Linear low-density polyethylene synthesis by high-throughput approach

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Linear Low-density Polyethylene Synthesis by High-throughput Approach

PROEFSCRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de rector magnificus, prof. dr. ir. C. J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op woensdag 21 December 2011 om 14.00 uur

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1 Introduction

1.1 History of Polyolefins

In 1933, the first discovery of polyethylene by Eric Fawcett and Reginald Gibson at ICI Chemicals\textsuperscript{1a} initiated a new era which was followed by the production of polyethylene at high pressure by Michael Perrin in 1936.\textsuperscript{1b} Their discovery forms the basis of the commercial low density polyethylene (LDPE) production, which requires high pressure (500-1200 atm) as well as high temperature (200-400 °C) and a radical initiator. Today, the highly branched, soft and pliable LDPE is used on large scale in applications ranging from plastic bags, containers, textiles, and electrical insulation, to coatings for packaging materials.

Ziegler and Natta were awarded the Nobel Prize in 1963\textsuperscript{2-5} for their discovery of a catalytic system based on titanium halides and organoaluminum reagents (TiCl\textsubscript{4} and AlR\textsubscript{3} R = alkyl, aryl, hydride) that produce almost perfect linear high density polyethylene (HDPE) and semi-crystalline isotactic polypropylene (i-PP) at even milder conditions than the silica-supported (Cr/SiO\textsubscript{2}) Phillips catalyst developed in 1950s.\textsuperscript{6} Because of its high crystallinity and solvent resistance, HDPE is suitable for high performance applications such as fuel tanks in the automotive industry and even as high performance fibers for bullet-proof vests if the molar mass is in the range of several millions. Nowadays, i-PP represents an important construction material for applications in the automotive sector (e.g. car bumpers) and in domestic goods (housings for vacuum cleaners, mobile phones and other household equipment). The advantage of Ziegler-Natta catalysts is their ability to produce a wide range of polyethylenes varying from high density (HDPE) to linear low density (LLDPE), while the range of products that can be obtained by the Phillips catalysts is more limited. Soon after the discovery of Ziegler-Natta catalysts, first generation metalloocene catalysts were discovered. However, these early complexes exhibited poor activity for ethylene polymerization, and failed to polymerize propylene.\textsuperscript{7a,b} Breslow and Chien\textsuperscript{7c} proposed that ethylene inserts into the Ti-C bond of the [Cp\textsubscript{2}TiR]\textsuperscript{+} cationic species formed by the Lewis acidic aluminum cocatalyst, following the Cossee-Arlman mechanism (see below). In 1976, Sinn and Kaminsky reported the bis(cyclopentadienyl)zirconium(IV)dichloride/AlMe\textsubscript{3} metalloocene catalyst system with the serendipitous discovery of the activating effect of small amounts of water.\textsuperscript{7d} The Ziegler-Natta
and metallocene catalysts have been proven to be flexible with regard to the incorporation of α-olefins and they became the basis for the olefin polymerization industry while optimization of the metallocene catalysts by varying the ligand systems and the transition metal led to higher activities and allowed the formation of various new polymeric microstructures ranging from syndiotactic to hemiisotactic PP and for example olefinic block copolymers. The discovery of methylaluminoxane (MAO) by partial hydrolysis of AlMe₃ in 1980 marked a breakthrough in the activation of single-site catalysts. It was rapidly followed by the development of structurally well-defined cocatalysts to yield well-defined catalytically active ion pairs. Up to the late 1990s, group 4 metallocenes and half-sandwich titanium-amido complexes have led the developments for controlling and improving the properties of polyethylene, polypropylene and copolymers of ethylene with α-olefins. The synthesis of the constrained geometry cyclopentadienyl-amido catalyst (CGC) was the beginning of a major impulse of developing so-called post-metallocene catalysts. Nowadays, post-metallocene single site catalysts outperform most metallocene catalysts and are for example able to produce multi-block copolymers or copolymers containing polar monomers. The discovery of nickel and iron-based active catalysts by Brookhart and Gibson signaled new lines of research beyond the group 4 metallocenes and constrained-geometry catalysts. Depending on the aryl group on the imine moiety, the conversion of ethylene to highly-linear HDPE or to linear α-olefins with a Schultz-Flory distribution was possible by Brookhart and Gibson’s 2,6-bis(arylimino)pyriydl iron, while branched polyethylene could be obtained without using additional α-olefin comonomer via the chain-walking mechanism initiated by Brookhart’s nickel α-diimine complex. The possibility of producing variable branched polyethylenes in a controlled fashion with the ligand variations on the α-diimine ligand makes these catalyst group prominent. Bulky substituents on the ortho position of α-diimine ligand effectively suppress the chain termination by blocking the axial positions. Therefore, high molar mass polymers can be produced with this group of catalysts. Catalysts bearing sterically undemanding ortho methyl groups produce α-olefins. Ligand variations together with different polymerization temperature and pressure tune the branching level and molar mass. Brookhart’s Pd(II) α-diimine complexes yields more branched polyethylene compared to the Ni(II) analogues irrespective of the ethylene concentration. In principle, the chain walking mechanism consists of repeating β-hydride transfer followed by reinsertion (Figure 1). In this process, the active site moves along the growing polymer chain. Monomer insertion after chain walking causes the formation of polyethylenes with substantial branching. (A detailed overview of the various classes of post-metallocene catalysts is given in section 1.4.)
Nowadays many research activities focus on gaining control over the microstructure and its influence on the properties of the copolymers. Arriola and coworkers made a breakthrough in polymer synthesis with the production of ethylene/α-olefin multi-block copolymers in a solution process using two catalysts (the so-called Dow Shuttle Chemistry),\textsuperscript{12} one of which gives low comonomer incorporation while the other one enables good comonomer incorporation. By the introduction of ZnEt\textsubscript{2} (the chain-shuttling agent), the growing polymer chain shuttles reversibly between the two catalysts to form a polymer consisting of alternating ‘hard’ and ‘soft’ blocks (Figure 2).\textsuperscript{12a} In other words, a polymer chain that starts to grow on one catalyst can be transferred to a chain transfer agent (CTA) like in a "normal" CCTP process.\textsuperscript{12b} The CTA can either transfer the polymer chain back to the same catalyst or to a different catalyst, which subsequently grows an additional block. Relative rates of chain transfer and chain growth are crucial for the system to work. The ratio of the different blocks is controllable by the relative amount of both catalysts, while adjusting the amounts of chain shuttling agent and monomer can control the length of the blocks.

\textbf{Figure 1.} Chain walking mechanism with Pd α-diimine complex.
Figure 2. Chain–shuttling system for ethylene/1-octene block copolymers (adapted from ref 12).

1.2 Polymerization Mechanism

In a typical activation of metallocene precatalysts with MAO, the initial halide precursor, Cp\(^8\_3\)MCl\(_3\), is alkylated and cationized affording the cationic 14 e\(^-\) cationic active species, [Cp\(^8\_3\)MCH\(_3\)]\(^+\). As an alternative to MAO, organoboron-based cocatalysts can be applied but they require an external alkylating agent, typically Al(iBu)\(_3\), or a pre-alkylated catalyst precursor. Generally, boron compounds like [Ph\(_3\)C][B(C\(_6\)F\(_5\))\(_4\)] \(^-\) or [HNMe\(_2\)Ph][B(C\(_6\)F\(_5\))\(_4\)] \(^-\) form ion pairs with truly non-coordinating anions [Cp\(^8\_3\)MR]\(^-\)[B(C\(_6\)F\(_5\))\(_4\)] \(^+\), while the Lewis acidic B(C\(_6\)F\(_5\))\(_3\) tend to yield weakly coordinated anions that form more stable, but commonly less reactive, zwitterionic complexes of the type [Cp\(^8\_3\)M\(^+\)(μ-R)B(C\(_6\)F\(_5\))\(_3\)].

Obviously, the catalyst has a strong influence on the product properties such as molar mass and stereoregularity. But besides the catalyst also the counter ion plays an important role during the catalytic process and can affect the rate of insertion and chain transfer as well as stereoregularity.\(^{15}\) Busico’s high-field \(^{13}\)C NMR studies on the polypropylenes produced by Waymouth and Coates\(^{16}\) oscillating \((2\text{-Ar-indenyl})_2\text{ZrCl}_2\) (Ar = 3,5-di-tert-butyl-4-methoxyphenyl) catalyst led to a better understanding of the effect of the cocatalyst/activator and solvent on the stereoregularity of the polymers. This catalyst is a captivating catalyst that produces stereoblock-isotactic propylene through reversible interconversion of the active cation between the enantiomorphous \textit{rac}-like conformation.\(^{15a,b}\) In this system, the transition from an oscillating to a conformationally locked state causes the fast interconversion of the two enantiomorphous \textit{rac}-like conformations, and this oscillation is induced by a sterically hindered contact-ion pair.\(^{15a,b}\) A comprehensive review of cocatalysts for metal-catalyzed olefin polymerization has been given by Chen and Marks.\(^{17}\)
After the formation of the active species, chain propagation proceeds via the so-called modified Cossee-Arlman mechanism (Figure 3). The Cossee-Arlman mechanism is based on olefin coordination to the available site of the metal, followed by the chain migratory insertion of the olefin via a 4-centered transition state.\(^{18,19}\) The insertion mechanism is assisted by an \(\alpha\)-agostic interaction (Figure 3). \(^{19c}\)

\[
\begin{align*}
  \text{Figure 3. Modified Cossee-Arlman Mechanism.}^{18,19}
\end{align*}
\]

Chain transfer processes determine the final molar mass of the polymers. For early transition metals, \(\beta\)-H elimination with formation of a metal hydride species is an unfavorable process and chain transfer proceeds via \(\beta\)-H transfer to monomer. However, for late transition metals the M-H bond is somewhat stronger than the M-C bond and they tend to form stable M-H-(olefin) species,\(^{10a}\) which also explains their tendency to undergo chain walking. For polypropylene, \(\beta\)-methyl transfer represents an additional chain termination mechanism resulting in the vinyl end group.\(^{20e,f,g}\)

The molar mass of the polymers can also be tuned by adding chain transfer agents. The most commonly used chain transfer agent is dihydrogen which leads to chain termination through hydrogenolysis and initiation of a new chain.\(^{20h}\) Chain transfer to aluminum or zinc is another highly useful chain transfer pathway.\(^{12,20i-m}\) Its reversible nature makes this chain transfer process very suitable for producing (multi-) block copolymers by either CCTP or Shuttle chemistry.\(^{12,20n-p}\)

### 1.3 Ziegler-Natta Catalysts

The classical Ziegler-Natta catalyst system is a versatile catalyst group consisting of a transition metal (Ti, V and Cr are widely used transition metals) catalyst and an organoaluminum compound as a cocatalyst.\(^{2-5}\)

After the breakthrough of Ziegler on ethylene polymerization, Natta and coworkers polymerized propylene with this particular catalyst system and for the first time isolated isotactic polypropylene. Based on the discovery of isotactic polypropylene, the principles of regio- and stereospecific polypropylenes were illustrated by Natta and coworkers.\(^{20q,r}\) Polypropylene chain microstructures are
categorized as isotactic (the polymer chain with chiral centers of the same configuration), syndiotactic (the polymer chain with chiral centers of the alternating configuration) and atactic (the polymer chain with chiral centers without configurational regularity). The properties of Ziegler-Natta system are influenced when they are employed with an inorganic compound, such as magnesium chloride. Stereospecific propylene polymerization in industrial application is carried out with heterogeneous Ziegler-Natta catalysts that are a combination of TiCl₄/MgCl₂/Internal donor/AlR₃ (R= Et, iBu₃), whereby active sites are on the edges of the MgCl₂.²⁰ By the addition of internal electron donors (Lewis base), such as ethyl benzoate the selectivity to isotacticity increases. The role of internal donor is to stabilize the MgCl₂ surface by controlling the distribution of TiCl₄. The loss of internal donor due to the alkylation during the polymerization was stabilized by the addition of external donors, such as alkoxy-silane that causes an increase in the stereoselectivity. Today, heterogeneous Ziegler-Natta catalysts are widely applied to produce i-PP, HDPE and LLDPE in industrial scale.

1.4 Development of Single-site Catalysts

After the discovery of heterogeneous Ziegler-Natta olefin polymerization catalysts in the mid-1950s, well-defined metallocene catalysts based on a ligand set consisting of two (substituted) η⁵-cyclopentadienyl groups have been developed. These organometallic complexes often contain group 4 metals. The first metallocene with the typical bend sandwich structure was Cp₂TiCl₂. Upon activation with Et₂Al and Et₂AlCl it polymerizes ethylene, but it is inactive for propylene polymerization.²³ Brintzinger and Ewen developed the stereoselective C₂-symmetric rac-(C₂H₄)(thInd)₂MCl₂ and rac-(C₂H₄)(Ind)₂MCl₂ anza-metallocene catalysts by ligand modification for stereoselective propylene polymerization.²⁴ The stereoselectivity for this group of catalysts is determined by the ansa-bis(indenyl) ligand system which oriantates the growing polymer chain. The incoming monomer chooses the opposite enantiomeric, avoiding the steric interactions between the growing chain and the monomer. Altering the symmetry of the metallocene structure led the formation of syndiotactic,²⁸ hemiisotactic,²⁵ or isotactic-atactic stereoblock polypropylene.²⁵ The selectivity in propylene polymerization with metallocene catalysts extensively reviewed by Resconi et al.¹⁸

In the early 1990’s, a new era in the polyolefin science has started by the development of a constrained geometry cyclopentadienyl-amido catalyst (CGC) by Dow and Exxon¹² (Figure 4, rightmost complex). This so-called constrained geometry catalyst is based on the variations on the ligand frame, which was firstly introduced by Shapiro and Bercaw in 1990 affording their organoscadium single-component olefin polymerization catalyst.²⁸ This group of catalysts has a considerably more open structure than the corresponding metallocenes. This key feature allows them to readily incorporate higher α-olefins, making them very suitable for producing LLDPE.
The palladium and nickel α-diamine complexes (Figure 4, third complex) developed by Brookhart in 1995\textsuperscript{13a} formed a breakthrough in the field of controlling the branching density and molar mass via chain-walking without the use of externally added α-olefin comonomers. Sterically hindered ortho-substituents on the aryl ring block the olefins to approach at the axial positions of the central transition metal. Thus, by tailoring the steric hindrance at the ligand system both chain transfer and chain walking can be tuned, which leads to polymer structures ranging from hyper-branched to linear polyethylenes of various molar masses.

2,6-Bis(arylimino)pyridyl iron complexes,\textsuperscript{14a,b} discovered by Brookhart and Gibson, are important examples of the developments in olefin polymerization catalysts because of their efficiency for the conversion of ethylene to HDPE and for obtaining oligomers with a Schultz-Flory distribution (Figure 5).\textsuperscript{32a,b} The substituents on the aryl ring play a key role in determining the molar mass of the product. Varying the steric hindrance of these substituents affords products ranging from high molar mass HDPE to α-olefin-based oligomers exhibiting a Schultz-Flory distribution.

\textbf{Figure 4.} Selected examples of non-metallocene catalysts.

\textbf{Figure 5.} 2,6-Bis(arylimino) pyridyl Brookhart-Gibson iron and cobalt complexes.\textsuperscript{14b}
Triazacyclohexane complexes of Cr(III)\textsuperscript{29a,b,c} form a nice example of how ligand variations offers a route for interconversion between polymerization and oligomerization.\textsuperscript{27} Modifications on the R group (R = linear alkyl chains) with substituents on the 2-position convert the polymerization catalyst into a selective trimerization catalyst (Figure 6). Another interesting feature of this catalyst system was reported by Nenu and Weckhuysen.\textsuperscript{29d} They treated triazacyclohexane ligand with Phillips polymerization catalyst.\textsuperscript{29e} Activation of the catalyst with [Me\textsubscript{3}PhNH][B(C\textsubscript{6}F\textsubscript{3})\textsubscript{4}] yielded 1-hexene and butyl branched LLDPE with low activity.

![Linear α-olefins](image1.png) ![HDPE](image2.png)

**Figure 6.** (Triazacyclohexane)CrCl\textsubscript{3} complexes.\textsuperscript{29}

The group 4 metal phenoxy-imine catalyst systems (Figure 4, the leftmost complex) developed by Fujita and coworkers, and known under the name FI catalysts, are able to produce a large diversity of polymers by tuning the electronic and steric environment of the catalysts.\textsuperscript{30} The polymers formed by FI catalysts range from ultra-high molar mass linear polyethylenes,\textsuperscript{30a-d} copolymers based on ethylene and polar comonomers,\textsuperscript{30e} syndiotactic\textsuperscript{30d} and isotactic\textsuperscript{30d} polypropylenes and even block copolymers such as PE-b-sPP and PE-b-EBR (EBR = poly(ethylene-co-but-1-ene))\textsuperscript{30a,f} Also by adding different monomers or monomer mixtures of different compositions, several poly(ethylene-co-α-olefin) copolymers can be manufactured.\textsuperscript{30g} The active species obtained from this catalyst group are highly electrophilic due to their O- and N-containing ligand groups which are even more electron-withdrawing than metalloocene and constrained geometry catalysts. Depending on the cocatalyst used (MAO or Al(iBu)\textsubscript{3}/[Ph\textsubscript{3}]C\textsuperscript{4}][B(C\textsubscript{6}F\textsubscript{3})\textsubscript{4}], the polymers formed with phenoxy-imine zirconium catalysts are either HDPEs or UHMWPEs, while titanium-based FI catalysts with specific ligands produce polymers with a significantly higher molar mass than zirconium-based FI catalysts.\textsuperscript{30} The modification of the ligands of the FI catalyst system with bulky substituents switched the polymerization catalysts into highly active oligomerization catalysts.\textsuperscript{30i} Kol’s Ti(IV) tetradentate [ONNO] type polymerization catalyst, which is active in isospecific and living polymerization of high-olefins,\textsuperscript{31a,b} and the pyridylamido hafnium and zirconium complexes\textsuperscript{31c} for ethylene/1-octene and propylene polymerizations are examples of recently developed group 4 metal post-metallocene catalysts.
Neutral group 3 and lanthanide alkyl complexes have been used as ethylene polymerization catalysts due to their isolability with cationic group 4 alkyl complexes. The advantage of this group of catalysts over group 4 analogs is that they do not require a cocatalyst. Cp-based scandium\textsuperscript{28,32a-c} and yttrium\textsuperscript{32d-i} have been described in literature with low to moderate activity, while Cp-based lanthanide complexes have been reported with moderate activity. \{\textit{Cp}^{+}\textit{Ln}[^{\mu}\textit{H}])\textsubscript{2}\} complexes\textsuperscript{32j-i} are reported to be highly active ethylene polymerization catalysts, however, they failed to polymerize propylene. Bercaw’s double-bridged yttrium system is the only group 3 metalloocene that polymerizes propylene.\textsuperscript{32m}

1.5 Olefin Oligomerization

Following the breakthrough advances in the synthesis of polyolefins with controlled microstructure with single-site catalysts that were outlined in the previous sections, attention has to be directed towards the development of the catalyst group that produces α-olefins. The oligomerization of ethylene to higher α-olefins represents an important research and industrial activity because of their possible use as for example comonomers in linear low-density polyethylene (LLDPE) production, as synthetic fluids and as precursors for e.g. plasticizer alcohols, tallow amines and surfactants. However, most commercial oligomerization processes yield Schulz-Flory or Poisson distributions,\textsuperscript{33a,b} which do not correspond to the market demand. Therefore, the development of catalysts capable of solely producing the desired oligomer, such as 1-hexene and 1-octene, is highly desirable. The development of the ethylene oligomerization process started with the discovery of zirconium and titanium alkoxide-base oligomerization catalysts. These complexes dimerize ethylene to 1-butene when activated by AlEt\textsubscript{3}, as found by Ziegler and Martin.\textsuperscript{33c} Their discovery led to the 1-butene production through the ‘Alphabutol process’.\textsuperscript{34} For the 1-butene formation a metallacyclic mechanism was proposed,\textsuperscript{35} although some recent work showed that the Cossee-Arlman mechanism could also explain its formation.\textsuperscript{36}

The first selective ethylene trimerization catalyst was based on chromium and was reported by Manyik \textit{et al.}\textsuperscript{37} Several chromium-based systems with different ligands such as symmetric PNP ligand (HN[CH\textsubscript{2}]\textsubscript{2}PR\textsubscript{2})\textsubscript{3},\textsuperscript{38} or Sasol’s SNS ligand (HN[CH\textsubscript{2}]\textsubscript{2}SR\textsubscript{2}),\textsuperscript{39} where both ligand systems coordinate to the Cr(III) metal center via a tridentate meridional coordination, are highly active and selective ethylene trimerization catalyst systems. Bollmann and coworkers developed the Cr(III)(acac)\textsubscript{3}/(Ph\textsubscript{2}P)\textsubscript{2}NR system which tetramerizes ethylene with a selectivity of up to 70%.\textsuperscript{38} A detailed review on olefin oligomerization has been recently published by McGuinness.\textsuperscript{41} The simplified Cr-catalyzed oligomerization mechanism is depicted in Figure 7. The chromium catalytic center generated by the activation with i.e. MAO coordinates the 2 ethylene molecules that form a chromacyclopentane species by subsequent oxidative coupling. Further ethylene insertion leads to metallacycle growth, which liberates 1-hexene via β-hydride transfer to the metal center as illustrated in Figure 7.
Innovene, Chevron-Phillips and Shell are the largest commercial producers of linear \(\alpha\)-olefins. Chevron-Phillips’ oligomerization process is based on Ziegler’s Aufbau reaction.\textsuperscript{33} The Aufbau reaction implies a series of ethylene insertion reactions into the Al-C bond under high pressure (100 to 400 bar) and high temperature (100 to 250 \(^\circ\)C). However, the boiling points of\(\text{AlEt}_3\) and the 1-dodecene produced are close to each other, which make it difficult to separate these two compounds. Innovene improved the Chevron-Phillips oligomerization system producing a distribution of 1-hexene and 1-octene. However, Shell’s Higher Olefin Process (SHOP) has been regarded as a leading oligomerization process among the commercial processes.\textsuperscript{42} Ligand variations were extended to \([\text{PO}]\) chelates.\textsuperscript{43,44} Since 2003, Chevron Philips produces 1-hexene in Qatar with the chromium-based ethylene trimerization catalyst.\textsuperscript{45}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{metallacycle.png}
\caption{Simplified metallacycle mechanism with Cr-based catalyst.}
\end{figure}

The development of catalysts selectively producing certain \(\alpha\)-olefins is highly important in view of their value in the petrochemical industry and their application as comonomers for the production of linear-low density polyethylene. In this respect, the selective trimerization of ethylene deserves particular attention. In the course of this thesis trimerization catalysts have been developed by 1) optimization of the catalyst’s ligand system, 2) the type and amount of cocatalysts and 3) the reaction conditions, all using a high-throughput approach. A second topic involved the combination of a trimerization and a polymerization catalyst, resulting in so-called tandem catalysis for the production of LLDPE.

1.6 Scope and Aims of the Thesis

Linear low-density polyethylene (LLDPE) is a random copolymer of ethylene and \(\alpha\)-olefins produced commercially with heterogeneous Ziegler-Natta catalysts or with homogeneous (post-)metalloocene catalysts in gas/slurry phase or solution phase processes, respectively. Traditionally, a mixed feed of ethylene and the \(\alpha\)-olefin (1-butene, 1-hexene or 1-octene) is used. Tandem catalysis, consisting of an
ethylene trimerization and an ethylene/1-hexene copolymerization catalyst, is an alternative way to synthesize LLDPE that has the advantage over the conventional approach in that it does not need a separate second monomer feed. Chemical and kinetic compatibility of the ethylene trimerization and copolymerization catalysts and their responses to different reaction conditions is the biggest challenge and, therefore, the major disadvantage of the tandem catalysis process. The majority of reported tandem catalysis for ethylene oligomerization/polymerization is based on homogeneous catalyst components. These unsupported systems are ideally suited to demonstrate the concept of concurrent tandem catalysis. However, due to the limited thermal stability of the applied ethylene oligomerization catalysts, generally these systems cannot be run above the melting temperature of the product. Performing the polymerizations at lower temperatures in homogeneous phase will result in severe reactor fouling, which prevents commercial application. Data on tandem catalysis using an ethylene oligomerization catalyst thermally stable enough to be used in a solution process, or using a supported copolymerization catalyst to avoid reactor fouling, hardly exist.

During this doctoral research, one aim was to look for alternatives to the classical tandem catalysis. A second target was to develop a tandem catalysis system that can be run at temperatures below the melting point of the LLDPE product.

In Chapter 2, a novel Cr-based ethylene oligomerization catalyst based on the monoanionic ancillary ligand \([([\text{t-Bu}]\text{NPN}\text{t-Bu})]\) is described, which is capable to switch its catalytic selectivity from oligomerization to polymerization by changing the alane activator. The idea was that this switching of the catalytic selectivity of a single catalyst could be an elegant alternative to the tandem catalysis. The effect on the catalytic behavior of NPN ligands with different substituents is described. Depending on the cocatalyst applied, this catalyst system affords different products: 1-hexene, a Schultz-Flory distribution or \(\alpha\)-olefins or polyethylene. TOFs of up to 20 000 h\(^{-1}\) were achieved.

The third chapter is focused on the arene-substituted cyclopentadienyl titanium catalyst system developed by Hessen and coworkers.\(^{46,47}\) This trimerization catalyst is the most active non chromium-based trimerization catalytic system. Different experimental techniques and activation protocols were applied in a high-throughput experimentation (HTE) setup to optimize the catalytic selectivity towards the formation of 1-hexene. The HTE approach was shown to be a promising strategy to rapidly generate kinetic data for mechanistic studies.

The research described in the second section of chapter 4, focused on the difference in catalytic behavior of homogeneous, partly-supported tandem catalysts. We compared the differences in product and catalytic behavior for systems where (i) both the trimerization \([\text{C}_3\text{H}_6\text{CMe}_2\text{Ph}]\text{TiCl}_3\) and copolymerization \((\text{Cp}^{\text{Bu}_2}\text{ZrCl}_2)\) catalysts are in the homogeneous phase, (ii) the trimerization catalyst is in the homogeneous phase while the copolymerization catalyst is supported on SiO\(_2\).
In the fifth chapter, we discuss the synthesis of LLDPEs with different comonomers using two different varieties of setups. The ethylene + 1-hexene and ethylene + 1-octene polymerizations were carried out in 200 mL Büchi reactors while another series of ethylene + 1-hexene polymerizations have been carried out using a HTE platform consisting of four fully automated 125 mL Premex reactors. These series of ethylene + 1-hexene and ethylene + 1-octene copolymers have been subjected to a thorough high-throughput characterization program, carried out in collaboration with the Friedrich-Schiller University Jena, Germany.

Chapter 6 is a technology assessment highlighting the most intriguing and important results along with perspectives for future research. This chapter shows the contribution of the doctoral work to the fundamental knowledge in the polyolefin field in relation to the industrial relevance of the doctoral work. The thesis finalizes with the summary of the most important outcome of the work carried out.
1.7 References


2. K. Ziegler, Angew. Chem. 1952, 64, 323.


2 Chromium Catalysts with Non-Innocent Ancillary NPN Ligands Having Switchable Catalytic Behavior*

Abstract

The synthesis and characterization of a series of chromium catalysts supported by non-innocent spectator ligands consisting of an NPN framework is described. Depending on the aluminum alkyl activator, catalytically active species switch selectivity from ethylene polymerization to non-selective oligomerization and even to selective ethylene trimerization. Attempts to isolate activated species resulted in the isolation of single-activating ethylene polymerization catalysts. The roles of the aluminum alkyl activator, ligand variation and the oxidation state of chromium during catalysis have been studied.

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2.1 Introduction

Selective ethylene tri- and tetramerization represent a scientifically challenging research topic which, stimulated by the strong market demand for 1-hexene and 1-octene as comonomers in LLDPE synthesis, receives significant interest from the industry. The selective trimerization of ethylene was first observed by Manyik and coworkers. Various transition metals (Ta$^2$, Ti$^3$, Cr$^{3+}$, V$^5$) have produced ethylene trimerization catalysts. Because of their high activity and selectivity, chromium-based catalytic systems have a noticeable dominant position in the selective tri- and tetramerization of ethylene.$^5$

The mechanism of ethylene trimerization is believed to follow a metallacyclic route that involves oxidative addition of two ethylene molecules to the metal, followed by insertion of one additional ethylene molecule. Subsequently, reductive elimination of the product restores the low valent metal species and, thus, completes the catalytic cycle. This metallacyclic route$^{4a, 7}$ represents the most widely accepted mechanism for the selective oligomerization and is fundamentally different compared to the migratory insertion (Cossee-Arlman)$^8$ process, which is accepted for olefin polymerization. Even the best trimerization catalysts produce small amounts of polyethylene as a side-product suggesting that the selective oligomerization and migratory insertion may be linked. The key for the selectivity is assumed to be dependent on the oxidation state of chromium. Recently, catalyst systems capable of selectively tetramerizing ethylene to 1-octene have been reported. The originally proposed mechanism is similar to that of ethylene trimerization with the only difference that the chromocyclopentane ring inserts two ethylene molecules rather than one before it collapses to form 1-octene and the low valent metal center.$^9$ More recently, an alternative mechanism for the formation of 1-octene that involves two metallacyclopentane moieties has been proposed by Rosenthal.$^{9g}$

Chromium is an ideal substrate to study the factors affecting catalyst behavior, since effective catalysts for both ethylene polymerization$^{10}$ and oligomerization (including selective tri-$^{11}$ and tetramerization$^{12a}$) have been reported for this element. Virtually all homogeneous chromium-based catalyst systems reported to date invariably consist of a di- or trivalent chromium precursor and an aluminum alkyl-based activator.$^{10}$ Besides the oxidation state of the metal precursor, the ancillary ligand system, the reaction conditions and the choice of cocatalyst can also have a profound effect on catalyst selectivity.$^{13}$

In this chapter, we are searching for alternatives to classical tandem catalysis for the production of LLDPE out of ethylene as the sole feedstock by using one precatalyst that can switch its selectivity. A few examples of tandem catalysis starting from a single precatalyst already exist. De Wet-Roos’s Cr/PNP/MAO system is known to change its selectivity from oligomerization to polymerization by changing the temperature profile.$^{14}$ Another interesting tandem catalytic system reported is a combination of rac-Et(Ind)$_2$ZrCl$_2$ and two cocatalysts (AlEt$_2$Cl and MAO). In their system, when rac-Et(Ind)$_2$ZrCl$_2$ is activated by AlEt$_2$Cl, it functions as an ethylene oligomerization catalyst, while rac-
Et(Ind)$_2$ZrCl$_2$ activated by MAO functions as copolymerization catalyst.$^{15}$ Triggered by the fact that the chromium (N-Me-pyrrole-dipyrrole) system, developed in our group, switches its catalytic selectivity from a Schultz-Flory (S-F) distribution of oligomers to polyethylene by changing the cocatalyst,$^{13}$ we thought we might be able to use such a switch in selectivity as an elegant alternative to tandem catalysis for the production of LLDPE. With the idea in mind that the [(tBu)NPN(tBu)]$_2^{2-}$ (I) ligand would not be very suitable to host a square planar Cr(II) species, we hoped to be able to avoid the undesired S-F distribution of oligomers and to favor the production of 1-hexene and/or polyethylene by applying an aluminum alkyl activator.

### 2.2 Chromium Catalyst stabilized by NPN ligands

Wass et al. and Overett et al. have clearly demonstrated the potential of the combination of nitrogen and phosphorous donor atoms in a three-atom array for obtaining selective trimerization$^{11f,i,k}$ and tetramerization catalysts.$^{12a}$ Previous mechanistic studies on selective trimerization led us to believe that a stable cationic organochromium (III) species might be the key to selectivity for the oligomerization process.$^{16b}$ These two arguments prompted us to use the established [(tBu)NPN(tBu)]$_2^{2-}$ (I) dianion,$^{17}$ since the particular geometry of the cage defined by the four-membered P$_2$N$_2$ ring of the ligand with two additional N donor atoms was assumed to be unsuited for accommodating the square-planar geometry of d$^4$ Cr(II).

In spite of our expectations for facial, octahedral d$^3$ trivalent complexes, the reaction of the dilithium salt of I with either CrCl$_2$(THF)$_2$ or CrCl$_3$(THF)$_3$ resulted in an unexpected cleavage of the P$_2$N$_4$ ligand structure into two monoanionic NPN fragments accommodating a divalent chromium metal center in the distorted square-planar complex (Figure 1). The affinity of divalent chromium for square-planar ligand fields as dictated by the d$^4$ electronic configuration is probably the reason for this unexpected behavior.

![Diagram](image)

**Figure 1.** Thermal ellipsoid plot of 1 with ellipsoids drawn at 50% probability. Selected bond distance(Å) and angles (°): Cr(1)-N(1) = 2.098(3), Cr(1)-N(2) = 2.103(3), N(1)-Cr(1)-N(2) = 70.50(10), N(1)-Cr(1)-N(1a) = 158.10(16), N(1)-Cr(1)-N(2a) = 114.08(11).

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2.2.1 Ethylene Polymerization and Oligomerization with a Chromium Catalyst Supported by a Non-Innocent Ancillary NPN Ligand and the Effect of Aluminum Alkyls

In this section, the catalytic activity and selectivity for ethylene oligomerization and polymerization of the divalent chromium catalyst precursor 1 was investigated and a selection of the results is listed in Table 1. When looking at the MAO-activated systems, several interesting features may be observed with respect to both selectivity and activity. Divalent 1 yields a Schultz-Flory distribution of α-olefins when activated with MAO. The Cr(II) pre-catalyst requires a considerable amount of MAO (1000 equiv.) before it shows significant ethylene oligomerization activity and the catalytic activity continues to rise with increasing the amount of MAO (Figure 2, Table 1). This contrasts, for example, the chromium PNP and SNS systems that show a clear optimum in activity for a much lower Al:Cr ratio of about 100-300, but a similar behavior was observed for amidinato and pyrrole-dipyrrolide chromium systems. Changing the Al:Cr ratio has no effect on the α-value of the S-F distribution.

![Graph](image)

**Figure 2.** Oligomers produced by [(tBuNPN(tBu)]2Cr (1) and [(ArNPN(tBu)]2Cr (6) versus the Al:Cr ratio.

The catalyst was found to be thermally stable, as catalytic tests with high catalyst loading showed drastic exotherms up to temperatures above 110 °C for prolonged periods of time. Interestingly, the selectivity of 1 was completely determined by the nature of the activator (Table 1). While MAO resulted in non-selective oligomerization of ethylene, activation with (tBuAl)2(μ-O) (TIBAO) gave polyethylene with a
similar activity as when activated with MAO. Interestingly, a small but significant amount of a mixture of exclusively 1-hexene and 1-octene (average ratio = 85:15) was formed as side product. In an attempt to track the origin of this selective oligomerization, it was argued that possibly Al(iBu)_3 (TIBA) present in the TIBAO might reduce the chromium to the monovalent state, which is believed to be responsible for selective oligomerization. While activated with TIBA, complex 1 indeed produced 1-hexene with excellent selectivity (>99.9% as determined by GC). Interestingly, during this experiment no 1-octene was formed. Although the activity was significantly lower compared to the activity when activated with MAO, it was still similar to that of most of the existing selective catalysts.\textsuperscript{11g,12b,16} The catalytic behavior of 1 resembles that of the recently reported N-Me-pyrrole, dipyrrolyl chromium system [N-Me, tripyrr]Cr(pyrindine)_2.(THF)_0.5,\textsuperscript{13} which also showed a complete lack of selectivity for the divalent state and a switch from non-selective ethylene oligomerization to ethylene polymerization upon changing the cocatalyst from MAO to TIBAO. Adding a strongly reducing aluminum alkyl as cocatalyst results in selective ethylene trimerization. These results support the current belief that Cr(II) is responsible for non-selective ethylene oligomerization whereas Cr(I) is responsible for selective oligomerization.

It was argued that using a combination of MAO and TIBAO as cocatalyst might \textit{in situ} produce a tandem system consisting of an oligomerization and polymerization catalyst, hopefully able to produce LLDPE from ethylene as the sole feedstock. Unfortunately, the reaction of 1, activated with a combination of MAO/TIBAO (50:50, Al:Cr = 500) with ethylene did not result in LLDPE. Instead, a small amount of linear polyethylene (5% wt of the total product) and 95% wt of Schultz-Flory distribution of \(\alpha\)-olefins were obtained. Clearly, the combination of MAO+TIBAO has a negative effect on the catalytic activity of the system. The exact reason for this is not understood.

### 2.2.2 Isolation of the Catalytically Active Species

The diversity of the catalytic behavior (Section 2.2.1 and Table 1) as a function of the activator clearly indicates that different catalytically active species are generated upon reaction of 1 with different alkyl aluminum reagents. To gain more insights into the structures of these species, we attempted to isolate intermediates by carrying out the reaction of 1 with various aluminum alkyls and testing their catalytic behavior as self-activating catalysts. When 1 was reacted with AlMe_3 (TMA) and (iBu)_2AlCl (DIBAC), the divalent chromium complexes \([([tBu]NP(Me)N(tBu)]AlMe_2)Cr([([tBu]NP(Me)(AlMe_3)N(tBu)]AlMe(\mu-Me)]) (2)\) and \([([tBu]NP(iBu)N(tBu)]AlCl(iBu)]Cr(\mu-Cl)_2Al(iBu)]_2) (3)\) were formed as was revealed by single crystal X-ray structure determination. In both cases the chromium is in its divalent state. The coordination sphere of the chromium in both complexes is somewhat different. In complex 2 chromium is bonded to the two \([RP(NtBu)_2AlMe_2])\] ligands, albeit adopting different modes. Whereas one of the ligand is \(\kappa^2-N,N\)-bonded, the other ligand is \(\kappa^2-C,N\)-bonded to the metal with a methyl bridging between chromium and
aluminum. This C,N-bonding mode also results in the coordination of the ligand phosphorous atom to a TMA molecule. In complex 3 one of the original NPN ligands has been displaced forming a complex in which chromium is ν2-N,N-bonded to one [RP(NtBu)2Al(iBu)2]− ligand and to a (iBu)2Al(μ-Cl)2− fragment through two bridging chlorine ligands (Figure 3). The different bonding modes of the ligands in 2 and 3 are most likely the result of the higher steric hindrance in 2, which might prevent the generally more favored ν2-N, N bonding mode of the ligand.

Figure 3. Reaction of 1 with aluminum alkyls affording 2 and 3. Thermal ellipsoid plot of 2 and 3 with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°) for 2: Cr(1)-N(1) = 2.135(3), Cr(1)-N(3) = 2.136(3), Cr(1)-C(14) = 2.344(5), Cr(1)-P(2) = 2.3505(12), N(1)-Al(2) = 1.940(3), N(2)-Al(2) = 1.839(3), Al(2)-C(14) = 2.025(5), P(1)-N(1) = 1.736(3), P(1)-N(2) = 1.667(3), Al(1)-P(1) = 2.5549(15), Al(3)-N(3) = 1.993(3), Al(3)-N(4) = 1.876(4), P(2)-N(3) = 1.710(3), P(2)-N(4) = 1.648(4) N(1)-Cr(1)-N(3) = 167.32(12), N(1)-Cr(1)-C(14) = 89.40(14), N(3)Cr(1)-C(14) = 103.24(14), N1-Cr1-P2 =
122.95(9), N(3)-Cr(1)-P(2) = 44.50(9), C14-Cr1-P2 = 145.67(12), Al(2)-C(14)-Cr(1) = 78.08(16); Selected bond distances (Å) and angles (°) for 3: Cr(1)-N(2) = 2.1256(12); Cr(1)-N(1) = 2.1305(13); Cr(1)-Cl(3) = 2.4041(5); Cr(1)-Cl(2) = 2.4063(5); Al(3)-Cl(3) = 2.2764(7); Al(3)-Cl(2) = 2.2765(7); Al(2)-N(1) = 1.9209(13); Al(2)-N(2) = 1.9283(13); Al(2)-C(13) = 1.9370(16); P(1)-N(1) = 1.7651(14); P(1)-N(2) = 1.7730(14); N(2)-Cr(1)-N(1) = 65.26(5); N(2)-Cr(1)-Cl(3) = 104.24(4); N(1)-Cr(1)-Cl(3) = 169.42(4); N(2)-Cr(1)-Cl(2) = 169.26(4); N(1)-Cr(1)-Cl(2) = 104.67(4); Cl(3)-Cr(1)-Cl(2) = 85.713(17); Cl(3)-Al(3)-Cl(2) = 91.88(2); N(1)-Al(2)-N(2) = 73.20(6); N(1)-P(1)-N(2) = 80.88(6).

The anionic charge of the [RP(NtBu)2AlR2]− ligand is formally located at the aluminum center that, at least for Al(3), is situated relatively far away from the chromium atom. Hence, the structure may be regarded to consist of a formally dicatonic chromium center stabilized by two anionic [RP(NtBu)2AlR2]− ligands. Such a structure resembles the earlier reported divalent cationic chromium species {[(CyN(PPh3)2]2CrClIME4}+ where a formally dicatonic chromium is stabilized by one weakly bonded Me3AlCl− fragment and two diphosphinoamine ligands.16a Although the latter complex required a co-catalyst before any catalytic activity is being observed, the presence of a positively charged chromium center containing a Cr-C bond made 2 a potential self-activating catalyst. Upon exposure of 2 to ethylene (35 bar, 50 °C) catalytic activity was indeed observed and polyethylene was formed with moderate activity. When 2 was treated with MAO, a radical switch in selectivity towards a statistic distribution of oligomers was observed with a similarly high activity as found for the 1/MAO system (see Table 1). Although there are no free coordination sites around chromium, nor are Cr-C bonds present which could possibly act as initiating functions, also 3 acts as a self-activating ethylene polymerization catalyst. Based on the similar activity and selectivity pattern as for 2, the most probable explanation for the activity of 3 is migration of an alkyl from the Al-R residue to chromium leading to [IBuP(NtBu)2Al(IBu)Cl]Cr([μ-IBu])([μ-Cl]Al(IGu)Cl or "[IBuP(NtBu)2Al(IGu)Cl]Cr([IGu])" that again can be regarded as a zwitterionic structure containing a cationic chromium alkyl. Alkyl shuttling from the alkylated P atom is another possibility that cannot be ruled out at this stage.

Since 2, 3 and TiBAO-activated 1 yield polymers of similar molar mass and 1-3 activated with MAO afford a S-F distribution of α-olefins with similar activity and α-value, it is likely that closely related active species were generated in the three systems. However, activation of both 2 and 3 with TiBA produced only polymer and no 1-hexene as was observed when 1 was activated with TiBA.

This unexpected behavior of the initially intended [{(tBu)NPN(tBu)}]2− ligand system gave access to a non-innocent spectator ligand, [{(tBu)NPN(tBu)}], which readily reacts with aluminum alkyls. The resulting [RP(NtBu)2AlR2]− anions result in thermally stable, self-activating chromium-based ethylene polymerization catalysts. To the best of our knowledge, after the earlier discovery of ether-coordinated Cr(III) alkyls18 as homogeneous single-component catalysts, our system is the second homogeneous
single-component catalyst. This desirable behavior is attributed to two characteristics of the [RP(NtBu)₂AlR₃]⁻ monoanion. The [RP(NtBu)₂AlR₃]⁻ anion has the potential to transfer an alkyl group to chromium (either from phosphorous or from the aluminum residue), which evidently yields robust chromium alkyl species, and it establishes a structure in which the Lewis acidity of the aluminum residue enhances the positive charge on chromium.

The observed switch in selectivity depending on the nature of the aluminum alkyl activator led us to attempt the isolation of other single component catalysts. This was done in view of studying the factors determining the selectivity towards polymerization versus oligomerization. Since the TiBAO-activated systems yielded 1-hexene and 1-octene as the only side products, we argued that traces of TiBA possibly present in TiBAO might be responsible for the formation of the tri- and tetramerization catalysts. To verify this, 1 has been reacted with 2 and 10 equivalents of TiBA in toluene. The reactions afforded divalent species (μ-[μ-(tBu)NP(iBu)N(tBu)]Al(iBu)₂)₂Cr (4, Figure 4) and [(μ-iBu)P(μ-N(tBu))₂Al(iBu)₂Cr(μ-H)]₂ (5, Figure 5), respectively.

![Figure 4](image_url)

**Figure 4.** Thermal ellipsoid plot of complex 4 with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)-N(2) = 2.129(3), Cr(1)-P(1) = 2.3989(10), Cr(1)-N(2a) = 2.129(3), N(1)-Al(1) = 1.898(3), N(2)-Al(1) = 1.988(3), P(1)-Cr(1)-P(1a) = 180.0, N(2)-Cr(1)-N(2a) = 180.0, P(1)-Cr(1)-N(2) = 44.51(7).
Table 1. Ethylene oligomerization and polymerization results for complexes 1, 2 and 3 (see Figure 3).^a

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<td>11 420</td>
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<td>920</td>
<td>0</td>
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</table>

^a Reaction conditions : T = 50 °C, 35 bar of ethylene, 100 mL toluene, 30 min. reaction duration; ^b 5 bar of ethylene; ^c Wax; ^d $\alpha$ characteristic for Schultz-Flory oligomer distribution determined from molar ratios $C_6$ - $C_{18}$.
Figure 5. Thermal ellipsoid plot of complex 5 with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): Cr(1)···Cr(1a) = 2.6142(16), Cr(1)-N(1) = 2.156(3), Cr(1)-N(2) = 2.141(3), Cr(1)-P(1) = 2.6178(15), N(1)-Al(1) = 1.953(3), N(2)-Al(1) = 1.956(3), N(1)-Cr(1)-N(2) = 65.20(11), N(1)-Cr(1)-P(1) = 41.88(8), N(2)-Cr(1)-P(1) = 42.27(8).

The crystal structure of 4 (Figure 4) reveals a divalent chromium atom in a square-planar coordination environment. In complex 4, both NPN ligands underwent the same addition of an iBu and Al(iBu)₂ residue across the N=P formal double bond. As a result, the P atom has been alkylated, the ligand formally acquired a second negative charge and the cationic Al(iBu)₂ residue was retained through coordination to the two N atoms. Treatment of complex 4 with 8 equivalents of TiBA or a convenient one-pot synthesis via reaction of 1 with 10 equivalents of TiBA afforded [(iBu)P{μ-N(tBu)}₂Al(iBu)₂]Cr(μ-H)]₂ (Figure 6). The crystal structure of complex 5 (Figure 5) revealed a hydride-bridged [(iBu)P{μ-N(tBu)}₂Al(iBu)₂]Cr(μ-H)]₂ dimer in which each chromium occupies only one alkylated ligand system. The other ligand has been substituted by a hydride, which bridges an identical unit by forming a Cr₂H₂ core. Complex 5 (Figure 5) is paramagnetic \( \mu_{\text{eff}} = 1.63 \mu_{\text{B}} \) with a magnetic moment that is expected on the basis of the presence of a fairly short Cr-Cr distance \( \text{Cr(1)···Cr(1a) = 2.6142} \) and two bridging hydrides.¹⁹

The \(^1\text{H}-\text{NMR}\) spectrum showed only broad features that could not be conclusively assigned.

The main difference between these two complexes is the bonding mode of the nitrogen and phosphorous atoms to the chromium center and the fact that in 5 one of the ancillary ligands has been replaced by a hydride. Two possible routes might explain the hydride formation. It can either be formed as a result of the abstraction of one ligand that forms the unstable iBu-Cr group that generates the chromium hydride upon \( \beta\)-H elimination, or alternatively isobutene elimination of TiBA might generate [(iBu)₂Al]₂(μ-H)₂ as a possible source of the hydride. However, attempts to more directly obtain complex 5 via reaction of 1 with [(iBu)₂Al]₂(μ-H)₂ resulted in complete decomposition to metallic chromium. In 5, the ligand nitrogen and the phosphorous atoms were bonded to the chromium center in a ‘tridentate’ facial mode, which resulted in a short Cr-P distance [2.6178(15) Å]. Therefore, the coordination geometry could be considered as being either square planar or distorted square pyramidal. This
difference in structure is most likely due to the release of steric hindrance and the increased Lewis-acidity of the metal because of the loss of one of the ancillary ligands in 5. The intermetallic distance was consistent with published divalent chromium hydride species.\textsuperscript{19} The catalytic behavior of 4 and 5 as single-component catalysts as well as in the presence of a cocatalyst has been summarized in Table 2.

**Figure 6.** Reaction of [(tBu)NPN(tBu)]\textsubscript{2}Cr with TiBA.

Complex 5 acts as a self-activating ethylene polymerization catalyst and its catalytic activity is of the same magnitude as that observed for the most active chromium catalysts.\textsuperscript{20} It is assumed that homolytic dimer-to-monomer dissociation of 5 leads to the active divalent species affording polyethylene via a non-redox mechanism. Complex 4, which does not have a preformed Cr-C bond, is also active as a single-component polymerization catalyst. The single-component character of 4 is most likely due to a spontaneous conversion of 4 into 5 under polymerization conditions. This assumption was supported by the fact that both complexes 4 and 5 produced high-density polyethylenes with nearly identical activities, molar masses and polydispersities.
Table 2. Oligomerization and polymerization results for 1, 4 and 5 either in the presence of a cocatalyst or as single component catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cocatalyst</th>
<th>Activity</th>
<th>PE (g)</th>
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<th>PE</th>
<th>1-hexene</th>
<th>$M_n$</th>
<th>PDI</th>
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<td></td>
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<td>$b_{PE}/$mmol$_{Cr}$</td>
<td>mL</td>
<td>%wt</td>
<td>%wt</td>
<td></td>
<td></td>
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<td>-</td>
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</table>

*Conditions: 20 μmol, TIBA cocatalyst, 50 °C, 35 bar, 30 min.; $^b$ in units of mL of (C$_5$H$_5$/mmol$_{Cr}$h); $^c$ in units of g of (PE/mmol$_{Cr}$h).

Complexes 4 and 5 showed a switch in selectivity from ethylene polymerization to selective trimerization when they were activated with an excess of TIBA (Figure 6). Complex 1 also resulted in a selective ethylene trimerization catalyst upon treatment with excess of TIBA. Therefore it is assumed that the same active species are generated, regardless which of the three complexes are used as a catalyst precursor. This could be confirmed by the nearly identical catalytic activities observed for 1, 4 and 5. It can be concluded that the large excess of TIBA triggers the transformation from ethylene polymerization toward selective trimerization. Alternatively, treatment of 2 and 3 with TIBA produced only polyethylene.

2.2.3 Ligand Effect on Trimerization of Ethylene

From the discussion above it is clear that the chromium NPN system switches its selectivity from ethylene polymerization to a non-selective oligomerization, and even to selective ethylene trimerization depending on the nature of the activator. We wondered how ligand substituents would influence this catalytic behavior. For this reason the aryl-substituted ligand has been prepared. The reaction of [(Ar)N(H)PN(tBu)]$_2$ (II)$^{137,22}$ with nBuLi followed by reaction with CrCl$_2$(THF)$_2$ yielded the divalent [(Ar)NPN(tBu)]$_2$Cr (6), where the ligand system underwent the same dimer to monomer dissociation generating two [(Ar)NPN(tBu)]$^-$ monoanions (Figure 7) as found for 1. The crystal structure of 6 (Figure 8) is very similar to that of 1 and did not show any relevant feature other than a divalent chromium center.
in an expected square-planar environment as defined by the four nitrogen atoms of the two NPN anions. The catalytic activity and selectivity for ethylene oligomerization and polymerization of the catalyst precursor 6 was investigated and a selection of the results is listed in Table 3. Besides oligomers, a small amount of polyethylene was formed. This behavior was very similar to that of the precursor 1 (see Figure 2) and it required a considerable amount of MAO (1000 equiv.) before significant ethylene oligomerization was observed. The catalytic activity continued to rise with increasing the amount of MAO. Upon activation with 500 equivalent of AlBu3 (TIBA) the selectivity of 6 switched to ethylene polymerization with a small amount of 1-hexene as side product. Interestingly, no 1-octene was obtained as was the case when 1 was activated with TIBA.

Table 3. Ethylene oligomerization and polymerization results for 6. a

<table>
<thead>
<tr>
<th>Cat</th>
<th>Co-cat.</th>
<th>Al:Cr</th>
<th>PE</th>
<th>Oligomer</th>
<th>Activity b</th>
<th>PE %wt</th>
<th>Olig. %wt</th>
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<td>&gt;99.9</td>
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a Conditions: 5 μmol, 50 °C, 35 bar, 30 min.; b In units of mL of (C6 /mmolCr*h).

Figure 7. Synthesis of 6 and reaction with TMA to the single-component catalyst 7.
Figure 8. Thermal ellipsoid plot of complex 6 with ellipsoids drawn at 50 % probability level. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 2.114(3), Cr(1)-N(2) = 2.086(3), N(1)-P(1) = 1.628(3), N(2)-P(1) = 1.612(3); N(1)-Cr(1)-N(2) = 71.02(13), N(1)-Cr(1)-N(2a) = 108.98(13), N(2)-Cr(2a)-N(1a) = 179.998(1).

In search for self-activating catalysts, 6 was reacted with several aluminum alkyls. Only the reaction of 6 with 4 equivalents of TMA resulted in an isolatable product in good yield formulated as \([[\text{Ar} NP(\text{Me}) N(\text{t-Bu})] AlMe_2] Cr[[\text{Ar} NP(\text{Me}) (AlMe_3) N(\text{t-Bu})] AlMe(\mu-\text{Me})]\) (7) (Figure 9). This complex is isostructural to 2.

Figure 9. Thermal ellipsoid plot of complex 7 with ellipsoids drawn at 50 % probability. Selected bond distances (Å) and angles (°): Cr(1)-N(3) = 2.144(4), Cr(1)-N(4) = 2.125(4), Cr(1)-C(38) = 2.289(6), Cr(1)-P(2) = 2.4035(16), N(4)-Al(2) = 2.026(4), N(2)-Al(2) = 1.899(4), Cr(1)-Al(4) = 2.8098(18), Al(2)-P(2) = 2.627(2), P(2)-N(2) = 1.659(4), P(2)-N(4) = 1.717(4), Al(4)-P(1) = 2.634(2), Al(4)-N(3) = 1.951(4), Al(4)-N(1) =
1.845(4), P(1)-N(3) = 1.746(4), P(1)-N(1) = 1.674(4), N(4)-Cr(1)-N(3) = 165.94(16), N(4)-Cr(1)-C(38) = 98.89(19), N(3)-Cr(1)-C(38) = 90.15(19), N(4)-Cr(1)-P(2) = 44.03(11), N(3)-Cr(1)-P(2) = 127.78(12), C(38)-Cr(1)-P(2) = 142.07(16), Al(4)-C(38)-Cr(1) = 79.9(2), Cr(1)...Al(4) = 2.8098(18).

Interestingly, whereas 2 is a self-activating ethylene polymerization catalyst, the isostructural complex 7 is a self-activating ethylene trimerization catalyst. Clearly, there is a delicate balance between the catalytic behavior of the catalyst and the ancillary ligand substituents. Its activity was of the same order of magnitude as that of other selective systems recently reported such as Sasol’s [SNS]CrCl₂ system.⁶ The activity and selectivity also depend on the reaction temperature. Namely, at 80 °C 1-hexene was no longer produced and polymer was formed instead. A similar behavior was observed by De Wet-Roos and coworkers for Sasol's PNP-type tetramerization catalyst system.¹⁴ At room temperature, the catalytic activity dropped and the catalysts deactivated. Reaction times up to 10 hours did not improve the productivity of 1-hexene (Table 4). Upon addition of aluminum-based cocatalysts the selectivity of complex 7 showed a dramatic switch. In the case of treatment with MAO, the selectivity switched to yield a statistical distribution of oligomers with an enormous increment of activity. Upon activation with TIBAO the selectivity switched to ethylene polymerization with a small amount of 1-hexene as side product. With TIBA as cocatalyst, no oligomers and only a small amount of polymer was formed. This switch of selectivity clearly demonstrates that selective trimerization and statistical oligomerization follow distinctive reaction mechanisms, given that the ligand and the initiating alkyl function (methyl) are the same for the two processes. The fact that at elevated temperature 7 becomes an ethylene polymerization catalyst suggests that the switch between the different mechanisms is rather easy.

The difference in reactivity (trimerization, non-selective oligomerization and polymerization) as a function of the ancillary ligand substituents as well as the presence/absence and nature of the aluminum alkyl is ascribed to different species generated in situ, probably with different oxidation states. Complex 7 has an existing Cr-Me bond, although it was bridged to an aluminum atom, and has no empty coordination sites. Therefore, one must necessarily concede that one ligand system may dissociate to generate the coordinative vacancy necessary to any C-C bond forming process. In fact, among the two alkylated ligands in 7, the one that shares the Me group with chromium could dissociate as a neutral (Me₃Al)[(Ar)NP(Me)N(tBu)]AlMe fragment, thus generating the coordinatively unsaturated “[(Ar)NP(Me)N(t-Bu)][AlMe₃]CrMe”. This species might well undergo further spontaneous reduction at the elevated temperature used for the trimerization and produce monovalent chromium, which is expected to be the artifex of the selective trimerization process. The importance of the ligand’s substituents are paramount, as the somewhat more electron donating ligand of 2 obviously prevents further reduction to Cr(I) and consequently produced polyethylene instead of 1-hexene. The added
aluminoxane or TIBA might facilitate ligand dissociation but clearly yielded different species depending on the type of aluminoxane used.

Table 4. Ethylene oligomerization and polymerization results for 7.

<table>
<thead>
<tr>
<th>Cat</th>
<th>Cat</th>
<th>Cocat.</th>
<th>Al:Cr</th>
<th>PE (g)</th>
<th>Olig.</th>
<th>PE Olig.</th>
<th>Activity</th>
<th>C_6</th>
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<td>wt%</td>
<td>g mmol^{-1} h^{-1}</td>
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<td>%</td>
<td>%</td>
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*Conditions: 100 mL of toluene, 35 bar of ethylene, reaction temperature 50 °C, reaction time 30 min; ^e reaction temperature 25 °C; ^f Reaction temperature 80 °C; ^f Reaction time 10 hours; ^e α = 0.57.

2.2.4 The Effect of Pendant Donor Functionalities on Cr-Based NPN Ligand System

The switchability of the catalytic behavior of the chromium NPN system described in the previous sections reflects the ability of the NPN ligand to stabilize different oxidation states. To improve our understanding of this versatile ligand system, we have attempted to assess its ability to affect the stability of the divalent and monovalent oxidation state of chromium as depending on the denticity and steric hindrance of the ancillary ligand system. In this section, we show the results of our further studies on this system, where a few variations of the ligand scaffold have been examined in relation to the catalytic behavior of these complexes. The ligands [(tBu)NPN(2-MeOPh)]_{2} (III) and [(t-Bu)NPNH[CH_{2}CH_{2}N(i-Pr)]_{2})_{2} (IV) were prepared via reaction of [(tBu)NPCl]_{2} with 2-methoxyaniline or (i-Pr)_{2}NCH_{2}CH_{2}NH_{2}, respectively (Figure 10). The reactions of both CrCl_{2}(THF)_{2} and CrCl_{3}(THF)_{3} with the deprotonated form of III were carried out at room temperature in THF affording the corresponding {[(tBu)NPN(2-MeOPh)]_{2}Cr}_{2} (8) and [(tBu)NPN(2-MeOPh)]_{2}CrCl (9), respectively (Figure 11).
Figure 10. Preparation of \([([tBu]NP Nh(2-MeOPh)]_2\) (III) and \([([tBu]NP Nh[CH_2CH_2N(iPr)_2])_2\) (IV).

Figure 11. Preparation of \([([tBu]NP Nh(2-MeOPh)]_2Cr)_2\) (8) and \([([tBu]NP Nh(2-MeOPh)]_2CrCl\) (9).

While targeting selective oligomerization catalysts, it is of primary importance that the ligand system may be capable of preventing disproportionation to the zero- and divalent states, respectively responsible for deactivation and unselective oligomerization. Apparently, by introducing a pendant 2-anisyl substituent to the ligand, the \(P_2N_2\) core stays intact and the reaction of the ligand dilithium salt with chromium trichloride affords a trivalent chromium complex, whilst the same reaction with the dilithium salt of I yielded the Cr(II) species 1. The extra donor helps stabilizing the trivalent chromium species but it does not prevent the formation of the divalent chromium complex, as was the initial motif of using this \(P_2N_4\)-ligand. As can be seen from Figure 12, complex 8 is a symmetry-generated dimer with two dianionic ligands surrounding the dimetallic unit with each metal in a distorted square planar coordination environment stabilized by coordination of one of the pendant methoxy donor functionalities. Each ligand adopts a curious bridging bonding mode. Each \(P_2N_2\) square core is capping a chromium center while none of the four atoms reaching a bonding contact with the metal. Instead the two nitrogen atoms of the two “arms” are bonding the chromium atoms. One of the two nitrogens
bridges the two metal center where as the other binds to only one chromium center. Each anisyl methoxy group also bonds to one of the chromium center. The second OMe group of the same ligand is not forming a bonding contact but is located on an equatorial vertex of an ideal trigonal bipyramid centered on the chromium atom.

Figure 12. Thermal ellipsoid plot of 8 with ellipsoids drawn at 50 % probability. Selected bond distances (Å) and angles (°): Cr(1)-N(4) = 2.056(3), Cr(1)-N(3) = 2.098(3), Cr(1)-N(3)A = 2.118(3), Cr(1)-O(1)A = 2.208(2), N(3)-Cr(1)A = 2.118(3), O(1)-Cr(1)A = 2.208(2). N(4)-Cr(1)-N(3) = 96.33(11), N(4)-Cr(1)-N(3)A = 168.74(12), N(3)-Cr(1)-N(3)A = 88.71(11), N(4)-Cr(1)-O(1)A = 95.83(10), N(3)-Cr(1)-O(1)A = 155.48(11), N(3)A-Cr(1)-O(1)A = 75.94(10), Cr(1)-N(3)-Cr(1)A = 91.29(11).

Structure 9 shows a monomeric complex with the chromium atom in a distorted trigonal pyramidal geometry (Figure 13). The coordination environment is defined by the two ortho located oxygen atoms of the two ligand’s methoxy groups, one terminally bonded Cl atom and three of the four nitrogen donor atom of the ligand system facially oriented. The fourth N atom is not engaged in a bonding interaction with the metal center.
Figure 13. Thermal ellipsoid plot of 9 with ellipsoids drawn at 50 % probability. Selected bond distances (Å) and angles (°): Cr(1)-N(1) = 1.912(5), Cr(1)-N(2) = 1.987(5), Cr(1)-O(1) = 2.098(4), Cr(1)-O(2) = 2.156(4), Cr(1)-Cl(1) = 2.326(2), N(1)-Cr(1)-N(2) = 98.2(2), N(1)-Cr(1)-N(3) = 73.3(2), N(1)-Cr(1)-O(1) = 78.88(19), N(1)-Cr(1)-Cl(1) = 94.58(17), O(1)-Cr(1)-O(2) = 169.8(2), N(3)-Cr(1)-Cl(1) = 104.09(14), N(2)-Cr(1)-Cl(1) = 166.26 (16), O(1)-Cr(1)-N(3) = 149.93(18), N(3)-Cr(1)-O(2) = 114.06(18), O(2)-Cr(1)-Cl(1) = 90.54(13), N(2)-Cr(1)-O(1) = 98.45(18).

The reaction of the ligand IV (See Figure 10) with CrCl₂(THF)₂ also afforded a dinuclear complex [{(tBu)NPN[CH₂CH₂N(iPr)₂]₂}₂CrCl]₂ (10) where the ligand is wrapped around the dimetallic unit consisting of two tetragonal planar chromium centers (Figure 14). Clearly, it seems to be a general feature that in the presence of pendant donor functionalities the original ligand structure remains intact. One chlorine atom was also retained on each of the two chromium atoms. Since unreacted chromium salt was invariably present in the reaction mixture, even after prolonged reflux, it was decided to carry out the reaction with the appropriate stoichiometry deduced from the formula elucidated by X-ray analysis.

Figure 14. Complex [{(tBu)NPNH[CH₂CH₂N(iPr)₂]₂}₂CrCl]₂ (10).
Structure 10 (Figure 15) shows the $\text{N}_2\text{P}_2$ core of the ligand symmetrically capping the dimetallic unit without bonding contact between any of the donor atoms and the metal centers. Each of the two N atoms of the ligand’s “arms” bridge the two metal centers with formation of a folded $\text{Cr}_2\text{N}_2$ core. The aliphatic pendant amino groups attached to each of the two nitrogens of the ligand’s arms coordinate to the metal centers which, with terminally bonded chlorine atoms on the fourth coordination site, achieves distorted square planar coordinated chromium centers.

![Diagram of 10](image.png)

**Figure 15.** Thermal ellipsoid plot of 10 with ellipsoids drawn at 50% probability. Selected bond distances (Å) and angles (°): $\text{Cr}(1)-\text{N}(5) = 2.081(4)$, $\text{Cr}(1)-\text{N}(3) = 2.114(4)$, $\text{Cr}(1)-\text{N}(6) = 2.232(5)$, $\text{Cr}(1)-\text{Cl}(1) = 2.3208(17)$, $\text{Cr}(1)-\text{Cr}(2) = 2.6354(13)$, $\text{Cr}(2)-\text{N}(3) = 2.071(4)$, $\text{Cr}(2)-\text{N}(5) = 2.144(5)$, $\text{Cr}(2)-\text{N}(4) = 2.245(5)$, $\text{Cr}(2)-\text{Cl}(2) = 2.3241(17)$, $\text{N}(5)-\text{Cr}(1)-\text{N}(3) = 84.97(17)$, $\text{N}(5)-\text{Cr}(1)-\text{N}(6) = 82.32(17)$, $\text{N}(3)-\text{Cr}(1)-\text{Cl}(1) = 95.23(12)$, $\text{N}(6)-\text{Cr}(1)-\text{Cl}(1) = 97.53(12)$, $\text{N}(3)-\text{Cr}(1)-\text{N}(6) = 161.76(18)$, $\text{N}(5)-\text{Cr}(1)-\text{Cl}(1) = 179.73(14)$, $\text{Cl}(1)-\text{Cr}(1)-\text{Cr}(2) = 127.78(6)$, $\text{Cr}(1)-\text{N}(5)-\text{Cr}(2) = 77.16(15)$, $\text{Cr}(2)-\text{N}(3)-\text{Cr}(1) = 78.03(15)$.

Attempts to form the trivalent analogue by treating $\text{CrCl}_3(\text{THF})_3$ with the dilithium salt of 1V only afforded oily materials, which were not further purified. The three complexes 8 - 10 described above have all been tested for their activity in ethylene oligomerization under standard ethylene oligomerization conditions using several activators (see Table 5). MAO seems to be the only effective activator. Activation of the two divalent complexes 8 and 10 with MAO gave a Schultz-Flory distribution of $\alpha$-olefins. The activities were in general quite high and, even more interestingly, the production of linear $\alpha$-olefins was not accompanied by the usual formation of waxes or polymer. TIBA and triethylaluminum (TEAL) gave no catalytic activity. Upon activation with TIBAO 8 gave a substantial amount of polymer aside a mixture of 1-hexene and 1-octene. No such behavior was observed for 10, which proved inactive on treatment with TIBAO.
The lack of selectivity of 8 and 10 when activated with MAO speaks for the stability of the divalent state of chromium in these two complexes, unlikely to undergo any further reduction towards the monovalent state. The presence of small amounts of 1-hexene and 1-octene in the reaction mixture in the case of the more reducing TIBAO, aside a large amount of polymer, indicates that some reduction occurs. MAO-activated 9 is catalytically inert, this might indicate that no reduction towards the Cr(II) or Cr(I) occurs with this ligand system.

Table 5. Ethylene oligomerization results for 8 - 10.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Cat</th>
<th>Cocat.</th>
<th>Al:Cr</th>
<th>PE</th>
<th>Oligo.</th>
<th>PE</th>
<th>Oligo.</th>
<th>Activity\textsuperscript{b}</th>
<th>C\textsubscript{6} \textsuperscript{c}</th>
<th>C\textsubscript{8} \textsuperscript{c}</th>
<th>C\textsubscript{10} \textsuperscript{c}</th>
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\textsuperscript{a}Conditions 100 mL of toluene, 35 bar ethylene, reaction temperature 50 °C, 5 μmol catalyst; \textsuperscript{b} g olefin/mmolecat.h; \textsuperscript{c} Calculated based on molar ratio of two oligomer fractions.

2.3 Conclusions

The synthesis, characterization and catalytic testing of a series of chromium complexes stabilized by non-innocent ancillary ligands of the type NPN and P\textsubscript{2}N\textsubscript{4} have been described. The NPN ligand derives from an unusual cleavage of the original P\textsubscript{2}N\textsubscript{4} ligand and produces the divalent species [RNPNR]\textsubscript{2}Cr (1, 6) regardless of the valence state of the chromium chloride used. Depending on the aluminum alkyl activator used, catalytically active species switched selectivity from polymerization to non-selective oligomerization and even to selective ethylene trimerization. Attempts to isolate the catalytically active
species afforded several self-activating catalysts that polymerize ethylene without the need of additional cocatalysts. Upon activation with MAO, complexes 2 and 3 produce the same S-F distribution of \( \alpha \)-olefins as 1 activated with MAO. Reaction of 1 with different amounts of TIBA afforded complexes 4 and 5. Both these species were found to be self-activating ethylene polymerization catalysts with no need for further activation. For reactions of ethylene in the presence of complexes 4 and 5 carried out with an excess of TIBA, a switch towards selective ethylene trimerization has been observed. The selective ethylene trimerization observed for 4 and 5 as well as 1 activated with an excess of TIBA can be explained by the reducing ability of TIBA.\(^{22}\) Although the oxidation state of the active species could not be elucidated, it is assumed that the reducing power of TIBA affords Cr(I) ethylene trimerization catalysts whereas the reducing power of MAO and TiBAO apparently is insufficient to reduce this chromium system to a lower than divalent state yielding either a S-F distribution of \( \alpha \)-olefins or polyethylene. Reaction of 6 with TMA afforded complex 7. Whereas 2 is a self-activation ethylene polymerization catalyst, the isostructural 7 proved to be a self-activating ethylene trimerization catalyst, clearly indicating the delicate balance between ligand substituents and catalytic behavior. Upon activation with MAO, 7 provides a non-selective ethylene oligimerization catalyst similar as 6, producing a statistical mixture of oligomers, while upon treatment with TiBAO it acts as a highly active polymerization catalyst. Thanks to the presence of pendant donor functionalities, the original \( \text{P}_3\text{N}_4 \) ligand system is preserved in complexes 8 - 10. Complexes 8 and 10 showed high activity toward oligomerization upon treatment with MAO without any PE formation, while complex 9 did not show any reactivity upon activation with MAO. High activity and lack of PE formation make complex 8 and 10 potentially interesting from the application standpoint. Activation of complex 8 with TiBAO gave substantial amount of polymer aside a mixture of 1-hexene and 1-octene. No such a behavior of complex 10 with TiBAO occurred. Complex 8 and 10 display a very comparable behaviour although the activation pathway of 10 remains unclear.

2.4 Experimental Section

General considerations

All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The reaction mixtures were analyzed using a CP 9000 gas chromatograph (GC) fitted with a 30 m × 0.32 mm capillary CP volamine column. NMR spectra were collected on a Varian Inova 400 MHz instrument. High temperature size exclusion chromatography analysis of the polyethylenes was carried out on a PL-GPC210 equipped with a refractive index detector using a 3*PLgel 10 \( \mu \)m MIXED-B column set at 160 °C with 1,2,4-trichlorobenzene as the solvent with a flow rate of 1 mL/min. Irganox was used as an antioxidant. The molar masses of the polymers were
referred to polystyrene standards. Samples for magnetic susceptibility were pre-weighed inside a drybox equipped with an analytical balance and measured on a Johnson Matthey Magnetic Susceptibility balance. Elemental analysis was carried out with a Perkin-Elmer 2400 CHN analyzer. Data for X-ray crystal structure determination were collected with a Bruker diffractometer equipped with a 1K Smart CCD area detector. TMA (1.3 M in heptane) was purchased from Acros, whereas TIBAO (10% in toluene) and MAO (10% in toluene) were purchased from Aldrich and Chemtura, respectively. MMAO-7 (in Isopar E; 7% Al) was purchased from Akzo Nobel. TIBA (1 M in heptane) was obtained from Fluka while diisobutylaluminum chloride was received from Aldrich. Ethylene was obtained from Air Liquide. All ligands and chromium complexes described in this chapter have been prepared by Khalid Albahily at the University of Ottawa, Canada. cis-\{tBu(H)NP(μ-NtBu)_2PN(H)\}tBu\(^{13}\) (I) and cis-\{(2,6-diisoproplyphenyl)\}NP(μ-N)(tBu)\}_2PN(H)(2,6-diisoproplyphenyl)\}^{21a,b,c} (II) have been prepared according to the literature procedures.

**Ethylene Oligomerization and Polymerization**

Samples were tested in a 200 mL high pressure Büchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in 10 mL of toluene under N\(_2\) and injected into the preheated reactor already charged with cocatalyst and toluene (total volume 100 mL). Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. Polymerizations were quenched by addition of acidified alcohol. The resulting polymer was isolated by filtration, sonicated with an acidified ethanol solution, rinsed with ethanol and thoroughly dried prior to mass determination in vacuum at 60 °C. The reaction mixtures of the oligomerization runs were cooled to 0 °C prior to releasing the overpressure and quenching with EtOH and HCl.

**Ethylene Oligomerization and Polymerization in the High-throughput Platform**

Polymerization reactions described in Table 3 have been carried out in either 200 mL high pressure Büchi reactors containing a heating/cooling jacket or in a high-throughput platform which was available at the Eindhoven University of Technology (developed by DSM Research and Innovene Chemicals), consisting of eight independently operated 125 mL Premex reactors. A preweighed amount of catalyst was dissolved in toluene (100 mL for the Büchi reactor, 50 mL for the HTE platform) under N\(_2\) prior to loading into the reaction vessel. Solutions were heated using a thermostatic bath and charged with ethylene, maintaining the pressure throughout the run. Polymerizations were quenched by release of the pressure and addition of acidified ethanol. The polymers obtained were isolated by filtration, sonicated with a solution of HCl, rinsed with ethanol, and dried prior to mass determination in vacuum at 60 °C. The reaction mixtures of the oligomerization runs were cooled to 0 °C prior to releasing the overpressure and quenching with acidified ethanol.
Preparation of [(tBu)NP(tBu)]_2Cr (1): A: To a solution of cis-{tBu(H)NP(μ-NtBu)_2PN(H)tBu} (I) (0.348 g, 1 mmol) in THF (20 mL) a solution of nBuLi (0.84 mL, 2.1 mmol, 2.5 M in hexane) was added at 0 °C. The mixture was allowed to stir at room temperature for 18 h. The resulting solution was added to a suspension of CrCl_2(THF)_2 (0.268 g, 1 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature overnight. The solvent was removed and then toluene (10 mL) was added. The solution was centrifuged and the resulting solution was stored at -30 °C for 4 days. Brown crystals of 1 separated during two days standing, which were filtered, washed with cold hexane (10 mL) and dried in vacuo to give analytically pure product 1 (0.294 g, 74%). [μ_{eff} = 4.98 μ_6]. B: To a solution of cis-{tBu(H)NP(μ-NtBu)_2PN(H)tBu} (I) (0.348 g, 1 mmol) in THF (20 mL) a solution of nBuLi (0.84 mL, 2.1 mmol, 2.5 M in hexane) was added at 0 °C. The mixture was allowed to stir at room temperature for 18 h. The resulting solution was added to a suspension of CrCl_2(THF)_2 (0.303 g, 1 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature overnight. The solvent was removed and then toluene (10 mL) was added. The solution was centrifuged and the resulting solution was stored at -30 °C for 4 days. Brown crystals of 1 separated during two days standing, which were filtered, washed with cold hexane (10 mL) and dried in vacuo to give analytically pure product 1 (0.294 g, 74%). [μ_{eff} = 4.98 μ_6].

Preparation of [(tBu)NP(Me)N(i-Bu)]Cr[(tBu)NP(Me)(AlMe_3)N(tBu)]AlMe(μ-Me) (2): A solution of 1 (0.398 g, 1 mmol) in toluene (10 mL) was treated with TMA (0.288 g, 4 mmol) at room temperature and stirred for 1 h. The solvent was removed in vacuo and then hexane (10 mL) was added. Storing the resulting solution at -30 °C in a freezer for 3 days afforded small purple crystals of 2 which were filtered and washed with cold hexane (10 mL) and dried in vacuo (0.386 g, 63%), [μ_{eff} = 4.97 μ_6].

Preparation of [(tBu)NP(i-Bu)N(tBu)]Cr(μ-Cl)_2Al(i-Bu) (3): A solution of 1 (0.398 g, 1 mmol) in toluene (10 mL) was treated with diisobutylaluminum chloride (0.704 g, 4 mmol) at room temperature and allowed to stir for 1 h. The solvent was removed by vacuum and then hexane (10 mL) was added. The solution was stored at -30 °C in a freezer for 3 days. The resulting product was filtered and washed with cold hexane (10 mL) and dried in vacuo to give 3 as blue crystals (0.282g, 46%), [μ_{eff} = 5.24 μ_6].

Preparation of {μ-[tBu]NP(iBu)N(tBu)]Al(iBu)_2}Cr (4): Neat TiBA (0.79 g, 4 mmol) was added at 0 °C to a solution of 1 (0.80 g, 2 mmol) in toluene (10 mL) and allowed to stir for 1 h at room temperature. The solvent was removed in vacuo and the residue redissolved in hexane (10 mL). Crystals of 4 separated from the resulting solution upon standing at -30 °C for 3 days. The brown crystals were filtered and washed with cold hexane (10 mL) and dried in vacuo (0.96 g, 60.3 %). [μ_{eff} = 4.74 μ_6]. El. Anal. Calcd. (found) for C_{40}H_{90}Al_2CrN_4P_2: C 60.43(60.41), H 11.41(11.39), N 7.05( 7.00).
Preparation of [(μ-(i-Bu)P(μ-N(tBu))$_2$Al(i-Bu)$_2$Cr(μ-H))]$_2$ (5): Neat TIBA (3.96 g, 20 mmol) was added at 0 °C to a solution of 1 (0.80 g, 2 mmol) in toluene (10 mL) and allowed to stir for 1 h at room temperature. The solvent and the excess of TIBA were removed in vacuo and the resulting solid residue was dissolved in hexane (10 mL). The solution was stored in a -30 °C freezer for 3 days. Red-purple crystals of 5 separated which were filtered, washed with cold hexane (10 mL) and dried in vacuo (0.751 g, 88.2 %) [$\mu_{\text{eff}} = 1.63 \mu_B$]. El. Anal. Calcd. (found) for C$_{48}$H$_{62}$Al$_2$Cr$_2$N$_4$P$_2$: C 56.58(56.55), H 10.92(10.88), N 6.60( 6.54).

Preparation of [(2,6-diisopropylphenyl)NPN(tBu)$_2$Cr (6): A solution of cis-[(2,6-diisopropylphenyl)(H)NP(μ-N)(tBu)$_2$PN(H)(2,6-diisopropylphenyl)] (II) (0.556 g, 1 mmol) in THF (20 mL) was treated with nBuLi (0.84 mL, 2.1 mmol, 2.5 M in hexane) at 0 °C. The mixture was allowed to stir at room temperature for 20 h. The resulting solution was added to a suspension of CrCl$_3$(THF)$_2$ (0.268 g, 1 mmol) in THF (10 mL). The reaction mixture was stirred at room temperature overnight. The solvent was evaporated in vacuo and the residue was dissolved in toluene (10 mL). The resulting suspension was centrifuged and stored at -30 °C. Brown crystals separated over four days and were filtered, washed with cold hexane (10 mL) and dried in vacuo to give analytical pure 6 (0.355 g, 59 %). [$\mu_{\text{eff}} = 4.96 \mu_B$].

Preparation of [(2,6-diisopropylphenyl)NPN(AlMe$_3$)N(tBu)]AlMe$_2$Cr([(2,6-diisopropylphenyl)NPN(AlMe$_3$)N(tBu)]AlMe(μ-Me)) (7): A solution of 6 (0.606 g, 1 mmol) in toluene (20 mL) was treated with TMA (0.288 g, 4 mmol) at room temperature and stirred for 10 minutes. Storing the resulting solution at -30 °C for 5 days afforded small purple crystals of 7 which were filtered and washed with cold hexane (5 mL) and dried in vacuo (0.455 g, 55 %). [$\mu_{\text{eff}} = 4.98 \mu_B$].

Preparation of cis-[(o-OMeC$_4$H$_4$)(H)NP(μ-N)(tBu)$_2$PN(H)(o-OMeC$_4$H$_4$)] (III): o-Methoxyaniline (7.16 g, 58.16 mmol) and Et$_3$N (11.9 g, 116.4 mmol) were added to a stirred solution of cis-CIP[(μ-N)(tBu)$_2$]PCl (8.0 g, 29.08 mmol) in THF (100 mL) and the reaction was refluxed for 1 day. After filtration all volatile compounds were removed by vacuum and hexane (25 mL) was added to the residue. After filtration and removal of the solvent the required product was obtained as white crystals (11.25 g, 86 %). $^1$H-NMR (CDCl$_3$, 300 MHz, 300K) δ 1.28 (s, 18H, C(CH$_3$)$_3$) 3.86 (s, 6H, OCH$_3$) 5.65 (s, 2H, NH) 6.8-7.0, 7.48-7.6 (m, 8H, Ph). $^{13}$C(CDCl$_3$, 300 MHz, 300K) δ 30.95 (C(CH$_3$)$_3$) 50.47 (C(CH$_3$)$_3$) 55.55 (OCH$_3$) 110.39, 119.78, 120.88, 133.22, 147.90 (Ph). $^{31}$P ($^1$H) (CDCl$_3$, 300 MHz, 300K) δ 97.93 (s). MS (ESI) m/z (M+H)$^+$ = 448.22. El. Anal. Calcd. (found) for C$_{22}$H$_{34}$N$_4$O$_2$P$_2$: C 58.92 (58.84), H 7.64 (7.58), N 12.49 (12.47).
Preparation of cis-\{([Pr]_2NHCH_2CH_2)(H)NP([μ-N](tBu))_2PN(H)([Pr]_2NHCH_2CH_2)\}_2 (IV):

2-(Diisopropylamino)ethylamine (7.16 g, 58.16 mmol) and Et_3N (11.9 g, 116.4 mmol) were added to a stirred solution of cis-ClP([μ-N](tBu))_2PCl (8.0 g, 29.08 mmol) in THF (100 mL) and the reaction was refluxed for 1 day. After filtration all volatile compounds were removed by vacuum and hexane (25 mL) was added to the residue. After filtration and removal of the solvent the required product was obtained as white crystals (11.25 g, 86 %) \(^1\)H-NMR (CDCl_3, 300 MHz, 300K) δ 0.975 (d, j = 22 Hz, 2H, CH(CH_3)_2) 1.24 (s, 18H, C(CH_3)_3) 2.44 (t, j = 23 Hz 4H, NHCH_2CH_2N([Pr]_2)) 2.8-3.1 (sep j = 22Hz, 4H, CH(CH_3)_2) 2.9 (m, 4H, NHCH_2CH_2N([Pr]_2)) (s, NH). \(^13\)C(CDCl_3, 300 MHz, 300 K) δ 20.90 (CH(CH_3)_2) 30.98 (C(CH_3)_3) 39.16 (NHCH_2CH_2N([Pr]_2)) 46.62 (CH(CH_3)_2) 47.90 (NHCH_2CH_2N([Pr]_2)) 50.9 (C(CH_3)_3). \(^31\)P \(^1\)H (CDCl_3, 300 MHz, 300 K) δ 90.32 (s). MS (ESI) m/z (M+H)^+ = 490.40. El. Anal. Calcd. (found) for C_{26}H_{58}N_8P_2: C 58.75 (58.70), H 11.50 (11.52), N 17.13 (17.15).

Preparation of \{([tBu]NPN[2-MeOPh])_2Cr\}_2 (8): nBuLi (0.84 mL, 2.1 mmol , 2.5 M in hexane) was added to a solution of III (0.448 g, 1.0 mmol) in THF (5 mL) at 0 ˚C and the resulting mixture was stirred at room temperature for 18 h. The resulting solution was added to a suspension of CrCl_2(THF)_2 (0.268 g, 1 mmol) in THF (5 mL). The reaction was allowed to stir overnight at room temperature. The solvent was removed in vacuo and toluene (10 mL) was added. The solution was centrifuged and the resulting solution was reduced to 3 mL and stored at -30 ˚C in the freezer for 5 days. The resulting crystals were filtered and washed with cold hexane (10 mL) and dried in vacuo to give 8 as green crystals (0.402 g, 40.3 %). \(\mu_{\text{eff}} = 4.97 \ \mu_\text{B} \). El. Anal. Calcd. (found) for C_{46}H_{64}Cr_2N_8O_2P_2: C 53.01 (53.11), H 6.47 (6.51), N 11.24 (11.31).

Preparation of \{([tBu]NPN[2-MeOPh])_2Cr\} (9): nBuLi (0.84 mL, 2.1 mmol , 2.5 M in hexane) was added to a solution of III (0.448 g, 1.0 mmol) in THF (5 mL) at 0 ˚C and the resulting mixture was stirred at room temperature for 18 h. The resulting solution was added to a suspension of CrCl_2(THF)_2 (0.375 g, 1 mmol) in THF (5 mL). The reaction was allowed to stir overnight at room temperature. The solvent was removed in vacuo and toluene (10 mL) was added. The solution was centrifuged and the resulting solution was reduced to 3 mL and stored at -30 ˚C in the freezer for 5 days. The resulting crystals were filtered and washed with cold hexane (10 mL) and dried in vacuo to give 0.205 g of product as green crystals (38.4 %). \(\mu_{\text{eff}} = 3.89 \ \mu_\text{B} \). El. Anal. Calcd. (found) for C_{22}H_{32}ClCrN_4O_2P_2: C 49.49 (49.45), H 6.04 (6.01), N 10.49 (10.35).

Preparation of \{([tBu]NP[NH[CH_2CH_2N([Pr]_2)_2])_2Cr\}_2 (10): nBuLi (0.84 mL, 2.1 mmol , 2.5 M in hexane) was added to a solution of IV (0.490 g, 1.0 mmol) in THF (5 mL) at 0 ˚C and the resulting mixture was stirred at room temperature for 18 h. The resulting solution was added to a suspension of CrCl_2(THF)_2 (0.536 g, 2 mmol) in THF (5 mL). The reaction was allowed to stir overnight at room temperature. The
solvent was removed in vacuo and diethylether (5 mL) was added. The solution was centrifuged and the resulting solution was reduced to 3 mL and stored at -30 °C in the freezer for 3 days. The resulting crystals were filtered and washed with cold hexane (10 mL) and dried in vacuo to give 9 as green crystals (0.460 g, 0.67 mmol, 69.3 %). \( \mu_{\text{eff}} = 4.01 \ \mu_B \). El. Anal. Calcd. (found) for C\(_{23}\)H\(_{24}\)ClCr\(_2\)N\(_6\)P\(_2\): C 43.44 (43.40), H 8.20 (8.18), N 12.66 (12.61).

**X-ray crystallography**

Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. Data collection was performed with three batch runs at phi = 0.00 deg (600 frames), at phi = 120.00 deg (600 frames), and at phi = 240.00 deg (600 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on F2. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.12 program library. Relevant crystal datas are given below.

**Crystal data. 1:** C\(_{16}\)H\(_{30}\)CrN\(_4\)P\(_2\), Formula weight 398.43 g/mol, orthorhombic, Pccn, \( Z = 4 \), \( a = 16.166(4) \ \text{Å}, \ b = 11.929(3) \ \text{Å}, \ c = 11.814(3) \ \text{Å}, \ V = 2278.1(11) \ \text{Å}^3, D = 1.162 \ \text{Mg/m}^3; \mu = 0.647 \ \text{mm}^{-1}. \ F(000) = 856; \ R_1 = 0.0446, \ wR_2 = 0.1054; \ G.o.F. = 1.118.

**Crystal data. 2:** C\(_{23}\)H\(_{24}\)Al\(_2\)Cl\(_3\)CrN\(_2\)P, Formula weight 613.97 g/mol, orthorhombic, P2(1)2(1)2(1), \( Z = 4 \), \( a = 8.6978(14) \ \text{Å}, \ b = 16.930(3) \ \text{Å}, \ c = 23.134(4) \ \text{Å}, \ V = 3406.6(10) \ \text{Å}^3, D = 1.197 \ \text{Mg/m}^3; \mu = 0.685 \ \text{mm}^{-1}. \ F(000) = 1312; \ R_1 = 0.0275, \ wR_2 = 0.0622; \ G.o.F. = 1.041.

**Crystal data. 3:** C\(_{25}\)H\(_{62}\)Al\(_3\)CrN\(_4\)P\(_2\), Formula weight 613.97 g/mol, Triclinic, P-1, \( Z = 2 \), \( a = 9.3177(13) \ \text{Å}, \ b = 11.7323(16) \ \text{Å}, \ c = 17.301(2) \ \text{Å}, \ \alpha = 90.963(2)^\circ; \beta = 95.876(2)^\circ; \delta = 94.465(2)^\circ; \ V = 1875.0(4) \ \text{Å}^3, D = 1.087 \ \text{Mg/m}^3; \mu = 0.479 \ \text{mm}^{-1}. \ F(000) = 766; \ R_1 = 0.0568, \ wR_2 = 0.1327; \ G.o.F. = 0.993.

**Crystal data. 4:** C\(_{40}\)H\(_{90}\)Al\(_2\)CrN\(_4\)P\(_2\), Mw = 795.06, Monoclinic, P2(1)/n, \( Z = 2 \), \( a = 12.604(3)\text{Å}, \ b = 13.740(3)\text{Å}, \ c = 14.445(4)\text{Å}, \ \theta = 97.494(4)^\circ; \ V = 2480.2(11)\text{Å}^3, D = 1.065 \ \text{Mg/m}^3; \mu = 0.359 \ \text{mm}^{-1}. \ F(000) = 876; \ R_1 = 0.0537, \ wR_2 = 0.1292; \ G.o.F. = 1.055. 5: C\(_{40}\)H\(_{92}\)Al\(_2\)Cr\(_2\)N\(_6\)P\(_2\), Mw = 849.08, Triclinic, P-1, \( Z = 1 \), \( a = 9.702(4)\text{Å}, \ b = 10.454(4)\text{Å}, \ c = 14.135(8)\text{Å}, \ \alpha = 107.554(6)^\circ; \beta = 95.139(9)^\circ; \delta = 101.520(6)^\circ; \ V = 1322.0(11)\text{Å}^3, D = 1.066 \ \text{Mg/m}^3; \mu = 0.532 \ \text{mm}^{-1}. \ F(000) = 464; \ R_1 = 0.0679, \ wR_2 = 0.1809; \ G.o.F. =
1.021.

Crystal data for 6: $\text{C}_{32}\text{H}_{52}\text{CrN}_4\text{P}_2$, $M_r = 606.72$, monoclinic, space group $P2(1)/n$, $T = 203(2) \text{ K}$, $a = 9.201(9)$ Å, $b = 21.91(2)$ Å, $c = 9.597(9)$ Å, $\beta = 113.947(11)^\circ$, $V = 1768(3)$ Å$^3$, $Z = 2$, $\mu(\text{Mo}_K\alpha) = 0.781 \text{ mm}^{-1}$; 10360 reflections were collected, of which 2937 were unique ($\text{Rint} = 0.0865$), $\text{GOF} = 1.039$, final $R1[I>2\sigma(I)] = 0.0559$, $wR^2 = 0.1350$.

Crystal data for 7: $\text{C}_{41}\text{H}_{76}\text{Al}_3\text{CrNa}_2\text{P}_2$, $M_r = 821.95$, monoclinic, space group $P2(1)/n$, $T = 203(2) \text{ K}$, $a = 18.9199(16)$ Å, $b = 14.7620(12)$ Å, $c = 18.1352(15)$ Å, $\beta = 102.7670(10)^\circ$, $V = 4939.9(7)$ Å$^3$, $Z = 2$, $\mu(\text{Mo}_K\alpha) = 0.781 \text{ mm}^{-1}$; 42194 reflections were collected, of which 8718 were unique ($\text{Rint} = 0.1409$), $\text{GOF} = 1.069$, final $R1[I>2\sigma(I)] = 0.0648$, $wR^2 = 0.1383$.

Crystal data for 8: $\text{C}_{47.5}\text{H}_{68}\text{CrN}_6\text{O}_4\text{P}_2$, $M_r = 1042.98$, space group $P1$, $T = 201(2) \text{ K}$, $a = 11.1140(8)$ Å, $b = 13.2931(10)$ Å, $c = 18.0547(14)$ Å, $\alpha = 80.2940(10)^\circ$, $\beta = 78.8410(10)^\circ$, $\gamma = 79.5040$, $V = 2548.5(3)$ Å$^3$, $Z = 2$, $\mu(\text{Mo}_K\alpha) = 0.602 \text{ mm}^{-1}$; $\text{GOF} = 1.016$, final $R1[I>2\sigma(I)] = 0.0494$, $wR^2 = 0.1091$.

Crystal data for 9: $\text{C}_{49}\text{H}_{75}\text{Cl}_2\text{Cr}_2\text{N}_6\text{O}_{1.5}$, $M_w = 1042.98$, space group $P4$, $T = 201(2) \text{ K}$, $a = 10.426 (3)$ Å, $b = 15.044(5)$ Å, $c = 19.059 (14)$ Å, $\alpha = 87.1611(5)^\circ$, $\beta = 77.551(5)^\circ$, $\gamma = 86.551(5)$, $V = 2911.8 (16)$ Å$^3$, $Z = 2$, $\mu(\text{Mo}_K\alpha) = 0.623 \text{ mm}^{-1}$; $\text{GOF} = 0.958$, final $R1[I>2\sigma(I)] = 0.0685$, $wR^2 = 0.1448$.

Crystal data for 10: $\text{C}_{25}\text{H}_{56.5}\text{Cl}_2\text{Cr}_2\text{N}_6\text{O}_{0.25}\text{P}_2$, $M_w = 682.10$, space group $P2(1)/c$, $T = 201(2) \text{ K}$, $a = 16.680 (3)$ Å, $b = 16.182 (3)$ Å, $c = 26.027(5)$ Å, $\alpha = 90$, $\beta = 92.078(2)^\circ$, $\gamma = 90$. $V = 7020(2)$ Å$^3$, $Z = 8$, $\mu(\text{Mo}_K\alpha) = 0.887 \text{ mm}^{-1}$; $\text{GOF} = 1.057$, final $R1[I>2\sigma(I)] = 0.0665$, $wR^2 = 0.1603$. 

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2.5 References


3 High-throughput Screening of a Titanium-based Ethylene Trimerization Catalyst

Abstract

The trimerization of ethylene to 1-hexene with \((\eta^5-C_5H_4CMe_2C_6H_3)Ti(CH_2Ph)_3\) in combination with a variety of cocatalysts was investigated using a high-throughput experimentation (HTE) approach. Cocatalysts MAO, MAO/BHT, TIBA/B\((C_6F_3)\), TIBA/[Ph_3C]\*\[B(C_6F_3)_4\], TIBA/[Me_2NHPH]\*\[B(C_6F_3)_4\] = [100:1], [TIBA/BHT = 1:1]/[Me_2NHPH]\*\[B(C_6F_3)_4\] = [100:100:1] were evaluated. Different experimental techniques and activation protocols were applied to optimize the catalytic selectivity towards 1-hexene formation. The overall productivity, the control over 1-hexene selectivity and PE formation revealed a dependence on the coordination ability of the cocatalysts. The HTE approach appeared to be a promising route to rapidly generate kinetic data for mechanistic studies.

3.1 Introduction

Many catalyst systems for the selective oligomerization of ethylene have been developed after Manyik\(^\dagger\) and Reagan’s discovery of the Phillips catalyst.\(^{1-4}\) General process variables and intrinsic catalyst features play an important role on the selectivity towards the formation of 1-hexene\(^5\) or even 1-octene.\(^7,8\) After Reagan’s discovery of the highly active and selective chromium-pyrrolyl based trimerization catalyst \(\textit{vide infra}\) the commercialization of selective 1-hexene production became feasible. Since its discovery, several improvements to the original system were reported. Mitsubishi Chemical Corporation made the most significant contribution by adding chloro-compounds and a non-coordinating strong Lewis-acid, \(\text{B}(\text{C}_6\text{F}_5)_3\), which yields up to 95.4% selectivity of 1-hexene (Figure 1). Even higher selectivity was achieved by using catalyst systems that were generated by mixing PNP \((\text{R}_2\text{PCH}_2\text{CH}_2_2\text{NH})^{50}\) and SNS \((\text{RSCH}_2\text{CH}_2_2\text{NH})^{50}\) ligands with chromium precursor (Cr(III) chloride) followed by their activation with MAO under ethylene pressure. Although the selectivity and the activity of trimerization and tetramerization of ethylene with chromium-based systems (see Chapter 2) are high, due to their toxicity, chromium catalysts require special handling. Ligand-free tantalum-based catalysts developed by Mashima and co-workers\(^9\) show selectivities up to 98.5 wt% with only some traces of polyethylene. Nevertheless, the trimerization activity of these are orders of magnitude lower than those of chromium- and titanium-based catalysts. (See review of McGuinness for a detailed overview of olefin oligomerization).\(^{10}\)

<table>
<thead>
<tr>
<th>Phillips catalyst</th>
<th>Mitsubishi modified catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cr}(2\text{-EH})_3 + \centerdot \text{C}_2\text{Cl}_6 + \text{Et}_3\text{Al})</td>
<td>(\text{Cr}(2\text{-EH})_3 + \centerdot \text{Et}_2\text{AlCl} + \text{Et}_3\text{Al})</td>
</tr>
<tr>
<td>Activity: 157 g/g(_{\text{Cr}})^*h</td>
<td>Activity: 3780 g/g(_{\text{Cr}})^*h</td>
</tr>
<tr>
<td>Selectivity (\text{C}_6): 93.2%</td>
<td>Selectivity (\text{C}_6): 95.4%</td>
</tr>
</tbody>
</table>

*Figure 1. Chromium-pyrrolyl catalysts for the trimerization of ethylene.*

The titanium \((\eta^5-\text{C}_5\text{H}_4\text{CMe}_2\text{Ar})\text{TiCl}_3\) catalyst discovered by Hessen \textit{et al.}\(^{11,12a,b}\) is one of the most active non-chromium-based ethylene trimerization catalysts known to date. The \((\eta^5-\text{C}_5\text{H}_4\text{CMe}_2\text{R})\text{TiX}_3\) catalyst system is a member of the \(\text{Cp}^*\text{TiX}_3\) family,\(^{13,14,15}\) but contains a labile pendant functionality, which is able

\(^\dagger\) Manyik’s chromium based catalyst is not only a trimerization catalyst but also is example of tandem catalysis from a single precatalyst because the 1-hexene formed was incorporated into the polyethylene.\(^2\)
to adapt its coordination mode according to the steric and electronic needs of the metal center. Variations of the R group (pendant arene, thiophene functionality\textsuperscript{16}) show that hemilabile coordination of the functional group to the metal center is essential for the catalytic activity and selectivity towards ethylene trimerization, and forms the basis of the effective reversible redox process between Ti(IV) and Ti(II), necessary for the redox mechanism of ethylene trimerization. Ring-slippage of the hemilabile pendant arene group appears to be the key to switch between trimerization and polymerization. Variable-temperature NMR studies showed the shuttle between \(\eta^1\), \(\eta^3\) and \(\eta^6\)-coordination of the arene ligand to the titanium metal center that occurs at various points during the metallacyclic mechanism.\textsuperscript{17} Hessen’s \((\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{-3,5-Me}_2\text{C}_6\text{H}_3)\text{TiCl}_3/\text{MAO}\) system shows 83% selectivity to 1-hexene. The main oligomeric side product observed is 5-methyl-non-1-ene, which is formed by incorporation of 1-hexene during trimerization. Approximately 1-2\% of polyethylene is also formed. The published results\textsuperscript{12-16} show that 1-hexene is formed through a metallacycle redox mechanism,\textsuperscript{17-19} while the polymer is believed to be formed through the Cossee – Arlman mechanism.\textsuperscript{19,20} The presence of an arene moiety at the cyclopentadienyl ring capable of coordinating to the titanium is crucial to stabilize the titanium species in the Ti(III)/Ti(IV) cycle as was demonstrated by density functional theory.\textsuperscript{21} The steps that lead to the catalytic cycle begin with the formation of a cationic Ti(IV) species that is stabilized by the intramolecular arene followed by reduction of the Ti(IV) to Ti(II). The divalent titanium species is able to capture two ethylene molecules and by a 2 e\textsuperscript{-} oxidative addition (with respect to the metal) the tetravalent titanocyclopentane is formed. This metallacycle is relatively stable and undergoes insertion of one ethylene molecule rather than \(\beta\)-H transfer, which would lead to the release of 1-butene and reforming Ti(II). The thus formed 7-membered metallacycle is labile and rapidly undergoes \(\beta\)-H transfer followed by reductive elimination of 1-hexene (Scheme 1). DFT calculations indicate that the formation of the 7-membered ring is the rate-determining step of the oligomerization mechanism, having a high Gibbs energy barrier.\textsuperscript{22} It is believed that two different ethylene polymerization catalysts are responsible for polymer formation while one active species is responsible for trimerization.\textsuperscript{17} At the early stages of the activation process the Ti(IV)[\((\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_3)\text{TiClMe}]^+ cation, formed during the activation process, rapidly polymerizes ethylene. Through the whole run, another slow formation of polyethylene occurs which is assumed to be due to the Ti(III)[\((\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{-3,5-Me}_2\text{C}_6\text{H}_3)\text{TiR}]^+ species that is gradually formed as a degradation product.\textsuperscript{23} Hence, rapid and complete activation of the tetravalent precatalyst to the divalent titanium species is crucial for high trimerization selectivity, a process that can be affected by the type of cocatalyst.

Further elaborating on these concepts, here we aim at finding a potent single catalyst/cocatalyst system that could switch its catalytic behavior between ethylene oligomerization and polymerization incorporating the \textit{in situ} formed \(\alpha\)-olefin into the polymer. Pelecchia’s Cp\textsuperscript{*}TiMe\textsubscript{3}/B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} system, which produces LLDPE with butyl branches from ethylene alone, exactly does this.\textsuperscript{15} Unfortunately, the short-chain branching extent cannot be controlled with their system. Our choice is Cp’TiR\textsubscript{3} (Cp’ = \(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\)-...
C₆H₃), which is special in the sense that mainly ethylene trimerization takes place, whereas PE is formed only as side product. 1-Hexene formed might be incorporated into the polyethylene product to produce LLDPE by tuning the catalyst/cocatalyst.

Scheme 1: Accepted catalytic ethylene trimerization mechanism (Courtesy of Dr. E. Otten).¹⁸

3.1.1 Cocatalyst Screening

Cocatalysts are known to affect the catalyst's behavior both with respect to activity and selectivity.²⁴ Recent developments in chromium-based ethylene oligomerization and polymerization demonstrated that changing the cocatalyst may result in a complete switch from non-selective ethylene oligomerization to trimerization or polymerization.²⁵ Generally, group 4 metal olefin polymerization precatalysts need to be activated by an appropriate activating agent which results in a catalytically active cationic metal alkyl species stabilized by a weakly- or non-coordinating anion. Comprehensive studies by Chen and Marks have provided valuable input to the activation process and the cation-anion relationship in the polymerization mechanism.²⁶ Conversely, there were only few investigations about cocatalyst effects on ethylene oligomerization.²⁷ Tight and loose counter ions such as [MeB(C₆F₅)₃]⁺ and [B(C₆F₅)₄]⁻ may have an influence on the catalyst activity, stability, selectivity and even on comonomer incorporation as shown by Sita and coworkers.²⁸
The thermodynamic and kinetic driving force of the activation process depends on the transition metal, ligand coordination and the nature of the cation-anion relationship, which is controlled by the Lewis-basicty and electron-withdrawing character of the anion.\textsuperscript{28} It is likely that cocatalysts may have a profound effect on the catalytic behavior (trimerization \textit{versus} polymerization). MAO is believed to alkylate the metal and to create a cationic active metal center in both oligomerization and polymerization systems.\textsuperscript{26} The "free" TMA in MAO will most probably scavenge impurities and alkylate the catalyst, which results in its reduction. TMA is a reducing agent and might play an important role in activating the oligomerization redox system. TMA is known to sometimes form inactive ato-complexes during olefin polymerization and can also function as chain transfer agent. Addition of BHT (4-Me-2,6-t-Bu\textsubscript{2}-C\textsubscript{6}H\textsubscript{3}OH) is known to selectively scavenge TMA from MAO and by doing so prevents ato-complex formation and chain transfer leading to more active catalysts and higher molar mass polymer products.\textsuperscript{28} How BHT affects the oligomerization catalysts (\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}CMe\textsubscript{2}C\textsubscript{6}H\textsubscript{3})TiCl\textsubscript{3} (1) and (\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}CMe\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Ti(CH\textsubscript{2}Ph)\textsubscript{3} (2) used in this chapter was thus far unknown and is of our interest.

### 3.1.2 Outlook to High-throughput Experimentation

High-throughput experimentation (HTE) is a technique that is well-suited for (co)catalyst screening and kinetic studies. A high-throughput approach under optimized conditions allows a much faster and more complete generation of kinetic data for mechanistic studies than traditional experimentation. The discovery of the Dow shuttle chemistry system for the production of ethylene/1-octene block copolymers is a striking example of the potential of high-throughput experimentation.\textsuperscript{29a} The amide-ether hafnium-based catalyst that polymerizes 1-octene was discovered with Symyx high-throughput screening (HTS). In that workflow, primary and secondary screenings were rapidly carried out to compose a catalyst library to survey this library for ethylene/1-octene polymerization capacity of the catalysts. Third screening was performed to validate the results from primary and second screening.\textsuperscript{29b} Without the use of HTE\textsuperscript{29a-c}, it would have been virtually impossible to identify the right combination of catalysts and conditions for those systems to work in an optimal way.

The aim of our study described in this chapter was to screen a library of cocatalysts, anion coordination strength, their effect on the catalytic behavior of the Hessen’ s catalyst, (\(\eta^5\)-C\textsubscript{5}H\textsubscript{4}CMe\textsubscript{2}C\textsubscript{6}H\textsubscript{3})Ti(CH\textsubscript{2}Ph)\textsubscript{3} with the particular interest of one-pot synthesis of LLDPE. Tuning the branching level by adjusting the catalyst/cocatalyst was also targeted. Hessen’ s catalyst was particularly chosen for its wide diversity in its catalytic behavior\textsuperscript{11,12,18,23} and a HTE system was required to test a large variety of parameters. The experiments were performed on a Symyx Parallel Pressure Reactor setup consisting of 32 parallel 5 mL reactors at the University of Naples as well as in 200 mL Büchi batch reactors for comparative purposes. Furthermore, the scalability and reproducibility of the catalytic runs in different reactor setups were studied. High-throughput primary screening was carried out to survey the catalytic activity of (\(\eta^5\)-
$C_3H_2CMe_2C_6H_3$Ti(CH$_2$Ph)$_3$ with different cocatalysts. The promising catalyst – cocatalyst combinations were subjected to the secondary screening, where 32 parallel experiments were carried and monitored individually controlled high-pressure reactors. In the third screening conventional batch reactors were used to validate the results.

### 3.2 Results and Discussion

#### 3.2.1 Effect of Cocatalyst on Trimerization and Polymerization Activity

For the appropriate precatalyst-cocatalyst match that can tune the selectivity and the performance towards 1-hexene or polymer formation, we evaluated different cocatalysts. Table 1 provides the preliminary polymerization results that have been obtained with ($\eta^5$-$C_3H_2CMe_2C_6H_3$)TiCl$_3$ (1) and ($\eta^5$-$C_3H_2CMe_2C_6H_3$)Ti(CH$_2$Ph)$_3$ (2) upon activation with MAO, MAO/BHT and TiBA/[Ph$_3$C]$^+$$[B(C_6F_5)_4]^-$. in toluene. The polymerization/oligomerization reactions were carried out in 200 mL Büchi reactors. Analyses of the liquid fractions were done by GC, GC/MS and NMR techniques.

**Table 1.** Catalytic ethylene conversion with 1/MAO, 2/MAO, 2/MAO/BHT [1:1]$^c$, 2/TiBA/[Ph$_3$C]$^+$$[B(C_6F_5)_4]^-$$[1: 100 :1]$.$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C$_6^+$ products$^a$ (wt%)</th>
<th>C$_{10}$+ products$^a$ (wt%)</th>
<th>PE (g)</th>
<th>PE (wt%)</th>
<th>Trimerization productivity$^b$</th>
</tr>
</thead>
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<td>1</td>
<td>82.0</td>
<td>4.8</td>
<td>0.71</td>
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<td>2$^c$</td>
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<td>10.7</td>
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<tr>
<td>2$^d$</td>
<td>51.3</td>
<td>11.0</td>
<td>1.45</td>
<td>34.0</td>
<td>120.0</td>
</tr>
</tbody>
</table>

Polymerization conditions: Ti = 10 μmol, [Al]/[Ti] = 1000, solvent = 100 mL toluene, 5 bar of ethylene, 30 °C, Reaction time = 30 minutes. $^a$ Determined by GC; $^b$$\text{g}_{\text{oligomer}}/\text{hr}$$^*$$\text{mmol}^{-1}$$^*$$\text{h}^{-1}$$^*$$\text{bar}^{-1}$; $^c$ Activated by MAO/BHT; $^d$ Activated by TiBA/[Ph$_3$C]$^+$$[B(C_6F_5)_4]^-$. The MAO-activated 1 was a moderately active trimerization catalyst, whilst activation of 2 with MAO yielded the highest trimerization activity. Interestingly, the 2/MAO/BHT system produced the lowest trimerization activity, while 2/TiBA/[Ph$_3$C]$^+$$[B(C_6F_5)_4]^-$ exhibited a higher trimerization activity than the MAO/BHT activated system. The differences in the selectivity to 1-hexene and the amount of polyethylene formed with different cocatalysts might have been due to the differences in the Ti-arene strength, which was affected by the interaction of the counter ion with the cationic active species. Apparently, the stronger the arene-Ti interaction, the lower the possibility of the partial dissociation or ring-slippage of the arene became, which might lead to catalyst inhibition. The preliminary results
presented here are in agreement with the trends obtained with a titanium-based trimerization catalyst with ligand and bridge modifications.\textsuperscript{18} The differences among the catalyst productivity were previously shown to be due to the differences in the Ti-arene strength.\textsuperscript{18}

Micro scale screenings of ethylene trimerization and polymerization were conducted in 5 mL reaction volumes of the Symyx PPR32 to gain more insight into the catalytic activities with catalyst/cocatalyst partners. Catalytic testing was performed using 0.07, 0.14, 0.22 and 0.45 μmol of catalyst loadings with [Al]/[Ti] = 500 at Tₚ = 40° C and 4.10 bar of ethylene pressure corresponding to an ethylene concentration of 0.37 M.

Figures 2a and 2b show the ethylene uptake profiles for the catalytic runs of 2 with MAO and MAO/BHT, respectively (performed in Symyx PPR32). Although there was a clear difference in the profiles, the total ethylene uptake was very similar in both cases. When activated with MAO, the system showed a much higher initial activity but this decreased rapidly and after about 5 minutes the catalytic activity merely ceased completely. For the system activated with MAO/BHT, a much lower initial activity was observed, but the system remained active for a considerably longer time. The product distributions determined at different reaction times (Figures 3a and Figure 3b) also showed a clear difference. The MAO-activated system displayed a considerably higher trimerization activity and lower polymerization activity compared to the MAO/BHT-activated system, which mainly yielded polyethylene. The results were in agreement with the preliminary experiments performed in Büchi reactors. The addition of BHT had a positive effect on the polymerization activity and resulted in an increase of molar mass of over one order of magnitude (MAO: \(2.3 \times 10^5\) g·mol\(^{-1}\); MAO/BHT: \(2.9 \times 10^6\) g·mol\(^{-1}\); see Figures 3 and 4).

![Figure 2](image)

**Figure 2.** (a) Ethylene uptake/kinetic profile with MAO-activated 2. (b) Ethylene uptake/kinetic profile with MAO/BHT activated 2. Experiments performed in Symyx reactors.
Figure 3. (a) Activity of 0.07, 0.14, 0.22 and 0.45 µmol of 2 versus time with MAO as precursor. (b) Activity of 0.07, 0.14, 0.22 and 0.45 µmol of 2 versus time with MAO/BHT as precursor. Experiments were performed in Synergy reactors. Oligomers and PEs are depicted with circles and squares, respectively.

Besides preventing possible ato-complex formation, the high polymerization activity upon activation with MAO/BHT might as well be explained by Ti-aryloxy formation. The observed activity was about a factor of two lower than the ethylene polymerization activities reported for Nomura’s non-bridged half-titancene Cp*TiCl2(OAr) (OAr = arylxy group) systems in the presence of MAO,30 and considerably higher than, for example Cp*TiCl2/MAO and Cp*TiMe2/MAO. On the other hand, BHT dramatically reduced the trimerization activity, especially at the beginning of the catalytic run. This indicated that the presence of a reducing agent like TMA does indeed help to transform precatalyst 2 into an oligomerization catalyst rather than a polymerization catalyst. However, the ethylene conversion experiment with precatalyst 2/MAO/(50 equivalents TMA) in our hands was rather disappointing with a lower trimerization activity.

In order to understand the chemistry behind the oligomerization versus polymerization, a set of experiments with different non-coordinating or weakly coordinating cocatalysts were performed with 0.035, 0.05, 0.07, 0.1 µmol of 2 and 2.0 µmol of TIBA. TIBA was added as a scavenger in view of the sensitivity of the catalyst. Activations with TIBA/[Ph3C][B(C6F5)4] and TIBA/B(C6F5)3 were tested with different numbers of equivalents of [Ph3C][B(C6F5)4] and B(C6F5)3. As it can be seen from Figure 5, according to the monomer uptake curves for the ethylene trimerization in the presence of TIBA/[Ph3C][B(C6F5)4] and TIBA/B(C6F5)3, negligible catalyst deactivation occurred compared to the ethylene trimerization with MAO and MAO/BHT. The overall ethylene uptake was higher than for the MAO- and MAO/BHT-activated systems and shows a different profile for the TIBA/[Ph3C][B(C6F5)4] and TIBA/B(C6F5)3-activated system.
Figure 4. (a) Comparison of PE formation by 0.07, 0.14, 0.22 and 0.45 μmol of 2/MAO (circles) and 2/MAO/BHT (squares) versus time. (b) Comparison of Oligomer formation by 0.07, 0.14, 0.22 and 0.45 μmol of 2/MAO (circles) and 2/MAO/BHT (squares) versus time. Experiments were performed in Symyx reactors.

The overall ethylene uptake was higher when 2 was activated with TIBA/[Ph₃C][B(C₆F₅)₄] and the system showed a fast initial and later a slightly lower ethylene uptake, typical for a slow-deactivating catalyst. Whereas the TIBA/B(C₆F₅)₃-activated system started with the same initial rate, but within 2 minutes the catalytic activity dropped to about half the initial activity. Interestingly, the activity was very steady throughout the whole reaction time.

Figure 5. (a) Ethylene uptake/kinetic profile for 2/|Ph₃C][B(C₆F₅)₄]/TIBA. (b) Ethylene uptake/kinetic profile of 2/B(C₆F₅)₃/TIBA. Experiments performed in Symyx reactors.
The reaction of 2 with [Ph$_3$C]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ or B(C$_6$F$_5$)$_3$ resulted in abstraction of a benzyl group, as was shown by $^{13}$C-NMR spectroscopy (Figure 6). The activation of 2 with a stoichiometric amount of [Ph$_3$C]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ in CD$_2$Cl$_2$ at -60 °C a signal at 3.97 ppm was observed belonging to the methylene resonance of CPh$_3$CH$_2$Ph. Consistently, the methylene moiety of the benzyl groups displayed a signal at 3.26 ppm, demonstrating the existence of 4 protons of the remaining benzyl groups. The aromatic region was very crowded, since it contained both phenyl resonances of the generated Ti complex and of CPh$_3$CH$_2$Ph. Traces of impurities or decomposition products were observed at 2.36 and 2.91 ppm.

![Figure 6. $^1$H NMR spectrum of 2/1 equivalent of [Ph$_3$C]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ in CD$_2$Cl$_2$ at -60 °C.](image)

With increasing in the B:Ti ratio, the polymerization activity increased, while the oligomerization activity decreased. This decrease in the oligomerization and increase in the polymerization activity might be due to the degradation of the catalyst as a result of the exchange between B(C$_6$F$_5$)$_3$/TIBA and [Ph$_3$C]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$/TIBA.$^{32a}$ Bochmann showed that the scrambling of alkyl and fluoro aryl groups between aluminum and boron in AlR$_3$ and B(C$_6$F$_5$)$_3$ or B(C$_6$F$_5$)$_4^-$ caused the deactivation of a metalloocene polymerization catalyst.$^{31}$ McGuinness investigated a similar exchange process for chromium-based ethylene trimerization and tetramerization catalysts.$^{25}$ The amount of AlR$_3$ in combination with B(C$_6$F$_5$)$_3$ and [Ph$_3$C]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ was found to affect the rate of catalyst deactivation. They were able to change the selectivity from trimerization to tetramerization and a high amount of polymer production was also observed due to the cocatalyst deactivation.$^{34}$ The deactivation of the oligomerization in the case of both 2/[TIBA/B(C$_6$F$_5$)$_3$] and 2/[TIBA/Ph$_3$C]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ could thus be explained by possible Al-R – B-R’ exchange.$^{33}$ However, the increase in polymerization activity was not in line with Bochmann’s
observations. A remarkable decrease in the polymerization activity was observed when TIBA/[Me₂N(H)Ph]⁺[B(C₆F₅)₄]⁻ was used as cocatalyst (Figure 7). With respect to the 1-hexene:polyethylene ratio, [Me₂N(H)Ph]⁺[B(C₆F₅)₄]⁻ produced the best oligomerization catalyst among all the activators that were evaluated. The reason for the decrease in the polymerization activity might be the presence of coproduct amine derived from [Me₂N(H)Ph]⁺[B(C₆F₅)₄]⁻. It was likely that this amine influenced the cation-anion strength, which suppressed the polymer formation. When TIBA/BHT was used as a scavenger with [Me₂N(H)Ph]⁺[B(C₆F₅)₄]⁻, the increase in the polymerization activity and decrease in the oligomerization activity were in line with our previous study shown in Figure 4a and Figure 4b where a similar effect of BHT on oligomerization and polymerization was observed. However, when TIBA/BHT was used as a scavenger with [Ph₃C⁺][B(C₆F₅)₄]⁻, there was a significant difference neither in the polymerization nor in the oligomerization activity. The concomitant polymer formation and titanium-catalyzed ethylene trimerization with MAO activator were also studied by Hagen et al. Two different active species were reported to be responsible for polymer formation. One of the two active species produced the polyethylene at the beginning of the reaction while another species produced polyethylene throughout the entire process but at a lower rate. Based on the study of Hagen, we can suggest that 2/[Me₂N(H)Ph]⁺[B(C₆F₅)₄]⁻/TIBA generates the Ti(III) species directly from [(η⁵-C₅H₅Me₂C₆H₅)Ti(CH₃Ph)₂]⁺ without allowing polymer chain growth from [(η⁵-C₅H₄Me₂C₆H₅)Ti(CH₃Ph)₂]⁺. The polymer obtained might be produced in the second stage of the whole process, which was slow but continuous.

![Graph](image.png)

**Figure 7.** Polymerization versus oligomerization with different activator/scavenger systems (oligomer: black and polymer: light gray)
Oligomerization/polymerization catalysts with B(C₆F₅)₃, [CPh₃]⁺[B(C₆F₅)₄]⁻ or [Me₂N(H)Ph]⁺[B(C₆F₅)₄]⁻ yielded highly electrophilic species that were stabilized by weakly coordinating counter anions. Both oligomerization and polymerization activity increased when the [Ph₃C]⁺[B(C₆F₅)₄]⁻/[Ti] and B(C₆F₅)₃/[Ti] ratios were increased from 1:1 to 2:1. When more than 2 equivalents of B(C₆F₅)₃ and [Ph₃C]⁺[B(C₆F₅)₄]⁻ were used, the oligomerization activity decreased whereas the polymerization activity increased slightly (Figures 8 and 9). Keeping in mind that B(C₆F₅)₃ is a Lewis acid and the activation process in principle is an equilibrium, it was understandable that increasing the amount of B(C₆F₅)₃ might increase the activity, but that the same was true for [CPh₃]⁺[B(C₆F₅)₄]⁻ was surprising.

![Graph](image)

**Figure 8.** (a) Oligomerization activity versus [Ph₃C]⁺[B(C₆F₅)₄]⁻/[Ti] ratio for the [Ph₃C]⁺[B(C₆F₅)₄]⁻/TiBA-activated catalyst. (b) Polymerization activity versus [Ph₃C]⁺[B(C₆F₅)₄]⁻/[Ti] ratio for the [Ph₃C]⁺[B(C₆F₅)₄]⁻/TiBA-activated catalyst. Experiments were performed in Symyx reactors. Oligomers and PEs are depicted with circles and squares, respectively.

The increase in the polymerization activity and decrease in oligomerization activity with two or more equivalents of trityl borate and borane could be due to the formation of dicationic ([Ti(η-C₆H₄CMe₂C₆H₄)₂]²⁺)[Ph₂CB(C₆F₅)₄]²⁻ species that were stabilized by the arene group, similar as was shown by Saßmannshausen.³³ Dicationic species might inhibit the reduction to Ti(II) due to the coordinative dimers. In order to determine this, low temperature NMR measurements were applied. 2 was treated with one and two equivalents of [Ph₃C]⁺[B(C₆F₅)₄]⁻ at 25 °C in CD₂Cl₂, respectively. The ¹H NMR spectra recorded at 25 and 0 °C were inconclusive as the intermediates formed were thermally unstable. Some decomposition products were observed. However, the ¹H NMR measurements at -30 °C and -60 °C did not show any evidence for the formation of covalent or coordinative dimers.
Figure 9. (a) Polymerization activity versus B(C₆F₅)₃/Ti ratio for the B(C₆F₅)₃/TIBA-activated catalyst. (b) Oligomerization activity versus B(C₆F₅)₃/Ti ratio for the B(C₆F₅)₃/TIBA-activated catalyst. Experiments were performed in Symyx reactors. Oligomers and PEs are depicted with circles and squares, respectively.

The absence of the dicatonic structure was also supported by the absence of a broad peak below 0 ppm which would be expected for the anion [PhCH₃B(C₆F₅)₄]⁻, although B(C₆F₅)₄ was observed in the ₁₉F NMR. Still, there were precedents in the literature for a similar behavior. Bochmann and Macchioni reported on the effect of ion pairing for zirconium complexes where an additional equivalent of [Ph₃C]⁺ [B(C₆F₅)₄]⁻ resulted in a more reactive ion pair.³⁴,³⁷ A similar ion pairing effect could also play a role in our titanium system (see Appendix 1).

3.2.2 Effect of Temperature and Cocatalyst on Trimerization and the Characterization of Polyethylenes Formed

By changing the reaction conditions (temperature, pressure) or ligand structures, it was possible to change the selectivity of the catalysts. In this section, different temperatures and different solvents were tested for 2/MAO to investigate their effect on oligomerization activity and the polymer products. The catalyst was thermally labile and showed significant deactivation with increasing temperature, but this did not influence its selectivity towards 1-hexene formation (Table 2).

Most of the polymer was formed in the early stage of the reaction. This was observed by the ethylene trimerization experiments that were performed during extended reaction times (5 to 60 minutes). Therefore it was likely that, prior to be transformed into the titanium (II) species, the intermediate cationic dialkyl titanium (IV) species was responsible for the polymerization of ethylene.
The $M_w$ values of the PEs ranged from 230,000 to 840,000 g/mol with molar mass distributions (MWD) of around 2.2 to 3.6. The melting temperature ranged from 128.8 to 131.4 °C. When the polymerization temperature was 50 °C, there was a maximum $M_w$ value and a polydispersity index of 3.6 was obtained. The differences in the molar masses at different polymerization temperatures could be explained by the mass transfer of ethylene, which was affected by reaction temperature and solubility of ethylene in the toluene solvent. An increase in the polymerization temperature from 30 to 50 °C obviously reduced the concentration of ethylene in the solvent, however, higher molar mass was observed due to the faster propagation rate. The $M_w$ value obtained at 80 °C was lower than that obtained at 50 °C due to the increased chain transfer. The effect of the polymerization temperature and the dissolution of ethylene in different solvents with Cp*$_2$Sm·2THF, which produces UHMWPE, were extensively studied by Kirti Garkhail.\textsuperscript{44}

**Table 2. Ethylene Trimerization with Z/MAO.**

<table>
<thead>
<tr>
<th>Temp [°C]</th>
<th>$C_6^+$ products$^a$ (wt %)</th>
<th>$C_6^+$ amount$^b$ mL</th>
<th>Activity $[g_{cat}\cdot h^{-1}\cdot mmol_{cat}^{-1}\cdot bar^{-1}]$</th>
<th>PE g</th>
<th>$M_w$ g/mol</th>
<th>$M_w/M_n$</th>
<th>$T_m$ °C</th>
<th>$\Delta H_m$ J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>89.8</td>
<td>9</td>
<td>242.3</td>
<td>1.03</td>
<td>230,000</td>
<td>2.2</td>
<td>129.6</td>
<td>104.4</td>
</tr>
<tr>
<td>50</td>
<td>83.0</td>
<td>5</td>
<td>134.6</td>
<td>1.00</td>
<td>840,000</td>
<td>3.6</td>
<td>128.8</td>
<td>69.5</td>
</tr>
<tr>
<td>80</td>
<td>94.2</td>
<td>1</td>
<td>26.9</td>
<td>1.33</td>
<td>294,000</td>
<td>2.4</td>
<td>131.4</td>
<td>19.4</td>
</tr>
</tbody>
</table>

Polymerization conditions: Ti : Al = 1000, solvent = 100 mL of toluene, ethylene = 5 bar $^a$ Determined by GC from liquid fraction, $^b$ Determined by integrating the intensity of the olefinic NMR resonances versus the aromatic protons of the toluene solvent, $^c$ Determined by SEC in trichlorobenzene using PE standards $^d$ Determined by DSC with heating rate of 10 °C/min from the second heating.

**Figure 10.** Melting temperatures of the LLDPE-like PEs obtained by Z/MAO at 20, 30, 50 and 80 °C from DSC (second heating).
The reaction medium also had an influence on the catalytic behavior of 2/MAO as the energetics of the cation-anion interactions were moderated by solvent polarity. In case of petroleum ether instead of toluene as the reaction medium, the selectivity to 1-hexene decreased from 90 to 71% and the total oligomerization activity decreased with 50% compared to the activity observed in toluene as the solvent. The polymerization activity decreased 1.5 fold with a TOF of 289,300 g [polymer]⁻¹mol⁻¹Ti⁻¹bar⁻¹[CH₄]⁻¹h⁻¹. This might be due to the lack of polarity of petroleum ether contrary to toluene that led to the lesser cation-anion separation.

Table 3. Ethylene trimerization/polymerizations with 2/TIBA/[Ph₃C][B(C₆F₅)₄] and MAO, MAO/BHT.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Co-catalyst</th>
<th>M_w [g/mol]</th>
<th>PDI</th>
<th>T_m [°C]</th>
<th>ΔH_m [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry 1</td>
<td>Toluene</td>
<td>MAO</td>
<td>230,000</td>
<td>2.2</td>
<td>129.6</td>
<td>104.4</td>
</tr>
<tr>
<td>Entry 2</td>
<td>Toluene</td>
<td>MAO/BHT</td>
<td>2,900,000</td>
<td>3.1</td>
<td>129.6</td>
<td>78.9</td>
</tr>
<tr>
<td>Entry 3</td>
<td>Toluene</td>
<td>TIBA/Borate</td>
<td>2,500,000</td>
<td>44.7</td>
<td>130.4</td>
<td>82.6</td>
</tr>
<tr>
<td>Entry 4</td>
<td>Toluene/1-octene</td>
<td>TIBA/Borate</td>
<td>1,700,000</td>
<td>44.6</td>
<td>132.7</td>
<td>137.5</td>
</tr>
<tr>
<td>Entry 5</td>
<td>Pet.Ether</td>
<td>MAO</td>
<td>300,000</td>
<td>2.7</td>
<td>138.3</td>
<td>180.4</td>
</tr>
</tbody>
</table>

Polymerization conditions: Ti : Al = 1000, Ti = B = 10 μmol, solvent = 100 mL, ethylene = 5 bar, 30 °C; Determined by SEC in trichlorobenzene; Determined by DSC with heating rate of 10 °C/min from second heating curve.

The polymerization reaction of 2 with [Ph₃C][B(C₆F₅)₄], MAO/BHT and MAO produced UHMWPE and HDPE (Table 3). The M_w of polyethylene obtained in the presence of just MAO (Entry 1) is 230,000 g/mol with a T_m of 129.6 °C with a heat of melting 104.4 J/g, which was indicative of HDPE while the polyethylene sample obtained in the presence of MAO/BHT (1:1) (Entry 2) exhibited a much higher M_w than the sample obtained by the MAO-activated system. The results showed that PEs obtained with MAO were HDPE, while PEs obtained with MAO/BHT were linear UHMWPE. This was confirmed by the ¹³C NMR analysis, which revealed hexene contents of <0.5 per 1000 C (<0.3 wt%) for the PEs obtained with MAO/BHT and 0.6 per 1000 C (0.4 wt%) for the PEs obtained with MAO. ¹³C NMR analysis of the PEs obtained by [Ph₃C][B(C₆F₅)₄] revealed 1.8 hexene content per 1000 C (1.1 wt%). The M_w of the polyethylene obtained using the borate [Ph₃C][B(C₆F₅)₄] as cocatalyst was 2,500,000 g/mol with a T_m of 130.4 °C. Entry 3 and Entry 4 showed different bimodal distributions according to the measurements performed with high temperature-SEC-IR (Figure 11). This technique not only gives the molar mass distribution but also the amount of short-chain branching across the entire molar mass distribution. The MWD of the first peak (lower MW belonging the Entry 3) had a shoulder at M_w ~ 30,000 g/mol and it contained low amounts of short-chain branching (SCB), close to the detection limit which resulted in a rather high signal to noise ratio (Figure 11). The SCB-density for the low molar mass fraction was 3.4 ±
1.7 SCB/1000 C. For Entry 4, SCB as a function of molar mass showed a different trend. Up to $M_w$ values of 100,000 g/mol branching varied from 17 to 22 SCB/1000 C, the short chain branches were somewhat scattered at the low molar mass side and significantly decreased in the higher molar mass region, approaching the same level as in the high molar mass region of Entry 3. Looking at the distribution shape of Entry 4, it may be concluded that the presence of branching within low molar mass side was apparent and might be due to the overlap of the high and low molar mass distributions. This might be indicative of a physical blend of a polymer with or without incorporated comonomer.

![Graph](image)

**Figure 11.** Molar mass distribution and SCB/1000 C of Entry 3 (duplicate measurement, red and blue) and Entry 4 (green).

The significant increase in the $M_w$ value of the samples obtained by using $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ as the cocatalyst could be assumed to be due to the coordinating behavior of the counter ion, which affected the rate of propagation and $M_w$ and $M_n$ of the samples. The weakly coordinating anions produced higher $M_w$ values.

### 3.3 Conclusions

The trimerizations of ethylene to 1-hexene with catalyst 2 in combination with a variety of cocatalysts were investigated using high-throughput experimentation. The cocatalysts MAO, MAO/BHT, TIBA/[(B(C$_6$F$_5$)$_3$)$_3$], TIBA/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$, TIBA/[Me$_2$N(H)Ph]$^+$[B(C$_6$F$_5$)$_4$]$^-$, [TIBA/BHT 1:1]/[Me$_2$N(H)Ph]$^+$[B(C$_6$F$_5$)$_4$]$^-$ and [TIBA/BHT 1:1]/[Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ were evaluated. The library of experiments with different activators presented in this chapter revealed that the type and the coordinating ability of the anion have a significant influence on the delicate balance between trimerization and polymerization while the overall productivity was not affected by the anion present.
The MAO-activated system showed a higher trimerization activity and a lower polymerization activity compared to the MAO-BHT-activated system. TMA had a predominant effect on the reduction of Ti(IV) to Ti(II), which was responsible for oligomerization. However, further investigations with the MAO/BHT-activated system are necessary because there are still unanswered questions concerning the transformation between oligomerization and polymerization. The evaluation of TIBA/[(B(C₆F₅)₃]−, TIBA/[Ph₃C]⁺[B(C₆F₅)₄]−, TIBA/[Me₂N(H)Ph]⁺[B(C₆F₅)₄]−, [TIBA/BHT 1:1]/[Me₂N(H)Ph]⁺[B(C₆F₅)₄]− and [TIBA/BHT 1:1]/[Ph₃C]⁺[B(C₆F₅)₄]− as cocatalysts led to a higher oligomerization activity compared to the MAO-activated system. The kinetic profile of the TIBA/[Ph₃C]⁺[B(C₆F₅)₄]−-activated system was found to be more stable for a longer period of time than MAO-activated system. Enhancing the amount of [Ph₃C]⁺[B(C₆F₅)₄]− boosted the overall activity. It is likely that the anion present has a significant effect on the Mₘₜ of the coproduct PEs, as the coordination behavior of the anion seems to affect the rate of propagation. The origin of the differences in polymerization activity with different cocatalysts is still not completely understood. However, polyethylene obtained as coproduct using (η⁵-C₅H₄CMε₂C₆H₃)Ti(CH₃Ph)₃ with 1 equivalent of [Ph₃C]⁺[B(C₆F₅)₄]− as an activator contained only a low amount of short-chain branches. It was likely that some of the 1-C₆− formed was subsequently incorporated into the PE formed. The unexpected bimodal distribution of the polymer obtained with 2/[Ph₃C]⁺[B(C₆F₅)₄]− could be attributed to multiple oxidation states occurring during polymerization. By adjusting the 2/[Ph₃C]⁺[B(C₆F₅)₄]− ratio it might be possible to tune the branching level. However, the incorporation of 1-C₆− we obtained was not effective, and the produced polyethylenes were all of the HDPE type whereas LLDPE-like polymers were expected for significant α-olefin incorporations. Nevertheless, with these experiments we showed that it was possible to control the relative amounts of ethylene trimerization and polymerization active species starting with one single catalyst precursor and by tuning the nature and stoichiometry of the cocatalyst system. We believe, these results could be valuable in perspective for tandem catalysis. The chemistry behind the different poly- and oligomerization activities with different cocatalysts was too complex and its elucidation requires further investigation. Moreover, future research should be focused on other experimental setups that could potentially lead to LLDPE synthesis. Since many additional catalytic experiments are expected to be required high-throughput experimentation is certainly needed to understand the realistic mechanism(s) involved.

Acknowledgements. I would like to thank to Prof. Dr. Busico, Prof. Dr. Macchioni and Dr. Lars-Christian Heinz (DSM Resolve) for their contributions.
3.4 Experimental Section

General procedures
All reactions were carried out under a dry nitrogen atmosphere. Solvents were dried using an aluminum oxide solvent purification system. The reaction mixtures were analyzed using a CP 9000 gas chromatograph (GC) fitted with a 30 m x 0, 32 mm capillary CP volamine column. NMR spectra were recorded on a Varian Inova 400 MHz instrument. Molar mass and molar mass-distributions of the polyethylene were determined by means of gel permeation chromatography on a PL-GPC210 equipped with refractive index and viscosity detectors and a 3*PLgel 10 μm MIXED-B column set at 160 °C with 1,2,4-trichlorobenzene as the solvent. BHT and Irganox were used as internal standards. The molar masses of the polymers were referenced to polyethylene standards with narrow molar mass distributions. Differential scanning calorimetry (DSC) was carried out with a Q100 differential scanning calorimeter (TA Instruments). The samples (4-6 mg) were heated to 160 °C and subsequently cooled to 20 °C at a rate of 10 °C/min. A second heating cycle was used for data analysis. Triethylaluminum (1.3 M in heptane) was purchased from Acros, TIBAO (10 % in toluene) was purchased from Aldrich. MAO (in toluene; 10% Al; 1.5 M) was purchased from Chemtura. TiBA (1 M in heptane) was obtained from Fluka. B(C₆F₅)₃ was synthesized according to literature procedures.¹⁶ [Me₂N(H)Ph]⁺[B(C₆F₅)₄⁻] and [Ph₃C⁺][B(C₆F₅)₄⁻] were generously donated by DSM Research B.V. Ethylene was obtained from Air Liquide. 1 and 2 were synthesized according to the corresponding literature procedures.¹⁷

Ethylene oligomerization procedures
Bench scale reactors. The oligomerization reactions were performed in a 200 mL Büchi reactor. The reactor was dried in an oven at 120 °C for two hours prior to each run and then evacuated for half an hour at 50 °C and rinsed with argon three times after repeated evacuation. After that, the reactor was charged with toluene and the desired amount of cocatalyst. After the solution was stirred for 10 minutes, it was saturated with ethylene and the pressure was kept constant at 5 bar. The catalyst solution was injected into the reactor by momentarily pressure release after which the reactor was immediately repressurized. After the required reaction duration, the reaction mixture was cooled to -5 °C and depressurized. A mixture of ethanol and diluted hydrochloric acid were subsequently injected to quench the reaction. The temperature was kept as low as possible during the work up to minimize loss of volatile products. The polymer was separated by filtration and dried at 60 °C for 18 hours under reduced pressure before the molar mass was determined. The liquid products were analyzed by GC chromatography. The overall catalytic activity was determined by integrating the intensity of the olefinic NMR resonances versus the aromatic protons of the toluene solvent.

Symyx PPR32 reactions. The polymerization experiments were carried out with a high-throughput parallel reactor setup (Symyx PPR32) with four reactor modules each containing eight reaction cells (5
mL working volume per cell). The system is totally housed in a triple MBraun LabMaster glovebox maintaining a pure nitrogen atmosphere (oxygen and water levels below 1 ppm). The monomer gas and quench gas line were plumbed directly into the reactors and controlled by automatic valves. Ethylene (Rivoira, polymerization grade) was fed after purification by passing it through columns containing a mixed bed of 4Å molecular sieves (3.2 mm pellets) and an activated copper catalyst (BASF R 3-11G). Liquid reagents are robotically added to the individual cells by syringes and the solvent (toluene, Romil) was previously purified in an MBraun SPS unit and dispensed inside the glove box using dedicated solvent line termini. Each cell was fitted with a pre-weighted glass vial insert and a disposable stirring paddle. The reactor modules were closed, and then the proper quantity of toluene was injected into each cell through a valve. The reactors were heated to the desired temperature and stirring was started at a speed of 800 rpm. The reactors were pressurized with ethylene, after which the desired amount of precatalyst and activator were premixed in a 1.2 mL glass vial (activators, MAO by Eurecen, BHT, 4-methyl-2,6-diterbutyl-phenol by Aldrich, B(C₆F₅)₃ and [Ph₃C][B(C₆F₅)₄] by Dow Chemical) and then injected into the reactors. The reaction was allowed to proceed for the proper time, after which an overpressure of 3.4 bar of oxygen was added to quench the reaction. The reactors were opened and the glass inserts were unloaded from the cells and transferred to a centrifuge/vacuum drying station (Genevac EZ-2 Plus). Subsequently the polymer samples were recovered and weighed on a Bohdan BA-100 Balance Automator unit.

**Activation of (η⁵-C₅H₄CMe₂Ph)Ti(CH₂Ph)₃ with [Ph₃C][B(C₆F₅)₄] in CD₂Cl₂**

A J-Young NMR tube was loaded with 15 mg of (η⁵-C₅H₄CMe₂Ph)Ti(CH₂Ph)₃ and 1 equivalent of [Ph₃C][B(C₆F₅)₄] (27.4 mg) within the glovebox. The tube was connected to a high vacuum line and approximately 0.7 ml of anhydrous methylene chloride was condensed in at -78 °C. The temperature was decreased to -60 °C and the mixture was gently shaken. The tube was immediately inserted into the pre-cooled NMR probe and the ¹H NMR spectrum was recorded.

**Analysis of comonomer distribution based on high temperature-SEC-IR measurements**

The samples were analyzed in 1,2,4-trichlorobenzene at DSM under standard SEC-MALS-IR conditions with the EOS MALS detector at 160 °C. The GPC column oven was set at 160 °C and an IR5 detector was used as concentration detector. The equipment used was a PL-GPC210 connected to a Wyatt DAWN EOS detector and a Polymer Char IR5 detector. Columns used were PL 20 μm mixed A columns (2*) LS. The column set was calibrated with ethylene-propylene copolymers with narrow molar mass distributions. For the determination of the amount of short chain branches SCB/1000 C < 10 as a function of molar mass no calibration is currently available. Therefore SCB/1000 C was calculated with a calibration suited for higher amounts of SCB.
3.5 References


44. K. Garkhail Sharma, Ph.D Thesis, **2005**.


3.6 Appendix

Figure A1. $^1$H NMR spectrum of 2/1 equivalent [Ph$_3$C][B(C$_3$F$_5$)$_4$] in CD$_2$Cl$_2$ at -60 °C immediately after preparation.

The spectrum in Figure 6 slowly changed during the period of two hours, during which three aromatic resonances emerged from the very broad signal close to 8 ppm (Figures A1 and A2). It is important to note that the relative integration of the resonances of the Ti complex is unaffected by the spectral change. The three resonances are due to the presence of an excess of CPh$_3^+$ due to the incomplete dissolution and activation of the precursor. This is confirmed by the observation in the $^{13}$C($^1$H) NMR spectrum of the downfield resonance bearing to the carbocation close to 210 ppm. It is interesting to note that the presence of such an excess of activator does not alter the resonance pattern of the cationic Ti complex. Consequently, it can be deduced that, at -60 °C, the second benzyl abstraction does not take place.
Figure A2. $^1$H NMR spectrum of 2/1 equivalent [Ph$_3$C]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ in CD$_2$Cl$_2$ at -60 °C after 2 hours.

To confirm the hypothesis, a complete NMR characterization of the product was achieved by using 2D scalar and Overhauser techniques (See Section 3.4 for details). It is important to outline that some of the aromatic resonances are overlapping with the signal of the CPh$_3$CH$_2$Ph moiety. The NMR experiment confirms that the activation leads to the $\eta^6$-coordination of the aromatic ring bound to the cyclopentadienyl. An indicative parameter that can be used to confirm the arrangement of the cation is the difference between the $^1$H NMR shifts of the monosubstituted Cp ring. In ansa-metalloccenes, the separation between $\alpha$ and $\beta$ Cp protons is directly related to the angle of the rings and, in the present case, $\Delta \delta H$ passes from 0.24 ppm for the neutral precursor to 1.22 for the corresponding cationic compound, thereby supporting the existence of $\eta^6$-coordination.

To investigate the level of self-aggregation in solution of [(C$_5$-$\text{C}_{3}$H$_2$CMe$_2$Ph)Ti(CH$_2$Ph)$_3$]$^+$$[\text{B(C}_6\text{F}_5)_4]^-$ a PGSE (Pulsed field Gradient Spin Echo) NMR measurement was performed in CD$_2$Cl$_2$ at -60 °C (Section 3.4 for details). The scope of the measurement is the determination of the self-diffusion coefficient (Dt) that is related to the hydrodynamic radius of the diffusing species as expressed by the Stokes Einstein equation:

$$D_t = \frac{k_b T}{6\pi \eta r_H}$$

Where: $k_b$ is the Boltzmann constant, $T$ is the temperature, $r_H$ is the hydrodynamic radius and $\eta$ is the viscosity of the solution. $f$ and $c$ are two coefficients that are related to the shape of the solvated species.
and the ratio between its hydrodynamic radius and that of the solvent, respectively. The experiment consists in the evaluation of the spin echo decay of signals belonging to different molecules diffusing in solution and exposed to a magnetic field gradient (G). This decay can be plotted as \( \ln \left( \frac{I}{I_0} \right) \) vs. \( G^2 \) where \( I \) and \( I_0 \) are the intensities of spin echoes in presence and absence of the gradient, respectively. This treatment gives linear trends in which the slope is directly proportional with the diffusion coefficient. Linear trends obtained from the PGSE investigation concerning the sample obtained as indicated before are reported in Figure A3. In these experiments cationic Ti complex had a concentration of about 5 mM and the excess of \([\text{Ph}_3\text{C}]^+\cdot[\text{B}(\text{C}_6\text{F}_5)_4]\) amounted to 25 mM.

![Graph](image)

**Figure A3.** PGSE investigation of cationic Ti complex (ca. 5 mM, circles) with an excess of 25 mM of \([\text{Ph}_3\text{C}]^+\cdot[\text{B}(\text{C}_6\text{F}_5)_4]\). CPh$_3$, CPh$_3$CH$_2$Ph and CD$_2$Cl$_2$ are depicted by diamonds, triangles and squares, respectively.

To obtain an accurate value of the hydrodynamic radius \( (r_H) \) it is necessary to know the correct values of temperature and viscosity. To overcome these complications an internal standard can be used. A natural internal standard is the solvent itself that has a known \( c \) factor and \( r_H \). A second standard is, in our case, the neutral species CPh$_3$CH$_2$Ph originating from the activation reaction. A simple relationship can be written:

\[
\frac{D_t}{D_t^{\text{st}}} = \frac{m_t}{m_t^{\text{st}}} = \frac{cr_H^{\text{st}}}{cr_H}
\]

In this equation \( m \) and \( m^{\text{st}} \) are the slope of the linear regressions of \( \ln \left( \frac{I}{I_0} \right) \) versus \( G^2 \) of the molecule and standard, respectively. By applying this methodology hydrodynamic volume values (VH) were obtained and these are reported in Table A1.
Table A1. Hydrodynamic volumes of the \( \text{CPh}_3\text{CH}_2\text{Ph}, \text{ Ti}^+ \) complex and \( \text{Ph}_2\text{C}^+ \)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( V_h ) ( \text{Å}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CPh}_3\text{CH}_2\text{Ph} )</td>
<td>470 ( \text{Å}^3 )</td>
</tr>
<tr>
<td>( \text{Ti}^+ ) complex</td>
<td>1100 ( \text{Å}^3 )</td>
</tr>
<tr>
<td>( \text{CPh}_3^+ )</td>
<td>714 ( \text{Å}^3 )</td>
</tr>
</tbody>
</table>

\( ^\text{a} \) All values are obtained imposing a \( c \) factor equal to 5.

As mentioned before, part of the precursor does not dissolve and, consequently, an excess of the activator is present when the NMR spectrum would be recorded. To activate all the titanium centers, the NMR tube was removed from the probe, vigorously shaken at room temperature for a few seconds and reinserted in the cooled probe. The \( ^1\text{H} \)-NMR spectrum was recorded after this operation. Figure A4 shows that the excess of the activator has been removed and the concentration of the titanium complex has been notably increased to 25 mM.

![NMR spectrum](image)

**Figure A4.** \( ^1\text{H} \) NMR spectrum of 2/1 equivalent \([\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-\) in \( \text{CD}_2\text{Cl}_2 \) at -60 °C after the activation of all titanium centers by removing the excess of \([\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-\).

After realizing such conditions, a new PGSE investigation was performed and the results are shown in Table A2 and Figure A5.
Table A2. Hydrodynamic volumes of the CPh₃CH₂Ph, Ti⁺ complex and Ph₃C after removing the excess of [Ph₃C]⁺[B(C₆F₅)₄]⁻

<table>
<thead>
<tr>
<th>Molecule</th>
<th>(V_n^a) [Å³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPh₃CH₂Ph</td>
<td>470 Å³</td>
</tr>
<tr>
<td>Ti⁺ complex</td>
<td>700 Å³</td>
</tr>
</tbody>
</table>

\(^a\) All values are obtained imposing a c factor equal to 5

Figure A5. PGSE investigation of PGSE investigation of cationic Ti complex (diamonds), after removing the excess of [Ph₃C]⁺[B(C₆F₅)₄]⁻. CPh₃CH₂Ph is depicted by triangles.

The hydrodynamic volume of the cation is compatible with that expected based on the chemical formula and it is not too different from that of CPh₃CH₂Ph. This indicates that a monomeric species is formed. It can be concluded that the stoichiometric activation leads to a single abstraction of a benzyl moiety forming a cationic and monomeric species. Likely, the same species is generated when the abstraction is carried out in the presence of an excess of activator (ca. five times excess). The higher value of the hydrodynamic volume observed in the latter case is most probably due to some interionic association (ion triples or ion quadruples) with trityl borate.

The above results are not indicative for the formation of covalent or coordinative dimers. A monomeric species forms when 2 is activated with 1 equivalent of [Ph₃C]⁺[B(C₆F₅)₄]⁻. Such species undergoes interionic association with trityl borate when the latter is in excess, which might lead to a more active species.
4 Linear Low-Density Polyethylene (LLDPE) Prepared by Tandem Catalysis and the Effect of Catalyst Immobilization*

Abstract

Linear low-density polyethylenes (LLDPEs) with narrow polydispersity indices have been synthesized from ethylene as the sole feedstock by a tandem catalysis approach. The concept of tandem catalysis applied in this chapter consists of two different strategies. In the first strategy both the trimerization catalyst $[\eta^5-C_3H_5CMe_2Ph]TiCl_3$ and the copolymerization catalyst $(\text{Cp}^{\text{Bu}_2}_2ZrCl_2)$ are present in the homogeneous phase. In the second strategy the trimerization catalyst is present in the homogeneous phase while the copolymerization catalyst is supported on SiO$_2$. We have clearly demonstrated that the synthesis of LLDPE applying a tandem catalysis approach using immobilized polymerization catalysts could be achieved and a series of branched polyethylenes with melting temperatures ranging between 123.7 and 127.4 °C have been obtained. However, the same dual system evaluated in a homogeneous system failed to produce branched PE.

4.1 Introduction

Linear low-density polyolefins (LLDPE) are random copolymers of ethylene and \( \alpha \)-olefins, commercially manufactured using Ziegler-Natta and single-site catalysts. The short chain branches impart a combination of stiffness, stress-crack resistance and transparency to the material, which raises the value of the copolymer product considerably with respect to the irregularly branched LDPE. The importance of polyolefinic materials in our daily life is responsible for extensive research activities both in industry and academia. The increasing need for high performance catalysts and polyolefins with tailor-made properties has resulted in some spectacular catalyst systems capable of producing polymers with novel microstructures.\(^{1a-c}\) An interesting development is the application of multicomponent systems (tandem catalysis) where two different catalysts (or two different cocatalysts) cooperate to give the desired product. Tandem catalysis can for example be employed to produce copolymers such as LLDPE by the copolymerization of ethylene and \emph{in-situ} formed \( \alpha \)-olefin comonomers (Scheme 1). The tandem catalysis process has the advantage over the more traditional two-monomers/one catalyst approach in that it does not need the separate production and subsequent addition of the second monomer. Obviously, finding compatible catalysts for a tandem system is challenging.

![Scheme 1. Tandem catalysis with an oligomerization catalyst and a polymerization catalyst.](image_url)

In the case of ideal tandem catalysis, the catalytic performance of the individual catalysts should not be influenced by the presence of the other. Unfortunately, this is not always the case. A number of factors must be taken into account when designing a successful tandem catalysis system for the production of LLDPE out of ethylene as the sole feedstock. Most importantly, the oligomerization and polymerization catalysts should not interfere with each other and should show an optimal activity (and selectivity) under the same reaction conditions. The control over the branching level can be provided by the relative amount of \( \alpha \)-olefin produced in the oligomerization cycle, simply by varying the oligomerization/polymerization catalysts ratio.
Beach and Kissin reported the earliest LLDPE tandem system consisting of heterogeneous Ziegler Natta catalysts Ti(OiPr)₄/AlEt₃ and TiCl₄/MgCl₂, where Ti(OiPr)₄/AlEt₃ produces 1-butene, while the TiCl₄/MgCl₂ incorporates the produced 1-butene into the polyethylene main chain.¹ ³ Chromium 2-ethylhexanoate activated by poly(isobutylaluminum oxide) has been demonstrated to yield a homogeneous tandem catalyst, which shows a dual oligomerization/polymerization nature.² Pellechia and coworkers reported another interesting catalyst system, viz. (η⁵-C₃Me₅)TiMe₂-B(C₆F₅)₃, which was shown to have a dual nature as it produces LLDPE out of ethylene as the only feedstock.³ In their system, ethylene is in-situ trimerized to 1-hexene, which is subsequently incorporated into the polymer chain. This behavior is attributed to the Ti(II)/Ti(IV) oxidation states, which lead to different mechanistic pathways.³ However, details of the mechanism behind the short chain-branched polyethylene are still missing. A successful implementation of the tandem catalysis has been shown by Bazan with triple tandem catalysts, indisputably demonstrating the importance and power of a high-throughput approach for catalyst developments, which optimized the reaction conditions even for a system consisting of three catalysts.⁴ They obtained branched polyethylenes that cannot be accomplished by a single- or a two-component catalyst combination.⁴ Bianchini’s tandem catalysts include a cobalt(II) complex that produces a Schultz-Flory distribution of α-olefins and a Ti(IV) constrained geometry polymerization catalyst that subsequently incorporates the α-olefins together with ethylene into an LLDPE-like product.⁵ De Wet-Roos’ and Dixon’s⁶ highly selective bis[2-decylthioethyl]amine-CrCl₃ ethylene trimerization catalyst⁷ in combination with metallocene catalysts produced LLDPEs with different levels of branching depending on the metallocene used. Fink and coworkers’ ‘Shop-type’ nickel-based catalyst for the in-situ non-selective ethylene oligomerization in combination with an alkyl-aluminum-free heterogeneous Ziegler catalyst⁸ is another reported example of tandem partners. An interesting tandem system, different from most reported tandem catalyst systems, consists of a single catalyst (rac-Et(Ind)₂ZrCl₂) and two cocatalysts (AlEt₂Cl and MAO).¹¹ When activated with AlEt₂Cl, rac-Et(Ind)₂ZrCl₂ functions as a non-selective ethylene oligomerization catalyst. Whilst activated with MAO it functions as polymerization catalyst. [η⁵-C₅H₄CMe₂Ph]TiCl₂/MMAO and a constrained geometry catalyst [{(η⁵-C₅Me₅)SiMe₂(tBuN)}TiCl₂/MMAO was reported by Zhu et al.,¹² as homogeneous tandem partners to synthesize LLDPEs with butyl branches and a small amount of 3-methylheptyl branches due to the C₁₀ fraction that is formed via co-trimerization of two ethylene and 1-hexene.

All these systems show interesting features but the authors seem to ignore the fact that LLDPE is either produced by a solution process above the melting temperature of the product or at lower temperatures using heterogeneous catalysts. Since ethylene oligomerization catalysts are commonly thermally unstable, a high temperature solution tandem process is generally not feasible. Hence, at least the polymerization catalyst will have to be a heterogeneous catalyst. Heterogeneous catalysts produce particles with a favorable morphology and a high bulk density and moreover avoid reactor fouling.

Disadvantages of classical Ziegler-Natta catalysts are the formation of broad MWD products and the
non-uniform distribution of the \( \alpha \)-olefin over the molar mass distribution. MgCl\(_2\)- or SiO\(_2\)-supported single-site catalysts generally still produce narrow MWD products with a uniform distribution of the \( \alpha \)-olefin, but often the catalytic activity is decimated compared to the original homogeneous system and not seldom the catalytic selectivity changes as well.\(^{16,20}\)

The number of reports on tandem catalysis where heterogeneous oligomerization/ polymerization catalysts are employed is very limited. Wang and co-workers have reported a heterogeneous tandem system to produce branched polyethylenes consisting of a bis(imino)pyridine iron oligomerization catalyst and Me\(_2\)C(Cp)(Flu)ZrCl\(_2\) as polymerization catalyst immobilized onto MAO-modified silica.\(^9\)

Okuda et al. used pyridyl-2,6-diisopropylphenylimine nickel dibromide in the homogeneous phase, while MAO pre-activated constrained geometry polymerization catalyst was immobilized onto a pyridylethysilsililane-modified silica support.\(^{10}\)

Examining the published tandem catalyst systems, it is clear that the use of tandem catalysts is a challenging research field and especially concerning heterogeneous tandem catalysis systems more research is required. In the study described in this chapter, we have investigated the catalytic behavior of ethylene oligomerization and polymerization catalysts present in the homogeneous and/or the heterogeneous phase. The catalysts have been tested individually as well as in tandem. For this study we have chosen the selective ethylene trimerization catalyst \([\eta^5\cdot \text{C}_5\text{H}_4\text{CMe}_2\text{Ph}]\text{TiCl}_3\) (1) and the polymerization catalyst Cp\(_{\text{Bu}}\)ZrCl\(_2\) (2).\(^{13}\) The main reason for choosing these catalysts is the fact that 1 and 2 show optimum performance under comparable conditions. We have compared the differences in product properties and catalytic behavior for systems where (i) both the trimerization 1 and polymerization 2 catalysts were present in the homogeneous phase, (ii) 1 was in the homogeneous phase while 2 was supported on SiO\(_2\). The third possibility where both 1 and 2 were supported has not been investigated further as SiO\(_2\)-supported 1 proved to be virtually inactive (vide infra).

### 4.2 Results and Discussion

#### 4.2.1 Independent Ethylene Trimerization Catalyzed by \([\eta^5\cdot \text{C}_5\text{H}_4\text{CMe}_2\text{Ph}]\text{TiCl}_3\) (1) and Ethylene/1-Hexene Copolymerization Catalyzed by Cp\(_{\text{Bu}}\)ZrCl\(_2\) (2) in Homogeneous Phase.

Before starting the tandem catalysis experiments, the catalytic behavior of both the ethylene trimerization (1) and the polymerization (2) catalysts was studied independently. 1/MAO shows \(>95\%\) trimerization selectivity affording mainly 1-hexene plus a small amount of a C\(_{10}\) fraction (co-trimers of ethylene and 1-hexene, mainly 5-methyl-non-1-ene) and up to 5\% of PE as a side product.\(^{13}\) As shown in Table 1, the combinations of 1/MAO and 1/TIBA/TBF\(_{20}\) (TIBA = Al(iBu)\(_3\), TBF\(_{20}\) = [Ph\(_3\)C]\([\text{B}((\text{C}_6\text{F}_5)_3]\)]\) result in active and selective ethylene trimerization catalysts and the results described in Table 1 are consistent with previously reported results.\(^{13}\) From entries a and b in Table 1 it was clear that the major
part of the 1-hexene was formed during the first 15 minutes, indicating that the lifetime of the catalyst is rather limited. Activation with MAO resulted in a slightly more selective catalyst than activation with TiBA/TBF$_{20}$ (entries b, c in Table 1), while activation with TiBA/TBF$_{20}$ resulted in higher activity and less polymer formation.

Table 1. Catalytic behavior of homogeneous [$\eta^5$-C$_5$H$_4$CMe$_2$Ph]TiCl$_3$ activated with MAO or TiBA/TBF$_{20}$.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst system</th>
<th>Reaction time (min)</th>
<th>C$_6$ * (wt%)</th>
<th>C$_6$ * (mL)</th>
<th>C$_{10}$ * (mL)</th>
<th>Trimerization Activity*</th>
<th>PE (g)</th>
<th>Polymerization Activity*</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1/MAO*</td>
<td>15</td>
<td>86.2</td>
<td>2.0</td>
<td>0.05</td>
<td>18000</td>
<td>0.5</td>
<td>6700</td>
</tr>
<tr>
<td>b</td>
<td>1/MAO*</td>
<td>30</td>
<td>87.6</td>
<td>2.4</td>
<td>0.04</td>
<td>11000</td>
<td>0.7</td>
<td>4700</td>
</tr>
<tr>
<td>c</td>
<td>1/TIBA/TBF$_{20}$*</td>
<td>30</td>
<td>83.2</td>
<td>3.4</td>
<td>0.15</td>
<td>15600</td>
<td>0.4</td>
<td>2700</td>
</tr>
</tbody>
</table>

Reaction conditions: * Solvent Isopar E, total volume 75 mL, 10 bar of ethylene, 40 °C, 30 µmol of [C$_5$H$_4$CMe$_2$Ph]TiCl$_3$, Al:Ti = 1000, 1 mmol of TiBA (scavenger); † 1.2 equivalent of TBF$_{20}$ 1 mmol of TiBA (scavenger); * Activity = g oligomer/mol catalyst·hour·bar; ‡ Activity = g PE/mol catalyst·hour·bar.

Table 2 lists the ethylene homopolymerization and ethylene/1-hexene copolymerization results of 2 in homogeneous phase. During all the polymerization reactions presented in Table 2, it was observed that the ethylene mass flow remained constant during the polymerization, which was an indication of a negligible catalyst deactivation. This lack of deactivation was confirmed by the comparable catalytic activity obtained after 15 minutes and 30 minutes of reaction duration. The highest molar mass and melting temperature were obtained when Cp$^{Bu}$ZrCl$_2$ was activated by TIBA/(TBF$_{20}$) although in this case the catalytic activity was significantly lower (Entry 3). PDI values were indicative for a single-site behavior of the catalyst, as was expected. However, deviations from the theoretical value of 2.0 were observed in the case of ethylene/1-hexene copolymerization reactions. The broadening of the PDI is most likely due to the composition drift during the polymerization. As expected, the melting enthalpies and the melting temperatures of the polyethylenes were influenced by the comonomer incorporation into the chain (Table 2). The decrease in catalytic activity and polymer molar mass when comonomer was added is ascribed to a change in the relative propagation and chain transfer rates in the presence of comonomer, a characteristic property of the metalloocene-based systems.$^{21}$
Table 2. Characteristics of polymers obtained by ethylene homopolymerization and ethylene/1-hexene copolymerization catalyzed by homogeneous \( \text{Cp}^\text{Bu}_2\text{ZrCl}_2 \) (2) activated with MAO and TIBA/TBF\textsubscript{20}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Monomers</th>
<th>Reaction time (min)</th>
<th>Activity(^c) kg mol(^{-1})</th>
<th>( M_n )</th>
<th>PDI</th>
<th>( T_m ) °C</th>
<th>( \Delta H_m ) J g(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2/MAO(^a)</td>
<td>( \text{C}_2^* )</td>
<td>15</td>
<td>1600</td>
<td>135</td>
<td>2.4</td>
<td>136.5</td>
<td>167.7</td>
</tr>
<tr>
<td>2</td>
<td>2/MAO(^a)</td>
<td>( \text{C}_2^* )</td>
<td>30</td>
<td>1520</td>
<td>164</td>
<td>2.3</td>
<td>136.6</td>
<td>159.7</td>
</tr>
<tr>
<td>3</td>
<td>2/TIBA/TBF\textsubscript{20}(^b)</td>
<td>( \text{C}_2^* )</td>
<td>30</td>
<td>840</td>
<td>230</td>
<td>1.8</td>
<td>139.1</td>
<td>178.0</td>
</tr>
<tr>
<td>4</td>
<td>2/MAO(^a)</td>
<td>( \text{C}_2^* + \text{C}_6^* ) (1 mL)</td>
<td>30</td>
<td>1360</td>
<td>43</td>
<td>2.5</td>
<td>126.5</td>
<td>133.8</td>
</tr>
<tr>
<td>5</td>
<td>2/MAO(^a)</td>
<td>( \text{C}_2^* + \text{C}_6^* ) (2 mL)</td>
<td>30</td>
<td>1240</td>
<td>71</td>
<td>2.6</td>
<td>125.3</td>
<td>125.6</td>
</tr>
<tr>
<td>6</td>
<td>2/MAO(^a)</td>
<td>( \text{C}_2^* + \text{C}_6^* ) (5 mL)</td>
<td>30</td>
<td>1280</td>
<td>67</td>
<td>2.7</td>
<td>119.8</td>
<td>113.4</td>
</tr>
</tbody>
</table>

Reaction conditions: \(^a\) Solvent Isopar E, total volume 75 mL, 10 bar of \( \text{C}_2^* \), 40 °C, 1 μmol of 2, Al:Zr=1000; \(^b\) 1 equivalent of TBF\textsubscript{20}, 1 mmol of TIBA (scavenger); \(^c\) kg of PE/mol of Zr-h-bar; \(^d\) Determined by DSC with heating rate of 10 °C/min from second heating curve.

4.2.2 Independent Ethylene Trimerization Catalyzed by \([\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph}]\text{TiCl}_3\) (1) and Ethylene/1-Hexene Copolymerization Catalyzed by \( \text{Cp}^\text{Bu}_2\text{ZrCl}_2 \) (2) in Heterogeneous Phase.

Utilization of a single-site olefin polymerization catalyst in a gas-phase or slurry process requires its immobilization on a carrier such as a MgCl\(_2\) or a silica support.\(^{15}\) However, catalyst immobilization often has a detrimental effect on the catalytic activity and can affect the selectivity of the catalyst as well.\(^{15,16,20}\) For example, it was shown that when 1 was immobilized on MgCl\(_2\) by heating the mixture of 1, MgCl\(_2\)/Al\(_r\)(OEt)\(_{3-n}\) support and toluene to 60 °C followed by decantation of the solvent, the original trimerization catalyst 1 turned into a potent ethylene polymerization catalyst producing UHMWPE instead of 1-hexene.\(^{14}\) On the other hand, using \([\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{Ph}]\text{TiMe}_3\) with a slurry of SiO\(_2\) with 5% MAO in toluene as a heterogeneous cocatalyst produced an ethylene trimerization catalyst that is even more selective (95% 1-hexene) than the corresponding homogeneous system.\(^{19}\) Hence, different immobilization protocols, *i.e.* pre-contacting the MAO cocatalyst with silica, or applying MgCl\(_2\)/Al\(_r\)(OEt)\(_{3-n}\) immobilization, can lead to an unexpected change in catalytic behavior. In this chapter, silica was chosen as an immobilization carrier because it is one of the two universal supports and MgCl\(_2\) has proven to turn catalyst 1 into a polymerization catalyst.

The results in Table 3 reveal the effect of immobilization of 1 and 2 onto SiO\(_2\). Immobilization in this case was realized by physisorption of the MAO-activated homogeneous catalyst on the support using the incipient wetness method.\(^{22}\) Our initial attempt was to investigate whether catalyst 1 would retain its ethylene trimerization ability once supported onto SiO\(_2\). Unfortunately, immobilization of 1 onto SiO\(_2\) resulted in a poor catalyst producing small amounts of polyethylene (200 kgPE/mol\(_{1\text{-h-bar}}\)) and only
traces of 1-hexene. \(^\dagger\) This switch in selectivity and activity as a result of different supportation methodologies (in-situ treatment of 1 with silica-supported MAO versus pre-supportation of MAO activated 1) was unexpected and clearly prevents the use of pre-supported 1 in a tandem system. The ethylene polymerization activity of silica-supported 2 proved to be significantly lower than the catalytic activity of 2 in homogeneous phase.\(^{16b,20}\) Nevertheless, the molar mass distributions (\(\approx 2\)) obtained with silica-supported 2 indicate that the single-site nature of the catalyst is preserved. We did not observe any significant difference between molar masses obtained by homogeneous and silica-supported 2. However, it is well-known that immobilized catalysts tend to afford higher molar masses than their homogeneous congeners.\(^{23}\) In the experiments shown in Table 3, two different solvents, namely toluene and Isopar E, were used to study the effect of the polymerization medium on the catalytic activity and on the polymer morphology. When the more polar solvent toluene was used as a polymerization medium the catalytic activity increased (Entry 8 and 12 in Table 3). Possibly, the toluene weakens the catalyst-cocatalyst interaction making the cation more accessible, resulting in a higher polymerization activity. The molar mass also seems to be solvent dependent as \(M_n\) values were generally lower in Isopar E compared with those obtained in toluene. The reason for this behavior is not fully understood.

For the copolymers, the polymer molar masses, melting points and heats of melting decreased with higher comonomer concentration (Table 3). The increase in the activities of the silica-supported catalyst in the presence of 1-hexene in Isopar could be attributed to the so-called comonomer effect: the more amorphous nature of the copolymer enhanced monomer diffusion into the catalyst particle.\(^{24,25}\) However, this effect in the activities of the silica-supported catalyst in the presence of 1-hexene in toluene is less pronounced. A possible explanation could be that in toluene the polymer tends to swell more and thereby lowering the diffusion limitation. Similar as observed for homogeneous 2 (Table 2), the molar masses of the copolymers obtained by 2+MAO/SiO\(_2\) decreased with increasing comonomer concentration. Interestingly, \(^{13}\)C-NMR spectroscopy revealed that the copolymers synthesized in Isopar E have a somewhat higher 1-hexene content (4.5 weight-%, which corresponds to 7.5 branches per 1000 C) than those synthesized in toluene (3.8 weight-%, which corresponds to 6.3 branches per 1000 C). Nevertheless, \(T_m\) and \(\Delta H\) reveal a slightly opposite trend (Entry 10 and 14). As expected, an increase in comonomer concentration resulted in a decrease in the melting enthalpies and melting temperatures of the polymers.\(^{13}\)C-NMR spectroscopy and DSC measurements suggested that catalyst supportation had very little, if any effect on 1-hexene incorporation. It was intriguing to compare the \(^{13}\)C NMR results with melting temperatures given in entry 6 in Table 2 and entry 10 in Table 3. Both samples contained 4.5 weight % of 1-hexene that corresponded to 7.5 branches per 1000 C. Still, the melting temperature in

\(^\dagger\) It has to be noted that 1 \(\mu\)mol of catalyst was used based on reference.\(^{14}\) The catalyst activity was expected to be higher at relatively low loadings.\(^{14}\)

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entry 10 of Table 3 is slightly higher (122.5 °C) than that of entry 6 in Table 2 (119.8 °C). Based on a melting enthalpy (ΔH) of 293 J/g for 100% crystalline polyethylene, the melting temperature and melting enthalpy values of entry 6 and entry 10 correspond to crystallinities of 38% and 42%, respectively. It was likely that the crystallinities of these LLDPEs were influenced not only by the presence of branched polyethylene but also by molar mass.

**Table 3.** Characteristics of polymers obtained by ethylene trimerization, homopolymerization and ethylene/1-hexene copolymerization using 1/SiO<sub>2</sub>/MAO, 2/SiO<sub>2</sub>/MAO and 2/SiO<sub>2</sub>/TIBA/TBF<sub>20</sub> catalysts systems: influence of solvent.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Monomer</th>
<th>Trimerization</th>
<th>Activity</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;</th>
<th>PDI</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;</th>
<th>ΔH&lt;sub&gt;n&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>1/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>trace</td>
<td>200</td>
<td>518</td>
<td>2.5</td>
<td>134.1</td>
<td>119.2</td>
</tr>
<tr>
<td>8</td>
<td>2/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>520</td>
<td>139</td>
<td>1.9</td>
<td>134.7</td>
<td>161.8</td>
</tr>
<tr>
<td>9</td>
<td>2/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; + C&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (1 mL)</td>
<td>-</td>
<td>520</td>
<td>58</td>
<td>2.6</td>
<td>128.0</td>
<td>137.4</td>
</tr>
<tr>
<td>10</td>
<td>2/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; + C&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (5 mL)</td>
<td>-</td>
<td>700</td>
<td>43</td>
<td>2.2</td>
<td>122.5</td>
<td>122.7</td>
</tr>
<tr>
<td>11</td>
<td>2/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; + C&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (9 mL)</td>
<td>-</td>
<td>740</td>
<td>47</td>
<td>2.5</td>
<td>118.8</td>
<td>84.0</td>
</tr>
<tr>
<td>12</td>
<td>2/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;</td>
<td>-</td>
<td>800</td>
<td>123</td>
<td>2.3</td>
<td>134.6</td>
<td>160.6</td>
</tr>
<tr>
<td>13</td>
<td>2/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; + C&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (2 mL)</td>
<td>-</td>
<td>560</td>
<td>126</td>
<td>2.2</td>
<td>126.6</td>
<td>134.0</td>
</tr>
<tr>
<td>14</td>
<td>2/MAO/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; + C&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (5 mL)</td>
<td>-</td>
<td>820</td>
<td>80</td>
<td>2.0</td>
<td>122.1</td>
<td>110.8</td>
</tr>
<tr>
<td>15</td>
<td>2/SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; + C&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt; (9 mL)</td>
<td>-</td>
<td>760</td>
<td>53</td>
<td>1.9</td>
<td>119.6</td>
<td>109.4</td>
</tr>
</tbody>
</table>

Reaction conditions: <sup>a</sup> Solvent Isopar E, total volume 75 mL, 10 bar, 40 °C, 1 μmol of [C<sub>5</sub>H<sub>4</sub>CMe<sub>2</sub>Ph]TiCl<sub>3</sub>/ 100 mg SiO<sub>2</sub>-supported MAO, 1 mmol of TIBA (scavenger); <sup>b</sup> Reaction conditions are same as a, 1 μmol of Cp<sup>Bu</sup>ZrCl<sub>2</sub>/100 mg SiO<sub>2</sub>-supported MAO, 1 mmol TIBA (scavenger); <sup>c</sup> Solvent Toluene, total volume 75 mL, 10 bar, 40 °C, 1 μmol of 2/100 mg SiO<sub>2</sub>, 1 mmol TIBA (scavenger); <sup>d</sup>Determined by DSC with heating rate of 10 °C/min from second heating curve.

The major advantage of employing silica-supported 2 is that spherical polymer particles are produced without any reactor fouling. The spherical morphology of the support was retained by replication as a result of homogenous distribution of active sites across the final catalyst particle. Scanning electron microscopy (SEM) micrographs of the spheroidal particle morphologies of polyethylenes obtained in Isopar E is shown in Figure 1.
Figure 1. SEM image of the PE (Entry 8 in Table 3) obtained using the 2/MAO/SiO$_2$ catalyst system in Isopar E.

4.2.3 Ethylene Polymerization with Tandem Catalyst Systems Based on Homogeneous and Heterogeneous Titanium and Zirconium Catalysts

The synthesis of LLDPE by tandem catalysis in homogeneous phase below the melting temperature of the polymer product is bound to suffer from severe reactor fouling and therefore will have no commercial value. Nevertheless, it can provide valuable information about the compatibility of the catalysts used in the tandem process. The homogeneous tandem catalysis results are listed in Table 4. In this section, TIBA/TBF$_{20}$ was chosen as a cocatalyst. Although it was shown that TIBA/TBF$_{20}$-activated 2 gave the lowest activity, the activity of TIBA/TBF$_{20}$-activated 1 was found to be higher than of MAO activated 1.

From the results described in Section 4.2.2 it could be concluded that a 1-hexene concentration in the range of 9-12% was required to obtain polymers with significant branching. To obtain this concentration of 1-hexene, a catalyst loading of 1 of approximately 15 μmol was required. From this simple calculation it was apparent that the Ti/Zr ratio would be large. However, as long as the catalysts do not interfere with each other, there should not be any problem. With the purpose of raising the concentration of 1-hexene to a certain level before the copolymerization started, we applied a pre-trimerization time of five minutes. In the ideal case, the production and consumption of 1-hexene should be the same so that the 1-hexene concentration would remain constant throughout the entire polymerization process. Since tuning the simultaneous 1-hexene production and consumption would require extensive optimization, we focused on a qualitative tandem catalysis study.
Table 4. Characteristics of polymers obtained with the tandem catalyst systems based on homogeneous 1 and 2 activated with TIBA/TBF\textsubscript{20}.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Ti/Zr</th>
<th>Reaction time</th>
<th>Activity ( \text{k}\text{PE/mol} \cdot \text{h-bar} )</th>
<th>( M_n ) ( \text{kg/mol} )</th>
<th>PDI</th>
<th>( T_m ) ( ^\circ \text{C} )</th>
<th>( \Delta H_m ) ( \text{J/g} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>2 (1 ( \mu \text{mol} )) + 1 (30 ( \mu \text{mol} ))</td>
<td>30</td>
<td>35</td>
<td>225</td>
<td>46</td>
<td>2.1</td>
<td>136.8</td>
<td>186.7</td>
</tr>
<tr>
<td>17</td>
<td>2 (1 ( \mu \text{mol} )) + 1 (60 ( \mu \text{mol} ))</td>
<td>60</td>
<td>35</td>
<td>315</td>
<td>40</td>
<td>2.4</td>
<td>131.7</td>
<td>166.3</td>
</tr>
<tr>
<td>18</td>
<td>2 (0.5 ( \mu \text{mol} )) + 1 (60 ( \mu \text{mol} ))</td>
<td>120</td>
<td>35</td>
<td>275</td>
<td>46</td>
<td>2.4</td>
<td>133.2</td>
<td>151.9</td>
</tr>
</tbody>
</table>

Reaction conditions: Solvent Isopar E, total volume 75 mL, 10 bar, 40 °C, 1 mmol TIBA (scavenger), 1.1 equivalents of TBF\textsubscript{20}. Determined by DSC with heating rate of 10 °C/min from second heating curve.

Except for the Ti/Zr ratio, all other polymerization conditions were kept constant. Compared to the copolymerization results presented in Table 2, it is clear that the activity of the tandem system (≈300 kg of PE/mol of Zr·h·bar) is significantly lower than the catalytic activity of 2 alone (≈1300 kg of PE/mol of Zr·h·bar; Table 4). This suggested that the two catalysts do affect each other at least to some extent. This interaction might well be emphasized by the large Ti/Zr ratio necessary to produce enough 1-hexene. Although the molar masses of the obtained polymers were comparable to those of the copolymerizations reported in Table 2, the melting temperatures and melting enthalpies were considerably higher and correspond to mainly linear polyethylene (Table 4). The tandem catalysis run carried out with a 1:2 ratio of 60 resulted in the lowest \( M_n \) and \( T_m \) value. Still the 1-hexene content in this copolymer was detected to be only 1.5 per 1000 C (based on \textsuperscript{13}C NMR), which corresponded to 0.9 weight-% (entry 17, Table 4). Why the branching density was so much lower than in Table 2 was not yet understood. The activity is not very different for entries 16-18. The difference was observed among the \( T_m \) values of the entries 16-18, which corresponded the differences in the branching level. DSC measurements revealed that entries 17 and 18 had crystallinities\textsuperscript{\dagger} of 56% and 52%, respectively (Table 4). On the other hand, melting temperature of entry 18 (133.2) was slightly higher than that of entry 17 (131.7). Crystallinity values of entry 17 and 18 were in contrast with the melting temperature values. It may be speculated that the minimal amount branching of entry 18 was heterogeneously distributed. For entries 21 - 24 (Table 5) the trimerization catalyst 1 was in the homogeneous phase while the copolymerization catalyst 2 was supported on SiO\textsubscript{2}. For entries 21 and 22, 1 was activated with TIBA/TBF\textsubscript{20}, whilst for entries 23 and 24 1 is activated with MAO. In all cases 2 was activated with TIBA/TBF\textsubscript{20}. Due to lack of time, we were not able to test fully heterogeneous tandem system that is the combination of 1 activated with SiO\textsubscript{2}-supported MAO in combination with SiO\textsubscript{2}-supported 2.

\textsuperscript{\dagger} Crystallinity (%) = \[ \Delta H_{\text{sample}} / \Delta H_{\text{PE (100\%)} \times 100} \] where \( \Delta H_{\text{PE (100\%)}} \) is the melting enthalpy value of 100% crystalline polyethylene (≈293 J/g) and \( \Delta H_{\text{sample}} \) is the melting enthalpy of the sample.
Table 5. Characteristics of the reaction products of the ethylene polymerization with tandem catalyst systems based on heterogeneous 2/SiO₂ and homogeneous 1 activated with TIBA/TBF₂₀ or MAO.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst/Cocatalyst System</th>
<th>Rxn. time</th>
<th>Activity</th>
<th>( M_n )</th>
<th>PDI</th>
<th>( T_m )°C</th>
<th>( \Delta H_m ) J/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>12²</td>
<td>2/MAO/SiO₂</td>
<td>30</td>
<td>800</td>
<td>123</td>
<td>2.3</td>
<td>134.6</td>
<td>160.6</td>
</tr>
<tr>
<td>19²</td>
<td>2/MAO/SiO₂/1000 MAO</td>
<td>30</td>
<td>380</td>
<td>306</td>
<td>2.0</td>
<td>136.5</td>
<td>159.5</td>
</tr>
<tr>
<td>20²</td>
<td>2/SiO₂/TIBA/TBF₂₀</td>
<td>30</td>
<td>380</td>
<td>134</td>
<td>2.0</td>
<td>135.0</td>
<td>154.5</td>
</tr>
<tr>
<td>21²</td>
<td>2 (1 µmol)/SiO₂/TIBA/TBF₂₀</td>
<td>35</td>
<td>120</td>
<td>113</td>
<td>2.2</td>
<td>123.7</td>
<td>100.5</td>
</tr>
<tr>
<td></td>
<td>1 (30 µmol/TIBA/TBF₂₀)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22²</td>
<td>2 (1 µmol)/SiO₂/TIBA/TBF₂₀</td>
<td>35</td>
<td>155</td>
<td>106</td>
<td>2.5</td>
<td>123.7</td>
<td>100.5</td>
</tr>
<tr>
<td></td>
<td>1 (60 µmol/TIBA/TBF₂₀)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23²</td>
<td>2 (1 µmol)/SiO₂/TIBA/TBF₂₀</td>
<td>35</td>
<td>430</td>
<td>385</td>
<td>1.7</td>
<td>133.5</td>
<td>122.6</td>
</tr>
<tr>
<td></td>
<td>1 (3.8 µmol)/1000 MAO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24²</td>
<td>2 (1 µmol)/ SiO₂/TIBA/TBF₂₀</td>
<td>35</td>
<td>290</td>
<td>252</td>
<td>2.2</td>
<td>127.4</td>
<td>119.4</td>
</tr>
<tr>
<td></td>
<td>1 (7.6 µmol)/1000 MAO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: ² Solvent toluene, total volume 75 mL, 10 bar, 40 °C, 1 µmol of 2/100 mg SiO₂, 1 mmol TIBA (scavenger) (the same as in Table 3) ³ Solvent: Isopar, total volume 75 mL, 10 bar, 40 °C, 1 µmol of 2/100 mg SiO₂, 1 mmol TIBA, 1 equivalent of TBF₂₀ ⁴ Solvent Isopar, total volume 75 mL, 1.1 equivalents of TBF₂₀, 1 mmol TIBA, 10 bar, 40 °C, reaction time 35 minutes. ⁵ Solvent toluene, total volume 75 mL, 1000 equivalents of MAO, 10 bar, 40 °C, reaction time 35 minutes; ⁶ Determined by DSC with heating rate of 10 °C/min from second heating curve.

The activity of the partly heterogeneous tandem system activated with TIBA/TBF₂₀ was even lower than that of the corresponding homogeneous tandem system. This was not surprising since the ethylene homopolymerization activity of 2/SiO₂/TIBA/TBF₂₀ (Entry 20) was also low. The LLDPEs obtained exhibited relatively narrow molar mass distributions with polydispersity indices ranging from 1.7 to 2.5, illustrative of the true single-site nature of the catalysts. The low melting temperatures and low melting enthalpies showed a definite incorporation of α-olefins into the polyethylene backbone in the presence of both cocatalysts. Not unexpectedly, based on the total amount of 1 present during runs 21 and 22 versus 23 and 24, the branching density of the polymers using TIBA/TBF₂₀ as cocatalyst were significantly higher than for the MAO-activated system (Tables 5 and 6). Unfortunately, all runs 21 – 24 produced significant reactor fouling. Clearly, at least part of the polymer is produced in homogeneous phase. For the runs where 1 was activated with MAO (entries 23 and 24) this is not very surprising. The excess MAO clearly induces leaching of the zirconocene from the silica support, as was proven in an independent experiment 19. But the same seems to happen when TIBA/TBF₂₀-activated 1 is used.
The melting temperature of the polymers prepared in runs 23 and 24 are somewhat higher compared to the \( T_m \)'s of the polymers prepared in runs 21 and 22. However, keeping in mind that the total amount of 1 is one order of magnitude lower than for the TIBA/TBF\(_{20}\) activated system the branching density was actually quite high. Doubling the amount of 1 (entry 23 and 24) showed a clear decrease of the melting point and enthalpy upon doubling of the loading of 1. Interestingly, doubling the amount of 1 in the TIBA/TBF\(_{20}\)-activated system did not lead to a lower melting temperature.

**Table 6.** 1-hexene contents determined by \(^{13}\)C-NMR with tandem catalyst systems heterogeneous 2/SiO\(_2\) and homogeneous 1 activated with TIBA/TBF\(_{20}\) or MAO.

<table>
<thead>
<tr>
<th>Entry</th>
<th>CH(_3) end groups per 1000 C</th>
<th>1-hexene incorporation per 1000 C(^c)</th>
<th>1-hexene incorporation weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>21(^a)</td>
<td>1.5</td>
<td>7.3</td>
<td>4.4</td>
</tr>
<tr>
<td>22(^a)</td>
<td>1.3</td>
<td>6.1</td>
<td>3.7</td>
</tr>
<tr>
<td>23</td>
<td>0.6</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>24(^a)</td>
<td>0.3(^b)</td>
<td>2.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^a\) sample colored brown after dissolution; \(^b\) end group values are barely visible. Relative high error is expected due to the difficulties in the dissolution; \(^c\) 1-hexene content was calculated from the integration area of the branching carbon signal and the integration area of the main signal of CH\(_2\)-chain. Chemical shifts are given in reference \(^{26}\).

### 4.3 Conclusions

In this chapter, we tried to apply two different approaches to tandem catalysis, based on a homogeneous and a mixed homogeneous – heterogeneous catalyst system. The difference in catalytic activity of 1 and 2 required a significant excess of 1 to obtain the required concentration of 1-hexene. It was found that when both 1 and 2 are in the homogeneous phase hardly any incorporation of 1-hexene was observed. On the other hand, for the partly heterogeneous tandem catalysts systems, incorporation of *in situ* formed 1-hexene was indeed observed. Summarizing, it can be concluded that monomodal LLDPEs can be produced using a 1 + 2/SiO\(_2\) tandem catalyst system. However, for the sake of fairness it has to be said that this system was far from ideal and it is clear that both the combination of the two catalysts as well as the necessary catalyst immobilization had a detrimental effect on the catalytic performance of the system. Besides, under the polymerization conditions 2 seems to leach partly from the support resulting in reactor fouling.
4.4 Experimental Section

All reactions and modifications of moisture- and air-sensitive compounds were conducted in a M-Braun glovebox under nitrogen atmosphere. Solvents were purchased from Biosolve and were purified by passing them through an alumina-activated column. MAO (1.5 M in toluene) was purchased from Chemtura. Ethylene (5.0) was purchased from Linde Gas. [Ph₃C][B(C₆F₅)₄] was a gift from DSM, while TIBA was purchased from Aldrich. Catalyst precursor 1 was synthesized by Fabian Karbach according to the literature. Zirconocene 2 was purchased from Strem Chemicals. 1-Hexene was purified by distillation and dried over 3 Å molecular sieves. The supports used in this work were prepared by Fabian Karbach. Catalyst immobilization was performed via incipient wetness method on non-pacified silica. Prior to use, silica particles have been calcined at 600 °C in a muffle furnace.

Immobilization of (CpBu)₂ZrCl₂ on SiO₂

(CpBu)₂ZrCl₂ (20.2 mg, 49.9 µmol) was dissolved in toluene (3.8 mL) and activated by the addition of methyl aluminoxide in toluene (7.7 mL, 1.5 M, 11.5 mmol, 230 eq. Al). The total volume of the solution (11.5 mL) equals 1.4 times the pore volume of the employed silica. After a pre-contacting time of 30 min the zirconocene-MAO-solution was added drop wise to a stirred bed of silica (5g, Tcalc=600 °C, pore volume 1.6 mL/g) cooled in an ice bath. When the addition was completed the stirring was stopped and the temperature was slowly increased to 55 °C. After 4 h at 55 °C and occasional agitation, high vacuum was applied to dry the silica and obtain a free flowing powder.

Polymerization procedure using reactor platform U118

The reactor was dried by heating it in vacuum at 130 °C (p≤6 mbar) for 3 minutes followed by purging N₂ (5 bar) and leaving it under pressure for 12 minutes. The drying procedure was repeated three times before the reactor was brought to the desired temperature (40 °C) and filled with Isopar E (50 mL). Subsequently a solution of TIBA (1 mmol) and 1-hexene (in case of co-polymerizations) in Isopar E (total volume 10 mL) was injected in the reactor and stirring was started (700 rpm). After the temperature inside the reactor was stable, it was pressurized with ethylene at a pressure corresponding to a partial pressure of 10 bar. The ethylene uptake was monitored and after the solution was saturated with ethylene a suspension of (nBuCp)₂ZrCl₂/SiO₂ (100 mg) in Isopar E (15 mL) was injected via the automated injection procedure. During injection the catalyst vial was shaken gently to maintain a homogeneous suspension of the heterogeneous catalyst.

After 30 minutes the polymerization was stopped by closing the ethylene feed and venting the reactor. The reaction mixture was poured onto acidified ethanol (20 mL), the produced polymer was isolated by filtration and dried under vacuum at 70 °C.
Homogeneous poly- and oligomerizations and reactions employing toluene as a solvent were performed following the same procedure.

Tandem catalysis was performed in a similar manner with the following deviations: When TIBA/TBF$_{20}$ was used as activator the trimerization catalyst (1) was mixed with TBF$_{20}$ in 10 mL of Isopar E and injected into the reactor containing solvent and scavenger (TIBA) after saturation with ethylene. In case MAO was used as a cocatalyst the MAO was injected together with the scavenger (TIBA) followed by saturation with ethylene as above. After saturation the trimerization catalyst dissolved in 10 mL of Isopar E was injected.

Independent of the activator employed, the trimerization was run for 5 minutes before the homogeneous or heterogeneous polymerization catalyst (2) was injected. After the polymerization catalyst was injected the reaction was run for additional 30 minutes before the reactor was vented and the mixture was quenched as described above.

**Characterization of the polymers**

SEC (High Temperature Size Exclusion Chromatography) was performed on a Polymer Laboratories PLTX-20 Rapid GPC Polymer Analysis System at 160° C with 3 PLgel Olexis (300 x 7.5 mm, Polymer Laboratories) columns. 1, 2, 4-Trichlorobenzene was used as a solvent at a flow rate of 1.0 mL/min. The column set was calibrated using universal calibration with narrow polyethylene standards in the range from 5 310 to 1 510 000 kg/mol. Mark Houwink constants of polyethylene were used for (k = 14 dl/g and α = 0.725). 1,2,4-Trichlorobenzene flows through the columns at a flow rate of 1 mL/min. 2,6-Di-tert-butyl-4-methylphenol (BHT) and Irganox 1010 were added to the mixture in order to stabilize the polymer against oxidative degradation. All samples were prepared by dissolving (at 160 °C) 4.5 – 6.0 mg of polymer in 4.5 mL of stabilized TCB and allowing the polymers to dissolve for 3 hours prior to injecting the polymer solution into the SEC instrument.

Thermal Analysis of the samples was conducted by using a DSC Q1000 apparatus (TA Instruments). The samples (4, 5 - 6 mg) were heated to 160° C and subsequently cooled to 20 °C at a rate of 10 °C/min. A second heating cycle was used for data analysis.

The $^{13}$C nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 400 MHz spectrometer by C$_2$D$_2$Cl$_4$ at 140 °C at DSM Resolve B. V. Stabilizer was added to prevent oxidation. 2000 scans were accumulated with 20 seconds relaxation delay.

**Acknowledgements.** I would like to thank to Fabian Karbach for his contribution and Harrie A. J. Linssen for the NMR measurements (DSM).
4.5 References


5 Characterization of Linear and Short-chain Branched Polyethylene utilizing High-throughput Approaches

Abstract

This chapter highlights the challenges involved in the high-throughput characterization of molecular as well as physical and mechanical properties of linear low-density polyethylenes (LLDPEs). A combination of various characterization methods such as DSC, SEC, SEC-IR, IR and Raman spectroscopy as well as nano-indentation provided comprehensive information on the molecular architecture at different dimensional levels. IR and Raman spectroscopy as well as nano-indentation were employed to screen the mechanical properties of the polyethylenes in a high-throughput way. Correlations between comonomer incorporation, elastic modulus and crystallization behavior were investigated. The obtained results showed that the combination of IR spectroscopy and DSC represents a better and more direct technique for the determination of the crystallinity index than DSC alone. Moreover, Raman spectroscopy delivered a mathematical approximation for the determination of the crystallinity index. The nano-indentation technique offered the possibility to screen the mechanical properties of the polymers by using only a small amount of sample. The high-throughput characterization techniques represented in this chapter are utilized as experimental strategies that speed up the characterization of polymers by measuring specified locations subsequently in one run. However, finally a close combination of high-throughput characterization with polymer synthesis and sample preparation techniques is necessary to avoid bottlenecks.
5.1 Introduction

The developments in polyolefin science are the result of the combination of improvements in catalyst design, polymer synthesis and polymer characterization methods as well as their interaction with each other. Today, hundreds of polyolefin varieties are commercially available from ultra-rigid thermosets to high-performance elastomers. These have applications from bottles to car bumpers, from packaging to medical devices. It is possible to produce polyolefins with well-defined and tunable microstructures by manipulating the reaction kinetics via customizing the catalyst and adjusting the process conditions. For this purpose, high-throughput experimentation (HTE) represents a highly advantageous and efficient approach: The possibility to vary a large number of parameters in a short time span speeds up the optimization of the synthetic procedures and catalyst design as shown in literature and Chapter 3. High-throughput techniques are mostly highly automated and minimize the time and labor demands per sample. First automated synthesizers for the organometallic compounds, supported catalysts and olefin polymerization reactions, were reported by Tuchbreiter and Mühlaupt. In addition, scientists at Symyx also described a fully-automated HTE system for the discovery of polyolefin catalysis. Moreover, the collaboration between Symyx and Dow led the discovery of a hafnium-based olefin polymerization catalyst. In their study, primary screening was performed by high-throughput 1-octene polymerization experiments (384 reactions in a time span of hours) with novel group (IV) polymerization catalysts resulting in the discovery of an amide-ether based hafnium catalyst. Secondary screening was performed by the amine-ether based hafnium catalyst library and demonstrated the ethylene-1-octene copolymerization capability of this catalyst library. Only the third screening was performed by conventional batch reactors to validate the results from the first and the secondary small-scale screening and to upscale the process. Needless to say, such a high quantity of polymerization reactions could not be carried out without HTE approach. In the same study, high molar mass polycatenes and LLDPEs were also characterized by rapid characterization techniques. Based on the results from the secondary screening of Symyx’s experiments, modifications on the ligand system of the hafnium catalyst were employed again using a HTE approach. As a result, it was discovered that this catalyst group was able to polymerize propylene in a highly isotactic fashion. Other illustrative examples of HTE approaches in kinetic studies and catalyst design are for example the studies by Arriola on the so-called Dow shuttle chemistry and Gibson’s high-throughput screening of ethylene oligomerization catalysts. Recently, hafnium heteroaryl-amido catalysts for the propylene polymerization were also discovered by applying strategies of HTE. These examples clearly demonstrate the impact of HTE on the innovations in the polyolefin field. Even though HTE represents a promising approach to develop new polyolefins, it is still challenging due to the need to operate under a controlled atmosphere because of the reactivity of the organometallic catalysts with water and oxygen.
To quickly assess the properties of a multitude of polymers obtained in a short time span, high-throughput characterization techniques are necessary for the thorough understanding of the formation of specific polymer microstructures. The analysis of polymers may be accelerated by several approaches such as: (1) The thermal analysis may be performed with an automated sampling system,\(^2\) (2) molar masses and polydispersity indices may be analyzed by high-speed columns, parallelization and flow-injection analysis as it was shown in the reviews of Hoogenboom et al. and Meier.\(^2\)k Moreover, analysis of polyolefin samples with a low branching level is difficult and time consuming with conventional NMR analysis whereas high-throughput SEC-IR analysis can be applied successfully to determine the branching level. Characterization with HTE is fast and accurate to determine structure-properties relationships in an efficient way, albeit that it has some limitations. Especially among the polyolefin materials with overlapping bimodal polydispersity indices with different amounts of comonomer concentrations, resolution can be a problem that limits the sample throughput in high-throughput SEC and SEC-IR analysis.

Since most synthetic HTE procedures yield very small amounts of polymer, only a minimum amount of sample is usually available for characterization using HTE. For this study it was decided to synthesize LLDPE samples in a 250 mL Büchi reactor and only perform the characterization with HTE. Moreover, several polymerizations were carried out in a HTE reactor setup consisting of 4 fully automated, parallel 125 mL reactors using a different catalyst (see below) for comparison of reactor performance and LLDPE characteristics.

In this chapter, various HTE characterization techniques were used to evaluate the molecular and the thermal/physical/mechanical bulk properties of different LLDPE grades. LLDPEs served as the model system for this study due to the good control over the side chains and well-defined microstructures leading to a library of polymers with predictable properties. Copolymerizations of ethylene/1-hexene and ethylene/1-octene were carried out using the \(\text{C}_2\)-symmetric metalloocene \textit{rac}-Me\(_2\)Si(2-Me-4-Ph-Ind)\(_2\)ZrCl\(_2\)/MAO\(^3\) catalyst to obtain short-chain branched polyethylenes with butyl and hexyl branches. This \(\text{C}_2\)-symmetric metallocone catalyst showed high activity for ethylene and propylene polymerization and reasonably good comonomer incorporation. The polymerizations in the HTE reactor setup were performed with a metallocene catalyst of the type Cp\(\text{Bu}^\text{Me}^\text{Bu}^\text{Bu}^\text{Bu}\)ZrCl\(_2\).

High temperature, high-throughput size exclusion chromatography (SEC) and SEC coupled to infrared spectroscopy (HT-SEC-IR) were used to analyze the short-chain branching distribution of the synthesized LLDPEs across the entire molar mass distribution. The crystallinity index of the LLDPEs was determined using high-throughput Raman and Infrared spectroscopy and compared to the results obtained by DSC. The crystallinity index is a relative value that is obtained by dividing the area of a crystalline band from the spectrum by the value of an amorphous band. The elasticity modulus of the surface with a depth down to the nanometer scale was characterized with a high-throughput nano-indentation technique. The influence of the length and the amount of branches on the crystallization and the mechanical
properties of the produced LLDPE materials is described in this chapter using the data obtained from all HTE characterization techniques mentioned above.

5.2 Results and Discussion

5.2.1 Molar Mass Determination with High-throughput SEC and SEC-IR

A series of ethylene/1-hexene and ethylene/1-octene (co)polymers was synthesized in a 250 mL Büchi reactor system to obtain short-chain branched materials. Linear polyethylenes, activated with two different Al:Zr ratios (250 and 500), were synthesized as reference materials to compare the properties of the copolymers to those of PE without branching. Both type of polymerization reactor and operating conditions were important factors determining the catalyst’s behavior. The reaction parameters, as well as the molar masses and polydispersity index (PDI) values for the linear and branched polymers are listed in Table 1.

During the homo- and copolymerizations, the high initial activity resulted in a rapid increase in temperature. This resulted in non-isothermal conditions. Lowering the catalyst concentration further resulted in too many failed runs compared to a few (approximately) isothermal runs that showed low activity. It appeared that the utilized Büchi reactor system did not have a sufficient cooling capacity for this highly active catalyst. This system led to uncontrolled homogeneous homo- and copolymerization reactions forming polymer deposits on the reactor walls that influenced the measured molar mass distributions and operability of the process.

For all copolymerization reactions an increase in the activity was observed up to a certain comonomer concentration, after which the activity decreased again. Interestingly, the effect was stronger for 1-octene than for 1-hexene. The comonomer effect was already described in the literature and it was observed that it was catalyst- and comonomer-specific, as was the case in our study. The presence of an optimum in activity with increasing comonomer concentration is a known phenomenon. This particular comonomer effect, which was also observed in our study, emerges from the participation of the comonomer on the activation of the active centers. This results in a decrease in the activation energy for the insertion of the monomer into carbon-metal bond.

The polymers produced by rac-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ activated with MAO at 40 °C had adequate molar masses but their polydispersity index values were relatively high and ranged between 2.0 to 7.5. The broadening of the molar mass distribution was assumed to be due to the non-isothermal conditions and reactor fouling which caused further heat and mass-transfer limitations. The molar masses of the polymers decreased with the increase in 1-octene incorporation, while there was no significant change observed with enhanced 1-hexene incorporation (Table 1).
Table 1. Ethylene/α-olefin (co)polymerization results (non-high throughput).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Comonomer</th>
<th>Feed</th>
<th>Al/Zr</th>
<th>Activity</th>
<th>$M_n$ kg/mol</th>
<th>PDI $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[vol-% in feed]</td>
<td>kg$<em>{polymer}$/mol$</em>{Zr}$+h$^+$bar</td>
<td>kg/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference 1</td>
<td>-</td>
<td>-</td>
<td>500</td>
<td>2800</td>
<td>470</td>
<td>3.0</td>
</tr>
<tr>
<td>Reference 2</td>
<td>-</td>
<td>-</td>
<td>250</td>
<td>2000</td>
<td>360</td>
<td>3.0</td>
</tr>
<tr>
<td>Sample 1</td>
<td>1-hexene</td>
<td>0.5</td>
<td>250</td>
<td>2760</td>
<td>215</td>
<td>5.4</td>
</tr>
<tr>
<td>Sample 2</td>
<td>1-hexene</td>
<td>1</td>
<td>250</td>
<td>3360</td>
<td>230</td>
<td>3.0</td>
</tr>
<tr>
<td>Sample 3</td>
<td>1-hexene</td>
<td>2</td>
<td>250</td>
<td>2580</td>
<td>220</td>
<td>2.5</td>
</tr>
<tr>
<td>Sample 4</td>
<td>1-hexene</td>
<td>3</td>
<td>250</td>
<td>2180</td>
<td>240</td>
<td>2.0</td>
</tr>
<tr>
<td>Sample 5</td>
<td>1-octene</td>
<td>0.5</td>
<td>250</td>
<td>3000</td>
<td>620</td>
<td>4.7</td>
</tr>
<tr>
<td>Sample 6</td>
<td>1-octene</td>
<td>1</td>
<td>250</td>
<td>3200</td>
<td>461</td>
<td>7.4</td>
</tr>
<tr>
<td>Sample 7</td>
<td>1-octene</td>
<td>2</td>
<td>250</td>
<td>4700</td>
<td>400</td>
<td>2.7</td>
</tr>
<tr>
<td>Sample 8</td>
<td>1-octene</td>
<td>3</td>
<td>250</td>
<td>4450</td>
<td>340</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Reaction conditions: 2.5 μmol Me$_2$Si[2-Me-4-Ph-Ind]$_2$ZrCl$_2$, 1 bar of C$_2$ (0.9 mol/L), reaction temperature = 40 °C, reaction duration 20 min, solvent 100 mL of toluene, 700 r.p.m. $^a$ Obtained by HT-SEC in a high-throughput way.

The branching density of three LLDPE samples was determined by HT-SEC-IR (Table 2). The analysis of these three ethylene/α-olefin copolymers involved both solvent and thermal fractionation. Compositional drifts were detected by HT-SEC-IR, for which the symmetrical and asymmetrical C-H stretching regions of the spectra were used. Differences in the proportions of methylene and methyl groups, and therefore the level of short-chain branching (SCB), in a sample were detected by measuring the relative intensities of the -CH$_3$ and -CH$_2$ absorption bands between 2800 and 3000 cm$^{-1}$.9

High temperature SEC-IR results for Samples 1, 5 and 9 showed that the level of co-monomer incorporation was constant across the molar mass distribution, as expected for a stable single-site catalyst. For Sample 1, $M_n$ values determined by HT-SEC-IR were higher than those found using typical SEC conditions while, on the other hand, the $M_n$ value for Samples 5 and 9 determined by HT-SEC-IR was lower. The differences in molar mass might be due to the different SEC instrument setups. Our in-house standard high temperature SEC instrument was optimized for handling very low sample concentrations.10 Low concentrations of high-molar mass samples result in inaccurate signal to noise ratios for the IR detector of the HT-SEC-IR, whereas, higher sample concentrations result in higher molar mass distributions as a result of column overloading.11
Table 2. High-throughput HT-SEC and HT-SEC-IR analysis of ethylene/α-olefin sample. Sample numbers correspond to those given in Table 1.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(C_6^a) feed [mL]</th>
<th>(C_8^a) feed [mL]</th>
<th>(M_n) (^a)</th>
<th>(M_w/M_n) (^a)</th>
<th>(M_n) (^b)</th>
<th>(M_w/M_n) (^b)</th>
<th>SCB/1000C(^c)</th>
<th>SCB/1000C(^d)</th>
<th>(T_m) (^e) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>-</td>
<td>0.5</td>
<td>93</td>
<td>4.7</td>
<td>130</td>
<td>2.4</td>
<td>1.2</td>
<td>0.24</td>
<td>135.2</td>
</tr>
<tr>
<td>Sample 5</td>
<td>0.5</td>
<td>-</td>
<td>130</td>
<td>5.4</td>
<td>110</td>
<td>4.3</td>
<td>4.2</td>
<td>2.00</td>
<td>132.8</td>
</tr>
<tr>
<td>Sample 9</td>
<td>-</td>
<td>5</td>
<td>220</td>
<td>2.7</td>
<td>150</td>
<td>3.4</td>
<td>5.9</td>
<td>n.d</td>
<td>116.0</td>
</tr>
</tbody>
</table>

Reaction conditions: 2.5 μmol rac-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂, 1 bar of \(C_2\) \(^f\) (0.9 mol/L), reaction temperature = 40 °C, solvent 100 mL toluene, 700 r.p.m.; \(^a\) Based on in-house HT-SEC; \(^b\) based on HT-SEC-IR; \(^c\) Measured by \(^13\)C NMR; \(^d\) Measured by DSC from the second heating; n.d means not determined.

For comparison, the measured data using both standard HT-SEC and HT-SEC-IR are shown in Table 2. The branching levels of the Samples 1 and 5 determined by \(^13\)C NMR analysis are not accurate due to low resolution of the spectra of the samples. The branching levels analyzed by \(^13\)C NMR and HT-SEC-IR are not well correlated.

5.2.2 Comparison of Crystallinity with DSC, High-throughput Raman Spectroscopy and IR Spectroscopy

Differential scanning calorimetry (DSC), high-throughput IR and Raman spectroscopy methods were used to investigate the degree of crystallinity of the copolymers. LLDPEs synthesized using heterogeneous catalysts exhibit a heterogeneity in the branching density along the molar mass distribution of the polymer. The branches are preferentially located in the lower molar mass chains, while the bulk LLDPE behaves as if it was a mixture of lower and higher molar mass copolymer and linear molecules. Theoretically, the comonomer incorporation using single-site catalysts occurs in a uniform way along the molar mass distribution of the polymer chains. Within our range of materials, the variations in the crystallinity and melting temperature are quite wide which, as mentioned above, is believed to be the result of reactor fouling and non-isothermal polymerization conditions. Vibrational spectroscopic methods in combination with DSC might enable to understand the morphology of the polymers in more detail.

In general and as expected, the crystallinity of the synthesized LLDPEs was decreasing with higher comonomer content incorporated into the polyethylene main chains and lamellae. There was also a strong dependence of the melting temperature of the copolymer on the content of the incorporated α-olefin comonomer. The melting temperature of the reference PE produced with a ratio Al:Zr = 250 was
137.9 °C. The melting temperature decreased from 132.8 to 116.0 °C when the 1-hexene incorporation was increased from 1.2 to 10.5 weight% (0.24 to 17.4 1-hexene incorporation per 1000C).

Raman and infrared spectra of crystalline and non-crystalline phases generally differ with respect to the position of the bands and their intensities. A careful analysis of these bands can be performed to calculate the relative crystallinity of a polymer sample in two distinct ways: (1) Comparison of Raman spectra of the PEs\textsuperscript{12} having different internal vibrational modes for crystalline and amorphous regions which show Raman shifts between 1000 and 1460 cm\textsuperscript{-1}. (2) Comparison of the ratio of the \textit{–CH\textsubscript{2}–} twisting vibration of the crystalline phase and the amorphous phase in Raman spectra, characteristically observed around 1295 cm\textsuperscript{-1} and 1303 cm\textsuperscript{-1}, respectively. Infrared spectroscopy is an absolute and direct technique,\textsuperscript{13} which is associated with the change in the dipole moment during vibration of the molecule. The crystalline and amorphous phases of the LLDPE show vibration bands at \textasciitilde1896 cm\textsuperscript{-1} and \textasciitilde1304 cm\textsuperscript{-1}, respectively.

Figure 1 shows the crystallinity index as determined by high-throughput IR and Raman spectroscopic analysis (left plot) and the crystallinity as determined by DSC analysis (right plot) as a function of the 1-hexene content in the feed during the copolymerization. IR and Raman spectroscopy analysis of the crystallinity index of Sample 1 (0.5% 1-hexene in the feed) and Sample 3 (2% 1-hexene in the feed) yielded almost identical results (see Figure 1 left side). For Sample 2 (1% 1-hexene in the feed), the crystallinity index obtained with IR spectroscopy was unexpectedly two fold higher than the value obtained from Raman analysis. For the ethylene/1-hexene copolymerizations, as a general trend, a decrease in crystallinity with increasing 1-hexene concentration in the copolymerization feed was observed with all three analytical methods, as expected.

\textbf{Figure 1}. Crystallinity index for ethylene/1-hexene copolymers obtained by high-throughput Raman (squares) and IR (circles) spectroscopy (left) as well as crystallinity obtained from DSC (triangles) analysis (right) (Al: Zr = 250) and DSC (Al: Zr = 500).
On the other hand, the measurements with IR and Raman spectroscopy for ethylene/1-octene copolymerizations were scattered (see Figure 2 left plot). Nevertheless, the measurements with DSC (Figure 2 right plot) did display the typical decreasing trend with increasing amount of 1-octene in the feed. Therefore, for determining the degree of crystallinity the results obtained from DSC seemed to be more reliable than the results obtained using IR and Raman spectroscopy.

**Figure 2.** Crystallinity index for ethylene/1-octene copolymers obtained by high-throughput Raman (squares) and IR (circles) spectroscopy (left) as well as crystallinity obtained from DSC (triangles) analysis (right) (Al: Zr = 250) and (Al: Zr = 500).

### 5.2.3 Nano-indentation

The elasticity modulus (E) of a sample is representing the resistance of the material to a deformation, which can also be defined as the stiffness of the material. With the high-throughput nano-indentation technique used in this study, the local E of each sample is determined by a depth-sensing indentation measurement.\textsuperscript{14-16} Indentation experiments are performed by pushing the tip of the indenter into the sample at a defined force, and then retracting the tip afterwards. This results in an indentation (force-displacement) curve. The sample is deformed elastically and plastically during loading and only elastically during unloading. Therefore, the elastic modulus is obtained from the unloading response.\textsuperscript{15} This method has been widely used in the HTE-analysis of poly(oxazoline)s\textsuperscript{17a,b} and in the field of coating technology\textsuperscript{17c} but has not yet been extensively applied for the analysis of LLDPEs.\textsuperscript{18} There are several limitations of this technique: (1) The broad temperature change during processing with compression molding of the polymer prior to nano-indentation might cause a local melting. This influences the elasticity modulus of the samples.\textsuperscript{19} (2) The viscoelastic behavior of a sample can also influence the indentation depth. Even if the pressure applied has been reduced, due to the viscoelastic property of the sample the displacement can continue.\textsuperscript{18} In this situation, it is difficult to obtain an accurate
unloading slope which also changes the elasticity modulus of the sample. This effect has been shown to occur for isotactic polypropylenes.\textsuperscript{20}

Nano-indentation applied to polyolefins is a relatively new technique. As a consequence a standardized method for the nano-indentation of polyolefins had to be developed. A polyolefin sample usually has a crystalline phase as well as an amorphous phase depending on the polymerization as well as crystallization conditions and depending on the amount of the comonomer present in its molecular structure. In each sample, there is a transition between plastic/viscoelastic and elastic phases. Therefore, by nano-indentation an average mechanical property is determined.

Nano-indentation tests were conducted on ten different linear-low density polyethylene samples with different comonomer contents ranging from 0.04 to 0.468 mol/L of 1-hexene and 0.03 to 0.303 mol/L of 1-octene in the polymerization feed. We assumed in our analysis that the sample behavior during unloading was predominantly elastic, and that therefore the determined $E_i$ corresponded to the elastic deformation of the sample.

The elastic modulus ($E_i$) depends on the amount of amorphous phase and the arrangement of the polymer chain. For both Al:Zr ratios (250 and 500) the elastic modulus decreases almost linearly with increasing 1-hexene content in the feed (Figure 3, left plot). The same trend was observed also for 1-octene, but not in a linear fashion (Figure 3, right plot). A decreasing stiffness with increasing amount of $\alpha$-olefin in the copolymerization feed was expected because higher 1-hexene (or 1-octene) contents in the feed, and accordingly very likely also in the copolymer obtained, correspond to a higher number of butyl (respectively hexyl) side-chains, resulting in a lower degree of crystallinity and, accordingly, in a lower stiffness of the polymer, which is reflected in a lower $E_i$. The lower crystallinity for increasing amounts of $\alpha$-olefin was shown earlier and, therefore, the lower stiffness with increasing comonomer content is in full agreement with the obtained high-throughput IR/Raman and the DSC data.

![Figure 3. Elasticity modulus $E'$ (GPa) of PEs obtained for copolyolefins synthesized with Al:Zr = 250 (squares) and 500 (diamonds) as a function of 1-hexene and 1-octene comonomer present in the feed during copolymerization.](image-url)
All the LLDPE samples examined in this section were viscoelastic, however, the mechanical properties differed depending on the comonomer and cocatalyst amount. Thus, as the interchain distance and the flexibility of the polymer chains increased by the incorporation of more short-chain branches, the material softened, which led to a decrease in the elastic modulus. In the future, the effect of the side chain length on the elasticity modulus should be studied using other comonomers (e.g. propylene, decene, dodecene and octadecene).

5.2.4 Indentation and Crystallinity Tests on PEs obtained with Homogeneous and Heterogeneous Polymerizations with a High-throughput Set-up

In this section, the polymers were synthesized in a recently installed high-throughput setup, which enabled polymerizations in high purity solvents with much better temperature control than possible in the Büchi reactors employed in the previous section. Copolymerizations of ethylene/1-hexene were carried out using the metallocene catalyst Cp$_{Bu}^+$ZrCl$_2$ to obtain short chain branched polyethylenes with butyl branches. Two different strategies were tested: (i) The catalyst was present in the homogeneous phase, and (ii) the catalyst was supported on SiO$_2$ using the supportation methodology discussed in Chapter 4. During the homogenous polymerization, the active sites are expected to be distributed homogenously across the catalyst, whereas in heterogeneous polymerization, the inhomogenous nature of the support is expected to be manifested in the catalyst product, as well as in the polymer product obtained. This section mainly provides the mechanical analysis of the polymers that were synthesized in homogenous and heterogenous polymerization.

The elasticity modulus ($E_t$) and crystallinity degrees of the PEs synthesized with the high-throughput reactor setup yielded results with similar trends to those obtained with the Büchi reactor system (Figure 4). $E_t$ and crystallinity degree measured with DSC resulted in a more linear decrease with increasing comonomer content. However, as with the PEs synthesized in the Büchi reactor system, the crystallinity degrees measured with IR and Raman spectroscopy were again scattered, suggesting that these techniques are not well suited for LLDPE samples. Immobilization of Cp$_{Bu}^+$ZrCl$_2$ onto silica revealed a clear increase of the $E_t$ but only slightly effected the crystallinity degrees obtained by DSC. The significant increase in the $E_t$ values obtained with silica-supported Cp$_{Bu}^+$ZrCl$_2$ could be due to the inhomogeneity of the supported-catalyst. The inhomogenous silica-supported material remained embedded in the polymer product which might be the cause of the increase in the $E_t$ values. Homo- and copolymerization with silica-immobilized Cp$_{Bu}^+$ZrCl$_2$ in Isopar E and toluene showed similar $E_t$ as well as crystallinity degrees, suggesting that the type of solvent had only a minor effect on crystallinity degree and $E'$. 
Figure 4. Elasticity modulus $E_i$ (gray circles) and crystallinity degree (black diamonds) of PEs obtained as a function of 1-hexene comonomer present in the feed during copolymerization.

Figure 5. Crystallinity indexes of PEs obtained with IR (gray squares) and Raman (black triangles) spectroscopy as a function of 1-hexene in the feed during copolymerization.
5.3 Conclusions

In this chapter, insights into the thermal and mechanical properties of a library of LLDPEs with different amounts of butyl and hexyl side chains, as well as the effect of different polymerization techniques on the thermal and mechanical properties were presented. A classical Büchi reactor set-up and a recently installed high-throughput setup were used for the preparation of LLDPEs. DSC, high-throughput depth-sensing nano-indentation (DSI), high temperature SEC-IR and SEC, as well as high-throughput IR and Raman spectroscopy were used for the molecular, mechanical and thermal analysis of the (co)polymers. High-throughput depth-sensing nano-indentation (DSI) has been shown to be a useful, rapid mechanical technique that can be performed in an automated manner requiring only small amounts of polymer. The polymers characterized here exhibit a continuous decrease in elasticity modulus with decreasing crystallinity. The samples show a more or less linear decrease in elasticity modulus (E) with increasing \( \alpha \)-olefin comonomer incorporation, regardless of the type of comonomer used. A decrease with increased incorporated amount of \( \alpha \)-olefin in the copolymers was also found for the \( T_m \) values of the samples. In conclusion, the side chains as well as the homogenous and heterogeneous nature of catalyst which were observed in the final polymer product had a significant effect on the thermal and mechanical properties of the product. It should be stated here that the elucidated structure-property relationships with varying the \( \alpha \)-olefin content in the copolymers are as expected, but we want to emphasize that this was the first time that such a relationship was established for polyolefins using predominantly high-throughput experimentation techniques. This represents a promising finding for the future evaluation of this class of polymers using HTE techniques.

5.4 Experimental Section

General considerations

All reactions and modifications of moisture- and air-sensitive compounds were conducted in a M-Braun glovebox under nitrogen atmosphere. Solvents were purchased from Biosolve and were purified by passing them through an alumina-activated column. MAO (1.5 M in toluene) was purchased from Chemtura. Ethylene (5.0) was purchased from Linde Gas. Zirconocene 2 was purchased from Strem Chemicals. 1-Hexene was purified by distillation and dried over 3 Å molecular sieves. The supports used in this work were prepared by Fabian Karbach (For details see section 4.4). \( \text{rac-Me}_2\text{Si(2-Me-4-Ph-Ind)}_2\text{ZrCl}_2 \) was kindly donated by B. Wang and N. Friederichs from Saudi Basic Industries Corporation (Sabic Europa). \( \text{Cp}^{\text{Bu}_2}\text{ZrCl}_2 \) was purchased from Strem Chemicals.
Ethylene homo and Ethylene/α-Olefin copolymerizations in a 250 mL Büchi reactor ("classical" equipment)

A glass insert (heated at 120 °C for 2 hrs) was placed in the reactor and the reactor was evacuated and backfilled with dry argon (3 x). Toluene (100 mL) and MAO (500 equivalents) were fed into the reactor by a syringe under argon after which the reactor temperature was stabilized at 40 °C under 1 bar of ethylene. The reactor was fed with 1 bar of ethylene. Catalyst solutions were injected under the flow of ethylene. The polymerization was stopped after 20 minutes by venting the reactor and injection of ethanol (5 mL). The polymers were precipitated into acidified ethanol, filtered and vacuum dried at 70 °C overnight.

Ethylene/α-Olefin copolymerizations in the HTE reactor setups

The reactor was dried by heating it in vacuum at 130 °C (p≤6 mbar) for 3 minutes followed by purging N₂ (5 bar) and leaving it under pressure for 12 minutes. The drying procedure was repeated three times before the reactor was brought to the desired temperature (40 °C) and filled with Isopar E (50 mL). Subsequently a solution of TIBA (1 mmol) and 1-hexene (in case of co-polymerizations) in Isopar E (total volume 10 mL) was injected into the reactor and stirring was started (700 rpm). After the temperature inside the reactor was stable, it was pressurized with ethylene at a pressure corresponding to a partial pressure of 10 bar. The ethylene uptake was monitored and after the solution was saturated with ethylene a suspension of (C₆H₅)₂ZrCl₂/SiO₂ (100 mg) in Isopar E (15 mL) was injected via the automated injection procedure. During injection, the catalyst vial was shaken gently to maintain a homogeneous suspension of the heterogeneous catalyst. After 30 minutes the polymerization was stopped by closing the ethylene feed and venting the reactor. The reaction mixture was pored onto acidified ethanol (20 mL), the produced polymer was isolated by filtration and dried under vacuum at 70 °C. Homogeneous poly- and oligomerizations as well as reactions employing toluene as a solvent were performed following the same procedure.

Differential Scanning Calorimetry (DSC) using classical equipment

Differential scanning calorimetry (DSC) analysis of the PE homopolymers and the LLDPE copolymers was performed with a non-high-throughput Q100 differential scanning calorimeter (TA instruments). The samples (4.00 to 6.00 mg) were heated in aluminum pans to 160 °C at a rate of 10 °C/min to eliminate the thermal history of the sample and crystallization was achieved by cooling the samples to 20 °C at the same rate. A second heating cycle was used for data analysis. Heating rates of 10 °C/min were chosen because this rate is the most commonly employed heating rate for the DSC analysis of polyethylenes. The DSC plots displayed a linear baseline, which enabled an accurate determination of the heat of melting from which the degree of crystallinity could be deduced. The crystallinity was then estimated as follows:
Crystallinity (%) = \[ \frac{\Delta H_{\text{sample}}}{\Delta H_{\text{PE (100\%)}}} \times 100 \] where \( \Delta H_{\text{PE (100\%)}} \) is the melting enthalpy value of 100% crystalline polyethylene (=293 J/g) and \( \Delta H_{\text{sample}} \) is the melting enthalpy of the sample under examination.

**Size Exclusion Chromatography (SEC) using a high-throughput instrument**

Size exclusion chromatography (SEC) measurements were carried out with a PL-XT 20-HT-SEC instrument. The column set consists of 3 × PLGel Olexis columns. The column set was calibrated using universal calibration with narrow polyethylene standards with molar masses in the range of 5310 and 1510 000 g/mol. Mark Houwink constants of polyethylene were used. (K = 14 dl/g and \( \alpha = 0.725 \)). 1,2,4-Trichlorobenzene flows through the column with 1 mL/min. 2,6-Di-tert-butyl-4-methylphenol (BHT) and Irganox 1010 were added to the mixture in order to stabilize the polymer against oxidative degradation. All samples were prepared by dissolving 4.5 to 6.0 mg of polymer in 4.5 mL of stabilized TCB (at 160 °C) subsequently allowing the samples to dissolve for 3 hours prior to injecting the solution into the SEC instrument. SEC-IR was processed with PolymerChar SEC-IR software in DSM, Heerlen. Preliminary calibration was based on PL standards and fractions of bimodal HDPE A6060. The molar mass calculation was done with PolymerChar software.

**Raman Spectroscopy (high-throughput technique)**

The Raman spectroscopy experiments were performed using a Raman Station from Avalon Instrument equipped with a 300 mW laser (wavelength: 785 nm) and a high-throughput experimentation stage.

**IR Spectroscopy**

The applied IR spectrometer was a Nicolet Avatar 370DTGS from Thermo Electron. The crystallinity index of the LLDPEs is calculated based on the extinction value of crystalline (\( e_{\text{crystalline}} \)) and amorphous (\( e_{\text{amorphous}} \)) bands that differ in their intensities. The extinction value \( e \) is taken from the spectrum. \( e = e \cdot c \cdot d \) where \( e \) is a material constant, \( c \) is the concentration and \( d \) is associated with the sample thickness. The extinction value of the crystalline part was calculated by K-X%, while the crystallinity degree of the amorphous part is A(1-X%). The crystallinity index was calculated as the Peak Area(crystalline) / Peak Area(amorphous).

**\(^{13}\text{C}-\text{NMR Analysis}**

The samples were dissolved in \( C_2D_2Cl_4 \) at 140 °C, stabilizer was added to prevent oxidation. All samples were measured on a Bruker Avance 400 MHz spectrometer. Over 2000 scans were accumulated with 20 seconds relaxation delay.
Compression Molding
20 mg of copolymer was deposited in the holes of an aluminum slide. The aluminum slide was sandwiched between a glass slide and another aluminum slide, the total thickness being 1.5 mm. The samples were molded in a preheated compression mold at 160 °C. Afterwards, the glass slide was removed and the aluminum slides with shaped samples were used for nano-indentation and Raman spectroscopy analyses.

Nano-indentation
Indentation tests were conducted using a TribolIndenter from Hysitron with a conospherical diamond indenter tip with a radius of approximately 4.7 μm. The measurements have been performed in an automated run overnight. Before every indent, the indenter was held in contact with the surface for piezoeactuator stabilization. A drift correction and a contact load were applied to prevent the deformation prior to the nano-indentation. The tip approached the surface until a threshold value for the force of 0.8 μN was reached. Subsequently, the tip was retracted and the position of the last contact was kept in the memory. This was used for the determination of the "zero-point", which determined the point where the tip touched the surface. Then, a second approach was done and the tip was held in contact with the surface for drift correction (preloading during drift correction was 0.1 μN for a time of 20 seconds). Compared to these values, the resulting deformation of the surface should be negligible. The forces for the measurements were 50 to 1000 μN. After lifting the tip and reapproaching the surface, the tip was loaded to maximum load in 10 s and unloaded in 2 s. The load displacement responses from depth-sensing nano-indentation DSI were analyzed using the Oliver and Pharr method.\textsuperscript{14-16} The $E_i$ modulus was calculated from the reduced moduli ($E_r$), where reduced moduli ($E_r$) was derived from the unloading segment ($v_{\text{sample}}$ and $v_{\text{indenter}}$ is the Poisson ratio of the sample and the indenter) with the following formula:

$$E_i = \frac{1 - v_{\text{sample}}^2}{1 - v_{\text{indenter}}^2} \cdot \frac{E_r}{E_{\text{indenter}}}$$

Acknowledgments: I would like to thank Dr. Lars-Christian Heinz at DSM Resolve for the HT-SEC-IR measurements and Erik F.−J. Rettler for the Raman, IR and Nano-indentation measurements.
5.5 References

6 Epilogue and Technology Assessment

Thermoplastic polyolefins form a class of polymers that covers a wide application range and show an exponential growth in the world plastic consumption since their original introduction during the mid 1950s. The requirements regarding good processability demand structural modifications to the polymerization catalysts. The latest generations of metallocene catalysts offer the possibility to obtain polypropylenes with different tacticities, thereby rendering isotactic, syndiotactic, atactic and hemi-isotactic-stereoblock polypropylene by simply changing the ligand structure of the complexes. Their discovery raised many mechanistic questions about the nature of the active sites and the enantio-selectivity of the monomer insertion. The stereochemistry and steric environment of the catalyst is of crucial importance as it has a direct impact on the microstructure of the polyolefin and, as a result, directly determines the crystallization behavior, flow and physical/mechanical properties. The cationic active sites are stabilized by an anionic methylaluminoxane or by another type of weakly bonding counterion like perfluorophenylborates. The strength and the steric hindrance of the ion-pairs can affect the catalytic activity, chain-transfer processes and the tacticity of the polymer. The key point is that the counter-ion coordinates poorly and allows the monomer to access the active site.

In this thesis mainly three approaches were used to synthesize linear low-density polyethylene (LLDPE). LLDPE is commercially produced by either a gas phase or a slurry phase process using heterogeneous catalysts or by a solution process at a temperature above the melting point of the product, where a homogeneous catalyst can be used. In all cases two different monomers, viz. ethylene and an \( \alpha \)-olefin, are fed to the system. On the laboratory scale, tandem catalysis represents an interesting alternative route to synthesize LLDPE. This concept has several advantages over the more traditional two-monomer/one catalyst approach in that it does not require a second monomer feed, since one catalyst produces the \( \alpha \)-olefin *in situ* from ethylene, after which the second catalyst copolymerizes it with ethylene. On the other hand, it is very challenging, as it requires two compatible catalysts with optimum activities under similar reaction conditions. In the course of Chapter 4, we developed the partially immobilized oligomerization/polymerization tandem catalysts that allowed us to control the microstructure of polyethylene by the distributing the comonomer along the polyethylene backbone. Our system demonstrated the concept of the concurrent tandem catalysis, however, this technique has
some difficulties that needs to be resolved. The interference between the two catalysts in one reactor proved difficult to prevent and matching their kinetic compatibility and optimum process conditions implied a real challenge. Taking into account the change in the kinetics of all reactions (i.e. the insertion process and the chain transfer processes) after the immobilization, the kinetic compatibility and the catalytic activities are even more difficult to predict and control. To the best of my knowledge, there is no tandem catalytic oligomerization/polymerization system commercially operating to date.

In Chapter 2 we attempted an alternative approach to tandem catalysis, where one catalyst could switch its selectivity from ethylene oligomerization to ethylene polymerization. In this way we aimed to produce LLDPE with one catalyst using ethylene as the only feedstock. The highlight of Chapter 2 is the development of a novel Cr-based catalyst system stabilized by a monoanionic NPN ligand system. This system indeed switches its selectivity from Schultz-Flory to selective trimerization or PE formation, depending on the cocatalyst used. Unfortunately, this particular catalyst does not incorporate α-olefins. Although our idea of synthesizing LLDPE by switching the selectivity of the catalyst by changing between different cocatalysts has failed, this chapter formed an important contribution to the field of ethylene oligomerization. The catalytic activity upon activation with MAO for non-selective ethylene oligomerization is impressive and since catalyst synthesis is simple and cheap, it could be a commercially interesting catalyst system. Although the selectivity in ethylene trimerization of the TiBA-activated system is very high, its catalytic activity is disappointing and not of any commercial value.

In the course of Chapter 3, we discussed the impact of different ion-pairs on the polymerization and oligomerization activity of MAO- or borate-activated ($\eta^5$-C$_5$H$_4$CMe$_2$C$_6$H$_5$)Ti(CH$_2$Ph)$_3$. The highlight of this chapter is the accurate control of the performance of the catalyst by different ion-pairs that result in different products ranging from α-olefins to ultra high molar mass polyethylene (UHMWPE) with some short-chain branching. However, the mechanistic reason behind the formation of different products, including 1-hexene incorporation into the polymer, demands further clarification. Computational studies (DFT calculations) and further NMR studies might elucidate the stereoregularity of the catalyst and the strength of the cation-anion interactions. Macchioni and coworkers will perform these studies.

Illustrative examples of the benefit of high-throughput experimentation (HTE) in kinetic investigations and catalyst design are the studies by Arriola on the so-called Dow shuttle chemistry, and for example by Gibson on the screening of ethylene oligomerization catalysts. In our study, HTE enabled us to evaluate and model the reaction kinetics of different catalysts with high accuracy and at a high speed. The HTE sample characterization approach for polyolefins, as it was demonstrated in Chapter 5, provided the desired characterization data in a rapid way. HTE experimentation significantly enhances the chance to discover kinetically compatible tandem partners. The development of new polyolefin architectures with different nanostructures can be achieved by new catalyst designs and tandem catalysis or chain shuttling chemistry, in which the high-throughput experimentation approach is expected to play a crucial role in the near future.
The fundamental studies described in this thesis could be significant with respect to both new academic developments and industrial applications. The reported Cr complexes of NPN monoanionic ligands in Chapter 2 not only produced Schultz-Flory distribution of oligomers and selective 1-hexene depending on the activator implemented, but also gave insights into the factors that are responsible for selectivity and activity. Further variations on the ligand scaffold selectivity yielded 1-hexene without any polymer as side product. All of which means that this Cr-based catalyst system has a potential for application. The results presented in Chapter 3, shows the significant influence of different cocatalysts on the C_6^+/PE balance obtained by Hessen’s trimerization catalyst.\(^\text{3-5}\) Albeit the tandem catalysis system shown in Chapter 4 is far from ideal, there is a probability to tailor the polymer properties with this technique. Nevertheless, the application of supported multicomponent catalysts prevents the interaction between two active sites that could have resulted in catalyst deactivation. High-throughput experimentation that was used during this thesis study aimed to speed up the design of new polyolefins by providing accurate kinetic data for mechanistical studies. High-throughput experimentation and characterization techniques can be applied for the tunability of chemical and physical characteristics of new polyolefins for current and future requirements. However, a suitable and perfectly operating HTE olefin polymerization platform is not easy to achieve. Realizing that the slowest process is determining the throughput, installing the reactors with individual experiment control, liquid-handling robots inside the box like Freeslate\(^6\) does, is probably the best solution to gain reliable results. Currently, the rate-determining step, if one wants to relate experimental polymerization conditions to polymer microstructure, is definitely the NMR characterization.

References

6. www.freeslate.com
Summary

Thermoplastic polyolefins form a class of polymers that covers a wide range of application. They show an exponential growth in the world plastic consumption. The requirements regarding good processability demand structural modifications in the catalysis field. The concept of the linear-low density polyethylene (LLDPE) synthesis, which is a random copolymer of ethylene and α-olefins, dates to 1980s. They are produced commercially with heterogeneous Ziegler-Natta catalysts or with homogeneous (post-)metallocene catalysts in gas/slurry phase or solution phase processes, respectively. There are different ways of synthesizing linear-low-density polyethylenes. Traditionally, a mixed feed of ethylene and the α-olefin (1-butene, 1-hexene or 1-octene) is used. Tandem catalysis, consisting of an ethylene trimerization and an ethylene/1-hexene copolymerization catalyst, is an interesting way to synthesize LLDPE that has the advantage over the traditional approach in that it does not require a separate second monomer feed. Chemical and kinetic compatibility of the ethylene trimerization and copolymerization catalysts and their responses to different reaction conditions is the biggest challenge and therefore the major disadvantage of the tandem catalysis process. The majority of reported tandem catalysis for ethylene oligomerization/polymerization is based on homogeneous catalyst components. These unsupported systems are ideally suited to demonstrate the concept of tandem catalysis. However, due to the limited thermal stability of the applied ethylene oligomerization catalysts, generally these systems cannot be run above the melting temperature of the product. Performing the polymerizations at lower temperatures in homogeneous phase will result in severe reactor fouling, which prevents commercial application. Data on tandem catalysis using an ethylene oligomerization catalysts thermally stable enough to be used in a solution process, or using a supported copolymerization catalysts to avoid reactor fouling, hardly exist. The aim of the work presented in this thesis was to study the challenges of tandem catalysis as well as to search for novel alternatives to the classical tandem catalysis. Where possible we used high throughput experimentation. Not so much to obtain large quantities of data but merely to investigate the usefulness of HTE in both polymer synthesis and characterization.

In the second chapter, we described a novel Cr-based ethylene oligomerization catalyst based on the monoanionic [(tBu)NPNR]⁻ (R = tBu, 2,6-dimethyl-phenyl) and their closely related dianionic cis-[μ-N](t-Bu)₂[PNNR]²⁻ (R = α-C₆H₅OMe, CH₂CH₂NMe₂) ancillary ligands, which are capable of switching their catalytic selectivity from oligomerization to polymerization by changing the alane activator. The idea was that switching the selectivity of a single catalyst could be an elegant alternative to the necessity of two independent catalysts in tandem catalysis. Depending on the ligand’s substituents as well as the cocatalyst applied, this catalyst system afforded different products: 1-hexene, a Schultz-Flory distribution or polyethylene. TOFs up to 20 000 h⁻¹ were achieved. The PEs obtained as side product during the oligomerization reactions did not contain any branches, indicating a low tendency of the
catalyst to incorporate α-olefins. When the polymerization catalyst, obtained upon activation with TIBAO, was treated with a mixture or ethylene and 1-hexene, also no branching was observed. Hence, although the catalyst system can switch its selectivity between ethylene oligomerization and polymerization it does not react with α-olefins and therefore is unsuitable to form LLDPE. To improve our understanding of this versatile ligand system, we have also examined a few variations of the ligand scaffold in relation to the catalytic behavior of these complexes. High ethylene oligomerization activity and lack of PE formation of the complexes with the ligand system containing pendant 2-anisyl substituent are potentially interesting from the application standpoint.

In the third chapter, we focused on the arene-substituted cyclopentadienyl titanium ethylene trimerization catalysts developed by Hessen and coworkers. These catalysts stand for the most active non-chromium-based ethylene trimerization systems. Different experimental techniques and activation protocols have been applied in a high-throughput experimentation setup to optimize the catalytic selectivity towards the formation of 1-hexene. The HTE approach has been proven to be a promising route to rapidly generate kinetic data for mechanistic studies and is certainly beneficial to understand the mechanisms involved. The interesting outcome of Chapter 3 is that polyethylene obtained as co-product using 1 equivalent of [Ph3C]+[B(AlF3)4] as an activator contains low amounts of short-chain branches. Some of the 1-C6 formed has subsequently been incorporated into the polymer which was proved by 13C NMR and SEC-IR measurements.

The research described in Chapter 4 focuses on the difference in catalytic behavior of homogeneous, partly- and fully supported tandem catalysts. In this study we compared the differences in product properties and catalytic behavior for systems where (i) both the trimerization [C3H3CMe2Ph]TiCl3 and copolymerization (Cp2B2ZrCl2) catalysts are in the homogeneous phase, (ii) the trimerization catalyst is in the homogeneous phase while the copolymerization catalyst is supported on SiO2. It was demonstrated that the α-olefin producing component in a tandem system to synthesize LLDPE should have high selectivity. Using immobilized tandem catalysts prevents reactor fouling and the problems resulting from uneven monomer diffusion to the catalyst particle, assuming that both catalysts are homogeneously dispersed inside the catalyst particle.

In the fifth chapter, we focused on the synthesis of conventional LLDPEs with different comonomers. Two different varieties of setups have been used for the synthetic part. The ethylene/1-hexene, ethylene/1-octene polymerizations were carried out in 250 ml Büchi reactors and recently installed high-throughput setup. These series of ethylene/1-hexene, ethylene/1-octene copolymers have been subjected to a thorough high-throughput characterization program, carried out in collaboration with the Friedrich-Schiller University Jena, Germany. Nano-indentation (DSI) has been shown to be a mechanical technique that can be performed in automated measurement run which requires only small amount of polymer and short measuring time. When optimized, this technique could be a useful alternative to NMR for rapidly determining the branching density of LLDPEs.
Summarizing, the major part of this work revolves around the ethylene oligomerization which leads to selective, non-selective and polyethylene formation and LLDPE synthesis with tandem catalysis starting from a single precatalyst and as well as traditional tandem catalysis under homogenous and heterogeneous conditions.
Samenvatting

Thermoplastische polyolefinen vormen een klasse polymeren met een breed toepassingsgebied. Binnen de wereldwijde consumptie van deze plastics vertonen deze polymeren een exponentiële groei. De vereisten voor een goede verwerkbaarheid vragen om structurele veranderingen op het gebied van de katalyse. Het concept van de synthese van lineair lage-dichtheidspolyetheen (LLDPE), een random copolymer van etheen en α-olefine, gaat terug tot de jaren tachtig van de vorige eeuw. Op commerciële schaal worden LLDPE’s geproduceerd met behulp van heterogene Ziegler-Natta katalysatoren in een gas/slurry fase proces of met behulp van homogene (post-) metalloecen katalysatoren in oplossing.

Er bestaan verschillende methoden om lineair lage-dichtheidspolyetheen te synthetiseren. Van oudsher wordt een gemengde voeding van etheen en het α-olefine (1-buteen, 1-hexeen of 1-octeen) gebruikt. De zogenaamde ‘tandem katalyse’, waarbij zowel een etheen trimerisatiekatalysator als een etheen/1-hexeen copolymerisatiekatalysator worden gebruikt, is een interessante manier om LLDPE te produceren met als voordeel, in vergelijking tot de klassieke methode, dat geen afzonderlijke voedingsstroom voor het tweede monomeer vereist is. De grootste uitdaging en daarmee ook het grootste nadeel voor het tandem katalyse proces wordt gevormd door de chemische en kinetische compatibiliteit van de etheen trimerisatie- en copolymerisatiekatalysatoren alsmede hun gevoeligheden ten opzichte van de verschillende reactiecondities. Het merendeel van de gepubliceerde tandem katalyse systemen voor etheen oligomerisatie/polymerisatie is gebaseerd op homogene katalyse componenten. Deze ongedragen systemen zijn uitstekend geschikt om het concept van tandem katalyse te demonstreren. Door de beperkte thermische stabiliteit van de gebruikte etheen oligomerisatie katalysatoren kunnen deze systemen echter niet toegepast worden boven de smelttemperatuur van het product. Als gepolymeriseerd wordt bij lagere temperaturen en in homogene fase, leidt dit tot voortijdig neerslaan van het product in de reactor (reactor fouling), hetgeen commerciële toepassing in de weg staat. Er is nauwelijks informatie te vinden over tandem katalyse met behulp van een etheen oligomerisatiekatalysator die thermisch stabiel genoeg is om te worden gebruikt in oplossing of over een gedragen copolymersatiekatalysator welke reactor fouling zou kunnen voorkomen. Het doel van het in dit proefschrift beschreven werk was enerzijds om de uitdagingen van tandem katalyse te bestuderen en anderzijds om te zoeken naar nieuwe alternatieven voor de klassieke tandem katalyse. Waar mogelijk is gebruik gemaakt van high throughput experimentation (HTE). Dit laatste niet zozeer om grote hoeveelheden data te verzamelen als wel om de bruikbaarheid van HTE in zowel polymeren synthese als karakterisatie te onderzoeken.

In het tweede hoofdstuk wordt een nieuwe Cr-gesegregeerde etheen oligomerisatiekatalysator beschreven, gebaseerd op monooanionische liganden [[tBu]NPNR]⁻ (R = tBu, 2,6-dimethyl-phenyl) en de nauw verwante dianionische liganden cis-[(μ-N)\{t-Bu\}]_2[PNR]_2²⁻ (R = α-C_6H_4OMe, CH_3CH_2NMe_2), welke in
staat zijn de katalytische selectiviteit te veranderen van oligomerisatie naar polymerisatie door verandering van de alaun co-katalysator. De achterliggende gedachte was dat het veranderen van de selectiviteit van één enkele katalysator een elegant alternatief kan vormen voor de vereiste voor twee onafhankelijke katalysatoren in tandem katalyse. Afhankelijk van het substitutiepatroon op het ligand en van de gebruikte co-katalysator, kan dit systeem verschillende producten opleveren: 1-hexeen, een Schultz-Flory verdeling of polyetheen. TOF’s tot 20 000 h⁻¹ bleken haalbaar. Het polyetheen dat als bijproduct gevormd werd tijdens de oligomerisatiereacties bevatte geen vertakkingen, hetgeen aangeeft dat de katalysator weinig α-olefinen inbouwt. Evenmin werden vertakkingen gezien als de katalysator verkregen door activering met TiBAO, werd blootgesteld aan een mengsel van eteen en 1-hexeen.

Hieruit blijkt dat, ofschoon dit katalysatorsysteem zijn selectiviteit kan wisselen tussen eteen oligomerisatie en polymerisatie, het niet reageert met α-olefinen en aldus niet geschikt is om LLDPE te maken. Om ons begrip van dit veelzijdige ligandsysteem te vergroten zijn ook een paar variaties van het ligand onderzocht in samenhang met het katalytische gedrag van deze complexen. Hierbij zijn de hoge eteen oligomerisatieactiviteit en de afwezigheid van polyetheen vorming door complexen met een 2-anisyl-gesubsitueerd ligandsysteem mogelijk interessant vanuit een toepassingsstandpunt.

In het derde hoofdstuk hebben we ons gericht op de aren-gebaseerde cyclopentadienyl titanium eteen trimerisatie katalysatoren die zijn ontwikkeld in de groep van Hessen. Deze katalysatoren representeren de meest actieve, niet op chroom gebaseerde trimerisatiekatalysatoren. Verscheidene experimentele technieken en activeringsprotocollen zijn toegepast in een zogenaamde high-throughput experimentation (HTE) opstelling en als doel de katalytische selectiviteit te optimaliseren voor de vorming van 1-hexeen. De HTE-aanpak bleek een veelbelovende methode om snel kinetische informatie voor mechanismistisch onderzoek te verschaffen en is zeker nuttig om de realistische mechanismen welke een rol spelen, te begrijpen. De interessante uitkomst van hoofdstuk 3 is dat het polyetheen dat als bijproduct verkregen wordt bij gebruik van 1 equivalent [Ph₂C]'[B(C₆F₅)₃]⁻ als activator, kleine hoeveelheden korte vertakkingen bevat. Het is aannemelijk dat een deel van het gevormde 1-hexeen vervolgens is ingebouwd in het polymeer.

Hoofdstuk 4 gaat in op het verschil in katalytisch gedrag tussen homogene, deels gedragen en volledig gedragen tandem katalysatoren. In dit deel worden de producteigenschappen en het katalytische gedrag van deze systemen onderzocht waarbij (i) zowel de trimerisatiekatalysator [C₃H₈CMe₂Ph]TiCl₃ en de copolymerisatiekatalysator (CpBu₂ZrCl₂) zich in de homogene fase bevinden, (ii) de trimerisatiekatalysator zich in de homogene fase bevindt en de copolymerisatiekatalysator is geïmmobiliseerd op SiO₂. Hierbij is aangetoond dat om LLDPE te synthetiseren in een tandem systeem, de α-olefine-producerende component een hoge selectiviteit moet hebben. Het gebruik van geïmmobiliseerde tandem katalysatoren voorkomt reactor fouling.

In het vijfde hoofdstuk hebben we ons gericht op de synthese van conventioneel LLDPE met verschillende comonomeren. Voor het synthetische gedeelte zijn twee verschillende soorten
opstellingen gebruikt. Eteneen/1-hexeen en eteneen/1-octeen polymerisaties zijn uitgevoerd in 200 ml Büchi reactoren. Deze eteneen/1-hexeen en eteneen/1-octeen copolymeren zijn nauwkeurig onderzocht middels een high-throughput karakterisatieprogramma, uitgevoerd in samenwerking met de Friedrich-Schiller Universiteit te Jena in Duitsland. Nano-indentation (DSI) bleek een mechanische techniek welke geautomateerd kan worden en slechts kleine hoeveelheden polymeer en korte meettijden vereist. Optimalisatie van deze techniek zou kunnen leiden tot een bruikbaar alternatief om snel de vertakkingsgraad van LLDPE’s te bepalen.

Samengevat beschrijft het merendeel van dit proefschrift de oligomerisatie van eteneen, resulterend in selectieve en niet-selectieve oligomerisatie en de vorming van polyetene evenals de synthese van LLDPE via tandem katalyse. Dit laatste is onderzocht uitgaande van één enkele prekatalysator en via traditionele tandem katalyse onder zowel homogene als heterogene omstandigheden.
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Curriculum Vitae

Ece Koç was born on the 11th of September 1978 in Bursa, Turkey. In 2001, she completed her BSc. degree at Istanbul Technical University, Istanbul, Turkey. In 2003, she moved to Hamburg, Germany where she started Diplom/M.Sc. She won a scholarship from International Center for Graduate Studies at University of Hamburg and DAAD STIBET (German Academic Exchange Service). The title of her master thesis was “Synthesis of Amorphous α-Olefins with Metallocene Catalysts” which was conducted under the supervision of Prof. dr. Walter Kaminsky with Degussa A.G as the industrial partner. In 2007, she moved to The Netherlands to start her PhD research in the Polymer Chemistry group at the Eindhoven Technical University under the supervision of Prof. dr. Cor Koning and Dr. Rob Duchateau, funded by Dutch Polymer Institute. The results of her research are presented in this PhD thesis.