Tailoring polyolefin properties by metallocene catalysis

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ACADEMIC DISSERTATION

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Helsinki 2006
Abstract

This doctoral thesis deals with the syntheses of olefin homo- and copolymers using different kind of metallocene catalyst. Ethene, propene, 1-hexene, 1-hexadecene, vinylcyclohexane and phenylborbornene were homo- or copolymerized with the catalysts. The unbridged benzyl-substituted zirconium dichloride catalysts (1-4), ansa- bridged acenaphthyl substituted zirconium dichloride catalysts, (5, 6), rac- and meso-ethylene-bis(1-indenyl)zirconium dichlorides, (rac- and meso-8), rac-ethylene-bis(1-indenyl)hafnium dichloride, (12), bis(9-fluorenyl)hafnium dichloride (14) enantiomerically pure (R)- phenylethyl[(9-fluorenyl-1-indenyl)]ZrCl₂ (11), 14 and asymmetric dimethylsilyl[(3-benzylindenyl-(2-methylbenzen[e]indenyl)] zirconium dichloride, (13), were prepared in our laboratory. Dimethylsilyl-bis(1-indenyl)zirconium dichloride, (9), isopropyldiene(9-fluorenyl-cyclopentadienyl)zirconium dichloride, (10), and were obtained commercially. The solid-state structures of the catalysts rac- and meso-1 were determined by X-ray crystallography. Computational methods were used for the structure optimization of the catalyst rac- and meso-1 in order to compare the theoretical calculations with the experimental results. Polymerization experiments were conducted in a highly purified autoclave system using low pressures (< 5 bar) of gaseous monomers. Experiments were designed to attain optimal catalytic activity and uniform copolymer composition. The prepared homo- and copolymers were characterized by the gel permeation chromatography, GPC, differential scanning calorimetry, DSC, nuclear magnetic resonance spectroscopy, NMR, and Fourier transform infrared spectrometry, FTIR. Molar mass (Mₘ, Mₜ), molar mass distribution (Mₙ/Mₚ), tacticity, comonomer content, melting temperature, glass transition temperature, and end group structures and content were determined. Special attention was paid to the correlation of the polymer properties with the catalyst structures and polymerization conditions. An intramolecular phenyl coordination was found in phenyl substituted benzyl zirconocenes 1-3 explaining the decreased activity of the catalysts. Novel copolymers poly(propene-co-phenylborbornene) and poly(propene co-vinylcyclohexane), were synthesized and high molar mass poly(ethene-co-1-hexene) and poly(ethene-co-1-hexadecene) copolymers with elastic properties were prepared. Activation of a hafnocene catalyst was studied by UV-Vis spectrometry and an activation process for the synthesis of ultra high molar mass poly(1-hexene) was found out.

(Keywords: metallocene, transition metal, aluminum alkyl, olefin, polyolefin, polymer, copolymer, catalyst, cocatalyst, molar mass, tacticity, )
Preface

The experimental work for this thesis was carried out in the Laboratory of Inorganic Chemistry at the University of Helsinki between the years 1998 and 2005. I gratefully acknowledge Academy of Finland and The Finish Technology Development Center, TEKES of the financial support.

I want to express my deepest gratitude to Professor Markku Leskelä for giving me the opportunity to carry out this experimental work, to learn and study and to write the articles and this thesis. Warm thanks go to Docent Timo Repo for his guidance in metallocene catalysis and for providing me with many interesting catalysts.

Warm thanks go also to Professors Franciska Sundholm and Heikki Tenhu and Docent Matti Elomaa for their efforts to make me a polymer chemist and to Dr. Ritva Dammert for her initiative in carrying out styrene polymerizations with these extremely interesting metallocene catalysts.

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A grateful mention is appointed to Docent Markku Sundberg and Docent Rolf Ugglä for their contributions to heavy calculations of the metallocene structures with
CSC-supercomputers. This work has given me many elementary ideas to understand metallocene chemistry.

I want to remember here the strong impact of our floorball team to my welfare; there have been many joyful events during the friday afternoon sessions with Antti Niskanen, Antti Pärssinen, Markus Lautala, Eero Rauhala, Viljami Pore, Tero Pilvi, Petro Lahtinen, Marianna Kemell and Arto Puranen.

This preface would not be complete without the mention of one permanent element in my life, The Band with Timo Korhonen, Tapio Orava and Janne Louhivuori. Training sessions at Timo's basement have been waited happenings to eliminate the stress acquired occasionally with computers or laboratory equipment and specially when connected to each other.

I wish warmly thank my mother Anja for her trust in me and her encouragement to develop my skills and talents in all areas of life, especially in arts and music. A grateful mention is appointed to Helena and Kalevi Kivinen for their role as loving and caring grandparents for Kaisa and Iiro. They have given me a lot freedom to concentrate on my work in laboratory. I thank my children Kerttu, Heikki, Minna, Kaisa and Iiro for giving me so much energy and inspiration to carry out this task. I am happy to express here that the births of my granddaughters Aada and Vilma have been especially golden events during the last years.

Most of all my wife Maarit deserves my deepest gratitude for her endless patience and female wisdom. Without her love and caring this work simply could not have come true.

Helsinki, November 2006 Erkki Aitola
List of original publications:


## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGC</td>
<td>constrained geometry catalyst</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>CSC</td>
<td>Center of Scientific Computing</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>EPDM</td>
<td>ethene propene diene rubber</td>
</tr>
<tr>
<td>EPM</td>
<td>ethene propene rubber</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>HDPE</td>
<td>high density polyethene</td>
</tr>
<tr>
<td>HF</td>
<td>Hartree-Fock</td>
</tr>
<tr>
<td>Ind</td>
<td>indenyl</td>
</tr>
<tr>
<td>i-PP</td>
<td>isotactic polypropene</td>
</tr>
<tr>
<td>LCBPE</td>
<td>long chain branched polyethene</td>
</tr>
<tr>
<td>LDPE</td>
<td>low density polyethene</td>
</tr>
<tr>
<td>LLDPE</td>
<td>linear low density polyethene</td>
</tr>
<tr>
<td>MAO</td>
<td>methylaluminoxane</td>
</tr>
<tr>
<td>MDPE</td>
<td>middle density polyethene</td>
</tr>
<tr>
<td>M</td>
<td>transition metal</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
<tr>
<td>M&lt;sub&gt;n&lt;/sub&gt;</td>
<td>number average molar mass</td>
</tr>
<tr>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>weight average molar mass</td>
</tr>
<tr>
<td>M&lt;sub&gt;n&lt;/sub&gt;/M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>molar mass distribution, polydispersity</td>
</tr>
<tr>
<td>MWD</td>
<td>molecular weight distribution, polydispersity</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>phNBN</td>
<td>phenynorbornene</td>
</tr>
<tr>
<td>PP</td>
<td>polypropene</td>
</tr>
<tr>
<td>(R)</td>
<td>optical activity, clockwise rotation</td>
</tr>
<tr>
<td>(S)</td>
<td>optical activity, counterclockwise rotation</td>
</tr>
<tr>
<td>sPS</td>
<td>syndiotactic polystyrene</td>
</tr>
<tr>
<td>T&lt;sub&gt;g&lt;/sub&gt;</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TIBA</td>
<td>trisisobutyl aluminum</td>
</tr>
<tr>
<td>T&lt;sub&gt;m&lt;/sub&gt;</td>
<td>melting temperature</td>
</tr>
<tr>
<td>TMA</td>
<td>trimethyl aluminum</td>
</tr>
<tr>
<td>TMS</td>
<td>trimethyl silane</td>
</tr>
<tr>
<td>TOF</td>
<td>turnover frequency</td>
</tr>
<tr>
<td>UHMWPE</td>
<td>ultrahigh molecular weight polyethene</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible light spectroscopy</td>
</tr>
<tr>
<td>VCH</td>
<td>vinylcyclohexane</td>
</tr>
<tr>
<td>VLDPE</td>
<td>very low density polyethylene</td>
</tr>
</tbody>
</table>
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1. Introduction

Organometallic catalysis is a fundamental method for the synthesis of new chemical substances from organic starting molecules.\textsuperscript{1} Transition metal complexes of Ti, Zr, Hf, Ni, Pd, Co, Cr etc. form a most remarkable group of these catalysts. The Nobel prize in chemistry for 2005 was awarded to Yves Chauvin, Robert. H. Grubbs and Richard R. Schrock for their ground braking work in organometallic synthesis and catalysis over three decades.\textsuperscript{2}

A great many high tonnage industrial petrochemical processes, including cracking\textsuperscript{3}, oligomerization\textsuperscript{4,5} and polymerization\textsuperscript{6,7} are based on organometallic catalysis. Petrochemical industry utilizes latest achievements and technologies in the catalytic processes to respond to the challenges on tightly competitive markets.

Polyolefin producers, comprising a significant part of the petrochemical industry, apply numerous catalytic processes in the polymerization plants. As the final properties of the polymers are strongly correlated with the structure of the used catalysts, the structure-property relationship is the key concept to develop new catalysts. The essential polymer properties such as molar mass, tacticity and crystallinity can be precisely tuned by the catalysts. New polymer materials with enhanced properties such as higher thermal and mechanical resistance can be synthesized. In addition a successful use of the highly tuned catalytic processes improves the energy efficiency in the industrial production.

During the last two decades there has been great academic and industrial enthusiasm to develop new polymerization catalysts. Organometallic metallocene catalysts have been the main focus on this research area and many new metallocene catalysts have been introduced and patented for industrial processes.

1.1 Polyolefins

Polyolefins are the most widely used thermoplastic materials in the modern world.\textsuperscript{8} Annual consumption of these plastics is about 80 million tonnes and the amount grows about five percent annually.\textsuperscript{9} Polyolefins cover a broad range of polyethenes, polypropenes and their copolymers with higher \(-\text{I}\)-olefins. High molar
mass linear and branched polyolefins are produced by polymerization of 1-olefin monomers (ethene, propene, butene etc.) by radical or catalytic processes.

Polyolefins begun to appear in the mid 1930s when the industrial process for the low density polyethene (LDPE) was introduced. LDPE is produced in high pressure (3000 bar) reactors at elevated temperatures, over 300°C, using organic peroxide initiators. Under these conditions the polymerization proceeds by radical mechanism and polyethenes with high polydispersity and high frequency of branching are produced. LDPE has many drawbacks due to the manufacturing process. It is a highly amorphous soft material having high creep tendency which limits its use. LDPE is used for plastic bags, packaging films and as protective coating on paper, for example in milk cartons.

Catalytic low pressure polymerization and high density polyethene (HDPE) was introduced in the mid 1950s. Compared with LDPE, HDPE has many improved physical properties which emerged it an important commercial plastic after the mid 1950s. Polyethene (PE) grades comprise a significant group of plastics with different material properties suitable for various practical purposes. A common classification of the main PE grades is done according to bulk density value (Table 1).

<table>
<thead>
<tr>
<th>PE grade</th>
<th>Abbreviation</th>
<th>Density, kg/dm³</th>
<th>Catalyst</th>
<th>Main Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very low density</td>
<td>VLDPE</td>
<td>0.880 - 0.915</td>
<td>Metallocene</td>
<td>Film</td>
</tr>
<tr>
<td>Low density</td>
<td>LDPE</td>
<td>0.910 - 0.940</td>
<td>Radical, peroxides</td>
<td>Bags</td>
</tr>
<tr>
<td>Mid density</td>
<td>MDPE</td>
<td>0.926 - 0.940</td>
<td>Metallocene</td>
<td></td>
</tr>
<tr>
<td>High density</td>
<td>HDPE</td>
<td>&gt;0.941</td>
<td>Ziegler-Natta, Phillips, Metallocene</td>
<td>Tanks, containers, canisters</td>
</tr>
<tr>
<td>Linear low density</td>
<td>LLDPE</td>
<td>0.915 - 0.925</td>
<td>Metallocene</td>
<td>Packaging films</td>
</tr>
<tr>
<td>Long chain branched</td>
<td>LCBPE</td>
<td>Like HDPE</td>
<td>Metallocene, Phillips</td>
<td>Same as HPDE</td>
</tr>
<tr>
<td>Ultrahigh molecular weight</td>
<td>UHMWPE</td>
<td>Less than HDPE</td>
<td>Ziegler-Natta, Metallocene</td>
<td>High tensile fibers</td>
</tr>
</tbody>
</table>

Polypropenes (PP) are another important group of polyolefin plastics and annual growth is following the same trend as for polyethenes. The chirality of the propene units in the polymer chains defines that the polypropene can form atactic,
isotactic and syndiotactic chain structures (Scheme 1). Isotactic and syndiotactic grades are highly crystalline polymers having elevated melting temperatures. Isotactic polypropene is commercially the most widely used of PP grades.

Olefin copolymers comprise a discrete group of plastics and elastomers. Some of them, such as LLDPE, a copolymer of ethene and 1-hexene or 1-octene, are classified among PE grades. Ethene-norbornene copolymers, introduced by Hoechst AG, are new commercial copolymers with special features. They are highly transparent having completely amorphous structure and high temperature resistance up to 200°C. Ethene-propene (EPM) copolymers and ethene-propene-diene (EPDM) terpolymers are widely used olefinic elastomers. Like natural rubber they are vulcanized with sulfur or peroxides to achieve elastic properties.

Polyolefins are ideal materials in many respects. They tolerate well liquid hydrocarbons, strong acids and other chemicals. They do not decompose or become contaminated by bacterial flora, and they are nontoxic for food packaging. After use they can easily be recycled or fed back to energy production. The physical toughness of specialty polyolefin grades is high enough to make durable products such as pressurized tanks and car bumpers, and even artificial joint implants for the human body.

Scheme 1: Orientation of methyl groups in polymer chain segments of iso-, syndio- and atactic polypropene.
1.2 Catalytic olefin polymerization

Olefin monomers are polymerized in large slurry and gas phase processes in polyolefin plants. Both processes are designed and adjusted to use heterogeneous catalyst. In the case of homogeneous catalyst, such as metallocenes, catalyst must be bound on disperse solid particles of silica or alumina to use in industrial processes.

1.2.1 Heterogeneous catalysis

In the early 1950s Karl Ziegler and his colleagues discovered and patented a catalyst that polymerizes ethene at low pressures (<50 bar) and temperatures to high density linear polyethene (HDPE).\textsuperscript{11} Ziegler’s catalyst consisted of a titanium chloride bound to solid magnesium dichloride carrier (Figure 1).\textsuperscript{16} To initiate and propagate polymerization, the catalyst had to be activated by aluminum alkyls such as trimethylaluminum, TMA.

HDPE is a highly crystalline linear polymer with high melting temperature and low creep tendency. Its arrival on the market initiated a new era in the use of polyolefins, as large number of novel plastic products, including gasoline canisters, chemical containers and bottles for cosmetics and hygiene were introduced.

![Figure 1. Schematic model of the Ziegler- Natta catalyst.](image-url)

Karl Ziegler's early co-worker Giulio Natta and his colleagues, working at the Technical University of Milan in the 1950s, focused their research on propene polymerization with the Ziegler's catalyst. In 1958 Natta patented a catalyst system...
that polymerizes propene stereoselectively to produce highly crystalline isotactic polypropene (i-PP). Isotactic PP has many superior properties including high resistance to chemicals, high melting temperature (up to 160°C), high impact resistance, surface gloss and good melt flow properties. Kitchen products prepared of i-PP are especially suitable for heating in microwave ovens.

About the same time in the United States, Banks and co-workers at Phillips Petroleum Co. developed a chromium oxide catalyst supported on calcined alumina or silica (Figure 2). This catalytic system was also capable of polymerizing ethene to high density linear polyethylene at low pressures and moderate temperatures. In contrast to Ziegler’s catalyst, the Phillips catalyst initiates and propagates polymerization without an additional activation and is therefore more cost effective in industrial processes. Today technologies based on the Phillips catalyst are highly tuned industrial processes covering the production of most commercial polyethylene grades including long chain branched polyethenes. It is estimated that one third of the worldwide production of polyethenes is carried out with Phillips processes.

![Figure 2. Activated Phillips-catalyst on solid carrier.](image)

Phillips and Ziegler-Natta catalyst are heterogeneous meaning that the catalyst particles are in solid state and polymerization takes place at the catalytic surface. Owing to the morphology of the catalytic surface, there are many sterically different active catalyst sites, which result in polymers with inhomogeneous material properties such as molar mass and molar mass distribution. One drawback of heterogeneous catalysis is that low molar mass volatile oligomeric components have to be removed from the final product to ensure the desired properties. Another drawback is that copolymerization of a higher olefin with ethene and propene is disadvantaged because of the poor coordination of higher olefins on the catalytic sites.
To overcome the drawbacks of heterogeneous catalysis there have been continuous efforts to develop homogeneous polyolefin catalysis parallel with Ziegler-Natta catalyst research.

1.2.2 Homogeneous catalysis

In 1957, *bis*-cyclopentadienyl titanium dichloride (Cp₂TiCl₂), a compound completely soluble in polymerization liquid, was reported to polymerize ethene when activated with cocatalysts AlEt₃²⁰ or AlEt₂Cl.²¹ The activity of this first homogeneous catalyst system was too low for industrial production of polyolefins, and the revolution in homogeneous olefin polymerization had to wait until 1975 when methyl aluminum oxide, MAO, was introduced as cocatalyst at the University of Hamburg.²²-²⁴ In the presence of MAO an enormous increase in catalytic activity of Cp₂TiCl₂ was achieved in ethene polymerization.²⁵ The zirconium analogue of Cp₂TiCl₂ was even more active, producing over 60 tonnes of high molar mass polyethylene in one hour per mole of catalyst at 2.5 bar of ethene pressure and temperature of 30°C.²⁶

MAO-activated Cp₂TiCl₂ and its derivatives were not suitable catalysts for propene polymerization due to their tendency to produce atactic polypropenes with low catalytic activity.²⁷ In the mid 1980s Brintzinger and his co-workers reported than an ethyl bridged *bis*-{(4,5,6,7-tetrahydro-1-indenyl)zirconocene catalyst, activated by MAO, was able to produce isotactic polypropene with good catalytic activity.²⁸

A few years later Ishihara et al. reported of the successful stereoregular polymerization of styrene with a homogeneous half metallocene catalyst, CpTiCl₃, activated by MAO.²⁹ The prepared syndiotactic polystyrene exhibited amazingly high melting temperature up to 250°C.

Homogeneous olefin catalysts can be divided into two classes: metallocenes and non-metallocenes. Non-metallocene late transition metal complexes of nickel, palladium and iron, introduced by Brookhart et al.³⁰-³² in the mid 1990s, are active catalysts for ethene polymerization producing highly branched polyethenes. This type of square planar catalysts, presented in Figure 3, have been reported to copolymerize olefins with polar monomers such as alcohols and acrylic acid.
In olefin polymerization with homogeneous catalysts, the optimal polymerization takes place at a single, precisely defined catalytic site, and the catalysts are denoted as single site catalysts (Figure 4.) Metalloocene catalysts offer improved control over the polymerization reaction and polymers with more precisely tailored properties can be synthesized. High degree of tacticity in polypropenes has been the primary property to benefit from metalloocene technology. The other remarkable feature of metalloccenes is their very good potential for copolymerization.

Faced with the complex patent issues associated with metalloocene catalysts and technologies, many companies have invested heavily in research on non-metalloocene olefin catalysis.\textsuperscript{33} Mitsui Chemical Co. has succeeded in developing group IV catalysts with a phenoxy-imine ligand system (figure 5).\textsuperscript{34,35} Some of these are reported to exhibit activities compared with those of the best metalloccenes when activated by MAO.\textsuperscript{36}
Combinatorial high throughput catalyst screening has resulted in inventions of some profitable catalysts. Combinatorial methods provide enormous ligand libraries to be tested in parallel polymerization experiments and have proved a powerful tool in catalyst research.

![Phenoxy-imine type catalyst as dichloride precursor](image)

**Figure 5.** Phenoxy-imine type catalyst as dichloride precursor developed by Mitsui Chemicals Inc.

### 1.2.3 Activation of catalysts

Organometallic dichloride catalysts precursors have to be activated with aluminumalkyls to monoalkylated cations which are the active polymerization species (Scheme 2). Cocatalyst MAO, containing free trimethylaluminum (TMA) has three important functions. First it exchanges one chloride ligand for a methyl group, then it abstracts the second chlorine leaving a free coordination site for the monomer, and finally it stabilizes the cation by loosely coordinating bulky methyl aluminum oxane anion. The weak cation-anion interaction is essential for the free access of the monomers to the catalytic center. A typical feature in the use of MAO is that it must be used in enormous overloads with respect to the catalyst to achieve optimal catalyst activity. The ratio of cocatalyst to catalyst falls in the range of 200 to 500 in highly purified reactor systems but for work as an efficient catalyst poison scavenger, ratios over 2000 are commonly needed. Lower ratios are sufficient with ansa-metalloocene having siloxy substituent in position-1 in the indenyl group. Owing to the complex nature of MAO (containing free TMA) the activation process is complicated and difficult to investigate by conventional methods.
Scheme 2. Alkylation of metallocene dichloride by trimethylaluminum, Al(CH₃)₃, and formation of active metallocene catalyst ionpair with methyl aluminum oxane, MAO.

Alternatively, alkylated metallocene catalyst precursors can be activated with borate anions (Scheme 3).⁴⁵ A metallocene/borate system is active with 1:1 stoichiometric ratios of cocatalyst but requires extreme purity of the polymerization system and is therefore difficult to carry out. The practical way to carry out polymerizations relying on borate activated metallocenes is to first alkylate the metallocene dichloride with tris-isobutylaluminum, TIBA, and afterwards add a stoichiometric amount of borate activator [V]. In this way excess of TIBA purifies the reactants by scavenging possible H₂O, O₂, and CO₂ contaminations, and polymerization takes place with optimal catalyst activity.

Scheme 3. Activation of monomethylated metallocene with borate anion.
1.2.4 Coordination-insertion mechanism

Catalytic coordination olefin polymerization takes place by coordination insertion mechanism,\textsuperscript{46,47} which has three characteristic phases: coordination, migratory insertion and chain termination. Coordination obeys general thermodynamical behavior and is defined by the electrostatic forces between the metal cation center and \( \sigma \)-orbitals of the coordinating monomer (Scheme 4, coordination). In the case of copolymerization some olefin monomers can be more favorable than others and the monomer will be enriched in the copolymer. Thanks to the spatial steering of the ligands of the catalyst, propene and higher prochiral \( \tilde{1} \)-olefins can have precisely defined coordination modes. This is an essential requirement for stereo- and enantioselective polymerization when the monomers insert exactly at the right positions in the growing polymer end.\textsuperscript{48-50}

During the polymer chain propagation, the coordinated monomer inserts between the initiating metal-alkyl or growing metal-polymeryl unit by migratory insertion mechanism (Scheme 4, insertion). This is the critical step for many catalysts and monomers. Insertion may be very slow or completely prohibited by steric factors and therefore one of the most important features for a metalloccene catalyst is how well the ligand environment steers and optimizes the insertion process.\textsuperscript{51,52} An \( \tilde{1} \)-olefin monomer, like propene, can have different insertion modes such as 1,2- or 2,1-insertions. Occasional 2,1-insertions induce regioerrors to the polymer chain and to produce highly regular chain structures, both stereo- and regiocontrol of the inserting monomer must be maintained during the whole catalytic cycle.
Scheme 4. Ethene coordination on active metalloocene catalyst cation and migratory insertion of ethene in the metal-carbon bond at the center metal atom.

1.2.5 Chain termination

After numerous coordination and insertion events polymer chain growth is quenched by chain termination reactions. There are three most favorable termination modes: $\alpha$-hydride elimination (chain transfer to metal), chain transfer to a coordinated monomer and chain transfer to the cocatalyst. The first two leave an unsaturated vinyl bond and the last leaves an aluminum alkyl group at the chain end (Scheme 5). Aluminum alkyl terminated end groups decompose when polymerization are quenched by alcohols and hydrochloric acid and a saturated chain is obtained. Chain end isomerization prior to the chain termination is widely studied mechanism in olefin polymerizations with metalloccenes (Scheme 6). Chain end isomerization takes place by the rotational movement of the coordinated polymeryl unit, successive formation of the bis-$\alpha$-agostic structure and termination by the chain
transfer to a coordinated monomer. Chain end isomerization result to a trans-vinylene chain end structure.

Careful chain end investigation provides information about the termination reactions, important for the evaluation of the catalyst properties[III]. If the catalyst-chain end interaction is unfavorable for the \( \alpha \) hydride eliminations chain propagation proceeds longer and high molar mass polymers are produced.\(^6\)

\textbf{Scheme 5.} Chain termination reactions by \( \alpha \)-hydrogen transfer to the metal or coordinated monomer.

\textbf{Scheme 6:} Mechanism for chain end isomerization and arrangement of \textit{trans}-vinylene chain end.
1.2.6 Catalytic activity and turnover frequency

The efficiency of a catalyst is measured in terms of *turnover frequency*, TOF, which expresses the number of catalytic cycles per time unit normalized to pressure of 101kPa. The highest TOF values measured for metallocene catalysts are ca. 50000 s⁻¹, which also represent the fastest known catalytic reactions. Activity is a calculated value for catalyst productivity in polymerization experiments and there are many ways to express it. Primarily activity is dependent on the character of the catalyst but secondary factors such as purity of monomers, inert gases, solvents and cocatalysts also play a role.

The usual way to express catalyst activity is to give the amount of synthesized polymer as kilograms per mole of catalyst precursor calculated as average activity in one hour polymerization: kgₚₒₒ/(molₙₐₙₜ * h). In this form, the pressure and monomer concentrations are disregarded and are normally given in table footnotes or in experimental sections. A good metallocene/MAO catalyst can easily reach an activity of 100*10³ kgₚₒₒ/(molₙₐₙₜ * h) at ethene (or propene) pressure of 3.0-5.0 bar at low temperatures (40-70°C). (The highest measured activity in polymerization experiments of this work was 205*10³ kgₚₒₒ/(molₙₐₙₜ * h) achieved with unbridged benzyl-substituted metallocene). The literature contains reports of catalysts with activities over 1000*10³ kgₚₒₒ/(molₙₐₙₜ * h) but these activities were obtained in very short experiments with huge overloads of cocatalyst.

Owing to the high polymerization activity of the metallocenes, strong heat formation and rapidly precipitating polymer may lead to severe reactor fouling. Maintaining stable polymerization conditions in reactors requires that the concentrations of the most active catalysts should be kept very low. On the other hand, extremely low catalyst concentrations require extreme purity of the polymerization system to prevent catalyst poisoning.

The chemical structure of cocatalyst MAO changes during comparatively short periods of storage by forming rearranged gels. Such changes are believed to cause variations in the activity values between polymerization sessions. Comparable activity values are achieved in extremely pure polymerization conditions in short periods of serial experiments. To avoid the disturbing effect on activity caused by the
unstable MAO, metallocene activation with borate/trialuminumalkyl may be preferred \[V\].

2. Metallocene catalyst

Metallocene is a generic term for transition metal complexes where two cyclopentadienyl units are $\gamma^5$ coordinated to the central metal atom. This structure was first described for ferrocene\textsuperscript{50} and later for tetrahedral bent metallocene dihalogens such as Cp$_2$ZrCl$_2$ (Figure 6).\textsuperscript{60}

![Figure 6: Structure of ferrocene, Cp$_2$Fe, and tetrahedral bent metallocene dichloride, Cp$_2$MCl$_2$.](image)

A general procedure for increasing catalyst performance is to modify its chemical structure by replacing hydrogens in cyclopentadienyl, indenyl and fluorenyl moieties by organic groups such as methyl, ethyl or phenyl (Chart 1).\textsuperscript{61} Numerous variations in catalyst structures have been achieved as a result of such modifications.\textsuperscript{62}

The most efficient metallocene catalysts for olefin polymerization are provided by the group IV metals:\textsuperscript{63} Ti, Zr and Hf, though many other transition metal complexes able to form $\gamma^5$ coordinative metallocene structure have been investigated.\textsuperscript{64,65} The behavior of the metallocene catalyst in polymerization reaction depends on the character of the center metal atom and steric and electronic properties of the ligands. The final polymerization performance is a net sum of all effects. In many cases it is difficult to distinguish the contributions of the metal atom and
ligands simply by characterizing the polymer properties and spectroscopic\textsuperscript{66-68} and computational methods have been widely used to investigate the subject.\textsuperscript{69-71}

\begin{center}
\begin{tabular}{c c c}
\includegraphics[width=0.3\textwidth]{chart1a} & \includegraphics[width=0.3\textwidth]{chart1b} & \includegraphics[width=0.3\textwidth]{chart1c}
\end{tabular}
\end{center}

\textbf{Chart 1:} Examples of 1-substituted indene ligands precursors.

\subsection{2.1 Unbridged metalloccenes}

\(\text{Cp}_2\text{ZrCl}_2\) activated with MAO is a highly active catalyst in ethene polymerization and its polymerization mechanisms have been widely studied by experimental and theoretical methods.\textsuperscript{72} \(\text{Cp}_2\text{ZrCl}_2\) has the simplest structure of any zirconocenes. The X-ray crystal structure shows distorted tetrahedral geometry and the interplanar angle between the \(\gamma^5\)-coordinated \(\text{Cp}\) rings is 122.1\(^\circ\) measured at 193K.\textsuperscript{73} As a dichloride it is a coordinatively saturated 16-electron molecule. When activated with MAO it forms an active 14 electron cation for polymerization. In an attempt to enhance its polymerization capabilities and a large number of derivatives have been synthesized and tested.\textsuperscript{74} Methyl substitutions to the \(\text{Cp}\) ring have been one basic procedure to further develop catalysts performance and clear variations in activity, molar mass and comonomer response have been achieved with such modifications.\textsuperscript{75}

Besides methyl substitution phenyl substitution is of special significance in catalyst design. The electron-rich phenyl ring is able to coordinate to metal center and can give additional stability to catalyst structure.\textsuperscript{76,77} A remarkable effect of the phenyl coordination is seen in polymerization of styrene with \(\text{CpTiCl}_3\) catalysts. The phenyl moiety of the last inserted monomer in the growing polystyrene chain coordinates to the titanium metal center so strongly that the catalyst steers the
syndiospecific polymerization of styrene by chain end control mechanism (Figure 7).78-80

![Figure 7: Chain end control in the syndiospecific polymerization of styrene with activated half-metallocene, CpTiCl₃.](image)

When phenyl moieties are linked with ethyl or longer spacers at the para-position of the indenyl group in unbridged bis\{\(\gamma\text{-}(1\text{-benzyl})\text{indenyl}\}\}ZrCl₂, the activity of the metallocene in ethene polymerizations can increase remarkably [II].81

As presented by Waymouth et al. unbridged metallocene catalyst with phenyl substituent at the 2-position of indenyl has a special polymerization behavior.82,83 Owing to the rotational movement of indenyl ligands (Figure 8), the catalyst is able to form two rotational conformers with unlike polymerization behavior. In propene polymerization, catalyst produces alternating isotactic and atactic blocks in polypropene giving the polymer elastomeric properties.

![Figure 8: Waymouth’s catalyst: rotational conformer left (rasemic-like) produces isotactic sequences and rotamer right (meso-like) produces atactic chain sequences to the polypropene.](image)
2.2 *ansa*-Bridged metalloccenes

Rotational instability of the cyclopentadienyl ligands\textsuperscript{84} in the unbridged metalloccenes disturbs the stereoselective coordination of the prochiral 1-olefin monomers on the catalyst and makes it impossible to obtain highly isotactic or syndiotactic chain structures with this type of catalysts.\textsuperscript{85} The problem was solved when ethylene bridge was constructed between indenyl ligands in the *bis*(4,5,6,7-tetrahydro-1-indenyl)ZrCl\textsubscript{2} to prevent the rotational movement.\textsuperscript{28} When activated with MAO, *rac*-ethylene-*bis*(4,5,6,7-tetrahydro-1-indenyl)ZrCl\textsubscript{2} polymerizes propene to high molar mass highly isotactic polypropene with excellent activity. Highly isotactic polypropenes are crystalline polymers owing enhanced material properties such as elevated melting temperature and low solubility to hydrocarbon solvents.\textsuperscript{86,87}

Metalloccenes with an intramolecular bridge between $\gamma^5$ coordinated Cp ligands are known as *ansa*-metalloccenes (Figure 9). The bridge has two important features. First, it binds the Cp rings tightly giving the desired rigid structure with exactly defined angles between ring planes. Secondly, it has a marked effect on the electron density of the center metal, which in turn has a strong influence on the polymerization.\textsuperscript{88} Many different *ansa*-bridge structures exists, the most common being ethyl, isopropyl and dimethylsilyl bridges (Figure 10).

![Figure 9: Optimized molecular structure of *ansa*-bridged metalloccene dichloride *meso*-ethylene-*bis*(1-indenyl)ZrCl\textsubscript{2}, *meso*-8. Optimization was performed by semi empirical PM3 method using Spartan '02 for Windows program.](image-url)
A stereoselective *ansa*-metallocene steers prochiral monomers to insert at exact coordination positions so that isotactic and syndiotactic\textsuperscript{89} chain architectures can be achieved. Errors in polymer chain are mostly caused by improper regional insertion (2,1-insertion) or missing spatial steering of the monomer.\textsuperscript{90} To achieve a completely regular polymer chain structure the catalyst has to exhibit both stereo- and regiocontrol over the incoming monomer.\textsuperscript{91}

The growing polymer chain is bound to the catalytic metal center by a strong \( \sigma \)-bond. An essential demand for the catalyst is that a \( \sigma \)-bonded polymeryl unit sits stably in the active center during the chain propagation process. In catalysts that produce highly regular structures, rotational movements of the polymeryl unit are blocked by the agostic bonds between chain end hydrogens and the metal center.\textsuperscript{92}

![Image of *ansa*-bridged zirconocene dichlorides as catalysts precursors.](image)

**Figure 10.** Common *ansa*-bridged zirconocene dichlorides as catalysts precursors.
2.3 Constrained geometry catalysts

An especially rigid molecular structure is in constrained geometry catalyst\textsuperscript{93} where the cyclopentadienyl ligand is liked with a silyl or phosphanyl bridge via a coordinating amido ligand to the metal center (Figure 11). The transition metal is usually titanium or zirconium but also chromium and vanadium complexes have been introduced.\textsuperscript{94} Activated constrained geometry Ti and Zr complexes are excellent catalysts in ethene-styrene\textsuperscript{95} and ethene-vinylcyclohexane copolymerization.\textsuperscript{96} They are also highly active, tolerate extreme reactor temperatures (up to 160°C) and produce long chain branched polyethenes.\textsuperscript{97}

![Constrained geometry chromium catalyst](image)

**Figure 11.** Constrained geometry chromium catalyst.

2.4 The scope of this work

The scope of this work was to investigate the structure-property relationship in olefin homo- and copolymerizations using the metalloocene catalysts synthesized in the Laboratory of Inorganic Chemistry in the University of Helsinki. The work was conducted by the serial polymerization experiments, and exact characterization of the product polymers. The objective was to find out steric and electronic properties in metalloocene catalysts, which affect on the polymerization mechanisms.
3. Experimental

The experimental work related to this thesis was primarily carried out in the Laboratory of Inorganic chemistry in the Department of Chemistry in the University of Helsinki. Most of the 13 metalocene catalysts were synthesized and characterized in the above laboratory. Catalysts 9 and 10 were obtained commercially. The polymerization experiments of 1-hexene with the hafnocene catalyst 14 and UV-Vis measurements of the activated catalyst solutions were performed in the Laboratory of Polymer Technology in the Technical University of Helsinki. The details of the experimental work summarized below can be found in the original publications I-V.

3.1 Metalocene dichloride synthesis and characterization

Unbridged metalocene catalyst chloride precursors were synthesized in a two part reaction. First the desired cyclopentadienyl derivatives were prepared by synthetic organic methods (Chart 2). After this their lithio salts were prepared using butyl lithium, BuLi. Finally the lithio salts were reacted with transition metal chlorides giving the required metalocene dichlorides (Scheme 7) [II].

Metalocene dichlorides substituted in 1-position of the cyclopentadienyl ring are able to form isomeric structures denoted as rac(emic)- and meso-forms. Isomerism is based on chirality of the carbon atoms at the position-1 (or position-3) in the cyclopentadienyl rings( Figure 12). During the trans-ligandation reaction with MeCl₄ 1-substituted indenyl ligand (and its derivatives) can form $\gamma^3$-bonding to the metal from the both sides of the Cp-plane giving an alternative to form an enantiomeric rasemic-pair of the complexes (racemate ) and a diastereomer (meso) complex. As the rac- and meso-forms of metalloccenes have different molecular structures they also have unlike polymerization behavior.

Separation of the meso-diastereomer from the racemate was carried out from toluene and dichloromethane based on the different solubility of the isomers. Small single crystals, suitable for X-ray diffraction measurements, were obtained for both isomers by slow crystallizing of the complexes from toluene or dichloromethane.
Figure 12: Meso-diastereomer and rac-enantiomers of 1-substituted bis(1-indeny1)ZrCl$_2$. In meso-complex the chiral carbon pairs (\text{*}, \text{*}) are R, S (defined by the optical activity) and in rac-complex the chiral carbons pairs (\text{*}, \text{*}) are R, R and S, S.

Bridged metalloccenes were synthesized by a similar procedure to that used for the unbridged metalloccenes except that alkyl- or silyl-bridges were first constructed between positions 1 of the two cyclopentadienyl rings. The bridged ligands were reacted with a group IV tetra chlorides to give the desired ansa-metalloocene dichlorides. All reaction steps with highly reactive reagents were carried out in nitrogen or argon, atmosphere and most reactions were performed using standard Schlenk techniques.
Chart 2: Cyclopentadienyl ligand derivatives used for metallocene catalyst.

Scheme 7: Synthetic route for the unbridged benzyl-substituted indenyl zirconocene dichlorides.

The three-dimensional molecular structures of the metallocene dichloride complexes were determined by single crystal X-ray crystallography (Figure 13). Determination of the structure is of great importance in evaluating catalyst behavior in
polymerization reactions. The most significant parameters in the catalyst structure are the orientation of $\gamma^\delta$-coordinated Cp derivatives, angular orientation of $\gamma^\delta$-ligand planes, and other molecular groups attached to the $\gamma^\delta$-ligands. If single crystal of the prepared metallocene dichloride precursor could not be obtained the characterization was made by NMR-methods instead.\textsuperscript{98}

![Figure 13](image)

**Figure 13.** Molecular structure of the *meso*-isomer of *para*-fluorobenzyl-substituted *bis*-indenylZrCl$_2$ (*meso*-3) determined by single crystal X-ray diffractometry.

### 3.2 Computational methods

With the enormously increased computer power now available quantum chemistry calculations have become a routine method. Complex molecular structures can be modeled with high accuracy using *ab initio* methods based on density functional theory, DFT [II]. A calculation of a metallocene catalyst cation nevertheless requires tens of hours of computer time. As an example optimization of the structure of ethylene *bis*(9-fluorenyl)Hf$^+$ isopropyl ethene cation as an initiating species for the polymerization required CSC/Corona supercomputer resources for over 70 hours.

Geometry optimizations of benzyl-substituted zirconocenes 1-4 were carried out with the Gaussian 03 program package using HF/3-21G$^*$ and hybrid density functional B3LYP/6-31G$^*$ methods.
3.3 Polymerization procedure

Polymerizations were performed in a thermostated 1000mL Büchi glass autoclave. The autoclave was loaded with 300mL of toluene and the required amount of 30% MAO in toluene. Ethene was fed to the autoclave until saturated ethene/toluene solution was achieved. Constant ethene pressure was maintained with an automated pressure controller. The polymerizations were started by injecting 20 mL of zirconocene dichloride precursor solution into the autoclave. Ethene consumption was monitored with a flow controller connected to a computer. Polymerizations were stopped by unloading ethene from the autoclave and pouring the polymerization solutions into HCl-methanol solutions. The precipitated polymer was washed with methanol, filtered, and dried overnight at 60°C.

3.4 Copolymerization procedure

Steady state copolymerization conditions are difficult to achieve in copolymerization experiments with metallocenes, due to the different coordination equilibrium of the monomers. The uneven change in the monomer concentrations during the polymerizations can result to copolymers with alternating monomer/comonomer ratios or even polymer/copolymers blends.

To solve this problem the copolymerizations were done in batch mode taking advantage of the short period when the rate of ethene (or propene) consumption was stable [I]. After loading of the required amount of toluene, MAO and comonomer, the reactor was pressurized to 2.5 bar with ethene and the polymerizations were started by adding the catalyst solution. Steady state polymerization conditions were achieved for a short period, as can be seen in the ethene pressure curve at Figure 14. In the pressure range 2.5–1.5 bar, the decrease in the pressure was linear indicating a constant rate of ethene consumption. In view of this finding all copolymerization reactions with ethene were stopped at 1.5 bar. The same procedure was utilized in the propene copolymerizations using different pressure intervals [I, IV].

The reaction time required for the pressure to decrease from 2.5 to 1.5 bar was dependent on the comonomer concentration and the catalyst. Since the rate of gaseous monomer consumption was constant and controlled by slower inserting
liquid comonomer (1-hexene, 1-hexadecene, phenylnorbornene or vinylcyclohexane), the copolymerization reactions followed steady state conditions, and even comonomer distributions in the copolymers were achieved.

**Figure 14**: Decrease of ethene pressure in ethene-hexene batch copolymerization with MAO activated metallocene catalyst.

### 3.5 Polymer characterization

Analysis of the chain structures of the prepared polymers were carried out to resolve catalyst behavior in polymerization reactions. Molecular and material properties of polymers such as molar mass, polydispersity, tacticity, chain end structures and thermal properties were characterized by applied methods (NMR, GPC, DSC, FTIR, UV-Vis).

#### 3.5.1 Nuclear magnetic resonance

Tacticities and comonomer contents in the copolymers we measured with $^{13}$C-NMR. Tacticity in propene copolymers were determined as an abundance of different pentads of methyl carbons at area of 19.0-21.5 ppm in the $^{13}$C-NMR spectrum (Figure 15). $^1$H-NMR was used in analysis of unsaturated chain ends of low molar mass copolymers.
**Figure 15.** Pentad sequences of methyl carbons of atactic and isotactic polypropenes determined with $^{13}\text{C}$-NMR.

### 3.5.2 Gel permeation chromatography

Molar mass and molar mass distributions of the polymers were analyzed with gel permeation chromatography, GPC. Owing to poor solubility of many olefin polymers in common solvents a high temperature GPC method with 1,2,4-trichlorobenzene as eluent was used. Measured polydispersity values were used to evaluate polymerization mechanisms since a optimal single site polymerization follows the statistical Flory-Schultz distribution giving optimal polydispersity value of 2.0.\textsuperscript{100}

### 3.5.3 Fourier transform infrared spectroscopy

In many cases, precipitated polyolefin polymers were insoluble in the common solvents and the only practical method for analyzing solid polymer samples was Fourier transform infrared spectroscopy, FTIR [II, III]. By FTIR analysis the amount and distribution of chain ends and number average molar mass were resolved. The superior benefit of FTIR was a very fast and simple sample preparation without need of hazardous solvents, merely pressing a thin tablet of polyolefin material and a direct measurement of the sample.
3.5.4 Differential scanning calorimetry

Thermal properties of polymers were determined by differential scanning calorimeter, DSC. The measured parameters were peak melting temperatures, \( T_m \), glass transition temperature, \( T_g \), and degree of crystallinity.

4. Results

The results of the polymerizations and copolymerizations with the metalloccenes are reported in the following. The effects of the changes in the ligand structure of the catalyst and the polymerization conditions were followed by characterization of polymer and copolymer products and these results are discussed in chapter 5.

4.1 Ethene homopolymerization with metalloccenes

Ethene polymerizes with MAO activated metalloccenes to a high molar mass polyethene with very high activity under mild reactor conditions. Catalyst properties can be effectively tuned by substitution of methyl, ethyl, isopropyl or phenyl groups in the cyclopentadienyl or indenyl ligands of the metalloccene. As a non prochiral and a small monomer ethene polymerizes well with both unbridged and bridged metalloccenes.

4.1.1. Ethene polymerization with unbridged benzyl substituted bis-indenyl zirconocenes

The influence of benzyl-substituent on the indenyl moiety in unbridged zirconocenes was investigated by polymerizing ethene with seven rac- and meso-isomers of catalysts 1-4 as presented in Scheme 7 [II]. The results are summarized in Table 2. Catalyst dichloride precursors were activated with MAO in cocatalyst/catalyst ratios ca. 2000. Substitution of the position-1 in the cyclopentadienyl ring with benzyl of phenyl derivatives had a marked effect on the performance of the catalyst. Variations in activity, molar mass and molar mass
distribution were achieved [II]. Differences in the distributions of end groups exposed the character of the chain termination reactions of the catalysts.

A notable feature of the benzyl-substituted zirconocenes 1-3 was the intramolecular coordination of the phenyl moiety to the metal center. This explained the lower activities of 1 and 3 than of rac-4 where the ethyl spacer pushes the phenyl moiety away from the vicinity of the coordination sphere of the cationic metal center. Ab initio calculations performed by Hartree-Fock and DFT methods confirmed these experimental findings.

Highest catalytic activity was obtained with the ethylphenyl-substituted catalyst rac-4. At pressure of 4.6 bar and temperature of 50°C, it produced over 200*10³ kgPE/mol_cat. This presents the highest activities in the polymerization experiments of this work. The activity of the reference catalyst rac-8 (rac-ethylene-bis(1-indenyl)ZrCl₂) showed activity 90*10³ kgPE/mol_cat at similar polymerization conditions.

Both isomers of the methoxy-substituted 2 were clearly less active than the catalysts rac-1 and meso-1. The interesting feature of the rac- and meso-2, was the broad molar mass distributions of the prepared polyethenes indicating existence on many different active sites. This and lower catalytic activity compared to other catalysts in this series of metallocenes were understood as a tight coordination of MAO species to free electronpairs of oxygen causing steric hinders to monomer to coordinate and insert.

The para-fluoro substituted catalysts rac-3 and meso-3 were the most active of the benzyl-substituted indenyl zirconium dichlorides. Activity increased with pressure for both the meso- and rac-catalysts: with the meso-form from 21 to 55 kgPE/MMol_cat*h and the rac-form 39 to 47 kgPE/MMol_cat*h. The molar mass of the polymers produced with rac- and meso-3 increased with ethene pressure: rac-3 from 475 to 700 kg/mol and meso-3/MAO from 450 to 600 kg/mol. In the same pressure range the polydispersities of the polyethenes prepared with meso-3 stayed almost constant at about 2.8, whereas with rac-3 it increased exceptionally high from 2.8 to 4.6.
Table 2. Results of ethene polymerizations carried out with MAO activated metalloenes 1-4 at pressures of 2.8, 3.8 and 4.6 bar.

<table>
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<th>Catalyst</th>
<th>Pressure Bar</th>
<th>Activity kgPE/ kg/mol (mmol&lt;sub&gt;cat&lt;/sub&gt; × h)</th>
<th>M&lt;sub&gt;n&lt;/sub&gt; kg/mol GPC</th>
<th>M&lt;sub&gt;n&lt;/sub&gt;/M&lt;sub&gt;w&lt;/sub&gt;</th>
<th>T&lt;sub&gt;d&lt;/sub&gt; /°C DSC</th>
<th>Trans- Vinylene% FTIR</th>
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<td>606.8</td>
<td>2.73</td>
<td>133.9</td>
<td>8.1</td>
</tr>
<tr>
<td>rac-4</td>
<td>2.8</td>
<td>105.6</td>
<td>471.0</td>
<td>1.94</td>
<td>135.7</td>
<td>10.2</td>
</tr>
<tr>
<td>rac-4</td>
<td>3.8</td>
<td>178.7</td>
<td>493.3</td>
<td>1.80</td>
<td>134.2</td>
<td>10.4</td>
</tr>
<tr>
<td>rac-4</td>
<td>4.6</td>
<td>205.7</td>
<td>444.7</td>
<td>1.78</td>
<td>134.7</td>
<td>6.9</td>
</tr>
</tbody>
</table>

4.1.2 Ethene polymerization with MAO activated catalyst 5 and 6

Benzannelated metalloene catalysts 5 and 6 (Figure 16) had characteristic features in ethene polymerization. First, they were unusually easily soluble in the polymerization solvent, toluene. Secondly, they produced granular polyethene particles, which precipitated during the polymerization keeping the polymerization solvent clear. The precipitation affected the reactor parameters so that heat formation and monomer feed and pressure remained exceptionally stable during the experiments. Results of ethene polymerizations with MAO activated catalyst 5 and 6 are collected in Table 3 [III].
Figure 16. Catalyst 5 and 6 as dichloride precursors.

### Table 3: Results of the ethene polymerizations with catalysts 5/MAO and 6/MAO.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Polym. pressure, bar</th>
<th>Polym. time, s</th>
<th>$n_{eq}$</th>
<th>Yield, g</th>
<th>Activity kg$<em>{poly}$(mol$</em>{cat}$*h$^{-1}$)</th>
<th>Mw by GPC kg/mol</th>
<th>Mw/Mn</th>
<th>$T_{onset}$ by DSC, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>2.5</td>
<td>1800</td>
<td>0.5</td>
<td>10.9</td>
<td>43 600</td>
<td>747</td>
<td>2.8</td>
<td>136.5</td>
</tr>
<tr>
<td>5</td>
<td>3.5</td>
<td>2460</td>
<td>0.5</td>
<td>9.29</td>
<td>45 302</td>
<td>640</td>
<td>2.6</td>
<td>135.0</td>
</tr>
<tr>
<td>5</td>
<td>4.5</td>
<td>1882</td>
<td>0.2</td>
<td>11.60</td>
<td>110 945</td>
<td>651</td>
<td>2.6</td>
<td>134.5</td>
</tr>
<tr>
<td>5</td>
<td>4.5*</td>
<td>903</td>
<td>0.2</td>
<td>9.25</td>
<td>190 200</td>
<td>544</td>
<td>2.8</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2.5</td>
<td>2033</td>
<td>0.2</td>
<td>1.40</td>
<td>12 366</td>
<td>902</td>
<td>2.7</td>
<td>133.0</td>
</tr>
<tr>
<td>6</td>
<td>3.5</td>
<td>1776</td>
<td>0.4</td>
<td>3.75</td>
<td>19 281</td>
<td>986</td>
<td>2.6</td>
<td>134.3</td>
</tr>
<tr>
<td>6</td>
<td>4.5</td>
<td>1845</td>
<td>0.4</td>
<td>3.13</td>
<td>27 696</td>
<td>812</td>
<td>2.5</td>
<td>135.3</td>
</tr>
</tbody>
</table>

Polymerization conditions: Toluene 200mL, Zr:Al = 1:2000, temp. 50°C, *70°C.

Catalyst 5 was highly active in ethene polymerization at 70°C, producing $190\times10^3$ kg$_{poly}$(mol$_{cat}$*h$^{-1}$). The molar mass of the polymer was 544 kg/mol. The high content of trans-vinylene chain end groups, determined by FTIR, indicated chain isomerization prior to the chain termination. The lower crystallinity values, slightly over 50%, suggested long chain branching, possibly caused by re-insertion of in-situ formed and released macromonomer. Highest molar mass polyethenes, 986 kg/mol, were obtained with 6 at temperature of 50°C, but because this catalyst was sterically more crowded it was distinctly less active than 5.
4.2. Copolymerization experiments with metallocene catalysis

Metallocene catalysts offer a versatile toolbox for the copolymerization of higher olefins with ethene or propene in various monomer/comonomer ratios and have provided numerous new copolymer compositions with diverse material properties.\textsuperscript{101} Synthesized \textit{ansa}-metallocene catalysts were applied in the copolymerization of propene and ethene with 1-hexene, 1-hexadecene phenylnorbornene and vinylcyclohexane.

4.2.1. Propene-phenylnorbornene copolymers

Copolymerization experiments with propene and phenylnorbornene were carried out to investigate the effect of bulky phenylnorbornene comonomer (Figure 17) on the properties of polypropene copolymers [I]. These experiments were done on the basis of earlier results obtained in ethene-norbornene and ethene-phenylnorbornene copolymerizations with \textit{ansa}-metallocene catalysts.\textsuperscript{102-104}

![Figure 17. Endo- and exo-isomers of phenylnorbornene.](image)

Metallocenes \textit{rac}-8 and \textit{meso}-8, 9, 10, 11 and 12 (Figure 18) showed that propene can be copolymerized with phenylnorbornene up to ratio of ca. 60/40 with moderate activity. The synthesized copolymers were amorphous or semi-crystalline with elevated glass transition temperatures. As an example with 16.7\% of phenylnorbornene feed, catalyst \textit{rac}-8 produced copolymer with 42.1\% of phenylnorbornene and a glass transition temperature of 73.3 °C.
Metallocene rac-8 was most active in copolymerizations with activity of 1930 kg/(mol_{cat}^*h). Its meso derivative meso-8 exhibited activity of 460 kg/(mol_{cat}^*h). The C₅-symmetric, 10, exhibited 40% of the activity of 1. The sterically most hindered catalyst, 11, was least active. The hafnium analogue of catalyst, rac-8, rac-ethylene-bis(1-indenyl)HfCl₂, 12, produced copolymer with activity of 320 kg/(mol_{cat}^*h).

The insertion of an incoming phenynorbornene unit requires at least one propene unit as the last inserted monomer and thus no higher than 50% comonomer can be inserted into the copolymer. The molar masses of the copolymers prepared with the zirconocenes were low due to the fast chain termination reactions after propene insertion. Hafnium analogue of rac-8, 12, produced significantly higher molar mass, but content of phenynorbornene in the copolymer remained low. Tacticities in the propene segments of the copolymers were similar to those obtained in homopolymerization with the same catalysts.

![Figure 18. Catalysts rac-8, meso-8, 9, 10, 11 and 12 as dichloride precursors.](image-url)
4.2.2 Ethene-vinylcyclohexane copolymer

Vinylcyclohexane, VCH, is a special comonomer which is pronounced to increase crystallinity in olefin copolymers. While many patents exist for ethene-vinylcyclohexane copolymers and preparation methods, only a few scientific papers have been published on this topic [IV]. Vinylcyclohexane copolymers have conventionally been prepared by two fold method: copolymerizing ethene with styrene and then hydrogenation of phenylic o-carbons of styrene to give the cyclohexane structure. Our goal was to carry out direct copolymerization of vinylcyclohexane with ethene and propene with selected metalloocene catalyst to find out characteristic features of this synthesis.

Catalyst rac-8 produced high molar mass ethene-vinylcyclohexane copolymers with high activity, but the amount of incorporated comonomer was only moderate (up to 3.5 %) even at high VCH feed concentrations (Table 4). The decrease of the molar mass at higher comonomer feeds was not as pronounced as anticipated from the findings in VCH homopolymerization.

In the FTIR spectra of the copolymers, the vinylidene peak at 888 cm\(^{-1}\) steadily increased with higher comonomer loads, indicating that termination after 1,2-insertion of the vinylcyclohexane becomes dominant. Melting temperatures and crystallinities of the copolymers decreased as a function of the comonomer content in the copolymer chain. In copolymerization solution, monomers compete for coordination to the metal center, and ethene is usually more favorably coordinated than a higher olefin. This, together with the fact that the cyclohexane ring is sterically rather bulky due to its vibrational conformations, makes VCH a difficult monomer to copolymerize and explains the low VCH incorporation. Following from this, VCH did not suppress the overall catalyst activity by blocking the free coordination site for the incoming monomer (ethene), and therefore moderately weakly coordinating VCH monomer behaved in these copolymerizations more or less like an additional solvent molecule.
Table 4. Results of the copolymerizations of vinlycyclohexane with ethene using MAO activated catalysts rac-8.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Feed, mol %</th>
<th>Activity, kgmol/(molcat*hr)</th>
<th>Mw, g/mol</th>
<th>Mw/Mn</th>
<th>VCH incorporation, % NMR</th>
<th>Peak Melting temp., °C DSC</th>
<th>Degree of crystallinity, % DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rac-8</td>
<td>0.531</td>
<td>79400</td>
<td>379100</td>
<td>2.8</td>
<td>0.51</td>
<td>129.0</td>
<td>54.5</td>
</tr>
<tr>
<td>Rac-8</td>
<td>0.703</td>
<td>109700</td>
<td>253944</td>
<td>3.68</td>
<td>1.21</td>
<td>122.7</td>
<td>43.0</td>
</tr>
<tr>
<td>Rac-8</td>
<td>0.779</td>
<td>137300</td>
<td>281016</td>
<td>3.50</td>
<td>2.92</td>
<td>123.0</td>
<td>43.6</td>
</tr>
<tr>
<td>Rac-8</td>
<td>0.825</td>
<td>79300</td>
<td>265301</td>
<td>3.14</td>
<td>3.46</td>
<td>121.5</td>
<td>41.3</td>
</tr>
</tbody>
</table>

4.2.4. Propene-vinlycyclohexane copolymer

Copolymerization of vinylcyclohexane with propene was a more challenging task than its copolymerization with ethene. In view of the prochirality of propene both regio- and enantioselective metalloccenes were chosen for the polymerization experiments. Results of the copolymerization experiments with C2-symmetric catalyst rac-8, C5-symmetric catalyst 10, asymmetric 11 and asymmetric 13 are presented in Table 5. Catalyst 13 is presented as dichloride precursor in Figure 19.

![Figure 19. Catalyst 13 as dichloride precursor.](image)

Activities of the catalysts in propene- vinlycyclohexane copolymerizations varied from good to moderate The common trend was low VCH incorporation of vinylcyclohexane in the copolymers. The highest comonomer content, 2.0%, was achieved with catalyst 13, while 10 and 11 both bearing a fluorenyl moiety, gave polymers with negligible amount of the comonomer.
In contrast to the ethene-vinylcyclohexane copolymerizations, high vinylcyclohexane loads decreased the rate of the polymerization reaction. This can be understood as follows: coordination affinities of propene and vinylcyclohexane to the cationic metal center are similar, but the insertion of the latter is less favorable, as indicated by the low vinylcyclohexane content in the copolymers.

**Table 5. Results of copolymerizations of vinylcyclohexane with propene using MAO activated catalysts rac-8, 10, 11 and 13**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>VCH feed, mmol</th>
<th>Activity, kgmol/ (mol, a*h)</th>
<th>Mw, g/mol GPC</th>
<th>Mw/Mn GPC</th>
<th>VCH incorporation, %, NMR</th>
<th>Peak Melting temp., °C DSC</th>
<th>Glass Transition Temp. DSC</th>
<th>Degree of cryst., % DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>rac-8</td>
<td>0.097</td>
<td>14583</td>
<td>39028</td>
<td>1.99</td>
<td>0.23</td>
<td>128.2</td>
<td>-4.23</td>
<td>46.6</td>
</tr>
<tr>
<td>rac-8</td>
<td>0.285</td>
<td>4914</td>
<td>49807</td>
<td>1.72</td>
<td>0.48</td>
<td>127.6</td>
<td>-13.7</td>
<td>47.5</td>
</tr>
<tr>
<td>rac-8</td>
<td>0.418</td>
<td>7472</td>
<td>51566</td>
<td>1.72</td>
<td>0.77</td>
<td>123.6</td>
<td>-12.5</td>
<td>44.0</td>
</tr>
<tr>
<td>rac-8</td>
<td>0.531</td>
<td>4278</td>
<td>41118</td>
<td>2.25</td>
<td>1.02</td>
<td>123.3</td>
<td>-9.0</td>
<td>38.2</td>
</tr>
<tr>
<td>10</td>
<td>0.289</td>
<td>2125</td>
<td>44360</td>
<td>1.7</td>
<td>&lt;0.1</td>
<td>132.6</td>
<td>-4.36</td>
<td>25.22</td>
</tr>
<tr>
<td>11</td>
<td>0.297</td>
<td>2111</td>
<td>32045</td>
<td>1.7</td>
<td>&lt;0.1</td>
<td>tactic</td>
<td>-23.9</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td>0.266</td>
<td>15401</td>
<td>61784</td>
<td>2.43</td>
<td>0.65</td>
<td>100.2</td>
<td>-5.7</td>
<td>11.00</td>
</tr>
<tr>
<td>13</td>
<td>0.426</td>
<td>3899</td>
<td>62301</td>
<td>2.15</td>
<td>2.0</td>
<td>92.45</td>
<td>-3.7</td>
<td>19.99</td>
</tr>
</tbody>
</table>

According to the enantiomorph control mechanism the repulsive interaction between the fluorenyl moiety of catalysts 10 and 11 the cyclohexyl group is strong thereby disturbing the monomer enchainment and causing the selective homopolymerization of propene.

Due to the C$_2$-symmetry of rac-8, the polymers prepared with it were clearly isotactic ([m..m..m..m..m..] above 91%) whereas the copolymers synthesized with C$_{1}$-symmetric catalyst 13 contained about 63% isotactic pentad sequences. Propene-vinylcyclohexane copolymers synthesized with catalyst 13 had also clear melting peaks at 100.2 and 92.5 °C depending on the vinylcyclohexane content.

Small amounts of vinylcyclohexane in the isotactic polypropenes affected on the melting temperature, crystallinity and glass transition temperature, but because of the alternations in the tacticities of the propene sequences the effects were not clearly recognized.
4.2.5. Ethene-hexene and ethene-hexadecene copolymers

Linear low density polyethenes (LLDPE) are the most widely produced new olefin copolymers based on metallocene technology. Commercial metallocene LLDPEs are copolymers of ethene and 1-hexene or 1-octene having up to 5% \( \text{1-olefin} \) component. Copolymerization of 1-hexene and 1-hexadecene with ethene was studied using MAO activated metallocenes 5, 6, and 11 [III].

Catalyst 5 produced very high molar mass ethene-hexene and ethene-hexadecene copolymers at low comonomer feeds, but the molar masses declined at higher feeds (Table 6). Except for catalyst 11 the activities decreased with higher comomer loads.

**Table 6.** Selected results of the copolymerization of hexene with ethene using MAO-activated catalyst 5, 6 and 11.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Comonomer Feed, mol%</th>
<th>Activity, ( \text{kg}_{\text{pol}}/(\text{mol} \text{cat} \cdot \text{h}) )</th>
<th>Molar mass/ Mw Kg/mol GPC</th>
<th>Comonomer content, mol% NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>16.7</td>
<td>29200</td>
<td>531</td>
<td>3.34</td>
</tr>
<tr>
<td>5</td>
<td>50.0</td>
<td>12900</td>
<td>199</td>
<td>10.9</td>
</tr>
<tr>
<td>6</td>
<td>16.7</td>
<td>2900</td>
<td>267</td>
<td>n.d</td>
</tr>
<tr>
<td>6</td>
<td>50.0</td>
<td>2200</td>
<td>183</td>
<td>7.86</td>
</tr>
<tr>
<td>11</td>
<td>16.7</td>
<td>3900</td>
<td>157</td>
<td>2.79</td>
</tr>
<tr>
<td>11</td>
<td>50.0</td>
<td>12100</td>
<td>54.6</td>
<td>9.27</td>
</tr>
<tr>
<td>11</td>
<td>67.0</td>
<td>19300</td>
<td>51.4</td>
<td>13.9</td>
</tr>
<tr>
<td>11</td>
<td>80.0</td>
<td>38600</td>
<td>39.7</td>
<td>21.4</td>
</tr>
</tbody>
</table>

Catalyst 11 showed unique behavior in the copolymerizations; the activity increased steadily, from 3900 to 38600 \( \text{kg}_{\text{pol}}/(\text{mol} \text{cat} \cdot \text{h}) \), with increase in the comonomer feed from 17 to 80%. Studies on 1-hexadecene copolymerizations showed the same trends as in ethene-hexene copolymerizations (Table 7). The synergetic comonomer effect in ethene- \( \text{1-olefin} \) copolymerizations is commonly known, but an unambiguous explanation for the effect has not yet been presented.\(^{106-108}\) Since this behavior is dependent on catalyst structure rather than the copolymerization conditions, the synergetic comonomer effects evidently have a mechanistic origin and are certainly the result of different steric and electronic properties of the catalysts.
Table 7: Ethene-1-hexadecene copolymerizations with catalysts 5 and 11

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Comonomer Feed, mol%</th>
<th>Activity, kgmol/(molecat*h)</th>
<th>Molar mass/ Mw Kg/mol GPC</th>
<th>Comonomer content, mol%</th>
<th>NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>16.7</td>
<td>28500</td>
<td>397</td>
<td>2.77</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>37.5</td>
<td>19400</td>
<td>224</td>
<td>6.95</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>54.5</td>
<td>6600</td>
<td>145</td>
<td>9.86</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>16.7</td>
<td>32900</td>
<td>121</td>
<td>n.d</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>37.5</td>
<td>69200</td>
<td>84</td>
<td>n.d</td>
<td></td>
</tr>
</tbody>
</table>

With all three catalysts, 5, 6 and 11 the molar mass of the copolymers decreased with increasing 1-alkene concentration. At highest comonomer feeds, 5 still produced copolymers with M_w above 100 kg/mol. Molar mass distribution values (M_w/M_n) varied from 1.8 to 3.4, which are typical for single site catalysts in copolymerizations.

Incorporation of 1-hexene to the polymer chains as a function of comonomer concentration was linear with catalysts 5 and 11, the former being more efficient in incorporating the comonomer. With catalyst 5, 1-hexene content of 17.4 mol % was achieved when 1-hexene concentration in the feed was 66.7%. When 1-hexene feed was increased up to 80%, the activity if catalyst 11 was further enhanced, but the product was wax-like polymer with 21.4% hexene incorporation. The other copolymers with high comonomer content and high molar mass were rubber-like elastic materials.

In ethene-hexene and ethene-hexadecene copolymers, the distributions of the three unsaturated end groups varied with the catalyst and the comonomer concentration in the feed. In general, the contents of the vinylidene end group (at 888 cm⁻¹ in FTIR) increased with comonomer concentration, showing that the termination after 1,2-insertion of the comonomer becomes dominant. A direct consequence of this is that the relative abundance of the vinyl end groups was decreasing strongly at higher comonomer feeds.

The end group distributions show that with catalyst 11 the relative rates for the chain termination mechanisms differ from those of 5 and 6. According to ¹H-NMR spectra, the copolymers made with 11 had a high content of saturated chain ends due to the extensive chain transfer to aluminum alkyls.¹⁰⁹
$M_n$ values the poly(ethene-co-1-hexene) copolymers were approximately twice as high when determined by FTIR as when determined by GPC, but the trends were same. In addition, trans-vinylene end groups were not present in polyethene homopolymers, but their amount increased with increasing 1-alkene concentration in copolymers. This indicates negligible possibility for chain end isomerization but instead high regioselectivity for 1-alkene comonomers. The chain transfer to aluminum alkyls alone does not explain the observed lower molar mass of the copolymer prepared with 11.

The results describing end group distributions indicates that the catalyst structure, that favors isomerization of the chain end is also capable of producing higher molar mass $\text{-}1$-olefin copolymers. The possibility for chain end isomerization decreases the overall chain termination rate via $\alpha$-H elimination.

Melting temperatures of the copolymers decreased rapidly with increasing comonomer content. Compared with the ethene-hexene copolymers, the degree of the crystallinity in the hexadecene copolymers did not show such a clear linear dependence on the comonomer content despite sharply decreased melting temperatures. At high 1-hexadecene content in the polymers, the hexadecene side chains can form small sub-crystallites, which increase the crystallinity relative to ethene-hexene copolymers.\textsuperscript{110}

### 4.3 Ultrahigh molar mass poly(1-hexene)

Hafnium analogues of ansa-zirconocenes have been found to produce higher molar mass polyolefins due to slower rate of chain termination.\textsuperscript{111} With this in mind catalyst ethylene-\textit{bis}(9-fluorenyl)HfCl$_2$, 14, (Figure 20) was investigated as polymerization catalyst for 1-hexene [V]. Activation of the catalyst with MAO/TMA led to poor catalytic productivity and low molar mass poly(1-hexene)s. Surprisingly, activation with TIBA/ borate system led to a highly active catalyst producing ultrahigh molar mass poly(1-hexene). The reason for this result was sought by studying catalyst activation with cocatalysts by UV-Vis spectrometry.
Ligand-to-metal charge-transfer (LMCT) absorptions give information about the changes of electron density around the active catalyst site. In the catalyst/cocatalyst systems examined, the absorption bands were strong and in the visible light region. The MAO/TMA activated catalyst system was blue after activation and after a certain time color became red. The TIBA/borate activated catalyst was greenish. Figure 21a shows the UV/Vis spectra of MAO activated ethylene-\textit{bis}(9-fluorenyl)HfCl$_2$ in toluene solution 10 minutes after start of the reaction with different catalyst-cocatalyst ratios. An activated ion pair was formed with an absorption maximum at 610-620 nm. Al:Hf ratios of ca. 2000 were needed to complete the complexation reaction, in agreement with expected activation of metallocene dichlorides with MAO. Shortly after this, the primary ion pair begins to decompose and a secondary complex adduct characterized by UV/Vis peak maximum at 525 nm begun to develop (Figure 21b). This reaction was completed within 24 hours at all studied Al:Hf ratios (Figure 21c) and the absorption peak at 610-620 nm vanished.
When monomer coordination to the complex was investigated by adding 1-hexene to the solution, no change was detected in the spectrum indicating that the reversion to the primary complex didn't take place. This was regarded as an evidence for the stability of the secondary complex adduct causing the poor polymerization capability of these species.

The activation/deactivation process with TIBA/borate cocatalyst was different. With TIBA, hafnocene dichloride forms a monoalkylated complex as indicated by a minor shift to the shorter wavelengths in the UV/Vis absorption (Figure 22d). When a stoichiometric amount of borate is added to the solutions, a fast and complete reaction takes place and an active alkylated ion pair is formed absorbing at same wavelength region (595-620 nm) as the primary MAO/TMA complex (Figure 22e). Compared with MAO/TMA complex, the borate ion pair is far
more stable. Only a very minor shift towards shorter wavelengths was detected after aging of the solution 24 hours with Al:Hf ratio of 30.

**Figure 22**: Activation of the hafnocene catalyst precursor with TIBA/borate system: d) hafnocene/TIBA with Al:Hr ratios of 0, 30, 100 and 300 after one hour of the reaction start. e) hafnocene/TIBA/borate at Al:Hf ratios of 30 after 0min, 11min, 60min and 24h of the reaction start. f) hafnocene/TIBA/borate at Al:Hf ratios of 300 after 1h, 24h, and 96h of the reaction start

Further aging of the catalyst/TIBA/borate solution for many hours resulted in the formation of secondary catalyst adducts absorbing at 535 nm. Even after these long experiments the absorbance at 590-610 nm did not completely disappear. The rate of formation of the secondary complex adduct is related to the TIBA concentration; the formation of secondary alkyl adduct and at higher TIBA concentrations was faster (Figure 22f). Nevertheless the increase of absorbance at 535 nm with the Al:Hf ratio of 300 was not detected before several hours. Addition of 1-hexene to this solution after 4 days caused further increase of the active ion pair peak at 610 nm. The decrease of the peak at 535 nm show that 1-hexene is able to shift the equilibrium from the inactive adduct to the active ion pair species (Figure 23g)
1-hexene stabilizes the complex by holding the equilibrium at the active species. This was seen in the UV-Vis Spectra of the catalyst system where the monomer was added simultaneously with TIBA and borate (Figure 23h and, 23g). With higher TIBA concentrations the stability of the active species is higher. With Al:Hf ratio of 300 no increase of the absorbance at 535 nm was detected earlier than 48 hours (figure 23h). During these last two experiments, the 1-hexene was polymerized and no monomer induced decrease in the stability of active catalyst ionpair was detected.

The TIBA/borate activation shows that the primary hafnium catalyst species that was formed during the activation absorbs at low energy band at 595-610 nm indicating a weakly coordinating borate ion pair. These may be the source of the high activity of the borate-activated catalyst. The borate-catalyst ionpair is also very stable against deactivation by alkylating agent TIBA. The formation of the secondary catalyst adduct characterized by the absorption peak at 535 nm was extremely slow. TIBA is not able form this complex alone and evidently this secondary complex adduct is a result of slow arrangement of the primary borate ionpair and coactivator
TIBA. Another interesting finding is also that the moderately bulky monomer, 1-hexene, is able to transfer the equilibrium from the inactive TIBA/borate adduct back to the active borate ion pair.
5. Influence of the catalyst structure on the polymerization and the polymer

The structure-property relationship was regarded most interesting aspect when new polyolefin materials were developed using metallocene catalysts 1-14. In this work was noticed that moderately small variations in catalyst structures affected markedly on the polymerization activity and changed noticeably properties of the polymers and the copolymers.

5.1 Catalyst activity

Catalysts activity is highly dependent on the catalyst properties and the polymerization conditions. Electronically MAO or borate activated zirconocenes are the most effective in group IV Cp2-metallocenes in polymerizing olefins. Increasing or decreasing the electron density at the M+ cation by different ligand substitutions does not increase catalytic activity by straightforward manner. Changing one parameter in the ligand environment alters the chemistry of the whole active catalyst complex.

Electron density of the metal center should be optimal, neither too low nor too high, to achieve good catalytic activity. Final electron density on the metal is defined by alkylation of the complex and the repulsive effects of the non-coordinating cocatalyst species. Ligand to metal charge transfer processes followed by UV-Vis spectroscopy showed that TMA, TIBA, MAO and borate anion all have characteristic effect on the electron density of the metal. With catalyst 14, highest activities were achieved with TIBA alkylation and borate counterion.

Orientation of the ligands in active complexes has an effect on the activity. In benzyl-substituted zirconocenes 1-4 intramolecular coordination of the phenyl substituent decreases the activity and the effect is apparently simple steric hindrance. The experiments with the catalysts rac-4 and meso-4 revealed that as well inductive effect of an electronegative fluoro substituent reasonably far from the metal changes the activity. A fluoro substituent at benzyl draws electrons from the metal by inductive effect via indenyl thus, weakening phenyl coordination and
giving ethene slightly more favorable access to the catalytic site. This result in somewhat higher activities of the fluoro complexes especially at high ethene feeds, although the effect of single fluoro substituent in indenyl is small.

The ethyl spacer between the phenyl group and the indenyl in catalyst 4 enhances the activity in ethene polymerization. This is a consequence of the prohibited phenyl coordination but also of the capability of the phenyl moiety to prevent cocatalyst species from too tight coordination to the active metal center.

Coordination of MAO/TMA species to the methoxy group close the catalytic center in catalysts rac-2 and meso-2 decreases activity dramatically and gives rise to chain transfer to the cocatalyst species.

The high activities of catalysts 5, 6 are probably the result of several factors. Catalyst 5, in particular, is sterically open enough for coordination of higher olefins to achieve good activity. The fused aromatic ring system around active metal center in 5 and 6 stabilizes the catalyst and protects it from poisoning and deactivation.

In copolymerizations with metallocones, the activity is determined by the coordination affinity and the rate of insertion of monomers and comonomers. The comonomer with lower rate of insertion defines the overall reaction rate. In propene- phenylnorbornene copolymerization bulky phenylnorbornene coordinates easily but inserts after a delay resulting in decreased activity but high phenylnorbornene content in the copolymer. Unfavorable coordination and slow insertion of vinylcyclohexane in turn did not prohibit coordination and insertion of ethene (or propene) but produced with high activities copolymers with very low content of vinylcyclohexane.

5.2 Molar mass

Highest molar mass, up to 4.0*10^6 g/mol was achieved with catalyst 14 when activated with TIBA/borate system. The low molar mass with MAO/TMA as cocatalyst can be explained by the fast chain transfer to coordinated TMA. When bulkier TIBA was used, the chain transfer to catalyst was not favorable due to the very weak coordination of TIBA to the active metal center. On the other hand also orientation of α-hydrogens in growing polyhexyl chain end did not promote fast α-
hydrogen eliminations. As the final molar mass is a result of many parameters (rates of chain propagation and termination and electron density of metal) it is impossible to estimate molar mass development without actual polymerization experiments.

The high molar mass of the polymers prepared with catalysts 5 and 6 resulted from prohibited direct α hydrogen elimination which in turn increased the possibility for the chain end isomerization. When ethene or propene is copolymerized with a higher olefin the decrease in molar mass is usually significant. Some monomers like norbornenes do not directly induce α hydrogen elimination due to the steric hindrance of lone α hydrogen in the bicyclo structure (Figure 24). Low molar mass of propene-phenynorbornene was attributed by the fast chain termination after propene insertion and was certainly affected by phenynorbornene units close to the last inserted propene.

![Figure 24: Schematic presentation of the steric hindrance for α hydrogen elimination in the inserted phenynorbornyl unit at the active meso-8 catalyst.](image)

### 5.3 Molar mass distribution (polydispersity)

Polydispersities of the prepared polyethenenes varied from 1.9 to 10.3 with the used catalysts. Catalyst 4 produced polyethenenes with the narrowest polydispersity values indicating optimal single-site polymerization behavior. Polydispersity was slightly increased with catalysts 1, 4, 5, 6 and 11 varying
between values of 2-4. Polydispersities were increased with rac-3 and meso-2 (4.2-4.5) indicating two or several active sites in the catalyst.

Methoxy substituted rac-2 produced polyethenes with exceptionally broad polydispersity values (6-10). The coordination of cocatalyst species on the methoxy oxygen, particularly with rac-2, can give rise to catalysts structures with several different ligand environments (Figure 25). In the case of its meso-derivative, meso-2, MAO species could be captured only one side explaining the narrower polydispersity values.

![Figure 25: Possible coordination sites for MAO species on the methoxy group in the active catalyst meso-2 (left) and rac-2 (right).](image)

1-Hexene polymerization with TIBA/borate activated catalyst 14 showed optimal polydispersity values of 1.8-2.0 In copolymerization experiments where steady state copolymerization conditions were achieved molar mass distributions were generally fairly close to the theoretical value of 2.0 but varied between values of 1.6 and 3.0

5.4 Tactility and regioregularity.

Steric factors in the catalyst structure can change the tacticity of the polymer in a dramatic way. With the catalyst systems investigated the polypropene segments in copolymers were syndio- or isotactic following the characteristic stereoregular homopolymerization of the catalyst. In propene-phenylnorbornene copolymers propene segments were isotactic with catalyst rac-8 and atactic with
catalyst 11 indicating the neutral effect of the phenylnorbornene unit on the stereoselectivity of the active catalyst. Findings were similar for propene-vinylcyclohexane copolymers.

Catalyst 11 was found to be exceptionally regioselective in ethene-1-hexene and ethene-1-hexadecene copolymerizations. An extremely low content of trans-vinylene chain ends indicated that 2,1-insertion of the incoming comomer was exceptionally unfavorable.

5.5 Chain end groups

Terminal chain end structures offer information about the termination mechanisms. Different chain end structures in polyethenes indicated that chain termination can take place with different ways. Vinyl chain end was a result of the α-hydride elimination and trans-vinylenes indicated chain end isomerization. A rare vinylidene chain end in polyethenes pointed possible 2,1-insertion of in situ formed macromonomer (oligomeric or low molar mass polyethylene chain released earlier from the active center) and a possible origin for long chain branches.

Chain termination is a highly sensitive reaction step in homo- and copolymerizations using metallocene catalysis. Distribution of the chain ends varied in polyethenes between used metallocene catalysts. Comonomers accelerate chain termination and generally the content of vinylidene chain end increases with the feed of the 1-olefin monomer. In the copolymerization of 1-hexadecene with ethene with catalyst 5 the content of trans-vinylenes increased also by the chain end isomerization caused by the 2,1-insertion of the comonomer.

6. Conclusions

Metalloocene catalysis has vastly enhanced the tailoring of polyolefin properties. According to our experiments with these metalloocene catalysts (Scheme 8), primary polymer properties such as molar mass and comonomer content can be adjusted through changes in the catalyst, cocatalyst, comonomer and polymerization setup.
The advantages of metallocene technology are many. Metallocene catalyst synthesis is relatively easy to perform using standard vacuum techniques in laboratories. Almost infinite ligand variations are possible and catalyst structures can be accurately resolved by X-ray crystallography. The single site feature provides exact control of the forming chain structure, making possible the preparation of highly stereo- and regioregular polymers. The strong coordination affinity of higher $\eta^1$-olefins to the activated metallocene catalysts provides excellent copolymerization properties and a broad selection of acceptable comonomers.

Single site catalysis promotes more complete use of monomers during the polymerization process and the final products are free from low molar mass oligomeric components. Catalytic activity of the best metallocenes is tremendous which means low catalyst cost per tonne of produced polymer and a product with extremely low amount of catalyst residuals. Two bottlenecks in the wider use of the metallocene technologies are the complex patent right issues and the utilization of industrial processes developed for heterogeneous Ziegler-Natta catalysts.

Scheme 8. Metallocene toolbox used in the polymerization experiments of this work.
7. References:

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Appendix: Chart of used metalloocene catalyst precursors

[rac-1]  [rac-2]  [rac-3]  

[meso-1]  [meso-2]  [meso-3]  

[rac-4]  [5]  [6]  

[rac-8]  [meso-8]  [9]  [10]  

[11]  [12]  [13]  [14]