a homogeneous titanium complex to an inorganic support and measuring its catalytic activity for the polymerization of α-olefins. Although different sites may be formed on the surface of the heterogeneous catalysts, the reactivity of the homogeneous and heterogeneous systems is rather similar. The covalent bonding between the pendant arm of the complex and the support provides a stable heterogeneous system. However, the release of part of the active sites cannot be excluded under the polymerization conditions, as the complex can be anchored either by the Si end group or to the Ti center. Although no major differences were found in the activity of the two types of catalysts, the polymer properties (molecular weights) were found to be rather different. In addition to the ability of constrained geometry complexes to give rise to long chain polymers, the immobilization of the complex provides polyethylene and polypropylene with much higher

molecular weight than the corresponding homogeneous complex.

5. Experimental

All manipulations of air sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual manifold Schlenk line, or interfaced to a high vacuum (10^{-5} Torr) line, or in a nitrogen-filled 'vacuum atmosphere' glovebox with a medium-capacity recirculator ($1–2$ ppm O$_2$). Argon, ethylene, propylene and nitrogen were purified by passage through an MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Styrene was freshly distilled under CaH$_2$, kept in the dark and vacuum transferred to another flask prior reaction. Ether solvents were distilled over argon from sodium benzophenone ketyl. Hydrocarbon deuterated solvents, C$_6$D$_6$ and CDCl$_3$, were distilled over nitrogen from Na/K alloy while C$_2$D$_2$Cl$_4$, 1,2,4-trichlorobenzene, BuLi, NH$_2$(CH$_2$)$_3$Si(OMe)$_3$ and Me$_2$SiCl$_2$ were used as obtained from Aldrich. The complex Ti(N(CH$_2$CH$_3$)$_2$)$_4$ [28a] and Li(C$_5$Me$_4$H) [28b] were prepared by literature procedures. All solvents for vacuum line manipulations were stored in vacuum over Na/K alloy in resealable bulbs. NMR spectra were recorded on a Bruker AM 200 spectrometer. Chemical shifts for ^{1}H- and ^{13}C-NMR were referenced to internal solvent resonances and are reported relative to TMS. The NMR experiments were conducted on Teflon valve-sealed tubes (J-Young) after vacuum transfer of the solvent in a high vacuum line.

5.1. Synthesis of compounds

A sample of Li(C$_5$Me$_4$H) (0.11 mol) was placed in 200 ml of THF at $-78°$C and 14.19 ml (0.11 mol) of Me$_2$SiCl$_2$ was added via syringe under argon. The mixture was allowed to warm to r.t. and stirred overnight, then THF was removed in vacuum leaving C$_5$Me$_4$HSiMe$_2$Cl as a yellow liquid. Hexane was added to the mixture, and LiCl precipitated. The white solid was washed several times with hexane and filtered, hexane was removed in vacuum and the crude product was vacuum distilled at 60°C, 0.01 mm Hg.

A sample of Cp'HSiMe$_2$Cl (5.78 g, 0.027 mol) was dissolved in 100 ml of hexane and cooled to $-78°$C. A sample of NH$_2$(CH$_2$)$_3$Si(OMe)$_3$ (12 ml, 0.054 mol) was added via syringe and the reaction mixture was stirred overnight at r.t. The ammonium chloride salt was removed by filtration under argon and the solvent was removed by vacuum yielding the product as a yellow oil.

^{1}H-NMR (C$_6$D$_6$, 25°C): $\delta = -0.54$ (s, 6H, Si(CH$_3$)$_2$), 0.58 (t, 2H, $J = 6$ Hz, CH$_2$–CH$_2$Si), 1.48 (m, 2H,

CH$_2$CH$_2$CH$_2$), 1.77 (s, 6H, CpCH$_3$), 1.90 (s, 6H, CpCH$_3$), 2.60 (m, CH$_2$NSi), 2.69 (m, 1H, NH), 2.75 (m, 1H, CH), 3.4 (s, 9H, CH$_3$O). ^{13}C-NMR (C$_6$D$_6$, 25°C): $\delta = -2.2$ (SiCH$_3$), 6.88 (CH$_2$Si), 11.42 ((CH$_3$)$_4$C$_5$), 14.65, ((CH$_3$)$_4$C$_5$), 25.50 (CH(Cp)), 28.19 (NH$_2$CH$_2$CH$_2$), 45.19 (NCH$_2$CH$_2$), 50.26 (OCH$_3$), 132.2, 135.6 (Cp).

5.2. Preparation of (C$_5$Me$_4$)SiMe$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$Ti(NEt$_2$)$_2$

A total of 2.5 mmol of C$_5$Me$_4$HSiMe$_2$NH (CH$_2$)$_3$Si(OCH$_3$)$_3$ was added via syringe to 2.5 mmol of Ti(NEt$_2$)$_4$ dissolved in 40 ml of toluene at -70°C. The mixture was heated under reflux overnight and the product was obtained as a clear brown oil after the by-products were removed at 130°C under high vacuum.

^{1}H-NMR (C$_6$D$_6$, 25°C): $\delta = -0.64$ (s, 6H, Si(CH$_3$)$_2$), 0.6 (t, 2H, $J = 6$ Hz, CH$_2$CH$_2$Si), 1.03 (m, 18H, NCH$_2$CH$_3$ amide, and HN(CH$_2$CH$_3$)$_2$ adduct), 1.50 (q, 2H, $J = 6$ Hz, CH$_2$CH$_2$CH$_2$), 1.77 (s, 6H, CpCH$_3$), 1.90 (s, 6H, CpCH$_3$), 2.49 (m, 1H, NH), 2.60 (m, 2H, $J = 6$ Hz, CH$_2$NSi), 3.4 (s, 9H, CH$_3$O), 3.48 (m, 12H, NCH$_2$CH$_3$ amide, and HN(CH$_2$CH$_3$)$_2$ adduct). ^{13}C-NMR (C$_6$D$_6$, 25°C): $\delta = -2.17$ (SiCH$_3$), 6.94 (CH$_2$Si), 11.42 ((CH$_3$)C$_5$), 14.65 ((CH$_3$)C$_5$), 15.5, 15.65 (N(CH$_2$-CH$_3$)$_2$), 16.1 (HN(CH$_2$CH$_3$)$_2$), 28.24 (CH$_2$CH$_2$CH$_2$−), 44.28 (N(CH$_2$CH$_2$CH$_2$)), 45.19, 45.46, 45.65, 46.71 (N(CH$_2$CH$_3$)$_2$), 47.43 (HN(CH$_2$CH$_3$)$_2$), 50.32 (OCH$_3$), 136.7, 137.6 (Cp).

Anal. Calc. for C$_{29}$H$_{64}$N$_4$O$_3$Si$_2$Ti, C 56.1%, H 10.32%, N 9.03%. Found C 55.48%, H 10.24%, N 9.15%.

5.3. Preparation of supported catalyst

5.3.1. Preparation of C$_5$Me$_4$SiMe$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$Ti(NEt$_2$)$_2$/SiO$_2$ or Al$_2$O$_3$

To 0.5 g of SiO$_2$ (160 m^2 g^{-1}, 60 Å, 63–200 μm) which was heated at 300°C under vacuum for 2 h, 0.2 g of C$_5$Me$_4$SiMe$_2$N(CH$_2$)$_3$Si(OCH$_3$)$_3$Ti(NEt$_2$)$_2$ in 20 ml of toluene were added, the suspension was heated to 100°C and stirred overnight. After the removal of the solvent the solid was washed several times with 20 ml of toluene and dried under vacuum for 10 h. The supported catalyst was obtained as a yellow powder. The washing solution was vacuum distilled to verify that no free ligand was present. The same procedure was used for the preparation of the alumina (γ 90 m^2 g^{-1}, 63–200 μm) -supported catalysts.

5.4. Olefin polymerization

Ethylene and propylene batch polymerizations were carried out at r.t. in a 100 ml round bottom flask equipped with a magnetic stirring bar. In the glovebox, an appropriate amount of the complex or supported catalyst and MAO was placed in the flask in an Al:Ti ratio of 800:1. A measured quantity of dry toluene (20 ml) was quickly added via syringe. The flask was attached to the high vacuum line, pumped down and back-filled three times, the flask re-evacuated, and a certain amount of olefin (ethylene $\rho = 1$ atm, propylene $\rho = 7.2$ atm.) was introduced through an MnO and a Davison 4 Å molecular sieve column. After a measured time interval, the reaction was quenched by addition of 20 ml of HCl/MeOH. Polyethylenes were collected by filtration, washed with acetone and dried. Polypropylenes were dissolved in hexane and washed several times with H$_2$O and the solvent was vacuum removed. The ^{13}C- and ^{1}H-NMR spectra of the polypropylene were recorded in CDCl$_3$ at r.t. and in C$_2$D$_2$Cl$_4$ and 1,2,4-trichlorobenzene at 120°C. Polymerization of styrene was carried out in a 100 ml flask equipped with a magnetic stirrer. Measured amounts of catalysts and MAO were placed in the reactor and 1.5 ml of styrene and 20 ml of toluene were added to the reaction mixture. Polymerization was carried out at 50°C over 17 h. The reaction was stopped by adding 20 ml of HCl/MeOH, and the product was washed with acetone and hexane, filtered and dried. The ^{13}C-NMR spectrum of the polystyrene was measured in C$_2$D$_2$Cl$_4$ or 1,2,4-trichlorobenzene at 120°C.

5.5. Molecular weight analysis

The molecular weight of the polymers was measured by the GPC method using a Waters 150-CV Plus instrument containing a set of standard high temperatures columns, fitted with a refractive index detector against polystyrene calibration standards. The solvent 1,2,4-trichlorobenzene flows continuously through the set of columns at 140°C and a controlled rate. The polymer is injected into the solution at a position upstream of the columns and the detector is located downstream of the last column. For chromatograms with multimodal distribution, each of the peaks has been taken individually (base line analysis) to calculate each M_w and M_n.

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