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**STRUCTURE-PROPERTY CORRELATIONS IN
METALLOCENE-CATALYZED OLEFIN HOMO-
AND COPOLYMERIZATION**

Doctoral Dissertation

Tanja Piel (née Seraidaris)



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Department of Chemical Technology
Laboratory of Polymer Technology**

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Abstract			
<p>The need for higher value-added materials has expanded the market for metallocene-catalyzed polyolefin products. The attractive features of metallocene polyethylene and polypropene are the uniform polymer structures, even comonomer and molar mass distribution, controlled molar mass and the possibility to tailor the polymer microstructure, and thereby the material properties, by modifying the catalyst structure.</p> <p>The focus of this thesis was on understanding of the structure–property relations in metallocene–catalyzed olefin polymerization. The polymerization process – activation, propagation, chain transfer and isomerization reactions – was examined for propene and ethene. The influence of the central metal atom on the activity of the catalyst and the molar mass and stereoselectivity of the polymer was studied and the influence of the leaving ligands, aluminum alkyls, and cocatalyst on propene polymerization behavior was investigated. The activity of the catalyst was improved by pre-alkylation with TMA or TIBA and pre-activation with MAO. UV/Vis and NMR spectroscopy revealed the formation of similar active species in the reaction of zirconocene complex with MAO regardless of the leaving ligands. The same result, but with different active species, was obtained in the reaction of zirconocene with [Me₂HNPPh]⁺[B(C₆F₅)₄]⁻/TIBA: leaving ligands did not significantly affect the structure of the active species. The cocatalyst had a significant effect on the catalyst activity and in some cases also on the molar mass of the polymer. The microstructure and thus the thermal behavior of the polypropene were dependent on the cocatalyst.</p> <p>Syndiotactic polypropene was rendered more elastic by copolymerizing a small amount of ethene into the syndiotactic polypropene chain. Copolymers of propene with very low ethene content were produced in liquid propene. High molar mass elastic polypropene was synthesized with the hafnocene/borate catalyst. The microstructure of the polymer and the mechanical properties were defined.</p>			
Keywords activation, cocatalyst, coordination polymerization, polyethylene, polypropene			
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<p>Parempien materiaaliominaisuuksien tarve on avannut markkinoita metallooseeni katalysoiduille polyolefiinituotteille. Metallooseeni polyeteenin ja polypropeenin hyötyjä ovat esimerkiksi yhtenäinen polymeerirakenne ja komonomeerijakauma, kapea moolimassajakauma ja säädettävissä oleva moolimassa. Polymeerin rakennetta ja siten materiaaliominaisuuksia on mahdollisuus räätälöidä muuttamalla katalyytin rakennetta.</p> <p>Tämän työn painopiste on rakenne-ominaisuus korrelaatioiden ymmärtämisessä metallooseeni katalysoidussa olefiinien polymeroinnissa. Polymerointiprosessin tutkiminen; aktivointi, polymeeriketjun kasvu, ketjunvaihto- ja isomerointireaktiot eteenin ja propeenin polymeroinnissa ovat työn keskeisessä osassa. Metallin vaikutusta tutkittiin katalyytin aktiivisuuteen, stereoselektiivisyyteen sekä polymeerin moolimassaan. Propeenin polymeroinnissa käsiteltiin lähtevien ligandien, alumiinialkyylien sekä kokatalyytin vaikutusta. Katalyytin aktiivisuuden huomattiin parantuvan, jos se esikäsiteltiin TMA:lla tai TIBA:lla tai esiaktivoitiin MAO:lla. UV/Vis ja NMR spektroskopiolla pystyttiin todistamaan, että aktiiviset keskukset, jotka muodostuvat zirkonoseenin ja MAO:n reaktiossa, olivat samanlaiset huolimatta erilaisista lähtevistä ligandeista. Sama ilmiö havaittiin zirkonoseenin reaktiossa $[Me_2HNPh]^+[B(C_6F_5)_4]$ (boraatti) kokatalyytin kanssa. MAO:n ja Boraatin kanssa muodostuneet aktiiviset keskukset olivat tosin keskenään erilaiset. Kokatalyytillä oli merkittävä vaikutus katalyytin aktiivisuuteen ja joissain tapauksissa myös polymeerin moolimassaan. Myöskin polypropeenin mikrorakenne ja siten lämpökäyttäytyminen olivat riippuvaisia käytetystä kokatalyytistä.</p> <p>Syndiotaktisen polypropeenin ominaisuuksia modifioitiin elastisemmaksi kopolymeroimalla pieni määrä eteeniä polypropeeniketjuun. Syndiotaktisen polypropeenin ja eteenin kopolymeerejä tehtiin käyttäen nestemäistä propeenin reaktioluoksena. Hafnoseeni/boraatti katalyytillä syntetisoitiin elastista polypropeenin, jonka mikrorakennetta ja mekaanisia ominaisuuksia tutkittiin.</p>	
Asiasanat aktivointi, kokatalyytti, koordinaatiopolymerointi, polyeteeni, polypropeeni	
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ABSTRACT

The need for higher value-added materials has expanded the market for metallocene-catalyzed polyolefin products. The attractive features of metallocene polyethylene and polypropene are the uniform polymer structures, even comonomer and molar mass distribution, controlled molar mass and the possibility to tailor the polymer microstructure, and thereby the material properties, by modifying the catalyst structure.

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Syndiotactic polypropene was rendered more elastic by copolymerizing a small amount of ethene into the syndiotactic polypropene chain. Copolymers of propene with very low ethene content were produced in liquid propene. High molar mass elastic polypropene was synthesized with the hafnocene/borate catalyst. The microstructure of the polymer and the mechanical properties were defined.

PREFACE

The experimental work for this thesis was carried out in the Laboratory of Polymer Technology at Helsinki University of Technology (HUT) between the years 2001 and 2005. A research period from February 2003 to March 2004 was spent in the group of Professor Kaminsky at the University of Hamburg (UH). The funding by TEKES, Borealis, Finnish Cultural Foundation and Neste Foundation is gratefully acknowledged.

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To my dear husband Christian, thank you for all the great moments together, your love and support. You and Justus bring so much joy into my life.

Gothenburg, April 2007

Tanja Piel

CONTENTS

LIST OF PUBLICATIONS	10
NOMENCLATURE	12
1 INTRODUCTION	14
1.1 Background.....	14
1.2 Description of the metallocene structure.....	15
1.3 Scope of the thesis	17
2 ACTIVATION OF METALLOCENE COMPLEXES AND ACTIVITY OF THE FORMED CATALYSTS	20
2.1 Leaving ligands.....	22
2.2 Aluminum alkyls	24
2.3 Cocatalysts.....	25
2.3.1 MAO	25
2.3.2 Boron-based cocatalysts.....	26
2.3.3 Effect of cocatalyst on catalyst activity and molar mass of the polymer.....	26
3 PROPAGATION AND CHAIN TRANSFER REACTIONS.....	29
3.1 Propagation reactions	29
3.2 Chain transfer and isomerization reactions	29
4 CHOICE OF THE CENTRAL METAL ATOM TITANIUM, ZIRCONIUM OR HAFNIUM	33
5 SYNDIOTACTIC POLYPROPENE AND ITS COPOLYMERS WITH ETHENE.....	35
5.1 Molar mass	36
5.2 Ethene incorporation.....	36
5.3 Microstructure of homo- and copolymers.....	37
5.4 Thermal behavior	38
6 ELASTIC POLYPROPENE	40
6.1 Microstructure of the polypropenes	41
6.2 Mechanical properties	43
7 CONCLUSIONS.....	46
REFERENCES.....	48

Appendices

Papers I-VI

LIST OF PUBLICATIONS

- I. Seraidaris, T., Mäkelä-Vaarne, N., Löfgren, B., Lehmus, P., Stehling, U. Activation and Polymerisation of *ansa*-Metallocene Chloroamido Complexes, *Macromol. Chem. Phys.* **205** (2004) 1064-1069.
- II. Seraidaris, T., Helaja, T., Vanne, T., Mäkelä-Vaarne N., Löfgren, B. Reactions of $\text{Me}_2\text{Si}(2\text{-Me-4,5-BenzInd})\text{Zr}(\text{Cl})(\text{NEt}_2)$ and $\text{Me}_2\text{Si}(2\text{-Me-4,5-BenzInd})\text{ZrCl}_2$ with TMA and MAO: Correlation of Spectroscopy and Propene Polymerizations, *Journal of Polymer Science Part A: Polymer Chemistry* **43** (2005) 6455-6464.
- III. Seraidaris, T., Kaminsky, W., Löfgren, B., Seppälä, J.V. Propene-Ethene Copolymers Synthesised with C_s -Symmetric Metallocenes and Different Cocatalysts, *Macromol. Chem. Phys.* **206** (2005) 1319-1325.
- IV. Seraidaris, T., Kaminsky, W., Löfgren, B., Seppälä, J.V. Copolymerization of Propene with Low Amounts of Ethene in Propene Bulk Phase, *Polymer* **47** (2006) 107-112.
- V. Seraidaris, T., Puranen, A., Karesoja, M., Repo, T., Löfgren, B., Seppälä, J.V, Leskelä, M. High Molar Mass Polypropene with Tunable Elastic Properties by Hafnocene/Borate Catalysts, *Journal of Polymer Science Part A: Polymer Chemistry* **44** (2006) 4743-4751.
- VI. Piel, T., Saarinen, T., Kokko, E., Maaranen, J., Pitkänen P., Löfgren, B. Effect of Metallocene Structures on their Performance in Ethene Polymerisation, *Macromol. Chem. Phys.* **208** (2007) 863-873.

The author's contribution to the appended publications

Publication I

Tanja Piel (née Seraidaris) planned the experiments with the coauthors and carried out the polymerization experiments and the polymer analysis. The UV/Vis measurements and preparation of the manuscript were done together with Nora Mäkelä-Vaarne.

Publication II

Tanja Piel participated in the planning work and carried out the polymerization experiments and the polymer analysis. The manuscript was written jointly with the coauthors.

Publications III and IV

Tanja Piel prepared the research plan under the supervision of Professor Kaminsky, carried out the experiments and characterization of the polymers, and wrote the manuscript.

Publication V

Tanja Piel drew up the research plan together with Arto Puranen, Timo Repo, and Barbro Löfgren and carried out the polymerizations as well as polymer characterization. DMA measurements were done under the guidance of Mikko Karesoja. The manuscript was written jointly with the coauthors.

Publication VI

Tanja Piel drew up the research plan together with Esa Kokko and Janne Maaranen, carried out the polymerizations and wrote the major part of the manuscript.

NOMENCLATURE

Al	aluminum
AlR ₃	aluminum alkyl
Cp	cyclopentadienyl
DMA	dynamic–mechanical analysis
DSC	differential scanning calorimetry
ePP	elastic polypropene
EtOH	ethanol
Flu	fluorenyl
FTIR	Fourier transform infrared spectroscopy
HCl	hydrochloric acid
ⁱ Bu	isobutyl
iPP	isotactic polypropene
Ind	indenyl
L	ligand
LMCT	ligand to metal charge transfer
M	metal
MAO	methylaluminoxane
Me	methyl
Mn	number average molar mass (kg/mol)
Mw	weight average molar mass (kg/mol)
MWD	molar mass distribution
NMR	nuclear magnetic resonance spectroscopy
Ph	phenyl
P-E	propene–ethene
PE	polyethene
PP	polypropene
R	alkyl chain
SAXS	small angle X-ray scattering
SBS	styrene–butadiene–styrene block copolymer
SEBS	styrene– (ethene–butene) –styrene block copolymer
sPP	syndiotactic polypropene

SSA	successive self-nucleation and annealing
^t Bu	tertiary butyl
T _c	crystallization temperature
TEA	triethyl aluminum
T _g	glass transition temperature
TIBA	tri-isobutyl aluminum
T _m	melting temperature
TMA	trimethyl aluminum
TPE	thermoplastic elastomer
UV/Vis	ultraviolet/visible

1 INTRODUCTION

1.1 Background

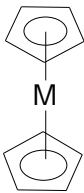
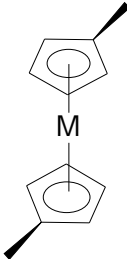
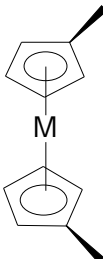
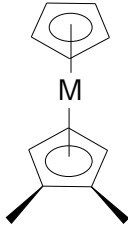
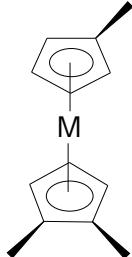
Polyethene (PE) was first produced with metallocene catalyst in 1957, when ethene was polymerized with $\text{Cp}_2\text{TiCl}_2/\text{AlEt}_3$ and $\text{Cp}_2\text{TiCl}_2/\text{AlEt}_2\text{Cl}$.^{1,2} The activity of these soluble catalyst systems was too low for industrial use, however, and the finding did not excite great attention. The real breakthrough of metallocene catalysts occurred in the early 1980s when Sinn and Kaminsky³ reported the extremely active polymerization of ethene with Cp_2TiCl_2 and Cp_2ZrCl_2 activated with methylaluminoxane (MAO). MAO, which is partially hydrolyzed trimethyl aluminum (TMA), is able to activate metallocenes in the polymerization of both ethene and α -olefins. MAO-activated Cp_2ZrCl_2 produced high molar mass PE and polypropene (PP) with good activity, but stereocontrol of the PP was lacking; the produced PPs were totally atactic.⁴

The first *ansa*-metallocene, producing isotactic PP (iPP), was *rac*-Et(Ind)₂TiCl₂ developed by Brintzinger's group⁵ in 1982. The research on metallocene catalysts quickly picked up speed and metallocenes with different ligand structures were developed. There have been two clear milestones in metallocene catalyst research. First it was found that alkyl substituents in cyclopentadienyl (Cp) ligands have a dramatic effect on catalyst activity and polymer microstructure as well as on polymer molar mass.^{6,7} Subsequently, it was found that use of *ansa*-metallocene structures makes it possible to control the enantioselectivity in α -olefin insertion.^{8,9} In 1985, Kaminsky and Brintzinger⁹ published the polymerization of highly isotactic PP with the pure racemic diastereomer of Et(IndH₄)₂ZrCl₂ as catalyst and MAO as cocatalyst. This discovery showed the possibility of tailoring the polymer microstructure and creating polymer products with improved material properties, such as better transparency, higher impact strength, stiffness, flexibility, or elasticity. Since then, both academic and industrial research groups have been highly effective in the development of controlled olefin polymerization systems, based on specific metallocene catalysts.

The industrial production of metallocene-catalyzed polyolefins has been relatively slow considering the huge research efforts. The main hindrances have been the difficulties in the processing of unimodal polymers and the complex immaterial rights. However, the growing demand for new material properties has accelerated the launch of metallocene polyolefins. The advantages of metallocenes are the possibilities they offer for homogeneous homo- and copolymer structures, controlled unimodal or bimodal molar mass distributions, and tailoring of polymer properties. Today about 10 % of PE and less than 3 % of PP produced worldwide are made using metallocenes. The trend is to build plants of high capacity which, at least in some cases, reduce the price of the product.

1.2 Description of the metallocene structure

An important advantage of metallocene catalysts is that polymer microstructure and thereby the material properties, can be tailored by modifying the catalyst structure. The configuration of the catalyst determines the stereoselectivity of monomer insertion and thus the stereochemistry of the polymer. Ewen and coworkers^{6,10-12} and Kaminsky and coworkers⁹ described a series of stereoselective metallocenes. The results have been collected together as “Ewen’s Symmetry Rules”, which summarize how the symmetry of the metallocene affects the stereochemistry of the formed poly(1-olefin) (Scheme 1).¹³

Symmetry		Sites	Polymer
C_{2v} Achiral		A,A Homotopic	Atactic
C_2 Chiral		E,E Homotopic	Isotactic
C_s Achiral		A,A Diastereotopic	Atactic
C_s Prochiral		E,-E Enantiotopic	Syndiotactic
C_1 Chiral		E,A Diastereotopic	Hemi-isotactic

Scheme 1. Ewen's Symmetry Rules. E = enantioselective site, A = nonselective site. Leaving ligands have been omitted for clarity.

Metallocene active species contain two active sites previously occupied by leaving ligands of the metallocene precursor. The last inserted monomer unit changes the nature of the corresponding site. If the monomer can coordinate to just one site, a limited number of polymer microstructures will be obtained. C_2 -Symmetric *ansa*-metallocenes produce isotactic PP by enantiomorphic control mechanism.^{9,14} There are many modifications of the ethyl-bridged bis(tetrahydroindenyl)zirconium dichloride complex designed by Kaminsky and Brinzinger working by the same mechanism. Use of these complexes makes possible a wide range of polymers with different isotacticities and molar masses.¹³ C_s -symmetric metallocenes have two coordination sites with enantiotopic nature, which leads to chain end control mechanism and the emergence of syndiotactic polymer chain.¹⁰ C_1 -symmetric metallocenes, in turn, have two diastereotopic coordination sites, which allows the stereochemistry of the monomer insertion to change from syndiotactic polypropene to the production of hemi-isotactic polypropene,^{10,15} and with certain ligand substitutions even to isotactic polypropene.¹⁶ Metallocene complexes possessing two nonselective sites produce mainly atactic polypropene. Closer examination of the matter reveals that with certain metallocene structures an aspecific site can convert to its isospecific state through a back-skip of the polymer chain.¹³ If the chain back-skip reaction is faster than the monomer insertion in the aspecific site, the polymer will be rich in isospecific insertions. These are only a few examples of the many polymer microstructures that can be created with use of metallocene catalysts.

1.3 Scope of the thesis

Understanding of the structure-property relations in metallocene-catalyzed olefin polymerization is essential in the development of new polymer materials, such as PP with properties like those of stiff plastomers and thermoplastic elastomers. The aim of this work was, on the one hand, to provide information about matters affecting the polymerization process – activation, propagation and chain transfer reactions – and, on the other, to explore the ways of modifying the material properties of polypropene through tailoring the metallocene structure and selecting appropriate experimental conditions. The thesis summarizes the results of the appended six publications. Chapter 2 discusses metallocene activation and the factors influencing the activation reactions. The influence of leaving ligands on the metallocene, aluminum alkyls, and cocatalysts on propene polymerization behavior is investigated.^{I,II} UV/Vis^{I,II} and

NMR^{II} spectroscopy are used to characterize the active species. Chapter 3 describes the propagation, isomerization, and termination reactions in ethene^{VI} and propene^I polymerization. The effect of the cocatalyst on the activity and molar mass of the polymer was considered.^{I,III,IV} Chapter 4 focuses on the influence of the central metal atom on catalyst activity, molar mass,^{VI} and stereoselectivity in propene polymerization.^{III} Chapter 5 deals with syndiotactic propene and its copolymers with ethene synthesized with C_s -symmetric metallocenes using different cocatalysts.^{III,IV} The factors contributing to molar mass, comonomer incorporation rate, polymer microstructure and thermal behavior are discussed. Chapter 6 presents a hafnocene/borate catalyst for the production of elastic polypropene.^V The microstructure of the polypropenes as well as the mechanical properties are described. The main results of the work are summarized in Chapter 7. The metallocene complexes employed are depicted in Figure 1.

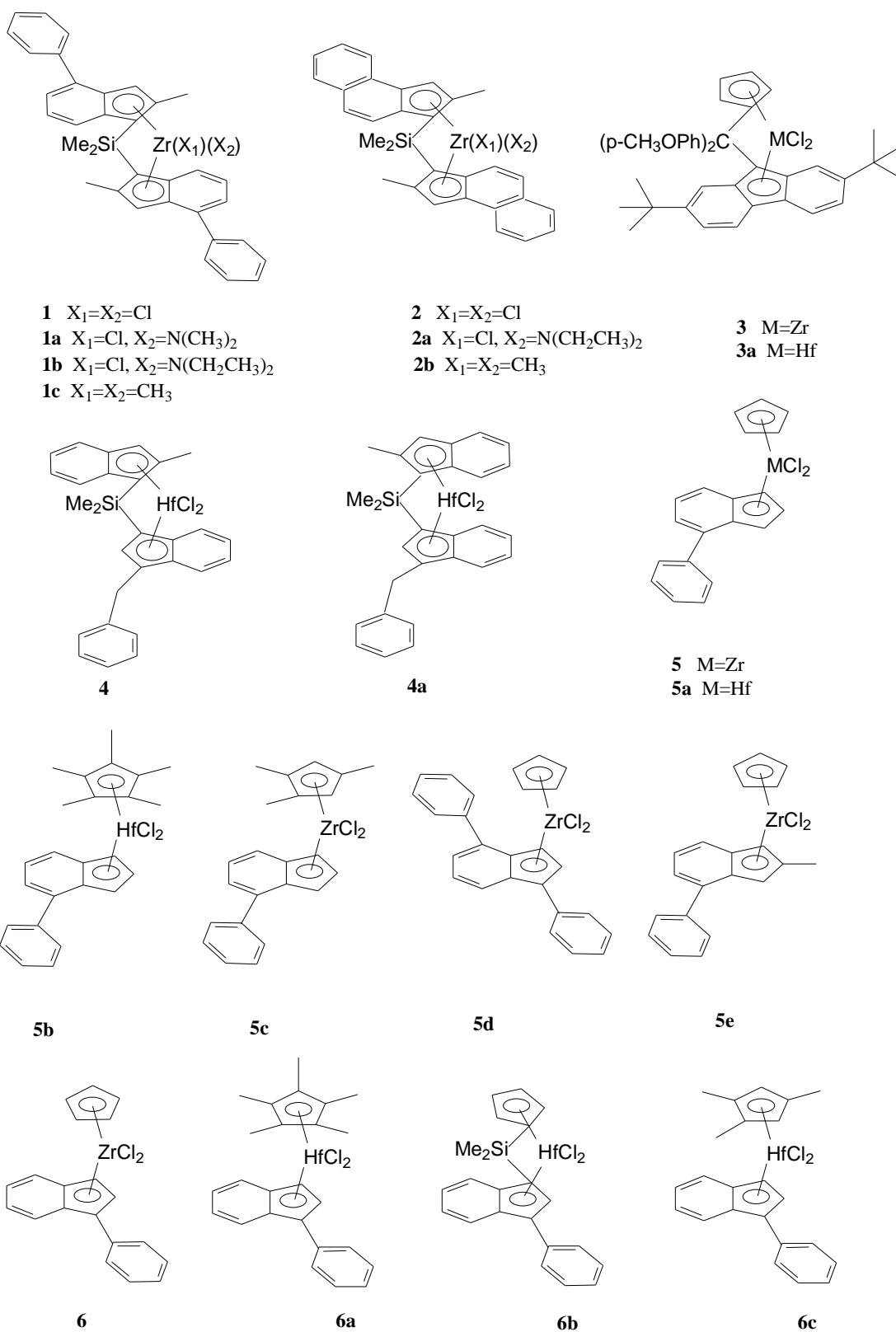
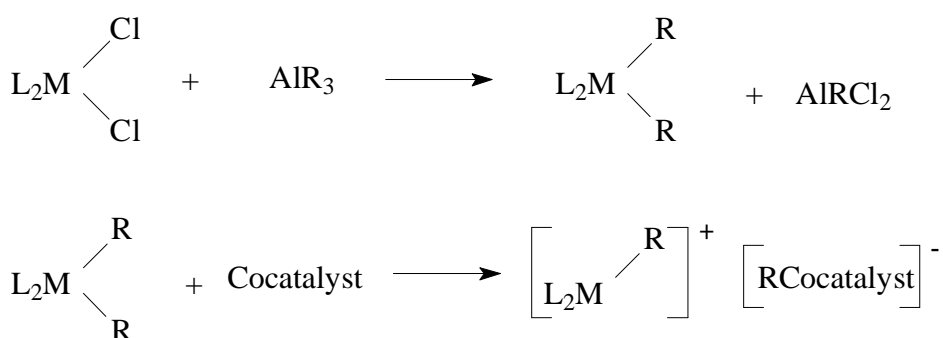


Figure 1. Metallocene complexes used in the study.

2 ACTIVATION OF METALLOCENE COMPLEXES AND ACTIVITY OF THE FORMED CATALYSTS

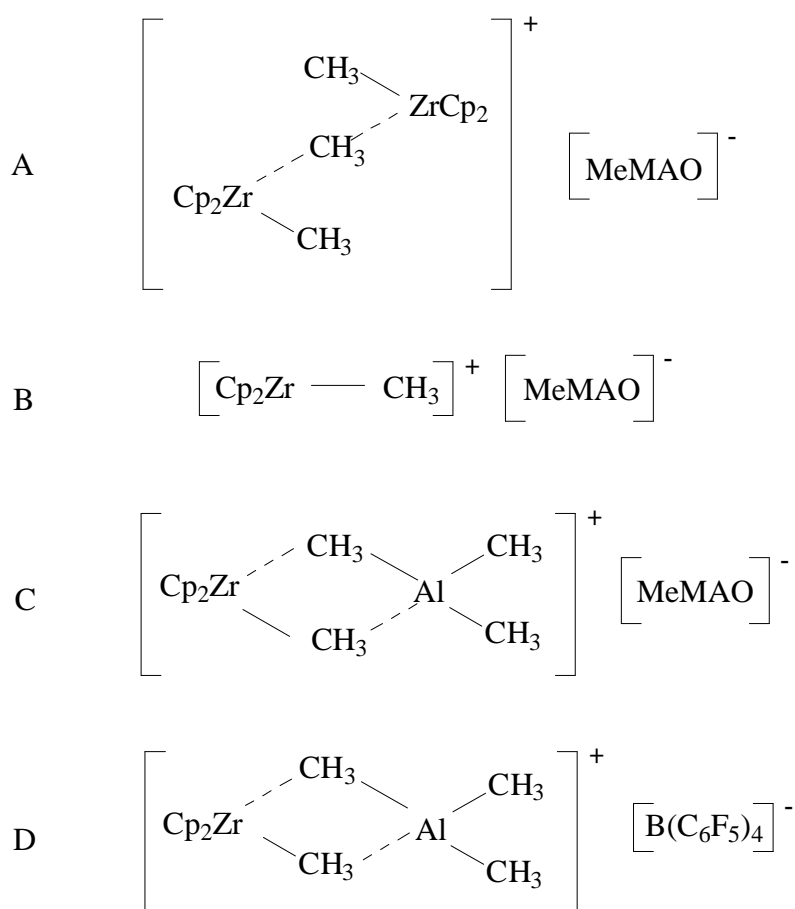
The formation of an active metallocene catalyst requires a metallocene precursor and an activating cocatalyst. Activation consists of two steps: alkylation of the initial complex by aluminum alkyl followed by cationization with a suitable Lewis acidic cocatalyst. The activated catalyst is electron deficient and a counter-anion is required to stabilize its structure. The general activation route for metallocene dichloride is shown in Scheme 2.



Scheme 2. Alkylation of metallocene dichloride with AlR_3 compound followed by cationization with Lewis acidic cocatalyst.

Many variables contribute to the activation process: structure of the metallocene, type and amount of the aluminum alkyl and cocatalyst and the reaction conditions. The exact structure of the active species has been of interest of several groups because knowing this would lead to an understanding of the activity of the catalyst and the molar mass and microstructure of the polymer.¹⁷⁻²² Metallocene dichlorides form monoalkyl monochloride complexes in reaction with aluminum alkyls or MAO at low Al/M ratios. Dialkylated complexes are formed with aluminum alkyls at high Al/M ratios.¹ In the reaction of Cp_2ZrMe_2 with MAO, binuclear μ -methyl complex A and a monomeric species B are formed, as shown in Scheme 3. At low Al/Zr ratios, the prevailing product is A, and when the Al/Zr ratio is increased, the trimethylaluminum (TMA)-complexed species C appears.²¹ The proportion of B increases as temperature and Al/Zr ratio increase toward the experimental laboratory polymerization conditions, suggesting that B is the active species in polymerization. The tightness of

the ion-pair $[L_2MR]^+[RCocatalyst]^-$ depends on the ligand structure, cocatalyst and the experimental conditions and has a marked effect on catalyst activity. The binuclear μ -methyl complex A is inactive as such, but it dissociates during the polymerization into Cp_2ZrMe_2 and monomethyl species B.^{23,24} The TMA-complexed C may also be dormant. It can dissociate into monomeric $[Cp_2ZrMe]^+[MeMAO]^-$ and free TMA. The same TMA-complexed structure is found in the reaction of Cp_2ZrMe_2 with $[Ph_3C]^+[B(C_6F_5)_4]^-$ and TMA (D in Scheme 3).²⁴ It is worth mentioning that there is a dynamic equilibrium in metallocene/ AlR_3 /MAO solution, and the proportion of a particular species is highly dependent on the reaction conditions.



Scheme 3. Species formed in the reaction of Cp_2ZrMe_2 with MAO (A–C) and Cp_2ZrMe_2 with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (D).

2.1 Leaving ligands

Leaving ligands play an important role in the activation process. To date group 4 zirconium dichlorides of type L_2ZrCl_2 have been the most frequently used metallocenes.^{13,25} However, the abstraction of the two chloride anions requires an excess of aluminum alkyl or MAO and the abstracted chloride anion can form a tight ion-pair with the zirconium vacant site, hindering the olefin coordination and insertion.²⁶ Jordan and co-workers^{27,28} have synthesized several C_2 -symmetric bis-amido zirconocenes. The advantage of these complexes is that they are relatively easy to synthesize by an amine elimination route and they can be activated by initial alkylation with AlR_3 reagents and subsequent reaction with MAO or other non-coordinating activators.^{29,30} Complex $Et(Ind)_2ZrX_2$ ($X=Me, NMe_2$ or CH_2Ph) needs notably less MAO to form the active cation than does the corresponding dichloride complex.³¹ Zirconocene dimethyl complexes are highly sensitive to impurities, such as oxygen, water, and carbon monoxide, which sets certain limitations on their use.^{32,33}

The reactivity towards aluminum alkyls depends on the electronic and steric effects in the complex structure.³⁴ According to UV/Vis measurements, complexes **1**, **1a**, and **1b** exhibit very low reactivity towards TMA and TIBA. With TMA at Al/Zr ratio of 400, **1a** is monomethylated, but **1** and **1b** show no reaction. **1** reacts with TIBA at Al/Zr=400 and **1b** at Al/Zr=800 producing the same, most probably monoisobutylated compound, $Me_2Si(2-Me-4-PhInd)_2ZrCl(iBu)$. This can be seen in the UV/Vis spectrum as ligand to metal charge transfer (LMCT) bands at the same wavelength and of similar form.^I

Benzindenyl zirconocenes **2** and **2a** react with TMA at low Al/Zr ratios producing different monomethyl species. Complex **2** forms a $L_2Zr(Cl)(Me)$ at Al/Zr=20. $L_2Zr(Cl)(Me)$ shows an LMCT band at 414 nm, which lies between the LMCT values of the pure complexes **2** (432 nm) and **2b** (387 nm). Complex **2a** forms $L_2Zr(Me)(NEt_2)$ species at Al/Zr=2. While this species shows no clear maximum in the studied wavelength area, its LMCT band is clearly different from that of dimethyl complex **2b**.^{II} One and two-dimensional NMR measurements confirm the formation of the $L_2Zr(Me)(NEt_2)$.^{II}

The different catalyst precursors, **2** and **2a**, also have an effect on the propene polymerizations, as can be seen from Figure 2.^{II} Without pre-reaction, **2**/MAO exhibits clearly higher activity than **2a**/MAO. Catalyst activity of both complexes is increased when they are monomethylated with TMA prior to polymerization. The form of the propene consumption curve remains the same as in the corresponding experiment made with the complexes without TMA pretreatment. When the complexes are pretreatment with MAO, polymerization kinetics and activities are increased and similar for the two complexes **2** and **2a**.

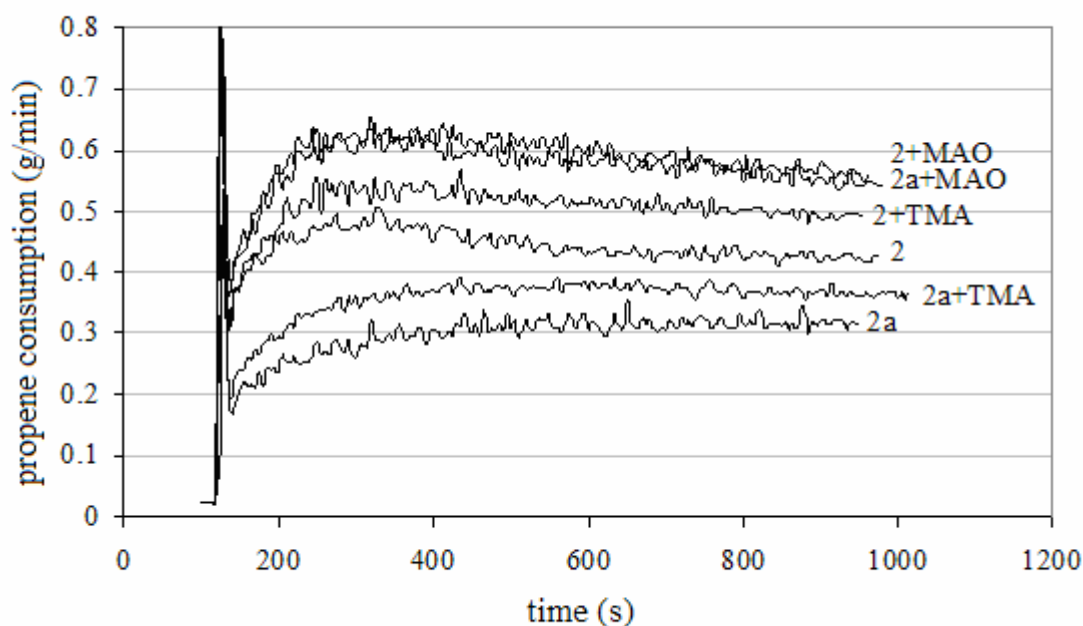


Figure 2. Propene mass-flow consumption curves from polymerizations with catalysts **2**/MAO and **2a**/MAO and when the complexes are pre-alkylated with either TMA or MAO.

The leaving ligands have only minor influence on the microstructure or molar mass of the polymer but a strong effect on the activity of the catalyst.^{I,II} The zirconocene dichlorides give the highest polymerization activity^{I,II,35} in a polymerization procedure where the zirconocene complex is fed to the reactor last and the alkylation and activation take place in the reactor.

Complexes **1**, **1a**, **1b** and **1c** form similar cationic species with MAO despite the leaving ligands. This can be seen from the similarly shaped LMCT absorption bands

at the same wavelengths (Figure 3). Cationic species formed at higher MAO concentrations (Al/Zr=8000) absorb at lower energies than the species existing at lower MAO concentrations (Al/Zr=400). This behavior is interpreted as the formation of a higher proportion of dissociated to associated zirconium species $[L_2ZrX]^+[MAOX]^-$.^{36-38,I}

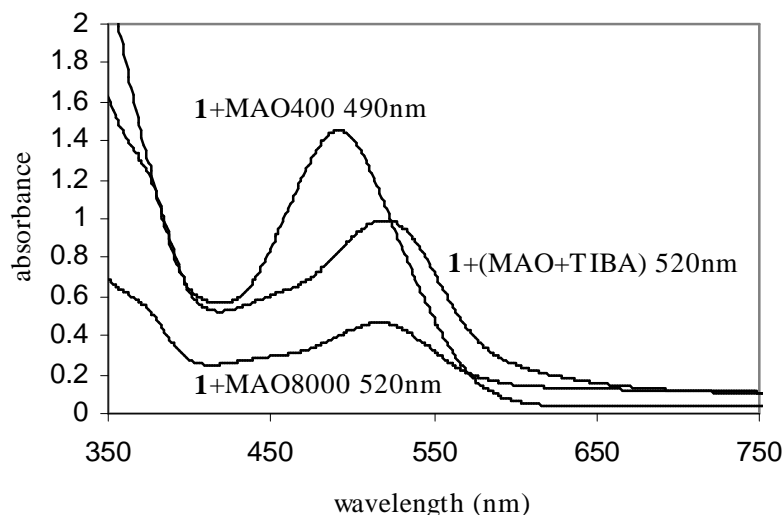


Figure 3. UV/Vis spectrum of complex **1** with MAO at Al/Zr=400 and Al/Zr=8000 and with a mixture of MAO (Al/Zr=5000) and TIBA (Al/Zr=3000).^I

The reactions of **2** and **2a** with MAO (Al/Zr=1000) give similar cationic species, which explains the similar polymerization behavior in Figure 2.

2.2 Aluminum alkyls

Aluminum alkyls (AlR_3) are used as cocatalysts, alkylating agents, and/or scavengers in olefin polymerization. AlR_3 have low efficiency as cocatalyst as such,¹⁸ but very high polymerization activities can be achieved when they are used together with boron-based non-coordinating anions.^{39,40} Metallocene dichlorides do not react with boron-based cocatalysts directly, but must be alkylated first. As mentioned in section 2.1, metallocene reactivity towards AlR_3 depends on the structure of the metallocene and the type of aluminum alkyl.³⁴ In addition, aluminum alkyls can reversibly inhibit catalysts or act as chain transfer agents, thus modifying the intrinsic behavior.^{24,41,42} Bulky aluminum alkyls, like triisobutyl aluminum (TIBA), show higher activity and

produce polymers with higher molar masses than less bulky TMA or triethyl aluminum (TEA). The explanation is that the bulkier isobutyl substituents prevent the formation of dormant $[L_2M(\mu-R)_2AlR_2]^+$ species⁴³ and thus the monomers have an easy access to the active site.^{29,44} Furthermore, monomer insertion is faster into metal–isobutyl bond than into the metal–methyl bond.⁴⁵ Unlike to TMA, TIBA is not an efficient chain transfer agent and therefore the molar mass of the produced polymer is not sensitive to the concentration of TIBA.^{1,29,46} When TIBA replaced part of MAO, the polymerization started at a slower rate, but no deactivation was detected in the whole polymerization, as shown in Figure 4.¹ The molar mass was also higher when the amount of MAO was reduced and TIBA was used in the polymerization.¹ The higher number of isobutyl end groups in the MAO-cocatalyzed polymerization experiments confirm the chain transfer reaction to aluminum.

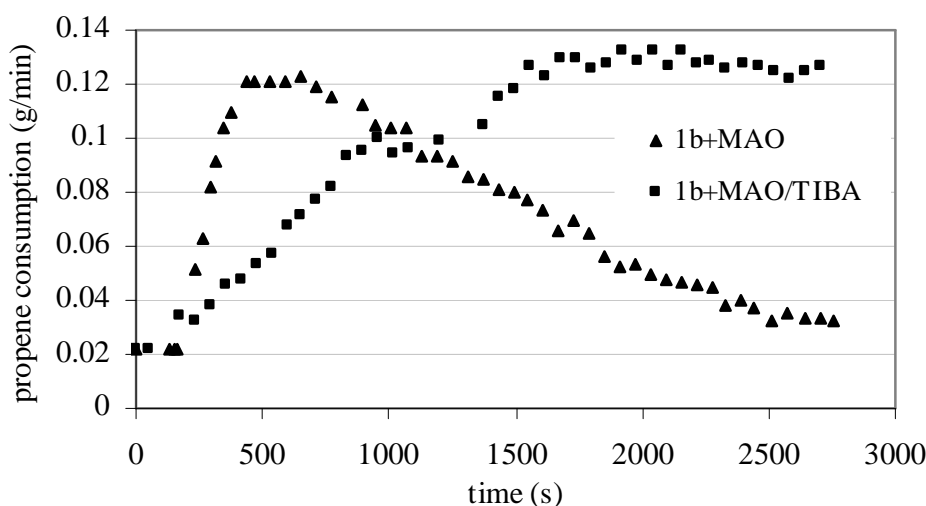


Figure 4. Influence of TIBA on the polymerization activity of **1b**.

2.3 Cocatalysts

2.3.1 MAO

MAO is the best-known and most used cocatalyst in metallocene-catalyzed olefin polymerization. MAO is a mixture of linear and cyclic oligomers containing –MeAlO– building blocks.³ It has been shown that MAO appears in solution in three-dimensional cage structures.^{40,47} Disadvantages of MAO are the high Al/M ratio that is required, which increases costs and may cause Al₂O₃ residuals in the polymer. The

limited preservability of MAO in solution can incur changes in the polymerization behavior.⁴⁸ In addition, characterization of the active species formed in the reaction of MAO and metallocene is difficult. MAO always contains TMA as a feedstock and decomposition material. The role of TMA in MAO is unclear. It has been suggested that TMA first alkylates the metallocene complex and then the methylated complex reacts with MAO to form the active catalyst.⁴⁹ Against this, Tritto *et al.*²⁰ have shown that the TMA in MAO remains intact and MAO is the actual alkylating agent. Because TMA is a good chain transfer agent, molar mass of the polymer is often decreased when content of TMA is high.^{39,44} Free TMA can be removed from MAO by vacuum distillation, but small amounts will be left in an associated form and can be removed only chemically.⁴⁰ Despite all this, MAO is widely used in industrial processes together with metallocenes, and it gives high polymerization activity at high operation temperatures.

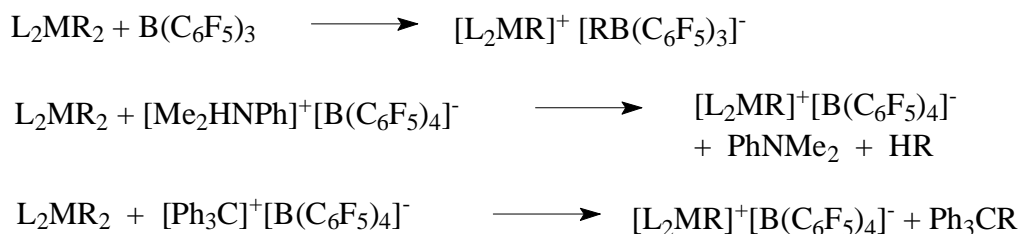
2.3.2 Boron-based cocatalysts

Boron-based compounds are the second largest group of cocatalysts for metallocene-catalyzed olefin polymerization. Marks's group⁵⁰ isolated and characterized the active species formed in the reaction of $B(C_6F_5)_3$ and L_2ZrMe_2 where $L=Cp$, Me_2Cp or Me_5Cp . Thereafter, the research in the area expanded markedly and modifications of $B(C_6F_5)_3$, like tris(2,2',2''-perfluorobiphenyl)borane⁵¹ and tris(β -perfluoronaphthyl)borane,⁵² were published. Trityl and ammonium borate salts, $[Ph_3C]^+[B(C_6F_5)_4]^-$ and $[Me_2HNPh]^+[B(C_6F_5)_4]^-$, respectively, are highly effective cocatalysts in olefin polymerization.⁴⁰ In comparison with MAO, borate anions are less bulky and more polar and have better coordinating ability.⁵³ Bochmann's group^{43,54,55} has synthesized a wide variety of different borate cocatalysts with reduced nucleophilicity based on $[CN\{B(C_6F_5)_3\}_2]^-$, $[M\{CNB(C_6F_5)_3\}_4]^{2-}$, and $[H_2N\{B(C_6F_5)_3\}_2]^-$ anions. These very weakly interacting cocatalysts are reported to give high polymerization activity with metallocene dialkyls.

2.3.3 Effect of cocatalyst on catalyst activity and molar mass of the polymer

$[Ph_3C]^+[B(C_6F_5)_4]^-$ as cocatalyst with complex **3** gave higher polymerization activity at 30 °C than $[Me_2HNPh]^+[B(C_6F_5)_4]^-$, $B(C_6F_5)_3$, or MAO.^{III,IV} System **3a**/MAO was not active at this temperature. When polymerization temperature was reduced to 0 °C $[Me_2HNPh]^+[B(C_6F_5)_4]^-$ gave clearly highest activity. At high propene concentration

effect was very pronounced: when polymerizations were conducted in liquid propene, $3/[\text{Me}_2\text{HNPh}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ exhibited activities up to 100 times those of $3/[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ or $3/\text{MAO}$.^{IV} At low temperatures the ion pair formation is slow in the case of MAO^{21,56}, and inactive species of the type $\text{L}_2\text{MCH}_3(\mu\text{-Cl})\text{Al}(\text{Me}_2)_2$, $\text{L}_2\text{M}=\text{CH}_2$ and $[\text{L}_2\text{M}(\text{Me})\text{OAl}(\text{Me})][\text{MAO}]$, where L=Cp-based ligand and M=Zr, Hf or Ti, may be formed.^{22,53} Combinations $3/\text{B}(\text{C}_6\text{F}_5)_3$ and $3\mathbf{a}/\text{B}(\text{C}_6\text{F}_5)_3$ show low activity compared with the borate-cocatalyzed polymerizations.^{III} The formed counter-anion $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ has a much higher activation barrier than $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ resulting in slower activation. One possible reason for the low activity of $\text{B}(\text{C}_6\text{F}_5)_3$ systems is the low Lewis acidity of $\text{B}(\text{C}_6\text{F}_5)_3$, which may lead to incomplete alkyl abstraction from the metal and thereby to lower catalyst activity.⁴⁰ $\text{B}(\text{C}_6\text{F}_5)_3$ can also react with TIBA under alkyl exchange to form potentially deactivating Al-C₆F₅ species.⁵⁷ The difference in the activity with the two borates $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $[\text{Me}_2\text{HNPh}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ shows that also the byproducts influence the polymerization. The reactions between alkylated complex and different boron-based cocatalysts are shown in Scheme 4.



Scheme 4. Activation with different boron-based cocatalysts.

The Lewis basic amine NPhMe_2 might interact with the zirconium center stabilizing the ion pair, while Ph_3CR is less reactive.⁵⁸ In some cases, amine can even displace propene from the vacant site leading to lower activity.^{I,59} Bochmann and Sarsfield⁵⁷ found that $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ can react with TIBA under hydride abstraction and alkene elimination leading to rapid consumption of the cocatalyst and thus lower the activity. We were able to minimize this reaction by first alkylating the complex and starting the polymerization by feeding $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ to the reactor last.^{III}

Cyclopentadienyl-indenyl based zirconium dichlorides together with MAO are one of the most active catalyst systems for ethene polymerization.²⁵ It is difficult to draw any universally applicable conclusions about the interaction of the catalyst precursor and the cocatalyst. The catalyst activity and molar mass of the produced polymer seem to depend on the match of the pair. The initial polymerization activity was high in all the ethene polymerizations with catalysts **5-5e**/[Me₂HNPh]⁺[B(C₆F₅)₄]⁻ and **6-6c**/[Me₂HNPh]⁺[B(C₆F₅)₄]⁻, causing rapid precipitation of the polymer. The catalyst was probably embedded in the polymer at an early stage of the polymerization which led to diffusion-controlled polymerization.

3 PROPAGATION AND CHAIN TRANSFER REACTIONS

3.1 Propagation reactions

After the formation of the cationic active species, monomer can coordinate to the catalyst vacant site. Monomer insertion is a two-step process: first the monomer coordinates forming a transition state between the metal, monomer and growing polymer chain, and then follows chain migratory insertion.⁶⁰⁻⁶³ Propene is a prochiral monomer and it can be coordinated and inserted in four different ways: primary (1,2-insertion) or secondary (2,1-insertion) and from right or left enantioface (*re*- or *si*-monomer).¹³ Whether the olefin insertion is primary or secondary determines the regioregularity of the polymer. Most propene insertions are primary and the 2,1-insertions are called regiodefects. The choice of the enantioface defines the stereoselectivity of the catalyst. The nature of the active site is changed after the olefin insertion, and the catalyst stereoselectivity is determined by the stereochemical relationships between the catalyst and the polymer chain. Depending on the symmetry of the metallocene (i.e. which enantioface is preferred), the formed poly(1-olefin) can be isotactic, syndiotactic, atactic, or hemi-isotactic.⁶⁴⁻⁶⁷

In ethene polymerization, where stereocontrol plays no role, unbridged metallocenes are the usual choice. For industrial purposes, the catalyst should be active at high temperatures and produce polymers with sufficient molar mass.

3.2 Chain transfer and isomerization reactions

The average degree of polymerization, which determines the molar mass of a polymer, is the ratio of chain growth to chain transfer reactions. Polymer end groups are fingerprints showing the type of chain transfer reactions that have occurred. End groups of PP are usually determined by ¹H and ¹³C NMR.⁶⁷ In the case of PE, low solubility sets some limitations on NMR analysis and FTIR is more often used in end group analysis.⁶⁸

Table 1 shows the most common chain transfer reactions and the formed end and initial groups in ethene and propene polymerization. Chain transfer to metal (unimolecular β -H transfer) and chain transfer to monomer (bimolecular β -H transfer)

are generally thought to be the prevailing termination mechanisms in olefin homopolymerization.^{39,69} The former is independent of monomer concentration and the latter proportional to it. β -Methyl transfer to metal is an important chain transfer reaction in propene polymerization. Chain transfer can also occur after 2,1 –insertion resulting in cis-2-butenyl end groups.⁷⁰ The longer the delay after a 2,1 –insertion, the greater is the possibility that the last 2,1 inserted unit undergoes isomerization to a 1,3 –unit.⁶³ Vinyl end groups can also isomerize to trans-vinylene end groups. High polymerization temperature and monomer concentration accelerate isomerization reactions.⁷¹ Hydrogen is a powerful chain transfer agent in metallocene-catalyzed olefin polymerization and widely used to control the polymer molar mass.⁷² Chain transfer to aluminum is a favored reaction in MAO-cocatalyzed propene polymerizations at high Al/M –ratios. It produces polymers with –AlR₂ end groups, but after washing with HCl/EtOH, which is a standard laboratory procedure, only saturated end groups are left. Chain transfer to aluminum plays a less important role in ethene polymerization.

There are also other chain transfer reactions, which are rare and seldom detected. The σ –bond metathesis results in a cleavage of the Zr–C bond of the growing ethene oligomer producing polymer having saturated end group and an initiating species, type L₂Zr⁺–CH=CH₂.⁷³ In principle β -H transfer after 2,1 –insertion can also be unimolecular, β -H transfer to metal, producing 4-butenyl end group and L₂M⁺–H initial group. In practice, however this reaction seems to be unfavorable and only the β -H transfer to monomer has been detected.^{70,74} β -Methyl transfer can also be bimolecular. It exists at high propene concentrations through C–C bond activation.^{75,76}

Table 1. The most common chain transfer reactions and corresponding end groups in ethene and propene polymerization.

Chain transfer reaction	Chain end group	Chain initial group
Chain transfer to metal (unimolecular β -H transfer)	PE:	PE: $L_2M^+ - H$
	PP:	PP: $L_2M^+ - \text{CH}_2\text{CH}_2\text{CH}_3$
Chain transfer to monomer (bimolecular β -H transfer)	PE:	PE: $L_2M^+ - \text{CH}_2\text{CH}_2\text{CH}_3$
	PP:	PP: $L_2M^+ - \text{CH}_2\text{CH}_2\text{CH}_3$
β -Methyl transfer to metal	PP:	PP: $L_2M^+ - \text{Me}$
β -H transfer after 2,1 - insertion (β -H transfer to the monomer)	PP:	PP: $L_2M^+ - \text{CH}_2\text{CH}_2\text{CH}_3$
Chain transfer to hydrogen	PE:	PE: $L_2M^+ - H$
	PP:	PP: $L_2M^+ - H$
Chain transfer to aluminum (AlR_3)	PE:	PE: $L_2M^+ - R$
	PP:	PP: $L_2M^+ - R$

The dependency of molar mass on the monomer concentration shows whether the chain termination is uni- or bimolecular. If molar mass is independent of the monomer concentration, β -H transfer to monomer is the dominant chain termination mechanism. This was the case with catalyst **5b**/MAO.^{VI} The increased proportion of trans-vinylene end groups at low ethene concentration supports this conclusion.^{77,78} Complex **6a** has similar ligand structure to **5b** and the molar mass of PE is also only slightly influenced by the monomer concentration. With all other complexes **5-5e** and

6-6c, the molar mass of the product increased with the ethene concentration, indicating that β -H transfer to metal takes place in varying degree.^{VI}

4 CHOICE OF THE CENTRAL METAL ATOM TITANIUM, ZIRCONIUM OR HAFNIUM

Group 4 transition metals have been found to give active metallocene catalysts. Ti, Zr and Hf are the frequently used central metals in olefin polymerization. Zr-based catalysts give the highest activities in olefin polymerization. Hafnium forms a strong metal-alkyl bond, which impedes the monomer insertion and leads to lower polymerization activities.⁷⁹ For electronic reasons⁸⁰, hafnocene-based catalysts generally produce higher molar mass than corresponding zirconocenes, and the strong Hf-alkyl bond suppresses the β -H transfer reaction.^{25,79} There are exceptions, as shown in Table 2: hafnocene **5a** produces lower molar mass than corresponding zirconocene **5.VI** Hafnocenes generally incorporate higher α -olefins better than zirconocenes.⁸¹⁻⁸³ In ethene polymerization, our studies showed, that hafnocenes require more MAO to reach the maximum polymerization activity than do zirconocenes^{VI} The activities of hafnocene/MAO catalysts were either increased or remained the same when the amount of MAO was increased from 5 mmol/l to 20 mmol/l. The activities of the studied zirconocenes were not very sensitive to the amount of MAO.^{VI}

Table 2. Ethene homopolymerization results with hafnocenes and zirconocenes. The polymerizations were carried out in heptane at 80 °C at 3 bar ethene overpressure. 1.5 mmol MAO was used as cocatalyst. Polymerization time was 30 min. Data from publication^{VI}

compl.	μmol	Cp1	Cp2	metal	bridge	yield g	activity ^a	Mn kg/mol	MWD
5	0.05	Cp	4-PhInd	Zr	-	2.53	33700	139	2.1
5a	1.6	Cp	4-PhInd	Hf	-	2.58	1100	93	2.4
5b	0.5	Me ₃ Cp	4-PhInd	Hf	-	4.70	6300	42	2.7
5c	0.05	1,2,4-Me ₃ Cp	4-PhInd	Zr	-	3.30	44000	113	2.7
5d	0.1	Cp	1-Ph-4-PhInd	Zr	-	2.02	13500	125	2.4
5e	0.05	Cp	2-Me-4-PhInd	Zr	-	1.37	18300	33	2.3
6	0.05	Cp	1-PhInd	Zr	-	10.1	134700	124	2.2
6a	0.2	Me ₃ Cp	1-PhInd	Hf	-	3.11	10370	39	2.8
6b	0.2	Cp	1-PhInd	Hf	Me ₂ Si	0.36	1200	98	2.5
6c	0.2	1,2,4-Me ₃ Cp	1-PhInd	Hf	-	3.00	10000	28	3.7

^akgPE/(molM*h*bar)

Ethene insertion to the M-Me bond is an exothermic reaction. Exothermicity increases with increasing Cp ligand substitution and is therefore dependent on the ligand structure. The cocatalyst too, has an effect on the methide abstraction enthalpy.⁸⁴ Modeling studies have shown that the methide abstraction reaction from SiH_2CpM (M=Zr, Hf or Ti) is least exothermic in the case of Ti⁸⁵, while the methide abstraction from $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(^t\text{BuN})\text{MMe}_2$ (M=Zr, Hf, Ti) complex is least exothermic in the case of Hf, followed by Ti and Zr.⁸⁴ Titanocenes suffer from low activity because of the small atomic radius and steric repulsion. When bulky substituents are introduced to the ligand frame, titanocenes are likely to be affected most. The steric effect of the growing polymer chain is also most significant in the case of titanocenes.⁸⁴

While ligand structure and the polymerization conditions have the strongest influence on the stereo- and regioselectivity of the catalyst, the metal plays also plays a role. Thus *rac*- $\text{Me}_2\text{Si}(\text{3-MeCp})_2\text{TiCl}_2/\text{MAO}$ produces polymers with lower regioregularity than its Zr and Hf analogues.⁸⁶ The effect of metal on the stereoselectivity is not well understood and it is difficult to draw general conclusions. Also, there are not enough examples of stereoselective Ti and Hf complexes to make an extensive comparison. In our studies the zirconocene complex **3** produced PP at 30 °C with syndiotacticity between 73 and 80%, depending on the cocatalyst, whereas the corresponding hafnocene **3a** produced PP with markedly lower syndiotacticity of 53-58%.^{III}

5 SYNDIOTACTIC POLYPROPENE AND ITS COPOLYMERS WITH ETHENE

C_s -symmetric metallocenes producing syndiotactic PP (sPP) were developed in 1988 by Ewen and Razavi.¹⁰ C_s -Symmetric catalysts follow the enantiomorphic site control mechanism, where two enantiotopic coordination sites lead to alternating enantiofacial orientation of propene insertion and thereby to the formation of syndiotactic polymer chain. The recent modifications of C_s -symmetric metallocenes produce polymers with syndiotacticity over 99%.⁸⁷ Highly syndiotactic PP is a tough thermoplastic material with relatively high melting point. Copolymers of sPP with low contents of ethene have lower melting points, lower glass transition temperatures, and higher impact strengths than pure sPP.

Thermoplastic elastomers (TPEs) are a diverse group of polymers combining the good processability of thermoplastics with elastomeric properties over a certain temperature range.^{87,89-91} Some TPEs have similar properties to conventional vulcanized rubbers and thereby have the potential to replace rubber in applications in the automotive, footwear, and sporting goods industries and in the area of medical devices. TPEs can also be used as compatibilizers in blends of crystalline polymers to obtain impact-strengthened polymers.⁹² TPEs contain two distinct polymer segments: hard, crystallizable segments, which bring stiffness to the material and act as physical cross-links, and soft, amorphous segments, which bring elasticity to the material (Figure 5). The properties of the material can be modified through control of the lengths of the crystalline and amorphous segments.

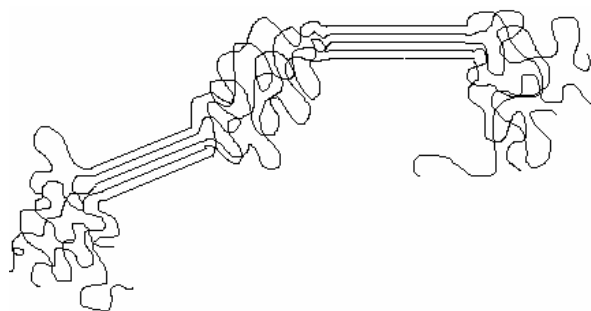


Figure 5. A schematic picture of thermoplastic elastomer.

There are many ways to modify the properties of PP in more elastic direction. Addition of a small amount of ethene to the PP chain creates a local disorder, which hampers the crystallization and leads to an amorphous segment. Copolymers of propene with small amounts of ethene are a relatively new class of TPEs.⁹³ Also, pure PP can be block-structured: the crystallizable blocks are formed from isotactic or syndiotactic segments and the amorphous blocks are either atactic segments or isotactic polymer structures with a certain number of single stereo errors in the polymer chain.^{94,95}

5.1 Molar mass

Sufficiently high molar mass is needed to obtain good tensile and creep properties. The hafnocene complex **3a** produces homo- and copolymers with very high molar masses, up to 980 kg/mol at 30 °C in toluene and at monomer concentration of 2.0 M. Under the same conditions, zirconocene **3** produces polymers with molar masses up to 220 kg/mol. Besides the catalyst structure, polymerization conditions have a significant influence on the molar mass. Low polymerization temperature and high monomer concentration lead to high molar masses with both complexes **3** and **3a**. At 0 °C, with 0.5 mol-% ethene in the feed and total monomer concentration of 4.0 M, molar masses around 400 kg/mol were produced with complex **3**. Homo- and copolymerizations were carried out in toluene or in liquid propene, where the propene concentration was as high as possible. Even though bulk phase polymerizations are used in industrial processes, there is little information available about the solubility of ethene in liquid propene in typical laboratory conditions of low pressure and temperature. In our copolymerization experiments, the amount of ethene in the copolymers increased linearly with the amount of ethene in the feed, as depicted in Figure 6. This result shows that ethene in the feed is dissolved in the liquid propene. β -Hydrogen transfer more easily takes place to the smaller ethene monomer than to the bulkier propene monomer, which appears as a decrease in molar mass.^{III}

5.2 Ethene incorporation

Because of the small size of the ethene molecule, the reactivity is higher than that of propene and the copolymer easily becomes rich in ethene. The reactivity of propene increases in the order C_{2v} symmetric (non-specific) metallocene < C_2 symmetric (isospecific) metallocene < C_s symmetric (syndiospecific) metallocene.⁹⁶ Fink's

group⁹⁷ explained this tendency in terms of the different size of the coordination gap of the π -ligand. In our studies the aim was to prepare P–E copolymers with low contents of ethene. Besides the catalyst structure, polymerization conditions have a marked effect on the ethene incorporation rate. Considerably lower portions of ethene were incorporated at 0 °C than at 30 °C. When the polymerizations were carried out in liquid propene, P–E copolymers were produced with ethene content as low as 1 mol-%.^{IV} Zirconocene complex **3** incorporated ethene faster than did the corresponding hafnocene **3a**. The cocatalyst had only minor influence on the ethene incorporation rate but a marked effect on the polymerization activity.^{III}

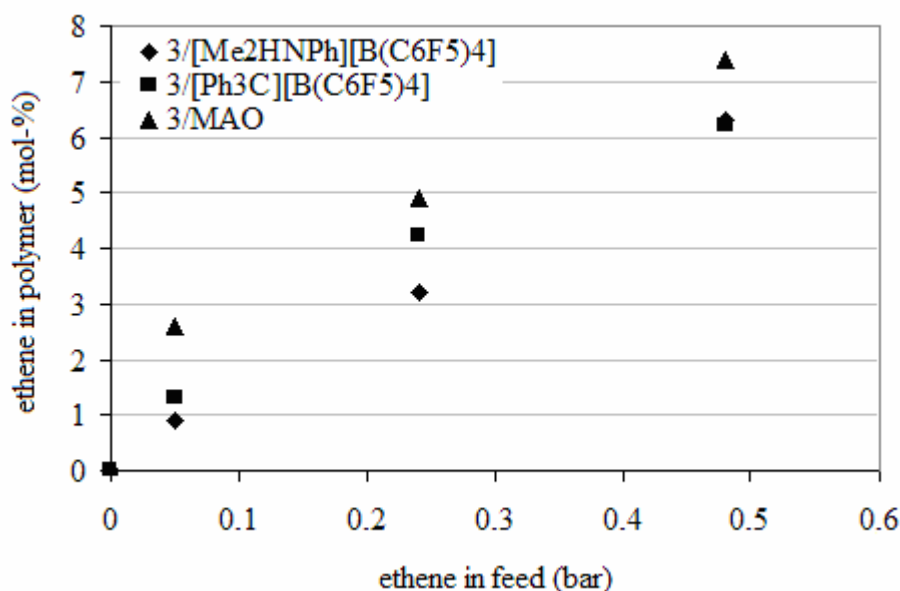


Figure 6. Ethene incorporation with catalysts **3**/[Me₂HNPh]⁺[B(C₆F₅)₄]⁻, **3**/[Ph₃C]⁺[B(C₆F₅)₄]⁻, and **3**/MAO.^{IV}

5.3 Microstructure of homo- and copolymers

The syndiotacticity of the homopolymer depends on the metallocene precursor and cocatalyst. At 30 °C and monomer concentration of 2.0 M **3**/MAO produced the most stereoregular polymer, with syndiotacticity of 81%. This was followed by **3**/B(C₆F₅)₃ 80%, **3**/[Me₂HNPh]⁺[B(C₆F₅)₄]⁻ 78% and **3**/[Ph₃C]⁺[B(C₆F₅)₄]⁻ 73%. As well, polymerization temperature and the total monomer concentration influence the polymer syndiotacticity. At 0 °C and total monomer concentration of 4.0 M, polymer made with **3**/[Me₂HNPh]⁺[B(C₆F₅)₄]⁻ showed syndiotacticity of 80%,

$\mathbf{3}/[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ 79% and $\mathbf{3}/\text{MAO}$ 75%.^{III} In liquid propene at 0°C, $\mathbf{3}/[\text{Me}_2\text{HNPh}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ produces clearly the highest syndiotacticity 90 % followed by $\mathbf{3}/[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ and $\mathbf{3}/\text{MAO}$, both having syndiotacticity of 81%.**IV** All the above catalyst systems produced both isolated [m] and [mm] stereodefects as a consequence of skipped insertions (site epimerization) as well as of monomer insertion with the wrong enantioface.⁹⁸ According to the ¹³C NMR spectra of the copolymers, ethene molecules were randomly distributed in the polymer chain in every case. No EEE triads were observed in the spectra and the number of alternating EPE triads was low, too.^{IV}

5.4 Thermal behavior

Syndiotactic PP (sPP) exhibits complex polymorphic behavior with four known crystalline forms.⁹⁹ It has been observed that the regio- and stereoregularity of the polymer has an effect on the structure of the crystalline lattice.¹⁰⁰ Characteristic for sPP are the double melting peaks in the differential scanning calorimetry (DSC) melting endotherms. The lower melting peak represents the melting of the primary and secondary crystals formed at the employed crystallization temperature. The melting peak at the higher melting temperature shows the melting of the recrystallized crystals grown during the heating endotherm.^{101,102} When the amount of ethene in the copolymer increases, the melting peaks fuse into a single peak, and with further increase in the amount of ethene, the material becomes amorphous. Homo- and copolymers made with complex **3a** were in general amorphous.^{III} Melting temperatures of the copolymers produced with complex **3** are dependent on the cocatalyst, as can be seen from Figure 7. With all the boron-based cocatalysts, the copolymers become amorphous after ethane content reached 8 mol-%. $\mathbf{3}/[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ shows a small melting peak at low temperatures indicating that some crystallinity remains in the copolymer. With MAO as cocatalyst clear melting peaks can be observed for copolymers containing up to 15 mol-% ethene. The explanation for this behavior is that syndiotacticity is higher for the polymers made at 30 °C at total monomer concentration of 2.0 M with $\mathbf{3}/\text{MAO}$ than for polymers made under the same conditions with borate or borane cocatalysts. Even the melting temperatures of the homopolymers are notably higher with MAO as cocatalyst. The highly stereoregular sequences in the copolymers are able to crystallize despite the higher content of ethene in the copolymer.^{III}

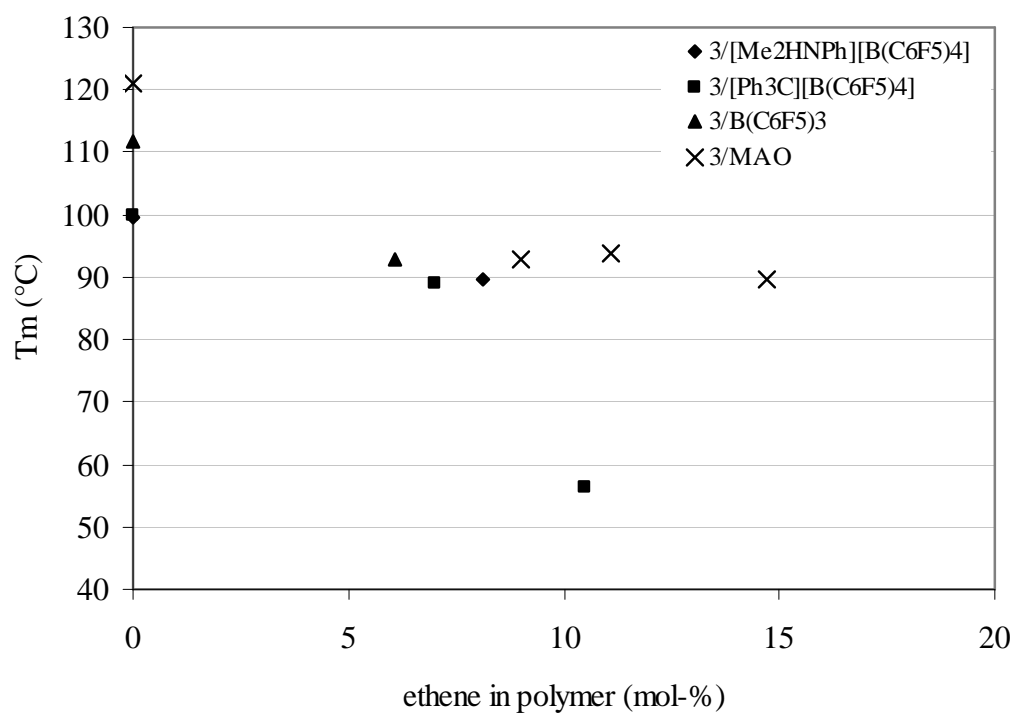


Figure 7. Effect of catalyst on the melting temperatures of the polypropenes and propene–ethene copolymers. Polymerizations were carried out in toluene at 30 °C with total monomer concentration of 2.0 M.

6 ELASTIC POLYPROPENE

PP is a versatile material whose properties of stiffness, elasticity, and transparency can be tailored by modifying the molecular architecture. Elastic PP (ePP) has awakened growing interest because of the straightforward homopolymer synthesis, easy of recycling of the material, good processability and, in the best cases, competitive material properties.¹⁰³⁻¹¹² Several C_1 -symmetric metallocenes produce PP owing good elasticity, but in most cases the molar masses are too low to provide good mechanical properties.^{104,113-115} Unbridged bis(2-aryindenyl)- and pentamethylcyclopentadienyl(2-aryindenyl) zirconocenes produce high molar mass elastic PP at room temperature. However, because of the free rotation of the ligands the produced polymers have an inhomogeneous block-like structure and broad molar mass distribution.^{107,108} Hafnium-based metallocenes have been reported to produce PP with higher molar mass and lower isotacticity than the corresponding zirconocenes, but with lower catalyst activity^{10,80,104} A noteworthy improvements in the synthesis of ePP was reported by Rieger's group^{105,106} The use of [1-(fluorenyl)-2-(5,6-cyclopenta-2-methylindenyl)ethane]HfMe₂/borate catalyst produces ultra high molar mass ePP with good catalyst activity. The creep–recovery properties of the ePP were comparable to those of commercial Kraton styrene(butadiene)styrene (SBS) block-copolymer, apparently because of the high molar mass.

In our study, *rac*- and *meso*-Me₂Si(3-benzyl Ind)(2-Me Ind)HfCl₂/[Me₂HNPh]⁺[B(C₆F₅)₄]⁻ catalysts **4** and **4a** were used to produce ePP. The racemic form **4** showed higher activity in propene polymerization and produced higher molar mass ePP than the meso form **4a**, as can be seen from Table 3.

Table 3. Experiments targeted at the production of elastic polypropene. Polymerizations were conducted in toluene with complexes **4** and **4a** with $[\text{Me}_2\text{HNPh}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ as cocatalyst.

run	cat	n (complex)	[prop]	Tp	time	yield	activity ^a	Mw	MWD	Tm	Tg (DSC)	crystallinity ^b
		10 ⁻⁶ mol	mol/l	°C	min	g		kg/mol		°C	°C	%
4_1	4	7	4	15	33	14.7	950	195	2.1	84.6	-6.3	17.0
4_2	4	5	6	0	80	17.0	430	538	2.1	78.2	-6.1	19.9
4_3	4	5	9	0	40	17.9	600	473	2.1	77.8	-6.0	22.6
4a_1	4a	15	4	15	45	12.1	270	150	2.2	80.5	-7.7	20.2
4a_2	4a	18.5	6	0	55	9.3	90	166	2.4	88.3	-7.5	35.5
4a_3	4a	15	9	0	150	20.7	60	250	2.5	85.1	-9.2	28.9

^a Activity/kg PP/(molHf*h*(mol/l))

^b Measured with SAXS

6.1 Microstructure of the polypropenes

The pentad distributions calculated from ¹³C NMR data shows the isotacticities of the polypropenes to range between 34 and 52% (Table 4). The zirconocene analogues *rac*- and *meso*-Me₂Si(3-benzyl Ind)(Ind)ZrCl₂/MAO produced similar microstructures to the hafnocenes **4** and **4a**, and isotacticities between 15 and 45%¹¹⁶ The zirconocene-catalyzed polypropenes showed elastic properties, but owing to the low molar mass the elastic recovery was poor. The pentad ratio of [mmmr]/[mmrr]/[mrrm] = 2:2:1 is typical for a chain migratory insertion mechanism and shows that the catalyst is working under enantiomorphic site control.^{13,67,117,118} The proportion of isotactic pentads increased with increasing propene concentration and decreasing temperature, indicating that there occur no polymer backskipping.^{105,116} Our suggestion, based on the polymer microstructure, is, that the polymer chain contains isotactic sequences with average lengths of 8.0-11.4 monomer units. These sequences can crystallize and form the hard phases in the TPE structure.¹¹⁷ The isotacticities of the polymers made with racemic complex **4** correlated well with the polymer crystallinities measured by small angle x-ray scattering (SAXS). The crystallinity increased with the number of [mmmm] pentads, as can be seen by comparing the data in Tables 3 and 4. The relationship is less straightforward for the polymers produced with the complex **4a** thus, **4a_2** has the highest crystallinity, 36%, but its tacticity is lower ([mmmm]=48%) than that of polymer **4a_3** ([mmmm]=52%) which has crystallinity of 29%. Successive self-nucleation and annealing (SSA) thermograms offer an explanation for the nonlinear behavior: the polymers produced with complex

4a have markedly broader melting curves than the polymers made with the complex **4**, as depicted in Figure 8. Especially polymers **4a_2** and **4a_3** have a particularly large number of fractions meaning a broad distribution of lamellae with different thicknesses. Polymers made with complex **4** have significantly fewer fractions indicating a more uniform material.^{V,119,120}

Table 4. Pentad distributions in percent calculated from ¹³C NMR.

run	mmmm	mmmr	rmmr	mmrr	mmrm+rmrr	rmrm	rrrr	rrrm	mrrm
4_1	33.8	16.8	3.8	15.6	9.8	4.2	2.8	5.9	7.1
4_2	37.5	15.9	3.8	15.3	8.5	4.0	2.8	5.5	6.5
4_3	40.1	15.3	4.3	14.4	8.1	3.6	2.6	4.5	6.9
4a_1	37.7	16.8	4.5	15.7	6.8	3.5	2.3	4.2	8.3
4a_2	47.8	15.4	3.5	14.4	5.0	2.0	1.7	3.0	7.1
4a_3	52.0	14.0	1.8	14.0	4.8	2.1	1.6	2.9	6.9

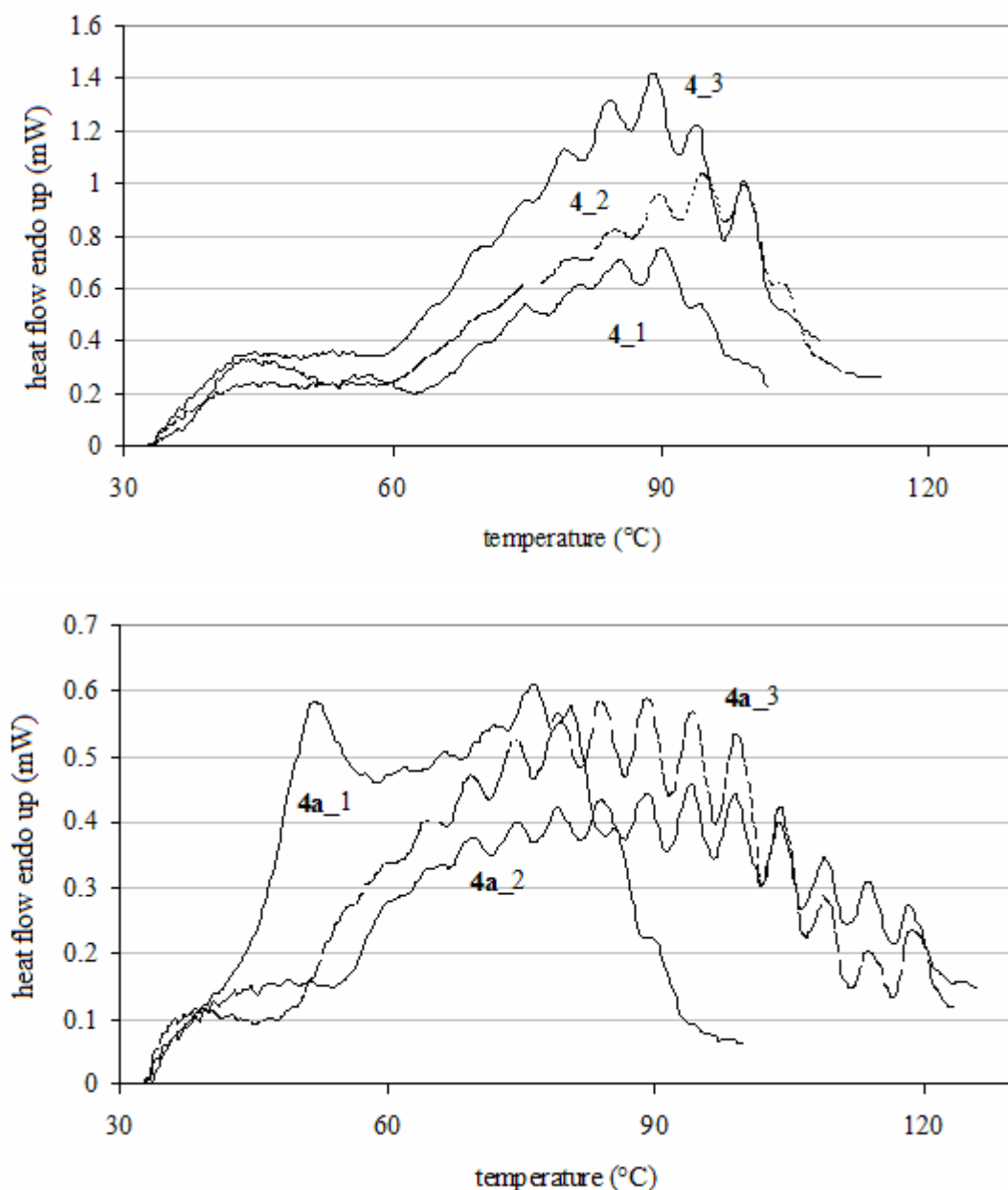


Figure 8. SSA melting curves of samples **4_1**, **4_2**, **4_3**, **4a_1**, **4a_2** and **4a_3**.

6.2 Mechanical properties

Dynamic mechanical analysis (DMA) creep-recovery tests demonstrate the relationship between crystallinity and elasticity. The most crystalline polymer, **4a_2**, is rather a flexible thermoplastic material than an elastomer. In the series shown in Figure 9, polymers **4_3**, **4a_1**, and **4a_3** stretched less than 30% under the test conditions, while polymer **4_1** with the lowest crystallinity gave a value of 270%. When the polymer sample **4_3** was exposed to higher stress of 3 MPa, it stretched

170% and recovered 78%. The stiffest tested polymer **4a_3** showed only 15% strain under 3 MPa stress, and the strain recovery was 96%.

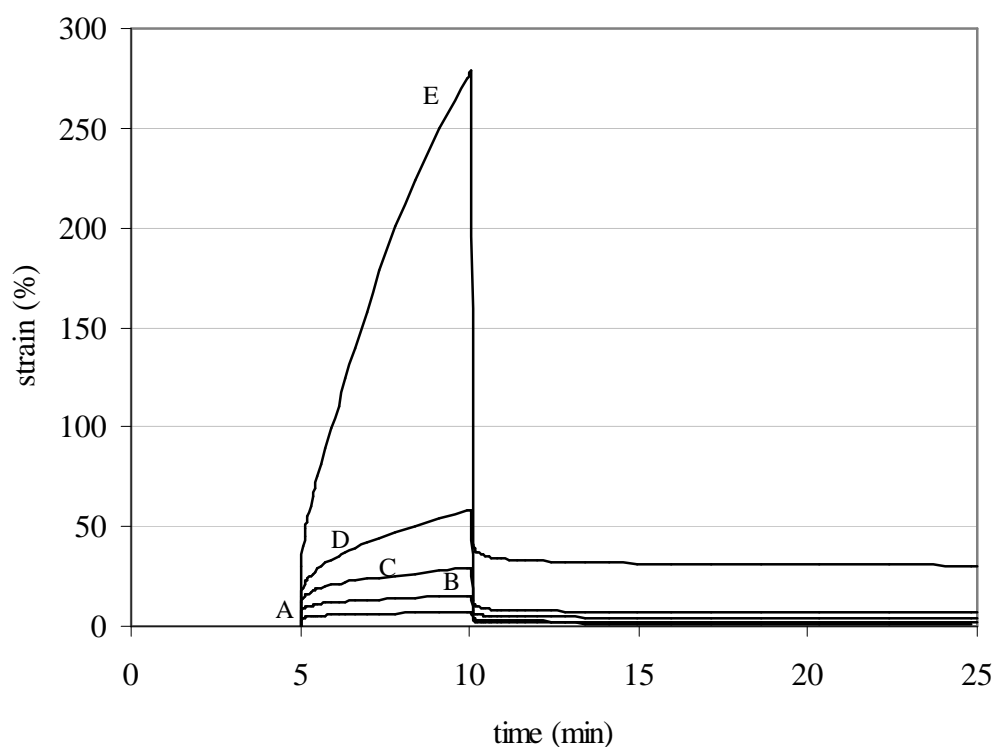


Figure 9. Results of DMA creep-recovery tests of the polymers A = **4a_3** (maximum strain 7%, strain recovery 99%), B = **4_3**(maximum strain 15%, strain recovery 98%), C = **4a_1**(maximum strain 29%, strain recovery 96%), D = **4_2**(maximum strain 59%, strain recovery 93%), E = **4_1**(maximum strain 279%, strain recovery 70%). The test pieces are exposed to 2 MPa stress for five minutes and after release the recovery is monitored for 20 minutes.

The dependence between molar mass and creep-recovery properties in this series cannot be fully explained. The polymer samples **4_2** and **4a_1** have similar isotacticities and crystallinities, but molar mass of **4_2** is three times that of **4a_1**. Interestingly, **4_2** stretched twice (59%) as much as **4a_1** (29%) at 2 MPa stress. The chain recovery of **4_2** was only 3 % less than that of **4a_1**, however (93% versus 96%). Evidently the greater molar mass and the more uniform structure of **4_2** influenced the creep-recovery behavior.^v

Kraton styrene(ethene-butene)styrene (SEBS) block copolymer is commercial TPE with good elastic properties.¹²¹ Compared with Kraton, our ePPs **4_1** and **4_2** are stiffer materials: **4_1** stretched 55% at 1.5 MPa stress and **4_2** yielded 90% at 2.5 MPa stress, when Kraton stretched 99% at 1 MPa stress (Figure 10). The elastic recovery of Kraton was 96%, whereas it was 95% for **4_1** and 92% for **4_2**. In order to see if the polymer **4_2** was creeping under use, the creep-recovery cycle was repeated 45 times. After the first elongation, there was always a viscous part that did not recover. When the new length of the sample was taken as sample length and the creep-recovery cycle was repeated, the elongation and recovery finally reached a constant value, where the chain recovery was more than 99%.^v

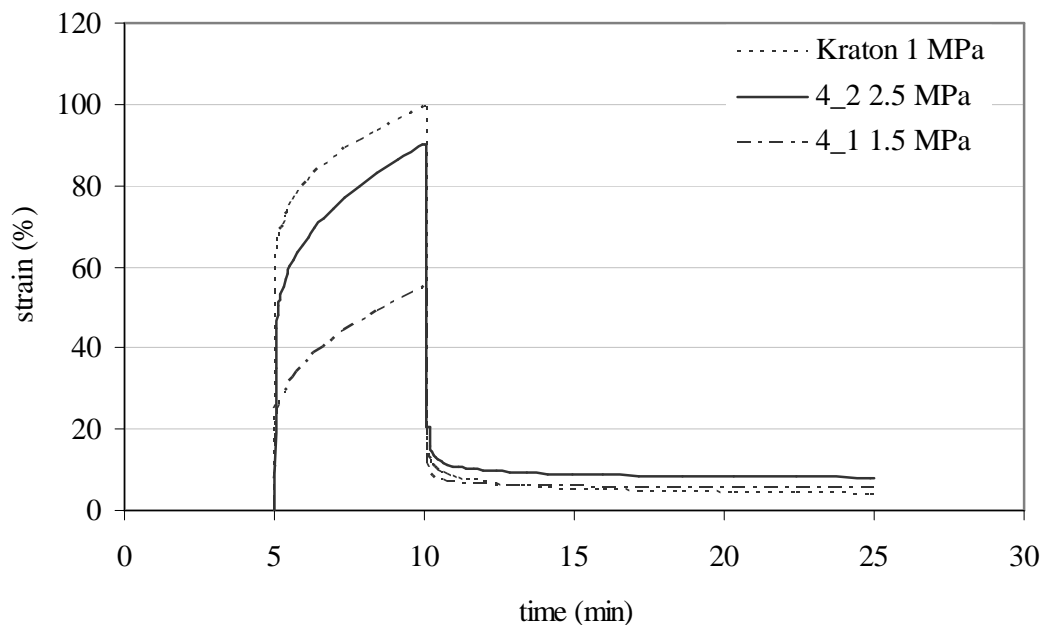


Figure 10. Results of DMA creep-recovery tests for the reference material Kraton SEBS block copolymer (maximum strain 99% and chain recovery 96% at 1 MPa stress) and for ePPs **4_1** (maximum strain 55% and chain recovery 95% at 1.5 MPa stress) and **4_2** (maximum strain 90 % and chain recovery 92% at 2.5 MPa stress).

7 CONCLUSIONS

This thesis shows how a wide variety of polymer structures can be obtained through a careful design of metallocene catalyst and a choice of cocatalyst and experimental conditions. Correlations were found between the catalyst structure and polymer properties through an investigation of the polymerization mechanism and the factors contributing to the polymerization process.

The main conclusions of this work can be summarized as follows:

- Polymerization activity is higher for metallocene dichlorides than for complexes with chloroamido leaving ligands. Pre-alkylation of the complex with TMA or TIBA and pre-activation with MAO influences the activity of the catalyst.
- According to UV/Vis and NMR measurements, similar active species are formed in the reaction of zirconocene complex with MAO regardless of the leaving ligands. The same phenomenon is observed in the reactions of zirconocene and $[\text{Me}_2\text{HNPh}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-/\text{TIBA}$: where leaving ligands do not significantly affect the structure of the active species. However, the active species formed in these two systems differ from each other. When used together with MAO, TIBA appears not to affect the active species.
- Cocatalysts – MAO, borates, and borane – have a great impact on the catalyst activity in ethene and propene polymerization. The stereoselectivity of propene insertion, and thereby the thermal behavior of the formed propene homo- or copolymer, is dependent on the cocatalyst. With some metallocenes and under certain polymerization conditions, the cocatalyst has a marked effect on the molar mass of the polymer. The cocatalyst also influences the catalyst regioselectivity and the chain transfer reactions. When MAO was partially replaced with TIBA, no catalyst deactivation is detected during the polymerization and the molar mass of the produced polymer is higher.
- Hafnocenes generally require more MAO than zirconocenes to reach their maximum activity in ethene polymerization.

- In propene–ethene copolymerization, hafnocenes incorporate less ethene than zirconocenes. Copolymers of propene with very low amounts of ethene were produced in propene bulk phase.
- In the production of elastic polypropene the distribution of the crystalline segments and the homogeneity of the material are important in defining the elasticity. Elastic polypropene with lower isotacticities, and thereby lower crystallinities, show the best creep-recovery properties.

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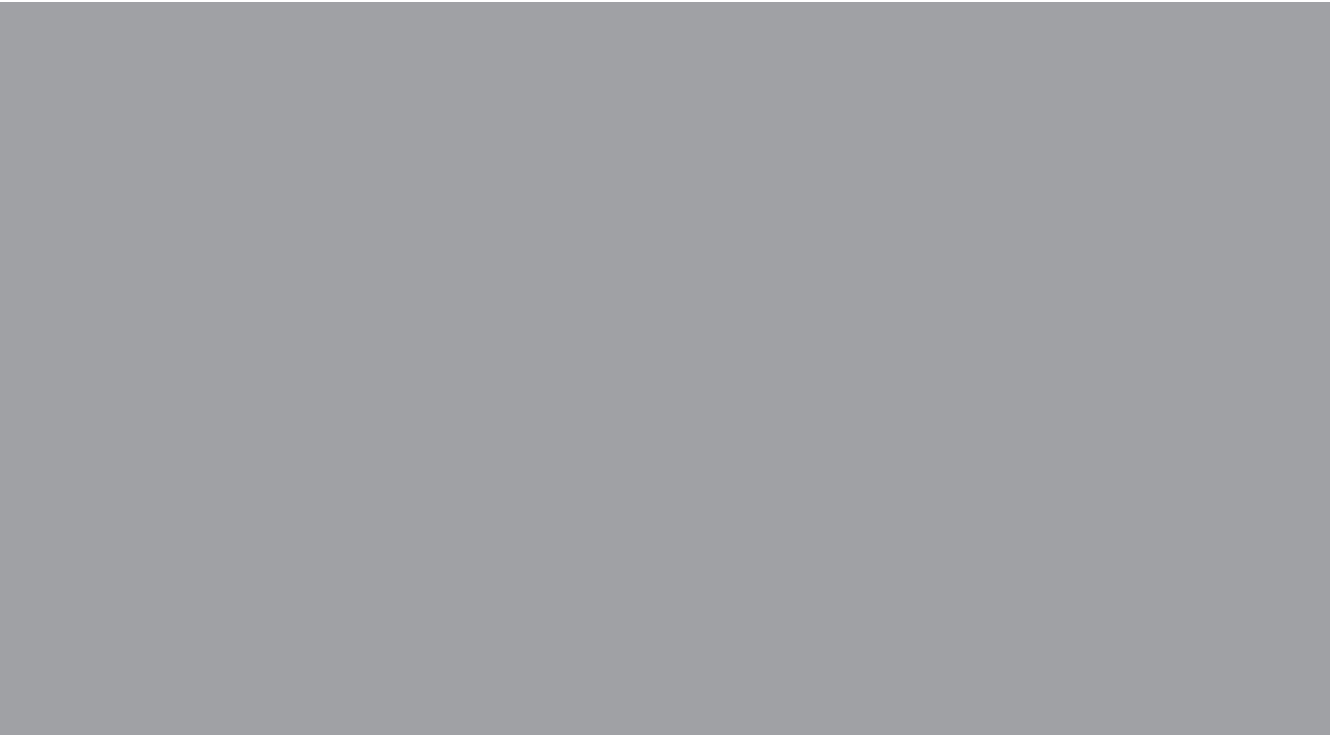
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