

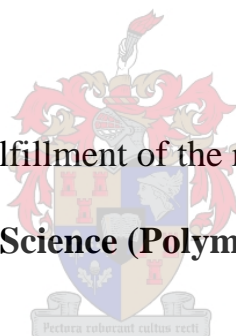
**An investigation of the effect of chain length on
stereo-regulation with C_2 symmetric
metallocene catalysts**

by

Ismael Amer

Thesis presented in partial fulfillment of the requirements for the degree of

Master of Science (Polymer Science)



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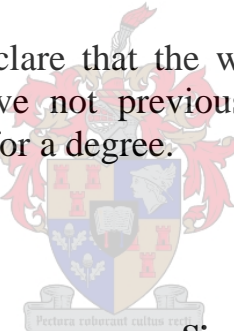
University of Stellenbosch

Promoter:
Dr A.J. van Reenen

Stellenbosch
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DECLARATION

I, the undersigned hereby declare that the work in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.



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ABSTRACT

This study concerns the polymerization of propylene both in the presence and absence of molecular hydrogen. The percentage of hydrogen used as a terminating agent in the polymerization reactions was varied from 0.1 wt% to 15.0 wt% in order to compare a variety of polymers with different percentages of hydrogen incorporated. Two *ansa* metallocene catalysts were used: (A) *rac*-[ethylene *bis*(indenyl)] zirconium dichloride (*rac*-Et(Ind)₂ZrCl₂) and (B) dimethylsilyl-*bis*(2-methyl benzoindenyl) zirconium dichloride (*rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂). Methylaluminoxane (MAO) was used as cocatalyst for both of the two catalysts.

Characterization of the polymers included using nuclear magnetic resonance spectroscopy (NMR) for information concerning the microstructure of the polymers, high temperature gel permeation chromatography (HT-GPC) for molecular weight and molecular weight distributions and differential scanning calorimetry (DSC) to investigate the melting point and crystallization behaviour of the polymers.

The polypropylenes prepared with the dimethylsilyl-*bis*(2-methyl benzoindenyl) zirconium dichloride catalyst system were compared to the polypropylenes synthesized with ethylene-*bis*(indenyl) zirconium dichloride. In particular, the effects of hydrogen on the microstructure, molecular weight, molecular weight distribution, melting point and crystallization behaviour were investigated.

OPSOMMING

Hierdie studie behels die polimerisasie van propileen in beide die afwesigheid en teenwoordigheid van waterstof-gas. Die persentasie waterstof gebruik as termineringsagent in die polimerisasie-reaksies is verander van 0.1 massa% tot 15.0 massa% om sodoende die polimere verky te kon vergelyk. Twee *ansa* metalloseen kataliste is gebruik: (A) *rac*-[ethileen *bis*(indeniel)] sirkonium dichloried (*rac*-Et(Ind)₂ZrCl₂) en (B) dimetielsiliel-bis(2-metiel benzindeniel) sirkonium dichloried (*rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂). Metielalumoksaan (MAO) is as ko-katalis gebruik.

Karakterisering van die polimere het die gebruik van kern-magnetiese resonans spektroskopie (KMR) ingesluit, om sodoende inligting te verkry oor die mikrostruktuur van die polimere. Hoë-temperatuur jel-permeasie chromatografie (HT-GPC) is gebruik om die molekulêre massa en verspreiding van molekulêre massa, en termiese analise (DSC) om smeltpunt en kristallasiepunt van die polimere te bepaal.

Die polipropileen deur die dimetielsiliel-bis(2-metiel bensoindeniel) sirkonium dichloried katalissistiem berie is vergelyk met die polimere bereie deur die etileen-bis(indeniel) sirkonium dichloried katalissistiem. Die uitwerking van waterstof op die mikrostruktuur, molekulêre massa en verspreiding, smeltpunt en kristallasie is ondersoek..

Dedicated to:

My Mother, Aisha

and

My Father, Salem

For their love, support and encouragement and
for giving me the opportunities they didn't have.

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I would like to thank Allah/God for giving me strength, health, opportunity and courage to face my reality. I thank him also for blessing me.

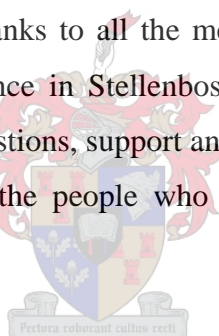
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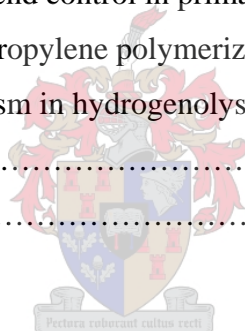
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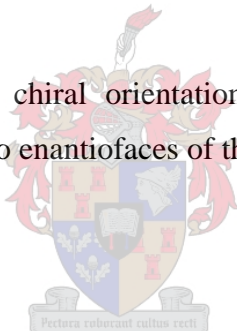
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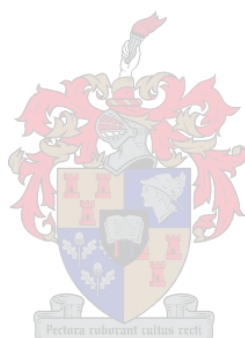


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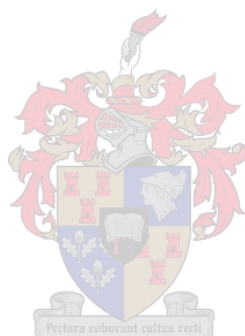
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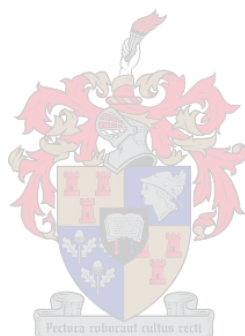
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LIST OF ABBREVIATIONS

Bz	Benzene
^{13}C	Carbon thirteen
COC	Cyclo-olefin copolymer
Cp	Cyclopentadienyl
DSC	Differential scanning calorimetry
ΔH_m	Heat of fusion
EI	<i>rac</i> -[ethylene <i>bis</i> (indenyl)] zirconium dichloride (<i>rac</i> -Et(Ind) ₂ ZrCl ₂)
Flu	Flourenyl
GPC	Gel permeation chromatography
^1H	Proton
HT-GPC	High temperature gel permeation chromatography
HDPE	High density polyethylene
Ind	Indenyl
<i>m</i>	<i>meso</i>
MAO	Methylaluminoxane
MBI	Dimethylsilyl-bis(2-methyl benzoindenyl) zirconium dichloride (<i>rac</i> -Me ₂ Si(2-MeBenz[e]Ind) ₂ ZrCl ₂)
M-C	Metal carbon
Me	Methyl
\overline{M}_n	Number average molecular weight
\overline{M}_w	Weight average molecular weight
MW	Molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance spectroscopy
PD	Polydispersity
PE	Polyethylene
PP	Polypropylene

<i>r</i>	<i>racemic</i>
TCB	1,2,4,-trichlorobenzene
TCE	1,1,2,2-tetrachloroethane
T _m	Melting temperature
TMA	Trimethyl aluminium
wt %	Weight fraction
X _c %	Crystallization percentage
1,2-insertion	Primary insertion
2,1-insertion	Secondary insertion
δ	Chemical shift (ppm)



CHAPTER 1

Introduction and objectives

1.1 Introduction

Metallocene catalyst systems in fact, have been around for just as long as the Ziegler-Natta systems.¹ Metallocenes are special members of a class of organometallic compounds. They are activated with methylaluminoxane (MAO) to form single-site catalyst systems, effective for α -olefin polymerization. These catalysts produce polymers with uniform and controlled properties.

Chiral metallocene catalysts possessing C_2 -symmetry have been widely studied in order to optimize and to better understand their ability to catalyze the stereo-regular polymerization of propylene.^{2, 3} *Ansa* C_2 -symmetric metallocene catalysts are highly iso-selective in propylene polymerization and have high activity. This allows for their use in most industrial applications for the production of polypropylene homopolymer and polypropylene copolymers.

Stereochemical control of the polymer is only possible if the active species during polymerization is chiral. Chirality might be located at the transition metal itself, or at the ligand attached to the transition metal, or on the growing polymer chain. Two basic mechanisms of stereo-chemical control are possible.⁴ Control can be at the catalytic site itself, or at the chain end. Catalytic site control (also known as enantiomorphic site control) leads to a Bernoullian distribution of stereo-errors in the polymer, while chain end control (chirality of the last inserted monomer unit) leads to a Markovian distribution of stereo-errors.

Control of molecular weight of polymers produced by C_2 -metallocene catalysts can be easily achieved by introducing hydrogen to the polymerization system or by increasing the reaction temperature. Unlike conventional Ziegler-Natta catalysts, metallocenes require only small amounts of hydrogen to significantly reduce the molecular weight of polymer produced.⁵

Hydrogen has also been used for mechanistic studies. For example, high hydrogen pressures have been used to produce propylene oligomers by the so-called hydro-oligomerization reaction⁶⁻⁸ in order to determine the regiochemistry and stereochemistry of initiation and propagation. By analyzing the structures of the propylene oligomers and measuring their optical rotations it was found that monomer insertion is predominantly primary and that after an occasional 2,1-insertion chain growth is terminated by hydrogen. The presence of *n*-butyl end groups in the presence of hydrogen strongly supports the above hypothesis, and that the catalyst preferentially selects the *re* monomer enantioface.

1.2 Objectives

The main objective of this study was to synthesize a series of polypropylenes and polyethylenes with different molecular weights by keeping a constant catalyst / cocatalyst / monomer ratio, and adding increasing amounts of hydrogen to the reaction mixture. To this end, two C_2 -symmetric *ansa* metallocenes that have a wide use, ethylene-bis(indenyl) zirconium dichloride (EI) and dimethylsilyl-bis(2-methyl benzoindenyl) zirconium dichloride (MBI), were used as catalyst systems in the polymerization reactions.

The synthesized polymers were to be characterized by nuclear magnetic resonance spectroscopy, high temperature gel permeation chromatography and differential scanning calorimetry to investigate the stereoregularity of these polymers and correlate them with the molecular weight. In addition, the polypropylenes prepared with the dimethylsilyl-bis(2-methyl benzoindenyl) zirconium dichloride catalyst system were to be compared with the polypropylenes synthesized with the ethylene-bis(indenyl) zirconium dichloride. In particular, the effect of hydrogen on the microstructure, molecular weight, molecular weight distribution, melting point and crystallization behaviour was to be investigated.

1.3 Thesis outline

- 1- Chapter 1 presents a short introduction to the study as well as the main objectives of the study.
- 2- Chapter 2 provides a brief historical overview of the development of metallocene catalysts. This chapter also presents the effect of the metallocene structure on the microstructure and the properties of the resulting polymers.
- 3- Chapter 3 describes propylene polymerization and stereo-selectivity mechanisms, as well as the influence of hydrogen on the propylene polymerization.
- 4- Chapter 4 explains the experimental work that was carried out. It includes an outline of the polymerization procedures, and describes the characterization and analytical techniques used in this study.
- 5- Chapter 5 discusses the microstructures and some of the thermal properties of the polyethylenes and polypropylenes produced using the *rac*-Et(Ind)₂ZrCl₂ catalyst system in the absence and presence of different amounts of hydrogen.
- 6- Chapter 6 discusses the microstructures and some of the thermal properties of the polypropylenes produced using the *rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂ catalyst system in the absence and presence of different amounts of hydrogen.
- 7- Chapter 7 summarizes the main conclusions of all the previous chapters and suggests some recommendations for future studies.

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CHAPTER 2

Historical and theoretical background

2.1 Introduction

Polyolefins are among the most important modern commodity polymers. Polyethylene and polypropylene are amongst the major tonnage plastic materials produced today. The industrial capacity for the production of polyethylene and polypropylene in 1990 was approximately 45 million tons.^{1,2} In the USA, in 2002, the annual production of polyethylene was approximately 55 million metric tons, which represented about \$35 billion in sales.³ Growth expectations are currently approximately 5% a year, reaching over 85 million metric tons in 2010.³ Polypropylene production was approximately 34 million metric tons in 2002. Projected growth estimates production in 2010 to be nearly 60 million metric tons.³

Metallocene catalyst systems are, as has been stated, just as old as the Ziegler-Natta systems,⁴ but the first metallocenes were found to have low activity. It was not until 1980, when they were used together with a methyl aluminoxane (MAO) as cocatalyst, that their full potential was realized.⁵

Metallocenes are positively charged metal ions, most commonly titanium or zirconium, sandwiched between two negatively charged cyclopentadienyl ligands. Polypropylenes produced by metallocene catalysts became available in the late 1990s. One such production process adopts a standard gas-phase process using a metallocene catalyst such as *rac*-dimethylsilylenebis(2-methyl-1-benz(e)indenyl)zirconium dichloride in conjunction with MAO as cocatalyst.⁶

By using metallocene catalysts, it was possible for the first time to produce:

- polyethylenes, polypropylenes and copolymers with narrow molecular weight distributions (MWD),⁷
- syndiotactic polypropylene (in commercial quantities),⁸
- syndiotactic polystyrene,⁹

- elastomeric polypropylenes,¹⁰
- long chain, branched polyethylenes,¹¹
- cyclo-olefin copolymers (COC) with high catalytic activity,¹²
- optically active oligomers¹³ and
- composite materials of biomass, solid oxides, and powdered metals with polyolefins.¹⁴

Group 4 metallocene catalysts exhibit high activities in olefin polymerization and their single-site nature enables the synthesis of polymers with narrow molecular weight distributions and tailored microstructures. They offer a significant advantage over the conventional, industrially used, heterogeneous Ziegler-Natta and chromium oxide catalysts, the structures of which contain several different active sites, making it difficult to control the polymer structure.¹⁵

For the synthesis of stereospecific metallocene catalysts for propylene polymerization, C_2 -symmetric precursors are necessary to obtain a catalyst for isospecific polymerization, and C_s -symmetric precursors to produce a catalyst for syndiospecific polymerization (Figure 2.1). Asymmetric precursors can be used to synthesize metallocene catalysts that produce hemi-isotactic and isotactic stereoblock polypropylene. A useful classification of metallocene catalysts based on their symmetry has been proposed.¹⁶

Chiral metallocene catalysts possessing C_2 -symmetry have been widely studied in order to optimize and to better understand their ability to catalyze the stereoregular polymerization of propylene.¹⁷⁻¹⁹

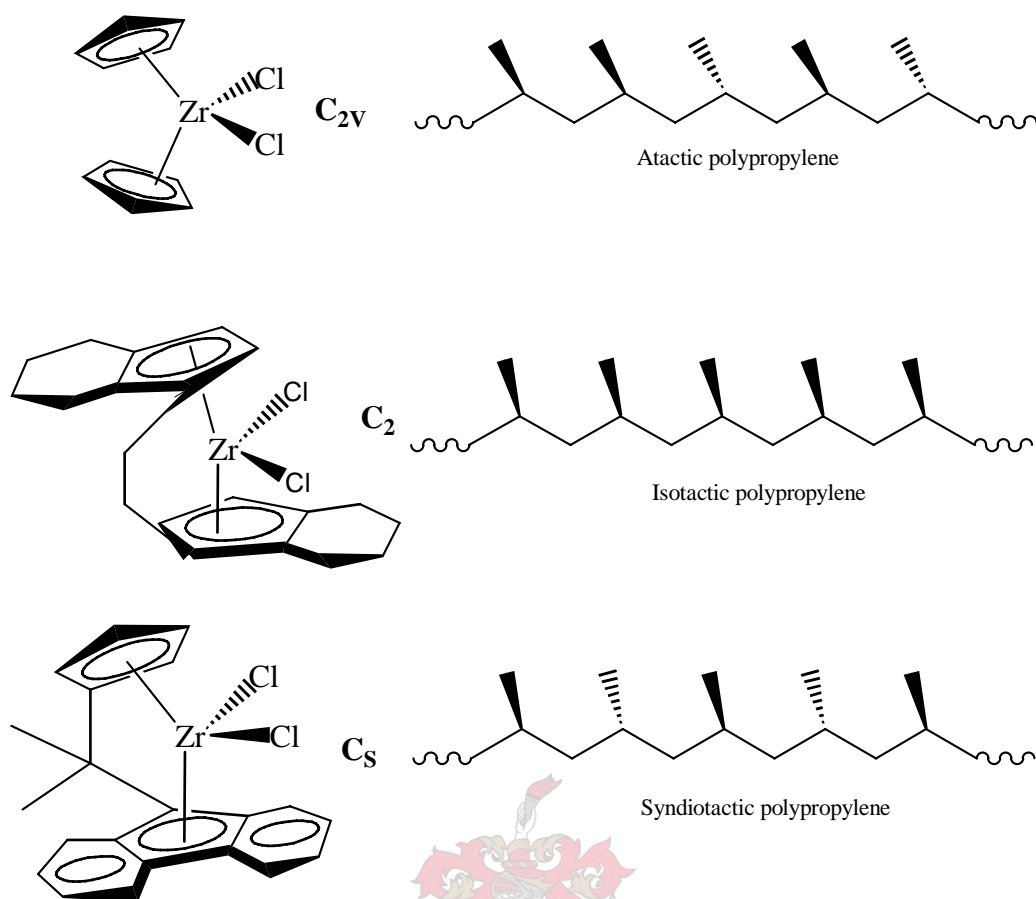


Figure 2.1 Symmetry effect on stereoselectivity of polypropylene.¹⁶

2.2 Historical background

The discovery in the 1980s of effective homogeneous transition metal catalysts for olefin polymerization is probably one of the most significant advances in polymer synthesis. The development of group 4 metallocene catalysts not only improved the properties of polyolefins but also made it possible to synthesize new types of polyolefins. Numerous studies have been carried out on the structure and properties of the polyolefins resulting from the advances in catalyst technology.²⁰

The first metallocene was discovered in 1951 in the form of ferrocene, $\text{Fe}(\text{Cp})_2$,^{21,22} as is shown in Figure 2.2. The sandwich structure of ferrocene was formulated in 1952 by Wilkinson and Woodward²³ and a number of other metallocenes were synthesized soon after this discovery.²⁴

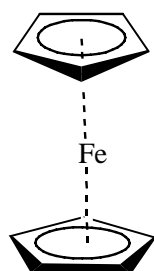


Figure 2.2 Structure of ferrocene.

In 1953 Karl Ziegler and co-workers²⁵ discovered catalyst systems based on transition metal compounds (zirconium and titanium halides), which were used to study the polymerization of α -olefins.²⁶ In the presence of aluminum alkyl activators these catalyst systems were able to polymerize ethylene to yield HDPE at low pressure, but could not polymerize propylene.

In 1954 Natta reported the successful polymerization of propylene using the same catalyst system.²⁷ After characterization of the resulting polymer, he was able to define the three stereo conformations of polypropylene: isotactic, syndiotactic, and atactic polypropylene. In 1957 titanocene dichloride was found to be active in olefin polymerization.^{28,29} In these experiments aluminium alkyls were used as activators but only low polymerization activities were obtained when using this metallocene system.

It was not until 1973 that the true potential of group 4 metallocene catalysts was recognized—it was observed that controlled addition of water into the titanocene/aluminium alkyl system increased the catalytic activity significantly.³⁰ The increase in activity was found to arise from the formation of aluminoxanes, *e.g.* methylaluminoxane (the general structure of it is shown in Figure 2.3), which can be obtained from the reaction of trimethylaluminium (TMA) and water.³¹

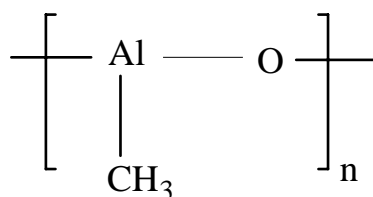


Figure 2.3 Simplified representation of methyl aluminoxane.

Many research groups proceeded to develop new metallocene complexes once the potential of metallocenes was established. One major advance was the synthesis of bridged zirconocene dichlorides with C_2 -symmetry by Brintzinger *et al.*³² Soon after this, Kaminsky and co-workers produced isotactic polypropylene with these bridged zirconocenes.³³ Their success spurred efforts to find more active and stereoselective catalysts for the polymerization of a wide range of monomers.³⁴

Presently, MAO-activated metallocene catalysts are still subjects of extensive research.^{33, 35} Although group 4 metallocene based catalysts are already being employed in the polyolefin industry, much work remains to be done in the field of catalyst design to improve the properties of the resulting polymers.

The historical development in the field of metallocene research can be summarized as is shown in Table 2.1.

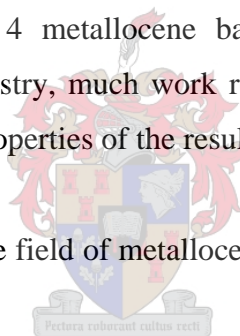


Table 2.1 Timetable and historical development in the field of metallocene catalyst research

1952	Development of the structure of metallocenes (ferrocene) by Fischer and Wilkinson ³⁶
1955	Metallocene as component of Ziegler-Natta catalysts, low activity with common aluminium alkyls ²⁹
1973	Addition of small amount of water to increase the activity (Al:H ₂ O = 1:0.05 up to 1:0.3) (Reichert, Meyer and Breslow) ³⁰
1975	Unusual increase in activity by adding water in the ratio Al:H ₂ O = 1:2 (Kaminsky, Sinn and Motweiler) ³¹
1977	Using separately prepared methylaluminumoxane as cocatalyst for olefin polymerization (Kaminsky and Sinn) ³¹
1982	Synthesis of <i>ansa</i> metallocenes with C ₂ symmetry (Brintzinger) ³⁷
1984	Polymerization of propylene using a <i>rac/meso</i> mixture of <i>ansa</i> titanocenes led to partially isotactic polypropylene (Ewen) ³⁸
1984	Chiral <i>ansa</i> zirconocenes produce highly isotactic polypropylene (Kaminsky and Brintzinger) ³⁹

2.3 Theoretical background

2.3.1 Metallocene catalyst systems

Metallocene catalyst systems result from the reaction of metallocenes and a cocatalyst, which is generally an organoaluminium compound. These catalysts play an important role in the polymerization of olefins, dienes and styrene. Today a significant part of the chemical industry is using these catalysts to produce increasing amounts of plastic materials. Metallocene catalysts are soluble in hydrocarbons, show only one type of active site and their chemical structures can be easily changed. These

properties allow one to accurately predict the properties of the resulting polyolefins. Molecular weight and distribution, comonomer content and tacticity can be controlled by careful selection of the catalyst and reaction conditions. In addition, the catalytic activity of the metallocene catalysts is 10-100 times higher than that of the typical Ziegler-Natta system.⁴⁰

Metallocene catalyst systems can be conveniently divided into two categories. In the first, an aluminoxane, an alkylaluminum, or a combination of aluminoxanes and alkylaluminums, is used to activate the metallocene catalyst. In the second category, an ion exchange compound is combined with the metallocene catalyst, forming what is generally called a cationic metallocene catalyst. It is now generally accepted that the catalytic active species for metallocene/aluminoxane/alkylaluminum systems is also cationic.⁴¹

Remarkable features of metallocene catalyst systems and their uses, in preference to other catalyst systems, include the following:

- 1- Very uniform homo- and copolymers with narrow molecular weight distributions, with $M_w/M_n = 2$, are typical for catalysts with only one type of catalytically active site ('single-site' catalysts).
- 2- Excellent control of molecular weight, end groups, stereochemistry, long- and short-chain branching is achieved.
- 3- Molecular weight-independent comonomer incorporation, including the less reactive comonomers such as long-chain α -olefins and styrenes, is possible.
- 4- Cyclo-olefins can be polymerized.
- 5- Morphology can be controlled and there is potential for production of reactor blends using metallocene blends.
- 6- Molecular weight distributions can be made in cascade reactors or hybrid metallocene-based processes.
- 7- New catalysts can be introduced into old plants to make new polymers ('drop-in' technology).
- 8- Polymers that are easier to recycle can be produced.
- 9- Only small quantities of catalyst are required.

Control of molecular weight of polymers produced by a metallocene catalyst can be easily achieved by introducing hydrogen to the polymerization system or by increasing the reaction temperature. Unlike conventional Ziegler-Natta catalysts, metallocenes require only small amounts of hydrogen to significantly reduce the molecular weight of polymer produced.⁴² On the contrary, a large excess of hydrogen is required to produce oligomers using conventional Ziegler-Natta catalysts.⁴¹ In addition, oligomers with unsaturated terminal vinyl or vinylidene groups can be produced by metallocene catalysts by increasing the polymerization temperature, because β -hydride elimination becomes the primary chain transfer pathway. The unsaturated oligomers can be further functionalized to make many useful chemicals.⁴³

The “single-site” nature of metallocenes simplifies mechanistic studies. Many powerful techniques are available for the characterizations of chemical structure. Although relatively inactive, the early metallocene catalysts with aluminum alkyl cocatalysts provided good systems for mechanistic study. The development of the aluminum-free cationic metallocene catalysts, using borane compounds such as $B(C_6F_5)_3$ as cocatalysts, provides ideal systems to study the mechanism and to understand the nature of the active species.⁴⁴⁻⁴⁶ Metallocene catalysts have prompted efforts from many companies to commercialize them for polyolefin production.⁴⁷ The commercial production capacity of polyolefins using metallocene catalysts continues to grow rapidly.

Disadvantages of metallocene catalyst systems are:

- sometimes extremely laborious preparation procedures are required,
- decay-type kinetics are evident with ethylene/higher α -olefin mixtures,
- higher Al/Zr ratios are required for obtaining high catalytic activity and a relatively stable kinetic profile,
- high cost of MAO cocatalyst,
- short shelf life of MAO, and
- incompatibility with slurry and gas-phase processes.

2.3.2 General structure of metallocene catalysts

The general structure of a group 4 metallocene catalyst precursor such as is used in olefin polymerization is presented in Figure 2.4. The most remarkable feature of these catalysts is that their molecular structure can be designed to create active centers to produce polymers with entirely novel properties.⁴⁸

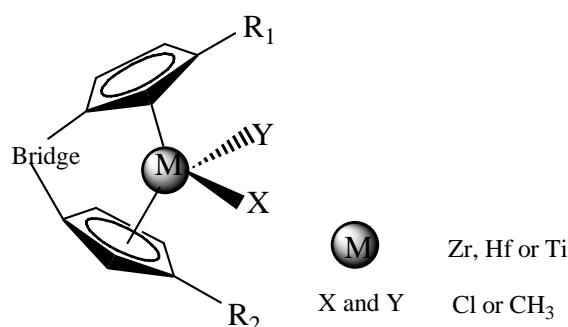


Figure 2.4 General structure of a bridged group 4 metallocene catalyst precursor.

The carbon atoms of the cyclopentadiene (Cp) ligands can bear hydrogen or other substituents such as alkyl, aryl, or silyl groups. Up to 10 different substituents are possible on a metallocene. Different substituents change not only the size and shape of the Cp ligands but also the Cp-Mt-Cp distances and angles, and that affects the activity of the metallocenes and the properties of the polymers produced by these catalysts.⁴⁹

Metallocenes used in olefin polymerization have been classified on the basis of their symmetry (Figure 2.5). In class I two η^5 -cyclopentadienyl ligands (represented by shaded rectangles) can be bridged or not; in the other classes they are bridged. In classes I and II, the two sites occupied by the η^5 -ligands are bisected by a horizontal mirror plane and are therefore achiral; they are related by a two-fold rotation axis in class III and are homotopic (equal). In class IV, the two sites are related by a vertical mirror plane and are enantiotopic (mirror image to each other). No symmetry elements are present in class V, and the two sites are diastereotopic (different).^{4,50-54}

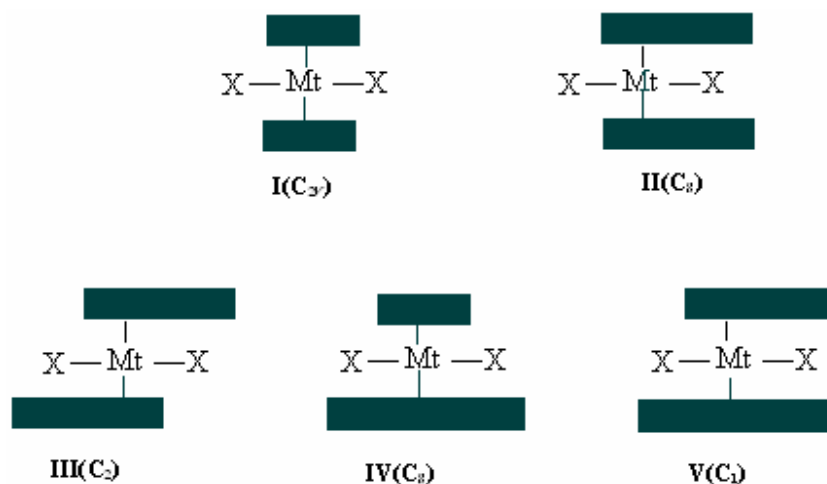


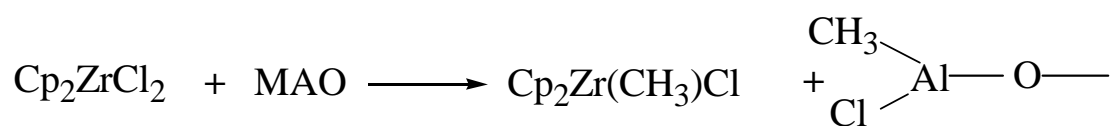
Figure 2.5 Classification of metallocene catalysts according to their symmetry.⁵⁰⁻⁵⁴

2.3.3 Catalyst activation

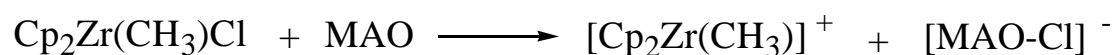
Group 4 metallocene complexes need to be activated before being used in olefin polymerization.⁵⁵⁻⁵⁸ The activator should be able to alkylate the metallocene. Further, the activator should be capable of reactivating the deactivated species (Scheme 2.1). MAO fulfils all the preceding requirements and is the most commonly used activator for metallocene catalysts. In addition, MAO acts as a scavenger of catalyst poisons by reacting with impurities such as oxygen and water that may be present in the catalytic system.

As described in Scheme 2.1, deactivation of the zirconocene catalyst in a pure zirconocene/MAO system occurs via methane abstraction through formation of a Zr-CH₂-Al bimetallic species. Fortunately, the deactivated bimetallic species can be reactivated by MAO through ligand exchange. This lengthens the lifetime of the catalyst in polymerization.⁵⁹⁻⁶³ Catalyst deactivation can also occur if a Lewis basic compound such as oxygen or water is present. The Lewis basic compound coordinates to and reacts with the Lewis acid metal centre, which then becomes inactive for olefin polymerization.

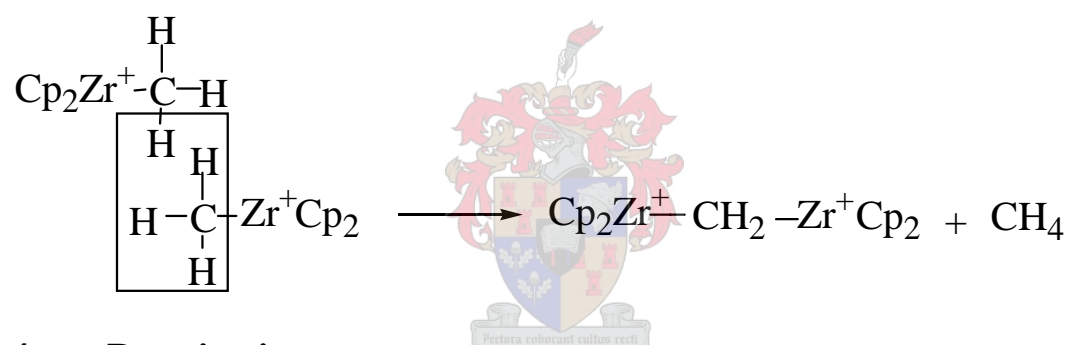
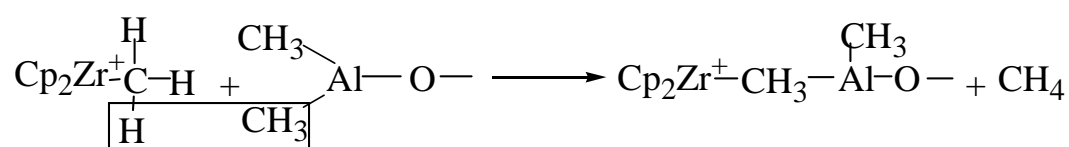
1. Methylation



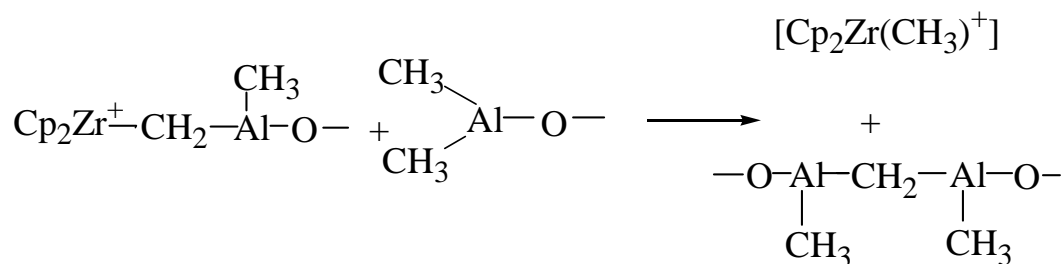
2. Cationization



3. Deactivation



4. Reactivation



Scheme 2.1 Reactions of group 4 metallocene with MAO. Zirconocene dichloride is presented as an example.⁵⁹⁻⁶²

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CHAPTER 3

Polypropylene: Stereochemistry and catalyst effects

3.1 Introduction

The use of metallocene catalysts in the preparation of polypropylenes reached commercial status with the production by Exxon of their Achieve[®] range in 1996 and in 1997 by Targor, the BASF-Hoechst joint venture, with the introduction of Metocene[®]. Such metallocene polypropylenes are, however, only a small proportion of the total polypropylene market, predicted at only about 3% of the total in 2005.¹ In a rapidly growing market many grades of polypropylene are available, but five main classes are well-known:

- homopolymers produced by Ziegler-Natta catalysis,
- block copolymers produced by Ziegler-Natta catalysis,
- random copolymers produced by Ziegler-Natta catalysis,
- rubber-modified blends of the above, and
- homopolymers and copolymers produced by metallocene catalysis.²

The microstructure of polypropylene in terms of the enchainment of the monomer units is determined by the regio- and stereo-specificity of the insertion of the monomer. Both primary 1,2-insertions and secondary 2,1-insertions are possible. Metallocenes favour successive primary insertions due to their bent sandwich structure. Secondary insertions are based on the structure of the metallocene used and the experimental conditions (generally temperature and monomer concentration).³

Secondary insertions cause increases in the steric hindrance to the next primary insertion, blocking the active center, which can be regarded as the resting state. This often leads to chain termination and isomerization processes.³

The propylene monomer is prochiral, and polymers of this monomer have pseudo-chiral centers at every tertiary carbon atom. The regularity of the configuration at these successive chiral centers is described by the tacticity of the polymer. If two

adjacent chiral centers have the same configuration then this "diad" of chiral centers is said to be *meso* in arrangement. If they have different configurations, they are said to be *racemic*. A polymer containing only *meso* diads is called isotactic, while a polymer containing only *racemic* diads is said to be syndiotactic. A mixture of *racemic* and *meso* diads gives an atactic polymer.³

Stereochemical control of the polymer is only possible if the active species during polymerization is chiral. Chirality might be located at the transition metal itself, or at the ligand attached to the transition metal, or on the growing polymer chain. Two basic mechanisms of stereochemical control are possible.⁴ Control can be at the catalytic site itself, or at the chain end. Catalytic site control (also known as enantiomorphic site control) leads to a Bernoullian distribution of stereoerrors in the polymer, while chain end control (chirality of the last inserted monomer unit) leads to a Markovian distribution of stereoerrors.

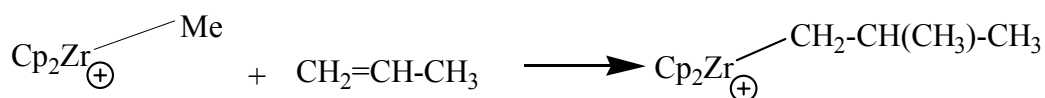
3.2 Mechanism of propylene polymerization using metallocene catalyst systems

The polymerization reaction of propylene with metallocenes is initiated by active centers of metallocene catalysts. Active species (chain initiators) are ionic pairs containing cationic species, like $\text{Cp}_2\text{M}^+\text{---R}$. These species are either synthesized or are formed in the reaction between metallocene complexes, such as Cp_2ZrMe_2 or Cp_2ZrCl_2 and MAO.^{5,6}

The mechanism of propylene polymerization with metallocenes can be summarized by a number of reaction steps, which are initiation reactions, propagation reactions and transfer reactions.

3.2.1 Initiation reactions

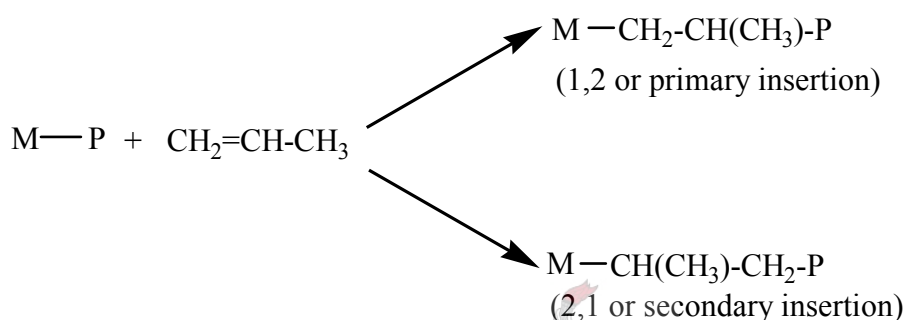
The polymerization reaction starts when a propylene monomer coordinates to the transitional metal atom bearing a positive charge, and subsequently inserts into the Zr-Me bond (probably by Me-migration), which is shown in Scheme 3.1



Scheme 3.1 Insertion of a propylene monomer to a Zr-Me bond.

3.2.2 Propagation reactions

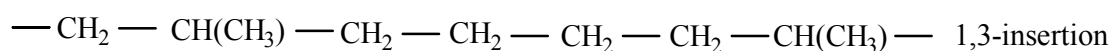
The insertion of a propylene monomer in the metal carbon bond may take place in two different ways, which is shown in Scheme 3.2



Scheme 3.2 Primary and secondary insertion of a propylene monomer in the metal-carbon bond.

It was proved by chain end-group analysis that the 1,2-insertion mode is predominant in isospecific polymerization of olefins with both heterogeneous^{7,8} and metallocene-based^{9,10} catalysts and in the syndiospecific polymerization of propylene with the homogeneous $\text{Me}_2\text{C}(\text{Cp},\text{F})\text{ZrCl}_2$ / MAO catalysts system.¹¹

Isospecific polypropylene obtained with chiral C_2 -symmetry group 4 metallocenes includes a small number (about 1%) of isolated regioirregular structural units resulting from 2,1- and 1,3-insertion of the monomer, as shown in Scheme 3.3.



Scheme 3.3 2,1- and 1,3-insertions for propylene polymerization.

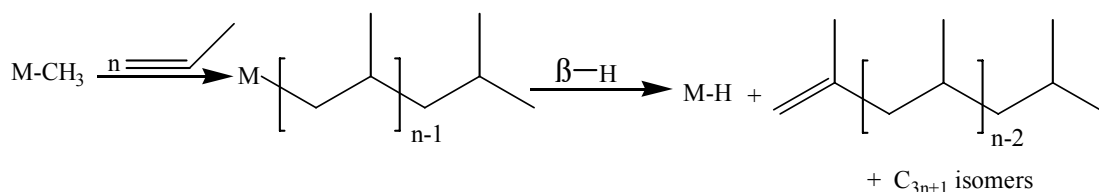
Regio-irregular insertions are revealed by the presence of $(\text{CH}_2)_2$ and $(\text{CH}_2)_4$ sequences in the polymer chain respectively. The content of the two regio-irregularities and their relative proportions depends on the π -ligands, polymerization temperature, and monomer concentration.¹² In general, regio-irregularities are mainly of the 2,1-type when the activity of the catalyst is very high.^{13, 14}

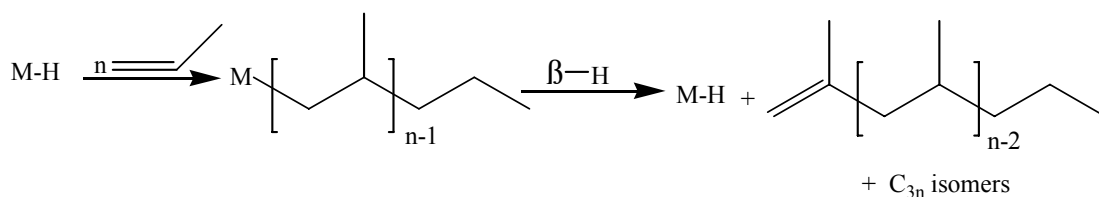
3.2.3 Transfer reactions

The investigation of transfer reactions is very important because it relates to the control of molecular weights and end-group structures of resultant polyolefins. In a reaction of polypropylene polymerization over a metallocene catalyst / MAO, where no external terminating agents (such as hydrogen) are involved, β -hydride transfer reactions (either after a primary or a secondary propylene insertion, and either unimolecular or bimolecular), β -methyl transfer reactions, chain transfer to the aluminum (mainly to trimethyl aluminum (AlMe_3) contained in MAO) and chain transfer to monomer constitute the entire set of chain transfer reactions. In general, β -hydride and β -methyl transfers are the two major chain transfer reactions in metallocene catalyst systems.^{15, 16}

(a) β -Hydride transfer reactions

β -Hydride transfer reactions after a primary insertion (Scheme 3.4) produce vinylidene-terminated chains. The other endgroups are predominantly n-propyl, except for those resulting from the chains initiated following a β -methyl transfer to metal.





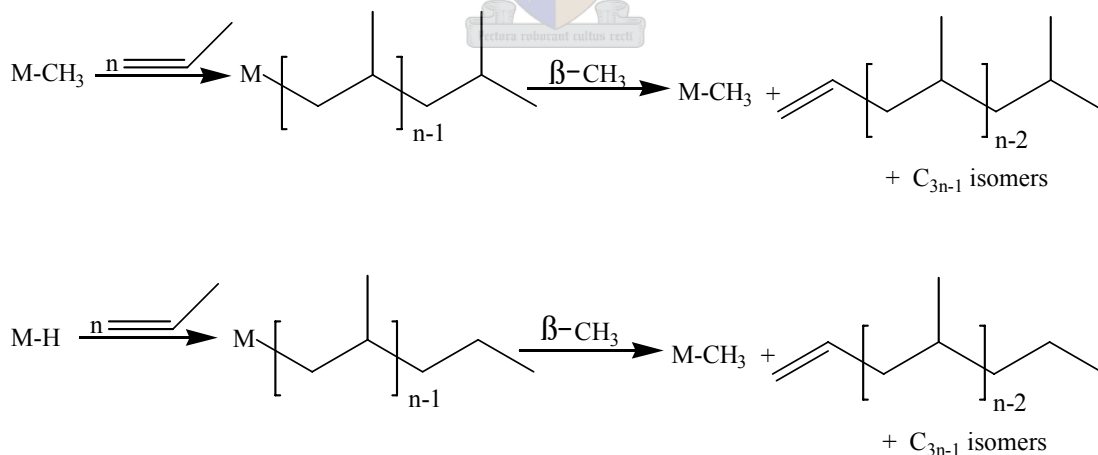
Scheme 3.4 β -Hydride transfer reactions.

β -H transfer reactions after a secondary insertion is also quite important, since it is the cause of the decrease in molecular weights observed in those metallocene systems for which a secondary insertion generates a slower propagating species.¹⁵

These transfer reactions can be unimolecular or bimolecular, producing a metal-hydride (or metal-propyl) initiating species and a polypropylene chain terminated with either a 3-butenyl (hydride transfer from the terminal CH_3) or a 2-butenyl end group (hydride transfer from the CH_2).

(b) β -Methyl transfer reactions

β -Methyl transfer reactions produce polypropylene chains initiated by isobutyl and terminated by allyl end groups ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{P}$), as shown in Scheme 3.5.

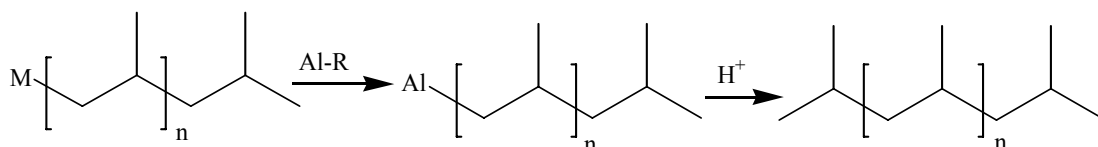


Scheme 3.5 β -Methyl transfer to the metal.

(c) Chain transfer to aluminum

These reactions, considered as transalkylation to the aluminum cocatalyst, produce (after hydrolysis), polypropylene with saturated end groups on both ends (Scheme 3.6). In the case of MAO cocatalyzed propylene polymerization, transalkylation is

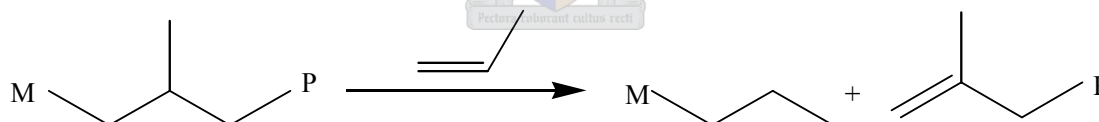
likely to occur with the AlMe_3 present in MAO, generating isobutyl end groups on both polymer ends. Chain transfer to aluminum reactions are not so relevant with metallocene systems, since they only occur at high Al/Zr ratios, or under conditions of low productivity.^{15,17}



Scheme 3.6 Chain transfer to aluminum.

(d) Chain transfer to monomer

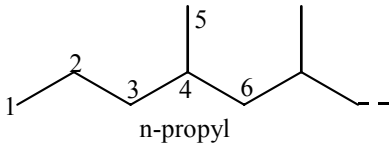
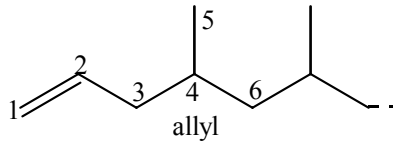
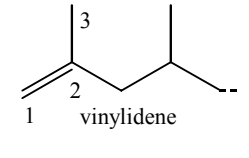
In the absence of hydrogen, and under normal polymerization conditions, chain transfer to monomer (Scheme 3.7) was found to be the most important chain transfer reactions in propylene polymerization with heterogeneous catalysts and a few metallocene catalyst systems. In the case of metallocene catalysts, they require a coordination gap with a wide "lateral extension" angle.¹⁸ This angle is narrowed by the presence of methyl substituents in the 2 position on the ligand.



Scheme 3.7 Chain transfer to monomer.

There are obviously a number of different end groups possible with metallocene polypropylene. These end groups can be detected by ^{13}C NMR.¹⁵ The structures and chemical shifts are summarized in Table 3.1.

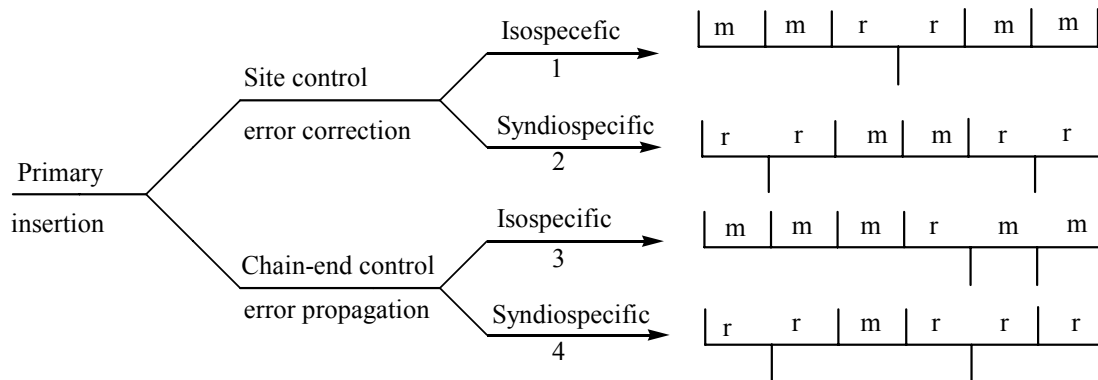
Table 3.1 ^{13}C NMR chemical shifts (ppm) and carbon numbering of common propylene chain end groups in 1,2,4-trichlorobenzene¹⁵

C			
1	14.47	115.37	111.38
2	20.12	137.67	144.87
3	39.68	41.38	22.6
4	30.50	30.80	-
5	20.81	20.64	-
6	45.98	45.33	-

3.3 Tacticity and stereoerrors

It is practically impossible to produce a polymer which has 100% stereoregularity, due to occasional errors that can occur during polymerization reactions.¹⁹⁻²³ During isotactic polymerization, monomers are inserted into the metal-carbon bond in a particular regular manner, with the methyl group pointing in the same direction with respect to the two ligands and the growing polymer chain (same enantioface). If a monomer is inserted in such a way that the methyl group points in a different direction, it causes an error in the growing polymer chain. Catalysts that produce highly isotactic polymers usually correct this error during the next insertion step of the monomer.

There are two types of errors that can occur (Scheme 3.8).²⁴ The first one is called a catalytic-site control error, which is also known as enantiomorphic site control. The second one is a chain-end controlled error and it is caused by the last monomer inserted.



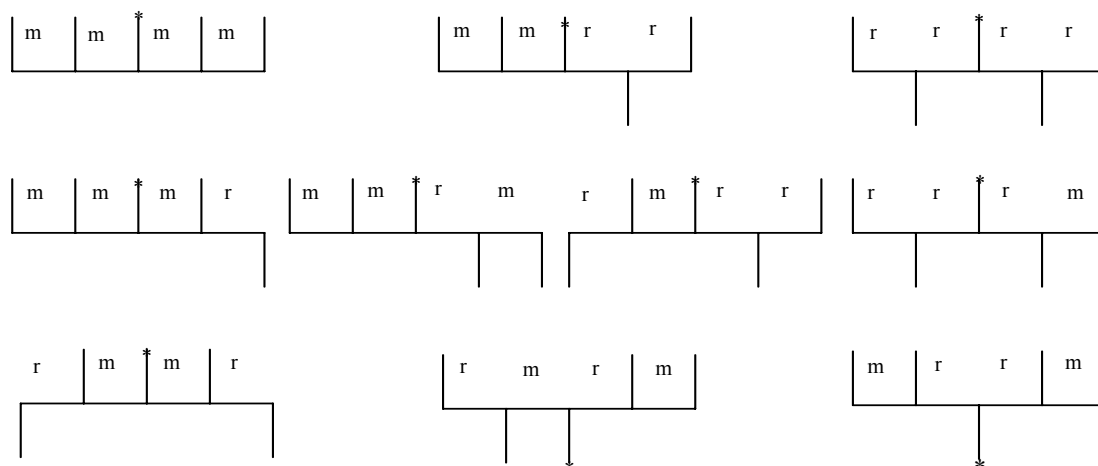
Scheme 3.8 Typical stereoerrors occurring during polymerization.²⁴

In polypropylene, the signal of the CH₃ group from ¹³C NMR measurement is usually used to determine the polymer microstructure. The ¹³C NMR chemical shift for CH₃ (Table 3.2) is determined by neighboring repeat units on both sides.

Table 3.2 Chemical shifts of CH₃ pentads in 1,2,4-trichlorobenzene⁽²⁶⁻²⁸⁾

Chemical shift (ppm)	Pentads
22.0-21.7	<i>mmmm</i>
21.7-21.4	<i>mmmr</i>
21.4-21.2	<i>rmmr</i>
21.2-21.0	<i>mmrr</i>
21.0-20.7	<i>mmrm + rmrr</i>
20.7-20.5	<i>rmrm</i>
20.5-20.3	<i>rrrr</i>
20.3-20.0	<i>rrrm</i>
20.0-19.7	<i>rmmr</i>

Each CH₃ signal is assignable to a particular "pentad" pattern, represented by the four consecutive *meso* (*m*) or *racemic* (*r*) designators framing the CH₃ (*) under consideration.²⁵⁻²⁸ The possible pentads are shown below in Scheme 3.9.



Scheme 3.9 Ten possible stereochemical pentads of a polyolefin.

All ten possible pentad signals (*mmmm*, *mmmr*, *rmmr*, *mmrm*, *mmrr*, *rmrr*, *rmrm*, *rrrr*, *rrrm*, *mrrm*) are observed in atactic polypropylene. Isotactic polypropylene is characterized by a single ^{13}C NMR signal for the *mmmm* pentad. The degree of isotacticity is expressed as the ratio of the *mmmm* pentad integral to the sum of all pentad integrals observed and is designated as [*mmmm*].

Syndiotactic polypropylene only contains *rrrr* pentads and is also characterized by a single ^{13}C NMR signal. The syndiotacticity is expressed as the ratio of the *rrrr* pentad integral to the sum of all pentad integrals and is designated as [*rrrr*].

3.4 Enantioface selectivity mechanism

The ethylene insertion mechanism has been extensively studied, yet only a few advanced calculations have been carried out on propylene insertion. This is due to the fact that propylene insertion is a much more complicated process.²⁹ As mentioned above, there are two well known mechanism that can occur, which are the enantiomorphic site control and the chain-end controlled error that can be caused by the last monomer inserted.

3.4.1 Mechanism of enantiomorphic site control in primary insertions

The driving force for the two stereospecific processes, originating from the chiralities of the catalyst active sites and referred to as enantiomorphic site control (isospecific⁹ and syndiospecific¹¹ site control), can be relatively strong, with differences in activation energy for the insertion of the two enantiofaces (*re* and *si*) up to 5 kcal/mol.

To understand in detail the proposed mechanism of stereocontrol, it must start looking at the role played by the ligand in directing the propylene enantioface selection. The first studies on propylene polymerization with heterogeneous catalytic systems indicated poor enantioselectivity for propylene insertion into the Ti-CH₃ bond.³⁰ This feature has also been confirmed for the metallocene-based homogeneous catalytic systems by different research groups.³¹⁻³⁴

As an example, the structures A and B of Figure 3.1 clearly show that the propylene methyl group is sufficiently far from the metallocene skeleton for both propylene coordination enantiofaces. That means the chirality of the ligand can not efficiently select between the two propylene enantiofaces in the absence of a growing chain larger than CH₃. This means that the first step of polymerization is essentially nonselective (random), but when the alkyl group is an isobutyl (which it would be after the first insertion), then the next insertion will be enantioselective (favour one enantioface).

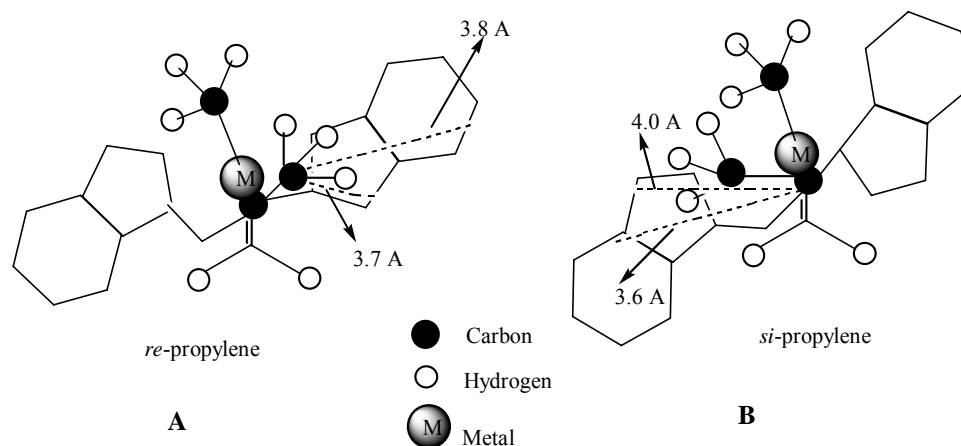


Figure 3.1 Molecular mechanics minimum geometry for *re* and *si* propylene coordination.¹⁵

Having established that the ligand chiral framework is unable to direct the enantioface selection of the incoming propylene monomer, we can now see that the chiral orientation of the growing chain is critical in forcing the incoming propylene monomer to differentiate between the two enantiofaces.

Looking at Figure 3.2, structure A, with a *re*-coordinated propylene,¹⁵ seems more stable than structures B and C, with a *si*-coordinated propylene. This is because there appears to be fewer repulsive interactions in structure A among the ligand framework, the growing chain, and the propylene molecule than is the case with B and C. This is reviewed extensively by Resconi *et al.*¹⁵

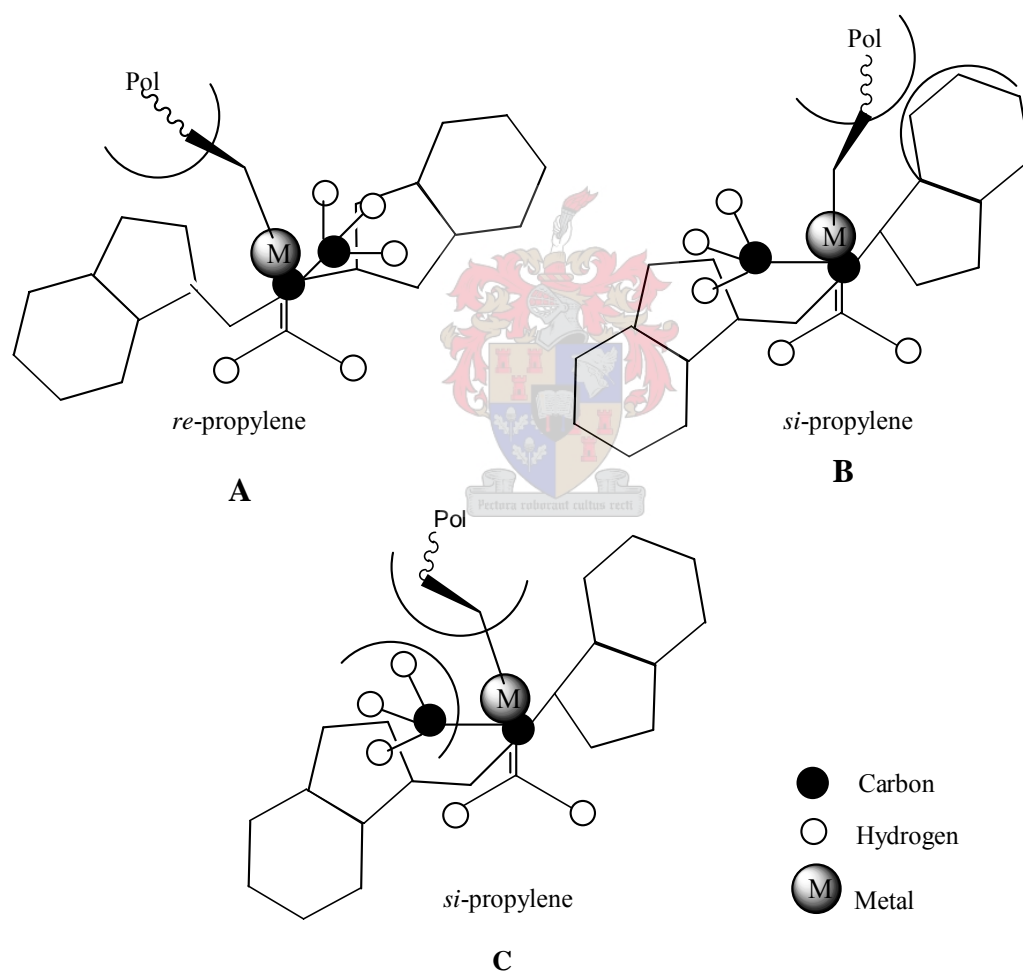


Figure 3.2 Ability of the chiral orientation of the growing chain to discriminate between the two enantiofaces of the incoming propylene monomer.¹⁵

The above scheme indicates that the growing chain is most likely to orient itself into an open sector, and that the methyl group of the coordinating propylene will point away from the growing chain (*anti* to the β -C atom of the growing chain¹⁵). This makes sense, as this orientation will minimize the steric interactions.

All of the above means that the enantioselectivity of the catalyst with respect a prochiral olefin is due to energy effects arising from the interaction of the incoming monomer with the growing chain, rather than the interaction of the monomer with the ligand framework. The interaction of the ligand framework with the chain will in turn guide the orientation of the chain. Of importance here, to us, is the assumption that only the first insertion is nonspecific.³¹⁻³⁴ We will test the theory during the controlled production of polypropylene with C_2 symmetric metallocenes.

3.4.2 Mechanism of chain-end control in primary insertion

Chain-end control is considered less effective than site control. The difference in activation energy between the insertions of the two enantiofaces is around 2 kcal/mol. Chain-end control can be effective only at low temperature, producing polypropylenes with low stereoregularity and low molecular weight.^{9,35}

3.5 Influence of hydrogen on propylene polymerization (hydrogenolysis)

Hydrogen molecules are used to regulate the molecular weight of polyolefins prepared in the presence of both heterogeneous and metallocene catalysts.^{12,36,37} Hydrogen response in metallocene-catalyzed propylene polymerization seems to be wide-ranging and reflects the strong dependence of the performance of metallocene catalysts on both their π -ligands structure and on the polymerization conditions.

Addition of molecular hydrogen leads to different levels of molecular weight depression depending on the hydrogen level, the concentration of the monomer, the type of catalyst, and the polymerization temperature.¹⁵

Catalyst productivity in the presence of hydrogen has been found to increase to a certain level, then it remained constant, or was slightly decreased by a further increase of hydrogen partial pressure. The hydrogen level required to reach maximum productivity is dependent on the nature of the catalyst. Productivity enhancement is mainly due to the increase of initial polymerization rate; catalyst decay with time is either not affected or slightly retarded by the presence of hydrogen.³⁸

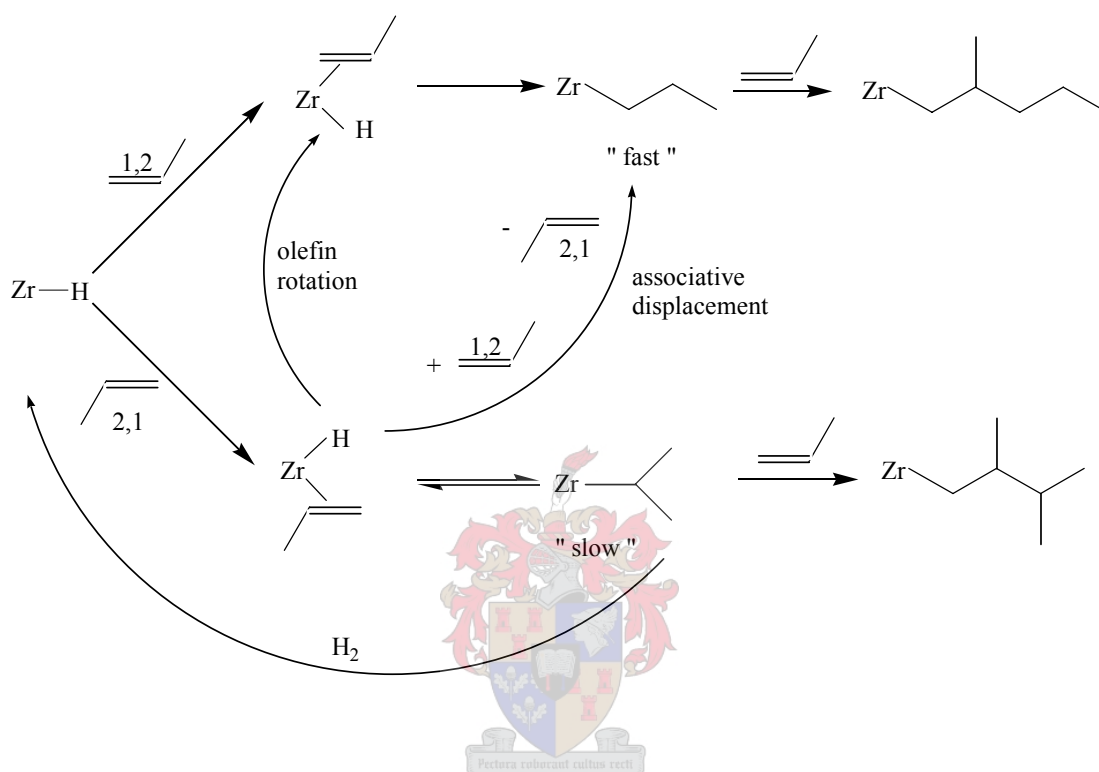
Hydrogen has also been used for mechanistic studies. For example, high hydrogen pressures have been used to produce propylene oligomers by the so-called hydro-oligomerization reaction³⁶ in order to determine the regiochemistry and stereochemistry of initiation and propagation. By analyzing the structures of the propylene oligomers and measuring their optical rotations, Pino³⁶ found that monomer insertion is largely predominantly primary and that after an occasional 2,1-insertion, chain growth is terminated by hydrogen. The presence of *n*-butyl end groups in the presence of hydrogen strongly supports the above hypothesis, and that the catalyst preferentially selects the *re* monomer enantioface.

3.5.1 Termination mechanism in the hydrogenolysis process

This process, which is practically used to control the molecular weight of polymers, involves coordination of a hydrogen molecule to the metal center of the β -agostic intermediate, activation of the coordinated H-H bond, and transfer of a hydride to the growing polymer chain to form a complex between the metal hydride and polymer, which eventually dissociates to give a isolated polymer with saturated end-groups.³⁹

Moscardi⁴⁰ has modeled the insertion of propylene into the Zr-H bond and found that secondary propylene insertion into the Zr-H bond with formation of the Zr(*i*-Pr) initiating species is certainly competitive with primary insertion, even on highly regioselective catalysts. This molecular modeling study has also exposed that the Zr(*i*-Pr) initiating species is slower compared to Zr(*n*-Pr) with respect to the following propylene insertion and that isomerization of Zr(*i*-Pr) to Zr(*n*-Pr) can follow a relatively low energy pathway by associative displacement with the monomer after β -H transfer on the Zr(*i*-Pr) species (Scheme 3.10).

Similar to the case of the propagation reaction, the attack of molecular hydrogen in the hydrogenolysis step may progress in two ways, depending on the relative position of the hydrogen molecule with respect to the β -agostic hydrogen. Thus, *syn* or *anti* processes must be considered that lead to reaction mechanisms known as frontside and backside. They are schematically explained in Scheme 3.11.⁴¹

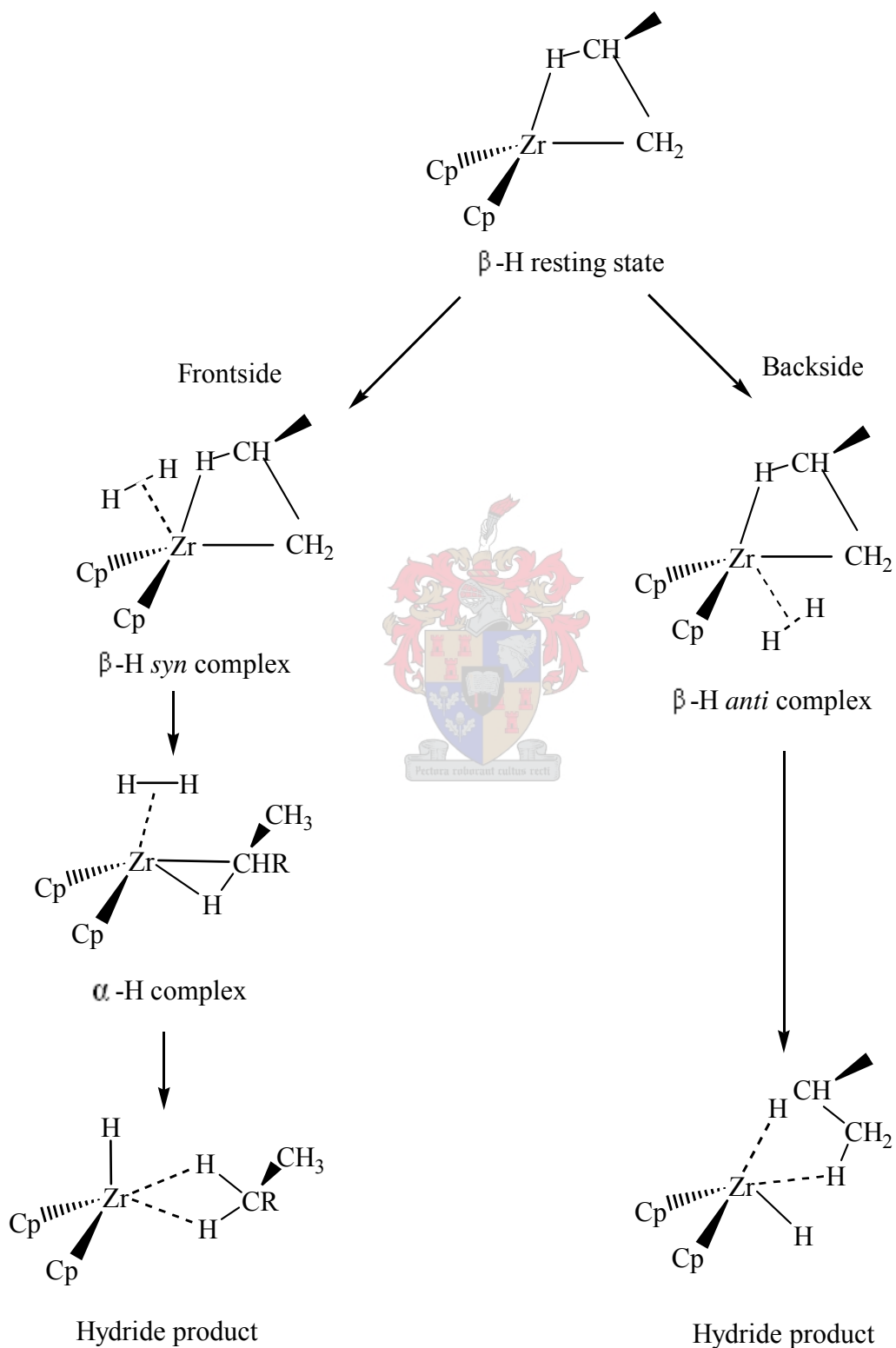


Scheme 3.10 Primary and secondary insertion mechanism into Zr-H bond and the isomerization process of Zr(*i*-Pr) to Zr(*n*-Pr).⁴⁰

The backside mechanism has the lowest energy pathway for hydrogenolysis reactions in metallocene catalysts. For ethylene polymerization, the hydrogenolysis reaction from the β -agostic intermediate, $\text{Cp}_2\text{Zr}(\text{CH}_2\text{CH}_2\text{CH}_3)_\beta^+$, is calculated to take place with a 3.4 kcal/mol for H-H activation and about 11.5 kcal/mol in the case of propylene polymerization.³⁹

In conclusion it can be said that a possible way to control the kinetics of the hydrogenolysis reaction can be considered. It involves the increase of steric hindrance in the middle plane of the system in order to hinder backside hydrogenolysis. A similar reasoning leads to the hypothesis that differences in hydrogen sensibility

between heterogeneous and homogeneous catalysts could be related to local symmetry around the metal center. Therefore, it may be possible to design new homogenous catalysts with reduced hydrogen affinity.⁴¹



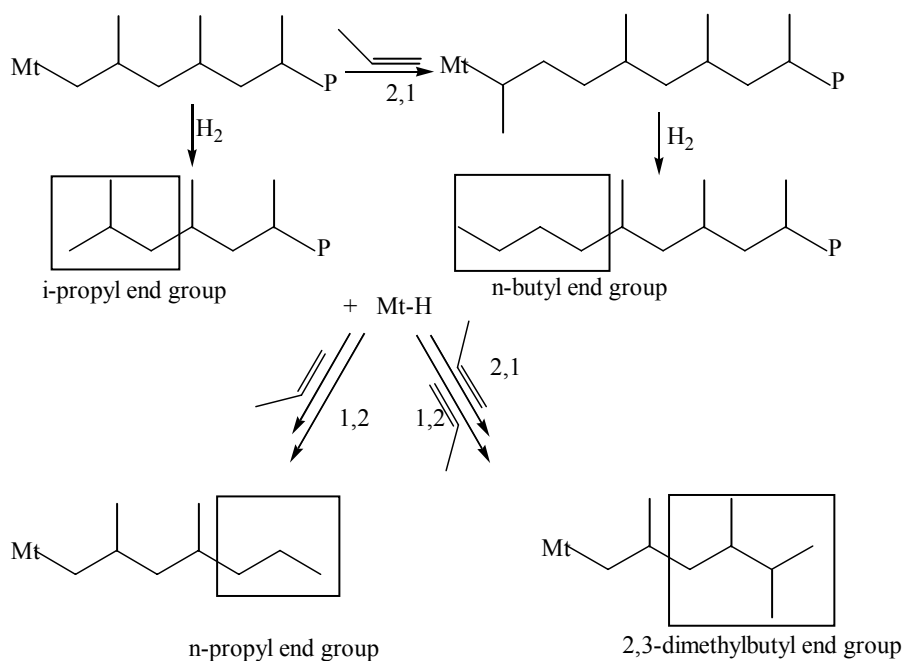
Scheme 3.11 Frontside and backside mechanism of the hydrogenolysis process.³⁹

3.5.2 Chain-end groups

The study of the chain-end structure of polyolefins is one of the most exciting subjects for many scientists and engineers because it introduces important key information on the explanation of propagation and termination mechanisms in olefin polymerization. Furthermore, the end structure often acts as a useful functional group in order to produce new functional polyolefins.⁴²⁻⁴⁶

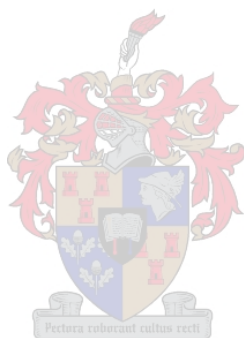
It is well known that metallocene-catalyzed polypropylene in the absence of any terminating agent has vinylidene end groups produced by β -hydride elimination. Recently, the terminal chain-end structures such as vinyl, butenyl and isobutenyl structures have been reported for polypropylene prepared by metallocenes that had different ligand structures.⁴⁵⁻⁴⁷

The structures of saturated polypropylene end groups that can be produced in the presence of hydrogen are shown in Scheme 3.12. Different types of chain-end groups could be detected such as i-propyl, n-butyl, n-propyl and 2,3-dimethylbutyl, which depend on the mechanisms of hydrogenolysis reactions for primary and secondary termination reactions.¹⁵



Scheme 3.12 Structures of saturated polypropylene end groups that can be produced in the presence of hydrogen.¹⁵

The i-propyl end-groups are generated by chain transfer after a primary insertion and the n-butyl end-groups are generated by chain transfer after a secondary insertion. The other end of the polymer chain (generated by insertion of a monomer into the metal-hydride bond) could be n-propyl or 2,3-dimethylbutyl which are due to either 1,2- or 2,1- propylene insertion in the metal-H bond respectively.

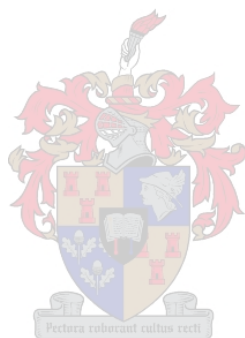


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CHAPTER 4

Experimental

4.1 Introduction

Polypropylenes and polyethylenes were synthesized by using two different types of C_2 -symmetric catalyst systems, *rac*-Et(Ind)₂ZrCl₂/MAO and *rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂/MAO, in the absence and in the presence of different amounts of hydrogen. These polypropylenes were characterized by nuclear magnetic resonance spectroscopy (NMR) to study the microstructures, high temperature gel permeation chromatography (HT-GPC) to measure the molecular weights and molecular weight distributions, and differential scanning calorimetry (DSC) to determine the melting points of these polymers. Preliminary work was done on polyethylenes, using the *rac*-Et(Ind)₂ZrCl₂/MAO catalyst system, to determine the effect of hydrogen as a terminating agent on the molecular weights of these polyethylenes.

4.2 Materials and methods

4.2.1 Purification of reagents

Propylene (polymerization grade, > 99%) and ethylene were obtained from Fedgas (SA) and purified by passing through three columns containing BASF catalyst R3-11G and molecular sieves. High purity hydrogen (total impurities < 7 vpm) was also obtained from Fedgas. Analytical grade toluene (Aldrich) was used as solvent in all the reactions. Toluene was dried by refluxing over sodium/benzophenone and then distilling under an inert gas atmosphere. Methylaluminoxane was purchased from Sigma-Aldrich and used without further purification (10 wt% solution in toluene).

The catalysts used in this study were the stereorigid C_2 -symmetric ethylene *bis*(indenyl)zirconium dichloride, *rac*-Et(Ind)₂ZrCl₂ and *rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂, hereafter abbreviated as EI and MBI respectively. These metallocene catalysts were obtained from Strem Chemicals and Boulder Scientific and used as received. Metallocene catalysts comprising group 4 metallocene

complexes and MAO are air and moisture sensitive, and thus experiments must be performed under an inert atmosphere and in dry solvents.

4.2.2 Polymerization procedure

All reactions were carried out under an inert gas atmosphere using standard Schlenk techniques. The polymerization reactions were carried out in a 350-ml stainless steel Parr autoclave with inlet and pressure gauge. Typically the reactor was charged with MAO (10 wt% solution in toluene), catalyst (0.55 μ mol in 5 ml toluene), and toluene (30 ml). The catalyst solution was stirred for 5 minutes and then the monomer was added. The reactor was pressurized with hydrogen and stirred for 2 hours at room temperature. The following polymerization conditions were used for all reactions:

- the catalyst/MAO ratio was kept at 1:6 000,
- 4-5 g propylene was used,
- all reactions were carried out at room temperature, and
- different amounts of hydrogen were used as terminating agent to control the molecular mass.

After 2 hours the reaction was quenched with 10% HCl/MeOH. The resulting polymer was filtered off, then washed several times with methanol and subsequently dried under vacuum at 80 °C for 15 hours to yield about 2-4 g of polypropylene as a white powder. The same procedure and conditions were used for the polymerization of ethylene.

4.3 Characterization and analytical techniques

Three different analytical techniques were used to characterize the polypropylene and polyethylene polymers in order to study the various properties of these polymers. The operation conditions of these techniques are now described in more detail.

4.3.1 Nuclear magnetic resonance (NMR)

NMR spectra (^{13}C NMR and ^1H NMR) were recorded at 120 °C on a Varian VXR 300 spectrometer. A pulse angle of 45 degrees and a relatively short repetition time of 0.82 seconds were used.¹ Some of the samples were also run on a 600 Varian Unity Inova NMR spectrometer equipped with an Oxford magnet (14.09 T), operating at 600 MHz, using a 5 mm inverse detection PFG probe. Resolution and accuracy were improved by zero-filling the data once before performing the Fourier transformation. Baseline correction was also applied in order to further enhance the accuracy and repeatability of the integrals measured for selected peaks in the spectra. Samples (60-80 mg) for ^{13}C NMR analyses were dissolved at 110 °C in a 9:1 mixture of 1,2,4-trichlorobenzene (TCB) and benzene- d_6 (Bz_6). Deuterated 1,1,2,2-tetrachloroethane (TCE-d_2) was also used as solvent for certain samples.

4.3.2 High-temperature gel chromatography (HT-GPC)

Number average molecular weight (\overline{M}_n), weight average molecular weight (\overline{M}_w) and MWD were determined by using high-temperature gel permeation chromatography (HT-GPC). Samples were analyzed with a PL-GPC 220 using a flow rate of 1.0 ml/min and a differential refractive index detector. Columns packed with a polystyrene/divinylbenzene copolymer (PL gel MIXED-B [9003-53-6]) from Polymer Laboratories were used. The length and diameter of these columns were 300 mm and 7.5 mm, respectively. Particle size was 10 μm . The analyses were carried out in 1,2,4-trichlorobenzene, stabilized with 0.0125% 2,6-di-tert-butyl-4-methylphenol, as solvent, at 140 °C. The calibration was done with monodisperse polystyrene standards (EasiCal from Polymer Laboratories).

4.3.3 Differential scanning calorimetry (DSC)

The melting points and the degree of crystallinity of polypropylenes and polyethylenes were determined by DSC. A TA instrument Q100 DSC system was used. It was first calibrated by measuring the melting temperature of indium metal according to standard procedure. All measurements were conducted under a nitrogen

atmosphere flow, at a purge gas flow rate of 50 ml/min. Three cycles were performed for each sample. First the samples (about 2 mg) were heated in crimped aluminium pans from -30 °C to 220 °C at a rate of 10 °C/min. Then they were cooled from 220 °C to -30 °C at a rate of 10 °C/min. The peak crystallization temperature, T_c (DSC) was determined from the cooling cycle. Lastly, the polymers were heated for the second time at 10 °C/min to 220 °C. This was done to determine the peak melting temperature (T_m) from the peak maximum of the second heating cycle.

4.4 General procedure of sample preparation for analysis

Sample preparation and choice of the solvent for compositional analysis of polypropylenes has been a subject of many literature reports. Various deuterated solvents have been used for characterization of polypropylene samples by ^1H and ^{13}C NMR spectroscopy. In order to obtain an informative and useful spectrum, samples need to be homogenous and without any defects or voids. This becomes even more crucial when running NMR spectra on higher resolution NMR spectrometers (600 MHz), since any inhomogeneity in the sample results in the validity and even the quality of data acquisition being suspect.

In the present study, as has been mentioned in Section 4.3.1, several deuterated solvents and different conditions have been used in order to optimize the quality of the spectra under existing condition and facilities. Weighed polymer samples were placed at the bottom of an NMR tube, and 0.5-0.8 ml of deuterated solvent was added gradually, to let the polymer swell and dissolve, and then samples were heated to the desired temperature (120 °C) for two hours in an oil bath before recording the spectra.

4.5 References

1. Brull, R, Raubenheimer, H.G, Pasch, H, Wahner, U, Sanderson, R.D. *J.Polym.Sci., A, Polym.Chem.*, **2000**

CHAPTER 5

Polymerization and characterization of polypropylene and polyethylene produced with *rac*-Et(Ind)₂ZrCl₂/MAO (EI)

Summary

Polypropylenes and polyethylenes were prepared both in the presence and absence of molecular hydrogen, using the C₂-symmetric, isospecific, bridged metallocene *rac*-ethylene bis(1-indenyl)zirconium dichloride (EI) as polymerization catalyst under standardized conditions. The effect of different amounts of hydrogen on the microstructure, molecular weight, molecular weight distribution, melting point and crystallization behaviour of these polymers was investigated. The polymers were characterized by nuclear magnetic resonance, high-temperature gel chromatography and differential scanning calorimetry.

5.1 Introduction

The length of the polymer chains obtained depends on the competition between chain propagation and chain termination reactions. In most cases, propagation is much easier than termination so that, in industrial production, the chain growth is regulated by injection of molecular hydrogen into the reactor. The sensitivity of heterogeneous catalysts to hydrogen is highly variable and is not completely understood. Therefore, a better knowledge of the hydrogenolysis process would be useful to efficiently control the chain growth of the polymer as well as its physical properties (molecular mass, melt index and crystallinity). Moreover, hydrogenolysis processes in metallocene catalysis are of substantial interest for industrial companies since, in practice, injection of hydrogen stops the polymerization, which renders control of the chain growth difficult.¹⁻¹²

This chapter reports on propylene and ethylene polymerization and studies the microstructure, molecular weight, molecular weight distribution and melting point of these polymers produced by using EI (Figure 5.1) as catalyst in the absence and presence of molecular hydrogen as terminating agent.

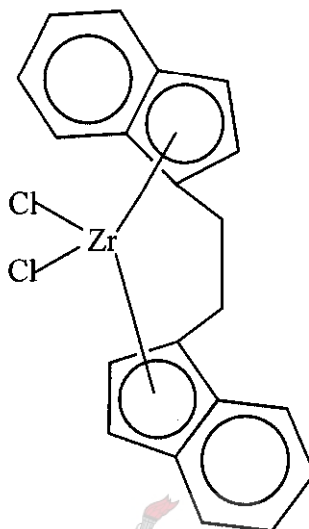


Figure 5.1 *rac*-Et(Ind)₂ZrCl₂ (EI).

5.2 Results and discussion of ethylene polymerization

The polymerization experiments with ethylene in the presence and absence of hydrogen were undertaken to gain some insight the practical aspects and limitations of using hydrogen during polymerization experiments. As will be noted, no serious attempt was made at this stage to quantify the amount of hydrogen that was used in the initial experiments. This is in no way a reflection on the ability to control the hydrogen added in later experiments, rather, in this instance hydrogen was added for differing amounts of time, with no effort made to accurately weigh the hydrogen added.

A series of polyethylenes with controlled molecular weights were obtained (Table 5.1) by keeping a constant catalyst/cocatalyst/monomer ratio, and adding increasing amounts of hydrogen to the reaction mixture.

In terms of theoretical studies, almost all studies have centered on ethylene polymerization due to the lower computational cost involved and because of the great importance of this olefin in industrial the field.¹³⁻¹⁷

Table 5.1 Results of ethylene polymerization carried out with various amounts of hydrogen

Run No.	Relative amount of hydrogen ^b	Activity (kg PE/(mol Zr.h))	M_w (g mol ⁻¹)	M_w/M_n	T_m (°C)	X_c^a (%)
1	None	5 480	155 528	3.56	133.94	52
2	1	15 385	62 255	4.69	129.83	43
3	2	20 702	29 151	7.38	128.56	69
4	4	12 473	23 426	4.52	128.58	71

^a Crystallinity degree, considering $\Delta H_m = 293$ J/g of PE 100% crystallinity^{17,18}

^b Relative times of hydrogen addition

5.2.1 Influence of hydrogen on ethylene polymerizations

The results in Table 5.1 show that the catalyst activity in the presence of small amounts of hydrogen increases significantly: from 5 480 kg PE/(mol Zr.h) in the absence of hydrogen to 20 702 kg PE/(mol Zr.h) in the presence of medium hydrogen content. This is probably due to reactivation of the deactivated species that could be formed, which lengthens the lifetime of the catalyst in the polymerization reaction. On the other hand, the presence of a high content of hydrogen leads to a decrease in the catalyst activity (12 473 kg PE/(mol Zr.h)) over the “medium” hydrogen content. This could result from a competition reaction of hydrogen with the active metal centers, whereby ethylene molecules are inhibited in their coordination.

A significant decrease in molecular weight ($\overline{M}_w = 155\,528$ g mol⁻¹ in the absence of hydrogen to $\overline{M}_w = 23\,426$ g mol⁻¹ in the presence of hydrogen) is observed. This clearly illustrates the effective chain terminating effect of hydrogen. The apparent

molecular weight distribution ($\overline{Mw}/\overline{Mn}$) increases as well, for instance to a value of 7.38 in the most extreme case. This broadness in molecular weight distribution (Figure 5.2) could be due to the way in which the peak was interpreted. There appears to be a bimodal distribution, with two peaks maxima apparent.

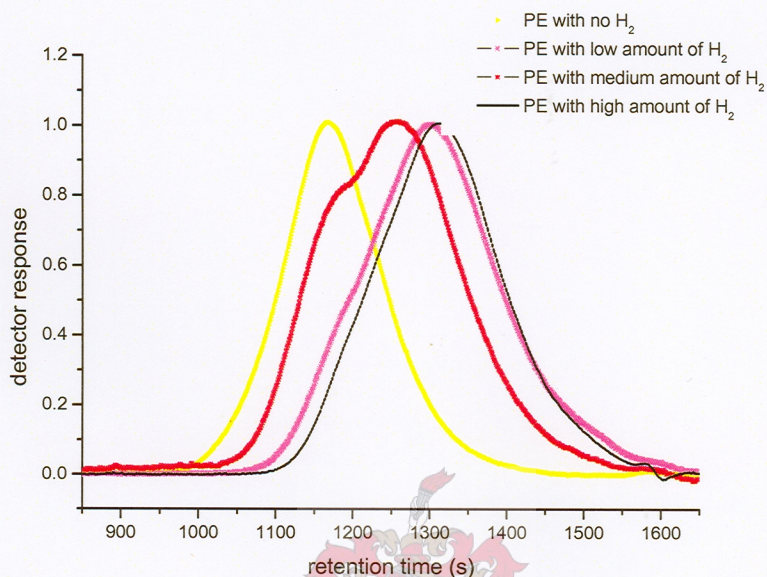


Figure 5.2 HT-GPC chromatograms of polyethylenes produced with the EI catalyst system with different amounts of hydrogen.

This broad shoulder could be due to more than one type of active center. That means that the catalyst species produces different molecular weight chains when hydrogen is used during the polymerization reactions. Uniform molecular weight distribution was transformed into a multimodal distribution of the molecular weights for the synthesized polymers.

Concerning the DSC results in Table 5.1, the melting temperature (T_m) of the obtained polymer in the absence of hydrogen (133.94 °C) was slightly higher than the temperatures obtained using different amounts of hydrogen (129.83 – 128.58 °C). This difference in the melting points is due to the differences in the molecular weights. With increasing the molecular weights the melting points also increase (Figure 5.3).

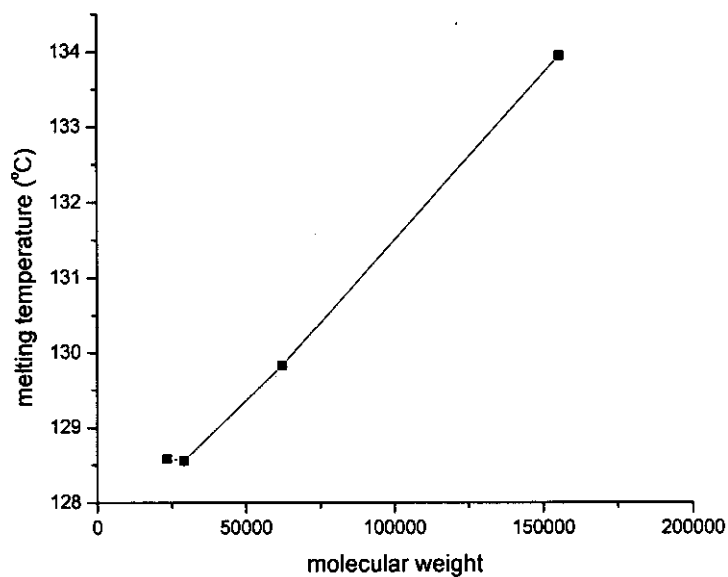


Figure 5.3 The molecular weights of polyethylenes versus melting temperatures.

Overall, the depression of melting temperature is quite small, and can be accounted for by the decrease in molecular weight.

5.3 Results and discussion of propylene polymerization

In this study a number of polypropylene polymers were prepared using the EI catalyst system in the absence and presence of different amounts of hydrogen. The reaction conditions were kept constant for all the polymerization reactions. A summary of these polymerization results is shown in Table 5.2.

Table 5. 2 Experimental parameters^{a,b} and results for propylene polymerizations carried out with EI catalyst system

Run No.	Amount of hydrogen (wt %) ^c	Activity ^d	M _w (g mol ⁻¹)	M _w /M _n	T _m (°C)	X _c ^e (%)
E1	0.00	1 462	76 640	2.22	144	49
E2	0.10	2 278	32 177	2.33	140	41
E3	0.30	3 656	27 876	2.12	142	39
E4	0.68	4 095	19 579	2.10	141	49
E5	1.50	3 802	15 227	2.00	141	48
E6	2.00	4 167	19 028	2.16	141	49
E7	2.65	4 313	15 431	2.13	141	46
E8	3.30	4 112	13 169	2.10	140	50
E9	3.90	5 118	14 844	2.10	140	52
E10	4.60	3 751	14 434	2.10	141	52
E11	6.27	3 620	10 191	1.92	139	46

^a Al/Zr ratio 1:6000

^b room temperature (25 °C)

^c (g H₂/g propylene) × 100

^d (kg PP/(mol Zr.h))

^e ΔH_m = 209 J/g of PP 100% crystallinity¹⁹

5.3.1 Propylene polymerization in the absence of hydrogen

The molecular weights, molecular weight distributions, catalyst activities, melting points, and crystallinity percentages observed in the absence and presence of hydrogen are tabulated in Table 5.2. Discussion of the above results, as well as details of microstructure changes, with full explanations, will be the subjects of the following sections (5.3.1.1 and 5.3.1.2).

5.3.1.1 Microstructure

The most powerful (if not the only) tool for the determination of the microstructure of polyolefins and the polymerization mechanism is solution ^{13}C NMR.^{2,20,21} The main advantage of NMR in the characterization of polymers is the unique molecular and structural information which can be obtained. For instance, the relative configurational distribution (tacticity) and regio-irregularities (defects) in homopolymers of polypropylene can be mapped out and represent a unique fingerprint of polymer microstructure.

Figure 5.4 shows a typical ^{13}C NMR spectrum of sample E1 (polypropylene prepared in absence of hydrogen), a relatively highly isotactic polypropylene. The spectrum contains three primary resonance signals which can be identified as those of (a) the methylene carbons (46.2 ppm), of (b) the methine carbons (28.62 ppm), and of (c) the methyl carbons (21.59 ppm) of polypropylenes. Often the methyl region is chosen for tacticity analysis due to its good chemical shift resolution. According to the spectrum the polymer is relatively highly isotactic and the resonances diagnostic of isolated regio-irregular units can also be observed. The isotacticity can be inferred from the intense peak at 21.59 ppm and the relatively few and small stereoirregularities.

Assuming stereochemical shifts of the methyl pentads are grouped together according to the central triad sequences *mm*, *mr* and *rr*, from low to high field, at least ten resonances can be assigned to the unique pentad sequences, observed in the order *mmmm*, *mmmr*, *rmmr*, *mmrr*, *mmrm*, *rmrr*, *mrmr*, *rrrr*, *mrrr*, and *mrrm*.²² The methyl region was chosen for tacticity analysis. The only peaks due to the stereoregular units *mmmm* (21.59 ppm) and the stereoirregular units *mmmr* (21.32 ppm), *mmrr* (20.77 ppm) and *mrrm* (19.60 ppm) of sample E1 can be seen in Figure 5.5, indicated as (c), (d), (e), and (f) respectively.

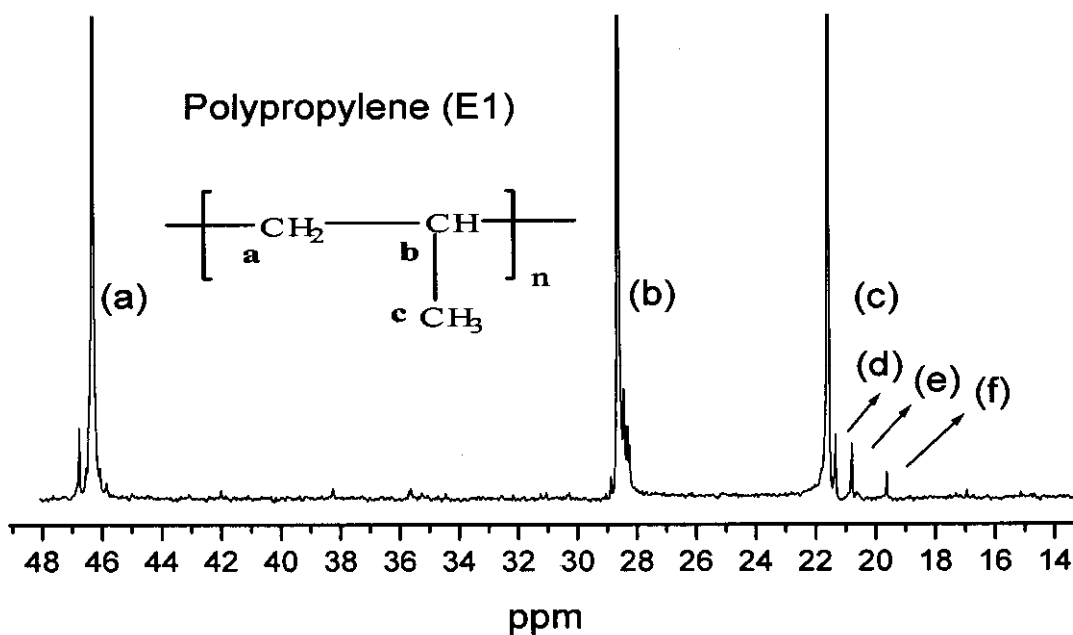


Figure 5.4 300 MHz ^{13}C NMR spectrum of isotactic polypropylene (E1) prepared in the absence of hydrogen. (Solvent: TCB:Bz₆ 9:1 volume ratio).

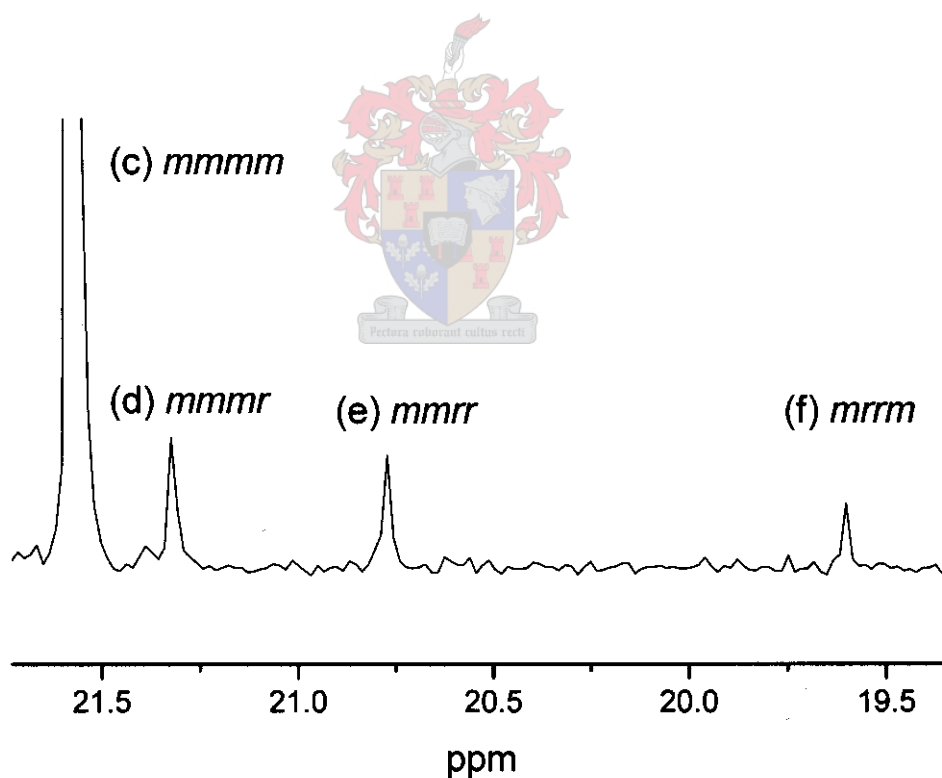


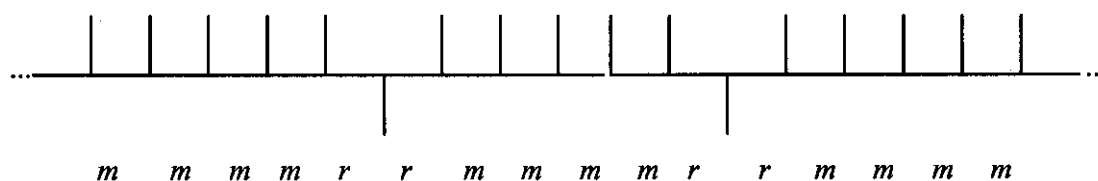
Figure 5.5 300 MHz ^{13}C NMR spectrum of the methyl region of sample E1. (Solvent: TCB:Bz₆ 9:1 volume ratio).

These assignments correspond what has been described in the literature.^{23,24} The relative ratios of the integrals of the *mmmm*, *mmmr*, and *mrrm* pentads are roughly 2:2:1,²¹ as expected from the statistical model of the enantiomorphic site control of the stereospecific propagation.^{25,26} The tacticity of this polymer was determined by integrating the methyl peak region in Figure 5.5, and this shows 86.5% isotactic polypropylene (Table 5.3).

Table 5.3 Steric pentad distributions evaluated from the ¹³C NMR spectrum of sample E1 in Figure 5.5

Pentad	Chemical shift (ppm)	Fraction %
<i>mmmm</i>	21.59	86.5
<i>mmmr</i>	21.32	5.8
<i>mmrr</i>	20.77	4.7
<i>mrrm</i>	19.60	2.1

According to Ewen⁹ the ¹³C NMR analysis of the steric pentads of this highly isotactic polypropylene is consistent with the polymer having the configurational microstructure represented by the idealized structure in Scheme 5.1.



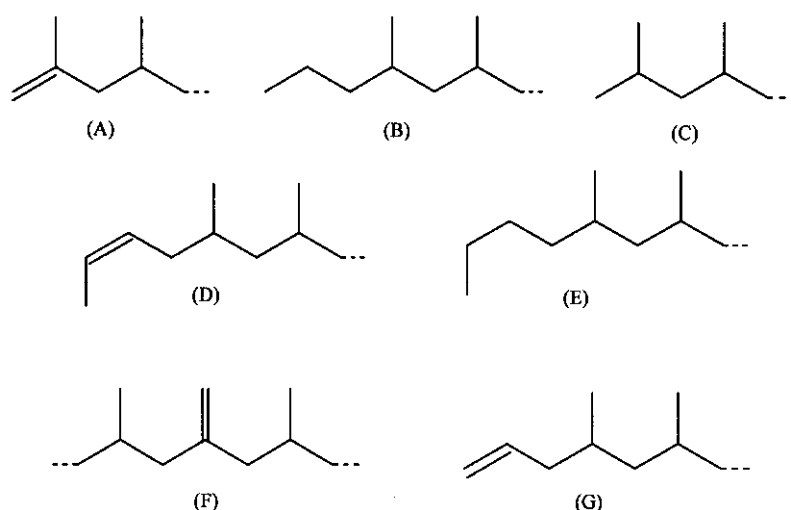
Scheme 5.1 Isotactic polypropylene chain segments with wrong configurations which represent stereodefects (isolated *rr* triads).⁹

Small peaks can be observed in Figure 5.4 in the areas of 17 ppm, 31 ppm and 38.2 ppm. These regio-irregularities result from 2,1-type insertion which produce head-to-head units. The intensities of these peaks however are low and correspond to

approximately 1 mol% of 2,1- and 3,1-misinsertions. These peaks are actually quite significant, because it indicates that 2,1-misinsertions actually occur, and that these do not, as is often the case with the heterogeneous catalysts, lead to chain termination and limits molecular weight. In the case where a monomer coordinates in the 2,1 fashion, insertion followed by termination will not lead to these units being enchainned and therefore showing up in the ^{13}C NMR spectrum.

5.3.1.2 Structure of the end groups

In the case of metallocene-catalyzed propylene polymerization, the termination reactions of the polymer chain are believed to result from the transfer of a β -hydride or a methyl group of the growing polymer chain owing to the detection of vinylidene, vinyl and vinylene groups as unsaturated chain end-structures.^{27,28} On the basis of the other papers that describe the assignment of NMR spectra,²⁹ 1,2-inserted chain ends could lead to vinylidene groups (A), n-propyl groups (B) and i-propyl groups (C), as described in Scheme 5.2. 2,1-inserted monomers leading to termination could give rise to 2-butenyl groups (D), n-propyl groups (B), i-propyl groups (C) and n-butyl groups (E). By allylic activation of the polymer chain, internal vinylidene (F) would also be generated. The i-propyl group (C) could also be derived from the 1,2-insertion of a monomer into the Zr-CH_3 bond.³⁰



Scheme 5.2 Different types of end-group structures that can be obtained in propylene polymerization.³⁰

The ^{13}C NMR spectrum of polypropylene in Figure 5.4 shows n-propyl end groups (represented by the signals at 15 ppm, 30.4 ppm and 42 ppm) and 2-butenyl end groups (represented by the signals at 31.3 ppm and 35.6 ppm). n-Propyl end groups are produced by β -hydride transfer reactions after 1,2-insertion and 2-butenyl end groups result from 2,1-propylene insertion followed by β -hydride transfer.

Figure 5.6 shows the ^1H NMR spectrum of sample E1 measured at 140 °C in TCB. In addition to the three major peaks at 0.95–1.85 ppm, corresponding to CH_3 , CH_2 and CH protons in the propylene repeating units, several minor peaks are observed at 4.5–6.0 ppm when the spectrum is adequately enlarged. These peaks are the fingerprints of polymer chain ends due to different chain transfer mechanisms. The peaks at 4.5–6.0 ppm (vinylidene **A**, allyl **G** and 2-butenyl **D**), assigned to protons on unsaturated groups formed by β -hydride and β -methyl transfer reactions, all show very weak intensities.³¹

The peaks at 4.85 and 4.92 ppm are attributed to vinylidene end groups and those at 5.02 ppm are attributed to an allyl end-group. In addition to the vinylidene and allyl end-group peaks, a more intense signal at 5.62 ppm is seen. The integrated intensity ratios between each of these peaks and the chain proton peaks at 0.95-1.85 ppm were recorded. Values of 0.13, 0.075 and 0.09 mol% were obtained for vinylidene, allyl and 2-butenyl groups, respectively. Comparing the amount of each chain-end group with the total chain-end amount gives the occurring frequency of the corresponding chain transfer reaction in the overall chain termination reactions. Values of 44%, 25.4% and 30.6% were obtained for β -hydride, and β -methyl transfer reactions after 1,2-insertion, and β -hydride transfer reactions after 2,1-insertion respectively, implying that a great majority of chain termination reactions occurred in the polymerization via β -hydride transfer reaction after 1,2-insertion. The above is what we would expect in the absence of hydrogen as terminating agent.

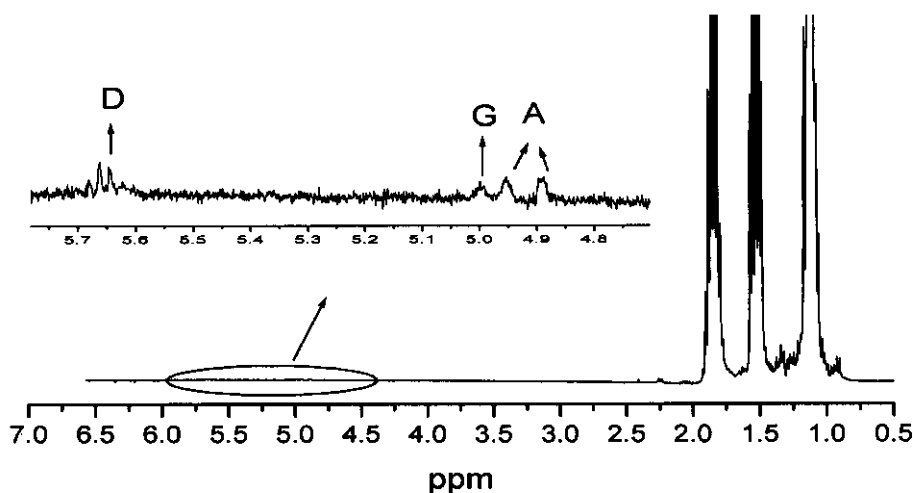


Figure 5.6 300 MHz ^1H NMR spectrum of isotactic polypropylene (E1) prepared using EI catalyst system in the absence of hydrogen. (Solvent: TCB:Bz₆ 9:1 volume ratio).

5.3.2 Propylene polymerization in the presence of hydrogen

A number of polypropylene polymers (samples E2-E11) were produced using the EI catalyst system in the presence of different amounts of hydrogen (0.1-6.27 wt%). The reaction conditions were kept constant for all the polymerization reactions. A summary of these polymerization results was shown in Table 5.2 (Section 5.3). As expected, the presence of hydrogen caused an increase in polymerization activity. Polymerization activity for EI increased (up to 3.5-fold in the presence of 3.9 wt% of hydrogen) from 1 462 to 5 118 kg PP/(mol Zr.h), as is shown in Figure 5.7. The most common explanation of this activating effect is the regeneration of an active species from the "dormant sites" formed after a regio-irregular olefin insertion (2,1-insertion).³²⁻³⁴ The chain transfer from a Zr-2,1 unit to hydrogen is about twice as fast as 1,2-insertion of propylene into this unit.

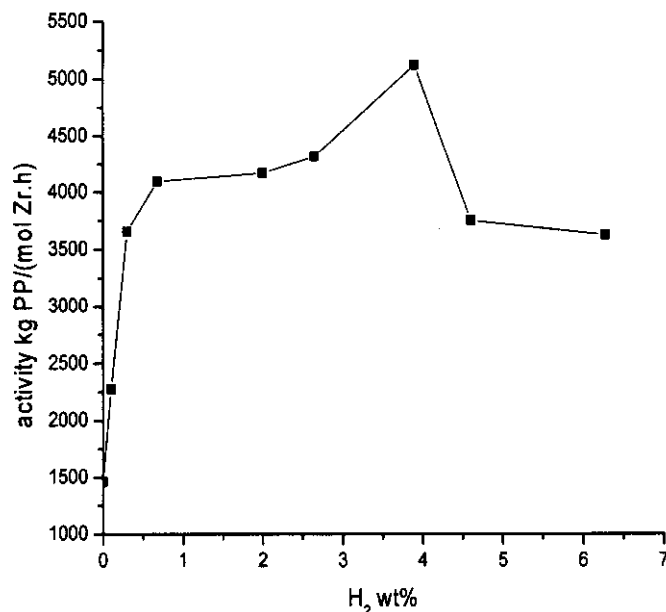


Figure 5.7 Activity kg PP/ (mol Zr.h) of propylene polymerization as a function of hydrogen content.

A slight decrease in the catalyst activity is caused by further increasing the hydrogen content (4.6-6.27 wt%, Figure 5.7). This decrease could be as a result of the slightly retarded level of propylene insertion into the Zr-C bond of the growing chain due to the high hydrogen level, and that depends on the nature of the catalyst.

5.3.2.1 Microstructure

As expected, the presence of hydrogen caused a reduction in polymer molecular weights (Table 5.2) due to chain transfer to hydrogen. The microstructures of the isotactic polypropylene samples were analyzed by solution ¹³C NMR. The ¹³C NMR spectra of different samples prepared with different amounts of hydrogen are shown in Figure 5.8, and the measured methyl pentad integrals at different amounts of hydrogen are summarized in Table 5.4.

Table 5.4 Microstructure of polypropylene samples determined by ^{13}C NMR

Run No.	Amount of hydrogen (wt %)	Methyl pentad distributions (%)								
		<i>mmmm</i>	<i>mmmr</i>	<i>rmmr</i>	<i>mmrr</i>	<i>mmrm</i> + <i>rmrr</i>	<i>mrnr</i>	<i>rrrr</i>	<i>mrrr</i>	<i>mrrm</i>
E1	0.00	86.5	5.8	-	4.7	-	-	-	-	2.1
E2	0.10	86.3	6.4	0.7	3.6	-	-	-	-	1.6
E3	0.30	86.4	6.4	0.7	3.5	-	-	-	-	1.5
E4	0.68	85.0	7.2	0.8	3.8	0.5	0.7	-	-	1.3
E5	1.50	84.2	7.1	0.6	4.0	0.7	0.8	-	0.5	1.4
E6	2.00	84.2	7.4	0.7	4.0	0.7	0.9	-	0.5	1.4
E7	2.65	84.0	7.1	0.7	4.0	0.7	0.9	-	0.5	1.5
E8	3.30	82.7	7.2	0.5	3.9	0.8	1.1	-	0.8	2.1
E9	3.90	81.8	7.7	0.5	3.9	0.8	1.2	-	0.9	1.9
E10	4.60	82.0	8.1	0.6	3.9	0.8	1.1	-	0.9	1.6
E11	6.27	81.3	8.2	0.6	4.1	0.9	1.3	-	1.1	1.7

The isotacticity (measured as *mmmm*%) is affected by hydrogen. Conflicting results have been reported for different systems. Tsutsui and Kashiwa⁹ reported a slight decrease in stereoregularity, from 91.7 to 89.0% *mm* triads for the *rac*-C₂H₄(1-Ind)₂ZrCl₂/MAO catalyst system. A stronger negative effect was found by Lin and Waymouth with *bis*(2-aryllindenyl)Zr/MAO catalysts.³⁵ No effect of hydrogen on isotacticity has been found in liquid propylene at 50 °C with the *rac*-Me₂C(3-*t*-Bu-1-Ind)₂-ZrCl₂/MAO catalyst system.³⁶ Carville *et al.* also reported that low hydrogen levels do not influence tacticity.³⁴

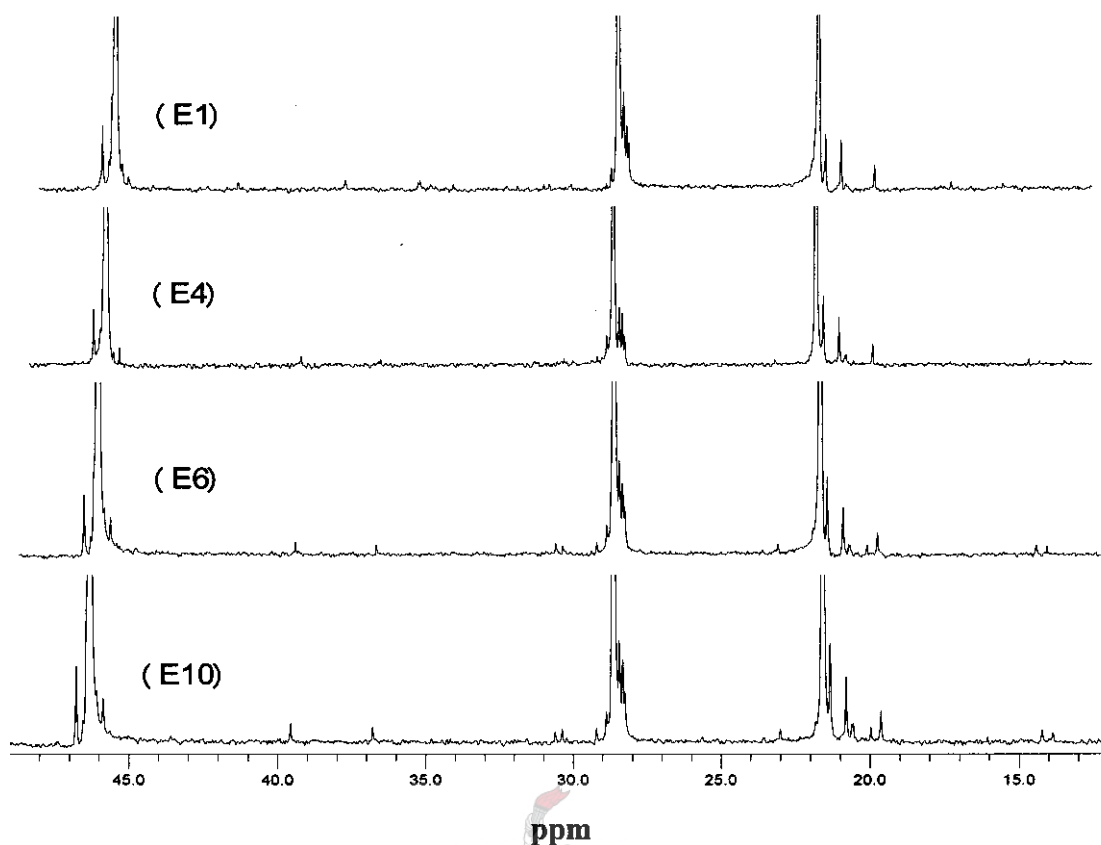


Figure 5.8 ^{13}C NMR spectra of polypropylenes prepared in absence and presence of hydrogen: E1 without hydrogen, E4 with 0.68 wt% H_2 , E6 with 2.0 wt% H_2 and E10 with 4.6 wt% H_2 , (Solvent: TCB:Bz₆ 9:1 volume ratio).

In the present study, under similar polymerization conditions, the isotacticity of polypropylenes produced by the EI catalyst system is slightly decreased, from $[mmmm] = 86.5\%$ in the absence of hydrogen to $[mmmm] = 81.3\%$ in the presence of 6.27 wt% of hydrogen, as can be seen from Table 5.4 and Figure 5.9. The drop in the isotacticity of these polymers is due to the increase of stereo-irregular pentads $[mmmr]$, $[mmrr]$ and $[mrrm]$, which could be attributed to the decreasing stereoselectivity of the catalyst with an increasing the amount of hydrogen.

The ^{13}C NMR spectra and the methyl region spectra of samples: E1 (with no hydrogen), and E4 (with 0.68 wt% of hydrogen), E6 (with 2.0 wt% of hydrogen) and E10 (with 4.6 wt% of hydrogen), respectively, are presented in Figures 5.8 and 5.10. It is apparent that the stereoirregular pentads $[mmmr]$, $[mmrr]$ and $[mrrm]$, indicated

respectively as (d), (e) and (f) in Figures 5.8 and 5.10, clearly increase when the amount of hydrogen is increased.

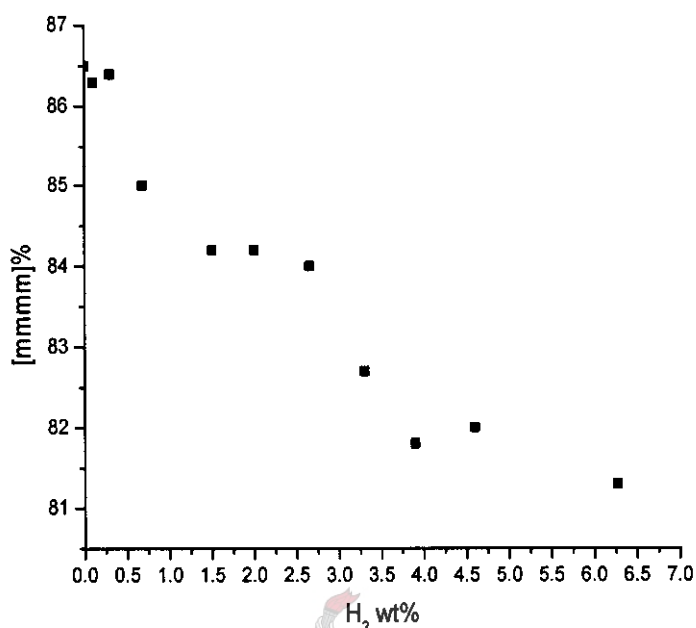


Figure 5.9 Dependence of isotacticity (*mmmm* pentad content) on hydrogen content of polypropylene polymers.

Additional small peaks *rmmr*, *mmrm*, *rmrr*, *mrmr* and *mrrr* which are due to stereo-irregular sequences are observed in Figure 5.10 as (g), (h), (i) and (j) in the case of propylene polymerization in the presence of different amounts of hydrogen. These stereoerrors were observed at different chemical shifts, as shown in Table 5.5. Propylene polymerization in the presence of 0.1 to 0.3 wt% of hydrogen (samples E2 and E3 in Table 5.4) gives new types of stereoerrors over polymerization in the absence of hydrogen, namely *rmmr* (20.93 ppm) stereo-irregular sequences. With increasing the amount of hydrogen from 0.3 to 0.68 wt% (sample E4), further peaks can be seen at 20.60 and 20.55 ppm, which are attributed to *mmrm* + *rmrr* and *mrmr* stereoirregular sequences.

Table 5. 5 Steric pentad distributions evaluated from the ^{13}C NMR spectra shown in Figure 5.10

Pentad	Chemical shift (ppm)
<i>rmmr</i>	20.93
<i>mrrm + rmrr</i>	20.60
<i>mrmm</i>	20.55
<i>mrrr</i>	20.00

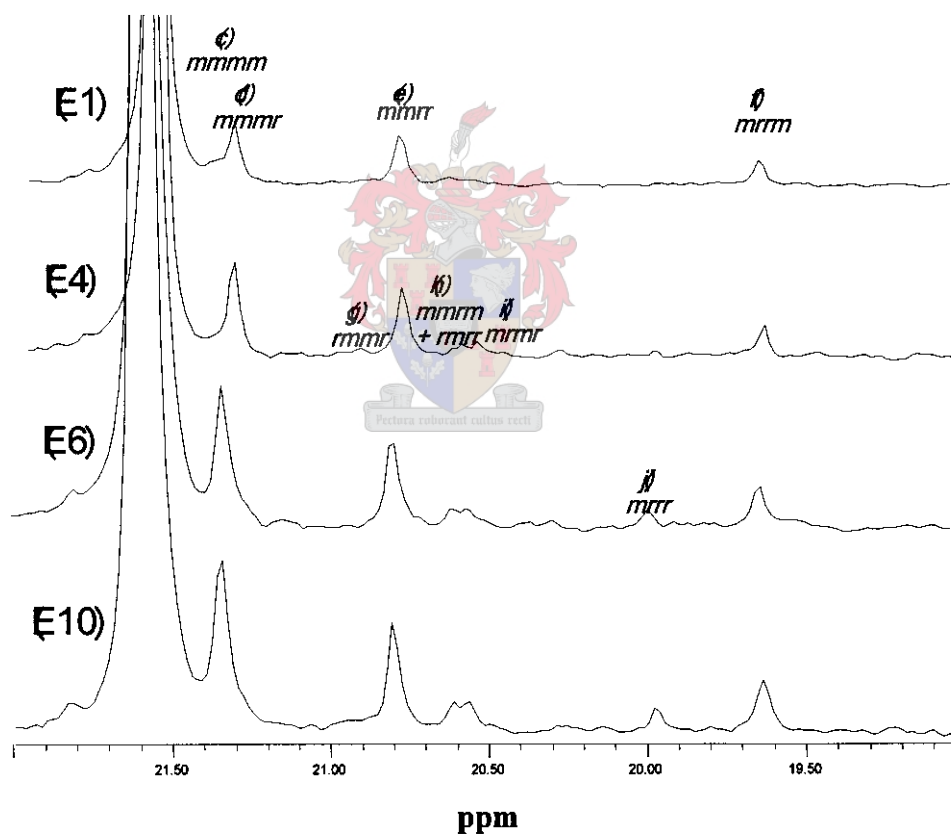


Figure 5. 10 ^{13}C NMR spectra of the methyl region of polypropylenes prepared in the absence and presence of hydrogen: E1 without hydrogen, E4 with 0.68 wt% H_2 , E6 with 2.0 wt% H_2 and E10 with 4.6 wt% H_2 , (Solvent: TCB:Bz₆ 9:1 volume ratio).

Further stereo-irregular pentads were observed with an increase in the amount of hydrogen (≥ 1.5 wt %), as can be seen from Table 5.4 and Figure 5.10. These stereo-irregular sequences *mrrr* appear in the area around 20.00 ppm and they are formed when successive misinsertions occur. So it means that the stereoselectivity of the catalyst decreases with increasing the amount of hydrogen and that the active-site control over the chain propagation is partially lost. It would appear, therefore, as if catalytic site control is significantly dependant on molecular weight. This would suggest that more random stereoerrors occur in the beginning of the chain growth than later.

To confirm the above results, ^{13}C NMR spectra were recorded at 120 °C, 600 MHz and using 1,1,2,2-tetrachloroethane- d_2 (TCE) as solvent of sample E10. As can be seen in Figure 5.11, which shows the spectrum of sample E10, much better resonance resolutions were observed. Figure 5.12 shows the methyl region of sample E10 in Figure 5.11. All the different stereo-irregular peaks observed in Figure 5.10 can once again be observed in Figure 5.12. These stereo-irregular peaks can however now be seen to be much clearer and better distinguishable.

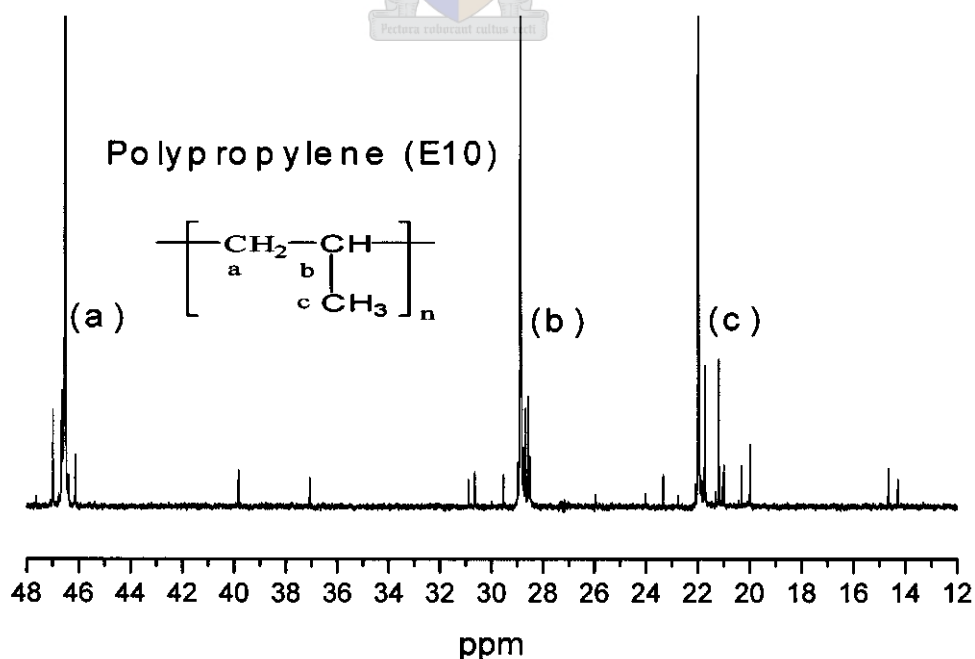


Figure 5. 11 600 MHz ^{13}C NMR spectrum of isotactic polypropylene (E10) in the presence 4.6 wt % hydrogen. (Solvent TCE).

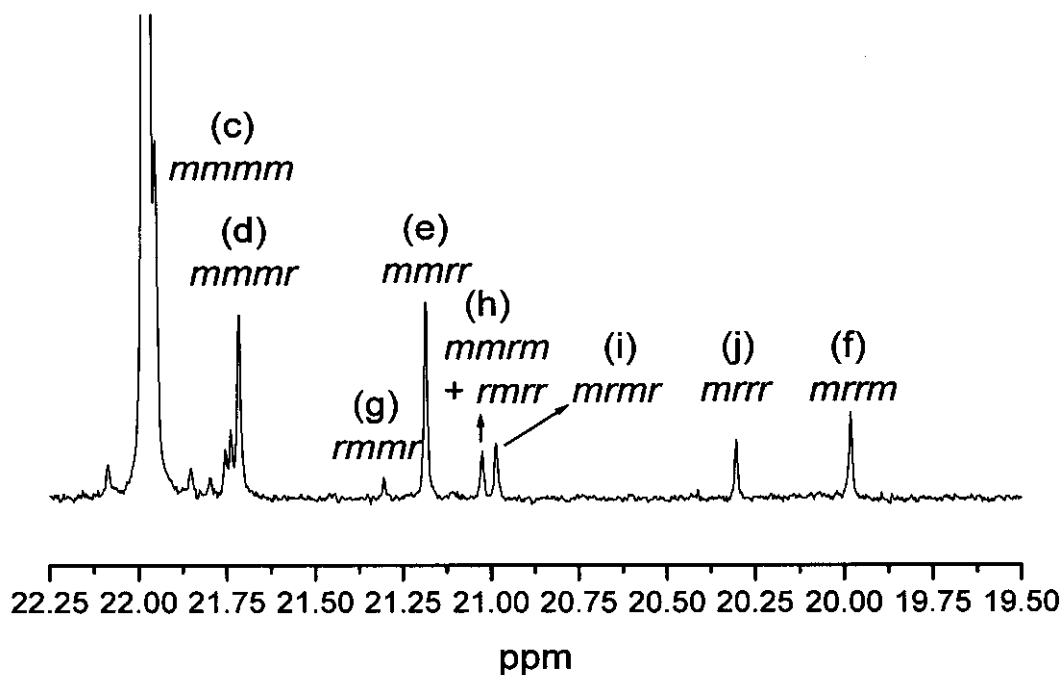


Figure 5. 12 600 MHz ^{13}C NMR spectrum of the methyl region of sample E10.
(Solvent TCE).

5.3.2.2 Regioselectivity

Reactivation of “dormant” (2,1-inserted) species via chain transfer with hydrogen explains the frequently observed activating effect of hydrogen in propylene polymerization, giving yields which may be around three times greater than those observed in the complete absence of hydrogen. These conclusions have been based on the ^{13}C NMR determination of the relative proportions of i-butyl and n-butyl terminated chains, resulting from chain transfer with hydrogen after primary and secondary insertion, respectively.³⁷

^{13}C NMR is a powerful tool for studying regioregularity in polypropylene, and the amount of regioerrors in the polypropylene chain can be calculated from the relative intensities of the peaks arising from the regio-irregular structures. In Figure 5.8 a series of ^{13}C NMR signals were assigned to various regio-irregular structures, including the structures formed by 2,1-insertion and 1,3-insertion. According to the

literature, the 1,3- sequences are formed by the transformation of a part of the 2,1- insertion through β -hydrogen exchange.³⁸ By comparing the spectra in Figure 5.8 in the case of the absence (sample E1) and the presence of hydrogen (samples E4, E6 and E10), it is apparent that the integrals of the peaks due to 2,1- and 3,1-misinsertion at 17 ppm and 38 ppm have decreased. A 2,1-misinsertion, as mentioned, leads to a dormant active site which, in the absence of hydrogen, may be reactivated through the incorporation of the defect into the chain, but in the presence of hydrogen will almost always lead to chain transfer rather than further propagation. This would seem to indicate that the presence of hydrogen will lower the amount of 2,1 misinsertions. This appears to be borne out with the results obtained.

5.3.2.3 Structure of the end groups

Nobuo *et al.*³⁰ indicated that chain-end structures depend on the species of catalysts. However, the effect of symmetry of the catalyst on chain propagation and a termination reaction has as yet never been clarified.

¹³C NMR spectra of polypropylene samples prepared in the presence of hydrogen with Ziegler-Natta catalysts reveal the presence of a greater number of n-butyl groups³⁶ (generated from chain transfer after a secondary insertion) compared to i-propyl groups (from chain transfer after a primary insertion) as terminating polymer chain-end. The initiating polymer chain-end invariably present in these spectra is n-propyl, which is due to the 1,2- propylene insertion in the metal-H bond.

By ¹³C NMR analysis (Figures 5.8 and 5.13), the changes of chain-end groups and thus the chain transfer reactions with different amounts of hydrogen can be clearly seen. Three types of saturated chain-end groups, namely n-propyl end groups (B1, B2 and B3) (represented by the signals at 14.7, 30.6 and 40 ppm), i-propyl end groups (C1, C2 and C3) (represented by the signals at 22.8, 24 and 26 ppm) and n-butyl end groups (E1, E2 and E3) (represented by the signals at 14.4, 23.4 and 29.5 ppm) were observed in polypropylenes synthesized by EI with hydrogen amounts that ranged from 0.1 to 6.27 wt%.

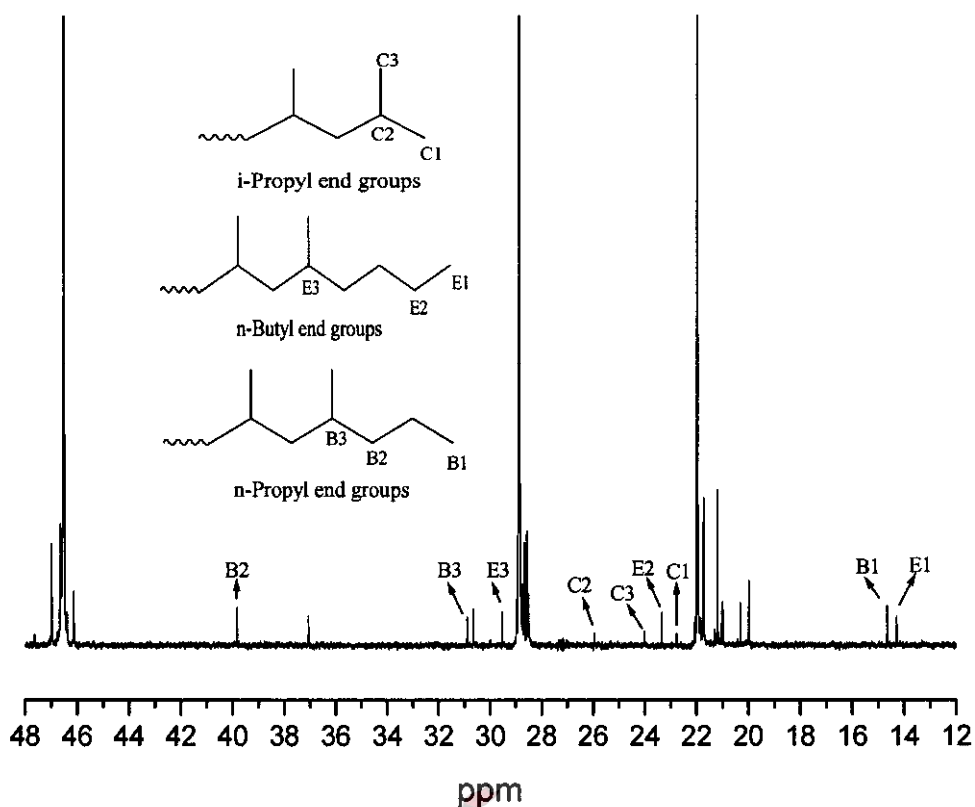


Figure 5.13 Chemical shifts of the various end groups observed by ^{13}C NMR spectrum of isotactic polypropylene (E10) in the presence 4.6 wt % hydrogen.

Table 5.6 A summary of chain-end group results for polypropylene prepared in the presence of hydrogen, evaluated from the ^{13}C NMR spectra in Figure 5.11

Chain-end group	Chain-end unit to total propylene units (mol%)	Percentage of each chain-end group (%)
n-propyl	0.0081	48
i-propyl	0.0026	16
n-butyl	0.0061	36

As can be seen in Table 5.6, the integrated intensity ratios between each of these end-groups and the total propylene units were recorded. Values of 0.0081, 0.0026 and 0.0061 mol% are obtained for n-propyl, i-propyl and n-butyl groups, respectively. Comparing the amount of each chain-end group with the total chain-end amount gives

the occurring frequency of the corresponding chain transfer reaction in the overall chain termination reactions. Values of 48%, 16% and 36% are obtained for 1,2-propylene insertion in the metal-H bond, chain transfer after a 1,2-insertion and chain transfer after a 2,1-insertion respectively, implying that a majority of chain termination reactions occurred in the polymerization via transfer reaction after 2,1-insertion.

By comparing the two different types of end-chain groups, i-propyl to n-butyl (chain transfer to hydrogen after 1,2- and 2,1-insertions respectively), it can be seen that the integrals of n-butyl end groups is about two times larger than i-propyl end groups, which means that chain transfer from Zr-2,1-units to hydrogen is faster than 1,2-insertion of propylene into this unit, and that the majority of sites that lead to termination reactions were in the “resting state” following secondary insertions.

As expected, increasing the amount of hydrogen leads to a decrease in the unsaturated chain-end groups. In Figure 5.14 the ^1H NMR spectra of resultant polypropylene polymers with different amounts of hydrogen are compared. As illustrated in this figure, the relative frequencies of vinylidene (A), 2-butenyl (D) and allyl (G) chain-end groups, which are due to β -hydride transfer reactions after 1,2-insertions, 2,1-insertions and β -methyl transfer reactions respectively, gradually decrease with an increase in the hydrogen amount. Polypropylenes prepared at high amounts of hydrogen (4.6 wt% H_2 , sample E10 in Figure 5.14), are completely saturated polymers and free of any terminal and internal vinylidene or allyl groups, implying the effective inhibition of β -hydride and β -methyl transfer reactions during the polymerization. This is due to the dominant chain transfer reactions to molecular hydrogen.

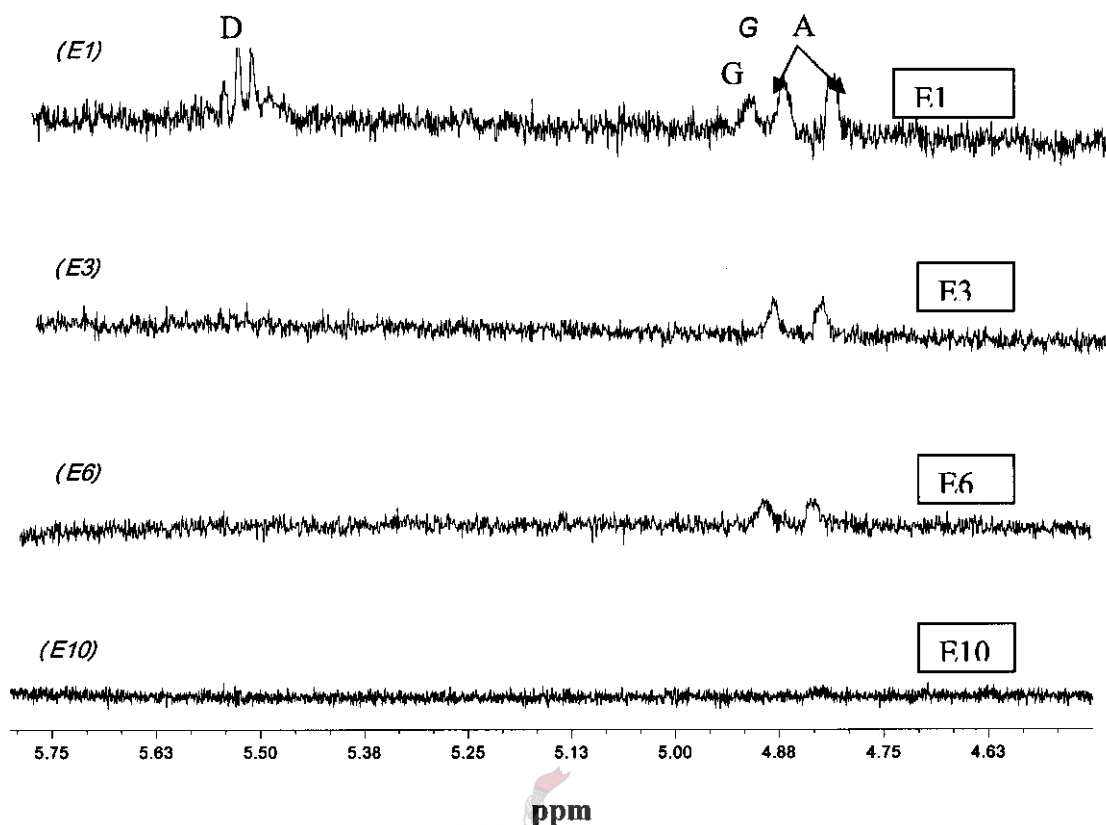


Figure 5.14 ^1H NMR spectra of polypropylenes prepared at different amounts of hydrogen: (E1) without hydrogen, (E3) 0.3 wt% hydrogen, (E6) 2.0 wt% hydrogen and (E10) 4.6 wt% hydrogen, (Solvent: TCB:Bz6 9:1 volume ratio).

5.3.2.4 Molecular weight and molecular weight distribution

The molecular weights and molecular weight distributions of polypropylenes that were produced by the EI catalyst system are shown in Table 5.2. As can be seen in Figure 5.15, as expected, the presence of hydrogen caused a dramatic reduction in polymer molecular weights ($\overline{M}_w \approx 76\,640 \text{ g mol}^{-1}$ in the absence of hydrogen to $\overline{M}_w \approx 10\,191 \text{ g mol}^{-1}$ in the presence of 6.27 wt% of hydrogen). This reduction in molecular weight can be explained as a result of a decrease in the propagation reactions due to an increase of chain termination caused by hydrogen.

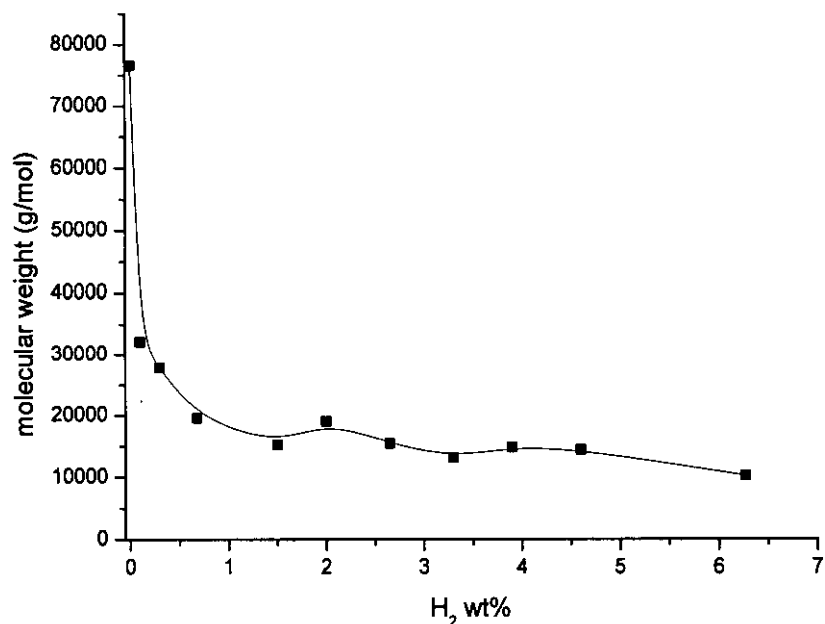


Figure 5.15 Dependence of molecular weight of the polypropylene polymers on the hydrogen content.

It can also be seen in Figure 5.15 that the molecular weight of polypropylenes in the presence of hydrogen decreases to a certain level then remains constant, or slightly decreases, by further increasing the hydrogen amount, which is dependent on the nature of the catalyst. The polydispersity of the polypropylene polymers in Table 5.2 are all in the region of 1.9-2.3 (Figure 5.16). This feature is very characteristic of single-site catalysts which produce polymers with uniform molecular weights.

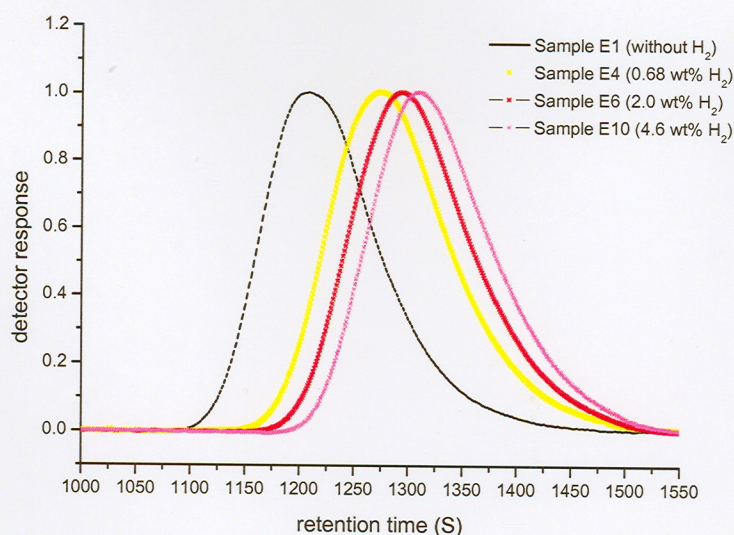


Figure 5.16 HT-GPC chromatograms of polypropylenes produced with the EI catalyst system at different amounts of hydrogen.

5.3.2.5 Melting behaviour

DSC is the most popular method to study the thermal properties of semi-crystalline polymers. Detailed structural information can be obtained by careful interpretation of DSC thermograms generated under different conditions (cooling and heating at various rates, multiple cooling and heating conditions, etc.).

Table 5.3 gives the results of the DSC analyses of the polypropylenes, with and without hydrogen, produced with the bridged EI catalyst. The degree of crystallinity was calculated by recording the ratio of the measured heat of fusion to that of a standard of known crystallinity. The heat of fusion of a perfect polypropylene crystal, used in the determination of the crystallinity, was taken as 209 J/g.^{19,39}

Typical melting exothermic DSC thermograms for the metallocene-catalyzed polypropylenes are shown in Figure 5.17. The melting temperature (T_m) of the obtained polymer in the absence of hydrogen (144 °C) is slightly higher than those obtained using different amounts of hydrogen (139 °C in the presence of 6.27 wt% of hydrogen). This decrease in the melting points is due to the amount of mis-insertions

and the low molecular weight ($\overline{M}_w = 10\,191$) of polypropylenes, which is usually caused by performing the polymerizations in the presence of 4.6 wt% of hydrogen. As the molecular weights decrease, so do the melting points. This can clearly be seen in Figure 5.18. However, of some note here is that even though the apparent tacticity decreases by some 5.5% from polymers produced in the absence of hydrogen to that produced in the presence of 4.7% hydrogen, the melting temperature is decreased by only 3°C. As peak melting temperature is a function of lamellar thickness, and as the total crystallinity does not decrease comparing polymer E1 to E10, this indicates that the decrease in tacticity does not have a real impact on the crystallizability of the polymer. There are two reasons for this: (a) most of the stereoerrors occur in the initial stages of chain growth (witness the increased amount of “odd” stereoerrors at lower molecular weights, Table 5.4), thus most of the stereoerrors are located at the chain ends, which are normally excluded from the crystalline areas in any case; and (b) the lessening of 2,1 misinsertions will counteract the lower tacticity.

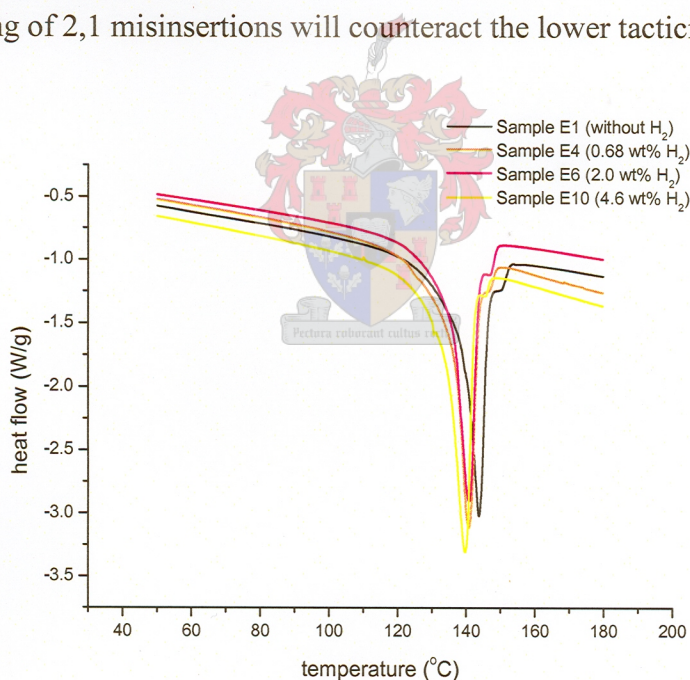


Figure 5. 17 DSC thermograms of polypropylenes produced with the EI catalyst system at different amounts of hydrogen.

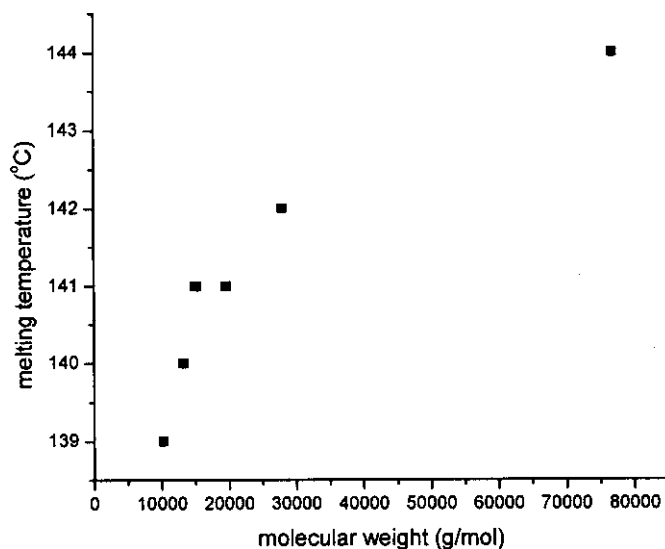


Figure 5. 18 The molecular weights of polypropylene polymers versus their melting temperatures.

5.4 Conclusions

When using the EI catalyst for propylene polymerization reactions, the addition of hydrogen has definite effects, some expected and others somewhat unexpected.

1. In the first place, the molecular weight is depressed, whilst the polydispersity remains constant.
2. The microstructure is affected; fewer 2,1 misinsertions are quantified from ^{13}C NMR spectra, as the hydrogen content is increased, and the tacticity ($[m m m m]\%$) is decreased. At the same time the amount of stereoerrors not consistent with enantiomorphic site control is increased as the molecular weight is decreased.
3. The melting temperature is depressed slightly as molecular weight is decreases, but crystallinity appears unaffected.
4. The combination of the conclusions under points 2 and 3 leads us to believe that the stereocontrol of this C_2 symmetric metallocene is dependant on molecular weight of the growing polymer chain; and as an extension of this, most of the errors should be observed predominately at the chain ends.

5.5 References

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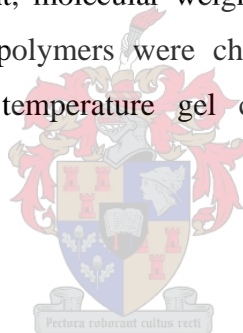
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CHAPTER 6

Polymerization and characterization of polypropylene produced with *rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂/MAO (MBI)

Summary

Polypropylenes were prepared in both the presence and absence of molecular hydrogen, using the homogeneous methylaluminoxane-activated racemic dimethylsilanediyl-bis(2-methylbenzo-[e]indenyl)zirconium dichloride (*rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂) (MBI) catalyst under standardized conditions. These polymers were used to investigate the effect of different amounts of hydrogen on the microstructure, molecular weight, molecular weight distribution, melting point and crystallization behaviour. The polymers were characterized by nuclear magnetic resonance spectroscopy, high temperature gel chromatography and differential scanning calorimetry.



6.1 Introduction

The MBI catalyst (Figure 6.1) was chosen as a suitable catalyst to compare to the EI catalyst discussed in the previous chapter. The latter catalyst produces fairly low molecular weight materials (around 70 000 g/mol) and low isotacticity ($[mmmm] = 86\%$) while the MBI catalyst has been shown to be industrially suitable.¹⁻³ This chapter reports on the influence of the molecular hydrogen on the polymer microstructure, molecular weight, molecular weight distribution, melting point and crystallization behaviour of propylene polymers. A comparison of the properties of the different types of propylene polymers synthesized by using the two different catalysts (EI and MBI) is also presented.

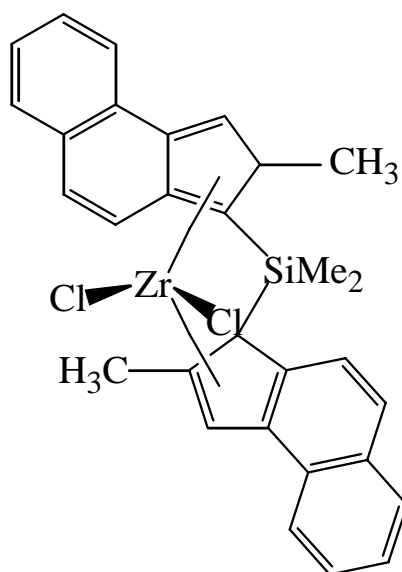


Figure 6.1 *rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂ (MBI).

6.2 Results and discussion of propylene polymerization

A series of polypropylene polymers were prepared by using the MBI catalyst system, in the absence and presence of different amounts of hydrogen. The reaction conditions were kept constant for all the polymerization reactions (see Section 4.2.2). A summary of these polymerization results is given in Table 6.1.

6.2.1 Propylene polymerization in the absence of hydrogen

The molecular weights, molecular weight distributions, catalyst activities, melting points and crystallinity (Table 6.1), and tacticity and distribution of regio-irregularities/end groups were evaluated for the polypropylene polymer (sample M1) prepared in the absence of hydrogen. Details of these properties with full explanations will be the subject of the following sections.

Table 6.1 Experimental parameters^{a,b} and results for propylene polymerizations carried out with MBI catalyst system

Run No.	Amount of hydrogen (wt %)	Activity ^c	\overline{M}_w (g mol ⁻¹)	$\overline{M}_w/\overline{M}_n$	T _m (°C)	X _c ^d (%)
M1	0.0	5 214	542 311	2.96	153	58
M2	0.16	9 385	68 241	2.00	153	53
M3	0.3	9 490	39 271	2.10	152	61
M4	0.7	11 434	33 852	2.00	152	54
M5	2.0	12 305	25 508	2.00	152	50
M6	3.0	17 248	18 745	2.00	151	65
M7	4.0	20 306	15 643	1.98	150	64
M8	10.0	24 874	9 660	2.00	148	54
M9	12.6	22 962	4 528	2.00	143	58
M10	14.0	22 288	3 059	1.58	138	51
M11	15.0	22 533	2 196	1.57	132	41

^a Al/Zr ratio 1:6000

^b room temperature

^c (kg PP/(mol Zr.h))

^d crystallinity degree, $\Delta H_m = 209$ J/g of PP 100% crystallinity

6.2.1.1 Microstructure

Figure 6.2 shows the ¹³C NMR spectrum of a polypropylene M1 produced in the absence of hydrogen using the homogeneous MBI catalyst system.

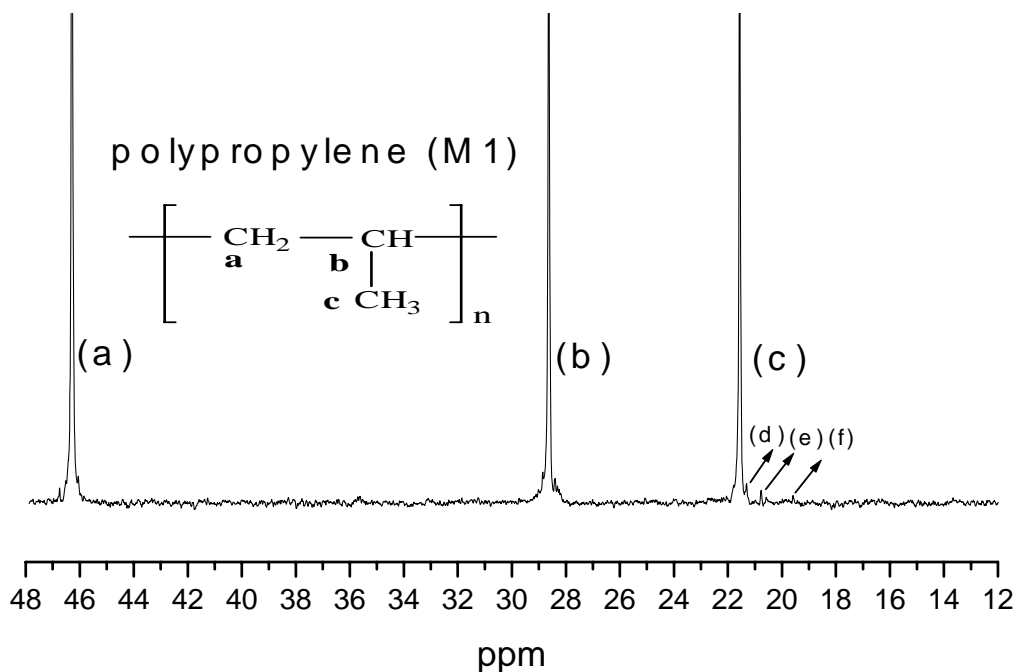


Figure 6.2 300 MHz ^{13}C NMR spectrum of isotactic polypropylene (M1) prepared in the absence of hydrogen. (Solvent: TCB:Bz₆ 9:1 volume ratio).

The primary resonance signals (a), (b) and (c) designate the methylene carbons ($\delta = 46.28$ ppm), the methine carbons ($\delta = 28.63$ ppm), and the methyl carbons ($\delta = 21.56$ ppm) of polypropylene respectively. As mentioned in the previous chapter (Section 5.3.1.1) the methyl region was chosen for tacticity analysis. Looking at the methyl region of the spectrum of sample M1 (shown in Figure 6.3) the stereo-irregularities (which are clearly visible) are at *mmmr* ($\delta = 21.31$ ppm), *mmrr* ($\delta = 20.77$ ppm) and *mrrm* ($\delta = 19.59$ ppm), indicated as (c), (d), (e), and (f) respectively.

The tacticity of this polymer (M1) was determined by integrating the methyl peak region in Figure 6.3 and found to be 98.0% [*mmmm*] (Table 6.2). It can therefore be concluded that this polymer is very highly isotactic, especially in comparison with sample E1 (Section 5.3.1.1).

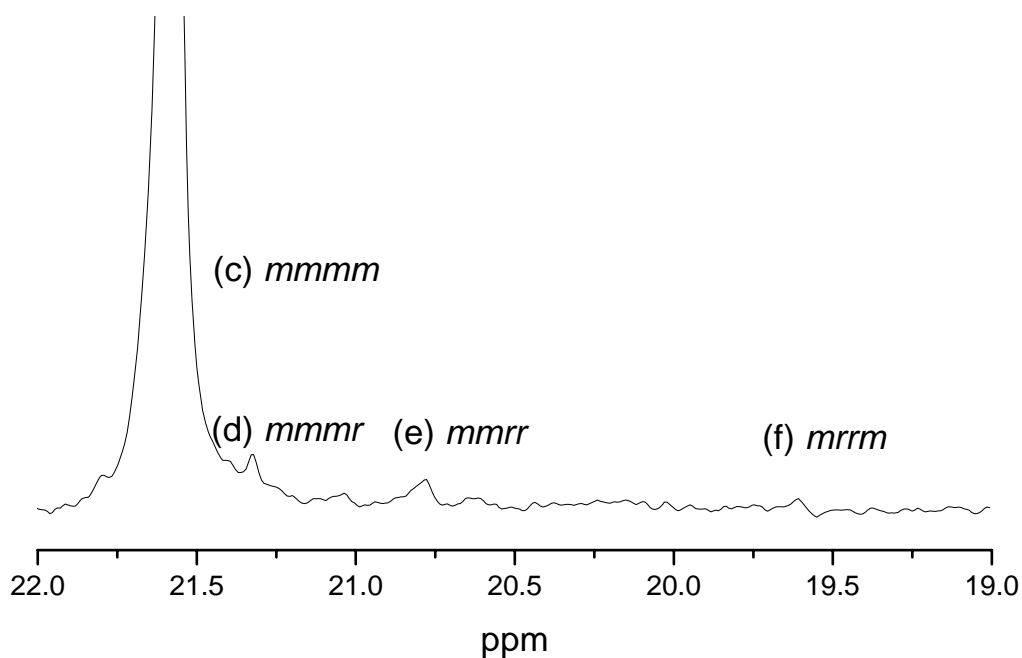


Figure 6.3 300 MHz ^{13}C NMR spectrum of the methyl region of sample M1.
(Solvent: TCB:Bz₆ 9:1 volume ratio).

Table 6.2 Pentad distributions evaluated from the ^{13}C NMR spectrum of sample M1, shown in Figure 6.3

Pentad	Chemical shift (ppm)	Fraction %
<i>mmmm</i>	21.56	98.00
<i>mmmr</i>	21.31	1.50
<i>mmrr</i>	20.77	0.55
<i>mrrm</i>	19.59	0.20

As can be seen from Figure 6.2, the peaks due to regio-irregularities (2,1- and 3,1-mis-insertions) are difficult to observe. It is proposed that this is due to the high regioselectivity of the catalyst and a very high molecular weight polypropylene (Sample M1 in Table 6.1), which makes these errors difficult to observe.

6.2.1.2 Structure of the end groups

The typical end groups found in low molecular weight polypropylenes produced by metallocene catalysts such as $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ or *rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$ in the absence of hydrogen are the vinylidene group, resulting from β -hydride transfer, and the n-propyl group, formed by the first insertion of propylene into the resulting Zr-hydride.³

The ^{13}C NMR spectrum of polypropylene (sample M1) in Figure 6.2 does not show any peaks due to end groups unlike the case of polypropylenes prepared with EI catalyst system (Figure 5.4). The reason for this is the very high molecular weight of sample M1 ($\overline{M}_w = 542\,311\text{ g mol}^{-1}$), which makes it very difficult to observe end-groups.

Figure 6.4 shows the ^1H NMR spectrum of the sample M1 measured at 140 °C in TCB. In addition to the three major peaks at 0.95–1.85 ppm, corresponding to the CH_3 , CH_2 and CH protons in the propylene repeating units, the vinylidene end group at 4.46 ppm (represented by the peak A in Figure 6.4) is the only end group found for this type of catalyst. The peaks for the n-propyl end-group are hidden in the area 0.95 – 1.8 ppm. It can be assumed that the majority of chain termination reactions occurred in the polymerization via a β -hydride transfer reaction after 1,2-insertion.

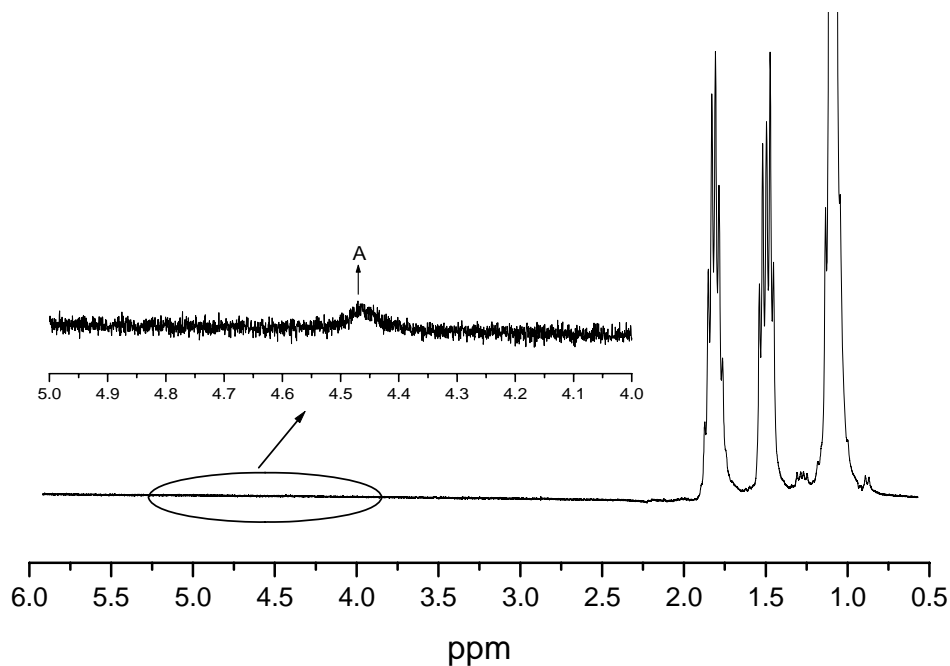


Figure 6.4 300 MHz ^1H NMR spectrum of isotactic polypropylene (M1) prepared by MBI in the absence of hydrogen. (Solvent: TCB:Bz₆ 9:1 volume ratio).

6.2.2 Propylene polymerization in the presence of hydrogen

A number of polypropylene polymers (samples M2-M11) were produced using the MBI catalyst system in the presence of different amounts of hydrogen (0.16-15.0 wt%). The reaction conditions were kept constant for all the polymerization reactions. A summary of these polymerization results were shown in Table 6.1.

Table 6.1 showed that, as expected, the presence of hydrogen caused an increase in polymerization activity. Polymerization activity for MBI increased (up to 5-fold in the presence of 10 wt% of hydrogen), from 5 214 to 24 874 kg PP/(mol Zr.h), as is shown in Figure 6.5. The most common explanation of this activating effect is the regeneration of an active species from the "dormant sites" formed after a regio-irregular olefin insertion (2,1-insertion).⁴⁻⁶ The chain transfer from a Zr-2,1-unit to hydrogen is about twice as fast as 1,2-insertion of propylene into this unit.

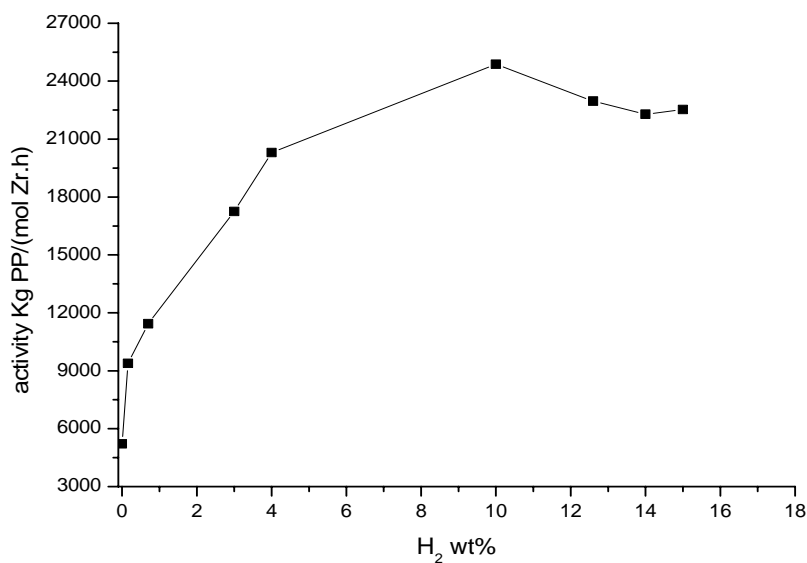


Figure 6.5 Activity (kg PP/ mol Zr.h) of propylene polymerization as a function of hydrogen content.

Figure 6.5 also shows that a slight decrease in activity is caused by a further increase in the hydrogen content (10 wt%). This decrease could be a result of the slightly retarded level of propylene insertion into the Zr-C bond of the growing chain due to the high hydrogen level, which also depends on the nature of the catalyst.

6.2.2.1 Microstructure

Table 6.1 also shows that, as expected, the presence of hydrogen caused a decrease in polymer molecular weights, due to chain transfer to hydrogen. The microstructure of the isotactic polypropylene samples was analyzed by solution ¹³C NMR. The ¹³C NMR spectra of different samples with different amounts of hydrogen are shown in Figure 6.6, and the measured methyl pentad integrals at different amounts of hydrogen are summarized in Table 6.3.

Table 6.3 Microstructure of polypropylene samples prepared with MBI catalyst as determined by ^{13}C NMR, (Solvent: TCB:Bz₆ 9:1 volume ratio).

Run No.	Amount of hydrogen (wt%)	Methyl pentad distributions (%)								
		<i>mmmm</i>	<i>mmmr</i>	<i>rmmr</i>	<i>mmrr</i>	<i>mmrm</i> + <i>rmrr</i>	<i>mrmm</i>	<i>rrrr</i>	<i>mrrr</i>	<i>mrrm</i>
M1	0.0	98.0	1.5	-	0.6	-	-	-	-	0.2
M2	0.16	97.1	2.1	0.1	1.1	-	-	-	-	0.3
M3	0.3	97.0	2.3	0.1	0.7	-	-	-	-	0.2
M4	0.7	96.6	2.5	0.2	0.7	0.1	0.1	-	-	0.2
M5	2.0	95.8	2.6	0.3	0.9	0.3	0.5	-	0.2	0.1
M6	3.0	92.7	4.2	0.4	1.0	0.3	0.8	-	0.3	0.5
M7	4.0	90.8	4.8	0.5	1.4	0.6	0.9	-	0.4	0.9
M8	10.0	90.4	4.9	0.7	1.2	0.2	1.2	-	0.5	0.5
M9	12.6	89.1	4.8	1.5	1.1	0.2	1.5	-	1.2	0.3
M10	14.0	85.2	5.3	2.1	0.7	0.4	2.0	-	2.0	0.3
M11	15.0	82.2	6.3	3.1	0.8	0.5	3.2	-	2.4	0.3

The isotacticity is affected by hydrogen, and different results have been reported for the MBI catalyst system at different polymerization conditions. Stephan *et al.*³ reported a slight decrease in stereoregularity, from 96.6 to 95.4% *mmmm* pentads of the MBI catalyst system at 0.35 bar partial pressure of hydrogen, 40 °C and [Zr/Al] ratio of 1:3000. A similar effect was found by Carvill *et al.*⁶ with same catalyst system.

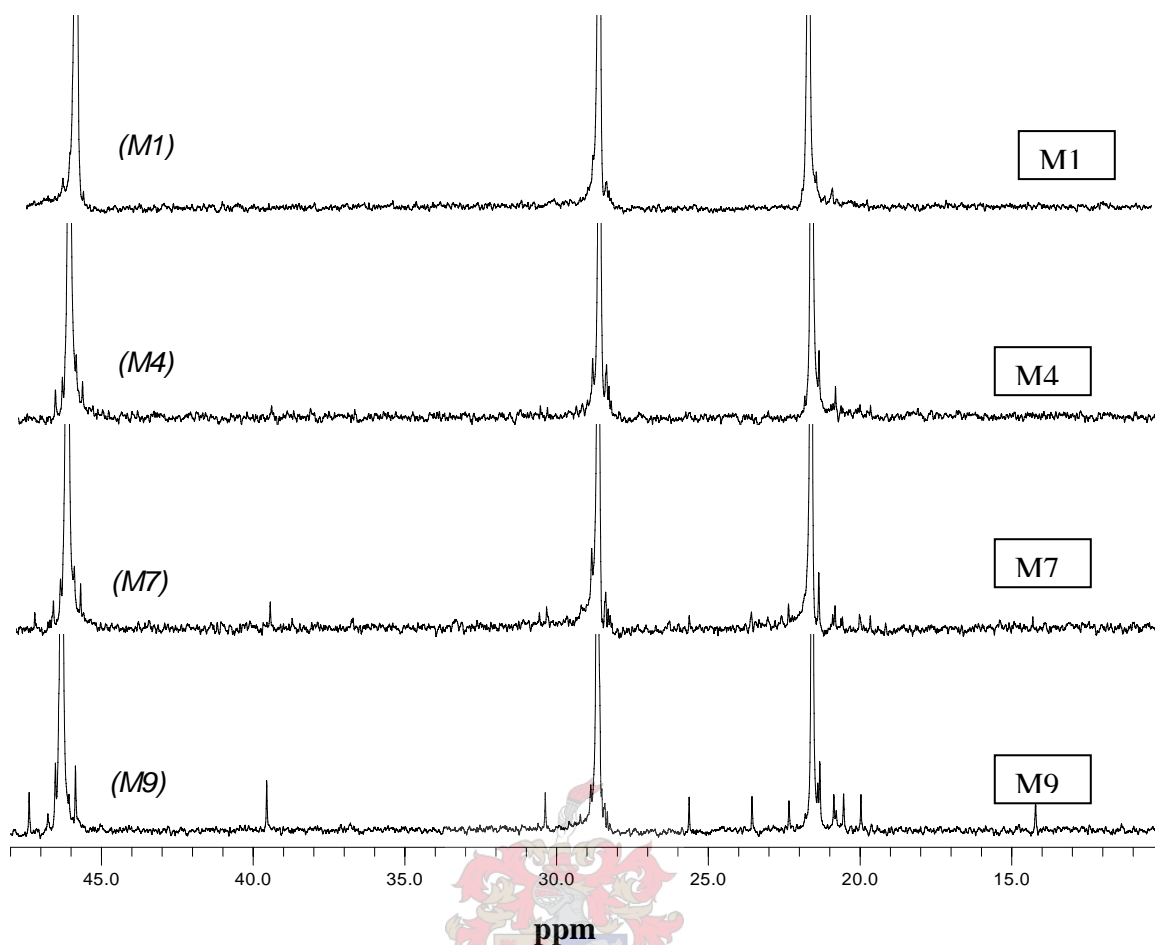


Figure 6.6 ^{13}C NMR spectra of polypropylenes prepared in the absence and presence of hydrogen: M1 without hydrogen, M4 with 0.7 wt% H_2 , M7 with 4.0 wt% H_2 and M9 with 12.6 wt% H_2 .

The isotacticity of polypropylenes produced by the MBI catalyst system in this study, under similar polymerization conditions, clearly decreases from $[m m m m] = 98.0\%$ in the absence of hydrogen to $[m m m m] = 82.2\%$ in the presence of 15.0 wt% of hydrogen, as can be seen from Table 6.3 and Figure 6.7. This decrease in the isotacticity of these polymers is due to the increase of stereo-irregular pentads $[m m m r]$, $[m m r r]$ and $[m r r m]$, which could be attributed to the decreasing stereoselectivity of the catalyst with increasing hydrogen amount. This can also be attributed to the decreasing molecular weights of these polymers with increasing hydrogen, which leads to loss in the active site control over the chain propagation, and chain-end control begins to play an important role.

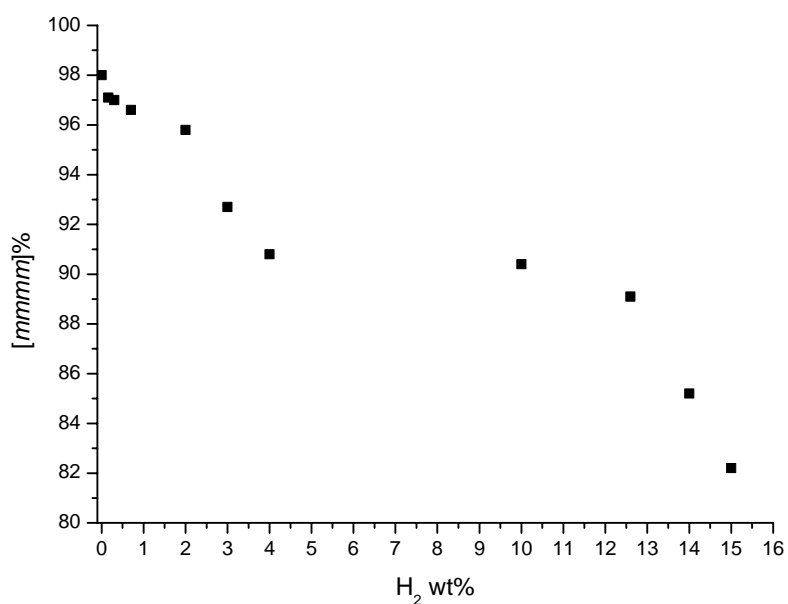


Figure 6.7 Dependence of isotacticity (*mmmm* pentad content) of propylene samples on hydrogen content.

The ¹³C NMR and the methyl region spectra of samples M1 (with no hydrogen), M4 (with 0.7 wt% of hydrogen), M7 (with 4.0 wt% of hydrogen) and M9 (with 12.6 wt% of hydrogen), respectively, are presented in Figures 6.6 and 6.8. It can be seen that the stereo-irregular pentads [*mmmr*], [*mmrr*] and [*mrrm*], indicated as (d), (e) and (f) respectively in Figure 6.8, clearly increase with increasing the amount of hydrogen.

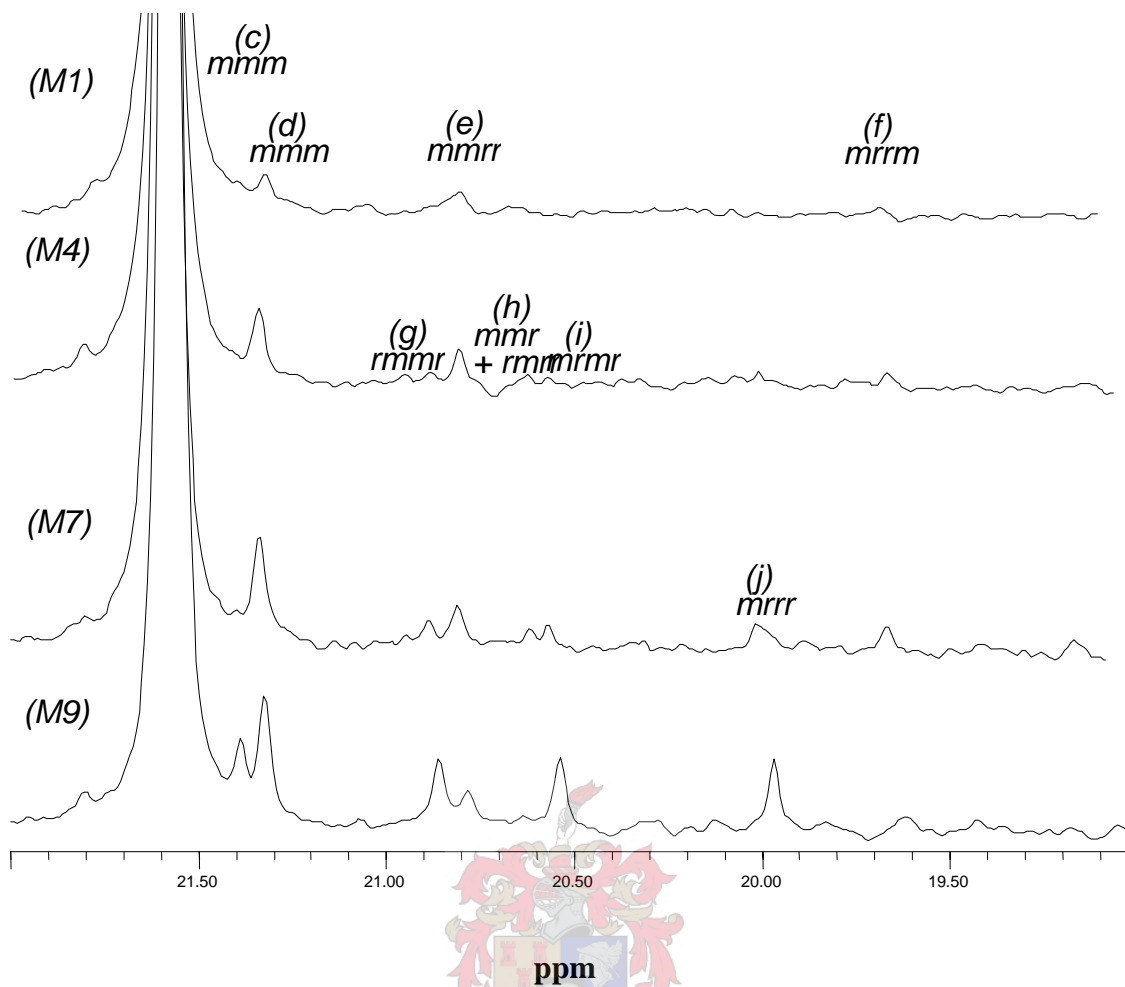


Figure 6.8 ^{13}C NMR spectra of the methyl region of polypropylenes prepared in the absence and presence of hydrogen: M1 without hydrogen, M4 with 0.7 wt% H_2 , M7 with 4.0 wt% H_2 and M9 with 12.6 wt% H_2 .

Other small peaks *rmmr*, *mmrm*, *rmrr*, *mrmr* and *mrrr* which are due to stereoirregular sequences can clearly be observed in Figure 6.8 as (g), (h), (i) and (j) in the case of propylene polymerization in the presence of different amounts of hydrogen. These stereoerrors were observed at different chemical shifts, as are shown in Table 6.4.

Propylene polymerization in the presence of 0.16 to 0.3 wt% of hydrogen (samples M2 and M3 in Table 6.3) gives a new type of stereoerrors compared to propylene polymerization in the absence of hydrogen, namely *rmmr* ($\delta = 20.86$ ppm) stereoirregular sequences. With increasing the amount of hydrogen from 0.3 to 0.7 wt%

(sample M4), other peaks could be seen at $\delta = 20.63$ and $\delta = 20.54$ ppm, which are attributed to *mrrm* + *rmrr* and *mrrr* stereo-irregular sequences.

Table 6.4 Steric pentad distributions evaluated from the ^{13}C NMR spectra of Figure 6.8

Pentad	Chemical shift (ppm)
<i>mrrr</i>	20.86
<i>mrrm</i> + <i>rmrr</i>	20.63
<i>mrrr</i>	20.54
<i>mrrr</i>	19.97

More stereo-irregular pentads were also observed with an increase the amount of hydrogen (≥ 2.0 wt% H_2 , Table 6.3 and Figure 6.8). These stereo-irregular sequences *mrrr*, observed in the area of 19.97 ppm, are formed when successive mis-insertions occur. This means that the stereoselectivity of the catalyst decreases with increasing the amount of hydrogen and that the active site control over the chain propagation is partially ineffective.

Similar and clearer results were obtained by running ^{13}C NMR spectra of sample M9 at 120 °C, and at 600 MHz, and by using TCE as solvent. As can be seen in Figure 6.9, which shows the spectrum of sample M9, much better resonance resolutions were observed. Figure 6.10 shows the methyl region of sample M9 (from Figure 6.9). All the different stereo-irregular peaks observed in Figure 6.8 can once again be observed in Figure 6.10, but they are now much clearer and better distinguishable.

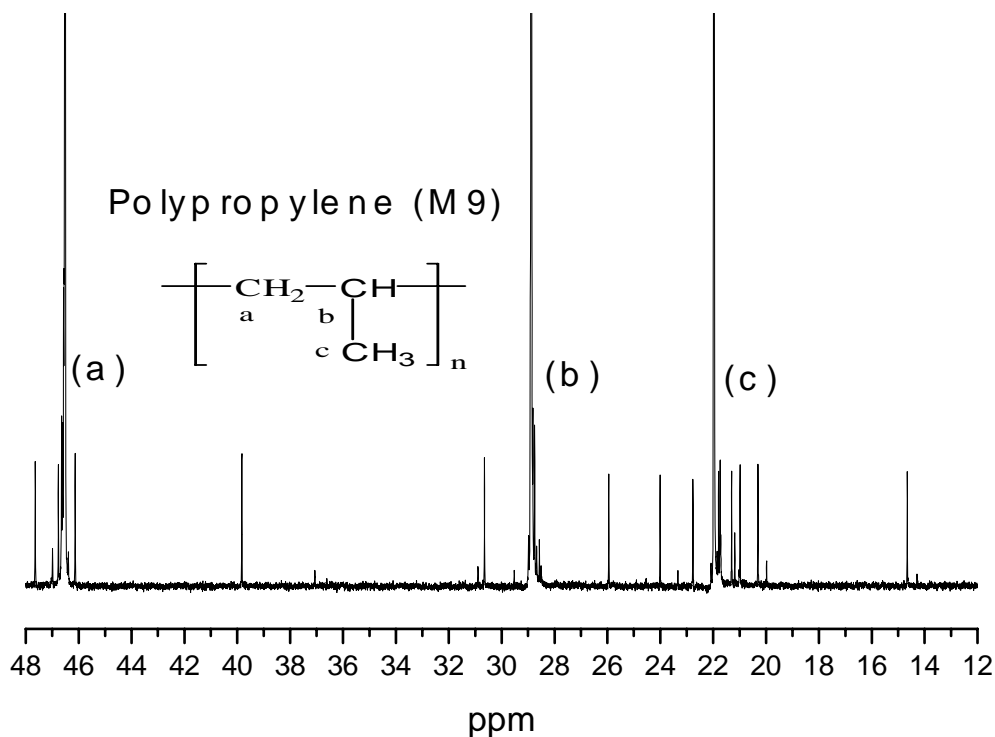


Figure 6.9 600 MHz ^{13}C NMR spectrum of isotactic polypropylene (M9) prepared in the presence 12.6 wt% hydrogen. (Solvent: TCE)

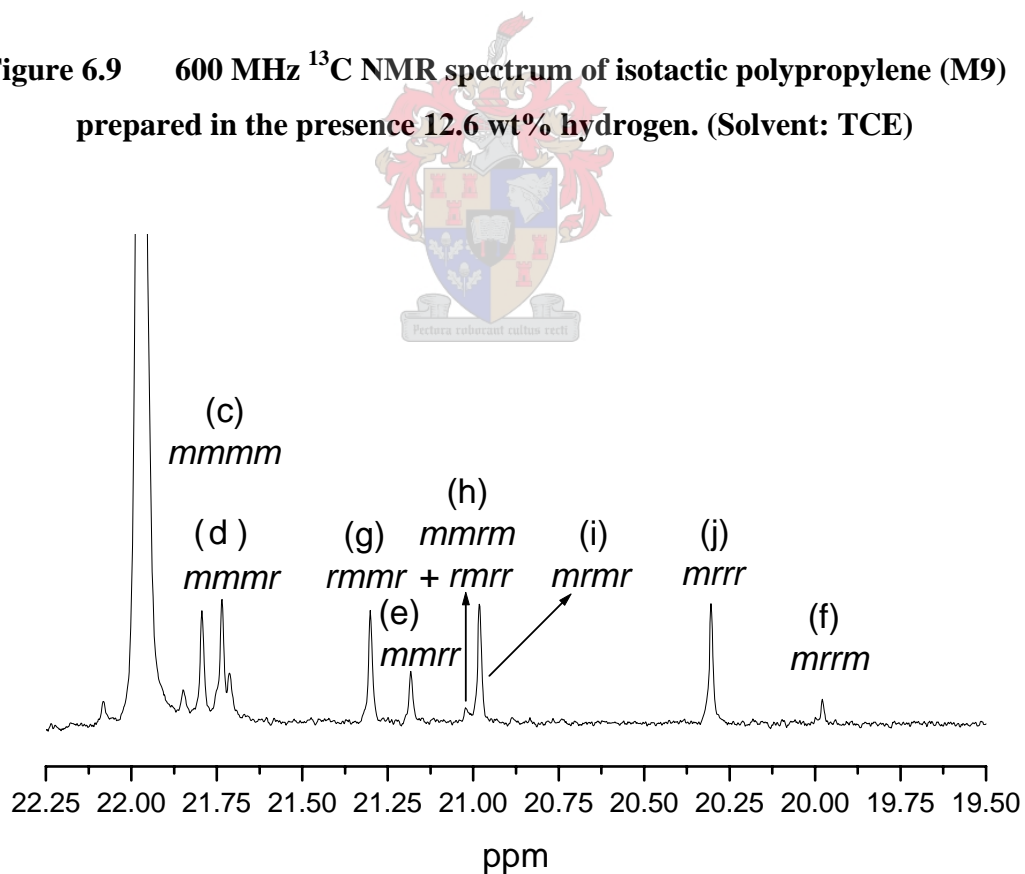


Figure 6.10 600 MHz ^{13}C NMR spectrum of the methyl region of sample M9. (Solvent: TCE).

In conclusion, much as in the case of the EI catalyst, it appears as if the molecular weight has an effect on the types of stereoerrors that occur. Stereocontrol is affected by chain length, and the effective anantiomorphic site control is not evident at low molecular weights. By extension this means that many “non-specific” errors occur when the chain is short, and that most errors of this nature will be found near the chain end of higher molecular weight materials.

6.2.2.2 Regioselectivity

Generally, C_2 -symmetric metallocenes are not exceedingly regioselective in propylene polymerization. Most polypropylene samples prepared with such catalysts have a content of regio-irregular enchainments in the range of 0.3-1.0 mol%. However, the regioselectivity is extremely sensitive to even small changes in the ligand framework.^{7,8}

^{13}C NMR is a useful tool for studying regioregularity in polypropylene, and the amount of regioerrors in the polypropylene chain can be calculated from the relative intensities of the peaks arising from the regio-irregular structures. In Figure 6.6 a series of ^{13}C NMR signals were assigned to various regio-irregular structures, including the structures formed by 2,1-insertion and 1,3-insertion. According to the literature, the 1,3- sequences are formed by the transformation of a part of the 2,1-insertion through β -hydrogen exchange.⁹

Looking at the spectrum in Figure 6.6, in the case of the absence of hydrogen (sample M1), it is unfortunately impossible to observe and quantify these regio-irregular structures. This is due to the very high molecular weight of this sample ($\overline{M}_w = 542\,311\text{ g mol}^{-1}$). It is known that adding hydrogen reduces 2,1-units in the polymer, and this reduction of incorporated 2,1-units is paralleled by an increase of n-butyl polymer end groups, as will be discussed in more detail in the following section. In the case of the presence of hydrogen (samples M4, M7 and M9), in Figures 6.6 and 6.9, the peaks due to 2,1- and 3,1-misinsertions at 31 and 37.2 ppm can be observed. The molecular weight of these samples is quite low ($\overline{M}_w = 33\,852 - 4\,825\text{ g mol}^{-1}$).

6.2.2.3 Structure of the end groups

The only end group found in the polypropylenes produced by the MBI catalyst system in the absence of hydrogen in this study, is the vinylidene end group (Section 6.2.1.2). In the presence of hydrogen the chain ends that formed are significant. ^{13}C NMR analysis (Figures 6.6 and 6.9), clearly show changes in the chain-end groups, and thus the chain transfer reactions with different amounts of hydrogen can be clearly seen. Three types of saturated chain end groups, namely n-propyl end groups (represented by the signals at 14.7, 30.6 and 39.8 ppm), i-propyl end groups (represented by the signals at 22.8, 24 and 26 ppm) and n-butyl end groups (represented by the signals at 14.4, 23.3 and 29.6 ppm) were observed in polypropylenes synthesized with MBI at hydrogen amounts that ranged from 0.16 to 15.0 wt%.

Table 6.5 shows the integrated intensity ratios of these end groups and the total propylene units. Values of 0.02, 0.018 and 0.0018 mol% were obtained for n-propyl, i-propyl and n-butyl groups, respectively. Comparing the amount of each chain-end group with the total chain-end amount gives the occurring frequency of the corresponding chain transfer reaction in the overall chain termination reactions. Values of 50, 45 and 5% were obtained for: 1,2 propylene insertion in the metal-H bond, chain transfer after a 1,2-insertion and chain transfer after a 2,1-insertion, respectively, implying that a great majority of chain termination reactions occurred in the polymerization via transfer reaction after 1,2-insertion. It can be seen that, the intensity ratio of i-propyl to n-butyl end groups (chain transfer to hydrogen after 1,2- and 2,1-insertions respectively) is about nine times greater.

Table 6.5 A summary of chain-end group results in the presence of hydrogen evaluated from the ^{13}C NMR spectra of Figure 6.9

Chain-end group	Chain-end unit to total propylene units (mol %)	The percentage of each chain-end group (%)
n-propyl	0.02	50
i-propyl	0.018	45
n-butyl	0.0018	5

Now, let us look at the effect of hydrogen on the unsaturated chain end groups. As expected, completely saturated polymers free of any terminal and internal vinylidene or allyl groups were obtained by using different amounts of hydrogen, implying the effective inhibition of β -hydride and β -methyl transfer reactions during the propylene polymerization reactions. This is due to the dominant chain transfer reactions to molecular hydrogen.

6.2.2.4 Molecular weight and molecular weight distribution

Table 6.1 and Figure 6.11 show that, as expected, the presence of hydrogen caused an impressive lowering of polymer molecular weights ($\overline{M}_w = 542\,311\text{ g mol}^{-1}$ in the absence of hydrogen to $\overline{M}_w = 2\,196\text{ g mol}^{-1}$ in the presence of 15.0 wt% of hydrogen). This decrease in the molecular weight can be explained as a result of an increase of chain termination by hydrogen.

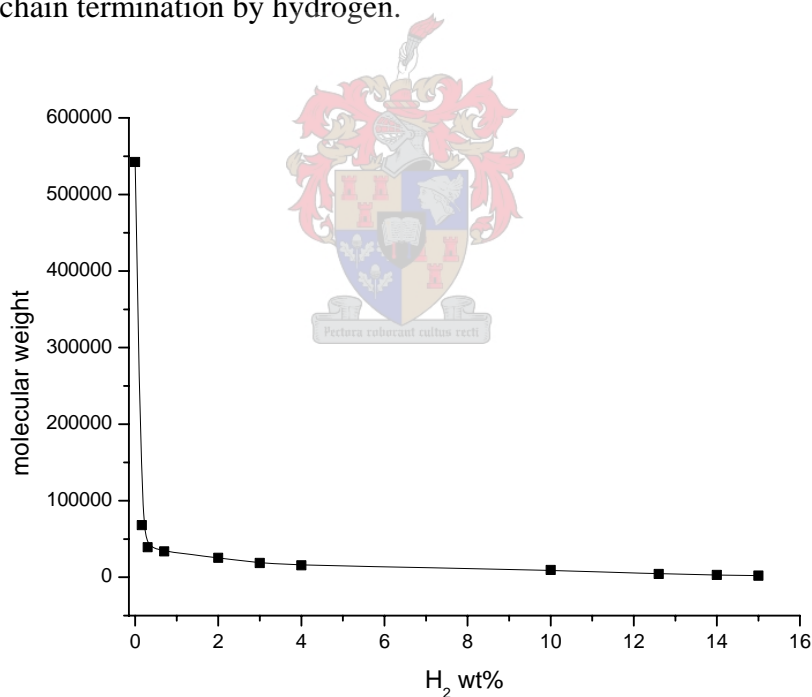


Figure 6.11 Dependence of molecular weight of polypropylenes on the hydrogen content.

As expected, the molecular weight distributions of the polypropylene polymers shown in Table 6.1 were all in the region of 1.57-2.96 (see Figure 6.12). This feature is very

characteristic of single-site catalysts, which produce polymers with uniform molecular weights.

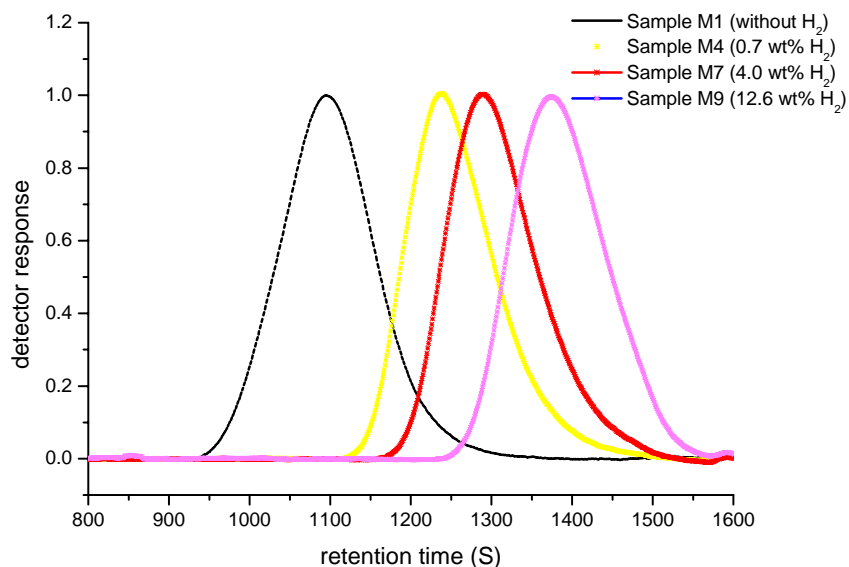


Figure 6.12 HT-GPC chromatograms of polypropylenes produced with the MBI catalyst system at different amounts of hydrogen.

6.2.2.5 Melting behaviour

Table 6.1 shows the results of the DSC analyses of the polypropylenes with and without hydrogen, produced with the MBI catalyst. The degree of crystallinity was calculated by taking the ratio of the measured heat of fusion to that of a standard of known crystallinity. The heat of fusion of a perfect polypropylene crystal, used in the determination of the crystallinity, was taken as 209 J/g.^{10,11}

Figures 6.13 and 6.14 show that the melting temperature (T_m) of the polymer obtained in the absence of hydrogen (153 °C) was clearly higher than the temperatures of the polymers prepared using different amounts of hydrogen (for example, 132 °C in the presence of 15.0 wt% hydrogen). This decrease in the melting points is due to an increase in the amount of defects ($[mmmm] = 82.2\%$ in the presence of 15.0 wt% hydrogen) and a decrease in the molecular weight ($\overline{M}_w = 2\,196\text{ g}\cdot\text{mol}^{-1}$ in the presence of 15.0 wt% hydrogen).

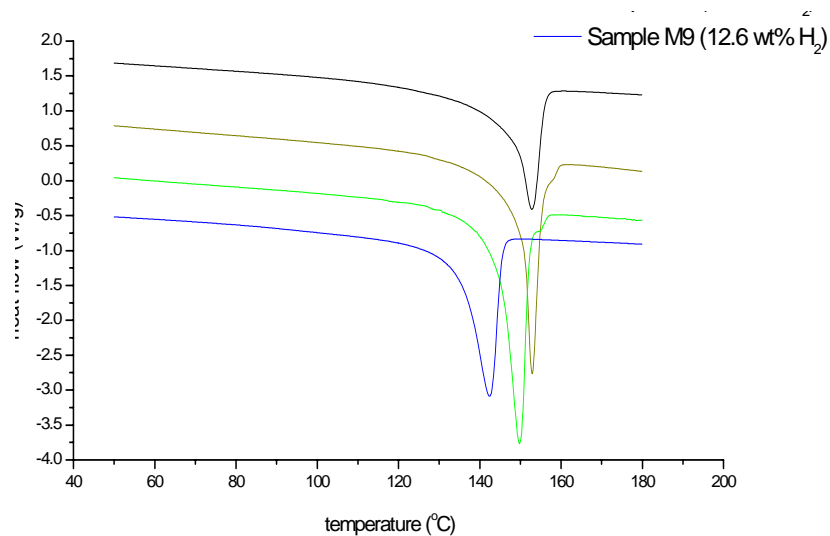


Figure 6.13 DSC exothermal thermograms of polypropylenes produced with MBI catalyst with different amounts of hydrogen.

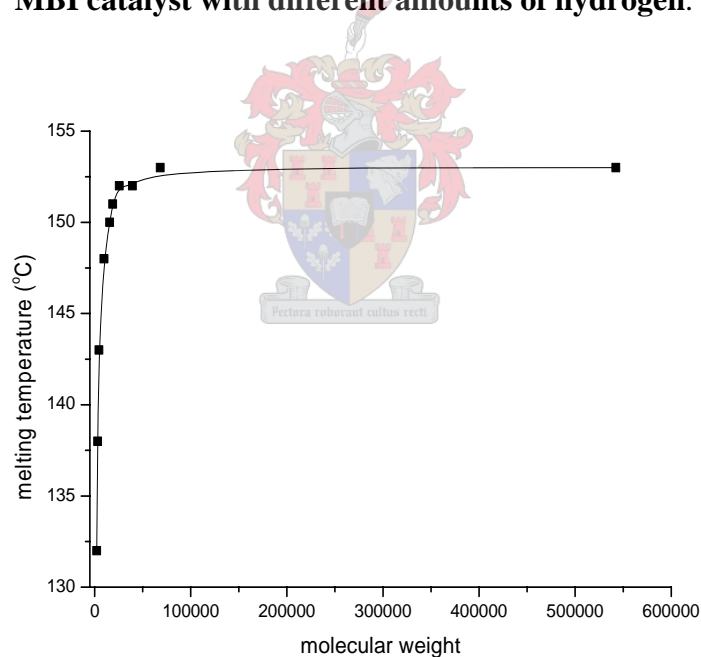


Figure 6.14 The molecular weights of polypropylenes produced with MBI catalyst versus melting temperatures.

Figure 6.15 shows the relationship between the melting temperatures and tacticity. It is noticeable that a linear decrease of T_m with decreasing tacticity is observed followed by a sharper decrease in melting temperature for samples with

lower molecular weights. It is at molecular weights of below 20 000 that the melting temperatures start being influenced by the chain length as well as the tacticity.

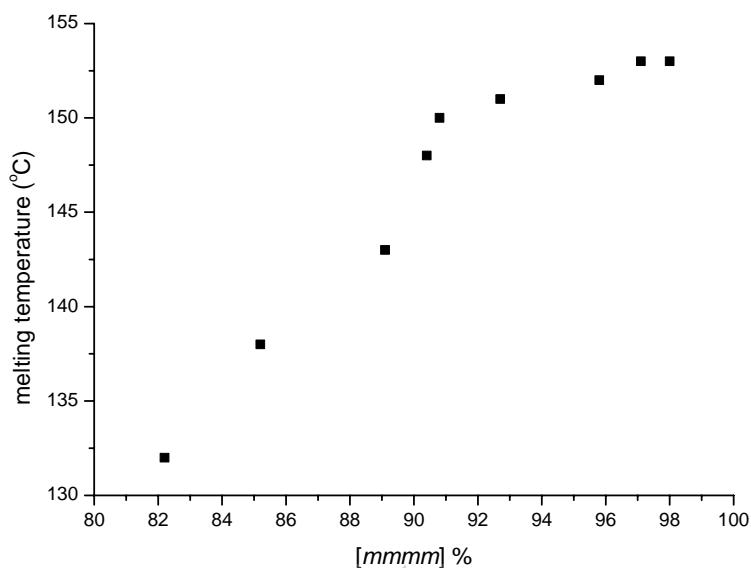


Figure 6.15 Dependence of melting temperature of polypropylenes on isotacticity (*mmmm* pentad content)

6.3 Comparison of results: EI and MBI catalysts.

6.3.1 Catalyst activity

The results as presented in Tables 5.2 and 6.1 are compared in Figure 6.16.

Polymerization activity for EI increased (up to 3.5-fold in presence of 3.9 wt% hydrogen) from 1 462 to 5 118 kg PP/(mol Zr.h) while in the case of MBI the polymerization activity increased up to 5-fold in presence of 10.0 wt% hydrogen (from 5 214 to 24 874 kg PP/mol Zr.hr). The increased activity of the MBI catalyst compared with the EI catalyst was expected, but it is difficult to really explain the greater effect of hydrogen on the activity for the former catalyst. What is noticeable is that the increased activity with increasing hydrogen content is maintained to higher levels of hydrogen for the MBI catalyst than for the EI catalyst.

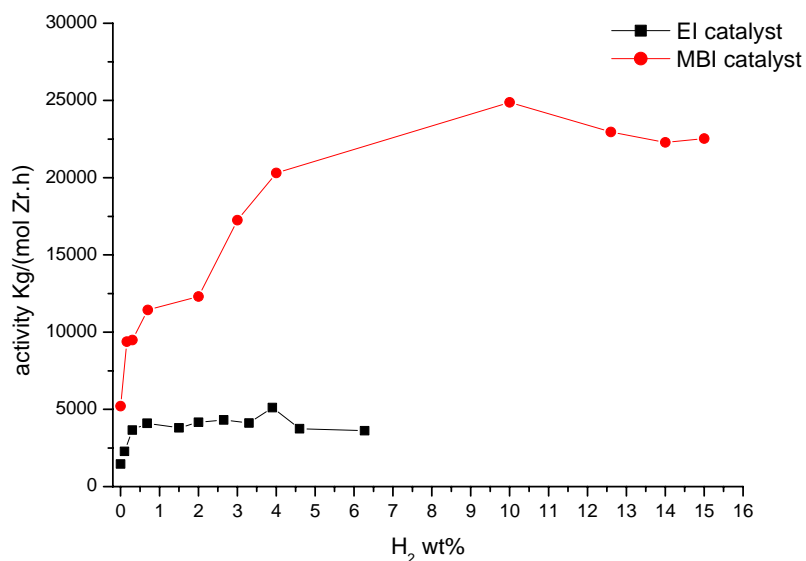


Figure 6.16 Catalyst activities of EI and MBI at different amounts of hydrogen.

6.3.2 Microstructure

Stereo-irregularities were found in propylene polymers produced by both catalyst systems. The extent of these defects however differs considerably between the different polymers depending on the type of catalyst used for the polymerization. Tables 5.4 and 6.3 show that the MBI catalyzed polymers contained fewer stereo-irregularities than the polymers produced using the EI catalyst system. Table 6.6 shows the difference in tacticities of the two different catalyst systems. It can clearly be seen the tacticity (*[mmmm]*) of the polymers produced using MBI catalyst system dropped significantly (from 98.0% in the absence of hydrogen to 89.1% in the presence of 12.6 wt% hydrogen), while in the case of EI catalyst system the reduction was somewhat less (from 86.5% in the absence of hydrogen to 81.3% with hydrogen), albeit in the presence of less hydrogen (see Table 6.6). It is therefore possible that with a higher hydrogen content, the percentage reduction in isotacticity would be greater for the EI catalyst.

Table 6.6 Summary of tacticities of polypropylenes prepared using the two different catalyst systems, EI and MBI

Sample entry	Type of catalyst system	Amount of hydrogen (wt%)	Tacticity range [mmmm] %
E1-E11	EI	0.0-6.27	86.5-81.3
M1-M9	MBI	0.0-12.6	98.0-89.1

Regio-irregular units typical of 2,1- and 3,1-insertions were visible in the case of propylene polymerization using EI, in the area of 17, 31 and 38.2 ppm, in the absence of hydrogen (Figure 5.4). These regio-irregular units were not observed in polypropylene produced using MBI (Figure 6.2). This is due to the substituent on the benzene ring in the 4-position that minimizes 2,1-misinsertions, leading to polypropylenes with a much higher molecular weight ($\overline{M}_w = 542\,311 \text{ g mol}^{-1}$) than polypropylenes produced using EI catalyst ($\overline{M}_w = 76\,640 \text{ g mol}^{-1}$). However, these regio-irregular units were formed in the case of both catalyst systems in the presence of hydrogen, but overall seemed less for the polymers produced with the MBI catalyst.

The nature of the stereoerrors are quite significant, if we compare the two polymers. In Figure 6.17 the stereoerrors produced with the EI catalyst are shown, while Figure 6.18 shows the stereoerrors produced by the MBI catalyst.

Of interest, Figure 6.17 shows the fact that the level of stereoerrors seem to remain reasonably constant, and that the “unexpected” errors occur in most cases once hydrogen is present (molecular weight is depressed). This is in contrast to the polymers produced with the MBI catalyst, where the level of all stereoerrors increase with increased hydrogen content.

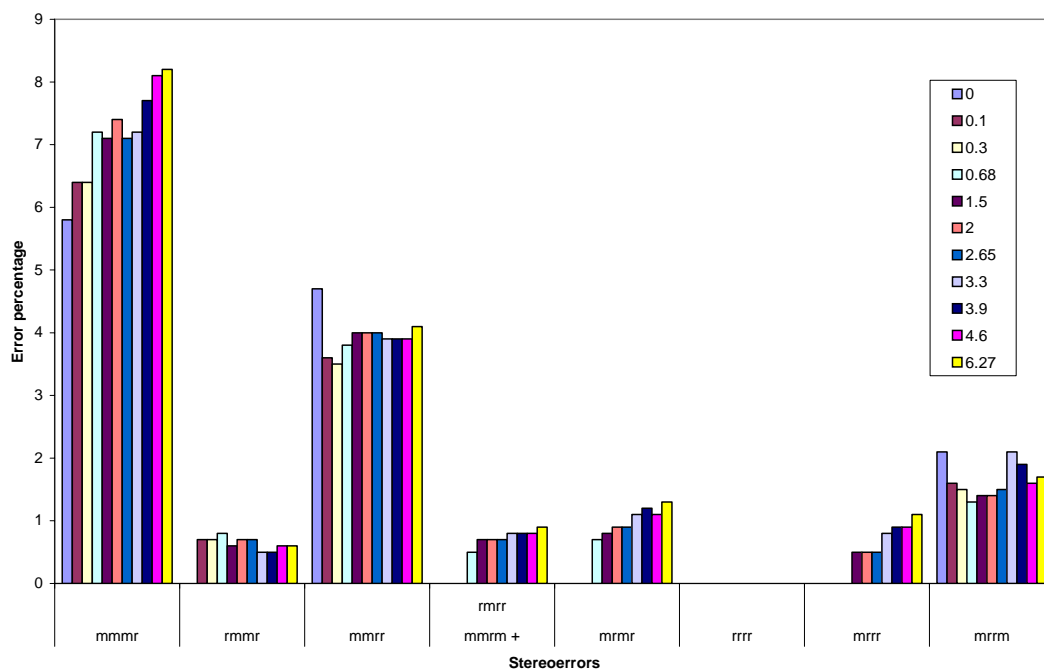


Figure 6.17 Stereoerrors produced by the EI catalyst in the presence and absence of hydrogen. The legend represents levels of hydrogen used in the polymerization.

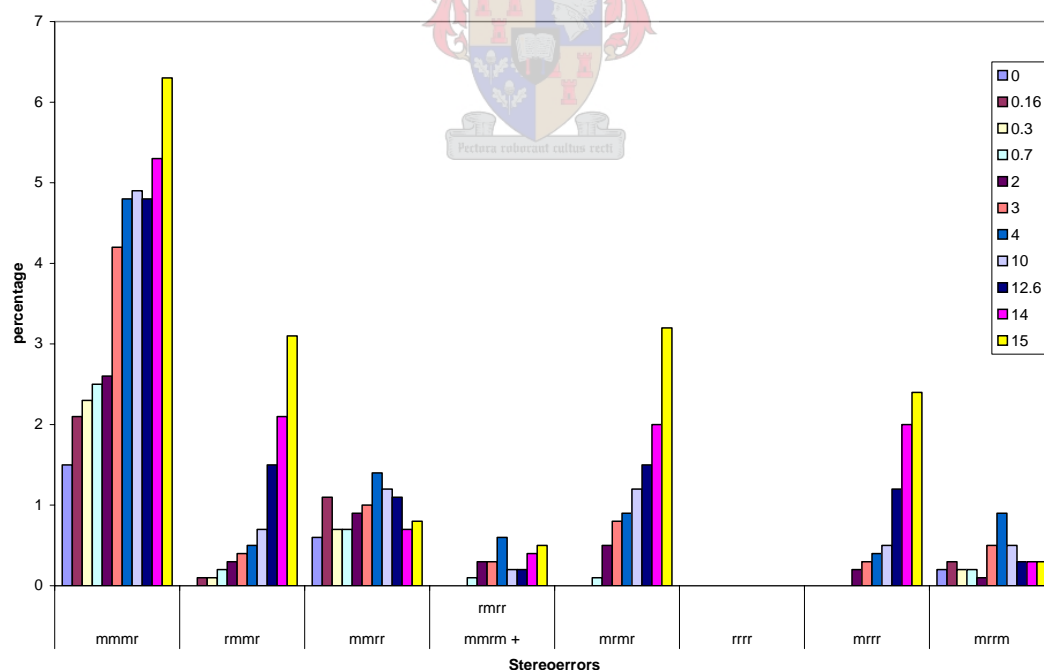


Figure 6.18 Stereoerrors produced by the MBI catalyst in the presence and absence of hydrogen. The legend represents hydrogen levels during polymerization.

6.3.3 Structure of the end groups

In the absence of hydrogen only vinylidene end groups were observed in the polypropylene produced by MBI catalyst. This is due to the very high molecular weight of this polymer. n-Propyl, 2-butenyl, vinylidene and allyl groups were observed in the polypropylene produced by the EI catalyst system in the absence of hydrogen.

n-Propyl, i-propyl and n-butyl end-groups were observed in polypropylenes synthesized by both of the catalyst systems in the presence of hydrogen. This is due to the low molecular weights of these polymers. End-group analyses indicate that far fewer termination reactions following 2,1 misinsertions occurred with the MBI catalyst than with the EI catalyst.

6.3.4 Molecular weight and molecular weight distribution

Table 6.7 shows that the MBI catalyzed polymers in the absence of hydrogen have much higher (almost seven times) number average molecular weight (\overline{M}_n) and weight average molecular weight (\overline{M}_w) than the EI catalyzed polymers. Stehling *et al.*¹ and Spaleck *et al.*¹² explained that ethano-bridged catalysts (such as EI) are less stereoselective than the dimethylsilano-bridged catalysts (such as MBI). Within the group of dimethylsilano-bridged catalysts, the addition of methyl substituents to the Zr-bonded ring in the 2-position was found to increase the molecular weight and stereoregularity of the polymers produced, as well as reducing the number of 2,1-insertions and almost eliminating the presence of 2-butenyl terminal end groups.

Table 6.7 Summary of molecular weight and molecular weight distribution of polypropylenes prepared with the two different catalyst systems

Sample entry	Type of catalyst system	Amount of hydrogen (wt%)	M_n (g mol^{-1})	M_w (g mol^{-1})	M_n/M_w
E1-E11	EI	0.0-6.27	34 407-5 302	76 640-10 191	2.22-1.92
M1-M11	MBI	0.0-15.0	183 284-1 400	542 311-2 196	2.96-1.57

Propylene polymerization in the presence of hydrogen caused a dramatic lowering of polymer molecular weights in the case of both catalysts, as can be seen in Table 6.7 and Figure 6.19.

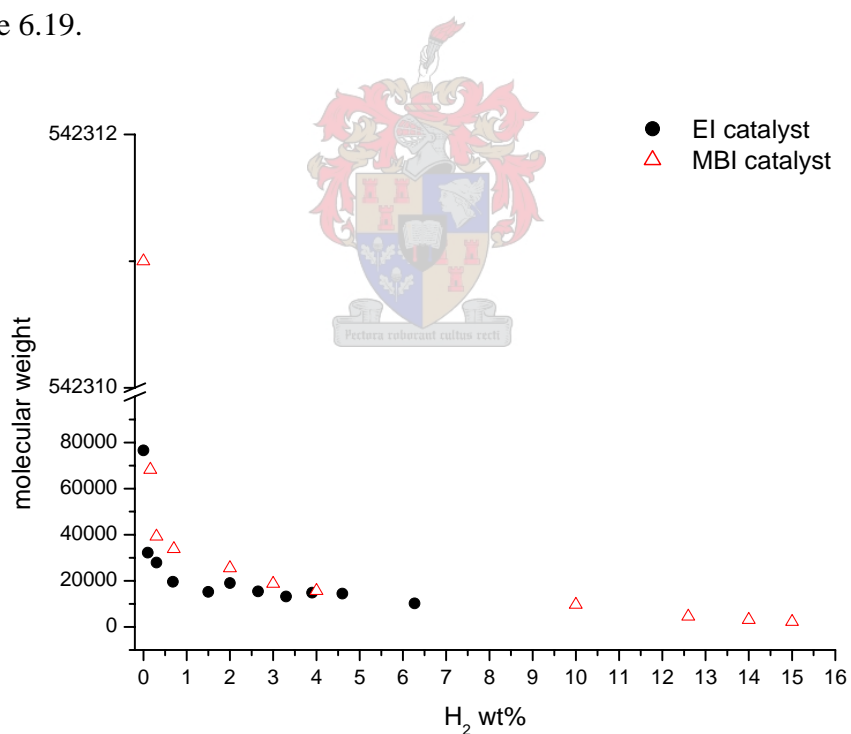


Figure 6.19 Dependence of molecular weight on hydrogen content of EI and MBI catalyst systems.

Of note here is that the MBI catalyst seemed far more sensitive to low amounts of hydrogen than the EI catalyst. As expected, the molecular weight distributions of the polypropylene polymers of both catalysts (Table 6.7) were all in the region of 1.57-

2.96. This feature is very characteristic of single-site catalysts which produce polymers with uniform molecular weights.

6.3.5 Melting behaviour

The MBI catalyzed polypropylene in the absence of hydrogen have much higher melting points than the EI catalyzed polypropylene. This is also reflected in the higher tacticity and apparently fewer 2,1 and 3,1 misinsertions (regiodefects).

The decrease in the melting points in the polypropylenes produced in the presence of hydrogen was larger in the case of MBI catalyzed polypropylenes than of the case of EI catalyzed polypropylenes. This decrease is due to the dramatic decrease in the molecular weight of MBI catalyzed polypropylenes ($\overline{M}_w = 2\,196\text{ g}\cdot\text{mol}^{-1}$ in the presence of 15.0 wt% of hydrogen).

The melting temperature of the polypropylenes produced with the EI catalyst decreased to around 139°C from 144°C. This could be directly related to the decrease in tacticity (86% to 82%). In the case of the MBI catalyst, the melting temperature was decreased from 153°C to 148°C from M1 to M8, which represents a lower molecular weight of around 10 000 g/mol. When the molecular weight decreases from 10 000 g/mol to around 2 500 g/mole, the melting temperature decreases a further 16°C, while the tacticity only decreases by a further 8% (similar to the decrease from M1 to M8). This clearly indicates the effect of molecular weight on melting temperature.

If one therefore compares E10 and E11 with M8, one sees that at the same molecular weight, the more isotactic M8 has a higher melting temperature than E10 or E11, as one would expect, but that comparing M11 with E10 and E11, we see that even if the tacticities are the same ($[\text{mmmm}] = 82\%$) the M11 polymer ($M_w = 2\,200\text{ g/mole}$) has a much lower melting temperature (132°C against 139°C). Once again this indicates the effect of the chain ends, in that the chain ends tend to be not crystallizable due to the fact that non-specific insertions occur near the chain ends.

6.4 References

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CHAPTER 7

Conclusions and Recommendations

7.1 Conclusions: *EI* catalyst

Addition of molecular hydrogen to propylene and ethylene polymerizations catalyzed using the *EI* catalyst system produced an increase in catalytic activity in the case of propylene polymerization. Furthermore, the polymer molecular weight was strongly reduced; polypropylene average molecular weight decreased from about 76 640 g.mol⁻¹ with no hydrogen to about 10 191 g.mol⁻¹ in the presence of 6.27 wt% hydrogen. The polydispersity of the polypropylenes were in the range of 1.92-2.33, which is typical for metallocene catalyzed polymers.

The isotacticity of polypropylenes produced by using the *EI* catalyst system is slightly reduced, from $[mmmm] = 86.5\%$ in the absence of hydrogen to $[mmmm] = 81.3\%$ in the presence of 6.27 wt% hydrogen. Apart from the expected stereo-irregular pentads $[mmmr]$, $[mmrr]$ and $[mrrm]$, the ¹³C NMR spectra of the methyl region of the polypropylenes showed additional small peaks due to the stereo-irregular sequences $rmmr$, $mmrm$, $rmrr$, $mrrm$ and $mrrr$, in the case of propylene polymerization in the presence of different amounts of hydrogen. This means that the stereoselectivity of the catalyst decreases with increasing the amount of hydrogen and that the active-site control over the chain propagation is partially lost. The effect of molecular weight on stereochemical control is therefore important. This indicates that most of the errors that are not due to enantiomorphic site control occur at the beginning of chain growth.

Using ¹³C NMR spectra and ¹H NMR spectra for end-group analyses showed that the use of hydrogen completely removed all β-H transfer reactions. It was also found that the majority of transfer reactions took place after a 2,1 insertion of propylene, with a concomitant decrease of 2,1 enchainments.

Finally, it was observed that the melting temperature (T_m) of the polypropylene synthesized in the absence of hydrogen (144 °C) was slightly higher than the T_m

values of polypropylenes obtained using different amounts of hydrogen (139 °C in the presence of 6.27 wt% hydrogen). This was in line with the decrease of tacticity as measured by $[m m m m]$ %..

7.2 Conclusions: MBI catalyst

The polypropylenes were successfully synthesized with the MBI catalyst system. The polymerization activity increased up to 5-fold in the presence of 10.0 wt% hydrogen, from 5 214 kg PP/(mol Zr.hr), to 24 874 kg PP/(mol Zr.hr).

From ^{13}C NMR spectra we can conclude that polypropylenes produced using the MBI catalyst system and in the absence of hydrogen are extremely isotactic. The isotacticity of the polypropylenes is significantly decreased from $[m m m m] = 98.0\%$ in the absence of hydrogen to $[m m m m] = 82.2\%$ in the presence of 15.0 wt% hydrogen. This decrease in the isotacticity of these polymers can be attributed to the decrease in stereoselectivity of the catalyst with an increasing hydrogen amount, as well as molecular weight effects. As in the case of the EI catalyst, stereoerrors not expected with enantiomorphic site control was found when the molecular weight was depressed. Unlike the polymers produced with the EI catalyst, these errors increased as the molecular weight decreased. Once again this indicates that the lower the molecular weight, the less effective the site control mechanism is.

The MBI catalyst system in the absence of hydrogen produced polypropylenes with much higher molecular weights ($\overline{M}_w = 542\,311\text{ g}\cdot\text{mol}^{-1}$) than the EI catalyst system ($\overline{M}_w = 76\,640\text{ g}\cdot\text{mol}^{-1}$). This is because the ethano-bridged catalyst ($\text{Et}(\text{Ind})_2\text{ZrCl}_2$) was less stereoselective than the dimethylsilano-bridged catalyst ($\text{rac-Me}_2\text{Si}(2\text{-MeBenz[e]Ind})_2\text{ZrCl}_2$), moreover the addition of methyl substituents to the Zr-bonded ring in the 2-position was found to lead to an increase in the molecular weights as well. In the presence of hydrogen, the molecular weight dramatically decreased to very low molecular weights ($\overline{M}_w = 2\,196\text{ g}\cdot\text{mol}^{-1}$ in the presence of 15.0 wt% hydrogen). As expected, the molecular weight distributions of the polypropylene polymers were all in the region of 1.57-2.96. This feature is very characteristic of single-site catalysts which produce polymers with uniform molecular weights.

Small regio-irregular units typical of 2,1- and 3,1-insertions were visible in the ^{13}C NMR spectra of the polypropylenes produced using EI, in the areas of 17, 31 and 38.2 ppm, in the absence of hydrogen, while these regio-irregular units were not observed in polypropylene produced using the MBI catalyst system. This could be due to substituent on the benzene ring in the 4-position minimizing 2,1-misinsertions, leading to much higher molecular weight ($\overline{M}_w = 542\,311\text{ g mol}^{-1}$) than polypropylenes produced using EI catalyst ($\overline{M}_w = 76\,640\text{ g mol}^{-1}$). However, these regio-irregular units were formed in both catalyst systems in the presence of hydrogen.

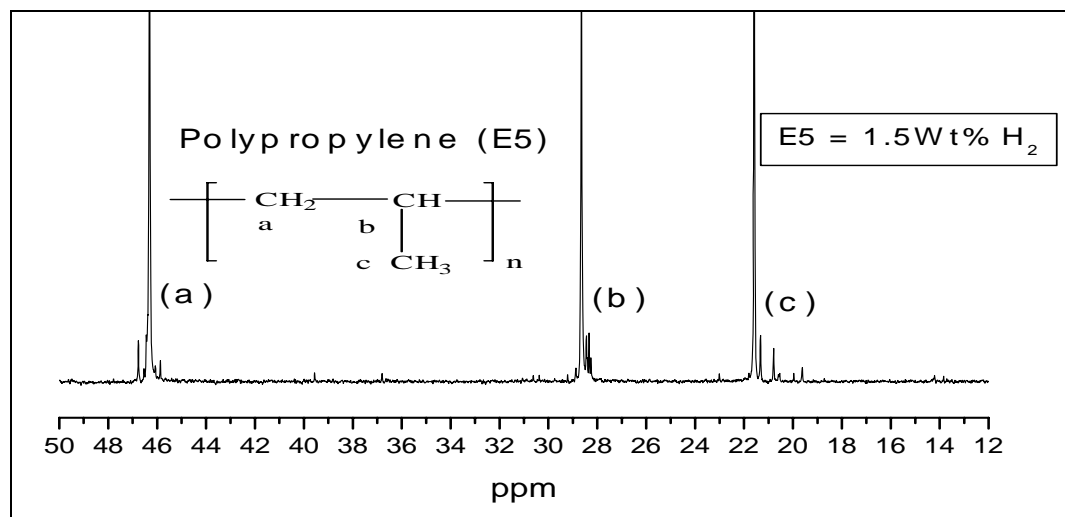
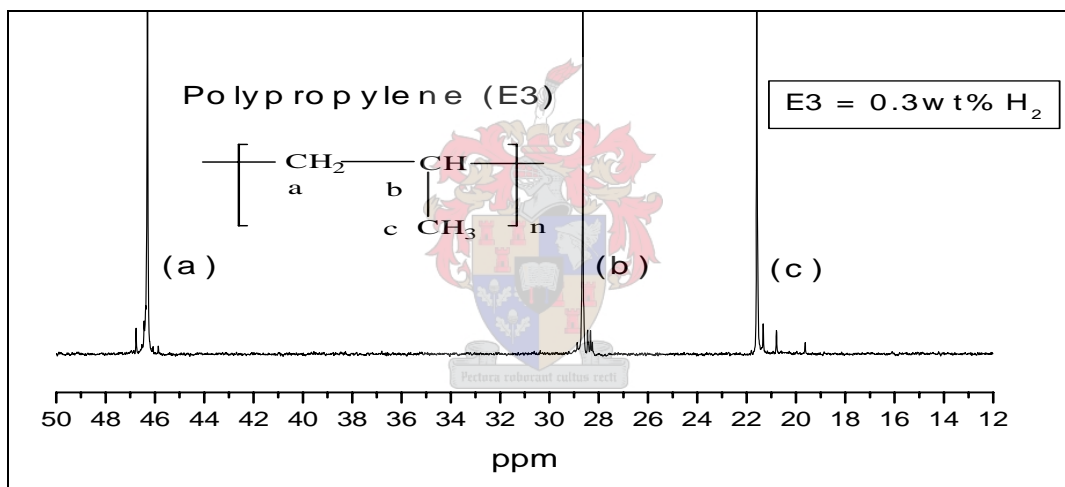
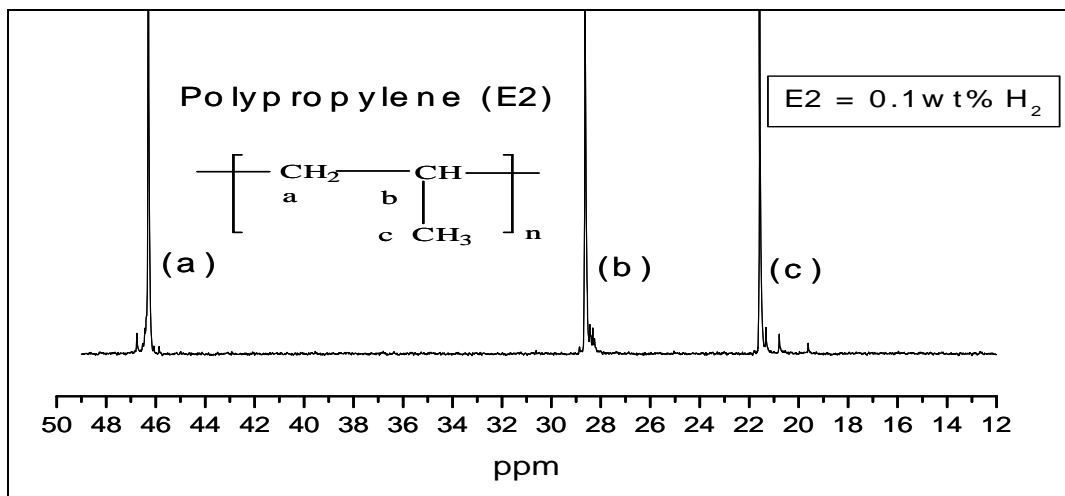
Vinylidene end-groups were the only end-groups observed in the polypropylene produced by MBI catalyst in the absence of hydrogen. In the presence of hydrogen, the transfer to hydrogen after 1,2 insertion was dominant, in contrast to the polymers produced with the EI catalyst.

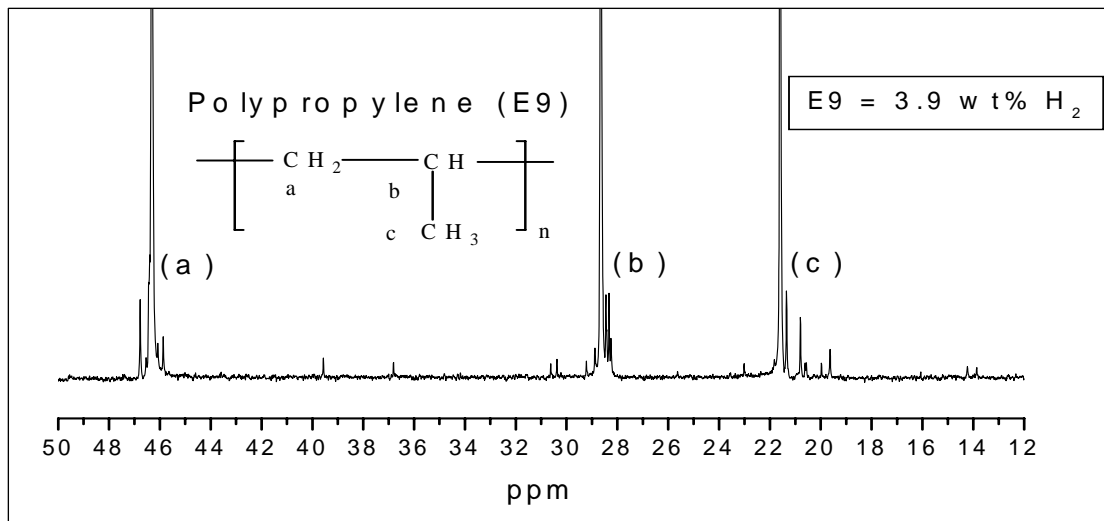
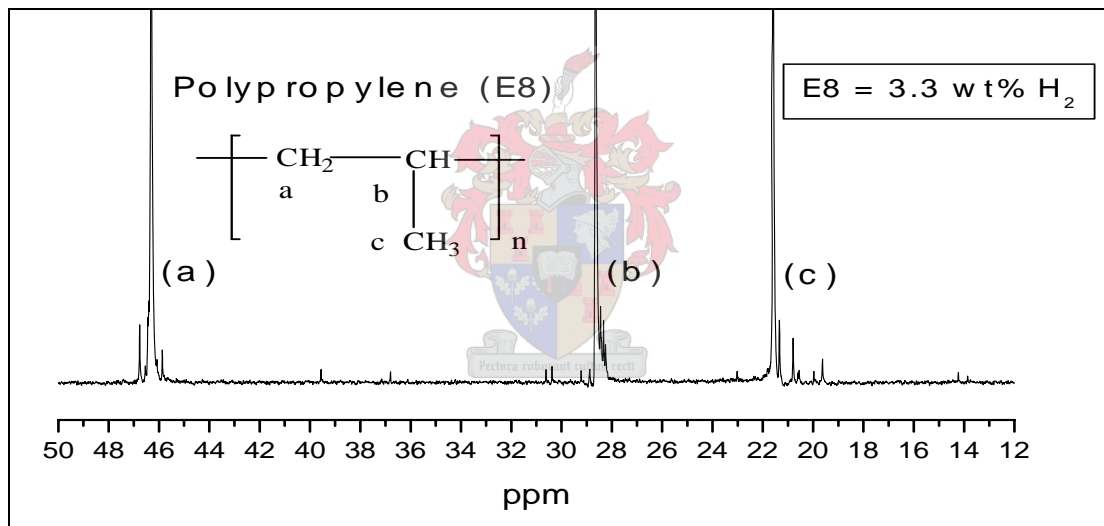
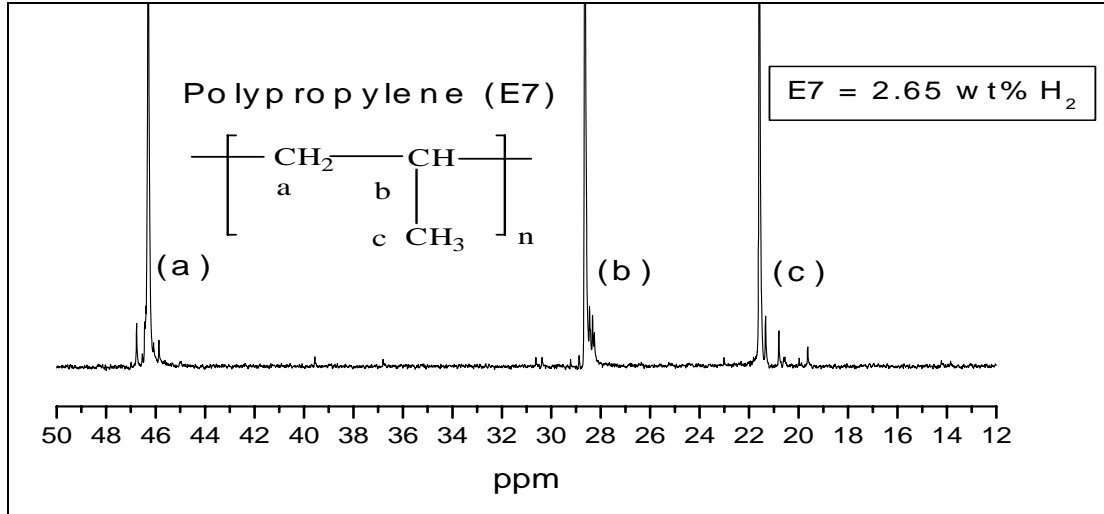
Finally, the melting temperature (T_m) of the polypropylene obtained in the absence of hydrogen (153 °C) was clearly higher than T_m values obtained for polypropylenes prepared using different amounts of hydrogen (132 °C in the presence of 15.0 wt% hydrogen). This decrease in the melting points is due to an increase in the amount of defects ($m m m m = 82.2\%$ in the presence of 15.0 wt% hydrogen) and a decrease in the molecular weight ($\overline{M}_w = 2\,196\text{ g}\cdot\text{mol}^{-1}$ in the presence of 15.0 wt% hydrogen).

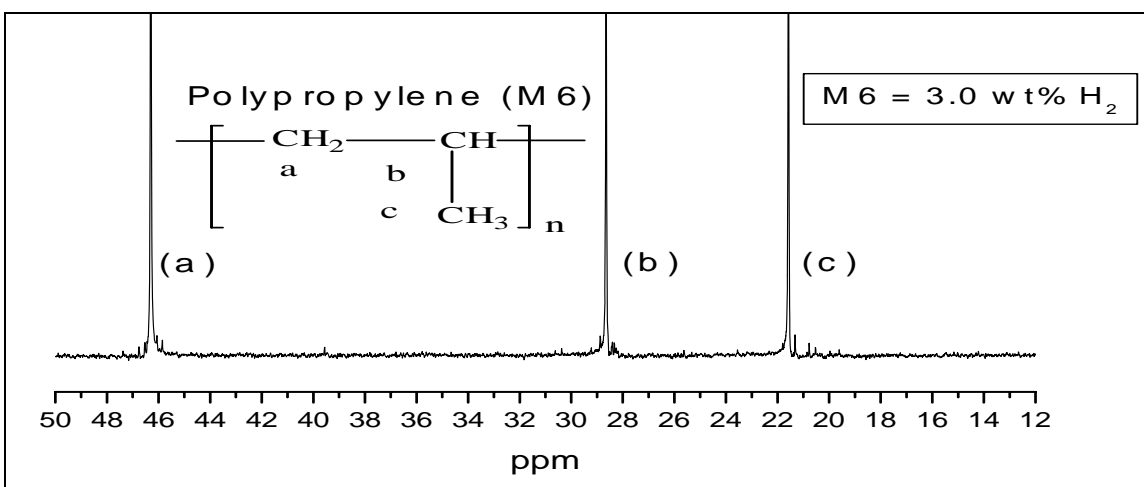
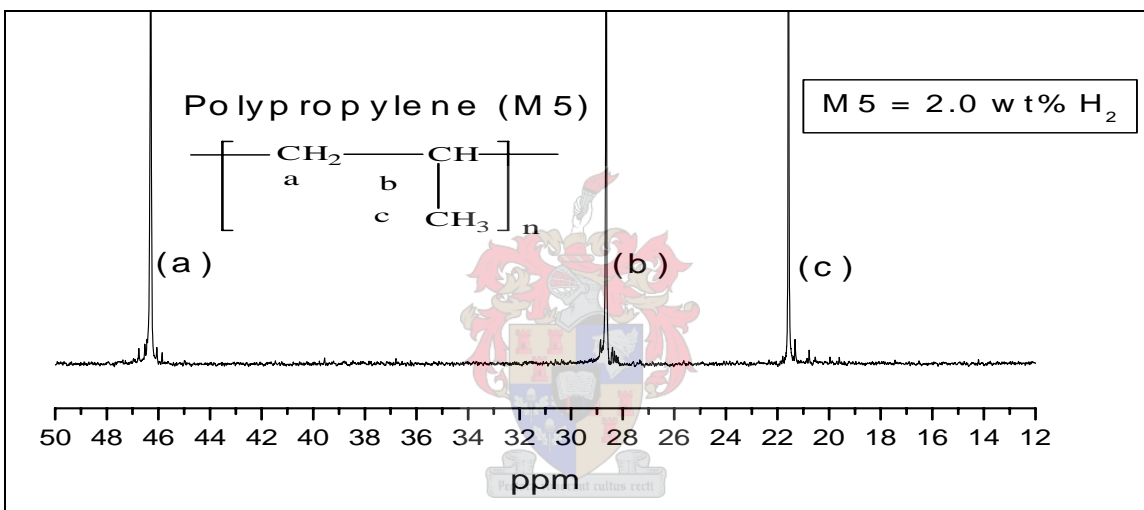
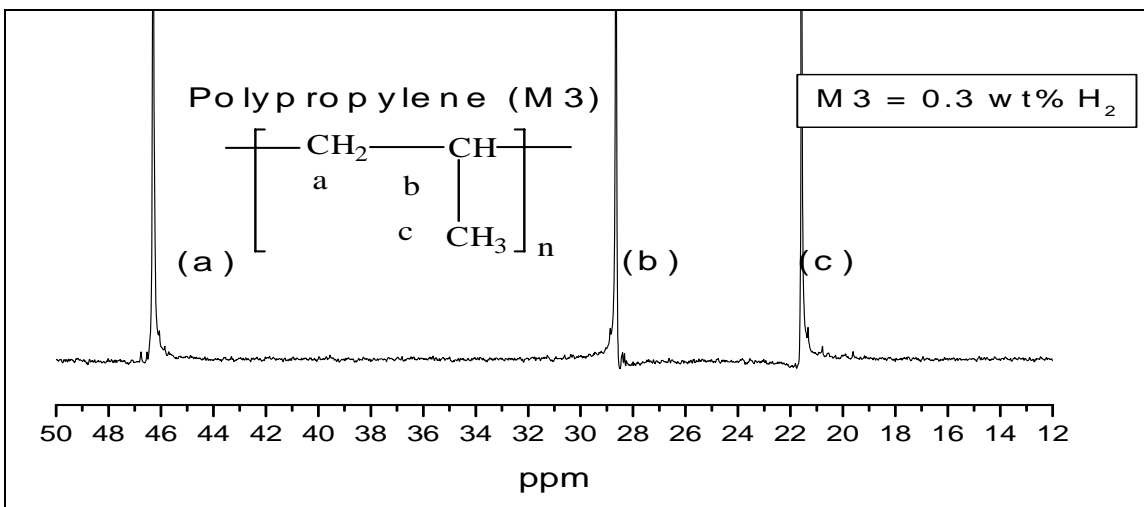
7.3 Recommendations for future work

The extension of this work to other catalysts, namely C_1 symmetric isospecific and C_s symmetric syndiospecific catalysts would give valuable insight into the way that these catalysts function and how the effect of chain length will affect catalyst control. Further extension of this research could also be seeing the effect of elevated temperatures on catalyst control when chain lengths are varied.

APPENDIX A ¹³C NMR CURVES







APPENDIX B HT-GPC CURVES

