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**TAILORING OF POLYPROPYLENE STRUCTURES AND
PROPERTIES WITH METALLOCENE CATALYSIS**

Doctoral Dissertation

Antti Tynys



**Helsinki University of Technology
Department of Chemical Technology
Laboratory of Polymer Technology**

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Abstract			
<p>Propylene was polymerised with individual and mixed metallocenes activated by methylaluminumoxane. Homogeneous as well as heterogeneous systems were applied, and copolymerisations were conducted with ethylene, 1-hexene and 1,9-decadiene.</p> <p>The copolymers showed lower heat of fusion values and melting temperatures as compared with the corresponding homopolymers. Copolymerisation with 1,9-decadiene resulted in the formation of long-chain branched structures, which was observed as an increase in molecular weight and broader molecular weight distribution. Homopolymers produced with combined heterogeneous catalyst systems had broader or bimodal molecular weight distribution and improved processability.</p> <p>In the case of <i>rac</i>-Me₂Si(2-Me-4-Ph-1-Ind)₂ZrCl₂, the presence of ethylene decreased the molecular weight due to β-H transfer to a coordinated ethylene monomer. For <i>rac</i>-Me₂Si(2-<i>i</i>-Pr-4-[3,5-Me₂-Ph]-Ind)₂ZrCl₂ this termination route was blocked due to the sterical hindrance created by the bulky substituents of the catalyst. Chemical treatment of methylaluminumoxane solution with a sterically hindered phenol was an effective method to remove trimethylaluminium residuals and suppress chain transfer to aluminium.</p> <p>Propylene was polymerised with a homogeneous binary catalyst system consisting of catalyst precursors Ph₂C(Cp)(Flu)ZrCl₂ (syndiospecific catalyst) and <i>rac</i>-Me₂Si(4-<i>t</i>-Bu-2-Me-Cp)₂ZrCl₂ (isospecific catalyst). The polymerisation behaviour of the catalysts in the binary catalyst system deviated from the behaviour observed for the catalysts individually, indicating an interaction between the catalysts. It was demonstrated that trimethylaluminium operated as a chain shuttling agent and transferred growing polymer chains between active catalyst sites; a stereoblock copolymer consisting of syndiotactic and isotactic blocks was formed. The binary catalyst system was also applied in 1,9-decadiene copolymerisations, and a novel copolymer structure was produced, in which diene linked together polypropylene chains of different tacticities. The copolymer was tested as compatibiliser in a blend of syndiotactic and isotactic polypropylenes. The compatibilised blend showed higher modulus and yield strength values than a 1:1 blend of syndiotactic and isotactic polypropylenes.</p>			
Keywords binary catalyst system, copolymer, metallocene, polypropylene			
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Väitöskirjan nimi Räätälöityjä polypropeenin rakenteita ja ominaisuuksia metalloseenikatalyysillä			
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<p>Yksittäisiä metalloseenikatalyytejä sekä metalloseenikatalyyttien seoksia tutkittiin propeenin polymeroinneissa. Polymerointeja suoritettiin sekä heterogeenisillä että homogeenisillä katalyyteillä käyttäen metyyli-alumiinioksaania kokatalyyttinä. Lisäksi tutkittiin mahdollisuutta valmistaa propeenin kopolymeerejä eteenin, 1-hekseenin ja 1,9-dekadienin kanssa.</p> <p>Kopolymeerien kiteisyys ja sulamislämpötilat olivat alhaisempia verrattuna vastaaviin homopolymeereihin. 1,9-dekadienikopolymeereissä havaittiin pitkäketjuhaarautuneisuutta, joka aiheutti moolimassan kasvua sekä moolimassajakauman leventymistä. Polypropeenin työstettävyyttä parannettiin polymeroimalla propeenin heterogeenisellä yhdistelmä-katalyytillä, jolloin saavutettiin joko leveämpi tai bimodaalinen moolimassajakauma.</p> <p><i>rac</i>-Me₂Si(2-Me-4-Ph-1-Ind)₂ZrCl₂ katalyytillä eteenin läsnä olo laski moolimassaa johtuen β-H vaihdosta koordinoituneeseen eteenimonomeeriin. Tämä terminaatiomekanismi pystyttiin estämään modifioimalla katalyytin rakennetta: polymeroinneissa katalyytillä <i>rac</i>-Me₂Si(2-<i>i</i>-Pr-4-[3,5-Me₂-Ph]-Ind)₂ZrCl₂ β-H vaihtuminen koordinoituneeseen eteenimonomeeriin oli estynyt. Metyyli-alumiinioksaani liuoksen kemiallinen käsittely steerisesti estyneellä fenolilla poisti vapaan trimetyyli-alumiinin kokatalyyttiliuoksesta, jolloin saatiin estettyä terminaatio ketjun vaihdolla alumiiniin.</p> <p>Homogeenista kaksoiskatalyyttisysteemiä, joka koostui katalyyteistä Ph₂C(Cp)(Flu)ZrCl₂ (syndiospesifinen) ja <i>rac</i>-Me₂Si(4-<i>t</i>-Bu-2-Me-Cp)₂ZrCl₂ (isospesifinen), tutkittiin propeenin polymeroinneissa. Katalyyttien polymerointikäyttäytyminen erosi polymerointikäyttäytymisestä, joka havaittiin yksittäisille katalyyteille osoittaen, että kaksoiskatalyyttisysteemissä aktiivisten katalyyttikeskusten välillä oli vuorovaikutuksia. Trimetyyli-alumiini siirsi kasvavia polymeeriketjuja aktiivisten katalyyttikeskusten välillä, joka johti stereoblokki kopolymeerin muodostumiseen. Kaksoiskatalyyttisysteemiä käytettiin lisäksi 1,9-dekadienin kopolymereinneissa, jolloin muodostui uudenlainen kopolymeerirakenne, jossa dieeni yhdisti isotaktisen ja syndiotaktisen polymeeriketjun toisiinsa. Muodostunutta kopolymeeriä seostettiin isotaktisen ja syndiotaktisen polypropeenin kanssa, joka paransi samanaikaisesti sekä moduulia että vetolujuutta verrattuna isotaktisen ja syndiotaktisen polypropeenin 1:1 seokseen.</p>			
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PREFACE

This work was carried out in the Laboratory of Polymer Technology at Helsinki University of Technology in 2003 and 2004, and in the Department of Chemical Engineering at the Norwegian University of Science and Technology in Trondheim between 2004 and 2007. Funding from the Finnish Funding Agency for Technology and Innovation, Borealis Polymers Oy, the Norwegian Research Council, the Department of Chemical Engineering at the Norwegian University of Science and Technology, the Research Foundation of Helsinki University of Technology, NordForsk and the Finnish Cultural Foundation is gratefully acknowledged.

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I wish to express my gratitude to Tapio Saarinen for his assistance, especially in the polymer characterisation by ^{13}C NMR. I am indebted to my co-worker Dr. Jan Lasse Eilertsen not only for fruitful co-operation and innumerable discussions but also for willingness to assist in diverse practical matters in Trondheim. His contribution to this work was invaluable. I am also grateful to the several co-authors for their contributions and comments.

I wish to thank the personnel at the Laboratory of Polymer Technology in Espoo and the Department of Chemical Engineering in Trondheim for creating inspiring and pleasant working environments. Sincere thanks to my colleagues as well, for the many enjoyable hours spent outside of office-hours.

Finally, my warmest thanks are expressed to my mother, father and brothers for their continuous support and encouragement throughout my studies.

Trondheim, February, 2007

Antti Tynys

LIST OF PUBLICATIONS

This thesis is based on the following five appended publications:

- I** Tynys, A., Saarinen, T., Hakala, K., Helaja, T., Vanne, T., Lehmus, P., Löfgren, B., Ethylene–propylene copolymerisations: effect of metallocene structure on termination reactions and polymer microstructure, *Macromol. Chem. Phys.* **206** (2005) 1043-1056.
- II** Tynys, A., Eilertsen, J. L., Rytter, E., Zirconocene propylene polymerisation: controlling termination reactions, *Macromol. Chem. Phys.* **207** (2006) 295-303.
- III** Tynys, A., Eilertsen, J. L., Seppälä, J. V., Rytter, E., Propylene polymerizations with a binary metallocene system – chain shuttling caused by trimethylaluminium between active catalyst centers, *J. Polym. Sci. Part A: Polym. Chem.* **45** (2007) 1364-1376.
- IV** Tynys, A., Saarinen, T., Bartke, M., Löfgren, B., Propylene polymerisations with novel heterogeneous combination metallocene catalyst systems, *Polymer* **48** (2007) 1893-1902.
- V** Tynys, A., Eilertsen, J. L., Seppälä, J. V., Rytter, E., Copolymerisation of 1,9-decadiene and propylene with binary and isolated metallocene systems, *Polymer* **48** (2007) 2793-2805.

The author's contribution to the appended publications was as follows:

- I** The author planned and carried out the polymerisation experiments and part of the polymer characterisation and wrote the corresponding part of the manuscript.
- II** The author planned and carried out the polymerisation experiments and the major part of the polymer characterisation. The manuscript was written with the assistance of the co-authors.
- III** The author planned and carried out the polymerisation experiments and polymer characterisation. The manuscript was written with the assistance of the co-authors.
- IV** The author planned and carried out the polymerisation experiments and part of the polymer characterisation and wrote the major part of the manuscript.
- V** The author planned and carried out the experimental work and prepared the manuscript with the assistance of the co-authors.

ABBREVIATIONS AND SYMBOLS

Benz[e]Ind	benz[e]indenyl
BHT	2,6-di- <i>tert</i> -butyl-4-methylphenol
Bu	butyl
¹³ C NMR	carbon 13 nuclear magnetic resonance
Cp	cyclopentadienyl
Et	ethyl
Flu	fluorenyl
GPC	gel permeation chromatography
Ind	indenyl
IndH ₄	tetrahydroindenyl
<i>i</i> -Pr	isopropyl
k_{β}	rate constant for β -H/ β -CH ₃ transfer to Zr
k_{Al}	rate constant for chain transfer to trimethylaluminium
k_M	rate constant for β -H transfer to monomer
k_p	rate constant for chain propagation
L	ligand
PE-LLD	linear low-density polyethylene
MAO	methylaluminoxane
[M]	monomer concentration (mol/L)
Me	methyl
M_n	number average molecular weight (kg/mol)
M_w	weight average molecular weight (kg/mol)
MWD	molecular weight distribution
M_z	z average molecular weight (kg/mol)
M_{z+1}	z+1 average molecular weight (kg/mol)
P	polymer chain
Ph	phenyl
<i>t</i> -Bu	<i>tert</i> -butyl
TIBA	triisobutylaluminium
TMA	trimethylaluminium

TAILORING OF POLYPROPYLENE STRUCTURES AND PROPERTIES WITH METALLOCENE CATALYSIS

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REFERENCES

1 INTRODUCTION

1.1 Thesis overview

The thesis comprises the present manuscript and the five appended papers. Background relevant to the subjects discussed in the papers is given in chapters 1–3. While the focus is on propylene polymerisations, ethylene polymerisation results are cited where relevant. The main results are collected and discussed in chapter 4, and a summary follows in chapter 5. The experimental procedures for polymerisation and characterisation can be found in the appended publications.

1.2 Scope of the work

The work had two main goals: 1) to tailor properties of metallocene based polypropylenes, including molecular weight, melt temperature and heat of fusion, and 2) to produce novel polypropylene structures with binary metallocene catalyst systems.

Different methods to control the molecular weight of polymers were investigated in publications **I**, **II** and **IV**. The molecular weight is strongly dependent on the metallocene structure, especially on the steric hindrance created by ligand substituents. The dependence of termination reactions on the catalyst structure was of interest in publication **I**, with the focus on termination reactions in ethylene/propylene copolymerisations. Trimethylaluminium (TMA), which is present in small amounts in methylaluminoxane (MAO) solutions, has a strong negative effect on molecular weight due to termination by chain transfer to aluminium. Suppressing chain transfer to aluminium by removing TMA residuals by chemical treatment of MAO solution was investigated in publication **II**. The control molecular weight and molecular weight distribution (MWD) by carrying out polymerisations with heterogeneous combined catalyst systems in propylene bulk phase was evaluated in publication **IV**.

Polypropylene properties can be greatly influenced by copolymerising with different comonomers. Copolymerisations are described in publications **I**, **IV** and **V**. The goal in study **I** was to produce ethylene copolymers with different ethylene contents in order to establish a correlation between ethylene content and the thermal properties of the copolymer. Additionally, the effect of catalyst structure on the

copolymer microstructure was evaluated. Publication **IV** focuses on the possibility to copolymerise 1-hexene in propylene bulk phase and thereby decrease the melt temperature and heat of fusion.

The poor melt strength of metallocene based polypropylene, which leads to processing limitations, can be improved by introducing long-chain branches into the polymer main chain. Long-chain branched polypropylene was prepared by carrying out copolymerisations with 1,9-decadiene; the results are presented in publication **V**. The effect of catalyst structure and polymerisation temperature on the tendency to form long-chain branched structures was studied.

Publications **III** and **V** present the results of polymerisations carried out with a binary metallocene catalyst system consisting of isospecific and syndiospecific catalyst precursors. The main goal in both studies was to synthesise polypropylene structures not obtainable with a single catalyst.

Publication **III** deals with the synthesis of stereoblock copolymer consisting of syndiotactic and isotactic blocks by chain shuttling polymerisation. The feasibility of using TMA as a chain shuttling agent to transfer growing polymer chains between active catalyst centres was investigated. Finally, in study **V**, a binary metallocene catalyst system was investigated in 1,9-decadiene copolymerisations for the purpose of producing a 1,9-decadiene copolymer structure in which 1,9-decadiene links syndiotactic and isotactic polymer chains. The copolymer was tested as compatibiliser in a blend of syndiotactic and isotactic polypropylenes.

1.3 Evolution of the metallocenes

Plastic production has grown exponentially since 1950, reaching 202.0 million tonnes worldwide in 2003. Consumption of polypropylene alone is expected to increase from 35.4 million tonnes in year 2003 to over 50 million tonnes in year 2010 with an annual growth rate of 6.0%.¹ The total demand for metallocene based polypropylene products in 2010 is estimated to be 12 million tonnes, equivalent to about 20% of the total global polypropylene consumption.²

The first steps towards controlled polyolefin polymerisation were taken by Karl Ziegler and his group in 1953. While investigating ethylene oligomerisation in the presence of aluminium alkyls, they discovered that transition metal compounds were efficient catalysts. In the presence of aluminium alkyl activators, zirconium and

titanium halides catalysed the polyinsertion process, which yielded high molecular weight, high density linear polyethylene. One year later Natta introduced the process of stereoselective α -olefin and diene polymerisation. The discovery of Ziegler-Natta catalysts together with Phillips-type (activator-alkyl-free $\text{SiO}_2/\text{CrO}_3$) catalysts initiated a rapid growth of polyolefin technology and the production of polyolefin materials exhibiting a broad range of properties. In 1963 Ziegler and Natta were awarded the Nobel prize in chemistry.³

The polymerisation of ethylene with a single-site, metallocene-type catalyst was reported for the first time in 1957. Initially, these catalysts showed very low polymerisation activity due to the cocatalyst employed (Et_2AlCl or Et_3Al).^{4,5} In 1973, Reichert and Meyer reported that traces of water, which was believed to be a catalyst poison, improved the activity of the catalyst system $\text{Cp}_2\text{TiEtCl}/\text{EtAlCl}_2$.⁶

The work of Sinn and Kaminsky⁷, reported in 1980, is considered to have triggered the evolution of highly active metallocene catalyst systems. They reported a highly active ethylene catalyst Cp_2ZrMe_2 activated by MAO, which was produced by partial hydrolysis of TMA. Motivated by the discovery of Sinn and Kaminsky, others proceeded to develop stereoselective metallocenes. In 1982 Wild *et al.*⁸ reported the synthesis of C_2 -symmetric *rac*- $\text{Et}(\text{Ind})_2\text{TiCl}_2$. In 1984 Ewen⁹ produced partly isotactic polypropylene with a *rac/meso* mixture of $\text{Et}(\text{Ind})_2\text{TiCl}_2$, and one year later Kaminsky *et al.*¹⁰ synthesised highly isotactic polypropylene with *rac*- $\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$. Since the discovery of the highly active metallocene catalyst family, research has been intense and a large number of articles and patents have been published on the subject of polymerisation with single-site catalysts.

The focus of catalyst research has shifted from improving catalyst productivity and stereoselectivity towards modifying morphological, mechanical, rheological and optical properties of polyolefins. The metallocenes enable control of molecular weight (M_w), regio- and stereoselectivity, end groups, polymer microstructure, morphology and especially comonomer incorporation.³ Such control is beyond the reach the commercially widely used heterogeneous Ziegler-Natta catalysts, which have several active sites with different polymerisation behaviour on one catalyst particle, thus hampering controlled polymer synthesis.

1.4 Metallocene catalyst systems

Active metallocene catalyst systems consist of two components, a metallocene precursor and a cocatalyst.

1.4.1 Catalyst precursor

Metallocene catalyst precursors are defined as d^0 , pseudotetrahedral organometallic compounds, in which a transition metal atom bears two cyclopentadienyl-type (Cp) ligands and two σ -ligands. The most common transition metal atom is zirconium and the σ -ligands are typically chloride ions. The aromatic Cp or substituted Cp ligands are π -bonded to the metal and often are connected to each other by a bridging unit.

A unique feature of the metallocene precursors is that they allow modification of the coordination environment of the metal centre through change in the bridging unit or the ligands, or through introduction of ligand substituents. These have been essential for rapid catalyst evolution.

1.4.2 Cocatalyst

The most widely used cocatalyst is MAO, which is able to activate the largest number of metallocenes. MAO is produced by controlled hydrolysis of TMA, but its exact composition and structure are unclear.¹¹ Several structures, from one-dimensional linear chains to three-dimensional clusters have been proposed,¹² and recently MAO was suggested to have a cage structure.¹³⁻¹⁵ The structure of MAO probably cannot be elucidated directly because of the many species in MAO solutions, and residual TMA may participate in equilibria that interconvert various MAO oligomers.¹²

MAO activates the metallocene precursor by formation of cationic alkyl complexes. MAO works as a counter ion to the formed active species, and stabilises the charged system. The reason for the high excess of MAO needed to obtain acceptable polymerisation activity and relatively stable kinetic profiles is not clear. Typically an Al/Zr ratio from 1000 to 10000 is used for homogeneous catalyst

systems, whereas Al/Zr ratios as low as 100 have proven sufficient for supported catalyst systems.¹⁶ One explanation for the high Al/Zr ratio is that MAO works as a scavenger for impurities; another is that high excess of MAO is needed to reactivate dormant catalyst species.¹⁷ It is also possible that a rare minor species is the active part of MAO. Eilertsen *et al.*¹⁸ have proposed that two large MAO clusters are required to stabilise an ion pair, which would partly explain the need for high excess of MAO.

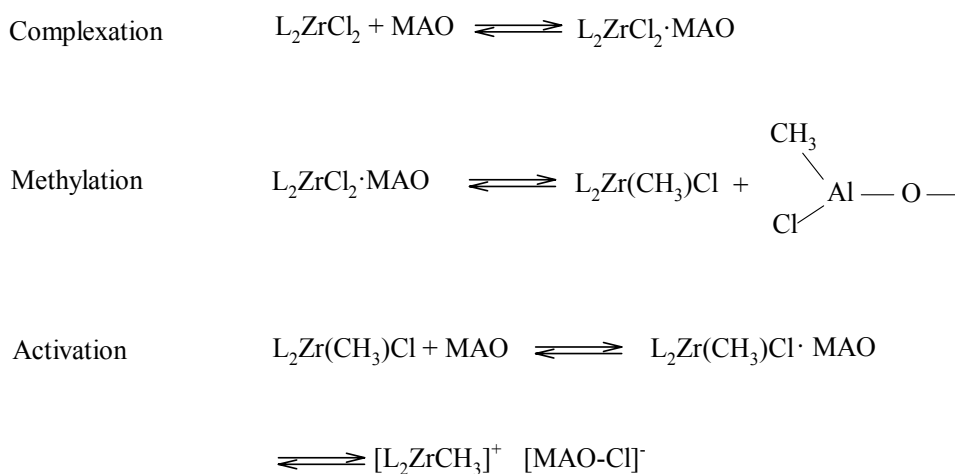
Additionally, boron compounds such as $B(C_6F_5)_3$, $NR_3H^+B(C_6F_5)_4^-$ and $Ph_3C^+B(C_6F_5)_4^-$ have been studied as cocatalysts in combination with metallocene dialkyls with the aim of producing simpler metallocene systems.¹⁶ The disadvantage of this class of cocatalysts is the incorporation of fluorine into the polymer, which may cause problems when polyolefins are thermally decomposed.¹⁹

1.5 Polymerisation mechanisms

The elementary reactions in olefin polymerisation can be described in terms of three key steps: activation, propagation and termination. Detailed understanding of the elementary reactions is necessary to produce efficient and versatile metallocene catalyst systems for olefin polymerisation. Propagation and termination reactions determine M_w and MWD, whereas the catalyst activation and deactivation processes influence the polymerisation kinetics.

1.5.1 Activation

The metallocene precursors are inactive without an activator. A strong Lewis acid (e.g. MAO) is needed for the formation of cationic species active in olefin polymerisations.^{12,20-22} The main steps in the formation of an active metallocene system by activation with MAO are complexation, methylation, and activation. Complexed MAO methylates the metallocene precursor by replacing a chloride ion with a methyl group. The active centre is then formed by abstraction of the other chloride ion. The activation steps are illustrated in simplified form in Scheme 1.

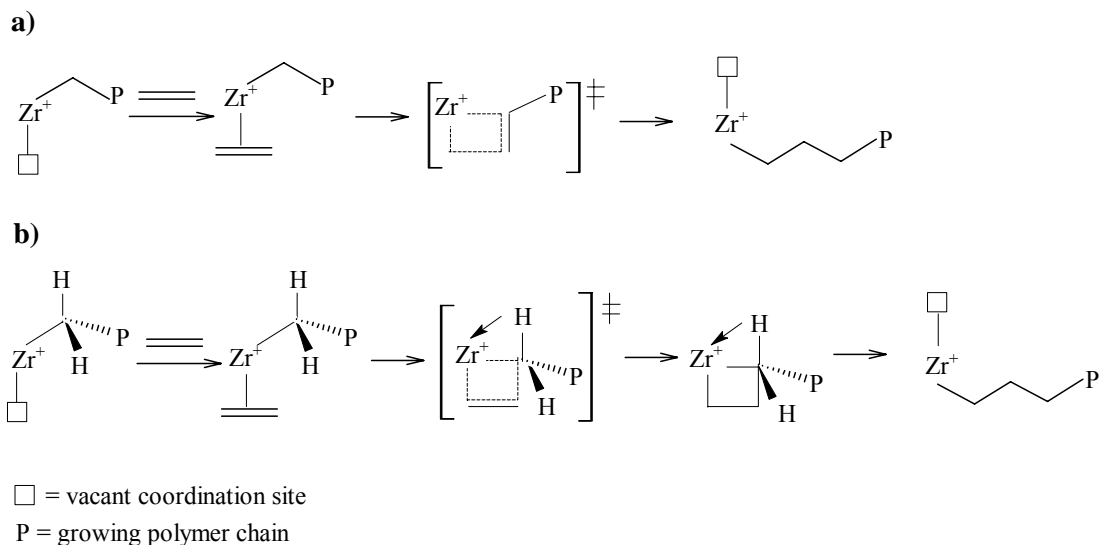
Scheme 1. Metallocene activation by MAO.¹⁷

As mentioned in section 1.4.2, MAO is produced by the controlled hydrolysis of TMA, and commercial MAO solutions always contain a certain amount of free TMA. The role of TMA in the metallocene activation process, and the effect of TMA concentration on catalyst activity, have received little attention, however. In ethylene polymerisations Liu and co-workers^{23,24} have reported that the effect of TMA is dependent on the structure of the metallocene precursor.

1.5.2 Propagation

The chain propagation is generally agreed to occur via olefin coordination and insertion into a metal-carbon bond via a transition state. The Cossee-Arlman direct insertion mechanism and the transition state α -agostic assisted insertion are the two main mechanistic schemes (Scheme 2) proposed for olefin polymerisation catalysed by group 4 transition metals.^{16,25}

Scheme 2. Propagation by the Cossee-Arlman direct insertion mechanism (a)^{26,27} and the transition state α -agostic assisted insertion mechanism (b).^{28,29}



The Cossee-Arlman mechanism was originally developed for conventional Ziegler-Natta catalysts.^{26,27} It involves basically two steps: 1) olefin coordination to the metal at a vacant site and 2) alkyl migration of the σ -coordinated growing chain to the π -coordinated olefin. At the end of the reaction, a net migration of the metal-chain σ -bond to the coordination position previously occupied by the olefin occurs.¹⁶ This cycle continues until termination of the growing polymer chain takes place.

The α -agostic assisted insertion mechanism is a modification of the Cossee-Arlman mechanism.^{28,29} This mechanism requires an interaction between the hydrogen atom on the α -carbon of the growing polymer chain and the metal centre in the transition state of the C-C bond forming step. The α -agostic interaction may lower the activation barrier to olefin insertion and help to orient the polymer chain into the open sector of the catalyst structure thus influencing the stereochemical outcome of the olefin insertion step.^{25,29} In addition to α -agostic interactions, γ -agostic interactions play an important role after the olefin insertion step by stabilising the insertion product.³⁰⁻³² The alkyl chain may also rotate from γ -agostic to more stable β -agostic conformation.³³

The ligand set of the metallocene catalyst and the growing polymer chain together influence the stereochemistry of the polymerisation reaction.³⁴ Enantiomorphic site control, which arises from the ligand set of the metallocene, provides the most

effective control of the polymer tacticity. C_2 -symmetric catalysts have two equivalent enantioselective coordination sites, and an isotactic polymer chain is formed as a result of multiple α -olefin insertions of the same enantioface. C_s -symmetric catalysts in turn are enantiotopic and α -olefin insertions are of alternating enantiofaces resulting in a syndiotactic polymer chain.¹⁶ If the stereogenic centre of the last enchainment monomer unit determines the stereochemistry of monomer addition, the mode of stereochemical regulation is referred to as chain end control.^{16,34} The enantiomorphic site control is typically more efficient and overrides the chain end control. Understanding of the propagation mechanism and the relationship between metallocene structure and tacticity has enabled the production of a wide range of polypropylene tacticities. Polypropylene with a certain tacticity cannot be precisely synthesised with the conventional heterogeneous catalysts.³⁴

Kinetic studies have shown that the reaction order in monomer is often higher than one.¹⁶ Different kinetic models have been proposed to explain this.^{16,35–37} Ystenes³⁵ has proposed a "trigger" mechanism, which involves a two-monomer transition state, where the entering of a new monomer unit triggers the insertion of the already complexed monomer. This mechanism is contested by Busico *et al.*,³⁷ who propose instead first-order kinetics at catalytic species that interconverts between a propagating and a dormant state.

1.5.3 Termination

Termination reactions compete with propagation, and the ratio of the rate of propagation to the rate of termination determines the M_w of the polymer. Thus, understanding and controlling termination reactions offers a way to control the M_w in metallocene catalysed olefin polymerisations.³⁸ The termination mechanisms in olefin polymerisations have been widely investigated and reviewed,^{16,38,39} and it is believed that chain termination starts from β -agostic structure.³² The termination in propylene polymerisations with zirconocene metallocenes with MAO as cocatalyst can occur by five principle routes: β -H transfer to Zr, β -CH₃ transfer to Zr, β -H transfer to monomer, chain transfer to aluminium and chain transfer to chain transfer agent, i.e. H₂. The most common termination reactions after propylene primary insertion are illustrated in Scheme 3.

End-group analysis, where the specific end-groups produced by each termination mechanism (Scheme 3) are differentiated by ^{13}C NMR spectroscopy, provides a powerful tool for determining the termination reactions in propylene polymerisations.

Additionally, analysis of the dependency of M_w on the polymerisation conditions, especially monomer and aluminium concentrations, allows conclusions to be drawn about the termination mechanisms.³⁸ Assuming insignificant chain transfer to MAO, and in the absence of an added chain transfer agent, the number average molecular weight (M_n) of a polymer produced with a metallocene catalyst can be described by the following equation:^{23,40}

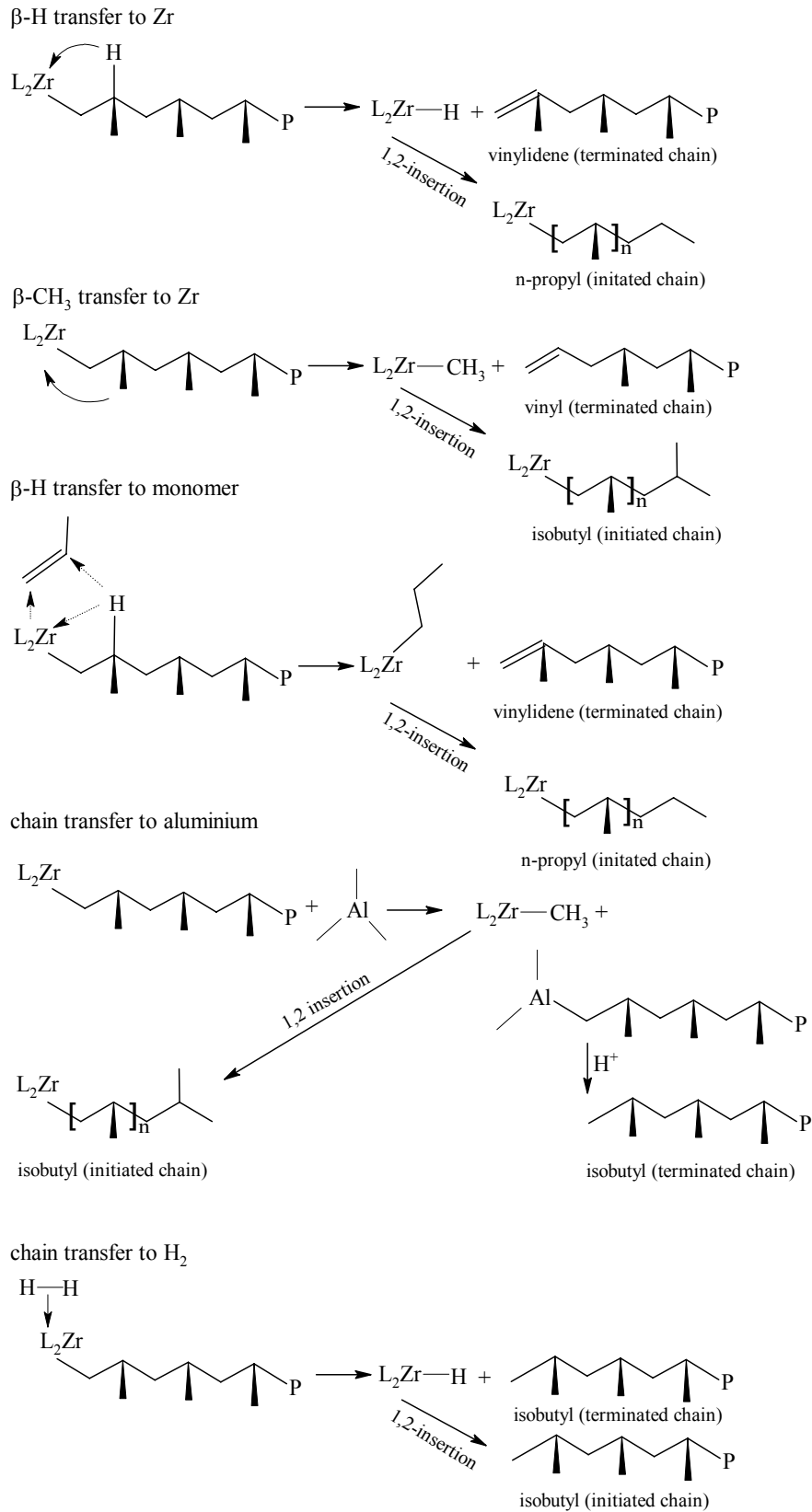
$$M_n = \frac{k_p [M]}{k_p [M] + k_\beta + k_{Al} [TMA]} \quad \text{Eq. (1)}$$

where k_p represents the chain propagation rate constant, and k_M , k_β and k_{Al} represent the rate constants for relevant termination reactions: β -H transfer to monomer (k_M), β -H/ β -CH₃ transfer to Zr (k_β) and chain transfer to TMA (k_{Al}). Here, $[M]$ represents the monomer concentration and $[TMA]$ is the concentration of free TMA in the polymerisation medium. The rate constant ratios can be estimated from the dependency of M_n on the TMA and monomer concentrations.

1.5.4 Isomerisation reactions

In propylene polymerisation, isomerisation side reactions lead to the formation of regioerrors and influence termination reactions. Regioerrors lower the crystallinity and melting point of isotactic polypropylene. It has been shown that catalyst structure and polymerisation conditions, especially polymerisation temperature and monomer concentration, have a major influence on isomerisation reactions.¹⁶

Scheme 3. Termination routes and resulting end groups in propylene polymerisations.³⁸



2 HETEROGENISED METALLOCENE CATALYST SYSTEMS

The advantage of carrying out polymerisation research with homogeneous metallocene systems is that the defined molecular based systems allow detailed studies of structure and mechanisms, and thereby facilitate the development of new and improved catalysts.³⁴ Most metallocene research this far has focused on homogeneous catalyst systems.

Since most industrial processes require heterogeneous systems, the results obtained with homogeneous catalyst systems are not easily implemented, however. Typically, metallocenes are heterogenised by immobilising them on a carrier. Many support materials have been utilised: silica and other inorganic porous oxides, starches, clays, metals and ceramics, metal halides and polymers.⁴¹ Silica is by far the most common carrier for metallocene catalysts, but catalyst homogeneity is typically poor and maximum metal content low. A novel emulsion based catalyst heterogenisation method has recently been developed to overcome these problems. The emulsion based method produces catalyst particles with inherently perfect spherical shape and unique intra- and interparticle homogeneity.^{42,43}

3 TAILORING OF POLYPROPYLENE PROPERTIES

3.1 Propylene copolymerisation

The properties of polypropylene can be significantly altered by copolymerisation of different comonomers. Propylene copolymerisations with ethylene, longer α -olefins, non-conjugated dienes and comonomers containing different functional groups have been investigated to obtain polypropylenes with specific properties.

3.1.1 Functional polypropylene

Because the lack of functional groups in polypropylene limits its application, it has been of interest to introduce functional groups to the polymer main chain by copolymerisation.^{44,45} Various functional polyolefins have been successfully synthesised with metallocene catalysts.⁴⁶⁻⁴⁹

3.1.2 Ethylene copolymers

Owing to their single-site nature, metallocene catalysts offer great potential for the production of ethylene/propylene copolymers and a new generation of elastomers. Copolymers with narrow intermolecular distribution of molecular properties can be prepared with metallocenes, something that is not possible with Ziegler-Natta catalysts.⁵⁰ A small amount of ethylene in the copolymer allows control of the melting and crystallisation behaviour.^{51,52}

The low M_w of metallocene based ethylene/propylene copolymers has been a limiting factor for some applications. Sufficiently high M_w , over 300 kg/mol, is necessary for good tensile and creep properties.⁵² The low M_w of ethylene/propylene copolymers is mainly caused by β -H transfer to a coordinated ethylene monomer.^{51,53} Although 2-methyl substitution in the ligand structure easily suppresses β -H transfer to the bulkier propylene monomer,⁵⁴ there is a need for catalysts that suppress β -H transfer to ethylene and propylene simultaneously.⁵¹

3.1.3 Longer α -olefin copolymers

The most common longer α -olefin used in copolymerisations with propylene has been 1-hexene, but other long α -olefins can be successfully applied as well.⁵⁵⁻⁵⁹ Poon *et al.*⁵⁷ showed that for 1-hexene/propylene copolymers with less than 10 mol-% of 1-hexene, the crystallinity is decreased and the melting peak is shifted to lower temperature with increasing comonomer content. This is due to the exclusion of short branches from the polypropylene crystals. Copolymers containing more than 10 mol-% of 1-hexene crystallise with a new crystal structure that permits incorporation of the 1-hexene units.

3.1.4 Diene copolymers

Copolymerisation of non-conjugated dienes with ethylene, as well as with propylene, has been investigated by several groups.^{56,60-70} One drawback of metallocene based polypropylenes is the low melt strength, and the main aim in copolymerisations with non-conjugated dienes has been to introduce long-chain branched structures to improve processability.^{56,70} Free double bonds in diene/propylene copolymers can be utilised as intermediates to introduce functional groups, and copolymers containing epoxy and maleic anhydride groups have been produced by this method.^{62,67} Besides symmetric non-conjugated dienes, asymmetrically substituted dienes, such as 6-phenyl-1,5-hexadiene,⁷¹ 7-methyl-1,6-octadiene^{56,65,68,71} and *R*(+)-5,7-dimethyl-1,6-octadiene,⁷¹ have been copolymerised with ethylene and propylene.

A diene monomer can be incorporated into a polymer main chain by either cyclo- or linear addition. In cycloaddition, both diene double bonds are incorporated into the same polymer main chain, whereas in linear addition only one double bond is incorporated into a main chain leaving the other double bond unreacted. The free double bond is then available for reaction during the polymerisation leading to long-chain branched structures and, eventually, polymer crosslinking. The amount of cyclic structures in a diene copolymer decreases with increasing length of diene chain,^{66,69} and the tendency to form crosslinked structures is reported to decrease with increase in the polymerisation temperature.⁶⁸

Naga and Imanishi⁶³ investigated the relationship between the diene addition mechanism and catalyst structure in ethylene copolymerisation with 1,7-octadiene. They reported that the catalyst structure had a strong effect on the mechanism; zirconocenes with Cp or Me₅Cp ligands produced a copolymer with both free double bonds and cyclic structures, whereas zirconocenes with indenyl ligands produced only cyclic structures. Arnold *et al.*⁶⁷ used a constrained geometry catalyst in propylene copolymerisation with 1,9-decadiene and found cyclic structures in the resultant copolymer. However, cyclic structures were not found in 1,9-decadiene/propylene copolymers synthesised with other types of metallocenes, showing that the linear addition typically dominates in 1,9-decadiene copolymerisations.^{56,62,63,70}

3.2 Metallocene mixtures

Relative to their Ziegler-Natta catalysed counterparts, metallocene based polypropylenes have a major drawback in their narrow MWD and hence their narrow processing window.⁷² A typical MWD for a metallocene catalysed polypropylene is about 2, whereas the MWD values for Ziegler-Natta catalysed polypropylenes typically vary between 5 and 7.

Several methods for controlling M_w and MWD of metallocene based polyolefins are available: (i) physical blending of polymers of different M_w ,⁷³ (ii) use of a series of reactors, each one run under different polymerisation conditions,⁷⁴ (iii) variation of operating conditions, such as temperature and hydrogen pressure, during polymerisation (non-steady-state polymerisation)^{75,76} and (iv) use of a mixture of metallocenes to produce polymers with different and controlled M_w and MWD.^{73,77} Using two or more metallocenes simultaneously to obtain a polypropylene mixture that consists of polymer fractions produced with the metallocenes individually is an attractive and economical method to control M_w and MWD. Polymerisation behaviour of both homogeneous and heterogeneous metallocene mixtures has been investigated.⁷⁸⁻⁸²

3.3 Novel polymer structures with catalyst mixtures

In a mixture of metallocenes, interactions may occur between active catalyst sites. In chain shuttling polymerisations, a third component (a chain shuttling agent) transfers growing polymer chains between active catalyst sites. The shuttling mechanism evidently offers an attractive method to synthesise novel polyolefin structures.

3.3.1 Stereoblock structures

Chien and co-workers^{78,79} investigated propylene polymerisation with homogeneous binary metallocene systems. With a binary catalyst system consisting of isospecific and aspecific catalyst precursors activated by triphenylcarbenium tetrakis(pentafluorophenyl)borate and tri-isobutylaluminium (TIBA), they were able to produce polypropylene products from tough plastomers to weak elastomers.⁷⁸ With a mixture of isospecific and syndiospecific metallocenes, they obtained stereoblock copolymers consisting of isotactic and syndiotactic blocks.⁷⁹ It was proposed that the chain shuttling agent, in their case TIBA, transferred growing polymer chains between the active catalyst sites, causing the formation of stereoblock copolymer.⁷⁹

The formation of stereoblock copolymer consisting of isotactic and syndiotactic blocks is also reported by Przybyla and Fink.⁸⁰ In their work, propylene was polymerised with a heterogeneous catalyst system in which isospecific and syndiospecific catalyst precursors were immobilised, and MAO was used as cocatalyst. The formation of stereoblock copolymer was confirmed by ¹³C NMR analysis, where a decrease in mmmm/mmmr and rrrr/rrrm pentad ratios was used as evidence. Further evidence was obtained by fractionation results (temperature rising elution fractionation analysis) and scanning electron micrographs. On the basis of the NMR analysis, they calculated that an average block length was 75 monomer units.

The formation of stereoblock polymer by chain shuttling is described by Marques and Chaves,⁸³ who polymerised propylene with a mixture of *rac*-Me₂Si(Ind)₂ZrCl₂ and Et(Cp)(Flu)ZrCl₂ activated with MAO. They concluded that Et(Cp)(Flu)ZrCl₂ incorporates the mmmm-rich polymer chains produced with *rac*-Me₂Si(Ind)₂ZrCl₂ by the chain shuttling mechanism, giving rise to stereoblock copolymer.

Lieber and Brintzinger⁸¹ investigated the effects of metallocene structure and the type of cocatalyst on chain shuttling reactions between an active catalyst site and the cocatalyst in propylene polymerisations with homogeneous binary catalyst systems. Four different metallocenes were investigated: a highly substituted isospecific *rac*-Me₂Si(2-Me-4-*t*-Bu-Cp)₂ZrCl₂, an isospecific *rac*-Me₂Si(2-Me-Ind)₂ZrCl₂, an aspecific Et(Flu)₂ZrCl₂ and a syndiospecific Ph₂C(Cp)(Flu)ZrCl₂. The cocatalyst was either MAO or TIBA with triphenylcarbenium tetrakis(perfluorophenyl)borate (borate). These catalysts were first studied individually with regard to their tendency toward chain shuttling with the respective alkylaluminium activator and then pairwise with respect to their capability to generate polymers with a stereoblock structure. With MAO as cocatalyst, the most highly substituted catalyst, *rac*-Me₂Si(2-Me-4-*t*-Bu-Cp)₂ZrCl₂, had the strongest tendency towards chain shuttling, and a stereoblock copolymer was produced when it was combined with the aspecific catalyst Et(Flu)₂ZrCl₂. It was also likely that a stereoblock copolymer was formed in a polymerisation with a mixture of *rac*-Me₂Si(2-Me-4-*t*-Bu-Cp)₂ZrCl₂ and Ph₂C(Cp)(Flu)ZrCl₂ activated by MAO. Chain transfer reactions were not observed for *rac*-Me₂Si(2-Me-Ind)₂ZrCl₂ underlining the importance of the catalyst ligand structure on chain shuttling reactions. Formation of stereoblock copolymer was not observed when borate/TIBA was used as cocatalyst. The observation that TIBA does not work as a chain shuttling agent is at variance with the results reported by Chien and co-workers.^{78,79}

Arriola *et al.*⁸⁴ report a binary catalyst system, that produces an ethylene block copolymer with alternating semicrystalline and amorphous segments. After extensive screening of different catalysts and possible chain shuttling agents, they chose zirconium bis(phenoxyiminine) and hafnium pyridylamide catalysts, with diethylzinc as chain shuttling agent. In octene/ethylene copolymerisation, these catalysts displayed a significant difference in comonomer response and there was evidence of chain shuttling by diethylzinc. The hard and soft polymer chains produced by the catalysts individually were shown to be efficiently transferred between the active catalyst centres by diethylzinc leading to the formation of the ethylene block copolymer.

3.3.2 Branched structures

Besides block copolymers, metallocene mixtures have been utilised to produce branched polymer structures. Ye and Zhu⁸⁵ synthesised a polypropylene structure having isotactic backbone and atactic side chains. The catalyst mixture they used consisted of an iron catalyst, $\{[2\text{-ArN}=\text{C}(\text{Me})]_2\text{C}_5\text{H}_3\text{N}\}\text{FeCl}_2$, and a zirconocene catalyst, *rac*- $\text{Me}_2\text{Si}(2\text{-MeBenz[e]Ind})_2\text{ZrCl}_2$, activated by modified MAO. The iron catalyst produced vinyl-terminated atactic macromonomers, and the macromonomers were incorporated into an isotactic polymer main chain in polymerisation with the zirconocene catalyst. A comb-like polypropylene structure was formed. Recently, Frediani *et al.*⁸⁶ reported that a mixture of a late transition metal oligomerisation catalyst with an early transition metal copolymerisation catalyst produced branched polyethylenes, with properties ranging from semicrystalline PE-LLD to amorphous, rubbery products.

4 RESULTS AND DISCUSSION

Five different metallocene precursors activated by MAO were of interest in the present work: *rac*-Me₂Si(2-Me-4-Ph-1-Ind)₂ZrCl₂ (**1**), *rac*-Me₂Si(2-*i*-Pr-4-[3,5-Me₂-Ph]-Ind)₂ZrCl₂ (**2**), *rac*-Et(2-[*t*-Bu-Me₂-SiO]-Ind)₂ZrCl₂ (**3**), Ph₂C(Cp)(Flu)ZrCl₂ (**4**) and *rac*-Me₂Si(4-*t*-Bu-2-Me-Cp)₂ZrCl₂ (**5**). The catalysts are depicted in Figure 1. Catalyst **4** is C_s-symmetric producing syndiotactic polypropylene, whereas the other catalysts are C₂-symmetric polymerising isotactic polypropylene.

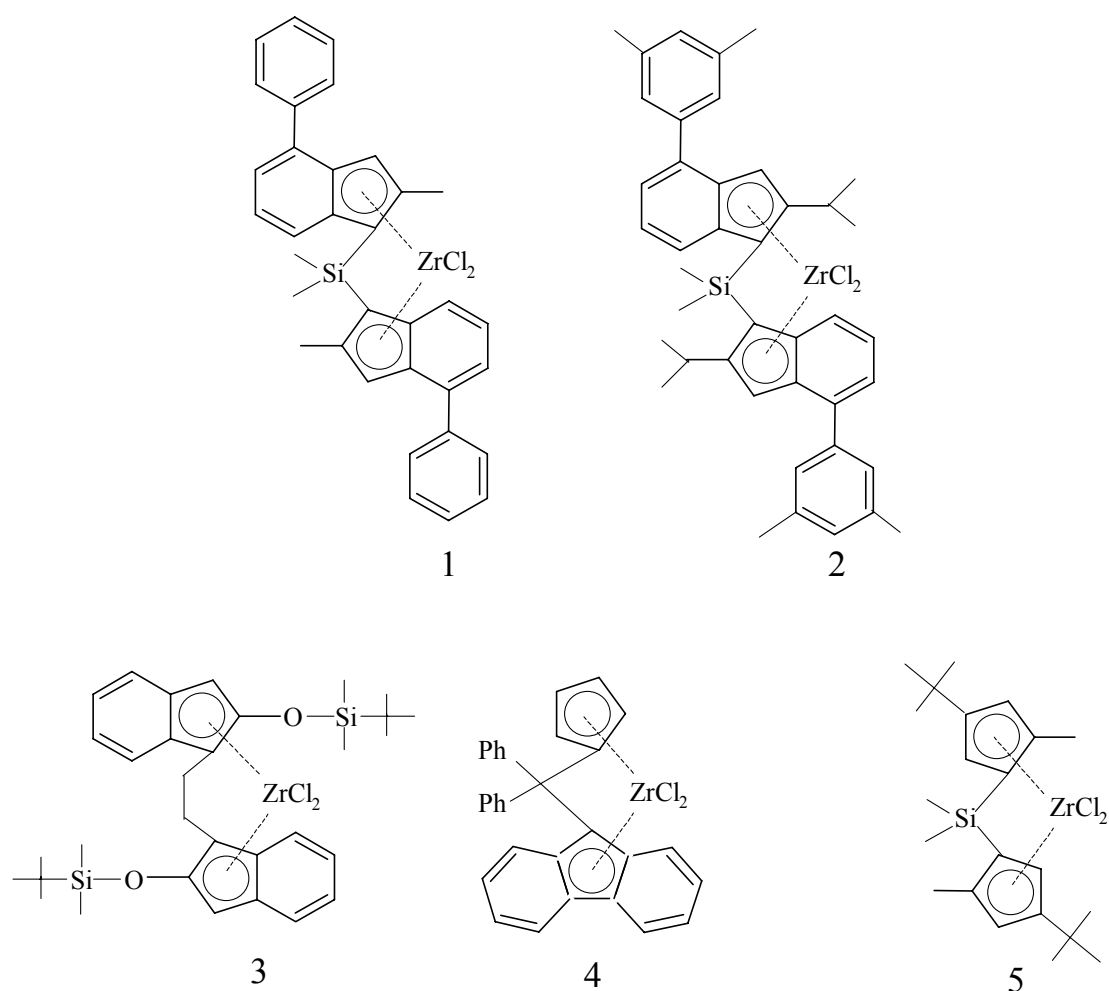


Figure 1. The metallocene precursors applied in this study.

Catalysts **1** and **2** were investigated separately as homogeneous catalysts in heptane solution at 70 °C, with total propylene pressure from 1.5 to 5.0 bar.^I Catalysts **4** and **5** were applied at 40 °C and 80 °C in toluene solution with total pressure of 2.0 and 4.0 bars.^{II} A homogeneous binary catalyst system consisting of a mixture of the metallocene precursors **4** and **5** was also applied.^{III,V}

Polymerisation behaviour of heterogeneous combined catalyst systems **1+2** and **1+3** produced by a novel emulsion based heterogenisation method^{42,43} was investigated in propylene bulk phase at 50 °C and 70 °C.^{IV} The heterogenised catalyst systems are described in Table 1.

Table 1. Heterogeneous catalyst systems applied in this study.^{IV}

	Percentage composition (mol-%/mol-%)	Al/Zr (mol/mol)
Catalyst 1+3	63.6 / 36.4	200
Catalyst 1+2	13.7 / 86.3	200

4.1 Effect of TMA on catalyst activity

The effect of TMA on catalyst activity was studied with catalyst precursors **4** and **5**. The results are reported in publication **II**. TMA-free polymerisation conditions were obtained by adding 2,6-di-*tert*-butyl-4-methylphenol (BHT) to the polymerisation reactor before the injection of the catalyst solution. Slightly more than two equivalents of BHT was added relative to the amount of TMA in the MAO solution. BHT reacts with TMA^{87,88} with formation of the product shown in Figure 2. The use of TMA-free MAO for catalyst activation was first reported by Busico *et al.*⁸⁹ and Carlini *et al.*⁹⁰

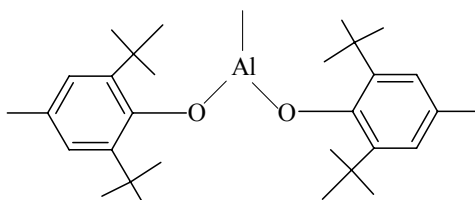
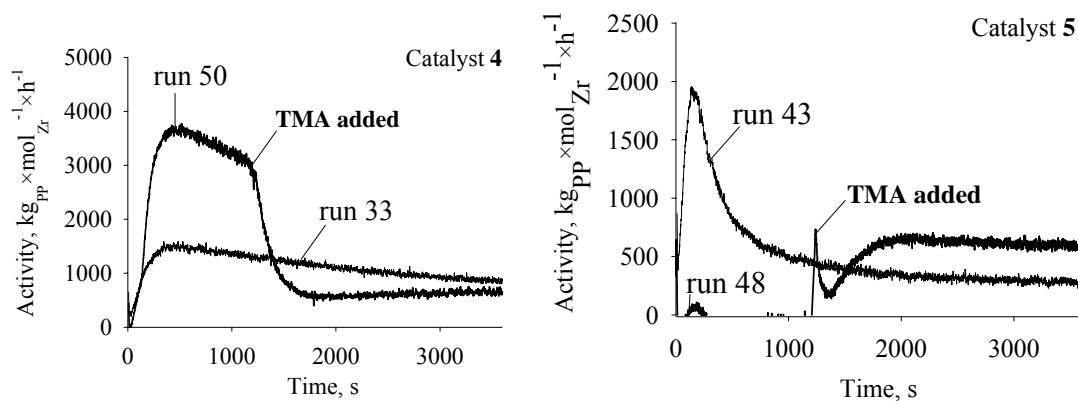


Figure 2. Reaction product of TMA and BHT.⁸⁸

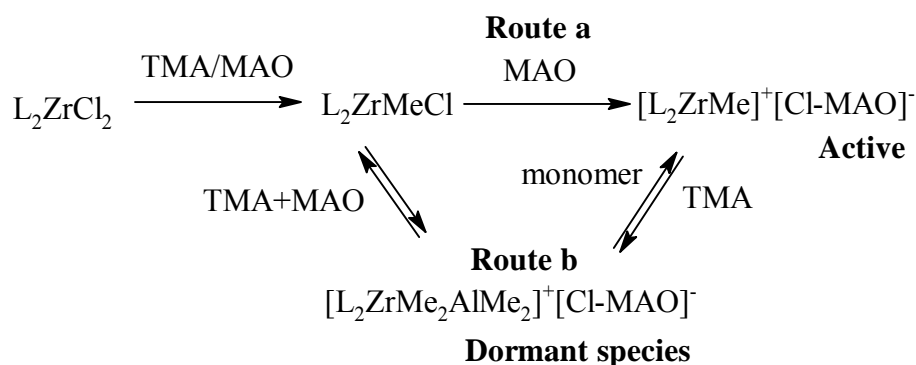
Activity trends for catalysts **4** and **5** at different TMA concentrations at 40 °C are presented in Figure 3. In polymerisation runs 33 (catalyst **4**) and 43 (catalyst **5**), the TMA concentration was 5.5 mmol/L, whereas runs 50 (catalyst **4**) and 48 (catalyst **5**) were started with TMA concentration of just 0.4 mmol/L, and the concentration was raised to 30.4 mmol/L by adding more TMA after 20 min polymerisation.



*Figure 3. Activity trends for catalysts **4** and **5** at different TMA concentrations at 40 °C. In runs 33 and 43 [TMA] was 5.5 mmol/L; in runs 50 and 48 [TMA] was 0.4 mmol/L at the beginning of the polymerisation, and TMA was added after 20 min.^{II}*

With catalyst **4**, the low starting TMA concentration (run 50) led to 2- to 3-fold higher activity, whereas with catalyst **5** (run 48) it resulted in nearly total loss of catalyst activity. When more TMA was added (after 20 min) during the polymerisation, the activity of catalyst **4** dropped sharply, whereas the activity of catalyst **5** recovered.

A possible mechanism for metallocene activation by MAO in the presence of TMA was constructed to explain the observed activity trends. The mechanism is illustrated in Scheme 4. The metallocene is mono-methylated by TMA or MAO. The mono-methylated metallocene is then activated by MAO (route a), and the catalytically active ion pair is formed. The catalytically active ion pair may then react with free TMA, whereupon a dormant and relatively stable inactive species is created, and the active centre is protected from terminal deactivation. Alternatively, the mono-methylated metallocene may react with MAO and TMA to form the dormant species directly (route b). This species is subsequently activated for the polymerisation by a monomer insertion.¹⁸

Scheme 4. Metallocene activation in the presence of TMA.^{II}

The decrease in the activity of catalyst **4** upon increase in the TMA concentration (run 50) is plausibly explained by the reaction of TMA with an active catalyst site, causing formation of the dormant species as depicted in Scheme 4. The low activity of catalyst **5** in the absence of TMA (run 48) may be related to the more sterically hindered structure of **5**. Possibly bulky MAO molecules are not capable of mono-methylating the catalyst precursor, or possibly the formation of the active ion pair after the mono-methylation is blocked due to steric reasons (route a). Evidently, for activation of catalyst **5**, TMA must be present for the mono-methylation or to form the dormant species (route b), which is activated by the monomer insertion.

4.2 Controlling termination reactions

Termination mechanisms in propylene homopolymerisations with catalysts **1**, **2**, **4** and **5** are reported in publications **I** and **II** and summarised in Table 2. The termination mechanisms of catalyst **3** are as reported by Lehmus *et al.*⁹¹ for ethylene polymerisations. Five different ways to influence the termination behaviour of the metallocenes are discussed below.

Table 2. Chain termination mechanisms for catalysts 1–5.

Catalyst	Termination mechanism(s)	Ref.
1	β -CH ₃ transfer to Zr Chain transfer to aluminium	I
2	β -CH ₃ transfer to Zr Chain transfer to aluminium	I
3	Chain transfer to monomer ^a	91
4	β -H/ β -CH ₃ transfer to Zr β -H transfer to monomer Chain transfer to aluminium	II
5	β -H/ β -CH ₃ transfer to Zr Chain transfer to aluminium	II

^aIn ethylene polymerisation.

4.2.1 Catalyst structure¹

The effect of catalyst structure was studied by applying two sterically different metallocenes, **1** and **2**, in production of ethylene/propylene copolymers containing different amounts of ethylene, as well as in propylene and ethylene homopolymerisations. Focus was on the effect of the steric hindrance created by bulky substituents of indenyl ligands on termination mechanisms and polymer microstructure. In catalyst **2**, the 2-methyl substituents of the indenyl ligands of catalyst **1** were replaced by bulkier 2-isopropyl substituents, and two methyl groups were introduced to the phenyl groups. The termination routes were determined by end-group analysis by ¹³C NMR and by M_w dependency on the polymerisation conditions.

In the case of catalyst **1**, in propylene rich polymerisations, the chain termination took place by chain transfer to aluminium and by β -CH₃ transfer to Zr. As expected, chain transfer to the bulky propylene monomer was suppressed by the 2-methyl substitution. In the presence of ethylene, chain transfer to a coordinated ethylene monomer became an important termination route, as reported earlier by Fan and Waymouth⁵³ and Voegelé *et al.*⁵¹

For catalyst **2**, the same termination pattern as for catalyst **1** was found in propylene homopolymerisation, but in the presence of ethylene the termination did not take place by chain transfer to the coordinated ethylene monomer. The result shows that it is possible to block simultaneously chain transfer to propylene and

ethylene monomer through proper tailoring of the steric hindrance of the metallocene precursor. Understanding of steric hindrance is essential to the development of improved catalysts for ethylene/propylene copolymerisation, as discussed in section 3.1.2.

Ethylene/propylene copolymer was also produced with the combined heterogeneous catalyst **1+2** in propylene bulk phase.^{IV} Supporting the results discussed above, ethylene did not have a negative effect on the M_w of the polymer fraction produced with catalyst **2**, but it caused a marked decrease in the M_w of the polymer fraction produced with catalyst **1**.

4.2.2 Eliminating TMA^{II}

The effect of TMA on termination reactions was investigated with catalyst precursors **4** and **5**. Polymerisations were conducted at different TMA concentrations at 40 °C and 80 °C. With both catalysts, higher TMA concentration caused a sharp decrease in the M_w of the polymers. The highest M_w values were obtained in the absence of TMA. Analysis of the end groups of the samples polymerised with catalyst **5** by ¹³C NMR showed the amount of iso-butyl end groups arising from chain transfer to aluminium to increase with increasing TMA concentration. No iso-butyl end groups were detected in the sample polymerised in the absence of TMA. Evidently, chain transfer to aluminium, especially to TMA, is significant for both catalysts. Additionally, the results show that i) free TMA can be efficiently removed by BHT and ii) marked chain transfer to aluminium does not occur in the absence of TMA.

4.2.3 Polymerisation temperature^{II,V}

Propylene was polymerised with catalyst **4** at different TMA and monomer concentrations at 40 °C and 80 °C. From Eq. (1) and the measured M_n values, the order of the rate constants of the termination reactions for catalyst **4** was determined to be $k_{Al} \gg k_M > k_\beta$ at 40 °C and $k_{Al} \gg k_\beta > k_M$ at 80 °C. While temperature did not have a significant effect on the $k_M \cdot k_p^{-1}$ value, the $k_\beta \cdot k_p^{-1}$ value showed substantial temperature dependency. The estimated reaction rate ratios for termination and

propagation at 40 °C and 80 °C are summarised in Table 3. The M_n dependency on TMA concentration at 40 °C and 80 °C is illustrated in Figure 4.

Table 3. Reaction rate ratios for termination and propagation with catalyst **4**.^{II}

	$k_{Al} \cdot k_p^{-1}$	$k_M \cdot k_p^{-1}$	$k_\beta \cdot k_p^{-1}$
40 °C	$2.68 \cdot 10^{-4}$	$5 \cdot 10^{-6}$	$4 \cdot 10^{-7}$
80 °C	$1.51 \cdot 10^{-3}$	$4 \cdot 10^{-6}$	$2 \cdot 10^{-5}$

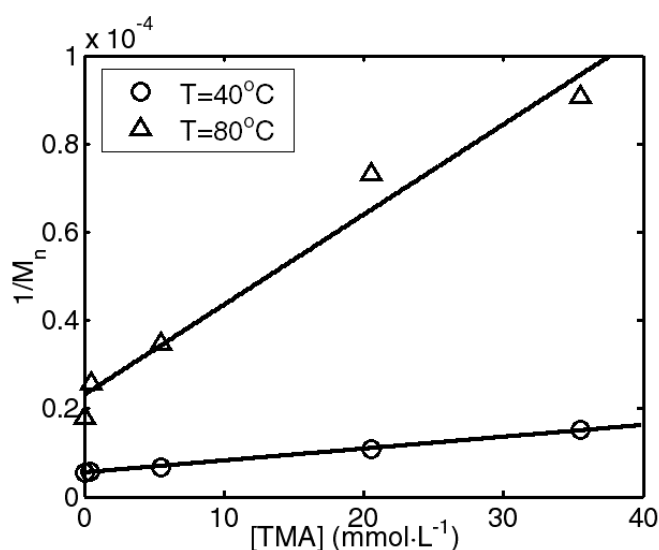


Figure 4. M_n dependency on TMA concentration with catalyst **4** at 40 °C and 80 °C.^{II}

End-group analysis of polymers produced with catalyst **5** at 40 °C and 80 °C showed that β -H transfer to Zr became more important at elevated temperature. The results discussed above show that an increase in the temperature favours the termination by β -H/ β -CH₃ transfer to Zr over β -H transfer to monomer. Additionally, it was seen that an elevated temperature favours termination by chain transfer to aluminium.

4.2.4 Chain transfer to molecular hydrogen^{IV}

The M_w of polyolefins is often controlled through use of molecular hydrogen as a chain transfer agent.⁹² The effect of hydrogen on M_w was evaluated in polymerisations with the heterogeneous combined catalysts **1+3** and **1+2** in propylene

bulk phase. As expected, a decrease in M_w was observed with both catalyst systems due to the inherent chain transfer reactions to molecular hydrogen.

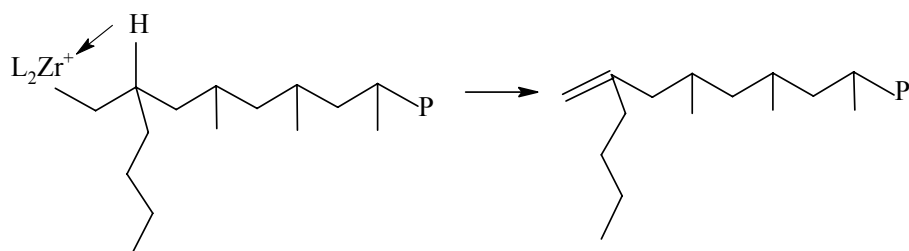
4.2.5 1-Hexene copolymerisation^{IV}

A negative effect of 1-hexene on M_w was observed in propylene copolymerisation in propylene bulk phase with the combined heterogeneous catalysts **1+3** and **1+2**. The M_w of the polymer fraction produced with catalyst **1** was decreased in the 1-hexene copolymerisations. Additionally, in the copolymer produced with **1+3**, the amount of vinylidene end-groups was increased, and it was concluded that, in the case of catalyst **1**, termination preferably took place immediately after incorporation of 1-hexene monomer into the growing polymer chain. The mechanism for the termination after 1,2 or 2,1 insertion of 1-hexene by β -H transfer to Zr is shown in Scheme 5.

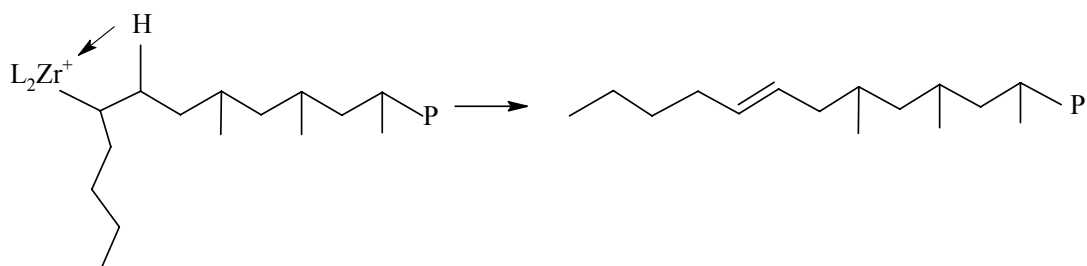
The strong negative effect of 1-hexene on the M_w was not expected, because the opposite effect has been reported.^{56,57} However, the negative effect of 1-hexene on M_w has been observed earlier for 1-hexene/ethylene copolymers.^{93,94}

Scheme 5. Chain termination after 1-hexene insertion.^{IV}

β -H transfer to Zr after 1,2 insertion of 1-hexene



β -H transfer to Zr after 2,1 insertion of 1-hexene



4.3 Propylene copolymerisations

In this work, propylene was copolymerised with 1-hexene, ethylene and 1,9-decadiene. The results are presented in publications **I**, **IV** and **V**. The effect of copolymerisation on the polymer properties is discussed below.

4.3.1 1-Hexene copolymers^{IV}

1-Hexene/propylene copolymers were synthesised with the combined catalyst systems **1+3** and **1+2** in propylene bulk phase. A copolymer containing 0.8 mol-% 1-hexene was produced with catalyst combination **1+3**. The 1-hexene copolymerisation decreased the M_w (from 286 to 144 kg/mol) due to the favoured termination after the 1-hexene insertion, as noted above. The melting point decreased from 147 °C to 135 °C, accompanied by a decrease in the heat of fusion. Catalyst **1+2** showed slightly better 1-hexene response, and a copolymer containing 1.1 mol-% 1-hexene was produced. In the case of catalyst **1+2**, the M_w decreased from 254 to 217 kg/mol, and the melting point decreased from 152 °C to 139 °C accompanied by a decrease in the heat of fusion. By the step crystallisation method⁹⁵ it was shown that all the metallocenes (**1**, **2** and **3**) were capable of incorporating 1-hexene.

4.3.2 Ethylene copolymers^{I,IV}

Ethylene copolymers were synthesised with catalysts **1** and **2** separately and with the heterogeneous combined catalyst system **1+2**. The effect of catalyst structure on the M_w and the termination reactions in ethylene copolymerisations were discussed in section 4.2.1.

Copolymers containing different amounts of ethylene were prepared with catalysts **1** and **2**. With catalyst **1**, the melting temperature and heat of fusion of the copolymers were decreased relative to the values for homopolymer samples, and amorphous material was obtained when the ethylene content was 21.9–63.6 mol-%. This result is in good agreement with that of Shin *et al.*,⁹⁶ who reported that propylene-rich copolymers contain only polypropylene crystals, whilst ethylene-rich copolymers contain only polyethylene crystals. The two types of crystals never coexist in the copolymers. Ethylene units in polypropylene disturb the formation of

polypropylene crystals, and weaken the melting peak and shift it to a lower temperature. As the ethylene content is increased, the melting peak corresponding to polyethylene develops. ^{13}C NMR analysis of the copolymers produced with catalyst **1** showed that a slightly blocky copolymer was obtained, where ethylene tended to form blocks randomly separated by propylene units.

The melting behaviour of the copolymers produced with catalyst **2** was not noticeably different from that of copolymers produced with catalyst **1**. However, a difference in the copolymer microstructure was observed; catalyst **2** produced random copolymer, not a slightly blocky copolymer as found for catalyst **1**.

A copolymer containing 3.0 mol-% of ethylene was obtained with the combined heterogeneous catalyst **1+2** in propylene bulk phase. As expected, the melting point and heat of fusion were decreased relative to the homopolymer produced with the same catalyst system. Additionally, ethylene decreased the amount of 1,3 misinsertions by incorporating into the polymer chain faster than propylene after 2,1 misinsertion and leaving less time for isomerisation reactions.

4.3.3 Diene copolymers^V

Diene copolymers were produced with catalysts **4** and **5** and with a mixture of these catalysts. The diene copolymerisation results with the catalyst mixture are discussed in section 4.5.3.

1,9-Decadiene copolymers with a comonomer content up to 0.98 mol-% were produced with catalysts **4** and **5**. The structures of the copolymers produced with **4** and **5** are presented in Figure 5, and the ^{13}C NMR spectra in Figure 6. Copolymerisations were carried out at 40 °C and 80 °C, and catalyst **4** showed a slightly better comonomer response at both temperatures. Compared with the homopolymers, the copolymers showed a decrease in the melting and crystallisation temperatures and an increase in the M_w and MWD values. The increase in the M_z and M_{z+1} values, which are sensitive to the high M_w fraction of a polymer, was pronounced confirming the formation of long-chain branched polypropylene. Catalyst **4** showed a greater tendency for long chain branching than did catalyst **5**, especially at 80 °C (Figure 7). As was expected, only linear addition of 1,9-decadiene was observed in copolymerisations with both catalysts; no cyclic structures were detected. A decrease in the rrrr pentad value was measured for the copolymers produced with

catalyst **4**, which indicates that stereoselectivity of **4** was influenced by 1,9-decadiene incorporation. This effect was not observed for catalyst **5**.

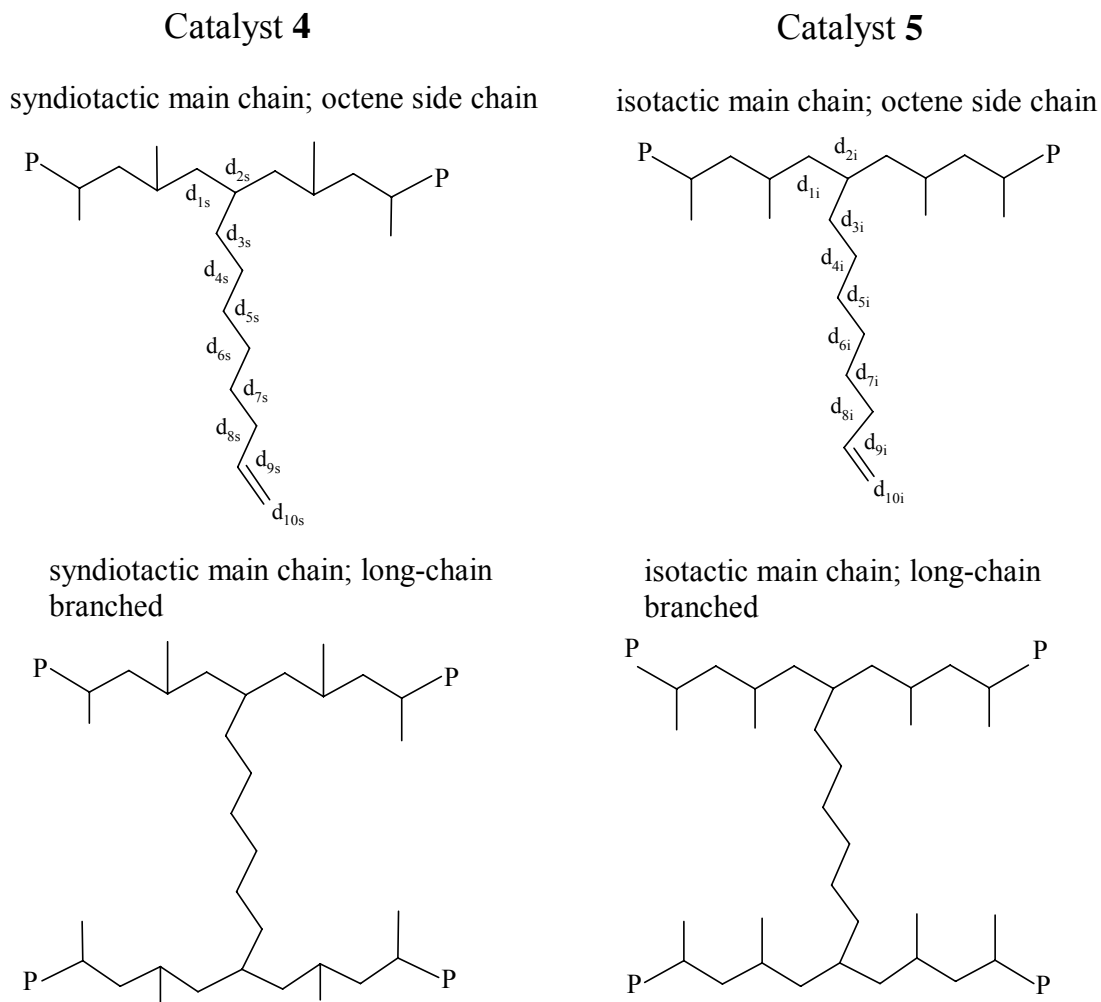


Figure 5. 1,9-Decadiene copolymer structures synthesised with catalysts **4** and **5**.^V

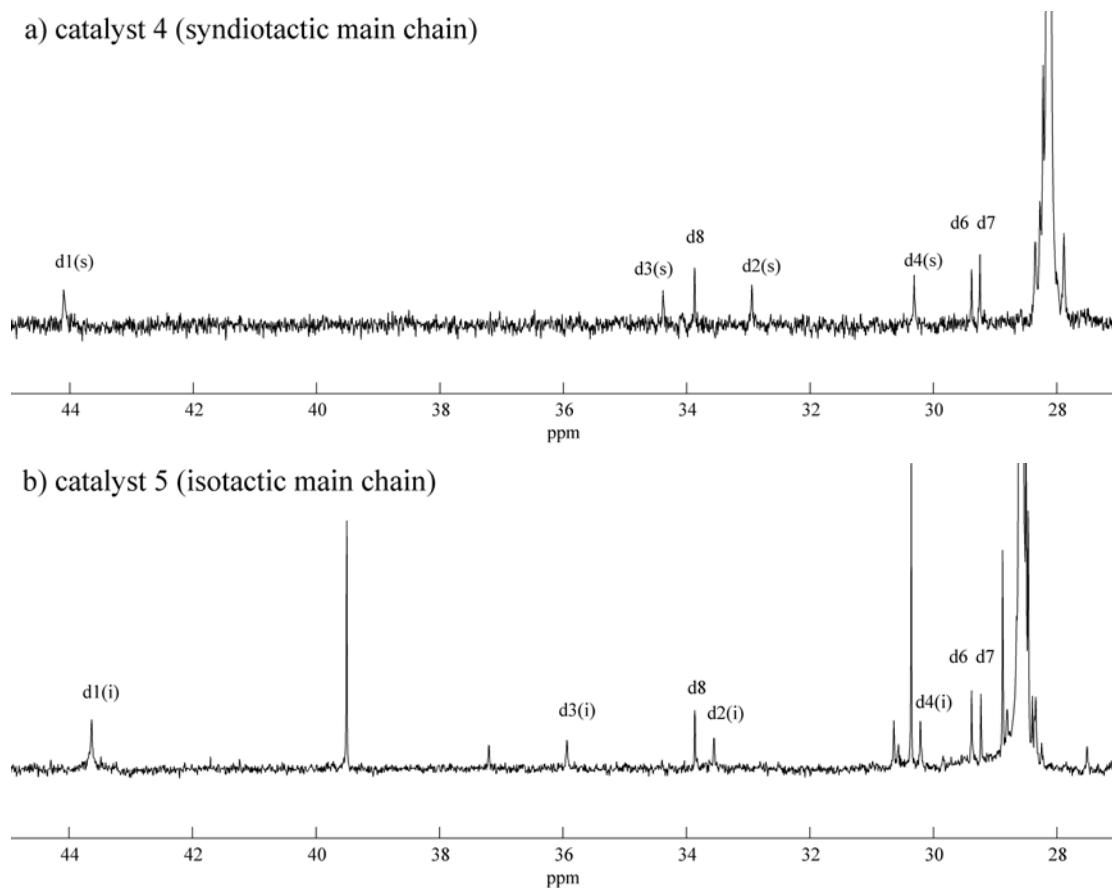


Figure 6. ^{13}C NMR spectra of 1,9-decadiene copolymers produced with catalysts **4** (a) and **5** (b).^V

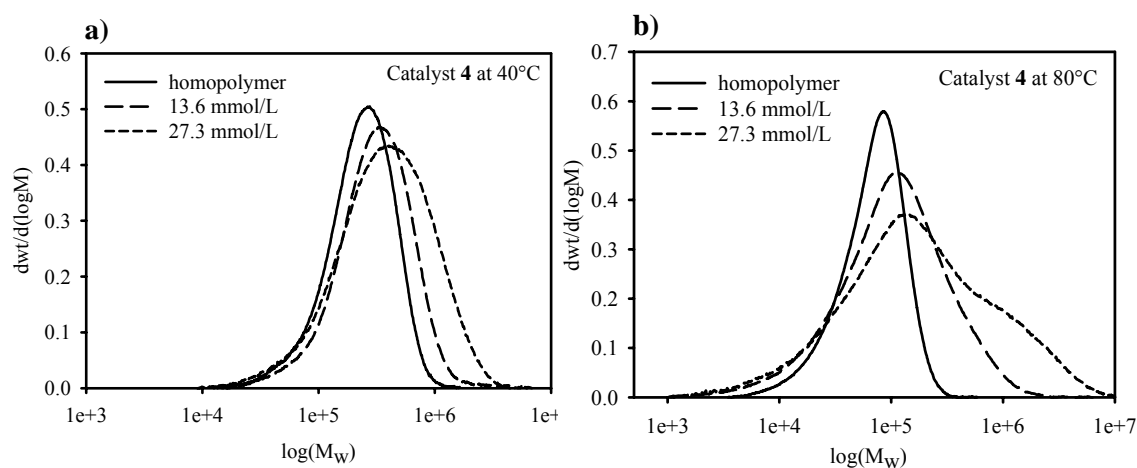


Figure 7. GPC curves of homo- and copolymers with increasing initial 1,9-decadiene concentration produced with catalyst **4** at 40 °C and 80 °C.^V

4.4 Controlling M_w and MWD with catalyst mixtures

Publication IV reports the polymerisation results with the heterogeneous combined catalysts **1+3** and **1+2** heterogenised by the emulsion-based heterogenisation method.^{42,43} The aim of the investigation was to overcome the processing limitations associated with narrow MWD metallocenes by using combination metallocene catalyst systems. The effects of polymerisation temperature and hydrogen on polymerisation behaviour and polymer properties were of interest, as well as the possibility of copolymerising 1-hexene and ethylene (discussed in sections 4.3.1 and 4.3.2).

Depending on the polymerisation conditions, M_w of propylene varied from 144 to 286 kg/mol for catalyst **1+3** and from 200 to 390 kg/mol for catalyst **1+2**. Combination **1+3** produced bimodal MWD with distinct low- and high- M_w polymer fractions. The MWD range was between 6.4 and 11.8, which was significantly broader than the MWD produced with **1+2**. GPC curves of the samples produced with **1+3** and **1+2**, including the modelled Schultz-Flory fractions, are illustrated in Figure 8. The presence of four Schultz-Flory fractions was due to variations in the polymerisation conditions. Because the catalyst and liquefied propylene were fed to the reactor at room temperature, some polymerisation took place while the temperature was being raised to the polymerisation temperature, causing broader MWD than predicted by Schultz-Flory theory.

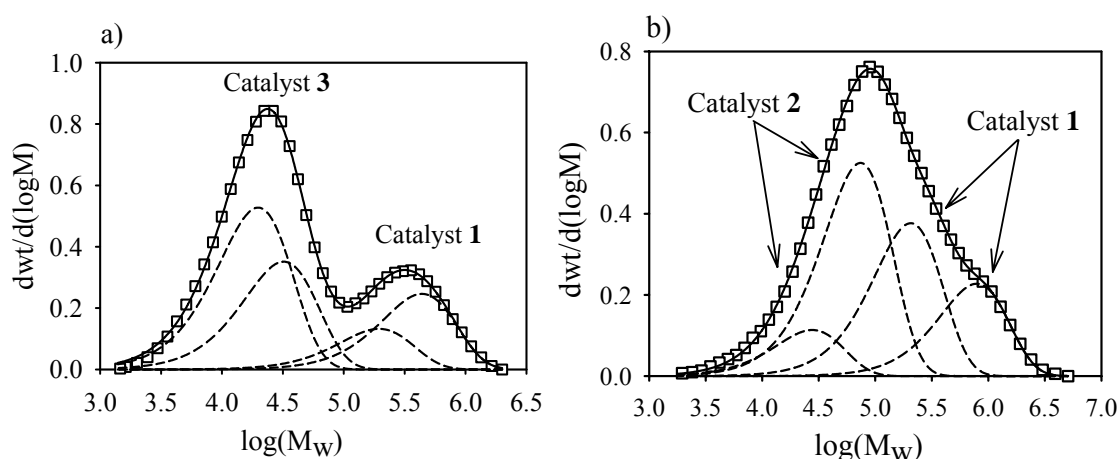


Figure 8. GPC curves and Schultz-Flory fractions of samples produced with catalyst combinations **1+3** (a) and **1+2** (b). Squares: observed GPC data points, dashed line: Schultz-Flory fractions, solid line: sum of Schultz-Flory fractions.^{IV}

There was no direct evidence of interactions between the active catalyst centres, and it is likely that the combined metallocenes worked individually in these polymerisations. The responses to polymerisation conditions of the individual metallocenes in the combined systems followed the patterns observed for the catalysts used separately. Since the studied metallocene systems produced polypropylene with the same tacticity as the individual catalysts, it would be virtually impossible to detect interactions on the basis of polymer properties such as microstructure.

4.5 Novel polypropylene structures with catalyst mixtures

As discussed in section 3.3, mixed catalyst systems can be used to produce polypropylene structures unavailable with single metallocenes. These systems were investigated in publications **III** and **V**.

4.5.1 Stereoblock copolymers^{III}

The homogeneous binary catalyst system consisting of metallocene precursors **4** (syndiospecific) and **5** (isospecific) activated by MAO was investigated for the production of a stereoblock copolymer having syndio- and isotactic blocks. The role of TMA as a chain shuttling agent was of interest. TMA-free polymerisation conditions were obtained by chemical treatment of the MAO solution with BHT. Catalysts **4** and **5** were considered to be good candidates to produce stereoblock copolymer by chain shuttling assisted by TMA because chain transfer to aluminium had earlier (publication **II**) been found to be an important termination route for both catalysts. The polymerisations were carried out at two temperatures (40 °C and 80 °C) and with different TMA concentrations. Typical GPC curves of samples obtained with the binary catalyst system **4+5** at 40 °C are presented in Figure 9(a). Melting thermograms of samples produced with the binary catalyst system **4+5** at different TMA concentrations at 40 °C are shown in Figure 9(b).

The polymerisation behaviour of catalysts **4** and **5** used together deviated from the polymerisation behaviour observed for the catalysts individually. Evidently, in the polymerisations conducted with the binary system, an interaction occurred between the active catalyst sites.

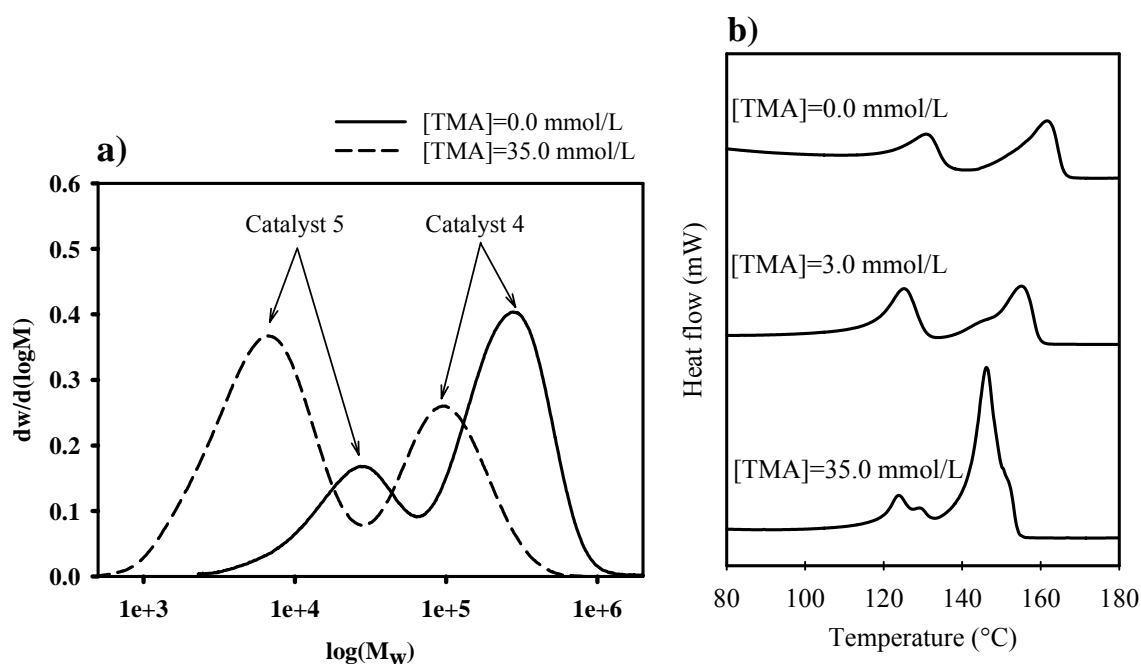


Figure 9. GPC curves of samples obtained with binary catalyst system **4+5** at TMA concentrations of 0.0 and 35.0 mmol/L (a), melting thermograms of samples produced with binary catalyst system **4+5** at TMA concentrations of 0.0, 3.0 and 35.0 mmol/L (b).^{III}

The melting behaviour of the polypropylene obtained with the binary catalyst system under TMA-free conditions deviated from the melting behaviour observed for a polymer sample consisting of neat syndiotactic and isotactic polypropylenes produced with catalysts **4** and **5** individually. This indicated that interaction between the active sites also took place in the absence of TMA. Under TMA-rich conditions, changes were observed in the high M_w peak maximum values and polymer microstructure. In particular, the *mmmm/mmmr* and *rrrr/rrrm* pentad ratios decreased, and it was concluded that TMA operated as a chain shuttling agent and caused the formation of a stereoblock copolymer consisting of syndiotactic and isotactic blocks.

It was demonstrated that polymerisation conditions, especially the TMA concentration, have a crucial effect on catalyst interaction mechanisms in the binary catalyst system. Additionally, different structures can be synthesised if the chain shuttling reactions can be controlled.

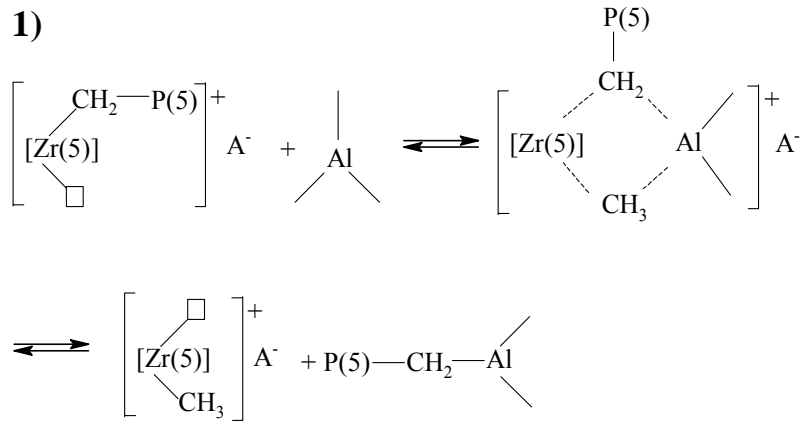
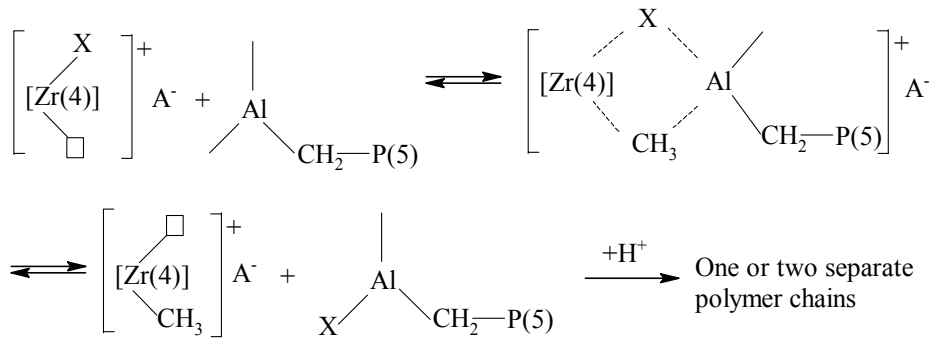
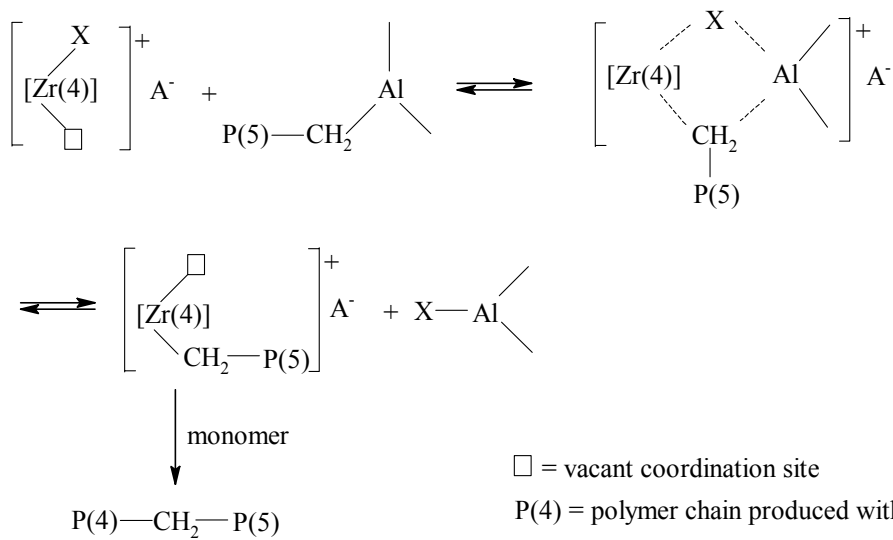
4.5.2 Chain shuttling reactions between TMA and active catalyst site^{III}

The proposed mechanism for chain shuttling by TMA is illustrated in Scheme 6. In the first reaction (path 1) the polymer chain from catalyst **5** is transferred to a TMA unit and one methyl group is replaced. At the same time the catalyst **5** is released for further polymerisation. It is possible that the same TMA unit, now carrying a polymer chain, interacts and exchanges ligands again, but this time with catalyst **4** (path 2). If the polymer ligands are exchanged (path 3), a stereoblock copolymer is formed.

Lieber and Brintzinger⁸¹ report that catalyst structure has a strong influence on chain shuttling reactions between active sites, and that it is likely that a polymer chain is transferred from a more sterically hindered catalyst to a less sterically hindered catalyst centre as presented in Scheme 6.

Scheme 6. Chain shuttling between TMA and active catalyst site.^{III}

1)

2) X = —CH₂—P(4) or —CH₃3) X = —CH₂—P(4) or —CH₃

4.5.3 Novel diene copolymers with binary catalyst system^V

The binary catalyst system **4+5** was applied in 1,9-decadiene copolymerisations to investigate the possibility of producing a novel type of 1,9-decadiene/propylene copolymer structure. On the basis of the copolymerisation results with the isolated catalysts **4** and **5** (discussed in section 4.3.3), polymerisation conditions were adjusted to give a high probability for the formation of a copolymer in which 1,9-decadiene links two propylene chains of different tacticity. The structure of the copolymer is presented in Figure 10 together with the ¹³C NMR spectrum.

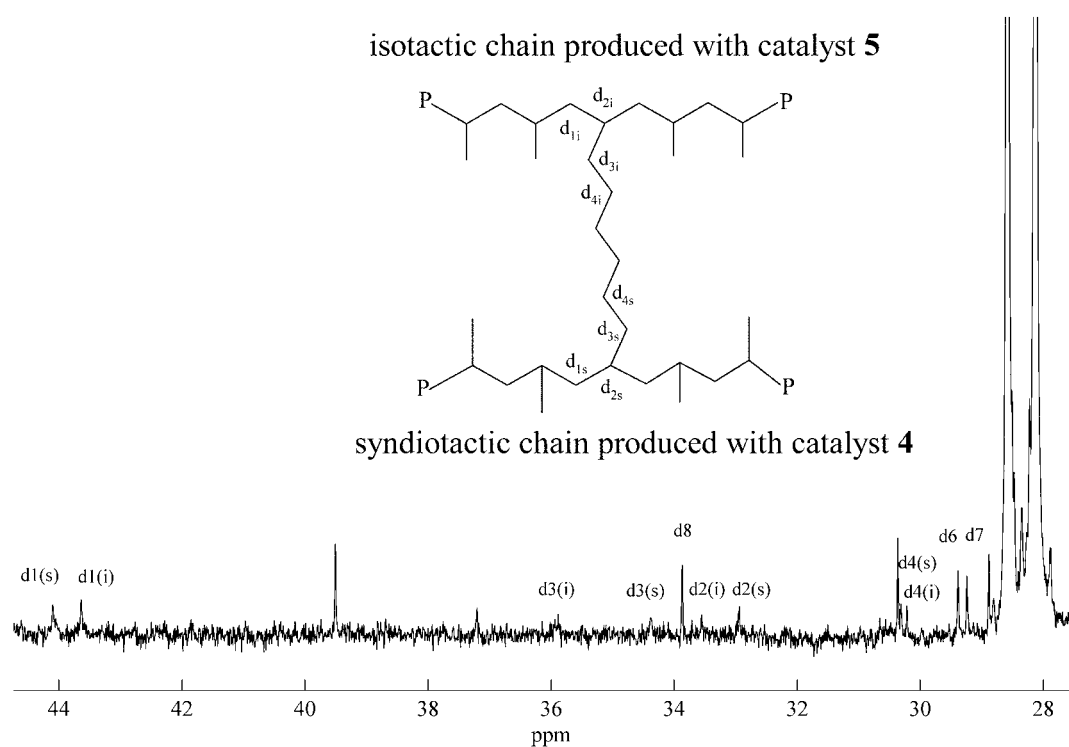


Figure 10. Structure and ¹³C NMR spectrum of 1,9-decadiene copolymer synthesised with the binary catalyst system **4+5**.^V

To produce a copolymer with high incorporation of 1,9-decadiene and large number of unreacted double bonds, the copolymerisation was started at 80 °C with catalyst **5**. Catalyst **4** was injected after 15 min polymerisation time because it has a strong tendency to form long-chain branched structures. In this way the isotactic macromonomers produced with catalyst **5** could be incorporated into the syndiotactic main chain. To minimise the low M_w fraction produced with catalyst **5** at 80 °C and to produce highly syndiotactic polypropylene with catalyst **4**, the polymerisation temperature was lowered to 40 °C immediately upon the injection of

catalyst **4**. As control experiments, homo- and copolymerisations were conducted with different catalyst injection orders and polymerisation temperatures.

The polymerisation method described above resulted in the formation of copolymer with the desired structure. The GPC data revealed the formation of a high M_w fraction (Figure 11), accompanied with strong increase in the M_z and M_{z+1} values showing the formation of long-chain branched polypropylene. ^{13}C NMR analysis confirmed the 1,9-decadiene incorporation into both syndiotactic and isotactic main chains (Figure 10). The proposed mechanism is that, during the first 15 min at 80 °C catalyst **5** incorporates 1,9-decadiene into the isotactic main chain without significant crosslinking; thereafter, at 40 °C, catalyst **4** incorporates the isotactic macromonomers into the syndiotactic main chain.

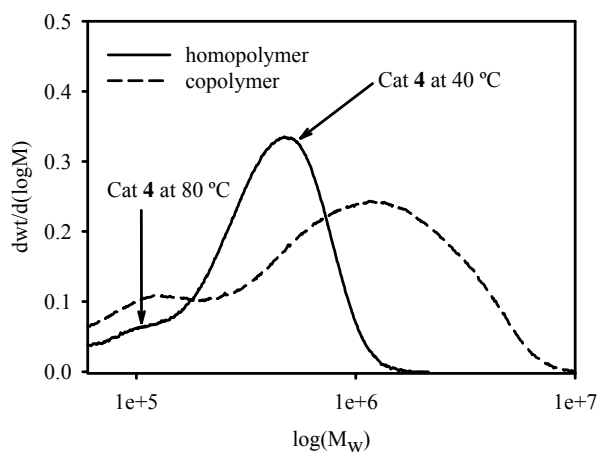


Figure 11. The effect of diene copolymerisation on the high M_w fraction produced with catalyst **4**.^v

Syndiotactic and isotactic polypropylenes are immiscible, and a phase separation occurs when they are blended.^{97–99} The novel type of 1,9-decadiene copolymer obtained as described above was tested as compatibiliser in a blend of syndiotactic and isotactic polypropylenes. The blend compatibilised with the copolymer showed a simultaneous increase in the modulus and yield strength values as compared with the values measured for a 1:1 blend of syndiotactic and isotactic polypropylenes. The result affirmed the formation of the desired copolymer structure, and showed effectiveness of this type of polymer as compatibiliser in a blend of syndiotactic and isotactic polypropylenes.

5 SUMMARY

Polypropylene properties and structures were tailored by polymerising propylene with metallocene catalysts. Polypropylene properties were tailored by modifying the metallocene catalyst system, fine tuning polymerisation conditions and copolymerising of different monomers, and novel polymer structures, not achievable with single catalysts, were synthesised in a controlled way with binary metallocene systems.

Several methods are available to control chain termination and M_w of polymers. In ethylene/propylene copolymerisations, the greater steric hindrance of *rac*- $\text{Me}_2\text{Si}(2\text{-}i\text{-Pr-4-[3,5-Me}_2\text{-Ph]-Ind})_2\text{ZrCl}_2$ than of *rac*- $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2$ suppresses chain transfer to coordinated ethylene monomer. Chain transfer to aluminium can be blocked by removing TMA residuals from MAO solution by chemical treatment of MAO solution with BHT. Additionally, polymerisation temperature has a strong effect on chain termination; higher temperature favours chain termination by $\beta\text{-H}/\beta\text{-CH}_3$ to Zr over $\beta\text{-H}$ -transfer to monomer.

Thermal properties of polypropylene are greatly affected by copolymerisation of 1-hexene and ethylene. Copolymerisation of 1-hexene decreases the melting temperature and heat of fusion, but has a negative effect on the M_w due to the favoured chain termination after incorporation of 1-hexene into the polymer main chain. Chain termination after incorporation of 1-hexene is particularly pronounced in copolymerisations with catalyst *rac*- $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2$. Ethylene copolymers are produced with catalysts *rac*- $\text{Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2$ and *rac*- $\text{Me}_2\text{Si}(2\text{-}i\text{-Pr-4-[3,5-Me}_2\text{-Ph]-Ind})_2\text{ZrCl}_2$. The melting temperature and heat of fusion are lower in ethylene copolymers than in the homopolymers, and amorphous materials are produced when the ethylene content is 21.9–63.6 mol-%.

Copolymerisation of 1,9-decadiene with catalysts $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and *rac*- $\text{Me}_2\text{Si}(4\text{-}t\text{-Bu-2-Me-Cp})_2\text{ZrCl}_2$ causes a decrease in the melting temperature and heat of fusion of polypropylene, whereas M_w and MWD values increase. The increase in M_w and MWD values is related to the formation of long-chain branched structures, which is desirable to improve the processability of metallocene based polypropylenes. Catalyst $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ has a stronger tendency to form long-chain branched structures, especially at elevated polymerisation temperature.

The processing limitations associated with narrow MWD of metallocene based polypropylene can be overcome by producing polypropylenes with combined metallocene systems prepared by a novel emulsion based heterogenisation method. Catalyst combinations $rac\text{-Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2/rac\text{-Et}(2\text{-[}t\text{-Bu-Me}_2\text{-SiO]-Ind})_2\text{ZrCl}_2$ and $rac\text{-Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2/rac\text{-Me}_2\text{Si}(2\text{-}i\text{-Pr-4-[3,5-Me}_2\text{-Ph]-Ind})_2\text{ZrCl}_2$ were investigated in polymerisations conducted in propylene bulk phase. Both catalyst systems produce polypropylene with broad MWD, and the combination $rac\text{-Me}_2\text{Si}(2\text{-Me-4-Ph-1-Ind})_2\text{ZrCl}_2/rac\text{-Et}(2\text{-[}t\text{-Bu-Me}_2\text{-SiO]-Ind})_2\text{ZrCl}_2$ yields bimodal MWD.

Novel polymer structures not achievable with isolated catalysts alone can be synthesised with a binary catalyst system consisting of catalyst precursors $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and $rac\text{-Me}_2\text{Si}(4\text{-}t\text{-Bu-2-Me-Cp})_2\text{ZrCl}_2$. It was demonstrated that these catalysts interact with each other in the binary catalyst system, and that TMA operates as a chain shuttling agent leading to the formation of a stereoblock copolymer consisting of syndiotactic and isotactic blocks produced with $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ and $rac\text{-Me}_2\text{Si}(4\text{-}t\text{-Bu-2-Me-Cp})_2\text{ZrCl}_2$, respectively.

When the binary catalyst system is applied in 1,9-decadiene copolymerisations, a novel 1,9-decadiene copolymer structure is obtained in which diene links syndiotactic and isotactic chain together. In the presence of 1,9-decadiene, catalyst $rac\text{-Me}_2\text{Si}(4\text{-}t\text{-Bu-2-Me-Cp})_2\text{ZrCl}_2$ produces isotactic polypropylene macromonomers, which are further incorporated into the syndiotactic main chain produced in polymerisation with catalyst $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$. When this copolymer is applied as compatibiliser in a blend of syndiotactic and isotactic polypropylenes, the compatibilised blend shows a simultaneous increase in the modulus and yield strength values compared with the values measured for a 1:1 blend of the two polypropylenes.

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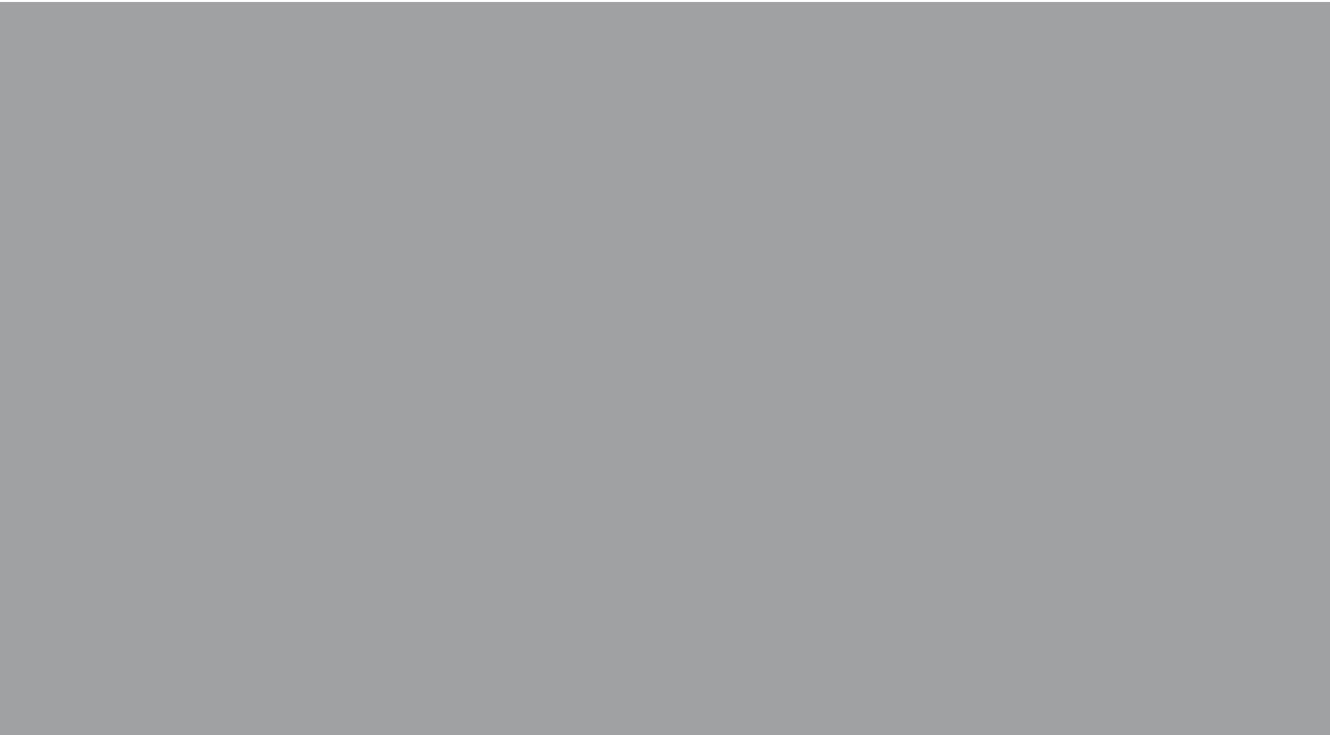
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