Titanium Complexes for the Polymerisation
of
Ethene and ε-Caprolactone

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Academic Dissertation

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Abstract

The literature part of the thesis mainly reviews the results of the use of titanium catalysts for ethene and ε-caprolactone polymerisation. The behaviour of titanium catalysts bearing phenoxy-imino ligands has been the focus of more detailed investigations in ethene polymerisation. Reasons for the production of multimodal polyethene for a range of catalysts are also given. The experimental part of the thesis is divided into two sections based on the monomers used in the polymerisations: Part A (ethene) and part B (ε-caprolactone).

Part A: Titanium(IV) complexes bearing phenoxy-imino ligands are known to possess high ethene polymerisation activities after MAO activation. Depending on the ligand, the activities of the catalysts in polymerisation can vary between 1 and 44000 kg\text{PE}/(mol_{cat}\cdot h\cdot bar). Depending on the polymerisation temperature and the electronic and steric properties of the catalyst ligands, low to high molar mass values and uni- and multimodal polydispersity values can been observed. In order to discover the reasons for these differences, 22 titanium(IV) complexes containing differently substituted phenoxy-imino derivatives as bi- and tetradeutentate ligands were synthesised with high yields and used as homogeneous catalysts in ethene polymerisations. Computational methods were used to predict the geometry of the synthesised complexes and their configuration after activation. Based on the results obtained, the geometry of the catalyst together with the ligand substituents seem to play a major role in defining the catalytic activity. Novel titanium(IV) complexes bearing malonato ligands were also synthesised. Malonates are considered to be suitable ligand precursors since they can be produced by the simple reaction of any primary or secondary alcohol with malonylchloride, and thus they are easily modifiable. After treatment with MAO these complexes had polymerisation activities between 10 and 50 kg\text{PE}/(mol_{cat}\cdot h\cdot bar) and surprisingly low polydispersity values when compared with similar types of catalysts bearing the O\cap O chelate ligands.

Part B: One of the synthesis routes in the preparation of the above mentioned phenoxy-imino titanium dichloride complexes involved the use of Ti(NMe$_2$)$_4$ with a range of salicylaldimine type compounds. On reaction, these two compounds formed an intermediate product selectively and quantitatively which was active in the ring-opening polymerisation of ε-caprolactone. Several mono-anionic alcoholates were also combined with Ti(NMe$_2$)$_4$ in different molar ratios and used as catalysts. Full conversion of the monomer was achieved within 15 minutes with catalysts having a coordination number of 4 while after 22 hours full conversion was achieved with catalysts having a coordination number of 6.
Preface

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Helsinki, December 2006

Antti Pärssinen
List of original publications

The thesis is based on the following original publications, which are referred by Roman numerals I-V.


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<tr>
<td>Ar</td>
<td>aromatic</td>
</tr>
<tr>
<td>ε-CL</td>
<td>ε-caprolactone</td>
</tr>
<tr>
<td>CpA</td>
<td>monocyclopentadienyl-amino</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>D_p</td>
<td>degree of polymerisation</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>FDA</td>
<td>Food and Drug Administrator</td>
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<tr>
<td>FI</td>
<td>phenoxy-imino</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
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<td>i-Bu</td>
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<td>L</td>
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<tr>
<td>PCL</td>
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<td>trimethylaluminium</td>
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PART A

1. Introduction

“The new development had its inception near the end of 1953, when I, together with Holzkamp, Breil and Martina, observed—during only a few days of an almost dramatic course of events—that ethene gas will polymerise very rapidly with certain catalysts that are extremely easy to prepare, at 100, 20 and 5 atmospheres and, finally, even at normal pressure, to a high molar mass plastic.” This sentence was part of Karl Ziegler’s speech when he and Giulio Natta received the Nobel Prize in 1963.1 The elementary invention was conceived by Ziegler2 (1953) which was exploited by Natta who presented the production of stereoregular polypropene (PP) with Ziegler’s catalyst system in 1954.3 With these fundamental observations the production of polyethene (PE) and PP begun from 17000 tonnes world wide in 1958 and increasing yearly being produced in Europe 33 million tonnes in 2004.4

Due to the large scale manufacturing of PE and PP even slight improvements in the catalytic cycle can decrease expenses and help companies to defeat their competitors. The easiest way for studying the influences of ligands in polymerisation cycle is to prepare soluble metal complexes which are in the first instance easy to analyse. Secondly all of the soluble catalyst particles have a similar environment without disturbing factors from the carrier material which is typical for heterogeneous systems.5 Despite benefits achieved by using homogeneous systems their only application in commercial polymerisation processes at present is in the production of elastomers and very low density ethene copolymers which are soluble in the reaction medium.5 A more common route for industrial processes is the design of highly active catalysts in solution followed by their heterogenisation to a suitable carrier which can be used in e.g. slurry and gas-phase processes.6

Research of soluble catalyst precursors was dominated by zirconium based metallocenes7 (1984) until the invention of late transition metal complexes bearing bidentate diimine ligands8 (1995) and a highly active Group 4 catalyst family bearing salicylaldiminato ligands9 (1999). The latter group is a successful example of the sophisticated ligand oriented research on finding optimal steric and electronic properties for catalysts. In our concern was to explain the dramatic differences in polymerisation activities of bis(salicylaldiminato) titanium dichloride catalyst precursors and why the formed PE have molar mass distribution curve (MMD) with the multimodal nature. For this purpose we synthesised 17 bidentate and five tetradeutate titanium catalyst precursors and carried out ethene polymerisations with them. In addition molecular modelling was used to predict the structures of the neutral titanium
complexes and their corresponding cationic forms which are responsible for actual polymerisation.\textsuperscript{10}

2. Background

2.1 History of $\alpha$-olefin polymerisation catalysis

The first Ziegler type catalyst for ethene polymerisation was a combination of Et\textsubscript{3}Al and TiCl\textsubscript{4}(IV) where after mixing the titanium is reduced to solid TiCl\textsubscript{3} (III)(s) followed by absorption of liquid Et\textsubscript{2}AlCl on its surface.\textsuperscript{11} This heterogeneous catalyst produced PE with moderate activity having broad molar mass distribution. Natta succeeded in increasing the activity and selectivity of these Ziegler-catalysts by isolating the crystalline $\beta$-form of the titanium trichloride followed by activation with alkylaluminum compounds.\textsuperscript{12} This is of particular importance since $\beta$-TiCl\textsubscript{3} consists of fibrous single chains of TiCl\textsubscript{6} octahedras which provide stereospecific polymerisation of propene whereas the other three crystalline forms of TiCl\textsubscript{3} share layer lattices having multiple non-uniform sites.

The second major improvement in the catalytic properties of titanium complexes arose from the use of magnesium based supports like Mg(OH)\textsubscript{2} and MgCl\textsubscript{2}.\textsuperscript{13} The crystal structures of these magnesium compounds after modification were identical to $\delta$-form TiCl\textsubscript{3} which was essential for maintaining the stereoselectivity in propene polymerisation.\textsuperscript{14} The activities of these supported catalysts with additional Lewis bases were 400 times higher when compared with the first Ziegler catalysts.

Research concerning homogeneous catalysts for polymerisation in mild conditions began quite rapidly after the invention of heterogeneous titanium catalysts. In 1957 Breslow et al. tested alkyl aluminium activated bis(cyclopentadienyl)titanium dichloride complex in ethene polymerisation with poor success.\textsuperscript{15} The same catalyst was tested again with a new accidentally discovered co-catalyst (methylaluminoxane (MAO)) after 16 years by Long and Breslow.\textsuperscript{16} Subsequent studies revealed that the high activity was due to hydrolysis of the trimethyl aluminium, Al(CH\textsubscript{3})\textsubscript{3} caused by water. Kaminsky used new type of co-catalyst with zirconocene complexes and achieved a dramatic increase in polymerisation of ethene as well as propene.\textsuperscript{17} The major problem with propene polymerisation was that formed PP was amorphous (atactic) and hence its mechanical properties were not suitable for commercial products.\textsuperscript{18} In 1984 Ewen\textsuperscript{7a} and co-workers reported the formation of isotactic PP by the use of a bridged titanocene system\textsuperscript{19} (ansa-metallocene) and the following year Kaminsky et al. published details of the first rasemic zirconocene capable of the production of highly isotactic PP.\textsuperscript{7b} The benefits achieved with these soluble group IV metallocene complexes were superior
when compared with conventional Ziegler-Natta systems in terms of activity, stereocontrol, “single-site” nature and control of chain branching.\textsuperscript{7c, 7d}

The major disadvantage of group four metal based catalysts is their strong oxophilic behaviour which excludes the use of monomers bearing polar functionalties (acrylates, vinylalcoholates etc.) in the polymerisation process.\textsuperscript{20} Previous limitation and the problem of practically throughout studied and patented metallocene catalysts forced researchers to explore other transition metals and ligands suitable for polymerisation of \(\alpha\)-olefins and as well as polar monomers.

The first milestone in this non-metallocene catalysis area was achieved by Brookhart \textit{et al.} nickel and palladium based \(\alpha\)-diimine catalysts capable of polymerising ethene, higher \(\alpha\)-olefins and co-monomers of ethene and methylacrylate with high activity in 1995.\textsuperscript{8, 21} Three years afterwards Gibson and Brookhart published details of iron complexes bearing bis(imino)pyridine ligands which possessed exceptionally high polymerisation activities and hence are considered as a second milestone in development of non-metallocene catalysts.\textsuperscript{22} These highly active late transition metal complexes were bearing neutral ligands having imino functionality which was easy to prepare by one pot condensation reaction between any primary amines and aldehydes. Grubbs and co-workers reported the synthesis of neutral Ni(II) complexes bearing monoanionic salicylaldiminato ligands and their ethene polymerisations.\textsuperscript{23} These ligand precursors were combined with Group 4 metals and used in ethene polymerisation quite soon after their utilisation with nickel metal leading to the third major breakthrough in homogeneous olefin polymerisation catalysis. The best of these MAO activated bis(phenoxy-imino)ZrCl\textsubscript{2} catalysts (FI Catalysts) were competitive with zirconocene polymerisation catalysts.\textsuperscript{9j}

\textbf{2.2 Titanium complexes for \(\alpha\)-olefin polymerisation}

As pointed out in many reviews the comparison of direct polymerisation activity between catalysts is tricky. Firstly reaction parameters for polymerisations \textit{e.g.} temperature, pressure, time and concentration of the catalyst can vary largely and secondly the influence of the co-catalyst (MAO, different borates etc.) and their ratios with the metal centre can be significant.

The history of titanium catalysts utilized for polymerisation coincides with the history of modern time production of thermoplastic materials (PE and PP) which all started 1953 as a result of the invention of Ziegler and co-workers.\textsuperscript{2} The activities of these first generation heterogeneous titanium catalysts were 0.5-1 kg PP/g (cat.) which today after 50 years are above 100 kg PP/g (cat.).\textsuperscript{5}
The progress of homogeneous titanium catalysts for olefin polymerisation in an industrial scale has been very slow due to manufacturing problems.\textsuperscript{5} Homogenous systems were mostly used for performing detailed studies of the polymerisation mechanism of titanium precatalysts. The first actual catalyst soluble in media was the bis(cyclopentadienyl)titanium(IV)dichloride-dialkylaluminum chloride catalyst system which possessed low polymerisation activity (17 kgPE/Ti\textsubscript{mol}).\textsuperscript{15,24} After heterogenisation to a suitable carrier the catalytic activities were not improved and therefore the interest towards these titanocene catalyst precursors faded away.\textsuperscript{25}

The interest toward Group 4 metallocene complexes arose again after the discovery of the co-catalyst MAO which vastly increased catalytic activity, especially in the case of zirconocene complexes.\textsuperscript{7c} The activities of the corresponding titanium catalysts (Scheme 1, 1A) were 10 times less, being around 700 kgPE/Ti\textsubscript{mol}·bar and greatly less when compared with the best zirconocene catalysts.\textsuperscript{7c,26} These catalytic differences in particular led to the development of titanium catalysts with non-Cp based ligand precursors in 1988 when Uoi \textit{et al.} exploited CpTiCl\textsubscript{3} (Scheme 1, 1B) in the polymerisation of syndiotactic polystyrene.\textsuperscript{27} As a continuation of these mono-Cp systems Okuba published details of \textit{ansa}-monocyclopentadienyl-amino (CpA) titanium complexes (Scheme 1, 1C) which possessed remarkable copolymerisation properties for e.g. styrene and ethene leading to series of patents.\textsuperscript{28} Homopolymerisation of ethene with the corresponding borate activated CpA-Ti complex possessed an average activity of 1500 kgPE/(mol\textsubscript{cat}·h·bar)].\textsuperscript{29}

Catalytic improvements were achieved by using the amino group as an intramolecular donor in the CpTiCl\textsubscript{3} complex (Scheme 1, 1D). Catalytic activity high as 4900 kgPE/(mol\textsubscript{cat}·h·bar) was achieved by using MAO as a co-catalyst.\textsuperscript{30} The extra electron pair from the nitrogen atom stabilizes the cationic species and inhibits the deactivation procedure of the titanium(IV) species. In 1997 Marks \textit{et al.} published details of a titanium complex (Scheme 1, 1E) bearing the dianionic Cp-phenoxy ligand.\textsuperscript{31} This variation didn’t drastically influence the polymerisation and an activity of 2100 kgPE/(mol\textsubscript{cat}·h·bar) was achieved.

![Scheme 1. Cp based titanium complexes.](image-url)
The utilisation of N, O chelating compounds (salicylaldimine) with Group 4 metals increased the polymerisation activities of ethene to the same as level achieved with zirconocene catalyst precursors. Salicylaldimines were used initially as ligand precursors for nickel complexes in 1998 by Grubbs and co-workers in ethene polymerisation. The highest activity was a mere 40 kgPE/(mol\text{cat}\cdot h\cdot bar). The most interesting aspect of the complexes was the influence of the substituents on molar masses and polymerisation activities. Both were enhanced when ligands were bearing bulky substituents in the 3-position or an electron-withdrawing group (NO$_2$) in the 5-position of the salicylaldimino ring. Similar observations were made coincidently by workers at Mitsui Chemicals Inc. who patented the use of bis(salicylaldimino) Group 4 complexes for $\alpha$-olefin polymerisations in 1998. The ligand modification resulted in a period of few years many catalysts having extremely high activities. For zirconium the maximum activity is 9350 kgPE/(mmol\text{cat}\cdot h\cdot bar)$^9$h (Scheme 2, 1F) while for titanium it is 44000 kgPE/(mol\text{cat}\cdot h\cdot bar)$^9$e (Scheme 2, 1G) which is the highest activity for non-metallocene catalyst precursors among titanium based catalysts.

Many research groups have tried to achieve high activities with comparable titanium complexes bearing N, O chelating ligands but none of them has been successful. The MAO activated complex (Scheme 2, 1H) exhibited an activity value of 100 kgPE/(mol\text{cat}\cdot h\cdot bar) and after activation with borate showed enhanced polymerisation activity (5900 kgPE/(mol\text{cat}\cdot h\cdot bar)). Similar activities (5000 kgPE/(mol\text{cat}\cdot h\cdot bar)) were achieved with titanium complexes bearing two $\beta$-enaminoketonato ligands (Scheme 2, 1I). One third of the FI-catalyst activity was achieved by using a complex bearing two pyrrrolide-imine ligands where the phenoxy group was replaced by anionic nitrogen based pyrrolide group (Scheme 2, 1J). These compounds form 5-membered rings with metals instead of 6-membered ring as with phenoxy-imino complexes. It adopts a distorted octahedral structure in which two chlorine atoms are located cis to one another thus being similar with bis(phenoxy-imino)TiCl$_2$ complexes. As a continuation for complex 1J complex (Scheme 2, 1K) bearing two indoline-imine ligands was introduced. The chelate structure of 1K consist of a 6-membered ring which seems to have negative effect on polymerisation activities as only 1100 kgPE/(mol\text{cat}\cdot h\cdot bar) was achieved.

Another approach to catalyst design is to use only one phenoxy-imino (Scheme 2, 1L and 1M) or phenoxy-amide ligand (Scheme 2, 1N) bearing soft pendant donors (P, S). In these cases catalytic activity as high as 19000 kgPE/(mol\text{cat}\cdot h\cdot bar) was achieved. A recently published highly active titanium catalyst (Scheme 2, 1O) 12000 kgPE/(mol\text{cat}\cdot h\cdot bar) is also bearing modified salicylaldimine (dianionic phenoxy-amide) as a ligand while two dimethyamine groups released during synthesis are used as additional external donors. The influence of the substituents at the amido aryl fraction is the same as observed for
FI Catalysts. Changing the *ortho* methyl groups to chlorides enhances the polymerisation activity $70 \rightarrow 12000 \text{ kg}_{\text{PE}}/(\text{mol}_{\text{cat}} \cdot \text{h} \cdot \text{bar})$.

Scheme 2. Selected titanium complexes possessing high activities in ethene polymerisation.

Scheme 3. Ethene polymerisation activities in $\text{kg}_{\text{PE}}/(\text{Ti}_{\text{mol}} \cdot \text{bar} \cdot \text{h})$ of selected titanium precatalysts (1A-1O) reported in literature.
2.3 Solid state structures of bis(salicylaldiminato)TiCl₂ complexes

Schiff base Group 4 metal complexes have been known since the 60s, but it is only during the last ten years that they have attracted considerable attention as possible catalyst precursors for olefin polymerisation. The phenoxy-imine ligands are especially attractive as they are easily achievable via a classical imine condensation reaction between a suitable salicylaldehyde and any primary amine, and thus modification possibilities for these ligands are plentiful. These complexes bearing two non-symmetric bidentate ligands can theoretically possess five isomers arising from coordinating modes of ligands in an octahedral geometry (Scheme 4).

The solid state structures of all published bis(salicylaldiminato)titanium dichloride complexes possess a six-coordinate titanium metal centre in an distorted octahedral geometry with a cis-Cl disposition (Scheme 4, A-C). The nitrogen and the oxygen atoms of the salicylaldiminato ligand can be oriented either trans or cis to each other leading to three possible geometries for titanium complexes which will be presented as cis, ciscis and trans (Scheme 4) in this text. The cis geometry is common for the complexes bearing an ortho substituent at the phenoxy group e.g. t-butyl and SiMe₃. The ciscis geometry is rare and is found only in structures bearing a cumyl substituent next to the phenoxy oxygen. The trans geometry is found among complexes bearing aliphatic substituents (methyl and isopropyl) at the iminato fraction. Geometry D (Scheme 4) exists only among complexes bearing tetradentate ligands and no crystallographic data has been published for geometry E according to our literature search.

First task in studying the polymerisation behaviour of the phenoxy-imino titanium complexes was to compare the crystallographic data of the neutral dichloride complexes with their MAO activated ethene polymerisation results and try to find correlation between them (Scheme 5 and 6).
Scheme 5. Titanium complexes (2A-2H) and herein synthesised complexes 2 and 7 and their ethene polymerisation activities after treatment with MAO. The chloride ions and the second ligand are removed for clarity.

The catalyst precursors (2C, 2D and 2G) presented in Scheme 5 all of which have cis-geometry possess the highest polymerisation activities in the series. The desired cis-geometry can be easily achieved by using ligand precursors bearing bulky t-Bu substituents at the phenoxy moiety. By using a phenoxy group without substituents increasing the size of the aryl group at the imino moiety trans-configuration is achieved (2B and 2). The behavior of the titanium complexes in solution can be significantly different when compared with the solid state structures. By choosing the right ligand precursors complexes can have a combination of isomers at different ratios.45

A comparison of the Cl-Ti-Cl bond angles of the complexes revealed that a narrow ~90° angle is most likely connected to low activity. This is evident for the complexes 2F and 2 which both have methyl substituents at imino groups. What is surprising is that these two complexes possess different geometries (2F=cis and 2=trans) and despite of this fundamental difference in geometry the angle between chlorides is almost the same (Scheme 6). The bond distances of Ti-Cl vary quite much among the selected complexes (2.24Å-2.36Å) and in many cases even the chloride ions attached to same metal possess unequal bond lengths revealing a

<table>
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distortion in the octahedral structure (Scheme 6). Generally it can be said that a short Ti-Cl bond distance indicates a weaker coordination of phenoxy-imino ligands which is known to enhance catalytic activities.\textsuperscript{9e} In the complexes 2C and 2G this bond shortening is clearly a result of the presence of fluorine substituents at the imino group. The complexes 2H, 2 and 7 having longer Ti-Cl bonds can polymerise ethene only with low activity. It is obvious that certain trends can be observed from the crystallographic data, however major conclusions cannot be drawn from these observations as the influence of the co-catalyst (MAO and borates) on polymerisation activity has not been taken into account.

\textbf{Scheme 6.} Cl-Ti-Cl bond angles and corresponding bond distances of titanium complexes (2A-2H, 2 and 7).

\textbf{2.4 Polymerisation of multimodal PE by transition metal complexes}

Traditionally the geometry of the complex is considered to be rigid enough to hold their stereochemical structure after activation with co-catalysts (MAO) (Scheme 7).\textsuperscript{46} This assumption remained unchallenged until Fujita \textit{et al.} published details of their dicumyl
substituted phenoxy-imino zirconium precatalyst. The MAO activated complex was capable of controlled production of uni-, bi- and trimodal PE (Figure 1), all of which after mathematical calculations were found to have gained PDI values of ~2 implying a single site polymerisation mechanism. 

Scheme 7. Schematic representation of the formation of the cationic species of bis(phenoxy-imino)TiCl₂ by treatment with TMA/MAO solution and propagation step in the polymerisation of ethene.

Figure 1. Molar mass distribution curve of PE polymerised with bis(phenoxy-imino)ZrCl₂ complex at different temperatures.

After these observations Fujita et al. ruled out some of factors which may have been causing the multimodal behavior. Firstly, they changed the Al/Zr ratio and since no noticeable effect on MMD was observed neither a chain transfer to MAO nor acid-base interaction between MAO and the heteroatoms of the ligands can be responsible for defining MMD. Secondly, the
results of recent investigations on the decomposition of activated complexes where either alkylation or reduction of the imine function by alkylaluminum or by intramolecular alkyl group migration from the metal centre. These explanations were excluded due to the fact that a benzylic proton did not appear in the $^1$H NMR spectra. This gives rise to the question of whether the different isomers can be responsible for the catalytic behavior of bis(salicylaldiminato) Group 4 transition metal complexes. Evidence of differing coordination spheres around the zirconium atom in two separate complexes was obtained by Fujita et al. using $^{15}$N NMR at three different temperatures (Figure 2). They observed that paired peaks indicating *ciscis*-configuration had more fluxional nature than the *cis* peak due to the fact that they coalesced at lower temperatures and the sharp singlet from the *cis*-configuration was broadened only slightly even at 50 °C indicating a rigid structure. These preliminary investigations were carried out with neutral dichloride complexes and no real data concerning the activated species were included.

Figure 2. $^{15}$N-NMR studies of bis(salicylaldiminato) zirconium complexes.

One year later the same research group published a work focused on dried MAO (DMAO) activated complexes. They managed to prove that during activation two different imine fractions are formed (Figure 3). The one marked with (*) can be a source of the active species. The peak marked by (●) is caused by a decomposition product which when present prevented polymer formation. The formation of this inactive species was possible avoid by doing the activation in the presence of a monomer which led to formation of new imine signal marked as (+) which was assigned as a cationic propagation species of $L_2Ti^+(CH_2CH_2)_nCH_3$. Brintzinger et al. developed a procedure for analyzing the activation by using $^{13}$CH$_3$ enriched MAO, thus decreasing the amount of undesired resonances in the $^1$H NMR spectra. In the NMR studies they used MAO with three different Al:Ti ratios (10, 15 and 50) which led to the formation of $L_2TiMeCl$ species (signal 2 in spectrums b and c in figure 3) with ratios of 10 and 15. When the ratio was increased to 50 (d spectrum in figure 3) the formation of a new
species was observed as broad signal which is assigned as active ion pair of [L₂TiMe(S)]⁺MeMAO⁻ (signal 3 in spectrum d). After introducing the ¹³C-enriched ethene to the ion-pair the resonance marked at position 3 in spectrum d was split two signals. After a short period the signal near 9.0 ppm disappeared and the remaining imine resonance was assigned to the cationic propagation species [L₂TiP⁺MeMAO⁻. No explanation for the disappearance of the imine signal was given. These sophisticated NMR studies of the activation procedure did not reveal any information which could provide an explanation for the multimodal behavior of PE; however the split resonance of 3 in spectrum d may indicate changes in geometry during activation.

Figure 3. Activation studies of phenoxy-imino Group 4 complexes carried out with ¹H NMR by Fujita (spectra on the left) and by Brintzinger (spectra on the right).

In the ¹H NMR spectrum of the MAO activated FI-complex (Figure 3) the signal marked as 3 in spectrum d splits into two imine signals. This may be a result of the formation of ciscis-configuration during activation or formation of the bimetallic complex where the original configuration of the ligands has changed. Prior to dissociation the bimetallic complex may form two different catalytic species and hence polymerise multimodal PE. There are no experimental data supporting this theory among FI Catalysts, however the existence of the bimetallic species was verified by NMR with MAO activated Group 4 metallocenes (Scheme 8) and in monoanionic dichelate titanium complexes.
Supportive information related to the appearance of bimetallic systems in polymerisation was achieved by Yan et al. who published details of a dimeric nickel complex bearing two dichelate ligands bridged via two chloride ions (Figure 4).\textsuperscript{50} They managed to control the modality of PE by varying both the Al/Ni ratio and temperature (Figure 5). At the critical co-catalyst/metal ratio the formed PE was clearly bimodal and by keeping the Al/Ti ratio constant the profile of MMD changed along with temperature from bimodal (0 °C) to broad unimodal (40 °C). According to their explanations for the production of multimodal PE there are several active centres with the most active being deactivated at elevated temperatures causing a decrease in polymerisation activity and the loss of the high $M_w$ fraction. The assumption that the varieties in molar mass are related to the ratio between the rate of the chain transfer and the rate of the chain propagation was also given.

It is possible that after treatment with MAO this bimetallic nickel complex decomposes to two separate catalytic species having different ligand environment thus causing the multimodal behaviour or alternatively MAO may form an intermediate with bimetallic nickel compound having two different active catalytic centres. The molar mass values achieved with nickel catalyst at different temperatures look similar with herein introduced 3/MAO (Figure 10).

Figure 4. Schematic presentation of [2-methyl-2,4-bis(2'-pyridyl)-1H-1,5-benzodiazepine]$_2$NiCl$_2$.\textsuperscript{53}
An interesting phenomenon was observed by Coates et al. during the polymerisation of propene with titanium FI Catalysts prepared by a combinatorial system. One combination polymerised syndiotactic PP having 92 % r-dyad placement in the polymer chain according to a Bernoullian statistical model. Cavallo and co-workers explained that the tacticity is caused by the fluxional behaviour of the octahedral chiral site. This phenomenon was described earlier by Jordan et al. with complexes bearing ancillary bidentate pyridine-phenoxy ligands using NMR studies (Scheme 9). In definite conditions dissociation of N-Ti bond appears followed by facile inversion of configuration. Multimodal PE can appear if the transformation of the catalyst species proceeds at a much slower rate than chain propagation implying that the intermediate can be one of the active polymerisation species. There is no experimental evidence for this however also all of the FI Catalysts polymerising syndiotactic PP have narrow PDI values.

Scheme 9. Facile inversion of configuration at the titanium bearing bidentate pyridine-phenoxy ligands.
In studies of the activation and deactivation of the phenoxy-imino catalysts two new catalytic species were discovered, in both of which the imino functionality is decomposed and altered to amine bearing benzyl or \(-\text{Bu}_2\text{Al}\) groups. In the first new catalytic species the benzyl derivate of tetradientate titanium complex possesses rapid 1,2-migratory insertion at the imine co-ligand changing the neutral coordination of nitrogen to an anionic one (Scheme 10).\(^{54}\) This clearly deactivates catalysis due to the loss of one coordination place. Whether or not the intramolecular imine reduction cause the low activity of tetradiotate Schiff-base Group 4 catalysts in \(\alpha\)-olefin polymerisation is unknown.

Scheme 10. Intramolecular 1,2,-migratory insertion of benzyl derivative to imine group. Second unchanged phenoxy-imino ligand was left out for clarity reasons.

The \(-\text{Bu}_2\text{Al}\) mentioned in the previous paragraph is part of \(\text{Ph}_3\text{CB(C}_6\text{F}_5)_4/i\text{-Bu}_3\text{Al}\) co-catalyst which can reduce imine to amine without loss of the coordination site which is required for polymerisation (Scheme 11).\(^{55}\) The aluminium compound on the amine nitrogen has an influence on the bonding energy of the nitrogen atom to metal, on the direction of phenyl substituents reflecting to the polymerisation activity and the properties of formed PE. Comparable behaviour with MAO activated complexes have not yet been published and the question remains open whether the TMA adduct at MAO solution can work as reducing agent.

Scheme 11. Reduction of imine nitrogen by \(-\text{Bu}_3\text{Al}. Second unchanged phenoxy-imino ligand was left out for clarity reasons.
3. Experimental

In this work easy and high yield synthesis routes for production of bis(phenoxyl-imino)TiCl₂ and titanium complexes bearing malonate ligands were studied. These complexes were utilized for ethene polymerisations after treatment with co-catalyst MAO.

From herein syntheses of all compounds and all complex syntheses were performed under argon atmosphere using standard Schlenk techniques and dry solvents. The ligand and catalyst precursors used for ethene polymerisation were characterized and are fully described in the experimental parts of the attached original publications.

3.1 Syntheses of salicylaldimines

Imine ligand precursors (Scheme 12) were prepared via a classical condensation reaction between aldehydes and amines (Scheme 13). Salicylaldimines (a-d and g-j) can be efficiently prepared by simply mixing of salicylaldehyde and corresponding aliphatic or aromatic amine in the absence of solvent and heating the mixture at 110 °C for overnight in a flask open to air. The imines (e, f, k and m-o) were synthesised from volatile or fluorine containing starting materials prepared in a closed flask in toluene at 100 °C in the presence of anhydrous sodium sulfate and catalytic amount of sulfuric acid. The imines having solid starting materials (p-v) were solvated to appropriate amount of toluene followed by heating at 110 °C for overnight in a flask open to air. The 3,5-Bis(α,α’-dimethylbenzyl)salicylaldehyde (starting material for compounds p, q and v) was prepared according to literature procedure.57
Scheme 12. The salicylaldimine ligand precursors.

Scheme 13. A schematic representation for synthesis of salicylaldimines.

3.2 Syntheses of malonates

Ligand precursors diethylmalonate and diethylphenyl-malonate were used as received (Scheme 14), while diphenylmalonate was prepared by dropwise addition of a phenol in toluene solution to a cooled (0 °C) malonyl chloride in toluene solution (Scheme 15). The reaction mixture was warmed to room temperature and stirred overnight. The reaction was then terminated by addition of water followed by neutralization with KHCO₃-solution. The organic phase was separated, dried with Na₂SO₄ and the solvent was removed under reduced pressure.
Scheme 14. The malonate ligand precursors.

Scheme 15. A schematic representation for synthesis of malonates.

3.3 Syntheses of titanium(IV) complexes bearing phenoxy-imino ligands

In the preparation of bis(salicylaldiminato)titanium(IV) dichloride complexes (Scheme 21) the aim was to find an easy and effective synthesis route to avoid complicated and lengthy purification processes. The traditional synthesis method described in the literature is the reaction of TiCl₄ with 2 equivalents of the lithium salt of the phenoxy-imine (Scheme 16).⁹ By this method the desired titanium complexes are obtained in moderate to good yields (20-80 %) depending on the chosen ligand precursor. An alternate synthesis exists in preparation of salicylaldiminato complexes (Scheme 17) although its use has been limited to one case according to our information.⁴⁰a It is performed by treatment of titanium tetrachloride with 2 equivalents of N-phenylsalicylaldimine in the presence of triethylamine with loss of 2 equivalents of HCl. The yields achieved were above 60 %. Both of these synthesis routes require filtration and the yields achieved are unsatisfactory.

Scheme 16. A schematic representation of reaction of TiCl₄ with 2 equivalents of the lithium salt of the phenoxy-imine ligand precursor (R is any aromatic or aliphatic group).
Scheme 17. A schematic representation of the reaction titanium tetrachloride with 2 equivalents of N-phenylsalicylaldimine in the presence of triethylamine.

In an ideal situation complexation can be performed in a one-pot procedure. An essential requirement for this is that all intermediate and side products be volatile and removable under mild conditions. Three different methods are used to achieve this.

In the first method a silylated phenolic hydroxyl group is used in complexation with TiCl₄ which leads to the formation of the trimethylsilyl chloride (bp. 75 °C) which can be readily removed under low pressure (Scheme 18). A common silylating reagent is Me₃SiCl but its use in this context would require extra reagents to avoid contact of liberated HCl with imine nitrogen which can lead to the formation of the undesired intramolecular iminium salt. To avoid salt formation 1,1,1,3,3,3-hexamethyldisilazane is used. Residues (bp. 125 °C) as well as the by-product 1-trimethylsilylamine (bp. 57 °C) can be easily removed in vacuo after formation of the desired silyl compound.

Complex preparation with silyl-substituted ligand precursors has some limitations. The silylated phenoxy-imine compounds react rapidly and unselectively with TiCl₄. This phenomenon was observed e.g. in the complexation of the silylated ligand precursor a. Together with the desired 1:2 complex (L₂TiCl₂), complexes with the stoichiometry LTiCl₃ and L₃TiCl were also observed. The unselectivity is caused by the lack of steric bulkiness in the aniline substituents. When ligand precursors (c and d) bearing bulky substituents were used the complexation proceeded selectively with nearly quantitative yields. The second disadvantage of silazane is that it requires space when forming silyl compounds and therefore all reactions where the phenoxy group was bearing a bulky substituent located in ortho position e.g. t-Bu failed. The complexes 3, 4₀, 4, 10, 11, 13 and 14 were prepared by this synthesis route.
Scheme 18. A schematic representation of the silylation reaction with 1,1,1,3,3,3-hexamethyldisilazane followed by complexation with TiCl₄ (R is any aromatic or aliphatic group).

In the second complex synthesis route Ti(NMe₂)₄ was utilized for compounds bearing ortho phenoxy substituents (g-i, p and q) and for all tetradentate ligand precursors (r-v). Titanium complexes bearing amido groups can react directly with compounds containing a phenolic hydroxyl proton followed by cleavage of dimethylamine (Scheme 19). This method led to smooth formation of the bis(salicylaldiminato) Ti(NMe₂)₂ complexes and proceeded with higher selectivity than with the previous method. Despite the low boiling point of the released (Me)₂NH, the complete removal of this by-product was unachievable even after an extended period under vacuum at 50 °C. This might be due to partial coordination of dimethylamine to the titanium complex as this occurs with ligands bearing non bulky substituents.

Titanium amido complexes are known to be less active catalyst precursors in ethene polymerisation than their dichloro derivatives, and hence the obtained bis(salicylaldiminato) Ti(NMe₂)₂ complexes were converted directly to the corresponding bis(salicylaldiminato)TiCl₂ complexes using an excess of chlorotrimethylsilane. The chlorinated complexes formed selectively and quantitatively. The amido complexes containing coordinated dimethylamine reacted with Me₃SiCl and formed an unidentified salt, the existence of which was possible to observe using ¹H NMR. The salt was removed by refluxing the complex solution in toluene followed by evaporation of the solvent in a high vacuum. When the coordinated (Me)₂NH was removed completely the only by-product from the chlorination procedure was Me₃SiNMe₂, which was easy to remove by high vacuum at 70 °C or by recrystallization of the corresponding bis(salicylaldiminato)TiCl₂ complex. The complexes 1⁴⁰a, 2, 5-9 and 16-20, 21⁴⁴e and 22 were prepared by this synthesis route.
Scheme 19. A schematic representation of the direct metallation synthesis between Ti(NMe₂)₄ and the corresponding ligand precursor (R is any aromatic or aliphatic group).

In the third complex synthesis route two equivalent of salicylaldimine (1 and o) reacts directly with one equivalent of TiCl₄ which leads to the quantitative formation of the bis(salicylaldiminato)TiCl₂ complex (12 and 15). As described earlier only the intramolecular iminium salt was achieved by this method which requires further treatment with external base to attain the desired 2:1 titanium dichloride complex. In the synthesis of the complex 12 and 15 the lone electron pair of the nitrogen at the imine group is capable of coordinating directly to titanium and hence salt formation is avoided.

3.4 Synthesis of titanium(IV) complexes bearing malonato ligands

Malonates (compounds w-y) are not acidic enough to be deprotonated by the methods described above therefore sodiumhydride (NaH) was used in this synthesis step (Scheme 20). After successful salt formation the sodium salt was introduced to a cooled TiCl₄ solution and the reaction mixture was stirred overnight at room temperature. The pure complex (23-25) was isolated as a red powder with high yields (~90%).

Scheme 20. A schematic representation of synthesis of titanium complex bearing diethylmalonate (compound w).
Scheme 21. A schematic representation of all the titanium complexes presented in this thesis.
3.5 Solid state structures of titanium(IV) complexes

The X-ray crystal structure analysis of complex 7 (Figure 6) bearing t-butyl substituents at the phenoxy fractions and benzyl substituents at imine group revealed a distorted octahedral geometry where the nitrogen and the chlorine atoms form the basal plane and the oxygen atoms of the phenoxy groups complete the coordination sphere of the Ti centre by occupying the axial positions with a dihedral angle of 168.48°. The chlorides have cis-orientation with a Cl-Ti-Cl bond angle of 96.85° and almost equivalent bond lengths (2.30 and 2.31 Å).

![Figure 6. Molecular structure of complex 7 with thermal ellipsoids at 50 % probability level. All hydrogen atoms are removed for clarity.](image)

The solid state structure of complex 2 (Figure 7) possesses trans geometry and it has an almost symmetrical octahedral coordination located in the plane of the O₂Cl₂. The apical vertices of the coordination octahedra are occupied by nitrogen atoms, while the equatorial positions are occupied by both oxygen and chloride ions. The atoms in the plane are oriented cis to each other with bond angles of (O-Ti-O) 92.98° and (Cl-Ti-Cl) 89.90°. The octahedral coordination of Ti is accomplished by a trans-orientation of the iminato nitrogen atoms with the dihedral angle (178.69°).

Interesting observations were made when structural properties of complex 2 and complex 3 were compared (Figure 7). First of all the Ti-N bond lengths are shorter in complex 2 than in complex 3 due to the fact that there is only slight distortion in the dihedral angle (1.3°). The shortening of the Ti-N bonds has a direct influence on Ti-Cl bond lengths which are 0.03 Å longer in complex 2 than in complex 3. Surprisingly these changes in the bond lengths of Ti-N and Ti-Cl do not affect the Ti-O distances which are almost the same in both complexes. Despite the similarities in Ti-O bond lengths, the O-Ti-O angles are less similar being 92.98° and 88.5° for the complexes 2 and 3 respectively. As expected the bulky substituents at the
iminato fraction in complex 3 force the N-Ti-N angle away from the theoretical 180° to 171.7° and simultaneously widen the Cl-Ti-Cl angle to 93.8°.

Figure 7. Solid state structure of complex 2 (left). All hydrogen atoms are removed for clarity. The solid state structure of complex 3 (right) *Inorganica Chimica Acta*, 2000, 300-302, 816.

When complex 9 was exposed to air, red crystals suitable for X-ray determination were obtained at room temperature from a saturated toluene solution (Figure 8). The formed complex is a dimer containing an anionic oxygen bridge between two titanium centres which is a result of the cleavage of two equivalents of hydrogen chloride. Both titanium centres with their surrounding atoms were mirror images of each other. The oxygen atoms of the phenoxy group were oriented *trans* to each other and the O-Ti-O angle amounts to 161.76°. Due to decomposition of the monomeric complex the cleavage of two 3-phenyl-1-propylamine groups and the formation of two salicylaldehyde ligands were observed.

Figure 8. The half molecular structure of the partly decomposed complex 9. All hydrogen atoms are removed for clarity.
Structural analysis revealed that in complex 23 titanium has a distorted octahedral coordination sphere, where the two chlorine atoms adopt the cis-configuration and the oxygens from malonato ligand fill the vacant coordination places (Figure 9). Bond lengths of Ti-O1 and Ti-O2 are 1.94 Å and 2.02 Å respectively which are more than 0.1 Å longer than the Ti-O bonds in phenoxy-imino titanium complexes. The angle (O1-Ti-O1) 164.9° is common for similar distorted octahedral structures. The Ti-Cl bond lengths are equivalent (2.271 Å) and the angle between them is 96.71°. Good correlation between interatomic distances and angles are found when comparing malonate complexes to similar dibenzoylmethanate titanium complexes since both can only adopt a single isomer. The bulky phenyl groups of the methanate ligand precursor increase the distortion of O-Ti-O by 2° when compared with the corresponding malonato bond angle. The distortion also has an influence on the Cl-Ti-Cl angle which is roughly 7° wider in malonato than in methanate (90.0°) while the bond lengths of Ti-Cl which are equal in the malonate complex have a difference of 0.155 Å in the methanate complex.

Figure 9. Molecular structure of the complex 23. Hydrogen atoms are removed for clarity. ORTEP plot of 23 with thermal ellipsoids drawn at 50 % probability level.

3.6 Ethene polymerisation behaviour of titanium(IV) complexes

Polymerisations were performed in a Büchi 1.0 L stainless steel autoclave equipped with Julabo ATS-3 and Lauda RK 20 temperature controlling units. Toluene (200 ml) and the co-catalyst (MAO) were introduced to the argon purged autoclave reactor. Once the polymerisation temperature had been reached, the reactor was charged with ethene to the appropriate pressure. Polymerisation was initiated by injecting 20 cm³ of the catalyst precursor solution (5-20 μmol solution in toluene) into the reactor. Mechanical stirring was applied at a speed of 800 r.p.m. During the polymerisations both the partial pressure of ethene and the temperature were maintained constant. Ethene consumption was measured with a calibrated mass flow meter and monitored together with the autoclave temperature and
pressure. The polymerisation reaction was terminated by pouring the contents of the reactor into methanol, which was then acidified with a small amount of concentrated hydrochloric acid. The solid polyethene was collected by filtration, washed with methanol and dried overnight at 70 °C.

### 3.6.1 Ethene polymerisation behaviour of MAO activated titanium complexes bearing bi- and tetradaentate phenoxy-imino ligands

Bis(salicylaldiminato)titanium dichloride complexes are an interesting group of catalyst precursors for a number of reasons. 1) The activities in ethene polymerisations vary between 1 and 4600 kg_{PE}/(mol_{Ti}⋅h⋅bar) (Scheme 22). 2) Depending on polymerisation conditions uni-, bi- and trimodal polyethene have been obtained. 3) All complexes revealed distorted octahedral geometry and regardless of the ligand precursor, chloride atoms were situated in cis positions which is a requirement for active α-olefin polymerisation catalysts. There are three possible structural isomers whose existence depends on the orientation of the nitrogen and oxygen atoms around titanium metal. 4) Some of the complexes have a tendency to change their coordination sphere in conjunction with temperature and the ligand framework. Also unsurprisingly the quantity of different molar mass areas in a multimodal PE curve varied with temperature.

Our aim was to discover the correlation between the structure of the catalyst and activity and to find a rational reason as to why discrete MAO activated catalysts polymerised multimodal PE. The research was started by utilizing the unsubstituted bis(N-phenylsalicylaldiminato)TiCl₂ complex for polymerisation due to the fact that it has only simple phenyl substitution on the imine nitrogen. 1/MAO was used as a reference catalyst. As pointed out previously temperature has a major role in polymerisation and therefore based on this knowledge three different temperatures for polymerisation were used (40, 60 and 80 °C). Traditionally, higher monomer pressures increase activities rectilinearly but because the catalytic behavior of the MAO activated phenoxy-imino titanium complex is unique the effect of pressure response was also studied in the range 3 bars to 10 bars.

The activity of 1/MAO was 67 kg_{PE}/(mol_{Ti}⋅h⋅bar) at 60 °C and 3 bar and rose constantly with increasing monomer pressure. When the pressure was kept constant at 5 bar, the activity was enhanced with elevated temperatures and the maximum 143 kg_{PE}/(mol_{Ti}⋅h⋅bar) was achieved at 80 °C. It is worth of mentioning that the molar mass curve was bimodal, consisting of two equal areas without overlapping. Otherwise the general trends were that polymerisations done at 40 °C produced unimodal PE while at 60 °C bimodal PE with strong overlapping was produced. Molar mass values were centered on three areas 200, 300 and 800 kg/mol.
Catalyst 2/MAO carrying additional 2,6-methyl substituents at the iminato fraction had activities of less than 10 kg_Pe/(mol_Ti⋅h-bar) in all polymerisation conditions and molar masses of PEs were twice as high than those obtained with 1/MAO. All GPC chromatograms represented polymers with unimodal polydispersities. Tailing toward a low molar mass region was enhanced at elevated temperatures causing an increase in polydispersity values. It is important to note that 2/MAO was the only catalyst in the present study to produce unimodal PE in all conditions.

The replacement of methyl substituents with isopropyl ones further increases the steric conquest around the active metal centre and results in quite interesting polymerisation behavior for 3/MAO. The polymer produced was clearly bimodal and the relative ratios between two molar mass areas varied as a function of temperature (Figure 10). The polymerisation carried out at 40 °C resulted in the strongly overlapping bimodal distribution curve having a PDI value as high as ~14. At 60 °C the amount of low molar mass PE was decreased leading to a M_w value above 1000 kg/mol. At 80 °C the molar mass of the PE was 600 kg/mol having a PDI value of 9. Polymerisation activities were at all conditions less than observed with 1/MAO, being around 20 kg_Pe/(mol_Ti⋅h-bar). Naphthyl substituted 4/MAO behaved similarly to 3/MAO.

The replacement of ortho substituents of aniline with difluoro ones brings about considerable changes in catalyst performance. At 40 °C the activity of 5/MAO was 165 kg_Pe/(mol_Ti⋅h-bar) and when the temperature was increased its activity decreased to the same level as with catalyst 1/MAO. This, together with the fact that the molar mass distributions were considerably expanded, having a bimodal behavior at higher temperatures might indicate changes in the active catalytic species (Figure 11). 5/MAO showed a rather linear...
enhancement of the activity with increasing ethene pressure. In fact, the highest activity for 5/MAO of 265 kg\text{PE}/(mol\text{Ti} \cdot h \cdot \text{bar}) was achieved at 100 °C and 10 bars. At lower ethene pressures the catalyst tended to produce polymers with bimodal molar mass distributions but with sufficient monomer concentrations (10 bar) single-centre behavior of the catalyst appeared and polydispersities of the polymers remained below 2 at all used temperatures (40→100 °C).

![Figure 11. GPC profile of PE obtained by complex 5/MAO at different temperatures.](image)

In general, 6/MAO showed similar trends to 5/MAO in terms of variation of the polymer properties with changes in the polymerisation conditions. However it was slightly more tolerant to thermal changes. The bimodal distribution curve was only observed only at 80 °C with 5 bar pressure and the chromatogram consisted of two overlapping curves with equal areas (Figure 12). Surprisingly the MMD curve achieved with 1/MAO was similar when using the same polymerisation conditions. The catalyst 6/MAO showed relatively high activity, 713 kg\text{PE}/(mol\text{Ti} \cdot h \cdot \text{bar}) and gave polyethene with the highest molar mass (2000 kg/mol).

![Figure 12. GPC profile of PE obtained by complex 6/MAO at 80 °C with 5 bars.](image)
After studying the effect of phenyl substituted ligands on polymer properties the next step was to investigate the effect of ligands bearing aliphatic substituents at the iminato nitrogen on polymer properties. The work began by testing complexes bearing sterically undemanding groups (\textit{i}-Pr and \textit{t}-Bu) at the imine group or at the phenoxy \textit{ortho} position (13-15/MAO). These complexes produced PE with activities of less than 30 kg\textsubscript{PE}/(mol\textsubscript{Ti} \cdot \text{h} \cdot \text{bar}). Only the PEs polymerised with 13/MAO were analysed and there was no observable trend in MMD or PDI values.

When the size of ligands around the metal atom were increased by using the bulky adamantyl group at the iminato fraction the activity of 10/MAO increased to slightly above 100 kg\textsubscript{PE}/(mol\textsubscript{Ti} \cdot \text{h} \cdot \text{bar}) while all molar mass curves were broad and multimodal. All efforts to increase activity by keeping adamantyl group constant and varying the substituents at the phenoxy \textit{ortho} position failed. The fluorine and \textit{t}-Bu groups actually decreased activities to levels below 40 kg\textsubscript{PE}/(mol\textsubscript{Ti} \cdot \text{h} \cdot \text{bar}). The next attempt at increasing activity involved keeping the phenoxy group constant while varying the iminato fraction by using different sized aliphatic chains linked to phenyl ring. This approach finally resulted in highly active catalysts.

Good monomer response was not achieved with MAO activated 7 which yielded low activities the maximum being 40 kg\textsubscript{PE}/(mol\textsubscript{Ti} \cdot \text{h} \cdot \text{bar}) at 80 °C. Undoubtedly, the catalyst 7/MAO also has different active centres; at 3 bar ethene pressure two separate molar mass areas appeared in the GPC chromatograph (Figure 13), the lower fraction of which decreased with increasing monomer concentration. We can assume that this particular phenomenon is linked to the benzyl substituent, which tend to block the active site at lower pressures. At higher ethene concentrations this trend fades away.

![Figure 13. GPC profile of PE obtained by complex 7/MAO at 60 °C with 3 bars.](image-url)
The catalyst 8/MAO possesses an ethyl group which acts as a link between the phenyl group and the imine nitrogen. This small structural change has a dramatic influence on the catalytic activity. Activities as high as 1700 kgₚₑ/(molₜₐₚ⋅h⋅bar) were observed while polymerisation properties of the catalyst resemble those typical for single site catalysts e.g. metallocenes. The polydispersity values were around two and the obtained molar masses varied between 200 and 600 kg/mol. Further lengthening of the space between the imino nitrogen and the phenyl ring was found to have a deteriorating effect on catalytic activity. The average activities recorded for 9/MAO bearing a propylphenyl imino substituent were in the range 220-1100 kgₚₑ/(molₜₐₚ⋅h⋅bar) and were depend on the polymerisation temperature. This catalyst also produced PE with unimodal and narrow polydispersities as is typical for single site catalysts.

The complexes 16/MAO and 17/MAO bearing bulky cumyl substituents at the phenoxy moiety had similar polymerisation behavior to that of 7/MAO and 8/MAO respectively. The bulky cumyl substituents enhanced the polymerisation activity of the 17/MAO to 6000 kgₚₑ/(molₜₐₚ⋅h⋅bar), the highest in the present study while with the 16/MAO only 40 kgₚₑ/(molₜₐₚ⋅h⋅bar) was achieved.

Regardless of the applied polymerisation temperature and monomer pressure, the polymerisation activities of all tetradeutate Schiff-base titanium complexes (18-22) possessed very low activities 1-6 kgₚₑ/(molₜₐₚ⋅h⋅bar). Interestingly for these complexes is the phenoxy ortho substituent has no influence on polymerisation activities. This behaviour is quite opposite with titanium complexes bearing bidentate ligand precursors. MAO activated titanium complexes (18-22) produced; in general, PE with uni- and bimodal distribution curves. The catalyst 22/MAO, bearing cumyl substituents, differs from the rest of the catalysts in that it has slightly increased activity 10-20 kgₚₑ/(molₜₐₚ⋅h⋅bar) and it produces trimodal PE at any polymerisation conditions (Figure 14). The MMD curve of PE made at 80 °C consists of three separate, almost equal molar mass areas with each of them having narrow PDI values (1.5-2.0). The molar mass of the polymer at the high Mₜₐₚ-part is around 1 000 kg/mol, in the middle the Mₜ is around 30 kg/mol, while it is only a few thousand kg/mol at the low Mₜₐₚ-part. The relative sizes of these molar mass areas are dependent on the polymerisation temperature.
3.6.2 Ethene polymerisation behaviour of MAO activated titanium complexes bearing malonic acid ester based ligands

After activation with MAO, catalyst 23 yielded activities of 55 and 57 kg\textsubscript{PE}/(mol\textsubscript{Ti}\ h\ bar) in polymerisations made at 40 and 60 °C respectively. At 80 °C the catalyst productivity was diminished to 34 kg\textsubscript{PE}/(mol\textsubscript{Ti}\ h\ bar). The 24/MAO catalyst system produced PE with an average activity of 25 kg\textsubscript{PE}/(mol\textsubscript{Ti}\ h\ bar) at all chosen polymerisation conditions. Complex 25 showed the lowest activity in the series, being less than 20 kg\textsubscript{PE}/(mol\textsubscript{Ti}\ h\ bar). All catalysts produced PE with high or ultra high molar masses, the \textit{M}_w values varying between 900 and 3000) kg/mol. The molar mass distributions of formed PE are rather narrow (2-4) when compared with the molar mass distributions of PE produced with related \textit{cis}-\textit{β}-diketonate catalysts (PDI=26).\textsuperscript{63} What was lost in the control of the polydispersity values was gained in the polymerisation activity. The latter catalyst precursor produced PE with activity high as 600 kg\textsubscript{PE}/(mol\textsubscript{Ti}\ h\ bar).

Scheme 22. The best ethene polymerisation activities achieved with each herein introduced catalyst precursors 1-25.
3.7 NMR–studies of phenoxy-imino titanium complexes

The first evidence for a change in geometry was observed with a titanium complex bearing a tetradentate ligand by $^1$H-NMR studies (Scheme 23). The complex 19 bearing amido co-ligands possesses octahedral geometry with a cis-N, trans-O and cis-NMe₂ disposition. After amine elimination by trimethylsilylchloride the stereochemical arrangement changed to cis-configuration (N, O and Cl). This was possible to observe in the $^1$H-NMR spectra due C₂-symmetric amido complex has one singlet resonance for the imino protons while the corresponding dichloride complex possesses C₁-symmetry with two singlet resonances of equal intensity for the imino protons.

Further investigations were carried out with bis(phenoxy-imino) titanium complexes to explore whether or not this fluxional behaviour was present, however all of the investigated complexes with the exception of complex 9 proved to be rigid enough to hold their structural configuration during converting process. Complex 9 possessed a cis-geometry as an amido complex and after conversion to the chloride form $^1$H-NMR (CDC₃) spectra revealed three singlets with intensity ratios 1:4:1 corresponding to a mixture of cis- and ciscis-isomers (2:1). If the volatile side products were removed by refluxing in toluene in high vacuum the intensity ratio of cis to ciscis-isomers changed to 5:1 indicating that the relative stabilities of the different isomers were temperature dependent.

To gain more detailed understanding about fluxional behaviour of 9, dynamic $^1$H-NMR (C₆D₅Br) measurements were carried out. In spectrum of 9 at room temperature there are three resonances arising from CH=N protons ligands and an aromatic signal at the same region 7.65 ppm (Figure 15). The imine proton signals, 7.805 and 7.66 ppm, can be assigned for ciscis-configuration (C₁-symmetry) isomer while the third imino signal at 7.73 ppm can be
assigned for cis-configurations (C₂-symmetry) isomer. With increasing temperature the signals arising from cis-cis imino protons approach the signal at 7.73 ppm. This is in accordance with the observed changes between the cis and cis-cis-conformer ratios during the above described purification process and underlines the dynamic changes in the coordination sphere of the complex.

Figure 15. Dynamic ¹H-NMR spectra of complex 9.

3.8 Theoretical calculations of phenoxy-imino titanium catalysts

As observed in the previous chapter the bis(phenoxy-imino) titanium complexes can alter their configuration upon heating (complex 9) and during changing of amido groups to the corresponding chloro ones (complex 19). It was in our interest to discover if a similar phenomenon was present in the polymerisation procedure because of the fact that the ratios of molar mass areas in multimodal PE (Figure 14) can change with temperature.

Because only a few crystal structures could be solved in this work, computational methods (Hartree-Fock (HF)/3-21G*) were used to solve the structures of selected bis(phenoxy-imino)TiCl₂ complexes (Table 1). The solid state structures of the calculated L₂TiCl₂-type complexes are in a good agreement with those measured experimentally by X-ray diffraction. By comparing the polymerisation activities with the geometries of the neutral complexes, a clear dependence can be observed, the catalyst precursors preferring imine nitrogen atoms in the cis-isomer are more active in ethene polymerisation than those having trans-configuration. This observation does not however provide the answer to the question of what will happen after activation and why the PE can have uni- and bimodal distribution curves. Therefore, the stability of the bis(salicylaldiminato)Ti⁺-Me species (Table 1) was the subject of further
calculations as the stability of the cationic complex is one of the crucial parameters, which determines polymerisation activity.

According to the data the relative stability of the structural isomers can change after activation, e.g. complex 8 prefers cis-orientation but for the cation the trans-isomer is responsible for the highest stability. The question is: Does the species responsible for the catalytic activity have the same conformation as the corresponding dichloro complex. Whenever the conformation of the complex is changed dissociation of one of the coordination bonds should occur, after which a rotation of the ligand can take place. This provides the option for the cis or trans-isomers to convert directly to the ciscis-isomer, which is also the required intermediate isomer whenever the exchange between cis- and trans-isomer takes place. Taking this possibility into account, the observed activities as well as the multisite behaviors of the complexes can be rationalized.

Complex 1 prefers cis–conformation and after MAO activation it produces polyethylene with moderate activity. At low polymerisation temperatures 1/MAO gives PE with unimodal PD while at higher temperatures bimodal behavior is apparent. According to the calculations all cationic isomers have same stabilisation energy. It is possible that the energy barrier between cis- and ciscis-isomers is exceeded at 80 °C which leads on to two stable catalytic species. This would explain the fact that the formed PE consisted of two clearly unconnected molar mass areas.

Both the neutral and cationic form of complex 2 prefer the trans-isomer configuration since the ciscis-isomer is significantly higher in energy, it is plausible to assume that the geometry of the catalyst remains as the initial trans-conformer with high stability. This assumption is in accordance with the observed low activity and unimodal behavior of the catalyst. The neutral complex of 3 favors the trans-conformer while in its cationic form the cis-isomer is most favorable. Due to the fact that ciscis- intermediate is low in energy, such a change in the coordination sphere is easily achievable which is reflected in the polymerisation behavior of 3/MAO. This interchange of catalyst geometries can be seen as a broad bimodal distribution curve in prepared PE.
Table 1. The relative stabilisation energies in kJ/mol of the different isomERIC structures of the dichloro complexes $E_{\text{Rel}}(\text{Cl}_2)$ and their cationic forms $E_{\text{Rel}}(\text{Ti}^+\text{Me})$. The most stable isomer has been marked. In calculations the trans-isomer of each catalyst precursor has been chosen as a point of reference. The complexes (1-6) are bearing aromatic imino substituents. The complexes (7-13) are bearing aliphatic imino substituents and complexes 18, 19 and 21 are bearing tetradentate ligands.

<table>
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<th>$E_{\text{Rel}}(\text{Ti}^+)$</th>
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The presence of electron withdrawing fluoro substituents on aniline is considered to be highly beneficial as they give the catalyst precursors with the highest activities. We have assumed that the coordination between imino-N and Ti weakens (5 and 6) during activation and therefore affords intramolecular exchange from cis to trans even at low temperatures (Figure 16). The trans-isomer is not stable enough at higher polymerisation temperatures of 60 °C and 80 °C and ciscis-conformation with higher stability control the polymerisation leading to lower activities (Scheme 24). This change in configuration can be avoided by increasing monomer pressure to 10 bars where the precatalyst 5 can hold its trans-configuration at all temperatures and hence only unimodal PE is observed.
Figure 16. HF-calculated structures of the most stable isomers as a neutral dichloride complex (right) and corresponding cationic one bearing methyl co-ligand (left).

Scheme 24. Schematic representation of the catalytic behavior of complex 5. At 40 °C high polymerisation activity was achieved (trans-conformation). At 60 °C low polymerisation activity was observed (ciscis-conformation). At (10 bar, 60 °C) polymerisations again possessed high activity (trans-conformation).

The alkylphenyl substituted catalyst precursors 7-9 have a similar activation profile to complexes 5 and 6 which have high polymerisation activities (Table 1) and indeed, complexes 8 and 9 also possess high polymerisation activities as expected (Scheme 22). Interestingly however, complex 7 bearing the benzyl group as a substituent at the imine nitrogen has a very low level of catalytic activity. A similar observation was made by Choukroun et al. who reported the detrimental effects of the presence of alkyl substituents at the amido fraction on the catalytic activity. They suggested that the alkyl groups increase steric congestion and therefore actively hinder the activation of the neutral dichloride complex by the co-catalyst.61 The influence of the benzyl group was also studied with unbridged metallocene catalysts; the benzyl substitution can retard the catalytic activity via coordination from the ortho-carbon of
the phenyl ring to the cationic metal centre. In the solid state structure of complex 7, the benzyl substituents are pointing outward from titanium due to the cis-geometry (Figure 6). According to the calculations, the trans-geometry is however preferable for the corresponding methylated cation (Table 1). This structural transformation brings the benzyl substituents into the vicinity of the titanium centre and gives them an opportunity to interact. This can also occur with the cis-cis-conformer (Figure 17).

Figure 17. Space filling of atoms at complex 7 showing steric hindrance in cis-cis- and trans-configurations caused by benzyl derivatives. Chloride atoms are represented by (orange), carbon (gray), hydrogen (yellow) and oxygen (red).

Catalysts 8/MAO and 9/MAO bearing ethyl and propyl groups respectively as phenyl substituents at the imino fraction have a reduced possibility of metal-phenyl interactions. The energetically favored anti-staggered configuration of the carbon chains forces the phenyl rings away from the metal centre in trans-conformer, leading to high polymerisation activities (Figure 18).

Figure 18. Stick representation of complex 8 (trans) calculated by HF. Chloride atoms are presented by (orange), carbon (gray), hydrogen (yellow) and oxygen (red).
A series of alkyl substituted complexes bearing sterically bulky adamantyl or small \textit{i}-Pr groups at imine fraction were prepared to demonstrate a unique feature of the alkyl phenyl substituents. Complex 10 with the adamantyl substituents favors \textit{cis}-geometry both for the dichloride and for the methyl cation. In ethene polymerisations 10/MAO established average activities of \(\sim 100 \text{ kgPE/(molTі\cdot h\cdot bar)}\) connected with broad (MMD) values up to 19 indicating multi-centre behavior of the catalyst. The steric conquest around the catalytic metal centre was increased by adding the electron withdrawing fluorine group at the phenoxy 3-position. As a result of the presence of these substituents, 11 favors the \textit{trans}-geometry both in the dichloro as well as in the cationic form which as observed earlier with catalyst 2/MAO decreased activities to very low level, being below 40 \(\text{ kgPE/(molTі\cdot h\cdot bar)}\) at all polymerisation conditions.

Catalyst 12 bearing the \textit{t}-Bu group which has been known to increase catalytic activity had a similar activation profile with complex 3 and hence low polymerisation activities were achieved 10 \(\text{ kgPE/(molTі\cdot h\cdot bar)}\). The isopropyl group, as a model for the small alkyl substituent at the imine nitrogen, was also studied. Catalyst 13 having also similar calculated profile with complex 3 revealed low activities less than 30 \(\text{ kgPE/(molTі\cdot h\cdot bar)}\) and produced non symmetric multimodal MMD at all polymerisation conditions.

In our studies on a series of non-bridged bis(phenoxy-imino) titanium catalysts it can be concluded that the highest activities in ethene polymerisation are achieved with complexes where the imino nitrogens have possibility for dissociation and hence alter their stereochemical configuration (Scheme 25). In order to find more supporting information for the phenomenon titanium complexes (18, 19 and 21) bearing rigid tetradentate ligand precursors where the nitrogen atoms are forced to remain coordinated and thus the dissociation of Ti-N cannot take place were utilized for ethene polymerisation. Ab initio calculations concerning the relative stabilisation energies of the bridged complexes (18, 19 and 21) are in agreement with the experimental results. The relative stabilisation energies of the \textit{cis} and \textit{ciscis}-conformers are very close to one other. Thus, depending on the conditions, they can both be present in a solution. Similarly, when activated, both isomers of the cationic species have the same stability. Thus at certain polymerisation conditions, PE with bimodal or unimodal with slightly broadened distribution curves is expected. As predicted the catalytic activities were all below 30 \(\text{ kgPE/(molTі\cdot h\cdot bar)}\). All data related to activation are shown in scheme 19 where it can be observed that only a \textit{cis}\(\rightarrow\text{trans}\) change in geometry yielded highly active catalysts.
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Scheme 25. The most stable configurations of neutral titanium dichloride complexes and their corresponding cationic ones according to calculations.
PART B

4. Introduction

Rising quantities of plastic waste materials have started to become a worldwide problem. Almost 60% of plastic waste in Western Europe has been accumulating in landfills. The remaining 40% consists of mechanical and feedstock recycling together with energy recovery.63 The general concern in relation to environmental issues has launched research with the aim of finding biodegradable polymers which decompose in controlled circumstances to water, carbon dioxide and biomass.64 At the moment their properties are close to thermoplastics but their manufacturing processes are too expensive when compared with the production of traditional plastics (PE, PP, PS and PVC).65 These biodegradable polymers e.g. PCL, PLA, PGA and PHA are ideal for medical applications (sutures, tissue engineering, bone fillers and controlled drug delivery) and for agricultural purposes (mulches, seeding trips, plant pots and tapes) and are already commercially available.66 In this context our interest towards the production of biopolymers arises because the titanium complexes used in ethene polymerisation are suitable for use in the polymerisation of cyclic esters. As an additional benefit a small number of these titanium complexes have already been accepted as food additives according to the FDA and are therefore possible to use in vivo.

5. Background

The first preliminary investigations focused on the polymerisation of cyclic esters were performed by Bischoff and Walden in 1893.67 They described the transformation of glycolide, under the influence of heat or a trace of zinc chloride, into a polymeric solid polyglycolide (PGA) melting at 220 ºC. Almost 40 years after the first ring-opening polymerisations Natta et al. invented the now commonly used poly-ε-caprolactone (PCL) and polylactide (PLA) polyesters.68 They observed that rapid polymerisation of ε-caprolactone (ε-CL) and lactide without any catalyst appears at 250-275 ºC. The polymers formed showed molar mass of about 4000 and 3000 g/mol respectively. In the presence of potassium carbonate a similar effect was observed at lower temperatures (~150 ºC).

The development of new catalysts for ring-opening polymerisation (ROP) of different cyclic esters was rather slow. The major reason for this was that all aliphatic polyesters investigated at that time (50’s) were susceptible to hydrolytic degradation and therefore no suitable application related to the decomposition of polymers was invented. Most of the catalysts for
ROP published in the 60’s provide the foundation for ongoing academic research in the area of biopolymer production.

In 1958 when Schneider et al. published an article focused on the polymerisation of different kinds of cyclic esters with selected catalyst precursors e.g. lead stearate and the combination of NaH and N-acetylcycloalactam. The following year Union Carbide Corp. published details of a series of catalysts based on tin compounds having the formula of X₂SnO or X₂SnY₂, in which X is e.g. alkyl or aryloxy radical and Y e.g. OH radical. Tin catalyst precursors are still in extensive use due to the fact that some of them are approved as GRAS (Generally Recognized as Safe) by the US Food and Drug Administration.

In 1962 Union Carbide Corp patented organometallic compounds having the formula of MR₁, where M is Li, Na, K, Rb or Cs and R₁ is e.g. hydrocarbyl radical. These catalysts possessed high catalytic activity in ROP of ε-caprolactone. After a few minutes of polymerisation at room temperature they produced polymers with molar mass above 250 kg/mol, and the conversion of monomer to polymer was, in general, nearly quantitative. A new set of compounds capable of ROP were introduced in patent by Farbenfabriken Bayer AG in 1964. They used the organometallic catalysts Et₂Zn, Et₂Cd; Et₃Al, Bu₃Al and Grignard compounds such as MeMgCl and PhMgBr in the polymerisation of substituted and unsubstituted ε-caprolactone.

The forerunner in catalyst design (Union Carbide Corp) published in 1965 details of a new and interesting set of catalysts having the following formulas: Al(OR)₃, where OR is an alkoxy radical and M′M″H₄ hybrid catalysts e.g. LiAlH₄. These compounds possessed high catalytic activity both in homo- and co-polymerisation of different cyclic esters.

5.1 Titanium catalysts for ring-opening polymerisation of ε-caprolactone

The first reports on the use of titanium complexes in ROP was published in 1958 by Hall and Schneider however no experimental data was included in the report that time. In 1970 the first titanium complexes were used for ring-opening polymerisations of different lactones by Union Carbide Corp. Polymerisation of e.g. ε-caprolactone gave a high molar mass linear polymer when using Ti(O-i-Pr)₄, Ti(C₁₈H₃₇O)₄ or Ti(O-n-Bu)₄. Almost two decades after the Carbide patent in 1988 Kricheldorf et al. published experimental data of polymerisation of cyclic esters with Ti(O-n-Bu)₄. A few years later Okuda et al. published details of a titanium complex of the general formula Ti(Ind)Cl₂OMe which possessed low activity in ROP. The catalytic activities were quite low however and the ε-caprolactone required over night polymerisations at 100 ºC to achieve full conversion. The research focused on finding
They achieved 100 % monomer conversion with the catalyst bearing the t-Bu group (Scheme 26, 3A) in 5 hours at 25 °C when 100 equivalents of ε-CL was added. Changing the phenoxy ortho substituent to phenyl (Scheme 26, 3B) led to a decrease in the catalytic activity to (1/4 of 3A) but better control of the MMD was gained resulting in a polydispersity of 1.1. According to GPC measurements the degree of polymerisation (Dp) of the polymers was almost half of the monomer/metal ratio suggesting that both isopropoxide groups initiate polymerisation. In continuation of Aida’s work Harada et al. published (2002) complexes with an extra donor atom (sulphur) in the biaryloxy backbone (Scheme 26, 3C). The effect of the extra donor on the catalytic activity and selectivity was negative. On comparison of molecules where either isopropoxide or chloride was the initiative group polymerisation results were clearly favoring the former. The initiating group evidently has a major role in ROP.

In 2004 Harada et al. used amido ligands in aryloxy titanium complexes and observed a slight decrease in activities compared with isopropoxo containing ligands (Scheme 26, 3D). During this year several publications have appeared where new ligand types are introduced. In the most significant of them, Bounor-Legare et al. published details of ε-CL polymerisations with Ti(O-n-Pr)₄ and Ti(OPh)₄ which possessed the highest activities so far amongst titanium based catalysts. Full conversion of monomer was achieved in less than ten minutes with both catalysts at 100 °C with the monomer/metal ratio of 300.

The best activities achieved with titanium catalyst are for electron poor complexes having a maximum coordination number of 4 e.g. Ti(OPh)₄. All attempts to achieve high polymerisation activities using complexes with higher coordination numbers have failed. The titanium complexes bearing the aryloxy or isopropoxide group can be considered as excellent initiators when compared with the corresponding chloro or amido ligands. The polymerisation temperature has a major role in defining activity. When polymerisations are carried out at
room temperature full conversion with a ratio of 100 can take 5 to 24 hours while at 100 °C polymerisations with the same catalyst are over in 10 minutes.

5.2 Mechanism of ring-opening polymerisation of \(\varepsilon\)-caprolactone

Polymerisation of cyclic esters can be carried out using several methods. In anionic ROP initiators such as hydroxides, alkoxides and oxides of alkaline and earth alkaline metal are used.\(^{81}\) The reaction involves the nucleophilic attack of a negatively charged \(\text{tert}\)-butoxy group on the carbonyl carbon resulting in a negatively charged alcoholate attack on the potassium cation (Scheme 27). The disadvantages of anionic polymerisation are related to the problems in controlling the molar mass and the equilibrium reaction between linear polymers and cyclic oligomers.\(^{81a}\)

![Scheme 27. The reaction mechanism of the initiation and chain growing of the polymer chain of PCL with KO-\(\text{tert}\)-Bu.](image)

The cationic polymerisation can be initiated by different acids, alkylating agents and acylating agents.\(^{82}\) The reaction involves the formation of a positively charged species which is subsequently attacked by a monomer (Scheme 28). The attack results in a ring-opening of the positively charged species through an S\(_{N2}\)-type process.\(^{82c}\) The disadvantage of cationic polymerisation is that it is difficult to control and often only low molar mass polymers are formed.
Scheme 28. The reaction mechanism for the cationic ring-opening polymerisation.

\[(P^+A^- \text{ can be } e.g. [\text{EtZn(OEt}_2\text{)_3}]^+[\text{B(C}_6\text{F}_5\text{)}_4]^-)\]

The pseudo-anionic ROP is often referred to as coordination-insertion ROP, since the propagation is thought to proceeds by coordination of the monomer to the active species followed by insertion of the monomer into the metal-oxygen bond (Scheme 29).\(^{77, 83}\) The growing chain remains attached to the metal through an alkoxide bond during the propagation. All herein introduced catalysts follow the coordination-insertion polymerisation mechanism having isopropoxide\(^{78}\) or dimethylamido\(^{79}\) chain end groups. There are also several minor ring-opening polymerisation methods \(e.g.\) free radical\(^{84}\), active hydrogen,\(^{85}\) zwitterionic\(^{86}\) and enzymatic.\(^{87}\)

Scheme 29. The reaction mechanism for the coordination-insertion ring-opening polymerisation.
6. Experimental

The aim of the work was firstly to discover complexes which can be synthesised with quantitative yields and utilized directly in ε-caprolactone polymerisation and secondly control the rate of polymerisation and the properties of produced PCL (e.g. $M_n$ and PDI values). This was activated by using aromatic and aliphatic alcohols as well as bi- and tetradeptate phenoxy-imines as ligand precursors with Ti(NMe$_2$)$_4$ as a metal source.

6.1 In situ generated titanium complexes

In screening of the different ligand precursors (Scheme 30) for use in titanium catalysts we used commercially available compounds without further purification ($4a$-$4i$, $5e$, $6a$-$6d$, $7a$-$7l$) together with our laboratory synthesised ligand precursors ($a$, $c$, $d$ and $e$),$^{42}$ ($g$, $i$, j-l),$^{56}$ ($3m$ and $3n$),$^{88}$ $5a$, $^{89}$ $5b$, $^{90}$ $5c^{91}$ and $5d$. $^{92}$ The ligands are divided into three groups: (i) monoanionic aromatic and aliphatic alcohols, (ii) chelating (N∩O, O∩O) ligands and (iii) tetradeptate bridged salicylaldimines. The metal precursors for the first experimental set were chosen so that they formed fully soluble combinations in toluene. Ti(NMe$_2$)$_4$ and Ti(O-i-Pr)$_4$ are the best choice for this due to the fact that they are both liquids and their chemistry with alcohols is well known.$^{42,80c,93}$ Other commercially available titanium alcoholates do not have similar properties to titanium isopropoxide e.g. Ti(O-n-Bu)$_4$ is known to possess lower activities in ROP$^{75}$ while Ti(O-t-Bu)$_4$ is both expensive and AIR sensitive.

6.2 Ring-opening polymerisation of ε-caprolactone

In total 46 different ligand precursors were used for complexation. In some cases more than one metal/ligand ratio was used increasing the number of tested titanium catalysts for ring-opening polymerisation to close to one hundred. All catalyst precursors were prepared in situ in a reactor facilitating 12 parallel reactions under argon atmosphere by mixing the ligand precursor and the corresponding metal compound in toluene (5 ml) at -78 °C in the appropriate ratio. The solution was allowed to warm to RT and stirred over-night to ensure the formation of the desired complex. The solution of dry toluene (5 ml) and in situ prepared complex (initiator) was heated to 75 °C followed by introduction of ε-caprolactone (3 ml) to reactor vessels. The polydispersity values of PCL produced with these catalysts were between 1.3 and 1.9 when the degree of conversion was over 60 %.
Scheme 30. Ligand precursors for *in situ* generated titanium complexes. Compounds marked only with letter are the same as those used in the synthesis of complexes for ethene polymerisation (Scheme 9).
A number of known [Ti(O-i-Pr)$_4$ and Ti(O-n-Bu)$_4$] and novel commercially available [Ti(OMe)$_4$ and Ti(O-t-Bu)$_4$ and Ti(NMe$_2$)$_4$] were used in ε-CL polymerisation to set minimum requirements for the new synthesised titanium catalysts. The first polymerisations were carried out at 75 °C and terminated after 15 minutes which is clearly ideal when monomer/titanium ratio of 270/1 is used (Scheme 31). All conversions were close to 90 % with one exception achieved with Ti(O-t-Bu)$_4$ possessing conversion of 76 %. The polymerisations carried out at 40 °C (Scheme 31) revealed increased differences in conversions. The highest conversion was achieved with Ti(NMe$_2$)$_4$ (32 %) and the lowest with Ti(O-t-Bu)$_4$ (2 %). The lower activity of the catalyst Ti(O-t-Bu)$_4$ can be explained by higher selectivity thus revealing higher molar mass values. $M_n$ and polydispersity values presented in the scheme 32 are for full conversions after 3 hour polymerisations. The highest molar mass value of PCL in the series ($M_n=38000$) was achieved with Ti(O-t-Bu)$_4$ and the lowest ($M_n=14000$) with Ti(O-n-Bu)$_4$. Theoretical $M_n$ values for PCL are 30780 (produced with catalysts having one active centre), 15390 (two active centres), 10260 (three active centres) and 7695 (four active centres) when the ε-CL/titanium ratio is 270/1.

![Scheme 31. Degree of conversion of monomer after 30 and 15 minute polymerisation with the commercial titanium complexes at 40 °C and 75 °C respectively.](image1)

![Scheme 32. Molar mass values (columns) and polydispersity values (line) of PCL polymerised with commercially available titanium complexes: Ti(O-t-Bu)$_4$, Ti(OMe)$_4$, Ti(O-i-Pr)$_4$, Ti(NMe$_2$)$_4$ and Ti(O-n-Bu)$_4$.](image2)
In the first polymerisation set the focus was on finding high catalytic activities by studying compounds having different ligand/metal ratios bearing N\(\cap\)O \((\text{a})\) type of chelating ligand (Scheme 33). When ligand precursor \(e.g.\) a is used in describing complex \((\text{a})\)Ti(NMe\(_2\))\(_3\) in the body text \((\text{a})\) means anionic deprotonated ligand.

Complexes I, V and VIII were synthesised by adding one, two and three equivalents of salicylaldimine respectively to a solution of Ti(NMe\(_2\))\(_4\). On warming the initial yellow colour of the solutions turns to red which is known to be evidence for the formation of titanium salicylaldiminato complexes. Compounds IV, VII and IX were prepared by the same method as described for the previous set of complexes by mixing Ti(O-i-Pr)\(_4\) with one, two and three equivalents of salicylaldimine respectively. The complexes II, III and VI bearing two different kinds of initiating groups were synthesised by treating the corresponding amidoxime adduct with one or two equivalent of isopropanol at RT for two hours.

From this set of experiments catalysts of the type \((\text{a})\)Ti(NMe\(_2\))\(_3\) \((\text{I})\) and \((\text{a})\)Ti(NMe\(_2\))\(_2\)(O-i-Pr) \((\text{II})\) provided the highest conversions of monomer after three hours of polymerisation and were suitable for more detailed polymerisations with the rest of the ligand candidates.

Scheme 33. \textit{In situ} generated titanium catalysts bearing different combinations of ligand \((\text{a})\) with dimethylamine and isopropanoxide as initiating groups. Degree of conversion of \(\varepsilon\)-CL after three hours polymerisation at 75 \(^{\circ}\)C with monomer/metal ratio of 270/1 with catalysts (I-IX).
As the conversion of monomer was 100 % after three hours of polymerisation with (a) Ti(NMe₂)₃, the time was reduced to 30 minutes to observe the differences in conversion with the other dichelate ligand precursors (Scheme 34). From the chosen salicylaldimine compounds almost all gave conversions above 80 %. The highest conversion in the series was achieved with ligand ı and 3n (95 %). The catalysts containing fluorine atoms either at the phenoxy (k) or imine fraction (e) possessed slightly lower conversions (below 70 %). The cause of this exception remains unsolved. Some possible reasons are: firstly that the fluorine atom has interactions with coordinating monomer influencing to chain growing mechanism and secondly the treatment of metal precursor with fluorinated compounds does not necessarily lead to selective cleavage of dimethylamine thus increasing the coordination number of titanium which is known to decrease activity in ROP.

From the commercially available dichelate O∩O type ligands only 4e and 4h showed high activities (above 84 %) after 30 minute polymerisation. A surprising finding in the polymerisation results was the difference in conversion between 4d (0 %) and 4e (83 %) which both have a similar dichelate OCCHCO type of backbone having delocalized electronic charge. A reason for this was found during the crystallization of compound 4d and Ti(O-i-Pr)₄ in 1:1 ratio. Instead of the formation of (4d)Ti(O-i-Pr)₃ rapid formation of (4d)₂Ti(O-i-Pr)₂ occurred. A similar imbalance in stoichiometry was observed in the attempted synthesis of (4d)₂ZrCl₂ as only (4d)₃ZrCl was possible to isolate.

Direct comparison of molar mass values is complicated. All catalysts with low conversion produced PCL with narrow PDI values however for catalysts with higher conversion, increase of the values was observed leading to lower Mₙ values. Molar mass values for a situation of 100 % conversion were estimated by linear extrapolation of the lower response values to the maximum. By this method catalysts produced very high Mₙ values always up to 50000. The maximum theoretical molar mass value for catalysts having one initiating group is only 30780. This value was closest to being achieved with the catalyst bearing ligand g (Scheme 34) which produced PCL with a Mₙ value of 25700 and 91 % conversion. As observed with similar type of catalyst in ethene polymerisation (7/MAO), the two benzyl derivatives are sterically blocking the catalyst centre reducing the activity to almost zero. In ε-CL polymerisation the above mentioned catalyst has only one benzyl derivative, leaving the other coordination site free for polymerisation. In ROP this is a clear advantage because control of the initiating species is usually achieved at the expense of activity.
Scheme 34. $M_n$ values of PCL produced with catalysts LTi(NMe$_2$)$_3$ and LTi(NMe$_2$)$_2$(O-$i$-Pr) in where L is dichelate ligand (a-4i).

The list of catalysts having both high activity and the ability to produce high molar mass $\epsilon$-CL is short and only complexes bearing g, i, j and e achieved $M_n$ values over 15000. The rest of the catalysts produced molar mass values between 8000 and 14000.

The activities of titanium complexes in ROP of $\epsilon$-CL can be further increased by reducing the coordination number to four as is the case with Ti(NMe$_2$)$_4$ and Ti(O-$i$-Pr)$_4$. The promising polymerisation results achieved with the Ti(NMe$_2$)$_4$ based catalysts provided a reason to continue their use as catalyst precursors. Initially three different ratios of Ti(NMe$_2$)$_4$ and basic aliphatic alcohols were tested (Scheme 35). The polymerisation time was reduced to 15 minutes because of the lowered coordination number. All catalysts achieved conversions above 74 % after 15 minute polymerisation and the highest values ($\geq$90 %) were achieved with the L$_2$Ti(NMe$_2$)$_2$ type catalyst bearing methoxy and isoproppoide ligands. In terms of molar mass values and activities, the methoxy complexes generally gave the best results from this experimental set of catalysts.
Scheme 35. 15 minute polymerisation with the LTi(NMe₂)₃, L₂Ti(NMe₂)₂ and L₃Ti(NMe₂) catalyst types in where L is alcohol (6a-6d). The degree of conversion (left) and MN values of PCL (right).

The search for highly active catalysts was expanded to include phenols and bulky aliphatic alcohols (7a-7l). In the first experiment polymerisations were carried out with four possible combinations of Ti(NMe₂)₄ and phenol 7a in ε-CL polymerisation (Scheme 36). The results were quite similar to the previous screening with aliphatic alcohols. The highest molar mass was achieved with the LTi(NMe₂)₃ type of catalysts and lowest with L₄Ti. After 30 minutes of polymerisation the observed behaviour was not so straightforward. L₂Ti(NMe₂)₂ achieved 80 % conversion but the rest of the combinations only achieved 55 %. Based on these preliminary observations, the complexes of type LTi(NMe₂)₃ and L₂Ti(NMe₂)₂ were chosen for polymerisation with the rest of the alcohols.

Scheme 36. Molar mass values (columns) and degree of conversion (line) of PCL polymerised with different ratios of phenol 7a (L) and Ti(NMe₂)₄ after 30 minutes of polymerisation.
Firstly the influence of electron donating and withdrawing groups (7b-7h) at the ortho and para position of phenol on catalytic properties was studied. The polymerisation time was reduced to 15 minutes because all except complex (7a)Ti(NMe2)3 achieved full conversion after 30 minutes of polymerisation. Among the studied catalysts no dramatic differences in activities nor in molar masses with LTi(NMe2)3 and L2Ti(NMe2)2 types of catalysts were observed (Scheme 37). Conversions were between 75-95 % after 15 minute polymerisation and molar masses of PCL varied between 8000 and 11000. The only catalyst capable of producing higher molar mass polymer was (7a)Ti(NMe2)3 having M_n=16900 with 60 % conversion. For some reason the polymerisation selectivity is lost when using the substituted phenols and so detailed investigations are required to provide an explanation for this.

In this context, a few aliphatic alcohols bearing bulky substituents were used, which one of (7i)Ti(NMe2)3 polymerised ε-CL with full conversion after 15 minutes which is the highest activity of the catalysts studied herein. Unfortunately these catalysts were not able to produce high molar masses and only 1/4 of the ideal M_n value 30780 was achieved.

![Scheme 37. 15 minute polymerisations with LTi(NMe2)3 and L2Ti(NMe2)2 bearing ligand (7b-7l). Conversion of monomer (left) and M_n values of PCL (right).](image)

All of the polymerisations up to this point were carried out at 75°C and so the polymerisation behaviour at various temperatures with the highly active complexes (6a)2Ti(NMe2)2 and (7i)Ti(NMe2)3 was tested (Scheme 38). The polymerisation time used was 30 minutes and the temperatures were between 40 and 75 with 5°C intervals. At 40°C the catalyst based on 6a achieved a 10 % monomer conversion while catalyst 6i showed no activity. At 65 °C polymerisation the degree of conversion was slightly better with 7i than with 6a. Generally the activities increased linearly with temperature.
Aluminium bearing tetradiantate salen types of ligands are known to produce stereoregular polylactide therefore these ligands are of interest.\textsuperscript{96} The strong preference for the production of stereoregular LA is apparently due to the stereogenic environment at the reactive metal site; i.e., polymerisation by a site-control mechanism. Salen ligands have been tested in ROP with many transition metals including titanium.\textsuperscript{97} Titanium(IV) salen complexes have not shown the same properties with corresponding aluminium complexes because there are two possible places for chain growth which can interfere with the site-control mechanism (Scheme 38).

In the preliminary work up with different kinds of dianionic ligand precursors (5a-5e and r-u) the influence of the orientation of the initiating groups on molar masses and PDI was studied for 22 hours polymerisations. In the traditional salen type complexes (5b and 5d) the initiating groups \textit{e.g.} isopropoxide occupy axial positions (\textit{trans}) having a O-Ti-O angle of around 180°
while in structures 5e and r-u the O-Ti-O angle is ~90° (cis). For titanium complexes of 5a and 5c no crystallographic data exists but their structures have been calculated by computational methods predicting trans-configuration although the differences in the stabilisation energies of the cis- and trans-configurations were small.98

The catalysts 5a-5c behave similarly in polymerisation. Mₙ values, polymerisations rates and even PDI values are much the same (Scheme 40). The behaviour of catalyst 5d differs much from the previous ones. The aromatic linkage between the imine nitrogen atoms stabilises the polymerisation reaction and a PDI value of 1.1 can be obtained. Unfortunately, however the activity decreased simultaneously and only 20 % conversion was observed. By replacing one amido group with isopropoxide the conversion of monomer increased to 47 % without loss of the low PDI value. Catalysts having the amido ligands cis to each other possessed lower activities than the corresponding trans ones while structures bearing a t-butyl group at the phenoxy ortho position (ligand s) or a methyl group at the biaryl backbone (ligand r) resulted in no catalytic activity whatsoever. The catalyst bearing binaftyl ligand t gave reasonable conversion (57 %) and PCL formed had a narrow PDI (1.2). Extrapolation of the molar masses to match 100 % conversion showed that these cis type catalysts may produce Mₙ values close to 25000. This is still not high enough to achieve the desired 30780 value for a one active site catalyst.

Scheme 40. Results of 22 hours polymerisation with titanium catalysts bearing dianionic ligand precursors. Degree of conversion (left) and Mₙ values of PCL (right).
7. Conclusions (part A and B)

It is possible to synthesise titanium(IV) complexes bearing differently substituted phenoxy-imino ligands almost quantitatively and selectively by choosing the appropriate synthesis route. The quantitatively formed intermediate product of any salicylaldimine and Ti(NMe₂)₄ can be converted into the corresponding titanium dichloride precatalyst. In addition, these amido complexes can be utilised without modification for ring-opening polymerisation of ε-caprolactone. Titanium complexes bearing malonates were prepared by the traditional method using sodium hydride as a deprotonation agent and yields around 90 % were achieved.

After MAO activation, the bis(salicylaldiminato) titanium catalysts 1-17 exhibit a range of catalytic activities from low to high [3-6000 kgPE/(molTi⋅h⋅bar)] in ethene polymerisation. According to the polymerisation results, the alkyl substitution at the imino nitrogen atoms has a essential role in determining the catalytic properties; the most active catalysts were 7, 8 and 17. When activated, these bis(salicylaldiminato)TiCl₂ complexes tend to change the relative coordination of the phenoxy-imino ligands from cis- to trans-conformation, according to computational calculations. Even though there is no unambiguous explanation for the observed structure-activity relationship, from a steric point of view the trans-configuration of the imine substituents seems to offer an ideal steric surrounding for the cationic metal centre.

Sterically small imine substituents (complexes 13-15) leave the metal centre available for participation in side-reactions, while more sterically bulky groups in the vicinity of the cationic metal centre can interfere with the chain growth process (complex 12). In calculations involving the cationic species the influence of the counter ion is too complicated to include in the modelling equation and therefore modelling alone can not predict ligand combination suitable for finding highly active Group 4 catalyst.

Bis(salicylaldiminato)TiCl₂ complexes are often described as catalyst precursors which are able to produce polyethene with narrow polydispersities and even a living polymerisation of α-olefins has been reported. The series of bis(salicylaldiminato) catalysts described here are extremely useful as they provide high activity with tunable multisite character and as an addition tolerate high polymerisation temperatures. Similar multisite behavior for the bis(salicylaldiminato)TiCl₂ catalyst precursor has been reported for bis[(3-(3,5-dicumyl)salicylidene)-anilinato]zirconium(IV)dichloride.

The multimodal MMD curves are often observed with the catalysts possessing low to moderate polymerisation activities. Some possible reasons observed here are: firstly the
isomers (cis, ciscis and trans) possess similar polymerisation activities (3/MAO) and the ratio of isomers is dependent on temperature, thus the resulting PE having unique MMD profile at the used temperature and secondly at higher temperature the quantity of the isomer responsible for high activity is reduced and the quantities of the isomers responsible for low activities are increased (6/MAO). In the terms of the MMD unimodal PDI curve achieved at low polymerisation temperature is replaced by the multimodal MMD achieved at high temperatures.

Ethene consumption during one hour polymerisation reactions is stable for the catalyst precursors 18-22, thus the observed average low activities and changes in modalities cannot be explained by the deactivation of the catalyst during the polymerisation. The bridged titanium complexes have two different catalytically active conformations (cis and ciscis) which are in competition after MAO activation. Their appearance and relative activity is dependent on the polymerisation conditions. It is not possible for these titanium complexes bearing tetradeinate ligands to undergo the cis to trans change in conformation that is characteristic of other highly active ethene polymerisation catalysts.

Homoleptic titanium complexes can clearly offer good selection of catalyst precursors for ε-caprolactone polymerisation. In the terms of activity Ti(NMe2)4 revealed highest conversion of monomer (32 %) of all the catalysts introduced herein at low temperatures. The best in situ synthesized catalyst (6a)2Ti(NMe2)2 revealed conversion of 22 % at the same polymerisation conditions. In the terms of molar mass values Ti(O-t-Bu)4 produced highest Mₘ value (38013). In this respect (g)Ti(NMe2)3 is the only catalyst which can challenge commercial catalysts in terms of molar mass values (31000) in reasonable polymerisation times. PDI values of the polymers produced with the commercial compounds were all higher than 1.38. This value can be diminished close to one by using catalyst (5d)Ti(NMe2)(O-i-Pr) which produce PCL with PDI value of 1.1. This is achieved at the expense of polymerisation activity (47 % conversion after 22 hours).

Ti(NMe2)4 is an ideal metal precursor for in situ synthesised catalysts as it is known to react quantitatively and selectively with compounds bearing an acidic proton, such as aromatic and aliphatic alcohols. For ε-CL polymerisation the best ligand candidates were clearly the monoaionic aliphatic alcohols which showed polymerisation activity even at 40 °C. The catalyst containing the ligand precursor g bearing a benzyl derivative had interesting polymerisation behaviour. It produced PCL with a molar mass value of 30 kg/mol which is close to the theoretically ideal value for single site catalysts. The high molar mass value is most likely due to steric disturbance at one of the coordination sites. Since only one initiating site is available for chain growth the resulting chain is longer. Since the loss of one of the active
polymerisation sites results from steric hindrance rather than coordination there is no observed decrease in activity.

Herein *in situ* synthesised titanium complexes can not compete with homoleptic titanium catalysts in ε-CL polymerisation activity. One possible benefit can be found when utilizing these *in situ* synthesised complexes for D, L-lactide polymerisation. The formed polylactide can have stereoregular sequences in the chain and to gain these the sterical environment around active titanium centre has to be highly controlled. This is not possible to achieve with the titanium complexes bearing only one type of ligand *e.g.* Ti(NMe$_2$)$_4$ and Ti(O-i-Pr)$_4$. 


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Crystal structure of the complex (4d)2Ti(O-i-Pr)2 have not been published.

Crystal structure of the complex (4d)3ZrCl have not been published.

