

# Polymerisation of 1,5-Hexadienes

By

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Thesis presented in fulfillment of the requirements of the degree of

**Master of Science (Polymer Science)** at the

University of Stellenbosch



Promotor

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September 2001

## **DECLARATION**

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not in its entirety or in part been submitted at any university as a degree.

**Madri Smit**

## ABSTRACT

In this study, the feasibility of the non-conjugated 1,5-hexadiene as monomer in metallocene catalysed cyclopolymerizations was considered. Homopolymers and copolymers with ethylene, propylene, 1-pentene, 1-hexene and 2-methyl-1,5-hexadiene as comonomers were synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  and *rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ . The microstructure (stereoregularity and cyclisation) and number-average molecular weight were determined from NMR analysis. Crystalline oligomers with functional (eg  $-\text{OH}$ ) and vinylidene end groups were obtained.

## SAMEVATTING

Die studie behels die ondersoek rakende die gebruik van ongekonjugeerde 1,5-heksadieen as monomeer in metalloseengekataliseerde polimerisasies. Homopolimere, sowel as kopolimere van etlieen, propileen, 1-penteen, 1-hekseen en 2-metiel-1,5-heksadieen, is in die teenwoordigheid van  $\text{Cp}_2\text{ZrCl}_2$  en *rac*- $\text{Et}(\text{Ind})_2\text{ZrCl}_2$  gepolimeriseer. Die mikrostruktuur (stereochemie en siklisering) en die getal-gemiddelde molekulêre gewig van die gesintetiseerde polimere is met behulp van KMR spektroskopie ondersoek. Die studie het getoon dat kristallyne oligomere met funksionele (bv  $-\text{OH}$ ) en vinilideen end-groepe gesintetiseer is.

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|                |   |
|----------------|---|
| Reaction nr 1  | Poly(1,5-hexadiene)                           |
| Reaction nr 15 | Poly(1,5-hexadiene)                           |
| Reaction nr 30 | Poly(1,5-hexadiene)                           |
| Reaction nr 26 | Poly(2-methyl-1,5-hexadiene)                  |
| Reaction nr 29 | Poly(2-methyl-1,5-hexadiene)                  |
| Reaction nr 5  | Poly(ethylene-co-1,5-hexadiene)               |
| Reaction nr 6  | Poly(ethylene-co-1,5-hexadiene)               |
| Reaction nr 32 | Poly(ethylene-co-1,5-hexadiene)               |
| Reaction nr 23 | Poly(propylene-co-1,5-hexadiene)              |
| Reaction nr 16 | Poly(pentene-co-1,5-hexadiene)                |
| Reaction nr 21 | Poly(pentene-co-1,5-hexadiene)                |
| Reaction nr 20 | Poly(hexane-co-1,5-hexadiene)                 |
| Reaction nr 31 | Poly(carbon monoxide-co-1,5-hexadiene)        |
| Reaction nr 27 | Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene) |
| Reaction nr 28 | Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene) |

### DYNAMIC MECHANICAL ANALYSIS

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|                |   |
|----------------|---|
| Reaction nr 1  | Poly (1,5-hexadiene)                          |
| Reaction nr 15 | Poly(1,5-hexadiene)                           |
| Reaction nr 23 | Poly(propylene-co-1,5-hexadiene)              |
| Reaction nr 16 | Poly(pentene-co-1,5-hexadiene)                |
| Reaction nr 21 | Poly(pentene-co-1,5-hexadiene)                |
| Reaction nr 20 | Poly(hexene-co-1,5-hexadiene)                 |
| Reaction nr 27 | Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene) |
| Reaction nr 28 | Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene) |

## INFRARED SPECTRA

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Reaction nr 31 Poly(carbon monoxide-co-1,5-hexadiene)

## NUCLEAR MAGNETIC RESONANCE SPECTRA (<sup>1</sup>H SPECTRA)

---

NMR 001 Poly(1,5-hexadiene)  
NMR 015 Poly(1,5-hexadiene)  
NMR 057 Poly(1,5-hexadiene)  
NMR 014 Poly(2-methyl-1,5-hexadiene)  
NMR 015 Poly(2-methyl-1,5-hexadiene)  
NMR 009 Poly(ethylene-co-1,5-hexadiene)  
NMR 054 Poly(ethylene-co-1,5-hexadiene)  
NMR 052 Poly(ethylene-co-1,5-hexadiene)  
NMR 056 Poly(propylene-co-1,5-hexadiene)  
NMR 012 Poly(pentene-co-1,5-hexadiene)  
NMR 055 Poly(pentene-co-1,5-hexadiene)  
NMR 008 Poly(hexene-co-1,5-hexadiene)  
NMR 010 Poly(hexene-co-1,5-hexadiene)  
NMR 016 Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)  
NMR 017 Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)

## WIDE-ANGLE X-RAY SCATTERING

---

Reaction nr 5 Poly(ethylene-co-1,5-hexadiene)  
Reaction nr 6 Poly(ethylene-co-1,5-hexadiene)  
Reaction nr 32 Poly(ethylene-co-1,5-hexadiene)



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**LIST OF ABBREVIATIONS**

|  |  |
|--|--|
| Cycloolefins   | CO   |
| Bis(cyclopentadienyl) zirconium dichloride                 | $\text{Cp}_2\text{ZrCl}_2$                         |
| Differential scanning calorimetry                          | DSC  |
| Dynamic mechanical analysis                                | DMA  |
| Glass transition temperature                               | $T_g$  |
| 1,5-hexadiene  | HD   |
| Melting temperature  | $T_m$  |
| Methylalumoxane  | MAO  |
| 2-methyl-1,5-hexadiene                                     | MHD  |
| Nuclear magnetic resonance spectroscopy                    | NMR  |
| Number-average molecular weight                            | $M_n$  |
| Polypropylene  | PP   |
| Racemic ethylene-bridged bis(indenyl) zirconium dichloride | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub> |
| Wide-angle x-ray scattering                                | WAXS   |

## ACKNOWLEDGEMENTS

I would personally like to thank the following people and institutions, without whom this study would not have been possible.

**Dr AJ van Reenen**, for his support and guidance throughout this study.

**SASOL Polymers**, for funding my research.

**Charl Morkel**, for all the DMA analysis.

Special thanks goes to my family, friends and colleges at the Polymer Science Division for their support and understanding.

# Chapter 1 Introduction and Objectives

## 1.1 INTRODUCTION

Propylene is supplied locally by SASOL South Africa and its versatility as monomer has extensively been demonstrated, not only by industry, but also in our own research group <sup>[1-4]</sup>.

The main aim of the present study was to consider the possible synthesis of new monomers from propylene and their potential applications. The focus was on the non-conjugated 1,5-hexadiene, a diolefin commonly observed as a by-product of anionic, cationic and Ziegler-Natta polymerisations <sup>[5]</sup>. This unique monomer is however produced in low yield and is very expensive to synthesise.

Recent studies <sup>[6]</sup> have shown that 1,5-hexadiene can be synthesised by the oxidative dimerisation of propylene. In order to better judge the feasibility of pursuing this method, it is necessary to evaluate the potential of this non-conjugated diene as a monomer in homo- and copolymerization reactions.

## 1.2 OBJECTIVES

The two main objectives of this study were:

### 1.2.1 Cyclopolymerisation of 1,5-hexadiene via metallocene catalysis

Metallocenes are special members of a class of chemical substances known as organometallic compounds. These molecular compounds are recognised by the general formula  $L_nMR$ .  $L_n$  represent an organic ligand set that remains bound to and thus modifies the reactivity of the active centre ( $M$ ) during the entire chemical reaction.  $R$  is the polymer or initiating group (see section 2.1.1 for further detail).

This section of the research included the determination of the reaction conditions for the homopolymerisation of the non-conjugated 1,5-hexadiene, as well as for the copolymerisations with ethylene, propylene, 1-pentene, 1-hexene and 2-methyl-1,5-hexadiene. Transition metal catalytic systems based on zirconocene dichloride ( $Cp_2ZrCl_2$ ) and *racemic* ethylene-bridged bis(indenyl) zirconium

dichloride (*rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>), with methylalumoxane (MAO) as cocatalyst were employed.

### 1.2.2 Analysis of the obtained polymeric materials

The microstructures of the polymeric materials were determined by Grant and Paul additivity chemical shift predictions, <sup>13</sup>C and APT (attached proton test) nuclear magnetic resonance spectroscopy (NMR). This information together with <sup>1</sup>H NMR data, was employed to determine the amount of cyclization of the diene, comonomer content in the polymer and the number-average molecular weight, M<sub>n</sub>, of the resulting material. Melting- (T<sub>m</sub>) and glass transition (T<sub>g</sub>) temperatures were obtained from differential scanning calorimetric (DSC) measurements and dynamic mechanic analysis (DMA), where possible. Wide-angle x-ray scattering (WAXS) experiments were also performed to determine the influence of the diene on the crystallinity of ethylene copolymers.

## 1.3 REFERENCES

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- [2] UM Wahner, UM; Brüll, R; Luruli, N; Pasch, H; Raubenheimer, HG; Sanderson, RD; Van Reenen, AJ; *Macromol Chem Phys*, submitted
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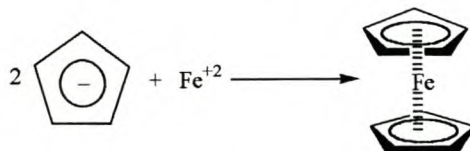
## Chapter 2 Historical and Theoretical Concepts

### 2.1 METALLOCENE CHEMISTRY

Research in single active-centre metal-catalysed polymerisation has seen explosive growth over the past two decades, advancing from questions of academic interest to solving problems in the commercial arena <sup>[1]</sup>. The active centre of the metallocene is tuned by the alternation of the ligand sphere of the central atom. It is thus possible to obtain uniform polymers with controlled properties.

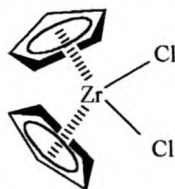
#### 2.1.1 History

Fischer and Wilkinson first determined the structure of ferrocene in 1952 <sup>[2,3]</sup>. Ferrocene (Scheme 2-1) can be described as a positively charged metal ion, sandwiched between two cyclopentadienyl anions through  $\pi$ -bonding.



**Scheme 2-1** Ferrocene, the first metallocene to be synthesised (Fischer and Wilkinson, 1952). <sup>[2,3]</sup>

Shortly thereafter, Wilkinson discovered metallocenes in which higher charged metal ions such as zirconium (+4) would bond with two chlorine atoms to obtain a stable system (Figure 2-1). The cyclopentadienyl rings will form an angle with respect to each other to facilitate the large chlorine ligands.



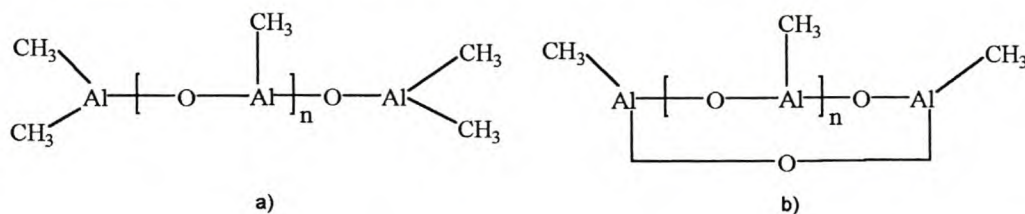
**Figure 2-1** Zirconocene dichloride (inactive metallocene catalyst).

Metallocenedichlorides with aluminium alkyl cocatalysts, used in Ziegler-Natta systems, were capable of polymerising ethylene, but only in very low activity.

Reichart and Meyer <sup>[4]</sup> found an increase in activity (20-100 times better) by adding small amounts of water to the  $Cp_2TiCl_2/C_2H_5AlCl_2$  catalytic system. The addition of water in a far greater amount resulted in an increase in activity up to 1 million times better than that previously observed <sup>[5]</sup>. The discovery and application of methylalumoxane (MAO) in 1977 in Hamburg, enhanced the activity by a factor of 10 000 <sup>[6,7]</sup>. A big milestone in metallocene catalysis was the synthesis of *ansa*-metallocenes with  $C_2$  symmetry. Brintzinger synthesised these chiral, bridged metallocenes in 1982 at the University of Konstanz <sup>[8]</sup>. In 1984 Ewen <sup>[9]</sup>, at Exxon, demonstrated that appropriate titanocenes could synthesise partially isotactic poly(propylene). A year later, highly isotactic material was obtained with analogous zirconocenes by Kaminsky *et al* <sup>[10]</sup>.

### 2.1.2 Activation of Metallocene catalyst

Methylalumoxane (MAO) is often employed as a cocatalyst for metallocene catalysts. MAO is an oligomeric compound with a molecular weight of 1 000 - 1 500g/mol, obtained by the controlled hydrolysis of trimethylaluminum ( $AlMe_3$ ) <sup>[5]</sup>. The exact structure of this compound has not yet been determined, although various plausible structures have been proposed (Figure 2-2).



**Figure 2-2** Plausible structures for methylalumoxane as proposed by Kaminsky *et al* – a) linear and b) cyclic <sup>[11]</sup>.

The most accepted structure consists of cage-like dimensions with trimethylaluminium dispersed throughout the complex (Figure 2-3).

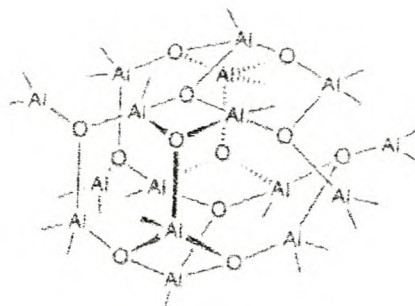
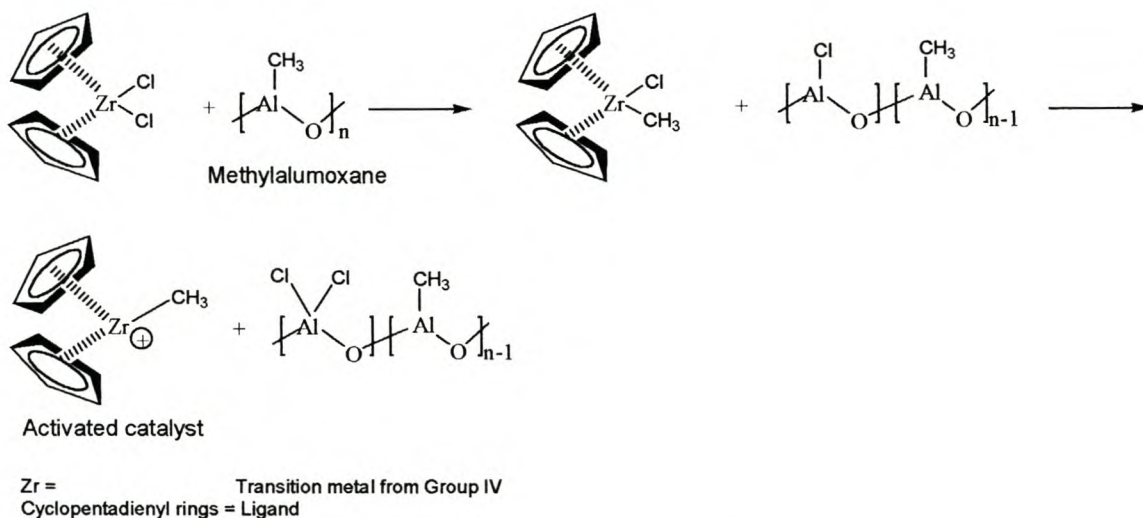


Figure 2-3 Suggested structure for methylalumoxane, clusters and cages, by Sinn et al. <sup>[12]</sup>

An important function of MAO, as cocatalyst, is the alkylation of the catalyst precursor (Scheme 2-2):



Scheme 2-2 MAO activation of metallocene catalyst precursors for polymerisations. <sup>[13]</sup>

A second function of MAO is the scavenging of polar compounds in the vicinity of the catalyst. Transition metals would easily react with these compounds, resulting in the deactivation of the catalytic system [5].

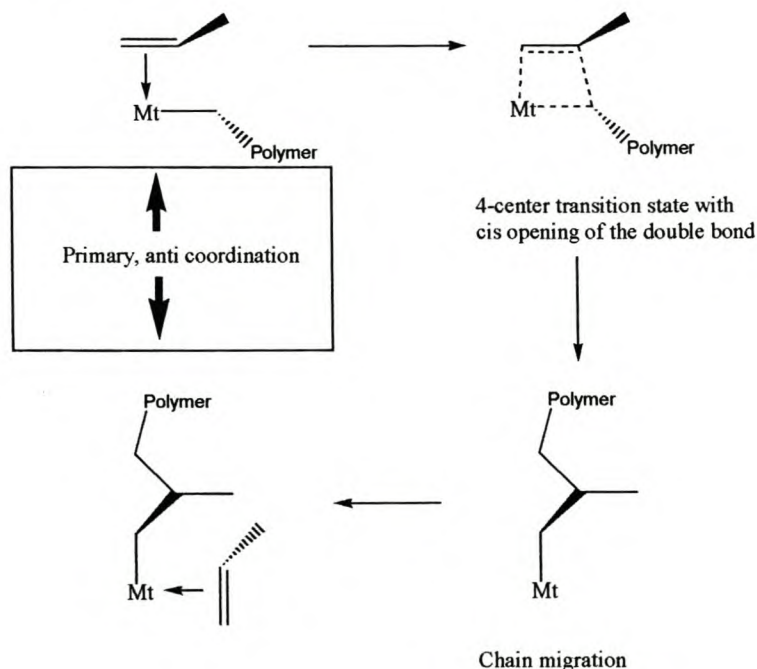
A third function of MAO as cocatalyst, is the reactivation of inactive species formed by hydrogen transfer reactions. This also explains the high catalyst-cocatalyst mole ratios required (eg 1: 1 000) for metallocene polymerisations with MAO as cocatalyst <sup>[5]</sup>.

### 2.1.3 Polymerisation mechanism

Polyolefins are produced by the multiple insertions of olefins into a metal-carbon bond. Olefin insertion occurs by the *cis*-opening of the double bond (both new bonds are on the same side of the inserting olefin) and with chain migratory insertion (it is the alkyl group on the metal that migrates to the olefin with a net exchange of two available coordination positions on the metal centre).

When we have PRIMARY insertion (1,2), then the 1-alkene enantioface that is inserted preferentially is the one, which in the transition state, places its substituent anti to the first C-C bond of the growing polymer chain (minimizes non-bonded interactions):

The active metal centre bearing the growing alkyl chain must have an available co-ordination site for the incoming monomer. Insertion occurs via chain migration to the closest carbon of the olefin double bond, which undergoes *cis*-opening, with the formation of the new metal-carbon and carbon-carbon bonds. The new C-C bond is then on the site previously occupied by the co-ordinated monomer molecule.



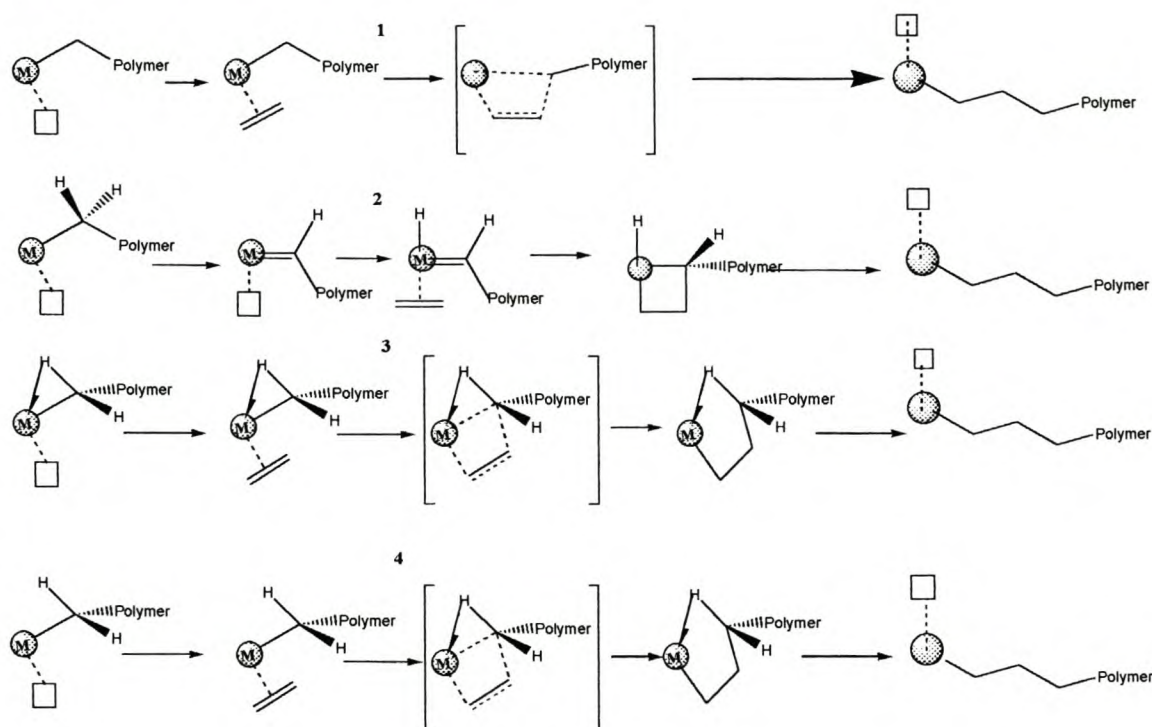
**Scheme 2-3** Schematic representation of coordination and insertion during olefin polymerisation with transition metals. (Mt = metal atom)



Points of importance in transition metal catalysed polymerisation of olefins:

- The metal atom must have a site for coordination
- Insertion occurs via chain migration to the closest carbon of the olefin double bond.

The four main proposed mechanisms for polymerisation are shown in Figure 2-4.<sup>[13,14]</sup>



**Scheme 2-4** Proposed polymerisation mechanisms for metallocene catalysed olefin polymerisation. (The dark circles are representative of the central metal atom.)

Scheme 2-4 is representative of, inter alia, two main mechanistic schemes (Scheme 2-4 (1 and 2)) that has been proposed for olefin polymerisation with Group III and IV transition metals.

The first mechanism (Scheme 2-4 (1, named after Cossee))<sup>(13)</sup>, involves two steps, eg olefin coordination and alkyl migration of the  $\sigma$ -coordinated growing chain to the  $\pi$ -coordinated olefin. The second mechanism (Scheme 2-4 (2)), involves the oxidative 1,2 hydrogen shift from the first C-atom of the growing chain to the metal, this results in  $\alpha$ -alkylidene hydride species bonded to the

metal. A 4-center metallacycle is then generated by reaction of the alkylidene species with the coordinated olefin. This mechanism can be ruled out, as the 14e cationic metallocenes lack the required number of d-electrons for formal oxidative addition.

The last two mechanisms shown above (Scheme 2-4 (3 and 4)) are improved versions of the Cossee mechanism. The third mechanism (Scheme 2-4 (3)) requires a stabilizing  $\alpha$ -agostic interaction in both the ground state and in the 4-center transition state. The mechanism shown in Scheme 2-4 requires the presence of an  $\alpha$ -agostic interaction in the transition state only. It is generally accepted that this  $\alpha$ -agostic interaction is necessary during the insertion step. The acceptable mechanisms all agree that:

- Monomer insertion is a two-step process; coordination followed by insertion.
- The active metal must have an available coordination site
- Olefin insertion occurs by *cis*-opening of the double bond, followed by chain migratory insertion.
- The olefin has to coordinate face-on to the metal, with its double bond parallel to the metal-carbon bond.

The ligands and substitution thereof, play an important role in the insertion of the monomer with reference to steric hindrance. The angle that the ligands form with each other is thus a vital variable and brings us to the concept of *ansa*-metallocenes. Control of the tacticity of the formed polymer is possible.

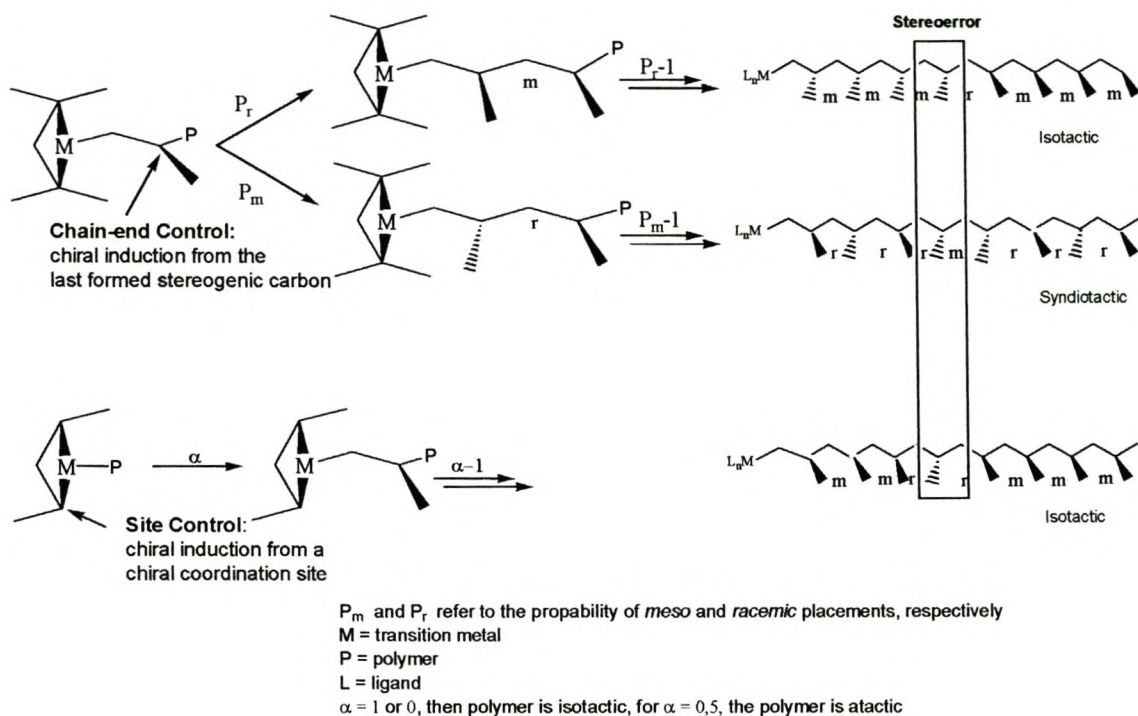
A distinction between the active centre and the active site of the catalyst precursor should be made: a metallocene type active centre has a minimum of two sites on which chain growth can take place. The nature of the active site is determined by the metal, the Cp ligands, geometry and the structure of the metal-bonded chain-end. Different types of last inserted monomer will thus increase the number of possible active sites. A difference in reactivity, regioselectivity and enantioface selectivity is therefore possible. The result is

that the active centre itself changes during a single chain growth but, statistically, behaves the same from one chain to another. Such a species can therefore be described as a single-centre catalyst <sup>[13]</sup>. The relationship between metallocene site symmetry and polymer stereochemistry will be discussed in section 2.1.5.

#### 2.1.4 Modification of the Catalytic System to obtain tailor-made polymers

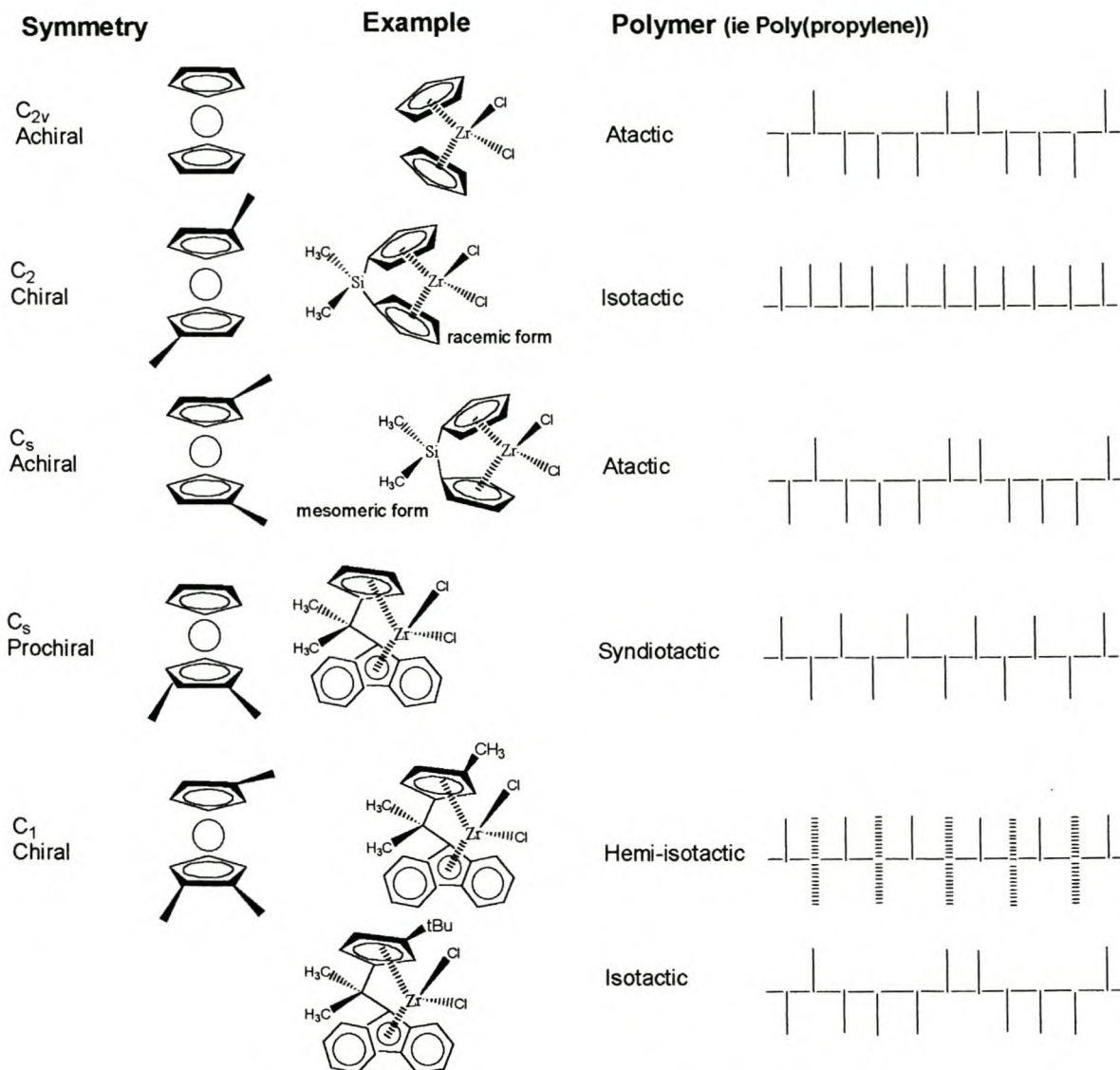
The versatility of metallocene catalysts is seen in the various modifications one can make to the system in order to create polymers with specific properties that meet the needs of the scientist and industry. Two possible sources of enantioface selectivity in olefin insertion are possible (see Scheme 2-5):

- a) Stereogenicity of the metal active site, based on enantiomeric site control mechanism for stereoselection. The relationship of the chirality of the two co-ordination sites of the catalytic complex determines the stereochemistry of the polymer.
- b) The last inserted monomer unit, based on chain-end control mechanism for stereoselection. Every monomer insertion generates a new stereogenic centre, chiral induction/ enantiophase preference can come from the last inserted monomer unit.



**Scheme 2-5** Chain-end and Enantiomorphic Site Mechanisms of Stereocontrol. <sup>[15]</sup>

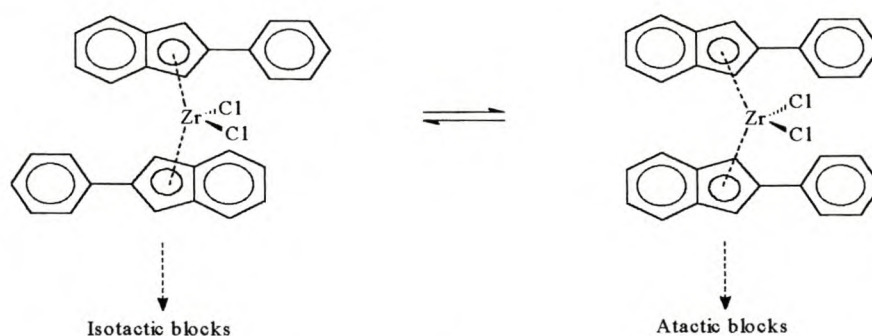
A predictable relationship between complex symmetry and polymer tacticity exists. This can be seen by Ewen's Symmetry rules (Figure 2-4), compiled by Ewen *et al* <sup>[9,16-20]</sup> and Kaminsky *et al* <sup>[10]</sup>.



**Figure 2-4** Steric Control as a Function of Metallocene Symmetry (Ewen's Symmetry Rules).  
[13,15]

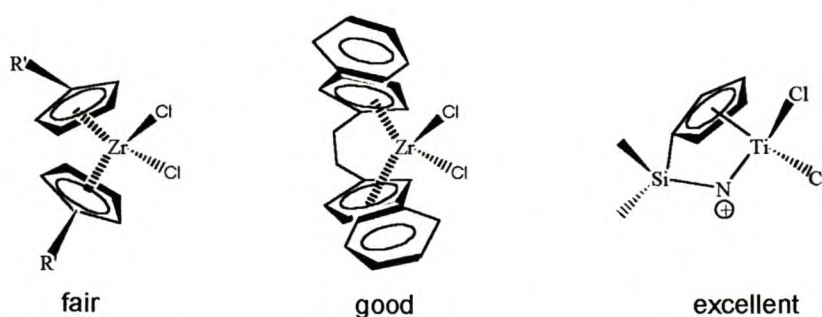
Single-site polymerisation catalysts can be divided into five major symmetry categories. It is assumed that the polymer rapidly equilibrates with the available co-ordination site for the purposes of assigning symmetry.  $C_{2v}$  symmetric metallocene catalysts produce atactic polymers or moderately stereoregular polymers by chain-end control mechanisms. Catalysts exhibiting  $C_s$  symmetry, consisting of mirror planes containing the two diastereotopic co-ordination sites, behave similarly and produce atactic polymers.  $C_s$  symmetric catalysts that have a mirror plane reflecting two enantiotopic co-ordination sites frequently produce

syndiotactic polymers.  $C_2$  symmetric complexes, both *racemic* and enantiomerically pure ones, typically produce isotactic polymers via a site-control mechanism. The fifth symmetry category, not mentioned in Figure 2-5, is oscillating metallocenes. Waymouth and Coates<sup>[21]</sup> reported on the production of stereoblock poly(propylene) with a non-bridged metallocene, bis(2-phenylindenyl)ZrCl<sub>2</sub>. The catalyst is able to switch its co-ordination geometry from aspecific to isospecific during polymerisation (Figure 2-5), resulting in a polymer consisting of atactic and isotactic blocks.

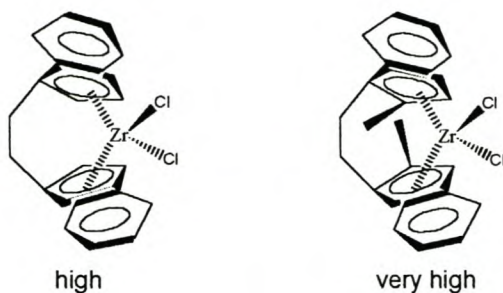


**Figure 2-5** Synthesis of stereoblock Poly(propylene) via an oscillating metallocene catalyst.<sup>[5]</sup>

The structure of the catalyst precursor also has a significant influence on the comonomer incorporation and molecular weight of the obtained copolymer, as can be seen in Figure 2-6 and Figure 2-7.



**Figure 2-6** Control of Comonomer Incorporation (ethylene copolymers) through the manipulation of catalytic structure.<sup>[22]</sup>

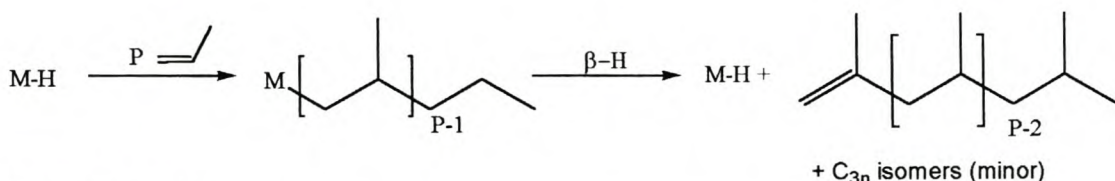
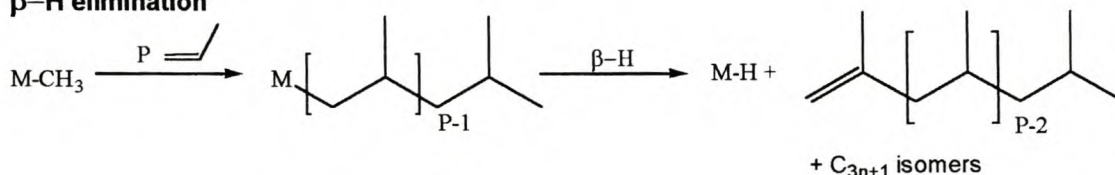


**Figure 2-7** Control of molecular weight (ethylene copolymers) through the manipulation of catalytic structure. [22]

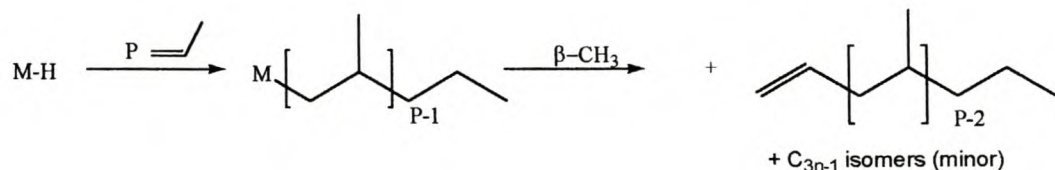
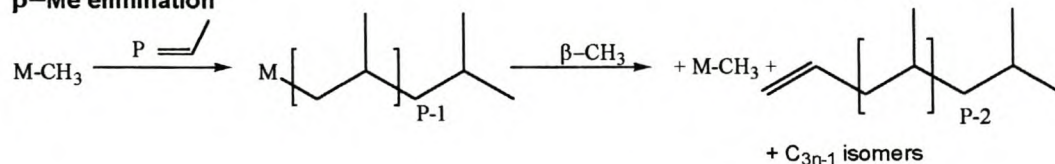
### 2.1.5 Chain termination possibilities in metallocene catalysed polymerisations

Various chain termination possibilities exist in the synthesis of polyolefins via metallocene catalysis (Schemes 2-6 and 2-7).  $\beta$ -H elimination is probably the most common mode of termination. Chain termination modes observed in cyclopolymerisation reactions will be discussed in Section 2.2.2.1.

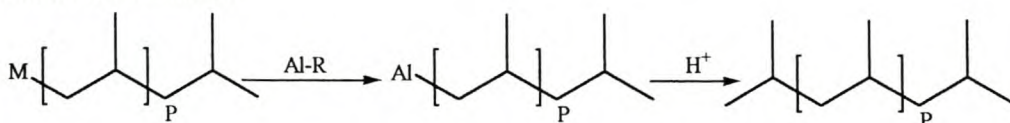
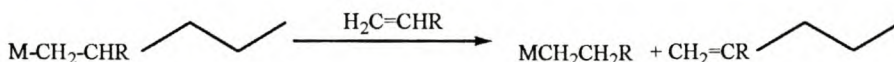
#### $\beta$ -H elimination



#### $\beta$ -Me elimination



**Scheme 2-6** Relevant chain termination possibilities in Metallocene catalysed polymerisation. [23,24]

**Transfer to Aluminum****Transfer to monomer**

**Scheme 2-7** Relevant chain termination possibilities in Metallocene catalysed polymerisation. [23,24]

## 2.2 CYCLIC OLEFINS AND NON-CONJUGATED DIENES

### 2.2.1 Cyclic Olefins

In the past, ring structures were incorporated into polymer chains by means of homo- and copolymerization of cycloolefins (Figure 2-8) such as norbornene. Metallocene catalysts polymerise these diolefins without any ring opening reactions.

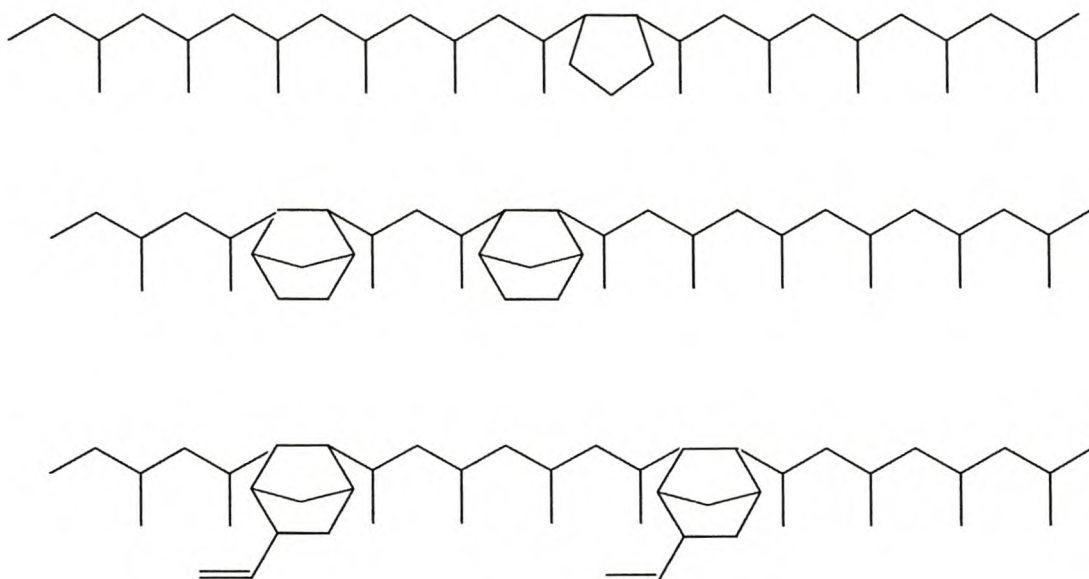


**Figure 2-8** Cycloolefins used for the polymerisation by metallocenes.

Such materials characteristically have excellent transparency and a very high continuous service temperature. Cycloolefin (CO) insertion rates equal to, and higher than, 10mole% result in an increase in amorphous character. CO show high solvent and chemical resistance, low uptake of moisture, high softening temperatures ( $T_g$  up to  $200^\circ C$ ) and can be processed on a thermoplastic basis. These characteristics make them interesting for optical and high impact applications. Ethylene-norbornene copolymers show high transparency and very good heat stability. Today, these copolymers, (Topas<sup>®</sup> : thermoplastic olefin polymers of amorphous structure), are offered by industry [25]. Arnold *et al* [26]

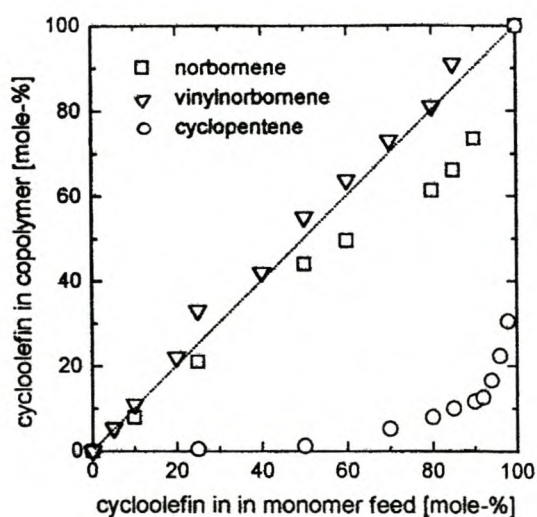


observed a strong influence of the incorporation behaviour on the structure of the cyclic olefin for the propylene-cyclic olefin copolymerisations (Figure 2-9).



**Figure 2-9** Polymer structures of some propylene copolymers synthesised by metallocene catalysis.

Monocyclic pentene is only incorporated when present in high concentrations, while bicyclic olefins norbornene and vinylnorbornene show good insertion into the growing propylene chain (Figure 2-10).



**Figure 2-10** Copolymerisation of propylene and cyclic olefins. <sup>[26]</sup>

Vinylnorbornene is incorporated into the polymer chain via the endocyclic double

bond; the exocyclic double bond is thus available for further modifications. It was concluded that a higher cyclic olefin concentration leads to a drastic decrease in polymerisation activity and molecular weight. Nevertheless, copolymers of every desired composition can be obtained by variation of the monomer ratio. Comonomer incorporation results in higher chain rigidity than can be detected by the investigation of the glass transition temperature ( $T_g$ ) of these polymers. Values that could be detected are shown in Figure 2-11.

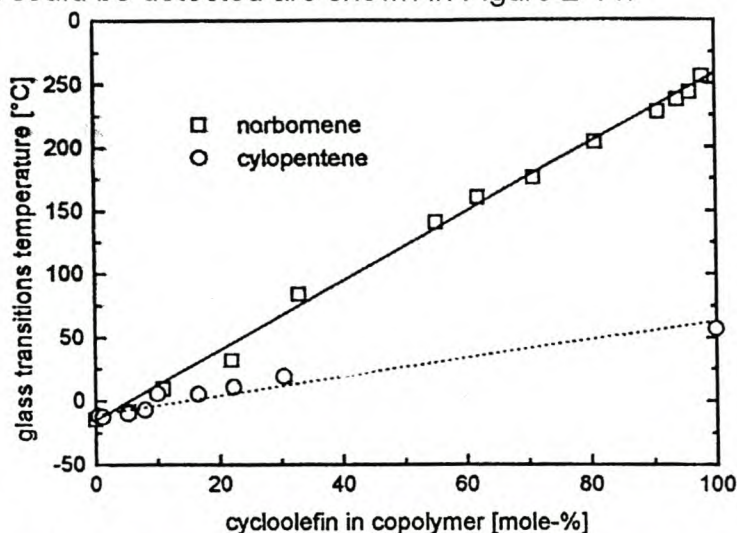


Figure 2-11 Glass transition temperatures of the system propylene/ cyclic olefin. <sup>[26]</sup>

The use of cyclic olefins as comonomers in propylene copolymerization by metallocene catalysis allows the synthesis of polymeric materials with adjustable  $T_g$  ranging from  $-10^{\circ}\text{C}$  to  $225^{\circ}\text{C}$ . The disadvantage of using cyclic olefins as comonomers, however, is low productivity.

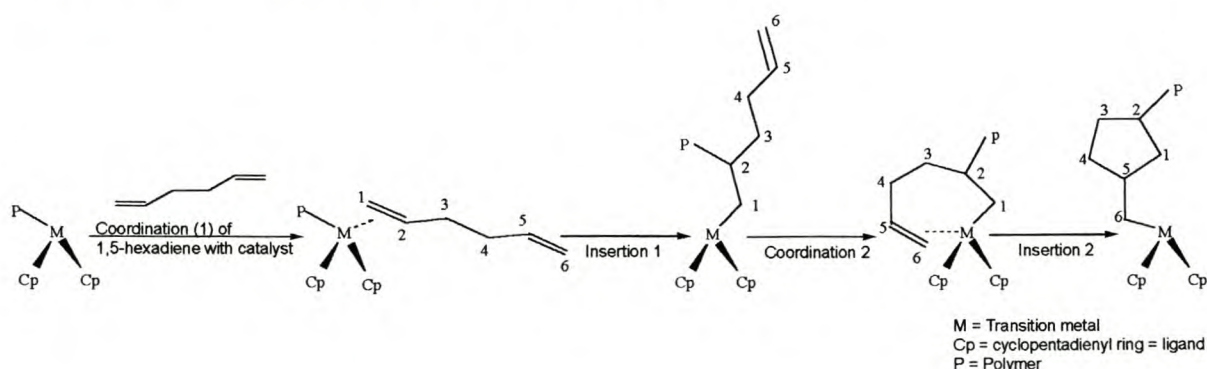
Recently, cyclopolymerisation was developed as a means of inserting cyclic structures into polymer chains by using linear monomers. Waymouth *et al* <sup>[27-30]</sup> performed detailed investigations on the cyclopolymerisation of non-conjugated dienes, in particular 1,5-hexadiene, with metallocene catalysts.

## 2.2.2 Cyclopolymerisation of Non-conjugated Dienes

### 2.2.2.1 Homopolymerisation

Marvel and Stille first prepared poly(1,5-hexadiene) in 1957 <sup>[33]</sup>, using triisobutylaluminum/ titanium tetrachloride as a catalytic system. This reaction

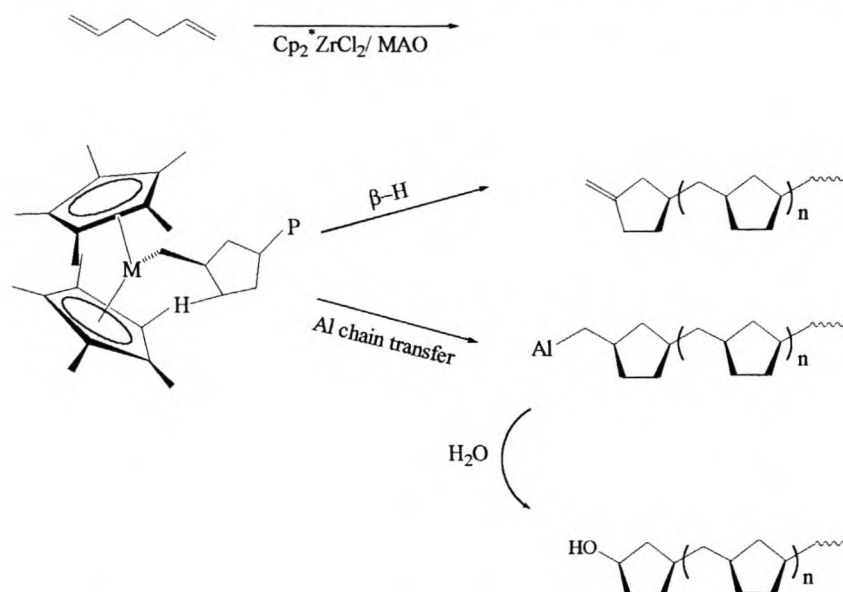
was unique, as it was the first time that cycloaddition was favoured above 1,2-addition. The most energetically feasible mechanism for the cyclopolymerisation of 1,5-hexadiene was that proposed by Marvel and Garrison (Scheme 2-8) [27,31]. Two distinct stereochemical events were identified: *enantioselectivity* of olefin insertion that determines the tacticity of the polymer chains and *diastereoselectivity* of olefin cyclization, which determines the formation of *cis*- and *trans* conformations of the rings in the polymer.



**Scheme 2-8** Cyclo- / intra-intermolecular polymerisation mechanism of 1,5-hexadiene (Marvel and Garrison).

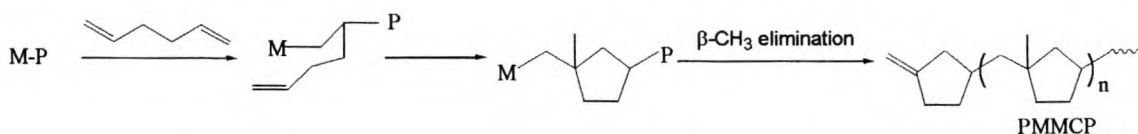
This theory was also supported by Cheng *et al* [33] who were the first to publish a detailed  $^{13}\text{C}$  NMR spectrum of poly(1,5-hexadiene). The polymer was shown to contain repeating five-membered rings separated by methylene bridges, with both *trans*- and *cis* placements. Makowski *et al* [34] reported on the highly crystalline properties of the materials obtained by titanium catalysis. The materials showed high tensile strengths (4360psi), melting points (up to 146°C), densities in the region of 1.00g/cm<sup>3</sup>, while still showing good flexibility. The substituents showed *cis*-conformation and the ring is in an envelope conformation. Due to the fact that full cyclization was not obtained, the polymer is referred to as an interpolymer rather than a homopolymer. Mogstad *et al* [29] looked into the chain termination possibilities.  $\beta$ -H elimination is generally accepted as the dominant chain transfer process. It is a unimolecular process, temperature dependent and yields unsaturated chain ends. Chain transfer to aluminium, on the other hand, is a bimolecular process and dominant at -25°C.

The result is end-functionalised hydrocarbons that can be used as macromonomers for the formation of block- and graft copolymers (Scheme 2-9).



**Scheme 2-9** Chain termination possibilities for cyclopolymerisation. <sup>[29]</sup>

Chain transfer via  $\beta$ -CH<sub>3</sub> elimination (Scheme 2-10) is the third possibility and reported to be applicable in the case of the highly chemo- and stereoselective cyclopolymerisation of 2-methyl-1,5-hexadiene to give *trans*-poly(methylene-1,3-(methylcyclopentane)).



**Scheme 2-10**  $\beta$ -CH<sub>3</sub> elimination as third chain transfer possibility. <sup>[35]</sup>

Control over the amount of cyclization via temperature and catalyst precursor provides a powerful tool for the control of polymer properties, eg crystallinity. Unsaturated chain ends, on the other hand, allow for grafting of polymers and the possibility for use as macromonomers.

### 2.2.2.2 Copolymerization

Research in the field of 1,5-hexadiene copolymerisation has mainly been focused on the synthesis of ethylene and propylene copolymers. Makowski *et al* <sup>[36]</sup> used

X-ray analysis and melting point composition behaviour to confirm the synthesis of poly(ethylene-co-1,5-hexadiene) block copolymer, in the presence of  $\text{AlR}_3/\text{TiCl}_3$  as catalytic system. The block nature of these copolymers was also confirmed by the crystallisation of the blocks into polyethylene and poly(1,5-hexadiene) crystals. Various physical properties were also determined as a function of weight % ethylene in the copolymer, as illustrated in Figures 2-12 to Figure 2-16.

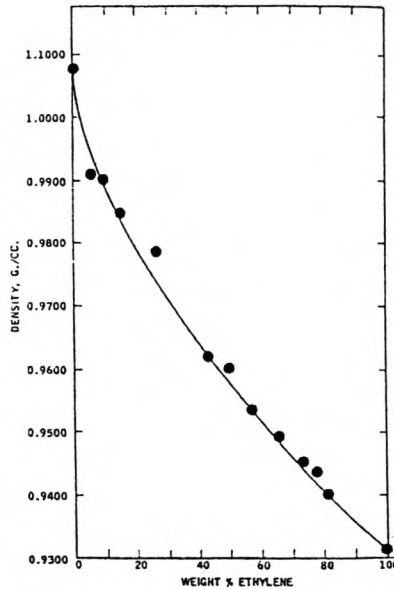


Figure 2-12 Effect of copolymer composition on Density. <sup>[36]</sup>

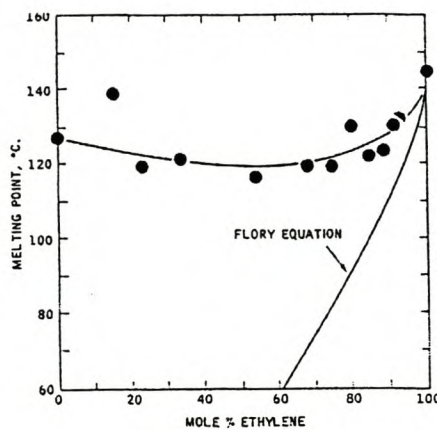


Figure 2-13 Effect of copolymer composition on Melting Point ( $T_m$ ). <sup>[36]</sup>

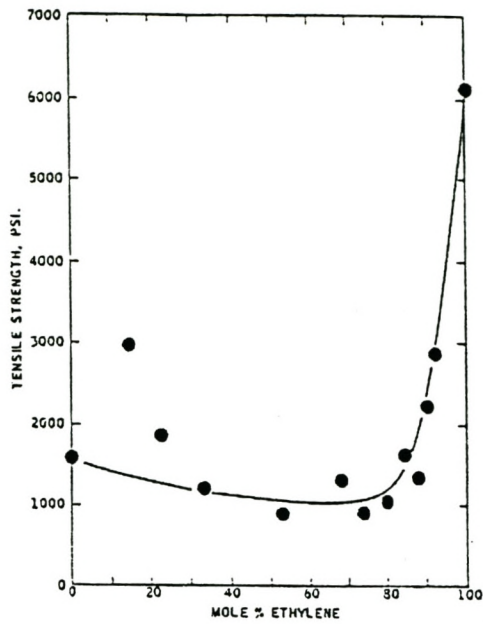


Figure 2-14 Effect of copolymer composition on Tensile strength. [36]

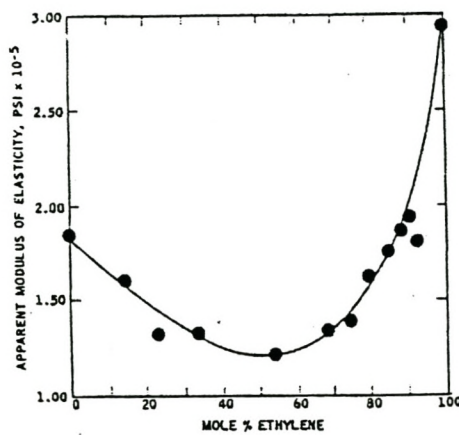


Figure 2-15 Effect of copolymer composition on Apparent modulus of Elasticity. [36]

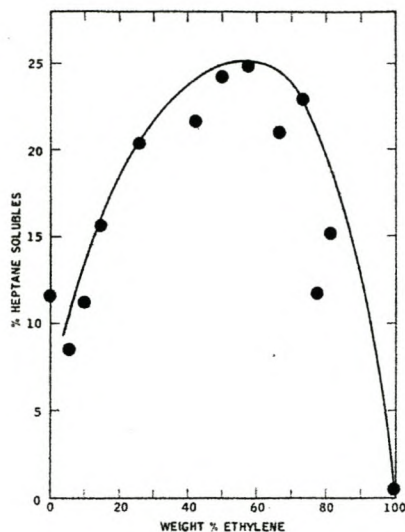
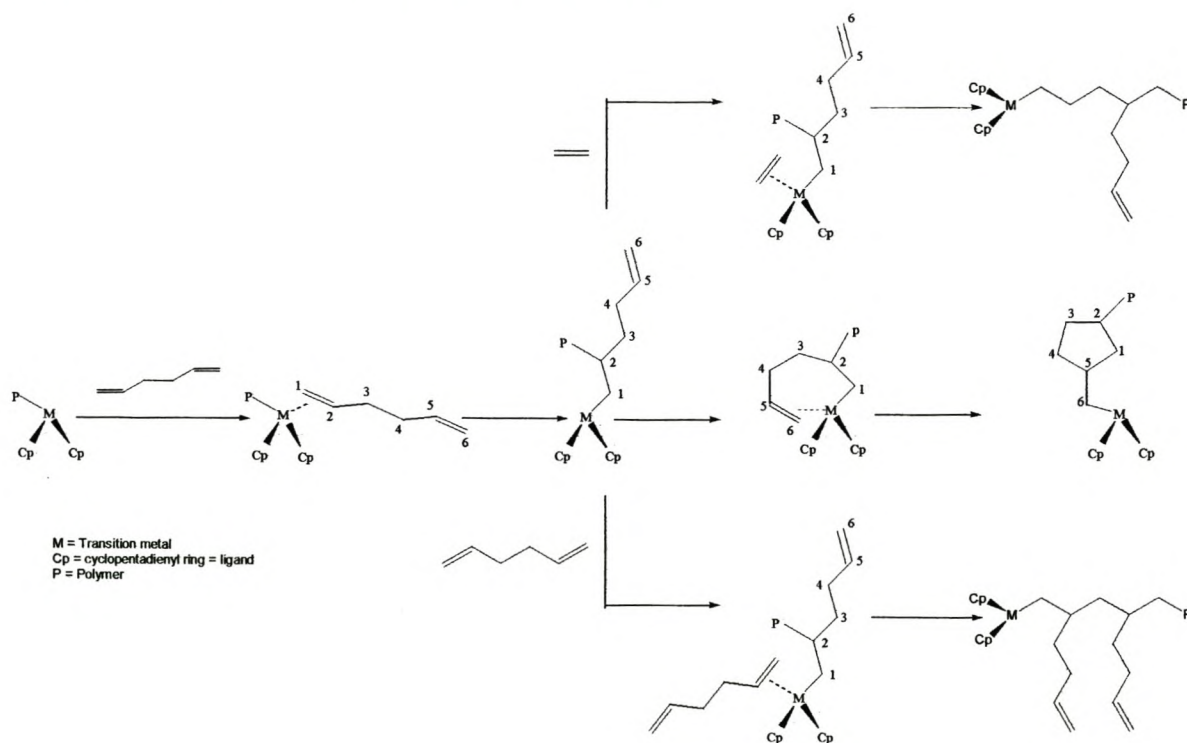


Figure 2-16 Effect of copolymer composition on Solubility of *n*-Heptane. [36]

Bergemann *et al* [37] reported the following reaction mechanism for the ethylene copolymerization of 1,5-hexadiene and ethylene:



Scheme 2-11 Reaction mechanism for the copolymerization of ethylene and 1,5-hexadiene. [37]

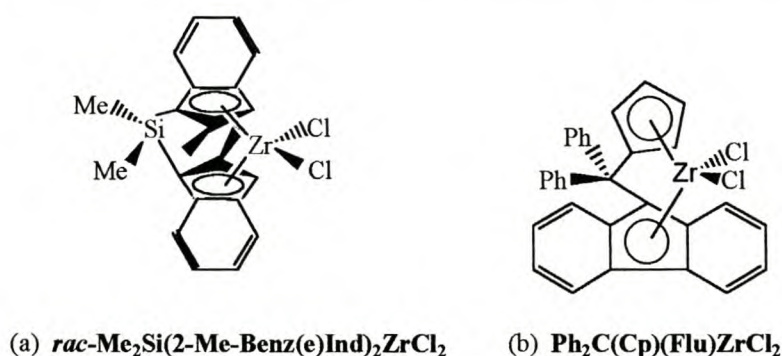
Their studies consisted of the high pressure (1 500bar) - high temperature (180°C) ethylene copolymerization of 1,5-hexadiene catalysed by  $\text{Cp}_2\text{ZrCl}_2$ , were

were compared to ethylene copolymerization with hexene copolymers under the same reaction conditions. The productivity of the copolymerisation was lower than that observed for ethylene homopolymerisation. Low diene concentration favoured cyclization of this monomer. A significant decrease in melting temperature with increasing diene content was also observed.

Crystallinity as high as ca 75% has been reported by Bergemann *et al.* Molecular weight as high as 432 000g/mole<sup>[38]</sup> and as low as 23 000g/mole<sup>[39]</sup> have been obtained by Pietikäinen *et al.* It has also been shown that *cis-trans* isomerism has a significant effect on the melting temperature of the material.

Literature was consistent that an increase in reaction temperature would result in a decrease in  $M_w$  and thus a decrease in the  $T_m$  of the material. More diene could also be incorporated at higher temperatures, although cyclization of this monomer is only favoured up to a certain concentration. One can therefore control the amount of cyclization and incorporation of unsaturated chain ends, for functionalisation and grafting, through the amount of the diene present in the reaction mixture.

Naga *et al* [38] compared the effect of isoselective (*rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub>) and syndioselective (Ph<sub>2</sub>C(Cp)(Flu)ZrCl<sub>2</sub>/ MAO) catalytic systems on 1,5-hexadiene and 1,7-octadiene during copolymerization with propylene. The structures of these catalytic systems used for these propylene copolymerisations can be seen in Figure 2-17.



**Figure 2-17** Catalytic systems for propylene copolymerisations: (a) *rac*-Me<sub>2</sub>Si(Ind)<sub>2</sub>ZrCl<sub>2</sub> and (b) Ph<sub>2</sub>C(Cp)(Flu)ZrCl<sub>2</sub>/ MAO.<sup>[40]</sup>



They concluded that propylene insertion could disturb the cyclization of 1,2-inserted dienes, except for 1,5-hexadiene with the syndiospecific catalyst (>98% cyclization). It was also found that the cyclization selectivity of 1,5-hexadiene was higher than for 1,7-octadiene. In both cases the cyclization activity decreased and the amount 1,5-hexadiene in the polymer increased with an increase in the diene concentration. Research from Naga *et al* also recorded detailed  $^{13}\text{C}$  NMR analysis, which will be referred to in section 4.2.

### 2.2.2.3 Terpolymerisation

Non-conjugated dienes, eg 1,5-hexadiene and ethylidene norbornene, are also well known for their use in EPDM rubber. This product normally consists of an ethylene/ propylene ratio of 55:45 with 2-5% incorporation of a non-conjugated diene <sup>[32]</sup>. Vanadium catalytic systems are currently commercially used in the production of EPDM rubber. There are however a few drawbacks to this system: low activity and productivity, the diene concentration is limited, the catalyst is poisonous and needs to be removed, and thus a restriction in application of the rubber <sup>[41,42]</sup>. Over the years researchers have identified certain requirements <sup>[40]</sup> for the catalysis of EPDM synthesis. Sufficient comonomer insertion rates are required; high yields - relative to catalyst amount and polymerisation time-random distribution of monomers; good control of molecular weight and distribution thereof, a low tendency to side reactions <sup>[42,43]</sup>. Most of these requirements are characteristic of metallocene catalytic systems. Dow and du Pont were also very impressed with what could be achieved with metallocenes and recently joined ventures to build a  $2 \times 10^8$  lb/yr plant for the use of metallocene technology in EPDM synthesis <sup>[44]</sup>.

## 2.3 **ECONOMICAL SYNTHESIS OF 1,5-HEXADIENE**

1,5-Hexadiene was previously synthesised as a by-product of cationic, anionic and Ziegler-Natta oligomerisations/ polymerisations. This was a very expensive method of synthesising this monomer, as only low yields were obtained.

Propylene is locally produced at SASOL, South Africa. The availability of this

versatile monomer makes the oxidative dimerisation of this olefin a very attractive solution for the feasible synthesis of 1,5-hexadiene:



**Scheme 2-12** Oxidative dimerisation of propylene for the synthesis of 1,5-hexadiene <sup>[43]</sup>

The oxidation of propylene is highly dependent on the catalyst used. Bukeikhanova *et al* <sup>[45]</sup> prepared amorphous microporous mixed oxides of indium and silicon (AMM –In<sub>x</sub>Si) via their acid-catalysed sol-gel method. It was shown that these materials are highly selective catalysts for the oxidative coupling of olefins. The high selectivity is attributed to the presence of isolated In-sites in the shape selective environment of the micropores of these materials. The best reaction conditions found were gas phase, atmospheric pressure and 550-600°C. Propylene conversion has reached 10% with selectivities higher than 80%.

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## Chapter 3 Experimental

### 3.1 MATERIALS AND EQUIPMENT

#### 3.1.1 Materials

All polymerisation reactions and the transferring of chemicals were done under an inert atmosphere. Nitrogen (Afrox) was used for this purpose.

##### 3.1.1.1 Solvents

Toluene and *n*-heptane (Aldrich) were dried by reflux over sodium. The reflux system was constantly kept under nitrogen and the drying process took about five hours.

Deuterated solvents (Aldrich) were placed on 4-Å molecular sieves (Merck) before use.

##### 3.1.1.2 Monomers

Ethylene (Afrox) was used as obtained. Propylene (Fedgas) was purified by passing it through two columns of copper-based catalysts (R3-11G and R3-12) from BASF and a column of 4-Å molecular sieves (Merck) to eliminate traces of water and oxygen. 1-Pentene (SASOL) and 1-hexene (SASOL) were dried on  $\text{LiAlH}_4$ .

1,5-Hexadiene (Aldrich) was dried over CaH (Merck) and distilled off before use. 2-Methyl-1,5-hexadiene (Aldrich) was used as supplied.

##### 3.1.1.3 Cocatalysts

Methylalumoxane, 10wt% solution in toluene (Aldrich), was used as purchased.

##### 3.1.1.4 Catalysts

$\text{Cp}_2\text{ZrCl}_2$  (Aldrich), *rac*-Et(Ind) $_2$ ZrCl $_2$  (Boulder Scientific) and *rac*-MeSi $_2$ [2-Me-Benz(e)Ind] $_2$ ZrCl $_2$  (Boulder Scientific) were used as supplied and stored under nitrogen atmosphere.

### 3.1.2 Polymerization equipment

The polymerisation reactions were carried out in teflon®-lined stainless steel Parr autoclaves (100ml and 350ml).



**Figure 3-1** Autoclaves used in polymerisations: a) 100ml (left) and b) 350ml (right).

The 100ml autoclave was used for the homopolymerisations and liquid-based copolymerisations. The autoclave was prepared under nitrogen atmosphere. A dry box equipped with a vacuum pump, nitrogen gas inlet and columns for the purification of the gas was used for this purpose. The 350ml autoclave, used for the gas-phase copolymerisations, was equipped with a gas inlet, two ball valves and a pressure gauge.

The reaction temperatures were controlled by the use of an oil bath and heater-stirrer equipped with contact thermometer.

The reactors, glass inlets and syringes were super-dried overnight in an oven at 120°C prior to use.

### 3.1.3 Analytical equipment

The microstructures of the polymers were determined by high temperature nuclear magnetic resonance (NMR) spectroscopy. Analysis was done on a Varian VXR 300 MHz NMR spectrometer. HMDS (hexamethyl disilane) was used as an internal standard with trichlorobenzene and tetrachloroethane (bp146°C) as solvents. Deuterated benzene was also used as an alternative lock solvent. Deuterated chloroform was used for the room temperature NMR analysis of oil-phase products and also obtained from Aldrich.

Differential scanning calorimetry (DSC) measurements were carried out on a PerkinElmer Pyris 1 instrument, at a heating rate of 10°C/ min.

Low temperature analysis was done on the PerkinElmer dynamic mechanical analyser (DMA 7e).

## 3.2 THE CYCLOPOLYMERISATION PROCESS

As mentioned in section 3.1.2, the 100ml autoclave was used for the homopolymerisation of 1,5-hexadiene (HD) and 2-methyl-1,5-hexadiene (MHD). The copolymerisations of HD with 1-pentene, 1-hexene and MHD were also carried out in the small autoclave.

The polymerisations were carried out as follows: a glass inlet (equipped with a magnetic stirrer bar), as well as the reactor, were dried overnight at 120°C in an oven and cooled under nitrogen atmosphere. The catalyst, still in powder form, was weighed in the dry box under nitrogen atmosphere. (The dry box, with the necessary equipment, was prepared with four vacuum-nitrogen purge cycles.) The catalyst was solvated by a predetermined amount of toluene and left overnight to ensure maximum solvation. Luer-lock glass syringes were used to add the solvent (*n*-heptane), cocatalyst (MAO), monomers and catalyst solution to the reactor. This was done under nitrogen atmosphere in a dry box. The reactor was assembled and placed in an oil bath to maintain the polymerisation temperature.

The 350ml autoclaves were used for the copolymerization of HD with ethylene and propylene.

The polymerisations were carried out as follows: a glass funnel, glass inlet (equipped with a magnetic stirrer bar), as well as the reactor, was super-dried overnight in a 120°C oven and cooled under nitrogen atmosphere. The catalyst, still in powder form, was weighed in the dry box under nitrogen atmosphere. (The dry box, with the necessary equipment, was prepared with four vacuum-nitrogen purge cycles.) The catalyst was dissolved by a predetermined amount of toluene and left overnight to ensure maximum dissolution. The reactor was assembled and cooled down under vacuum for 20 minutes. Purging with nitrogen followed to ensure an inert atmosphere. The solvent, cocatalyst, HD and catalyst solution were added whilst purging the reactor with nitrogen. The reactor was then weighed and then filled with the comonomer for the required amount of time. The reactor was then weighed again and the weight difference noted. The required polymerisation temperature was obtained by placing the autoclave in the pre-heated oil bath.

After polymerisation, both reactors were cooled, degassed and disassembled. The reaction product was quenched with a 10% acidic methanol solution. The solution was stirred overnight to ensure that the catalyst and cocatalyst were deactivated. The solution was then stirred while open to the atmosphere to allow the methanol to evaporate and then dried in a vacuum oven at 50°C.

The reaction conditions for all polymerisation reactions used in this study are summarised in Table 3-1.



**Table 3-1** Summary of reaction conditions used for the homo- and copolymerisations of 1,5-hexadiene.

| HOMOPOLYMERIZATIONS |                 |                            |  |                        |        |                     |                        |
|---------------------|-----------------|----------------------------|--|------------------------|--------|---------------------|------------------------|
| Reaction nr         | Monomer         | HD (mmole)                 | Catalyst   | Catalyst ( $\mu$ mole) | Al:Zr  | T <sub>r</sub> (°C) | t <sub>r</sub> (Hours) |
| 1                   | HD              | 25,27                      | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 1,026                  | 1000:1 | 25                  | 4                      |
| 14                  | HD              | 16,85                      | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 1,700                  | 2000:1 | 74                  | 4                      |
| 2                   | HD              | 25,27                      | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>                             | 2,400                  | 2000:1 | 25                  | 4                      |
| 15                  | HD              | 25,27                      | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>                             | 2,400                  | 2000:1 | 74                  | 4                      |
| 30                  | HD              | 25,27                      | <i>rac</i> -MeSi <sub>2</sub> (2-Me-Benz(e)Ind) <sub>2</sub> ZrCl <sub>2</sub> | 1,208                  | 1000:1 | 25                  | 4                      |
| 26                  | MHD             | 4,442                      | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 0,600                  | 1000:1 | 25                  | 4                      |
| 29                  | MHD             | 4,442                      | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>                             | 0,900                  | 2000:1 | 25                  | 4                      |
| COPOLYMERIZATIONS   |                 |                            |  |                        |        |                     |                        |
| Reaction nr         | Comonomer (CM)  | Monomer mole ratio (HD:CM) | Catalyst   | Catalyst ( $\mu$ mole) | Al:Zr  | T <sub>r</sub> (°C) | t <sub>r</sub> (Hours) |
| 5                   | Ethylene[1]     | 14,32/ 1MPa                | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 3,420                  | 2000:1 | 80                  | 1                      |
| 6                   | Ethylene[1]     | 35,38/ 1MPa                | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 3,420                  | 2000:1 | 80                  | 1                      |
| 32                  | Ethylene        | 15,16/ 1MPa                | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>                             | 2,309                  | 2000:1 | 80                  | 1                      |
| 33                  | Propylene       | 1:6.6                      | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 1,170                  | 2000:1 | 80                  | 18                     |
| 23                  | Propylene       | 1:6.6                      | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>                             | 1,194                  | 3000:1 | 80                  | 18                     |
| 16                  | 1-pentene       | 1:0.33                     | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 1,710                  | 2000:1 | 80                  | 3                      |
| 22                  | 1-pentene       | 0.33:1                     | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>                             | 1,194                  | 2000:1 | 90                  | 18                     |
| 17                  | 1-Hexene        | 1:0,5                      | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 1,710                  | 2000:1 | 80                  | 3                      |
| 20                  | 1-hexene        | 0.33:1                     | <i>rac</i> -Et(Ind) <sub>2</sub> ZrCl <sub>2</sub>                             | 1,194                  | 2000:1 | 90                  | 18                     |
| 31                  | Carbon monoxide | 15.16/ 1MPa                | <i>rac</i> -MeSi <sub>2</sub> (2-Me-Benz(e)Ind) <sub>2</sub> ZrCl <sub>2</sub> | 1,208                  | 2000:1 | 80                  | 1                      |
| 27                  | MHD             | 1:1                        | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 1,026                  | 2000:1 | 80                  | 4                      |
| 28                  | MHD             | 1:0.33                     | Cp <sub>2</sub> ZrCl <sub>2</sub>  | 1,026                  | 2000:1 | 80                  | 4                      |

All yields, except in the cases of ethylene- and propylene copolymers, were less than 1g.

### 3.3 REFERENCES

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## CHAPTER 4 Results and Discussion

For the sake of simplicity, “n” refers to polymers synthesized in the presence of  $\text{Cp}_2\text{ZrCl}_2$  as catalytic precursor, while “b” denotes synthesis in the presence of the *ansa* metallocene, *rac*-Et(Ind) $_2$ ZrCl $_2$ .

### 4.1 PHYSICAL STATE OF POLYMERS

Characterisation methods used for the various polymers synthesised were largely limited by their physical state – this can be seen in Table 4-1. Solubility is a determining factor in the use of NMR spectroscopy and molecular weight analysis. None of these polymeric materials listed in Tables 4-1 and 4-2 was soluble in tetrahydrofuran or trichlorobenzene, the result was that no gel permeation chromatography analysis at room- or at high temperature could be done for molecular weight determination. NMR analysis was thus used for this purpose where possible.

**Table 4-1** Homopolymers synthesised: their physical state and resulting analysis possibilities.

| HOMOPOLYMERS |                        |                 |     |     |     |      |
|--------------|------------------------|-----------------|-----|-----|-----|------|
| React nr     |                        | PHYSICAL STATE  | NMR | DMA | DSC | WAXS |
| 1            | 1,5-Hexadiene          | Viscous gel     | √   | √   | √   |      |
| 13           | 1,5-Hexadiene          | Viscous gel     |     |     |     |      |
| 15           | 1,5-Hexadiene          | Solid           | √   |     |     |      |
| 30           | 1,5-Hexadiene          | Insoluble Solid |     |     | √   |      |
| 34           | 1,5-Hexadiene          | Oil             | √   |     |     |      |
| 29           | 2-Methyl-1,5-Hexadiene | Viscous gel     | √   |     | √   |      |
| 26           | 2-Methyl-1,5-Hexadiene | Viscous gel     | √   |     | √   |      |

**Table 4-2** Copolymers synthesised: their physical state and resulting analysis possibilities.

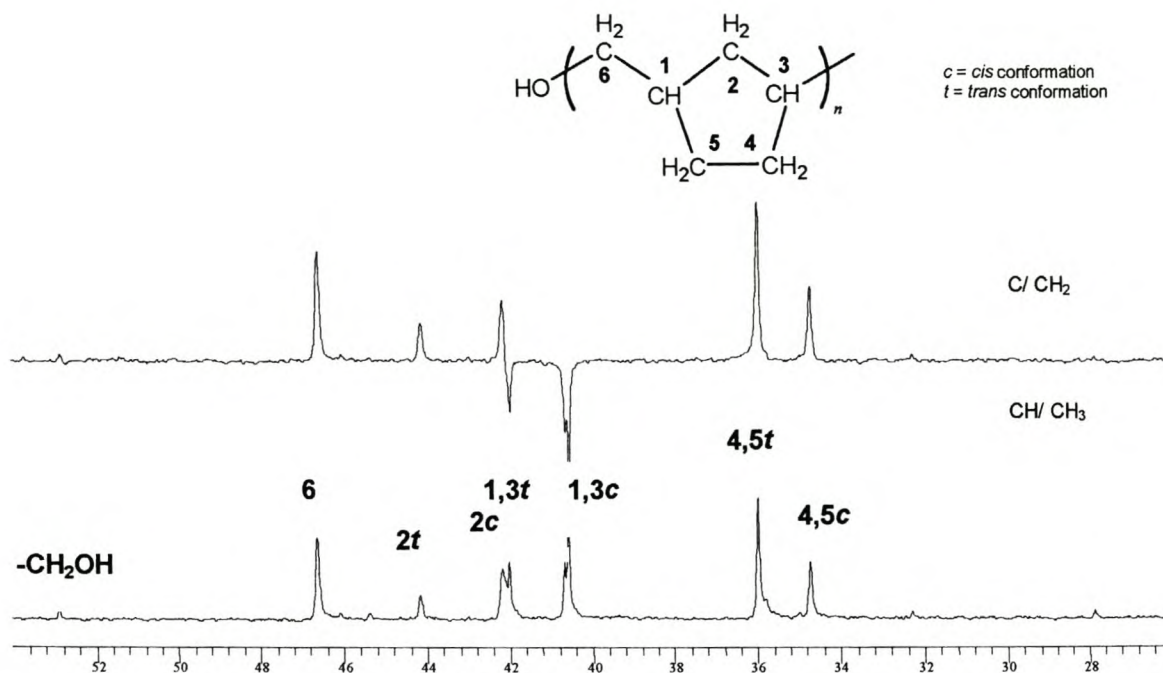
| COPOLYMERS |                        |                |     |     |     |      |
|------------|------------------------|----------------|-----|-----|-----|------|
| React nr   |                        | PHYSICAL STATE | NMR | DMA | DSC | WAXS |
| 5          | Ethylene               | Solid          | √   |     | √   | √    |
| 6          | Ethylene               | Solid          | √   |     | √   | √    |
| 32         | Ethylene               | Solid          | √   |     | √   | √    |
| 33         | Propylene              | Oil            | √   |     |     |      |
| 23         | Propylene              | Sticky solid   | √   | √   |     |      |
| 21         | 1-Pentene              | Viscous gel    | √   | √   | √   |      |
| 16         | 1-Pentene              | Viscous gel    | √   | √   |     |      |
| 20         | 1-Hexene               | Viscous gel    | √   | √   |     |      |
| 17         | 1-Hexene               | Viscous gel    | √   |     | √   |      |
| 28         | 2-Methyl-1,5-Hexadiene | Viscous gel    | √   | √   | √   |      |
| 27         | 2-Methyl-1,5-Hexadiene | Viscous gel    | √   | √   |     |      |

The determination of hard-to-detect transitions, like  $T_g$ , was mainly done by DMA, as DSC lacked the sensitivity for the detection of these transitions. Unfortunately, only samples that could be pressed into films could be analysed in this manner. In some cases, the samples degraded prior to melting, hence no films could be formed for DMA analysis.

#### 4.2 Characterization done by NUCLEAR MAGNETIC SPECTROSCOPY

All references made to literature in Section 4-2 refer to the work done by Cheng *et al*,<sup>[1]</sup> unless otherwise stated. In this section, NMR spectroscopy was used to comment on the microstructure, amount of cyclisation of the diene, stereoregularity, comonomer incorporation, number-average molecular weight and functionalisation of the obtained polymeric materials.

Peak assignments were made by use of literature and APT (attached proton test) experiments. APT spectra allowed us to differentiate between methylene/ quaternary carbons and methyl/ methine carbons. Figure 4-1 illustrates how peak assignments were confirmed by consideration of the corresponding APT spectra.



**Figure 4-1** APT (top) and  $^{13}\text{C}$  (bottom) NMR spectra of poly(1,5-hexadiene) synthesised at 74°C in the presence of  $\text{Cp}_2\text{ZrCl}_2$ .

These values were then correlated with the chemical shift assignments predicted by the additivity rules described by Grant and Paul [2]. Chemical shift predictions of a specific carbon, according to the additivity rules of Grant and Paul, are made by determining the combined effects of the neighbouring ( $\alpha$  up to  $\epsilon$ ) carbons. The following equation was proposed for this purpose:

$$\delta_{\text{C}} = \text{B} + \sum \text{A}_i n_i + \sum \text{S}_i$$

*Equation 4-1*

where

- B = Regression constant given by the chemical shift of methane (-1.87)
- $\text{A}_i$  = Additive shift due to carbon  $i$
- $\text{S}_i$  = Term included to account for branching
- $n_i$  = Number of carbons at position  $i$  away from carbon in question

The amount of carbons in the  $\alpha$ ,  $\beta$ ,  $\chi$ ,  $\delta$  and  $\epsilon$  position relative to the carbon in question, are counted and multiplied by the respective constants, given in Table 4-3.

**Table 4-3** Parameters for calculation of chemical shifts of alkanes, using the Empirical Additivity Relationships.

| Carbon Position | $A_i$ (ppm) |
|-----------------|-------------|
| $\alpha$        | 8.61        |
| $\beta$         | 9.78        |
| $\chi$          | -2.88       |
| $\delta$        | 0.37        |
| $\epsilon$      | 0.06        |

Apart from the standard influences of the neighbouring carbons, branching of the carbon chain also affects the chemical shift values. The following correction factors, shown in Table 4-4, must therefore be taken into account during the calculation of the chemical shift of a specific carbon:

**Table 4-4** Corrective term  $S_i$  for calculation of chemical shifts for branched alkanes, using the chemical shift relationships.

|                    | $S_i$ (ppm)      |
|--------------------|------------------|
| $1^\circ(3^\circ)$ | -1.40            |
| $1^\circ(4^\circ)$ | $-3.35 \pm 0.35$ |
| $2^\circ(3^\circ)$ | -2.45            |
| $2^\circ(4^\circ)$ | -7.50            |
| $3^\circ(2^\circ)$ | -2.65            |
| $3^\circ(3^\circ)$ | -9.45            |
| $4^\circ(1^\circ)$ | $-1.50 \pm 0.10$ |
| $4^\circ(2^\circ)$ | -8.35            |

$1^\circ(3^\circ)$  represents a methyl group attached to a tertiary carbon,  $2^\circ(3^\circ)$  represents a secondary carbon attached to a tertiary carbon and  $3^\circ(2^\circ)$  is a representation of

a tertiary carbon attached to a secondary carbon.

#### 4.2.1 Microstructure determination

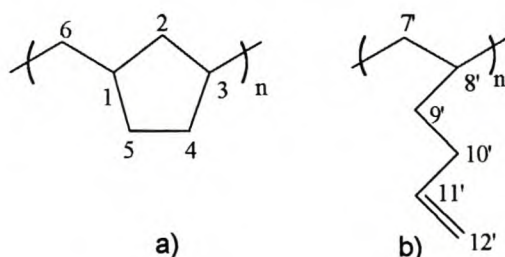
NMR analysis is the most important technique in polyolefin research for the determination of the microstructure of polymers. The chemical shift values for the carbons in 1,5-hexadiene oligomers/ polymers are quite complex. Not only do we need to consider cyclization-, termination- and side reactions, but tacticity and *cis*- and *trans*- conformations also contribute to the complexity of these spectra.

##### 4.2.1.1 Homopolymers

In this section, possible microstructures of the homopolymer poly(1,5-hexadiene) (HD) and poly(2-methyl-1,5-hexadiene) (MHD) will be presented and identified. The NMR spectra of homopolymers synthesised with various catalyst precursors and at different temperatures will also be compared.

##### a) Poly(1,5-Hexadiene)

The probable repeat unit structure of poly(1,5-hexadiene) is shown in Figure 4-2.

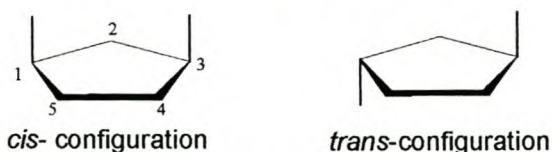


**Figure 4-2** Cyclised (a) and linear (b) repeat units in poly(1,5-hexadiene).

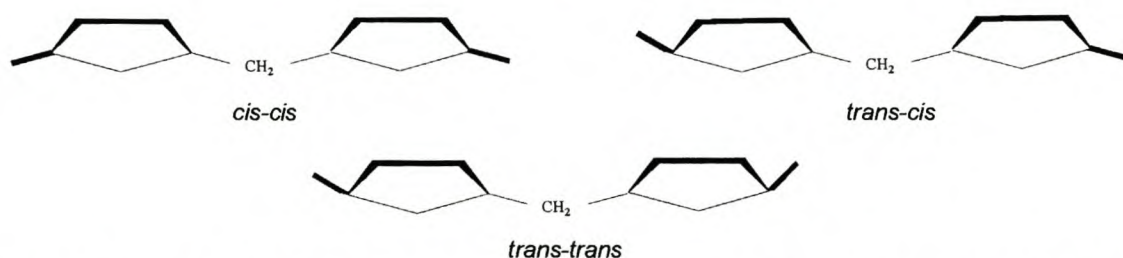
A number of stereochemical variations, with reference to the cyclised repeat unit structures (Fig 4-2(a)), are possible. The first is the effect of the placement of substituents (*cis-trans*) in the 1 and 3 positions of the cyclopentane ring (Fig 4-3). Then there are obviously the arrangements of the substituents on two adjacent rings, which can be *cis-cis*, *trans-cis* and *trans-trans*, as shown in Figure 4-4.

Cheng *et al* reported that the first stereochemical variations (Fig 4-3) have far

greater effect, evident in NMR spectra (ca. 1.7ppm), than the second stereochemical variations (Fig 4-4, around 0.05ppm).



**Figure 4-3** Stereochemical effects due to *cis-trans* placements of substituents on position 1 and 3 across the cyclopentane ring.



**Figure 4-4** Smaller stereochemical effect due to the same isomerism over the methylene bridges.

Cheng and his group were also the first to publish detailed  $^{13}\text{C}$  NMR spectrum of poly(1,5-hexadiene). This group of researchers made their assignments after consideration of APT NMR spectra and empirical additive rules as stated by Grant and Paul. Table 4-5 tabulates their findings:

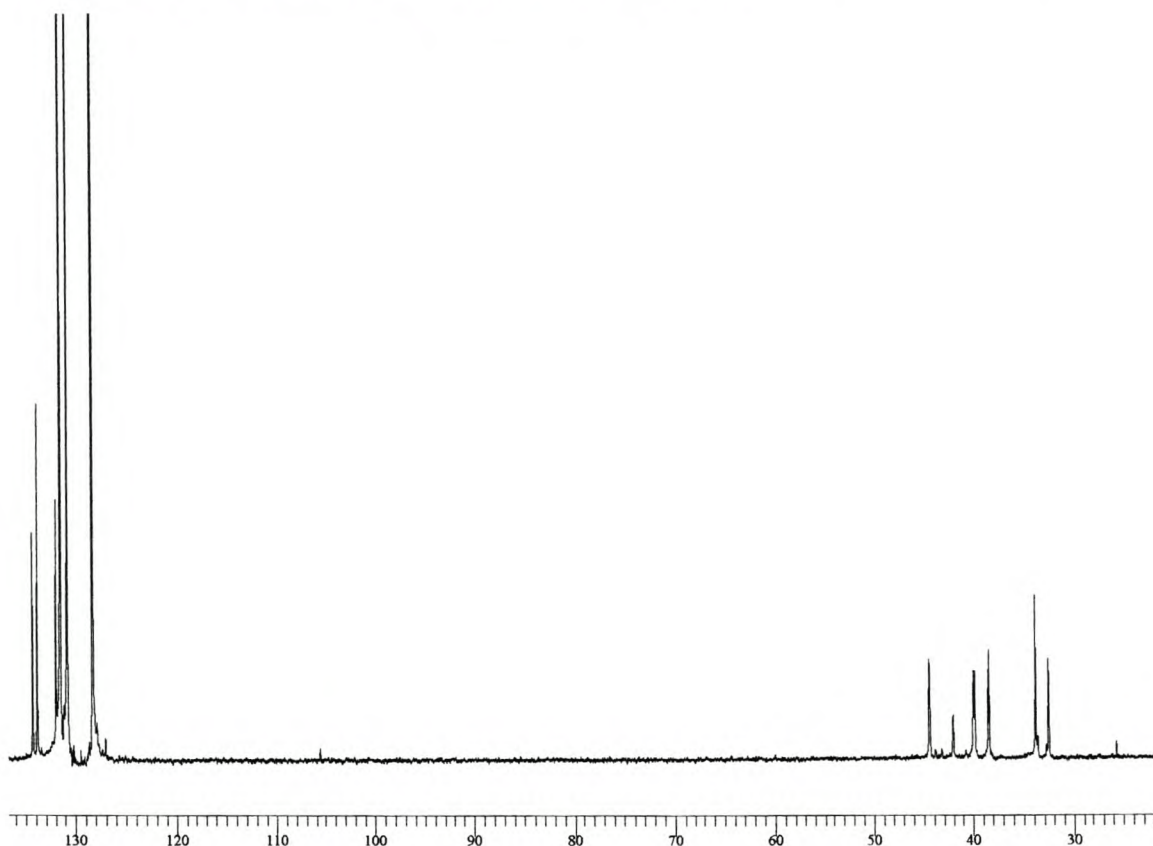
**Table 4-5**  $^{13}\text{C}$  NMR chemical shift assignments for the isomerism of the cyclic repeat units in poly(1,5-hexadiene), as observed by Cheng et al.

| Carbon <sup>a</sup> | Isomerism across ring | Isomerism across bridge | $^{13}\text{C}$ shift (ppm) |
|---------------------|-----------------------|-------------------------|-----------------------------|
| 6                   |                       | <i>trans-trans</i>      | 44.30                       |
|                     |                       | <i>cis-trans</i>        | 44.25                       |
|                     |                       | <i>cis-cis</i>          | 44.20                       |
| 2                   | <i>cis</i>            | <i>cis, trans</i>       | 41.93, 41.88                |
|                     | <i>trans</i>          |                         | 39.90                       |
| 1,3                 | <i>cis</i>            | <i>cis</i>              | 39.82                       |
|                     |                       | <i>trans</i>            | 39.75                       |
|                     | <i>trans</i>          | <i>trans</i>            | 38.45                       |
|                     |                       | <i>cis</i>              | 38.40                       |
| 4,5                 | <i>trans</i>          |                         | 33.72                       |
|                     | <i>cis</i>            |                         | 32.50                       |

<sup>a</sup>Carbons numbered as in Figure 4-2

The structure of the catalysts used in the polymerisation of 1,5-hexadiene, as well as the reaction conditions, has a significant influence on the microstructure and molecular weight of the formed oligomers/ polymers.

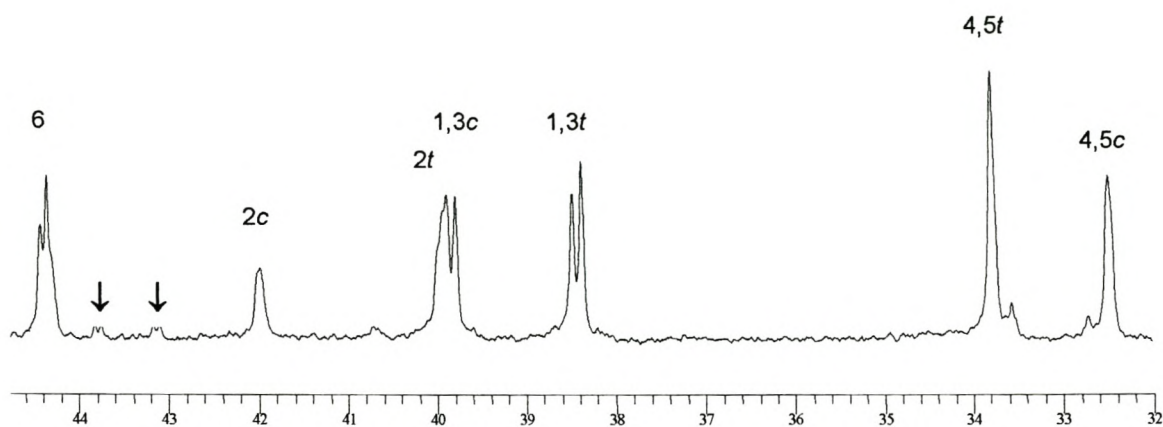
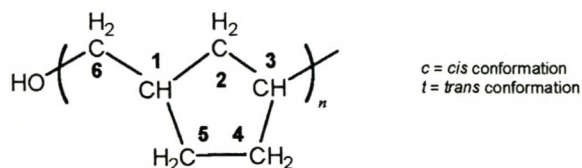
The first consideration was the influence of temperature on oligomers/ polymers synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  as catalyst. The full  $^{13}\text{C}$  NMR spectrum of poly(1,5-hexadiene), synthesised at 25°C, is shown in Figure 4-5, while the aliphatic/ cycloaliphatic region is shown in Figure 4-6.



**Figure 4-5** The full  $^{13}\text{C}$  NMR spectrum of poly(1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  at room temperature.

Trichlorobenzene and deuterated benzene relaxation peaks is observed in the 125-135ppm region. Carbon numbers identified in Figure 4-6 relates to the carbon assignments for the cyclic repeat unit, as seen in Figure 4-2, while *c* and *t* denote *cis*- and *trans* isomerisms respectively. The chemical shift assignments are summarised in Table 4-6.





**Figure 4-6**  $^{13}\text{C}$  NMR spectrum (aliphatic/ cyloaliphatic region) of poly(1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  at room temperature.

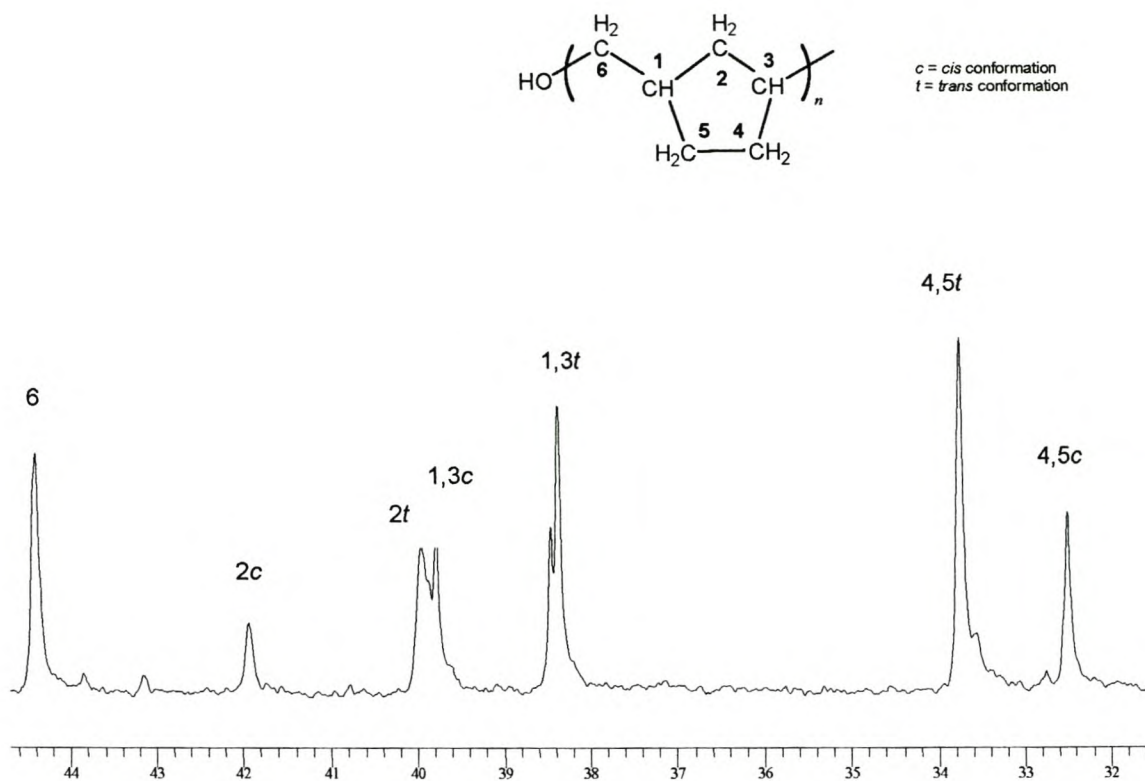
The chemical shift assignments, as determined from the  $^{13}\text{C}$  and APT NMR spectra, are tabulated in Table 4-6 and compared to the values reported (theoretical) by Cheng *et al* in Table 4-5.

**Table 4-6** *Poly(1,5-hexadiene), synthesised at room temperature in the presence of Cp<sub>2</sub>ZrCl<sub>2</sub> - Comparison of actual and theoretical <sup>13</sup>C NMR chemical shift values.*

| Carbon | Isomerism across ring | Isomerism across bridge | <sup>13</sup> C Shift (ppm) (Actual) | <sup>13</sup> C Shift (ppm) (Cheng et al) |
|--------|-----------------------|-------------------------|--------------------------------------|---|
| 6      |                       | <i>cis-trans</i>        | 44.35                                | 44.25                                     |
|        |                       | <i>cis-cis</i>          | 44.20                                | 44.20                                     |
| 2      | <i>cis</i>            | <i>cis, trans</i>       | 41.98                                | 41.93, 41.88                              |
|        | <i>trans</i>          |                         | 39.90                                | 39.90                                     |
| 1,3    | <i>cis</i>            | <i>cis</i>              | 39.77                                | 39.82                                     |
|        |                       | <i>trans</i>            | 38.36                                | 38.40                                     |
|        | <i>trans</i>          | <i>trans</i>            | 38.47                                | 38.45                                     |
| 4,5    | <i>trans</i>          |                         | 33.79                                | 33.72                                     |
|        | <i>cis</i>            |                         | 32.49                                | 32.50                                     |

As can be seen from Table 4-5, there is excellent correlation between the predicted and the experimentally determined <sup>13</sup>C NMR chemical shift values. In addition, very little evidence of uncyclised (pendant vinyl) monomer could be found. This will be addressed in further detail in Section 4.1.2.

The <sup>13</sup>C NMR spectrum (aliphatic and cycloaliphatic region) of poly(1,5-hexadiene) synthesised at 74°C is shown in Figure 4-7. The same catalyst was used as for the synthesis of the polymer in Figure 4-6.



**Figure 4-7** ***<sup>13</sup>C NMR Spectrum (aliphatic/ cycloaliphatic region) of poly(1,5-hexadiene) synthesised in the presence of Cp<sub>2</sub>ZrCl<sub>2</sub> at 74 °C.***

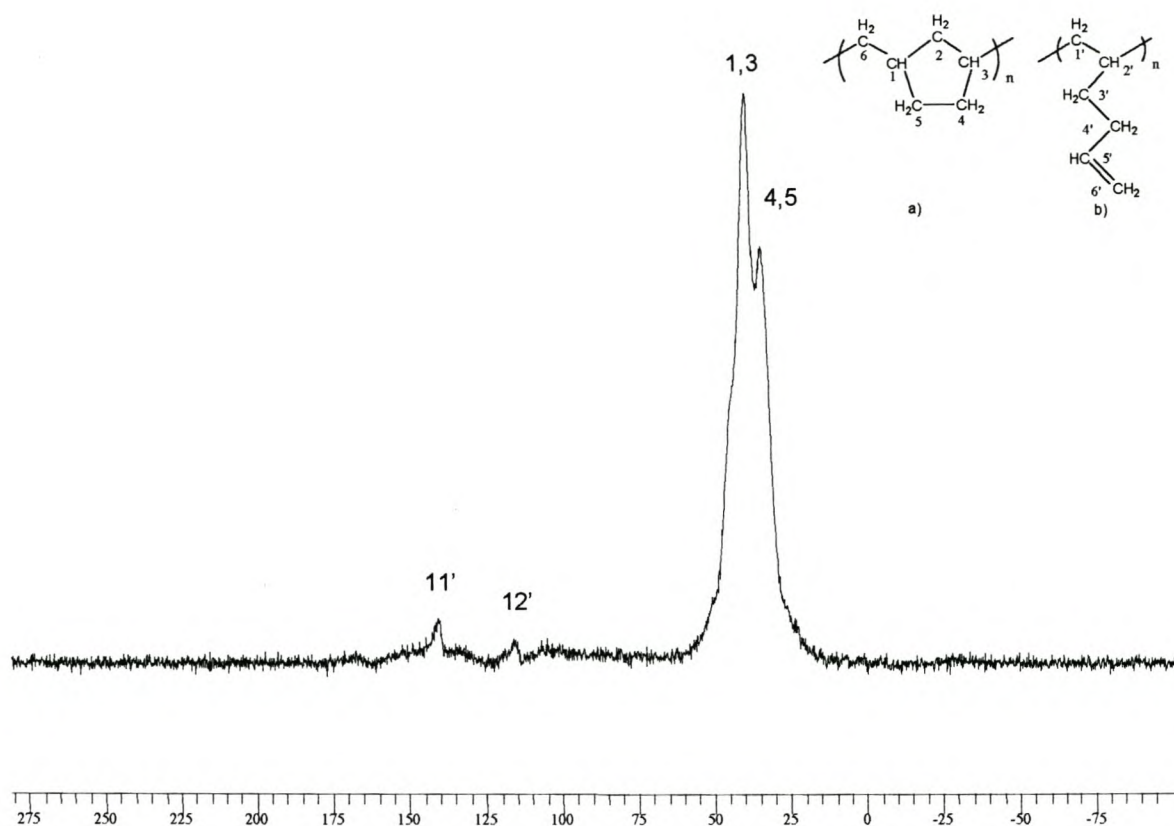
The spectra in Figures 4-6 and 4-7 are virtually identical. Differences observed refer to C<sub>6</sub> isomerism. The shoulders observed on the C<sub>4,5</sub> resonance peaks are probably due to tacticity. It is noticeable that only the *cis*-*trans* isomerism is present. All peaks identified in the above <sup>13</sup>C NMR spectra supported cyclization. The two resonance peaks observed at 43ppm, in both spectra, could possibly be explained through the observation of last monomer insertion discrepancies and chain termination possibilities. The chemical shift and peak assignments for Figure 4-7 are summarised in Table 4-7.

**Table 4-7** Poly(1,5-hexadiene), synthesised at 74°C in the presence of Cp<sub>2</sub>ZrCl<sub>2</sub>- Comparison of actual and theoretical <sup>13</sup>C NMR chemical shift values.

| Carbon | Isomerism across ring | Isomerism across bridge | <sup>13</sup> C shift (ppm) (Actual) | <sup>13</sup> C shift (ppm) (Cheng et al) |
|--------|-----------------------|-------------------------|--------------------------------------|---|
| 6      |                       | <i>cis-trans</i>        | 44.42                                | 44.30                                     |
| 2      | <i>cis</i>            | <i>cis, trans</i>       | 41.95                                | 41.93, 41.88                              |
|        | <i>trans</i>          |                         | 39.96                                | 39.90                                     |
| 1,3    | <i>cis</i>            | <i>cis</i>              | 39.97                                | 39.82                                     |
|        | <i>trans</i>          | <i>trans</i>            | 38.46                                | 38.45                                     |
|        |                       | <i>cis</i>              | 38.35                                | 38.40                                     |
| 4,5    | <i>trans</i>          |                         | 33.76                                | 33.72                                     |
|        | <i>cis</i>            |                         | 32.49                                | 32.50                                     |

Peak identification was once again mainly based on literature and supported by APT spectra. Both *cis-trans*- and *cis-cis* isomerism across the methylene bridge of C<sub>6</sub> were favoured during polymerisation at room temperature (Figure 4-5), while only *cis-trans* isomerism was favoured in the case of cyclopolymerisation at 74°C (Figure 4-6).

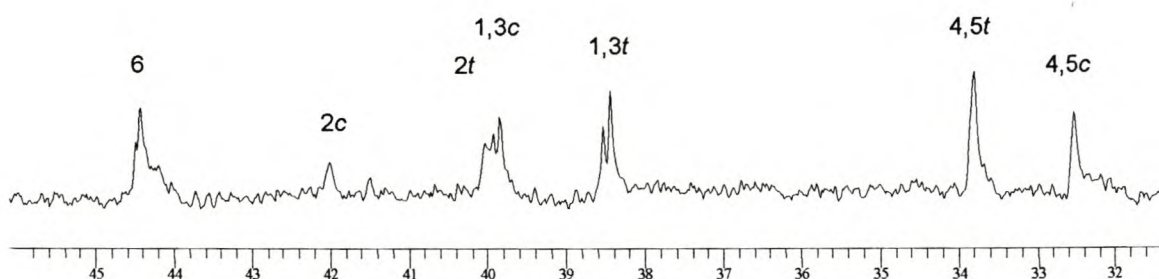
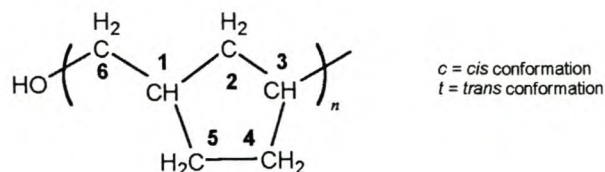
Figure 4-8 illustrates the solid state NMR spectrum obtained for the homopolymer synthesised at room temperature with the C<sub>2</sub> symmetric *ansa* metallocene, *rac*-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub>, as the catalyst precursor.



**Figure 4-8** The full solid state NMR spectrum of poly(1,5-hexadiene) synthesised in the presence of  $\text{rac-Et(Ind)}_2\text{ZrCl}_2$  at room temperature.

One can clearly identify the C relaxation peaks due to cyclization (at 38.94ppm and 30.00ppm), as well as those related to 1,2-insertion of the monomer (at 140ppm and 116ppm). It is thus clear that 1,5-hexadiene was polymerised. Solid State NMR spectra can unfortunately not be used for quantitative measurements. The insolubility of this polymer is a result of the presence of pendant vinyl groups, which results in cross-linking of the polymer.

A soluble homopolymer was obtained, using the  $C_2$  symmetric *ansa* metallocene at 74°C, as seen in Figure 4-9.



**Figure 4-9**  $^{13}\text{C}$  NMR spectrum (aliphatic/ cycloaliphatic region) of poly(1,5-hexadiene) synthesised in the presence of  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$  at  $74^\circ\text{C}$ .

Figures 4-6, 4-7 and 4-9 illustrate the large effect the choice of catalyst, as well as reaction temperature has on the microstructure of the polymer. The largest effect can be seen by comparing the stereoregularity data obtained for  $\text{C}_6$  and  $\text{C}_{1,3}$ . In Figure 4-6, *cis-cis* and *cis-trans* isomerism across the bridge was observed for  $\text{C}_6$ , while the data in Figure 4-7 only denotes *cis-trans* isomerism. A change in catalyst precursor, results not only in the presence of *trans-trans* isomerism across bridge (Figure 4-9), but also *cis-trans*- and *cis-cis* isomerism. Variation of the above reaction conditions also result in control of the isomerism observed for  $\text{C}_{1,3}$ .

Table 4-8 tabulates the chemical shift assignments for Figure 4-9 and a comparison is made to the theoretical values.

**Table 4-8** *Poly(1,5-hexadiene), synthesised at 74°C in the presence of rac-Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> - Comparison of actual and theoretical <sup>13</sup>C NMR Chemical Shift values.*

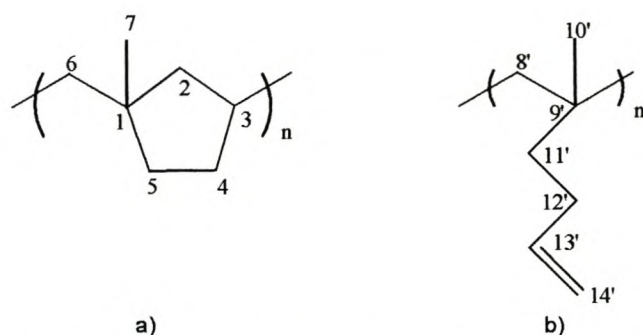
| Carbon | Isomerism across ring | Isomerism across bridge | <sup>13</sup> C shift (ppm) (Experimental) | <sup>13</sup> C shift (ppm) (Cheng <i>et al</i> ) |
|--------|-----------------------|-------------------------|--|---|
| 6      |                       | <i>trans-trans</i>      | 44.47                                      | 44.30   |
|        |                       | <i>cis-trans</i>        | 44.42                                      | 44.25   |
|        |                       | <i>cis-cis</i>          | 44.21                                      | 44.20   |
| 2      | <i>cis</i>            | <i>cis, trans</i>       | 41.98, 41.48                               | 41.93, 41.88                                      |
|        | <i>trans</i>          |                         | 40.00                                      | 39.90   |
| 1,3    | <i>cis</i>            | <i>cis</i>              | 39.90                                      | 39.82   |
|        |                       | <i>trans</i>            | 39.80                                      | 39.75   |
|        | <i>trans</i>          | <i>trans</i>            | 38.51                                      | 38.45   |
|        |                       | <i>cis</i>              | 38.41                                      | 38.40   |
| 4,5    | <i>trans</i>          |                         | 33.78                                      | 33.72   |
|        | <i>cis</i>            |                         | 32.50                                      | 32.50   |

A closer look to the isomerism results summarised in Tables 4-6 to 4-8 indicates that the *ansa* metallocene has a far greater influence on the polymerisation mechanism of the 1,5-hexadiene, in comparison to Cp<sub>2</sub>ZrCl<sub>2</sub> as catalytic precursor. The chiral catalyst must obviously direct the stereochemistry of the cyclization reaction. This is evident by the change in microstructure as observed in Figures 4-6, 4-7 and 4-9.

*b) Poly(2-Methyl-1,5-hexadiene)*

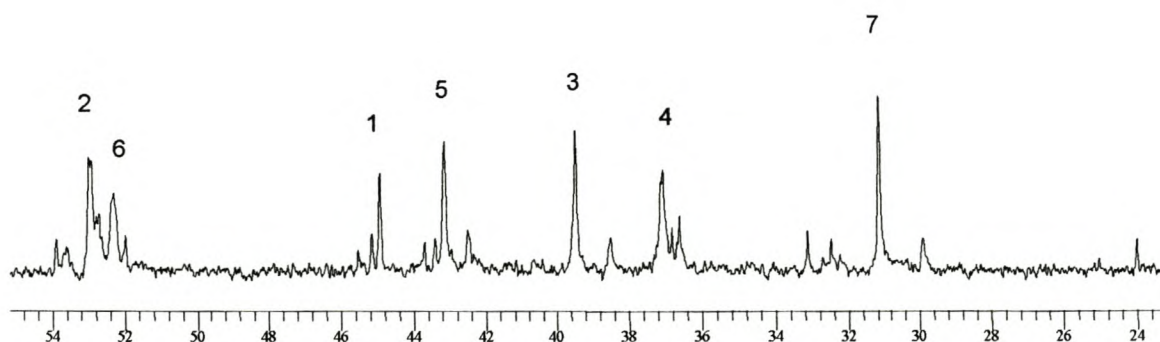
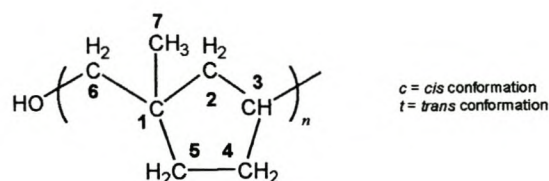
The presence of the methyl group in the 2 position of 1,5-hexadiene was expected to have a pronounced influence on the cyclization and the microstructure of the polymers in comparison to the 1,5-hexadiene homopolymers. The methyl group served as a source of steric hindrance, with reference to the insertion of the monomer in the polymer chain via metallocene catalysis.

Possible repeat units for poly(2-methyl-1,5-hexadiene) can be seen in Figure 4-10:



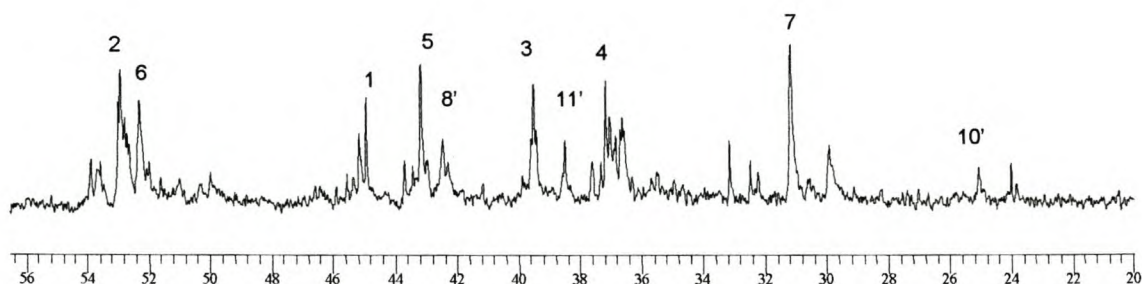
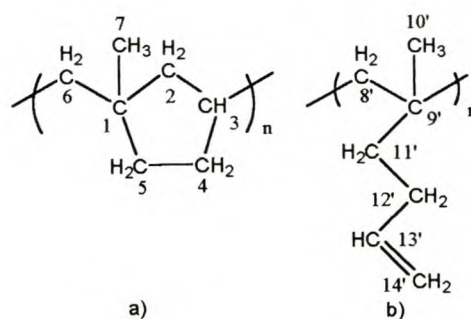
**Figure 4-10** Cyclised (a) and linear (b) repeat units for poly(2-methyl-1,5-hexadiene) (aliphatic/cycloaliphatic region).

Analysis of 2-methyl-1,5-hexadiene homopolymers were a lot more difficult and complex compared to the analysis of 1,5-hexadiene.  $^{13}\text{C}$  NMR spectra of poly(2-methyl-1,5-hexadiene) is shown in Figures 4-11 and 4-12.



**Figure 4-11**  $^{13}\text{C}$  NMR Spectra (aliphatic/ cycloaliphatic region) of poly(2-methyl-1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$ .





**Figure 4-12**  $^{13}\text{C}$  NMR Spectra (aliphatic/ cycloaliphatic region) of poly(2-methyl-1,5-hexadiene) synthesised in the presence of *rac*-Et(Ind) $_2$ ZrCl $_2$ .

In Figure 4-11 and Figure 4-12, it was possible to identify the resonance peaks that resulted from the cyclopolymerisation of 2-methyl-1,5-hexadiene. Speculations regarding the chemical shifts for the linear repeat units were also made as far as possible and confirmed with APT spectra and theoretical values. In Table 4-9, the  $^{13}\text{C}$  NMR chemical shift values for poly(2-methyl-1,5-hexadiene), synthesised by the  $C_{2v}$  symmetric ( $\text{Cp}_2\text{ZrCl}_2$ ) and  $C_2$  symmetric *ansa* (*rac*-Et(Ind) $_2$ ZrCl $_2$ ) metallocenes, are presented and compared (Figure 4-11 and Figure 4-12). Chemical shifts between 54ppm and 53ppm are most probably the result of  $-\text{CH}_2\text{OH}$  end groups, resulting from chain transfer to aluminium. (APT spectra confirmed that these peaks are due to methylene carbons)

**Table 4-9** *Poly(2-methyl-1,5-hexadiene) synthesised at room temperature in the presence of  $Cp_2ZrCl_2$  and  $rac-Et(Ind)_2ZrCl_2$  - Comparison of actual and theoretical  $^{13}C$  NMR Chemical Shift values.*

| Carbon | $^{13}C$ shift (ppm)<br>( $Cp_2ZrCl_2$ ) | $^{13}C$ shift (ppm)<br>( $rac-Et(Ind)_2ZrCl_2$ ) | $^{13}C$ shift (ppm)<br>(Theoretical) |
|--------|--|---|---------------------------------------|
| 1      | 44.91                                    | 44.89   | 46.73                                 |
| 2      | 52.94                                    | 52.93   | 52.63                                 |
| 3      | 39.49                                    | 39.47   | 32.24                                 |
| 4      | 37.06                                    | 37.15   | 29.45                                 |
| 5      | 43.11                                    | 43.13   | 42.48                                 |
| 6      | 52.32                                    | 52.29   | 43.36                                 |
| 7      | 31.12                                    | 31.17   | 31.78                                 |
| 8'     |  | 42.43   | 44.30                                 |
| 9'     |  |   | 38.71                                 |
| 10'    |  | 23.99   | 22.01                                 |
| 11'    |  | 39.49   | 39.97                                 |
| 12'    |  |   | 19.36                                 |
| 13'    |  | 112.35  | 137.70                                |
| 14'    |  | 137.94  | 114.30                                |

Methyl peaks observed at 23.99ppm in Figure 4-11 and Figure 4-12 are in the region where methyl groups due to polymer chain termination are observed. The presence of vinyl end groups was observed for the homopolymer synthesised in the presence of  $rac-Et(Ind)_2ZrCl_2$  as catalyst. (Full cyclization was thus not obtained (Section 4.1.2.3).) The relaxation peak of C9', a quaternary carbon, is very difficult to observe and often noted very lower than the predicted value.

#### 4.2.1.2 Copolymers

In this section, possible microstructures of copolymers will be proposed. 1,5-Hexadiene copolymers were synthesised with ethylene, propylene, 1-pentene, 1-hexene and 2-methyl-1,5-hexadiene as comonomers. The NMR spectra of copolymers synthesised with various catalysts will also be compared. The proposed insertion modes of 1,5-hexadiene when copolymerised with ethylene are shown in Figure 4-13.

## a) Poly(ethylene-co-1,5-hexadiene)

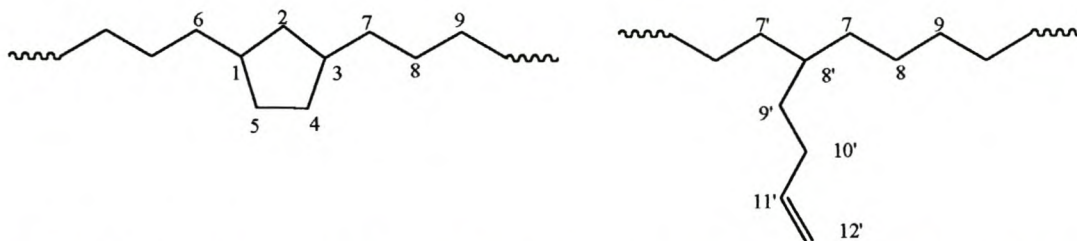


Figure 4-13 Simple cyclised- (a) and linear (b) repeat units in poly(ethylene-co-1,5-hexadiene).

Figure 4-14 shows the  $^{13}\text{C}$  NMR spectra for the synthesised ethylene copolymers.

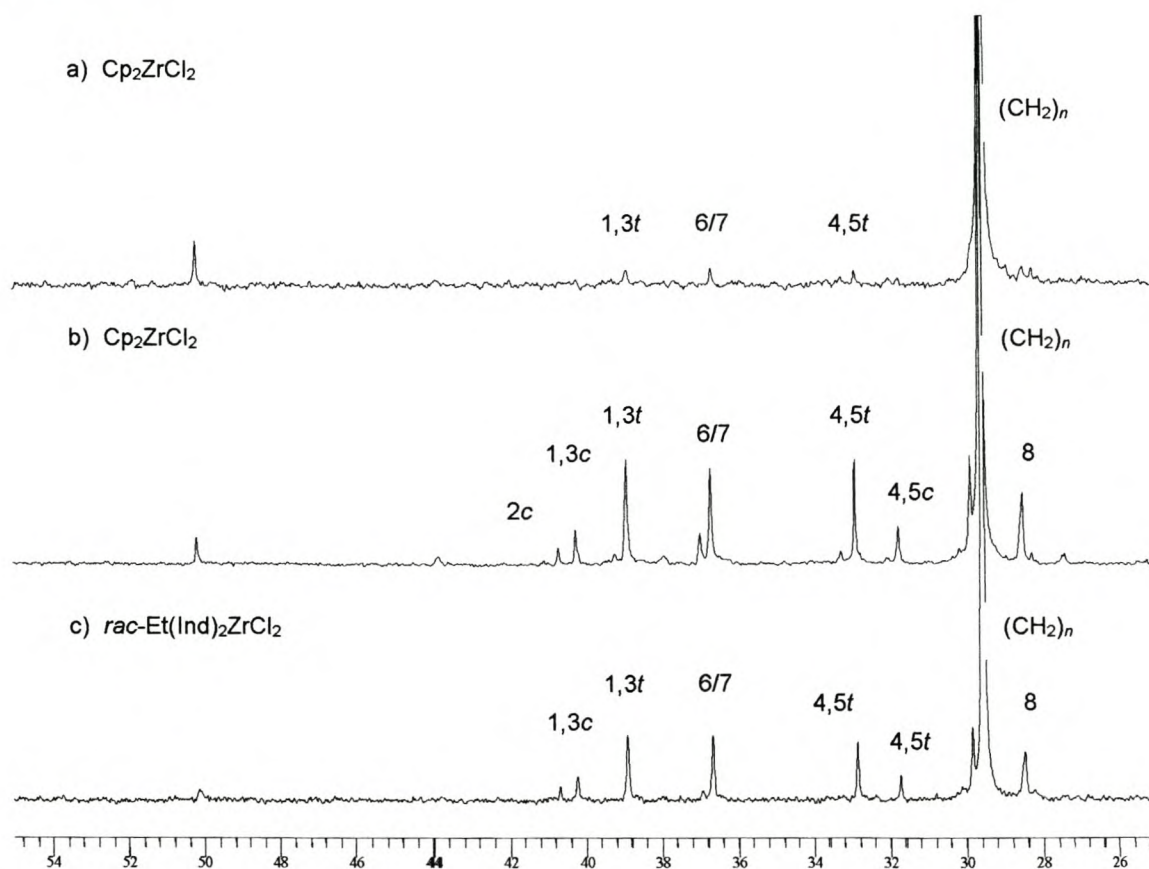


Figure 4-14  $^{13}\text{C}$  NMR Spectra (aliphatic/ cycloaliphatic region) of poly(ethylene-co-1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  (top and middle) and  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$  as catalysts.

The chemical shift values for the three ethylene copolymers, synthesised under different reaction conditions, are tabulated and compared to theoretical values in

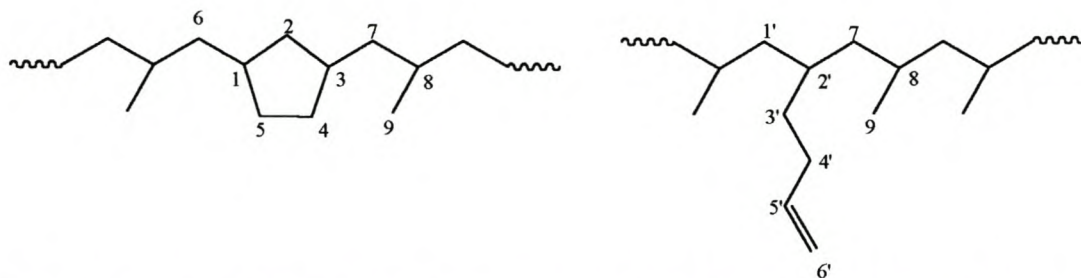
table 4-10.

**Table 4-10** Poly(ethylene-co-1,5-hexadiene) - Comparison of actual and theoretical  $^{13}\text{C}$  NMR chemical shift values.

| Carbon            | $^{13}\text{C}$ Shift (ppm)<br>(a) $\text{Cp}_2\text{ZrCl}_2$ | $^{13}\text{C}$ Shift (ppm)<br>(b) $\text{Cp}_2\text{ZrCl}_2$ | $^{13}\text{C}$ Shift (ppm)<br>(c) <i>rac</i> - $\text{et}(\text{Ind})_2\text{ZrCl}_2$ | $^{13}\text{C}$ Shift (ppm)<br>(Theoretical) <sup>A</sup> |
|-------------------|---|---|--|---|
| 1,3c              |   | 40.24   | 40.21  | 33.70   |
| 1,3t              | 38.88   | 38.90   | 38.89  | 33.70   |
| 2c                |   | 40.69   | 40.66  | 35.00   |
| 2t                |   |   |  | 35.00   |
| 4,5c              |   | 31.75   | 31.71  | 28.10   |
| 4,5t              | 32.85   | 32.87   | 32.83  | 28.10   |
| 6/7               | 36.65   | 36.96/ 36.69  | 36.66  | 34.70   |
| 8                 | 28.44/ 28.18  | 28.48   | 28.45  | 28.10   |
| 9                 |   | 29.85   | 29.81  | 30.60   |
| $(\text{CH}_2)_n$ | 29.52   | 29.57   | 29.53  | 30.30   |

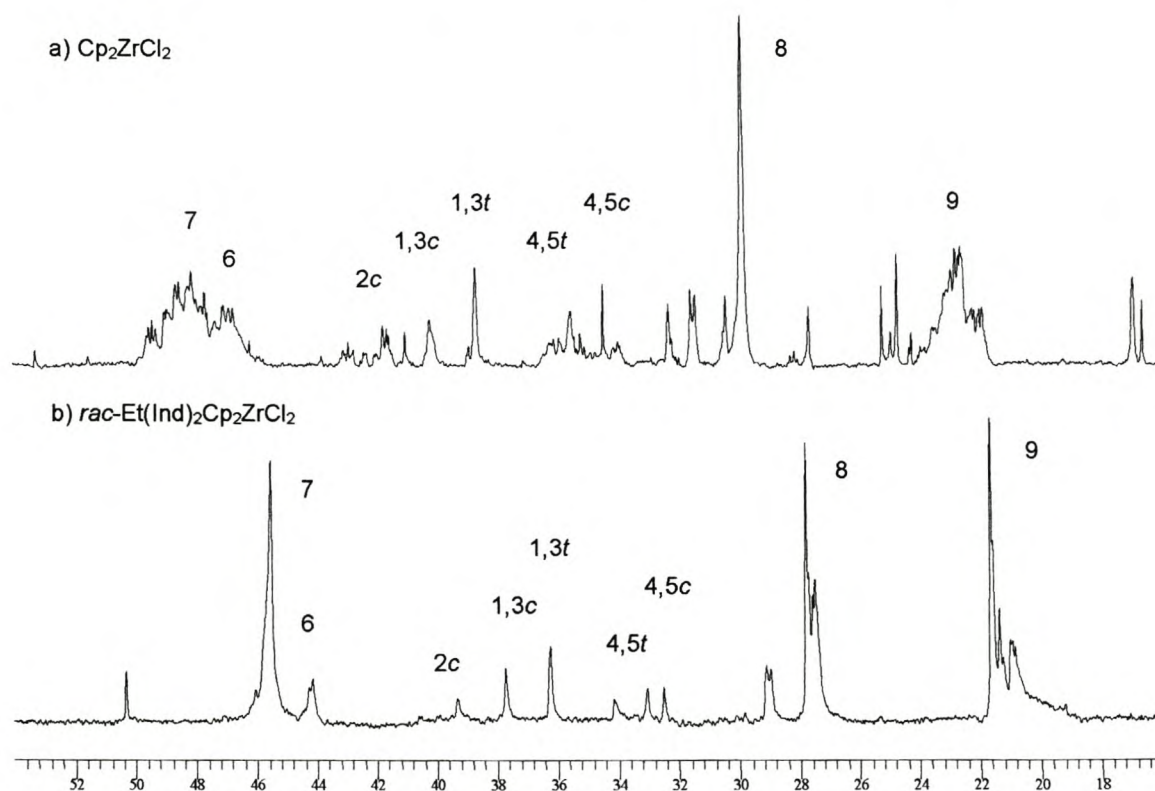
Figure 4-14 (b) is that of the ethylene copolymer synthesised under the same polymerisation conditions as used in obtaining the polymeric material in Figure 4-14 (a). The former, however, was made with double the amount of 1,5-hexadiene monomer than the latter (see Table 3-1). In all three cases,  $-\text{CH}_2\text{OH}$  end groups (transfer to aluminium) were observed in the region of 53ppm. Ethylene peak assignments, as well as identification of the carbons for the cyclic repeat unit for 1,5-hexadiene, were made possible by detailed  $^{13}\text{C}$  NMR work done by Pietikäinen *et al*<sup>[3]</sup>. The presence of the  $-\text{CH}_2\text{OH}$  end group (in region of 53ppm) in all three the spectra and the intensity with which they are observed. Significant differences in the microstructure of carbon 8 were observed in Figure 4-14.

The proposed insertion modes of 1,5-hexadiene, when copolymerised with propylene, are shown in Figure 4-15.

b) *Poly(propene-co-1,5-hexadiene)*

**Figure 4-15** Simple cyclised- and linear repeat units in *poly(propene-co-1,5-hexadiene)*.

The  $^{13}\text{C}$  NMR spectra of the propylene copolymers, are given in Figure 4-16.



**Figure 4-16**  $^{13}\text{C}$  NMR Spectra (aliphatic/ cycloaliphatic region) of *poly(propene-co-1,5-hexadiene)* synthesised in the presence of (a)  $\text{Cp}_2\text{ZrCl}_2$ , with chloroform as solvent for NMR analysis, and (b)  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ , with trichlorobenzene as solvent for NMR analysis.

The  $^{13}\text{C}$  NMR spectra in Figure 4-16 are excellent examples of the difference between atactic (a) and isotactic (b) polymeric materials. The shift of the

propylene relaxation peaks from one spectrum to the other is due to the difference in solvents used for the NMR analysis. The *ansa* metallocene shows much more control with reference to the way of monomer insertion, than observed in the case of zirconocene dichloride as metallocene catalyst. Relaxation peaks in the region of 53ppm (Figure 4-16(a)) and 50ppm (Figure 4-16(b)) relates to  $-\text{CH}_2\text{OH}$  end groups resulting from chain termination via transfer to aluminium. In Figure 4-17 (b) peaks in the region of 22ppm are observed and noted as  $-\text{CH}_3$  end groups. These peaks might also be present in Figure 4-16(a), but are over shadowed by the relaxation peaks for  $\text{C}_9$ . Table 4-11 summarises the  $^{13}\text{C}$  NMR chemical shifts as concluded.

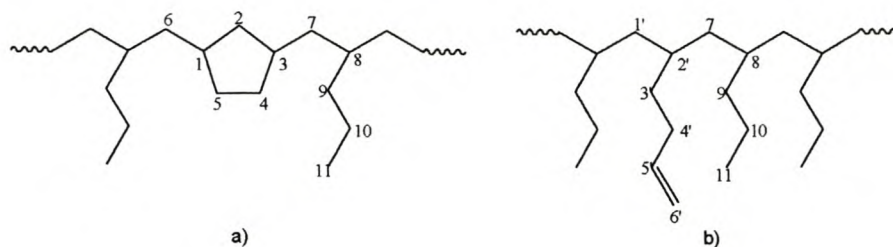
**Table 4-11** *Poly(propene-co-1,5-hexadiene) - Comparison of actual and theoretical  $^{13}\text{C}$  NMR Chemical Shift values.*

| Carbon | $^{13}\text{C}$ Shift (ppm)<br>( $\text{Cp}_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ Shift (ppm)<br>( $\text{rac-et}(\text{Ind})_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ Shift (ppm)<br>(Theoretical) <sup>a</sup> |
|--------|---|---|---|
| 1,3c   | 41.10   | 38.40   | 35.04   |
| 1,3t   | 38.59   | 36.04   | -   |
| 2c     | 41.66   | 39.10/ 39.00/ 38.90   | 37.06   |
| 2t     | 41.15   |   | -   |
| C4,5c  | 34.93   | 31.81   | 29.62   |
| C4,5t  | 35.44   | 32.87   | -   |
| 6      | 46.69/46.58   | 44.58/ 44.12  | 33.50   |
| 7      | 47.95   | 46.09-45.03   | 33.87   |
| 8      | 30.21/ 29.86  | 27.79/ 27.24  | 20.35   |
| 9      | 23.98/ 23.73/ 23.37/ 23.22                                    |   | 11.60   |

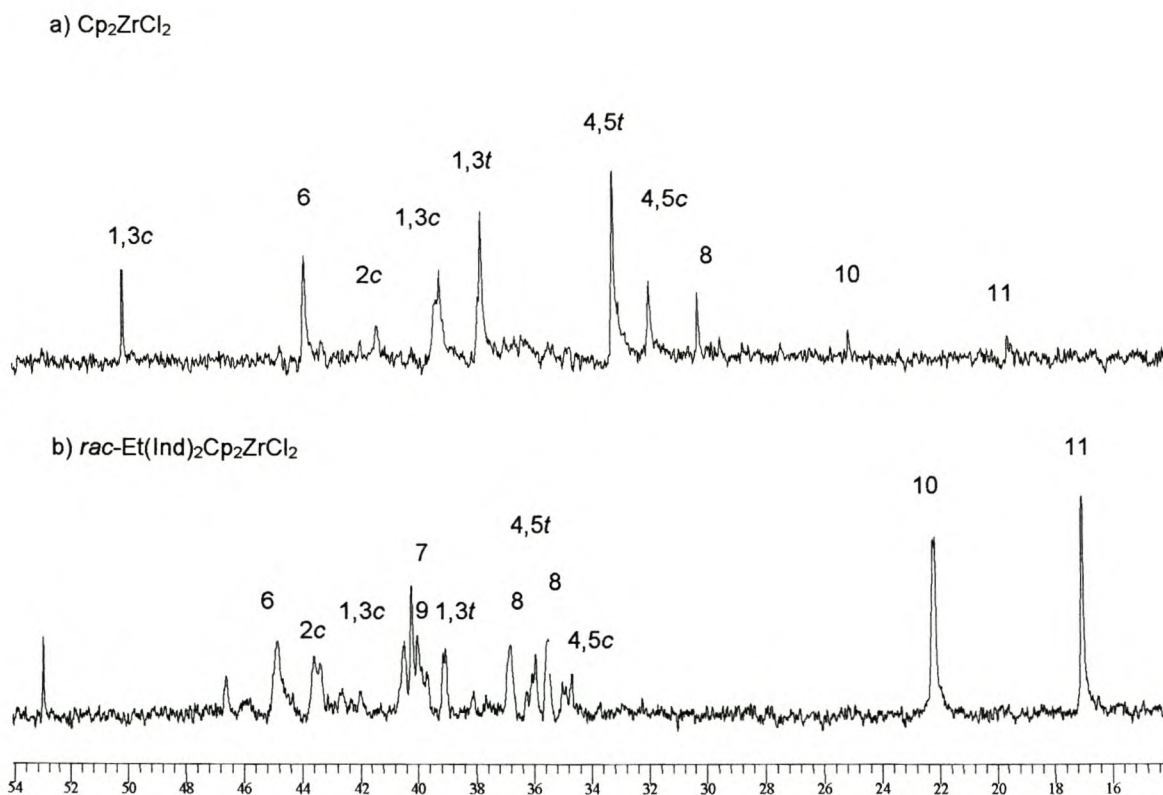
<sup>a</sup> Tacticity not taken into account with calculation

c) *Poly(pentene-co-1,5-hexadiene)*

The repeat units for poly(pentene-co-1,5-hexadiene) are shown in Figure 4-17. The carbon numbering is used to create a correlation between the structures and the corresponding relaxation peaks for the  $^{13}\text{C}$  NMR spectra (Figure 4-18).



**Figure 4-17** Simple cyclised (a) and linear (b) repeat units in poly(pentene-co-1,5-hexadiene).



**Figure 4-18**  $^{13}\text{C}$  NMR Spectra (aliphatic/ cycloaliphatic region) of poly(pentene-co-1,5-hexadiene) synthesised in the presence of (a)  $\text{Cp}_2\text{ZrCl}_2$  and (b)  $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$  as catalysts.

Figure 4-18 shows that 1-pentene was incorporated into a polymer chain consisting mainly of cyclic 1,5-hexadiene units for the polymer synthesised with zirconocene dichloride (Figure 4-18 (a)). The opposite is true for the polymer synthesised with the *ansa* metallocene (Figure 4-18 (b)). This was the intention,

as is shown in Table 3-1. This supports the versatility of 1,5-hexadiene as comonomer. In both cases, 1,5-hexadiene repeat units were observed to be cyclic structures.  $^{13}\text{C}$  NMR chemical shift values for the 1-pentene copolymers are summarised in Table 4-12.

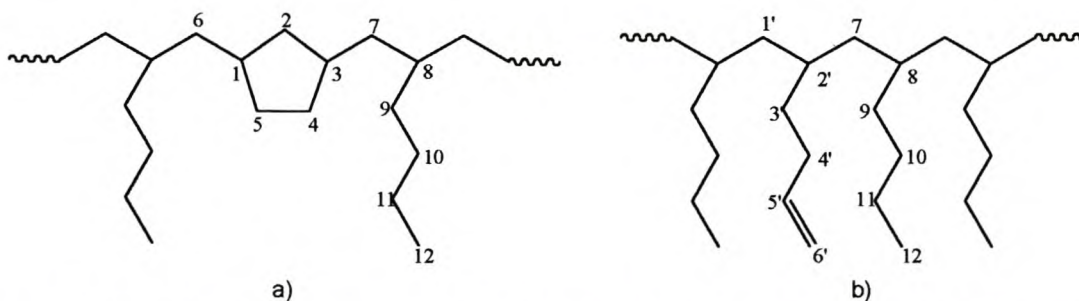
**Table 4-12** *Poly(pentene-co-1,5-hexadiene) - Comparison of actual and theoretical  $^{13}\text{C}$  NMR Chemical Shift values.*

| Carbon | $^{13}\text{C}$ NMR Chemical shift (ppm)<br>( $\text{Cp}_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ NMR Chemical shift (ppm)<br>( <i>rac-ef</i> (Ind) $_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ NMR Chemical shift(ppm)<br>Theoretical <sup>a</sup> |
|--------|--|---|---|
| 1,3t   | 39.12  | 39.11/ 39.03  | 37.95(P)/ 38.57(HD)   |
| 1,3c   | 37.81  | 40.45   |   |
| 4,5t   | 33.19  | 35.87   | 33.30(P)/ 33.10 (HD)  |
| 4,5c   | 31.90  | 34.95/ 34.88/ 34.67   |   |
| 6      | 43.87  | 44.80   | 39.43(P)/ 38.63(HD)   |
| 2t     | 39.33  | 42.58   | 43.06 (P)/ 42.84 (HD)   |
| 2c     | 41.94/ 41.34   | 43.55/ 43.35  |   |
| 7      |  | 40.22   | 41.43   |
| 8      | 30.29  | 36.80/35.48   | 33.35   |
| 9      |  | 39.98   | 39.67   |
| 10     | 25.07  | 22.19/ 17.01  | 21.49   |
| 11     |  |   | 14.49   |

<sup>a</sup>Tacticity not taken into account with calculation; Predictions were obtained from [WWW2.ACDLABS.COM/ilab](http://WWW2.ACDLABS.COM/ilab)

d) *Poly(hexene-co-1,5-hexadiene)*

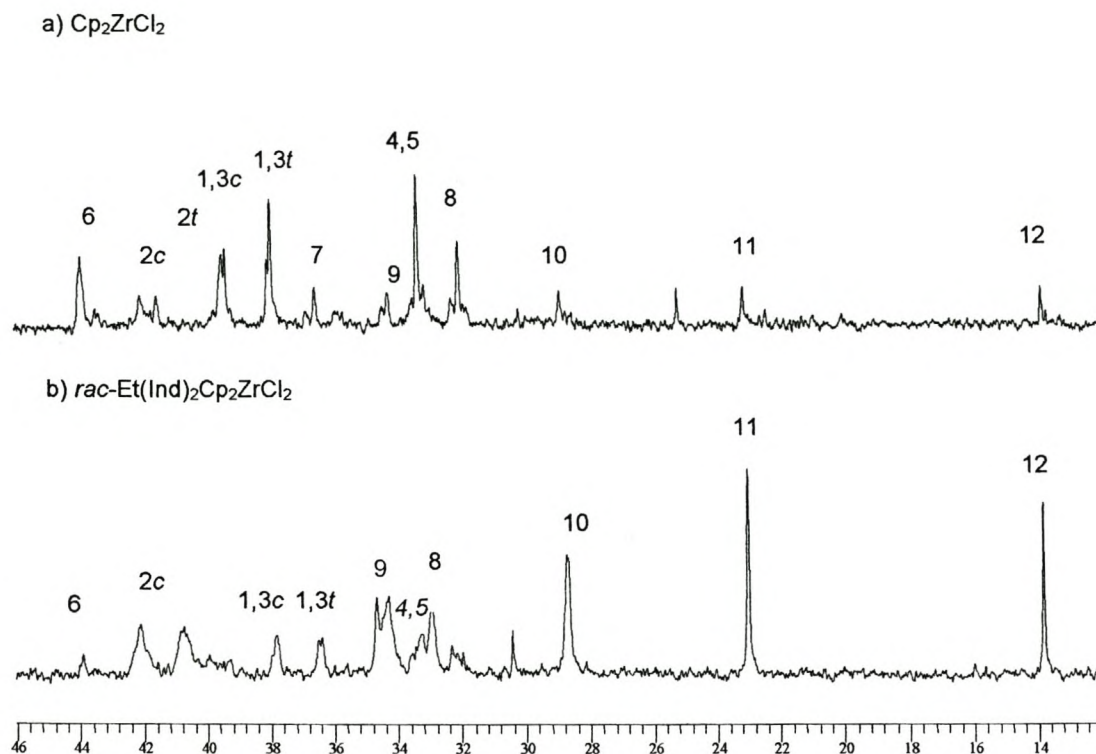
The proposed insertion modes of 1,5-hexadiene when copolymerised with 1-hexene are shown in Figure 4-19.



**Figure 4-19** *Simple cyclised (a) and linear (b) repeat units in poly(hexene-co-1,5-hexadiene).*



Poly(hexene-co-1,5-hexadiene) was synthesised under similar reaction conditions (Table 3-1), with zirconocene dichloride and the *ansa* metallocene as catalyst. A comparison of the two  $^{13}\text{C}$  NMR spectra can be seen in Figure 4-20.



**Figure 4-20**  $^{13}\text{C}$  NMR Spectra (aliphatic/ cycloaliphatic region) of poly(hexene-co-1,5-hexadiene) synthesised in the presence of (a)  $\text{Cp}_2\text{ZrCl}_2$  and (b)  $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ .

Table 4-13 tabulates chemical shift assignments for poly(hexene-co-1,5-hexadiene).

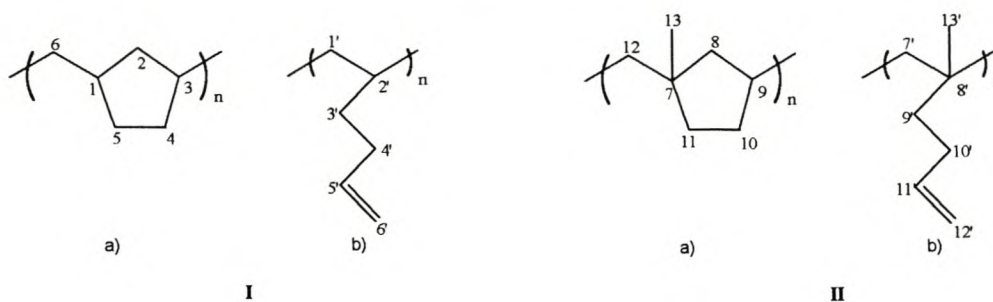
**Table 4-13** *Poly(hexene-co-1,5-hexadiene) - Comparison of actual and theoretical  $^{13}\text{C}$  NMR chemical shift values.*

| Carbon | Isomerism across ring | Isomerism across bridge | $^{13}\text{C}$ Shift (ppm) ( $\text{Cp}_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ Shift (ppm) ( $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ Shift (ppm) (Theoretical) |
|--------|-----------------------|-------------------------|--|---|---|
| 6      |                       | <i>trans-trans</i>      | 43.95  | 43.95   | 39.1                                      |
| 2      | <i>cis</i>            | <i>cis, trans</i>       | 42.07  | 42.16   | 41.93                                     |
|        | <i>trans</i>          |                         | 39.51  | 40.75   | 39.90                                     |
| 1,3    | <i>cis</i>            | <i>cis</i>              | 39.34  | 37.80   | 39.82                                     |
|        | <i>trans</i>          | <i>trans</i>            | 37.94  | 36.35   | 38.45                                     |
| 4,5    | <i>trans</i>          |                         | 33.35  | 33.41   | 33.72                                     |
|        | <i>cis</i>            |                         | 33.18  | 33.23   | 32.50                                     |
| 7      |                       |                         | 36.35  |   | 38.96                                     |
| 8      |                       |                         | 34.26  | 32.93   | 36.34                                     |
| 9      |                       |                         | 34.45<br>34.27   | 34.63<br>34.25  | 37.36                                     |
| 10     |                       |                         | 28.87  | 28.70   | 29.52                                     |
| 11     |                       |                         | 23.07  | 22.98   | 22.95                                     |
| 12     |                       |                         | 13.84  | 13.80   | 14.26                                     |

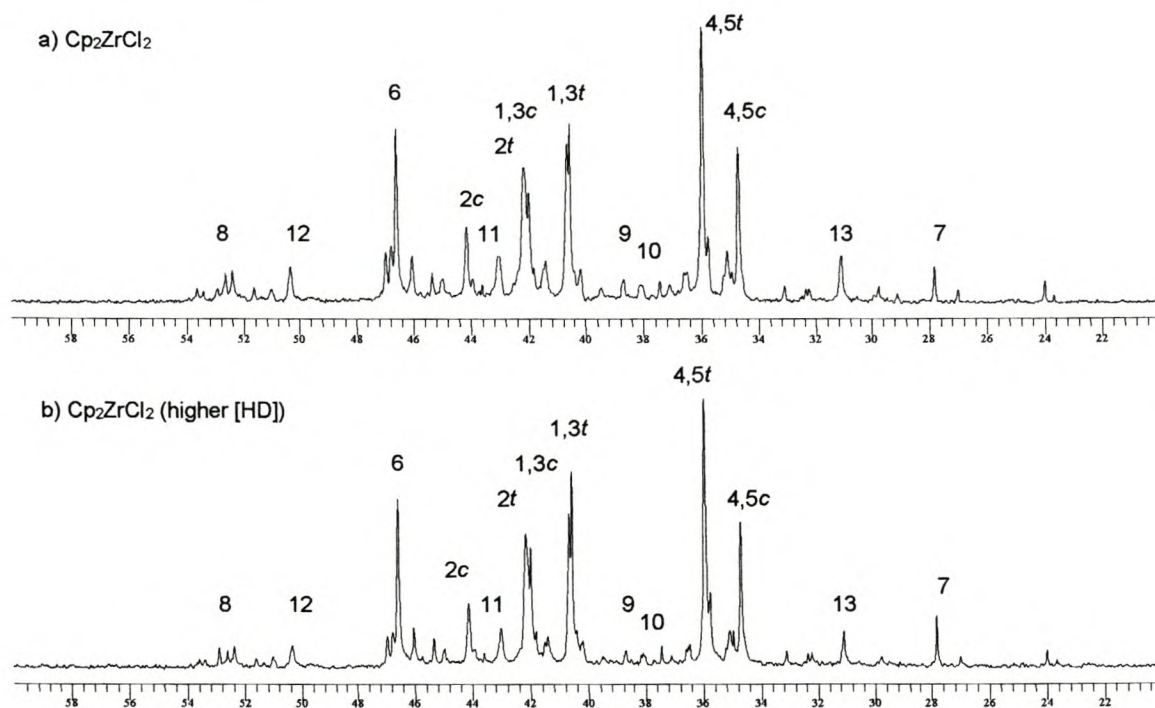
The peaks observed in Figure 4-20(b) at 39.90ppm and 30.30ppm are due to methine carbons (according to the corresponding APT spectra) and the presence thereof cannot be explained. It is also interesting to note that two relaxation peaks for  $\text{C}_9$  are observed in both cases. These polymers were dissolved in different solvents (trichlorobenzene and tetrachloroethane) and this should be kept in mind with the consideration of discrepancies between the relaxation peak identification between the two spectra.

e) *Poly(1,5-hexadiene-co-2-methyl-1,5-hexadiene)*

The synthesis of this copolymer was interesting with reference to the influence of the extra methyl group on the insertion of the comonomer into the polymer chain, as well as the effect on cyclisation of both these monomers. Figure 4-21 illustrates the possible repeat units in this polymer. The carbon numbering will be used to create a correlation between the actual repeat units and the relaxation peaks in the  $^{13}\text{C}$  NMR spectra (Figure 4-22).



**Figure 4-21** Cyclised (a) and linear (b) repeat units for both 1,5-hexadiene (I) and 2-methyl-1,5-hexadiene (II) monomers.



**Figure 4-22**  $^{13}\text{C}$  NMR Spectra (aliphatic/ cycloaliphatic region) of (a) poly(MHD-co-1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  (b) poly(MHD-co-1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  (higher HD incorporation).

The  $^{13}\text{C}$  NMR spectra in Figure 4-22 clearly indicate the presence of both monomers in the form of cyclic repeat units. Chemical shift assignments are summarised in Table 4-14.

**Table 4-14** Poly(MHD-co-1,5-hexadiene) - Comparison of actual and theoretical  $^{13}\text{C}$  NMR chemical shift values.

| Carbon | Isomerism across ring | Isomerism across bridge | $^{13}\text{C}$ shift (ppm) ( $\text{Cp}_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ shift (ppm) ( $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ ) | $^{13}\text{C}$ shift (ppm) (Theoretical) |
|--------|-----------------------|-------------------------|--|---|---|
| 6      |                       | <i>trans-trans</i>      | 46.95  | 46.96   | 44.30                                     |
|        |                       | <i>cis-trans</i>        | 46.76  | 46.76   | 44.25                                     |
|        |                       | <i>cis-cis</i>          | 46.57  | 46.58   | 44.20                                     |
| 2      | <i>cis</i>            | <i>cis, trans</i>       | 44.11/43.92  | 44.12/43.92   | 41.93/41.88                               |
|        | <i>trans</i>          |                         | 42.13  | 42.13   | 39.90                                     |
| 1,3    | <i>cis</i>            | <i>cis</i>              | 41.95  | 41.96   | 39.82                                     |
|        |                       | <i>trans</i>            | 41.78  | 41.79   | 39.75                                     |
|        | <i>trans</i>          | <i>trans</i>            | 40.62  | 40.63   | 38.45                                     |
|        |                       | <i>cis</i>              | 40.53  | 40.54   | 38.40                                     |
| 4,5    | <i>trans</i>          |                         | 35.92  | 35.92   | 33.72                                     |
|        | <i>cis</i>            |                         | 34.67  | 34.68   | 32.50                                     |
| 7      |                       |                         | 27.80  | 27.79   | 46.73                                     |
| 8      |                       |                         | 52.88/52.59/<br>52.36                                      | 52.90/52.62/<br>52.37   | 52.63                                     |
| 9      |                       |                         | 38.70/38.48  | 38.69   | 32.24                                     |
| 10     |                       |                         | 38.07/37.43/<br>37.09                                      | 38.08/37.43/<br>37.09   | 29.45                                     |
| 11     |                       |                         | 42.96  | 43.00   | 42.48                                     |
| 12     |                       |                         | 50.31  | 50.34   | 43.36                                     |
| 13     |                       |                         | 31.06  | 31.09   | 31.78                                     |

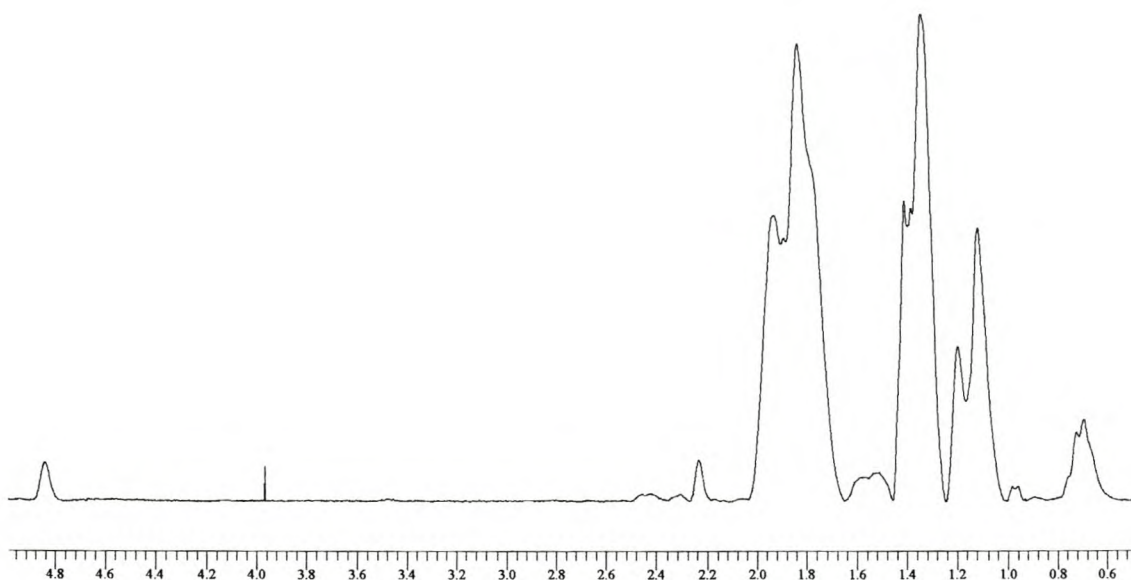
#### 4.2.2 Percentage cyclisation in homo- and copolymers

The amount of cyclisation of 1,5-hexadiene in the polymers were determined through the integration of relaxation peaks in  $^1\text{H}$  NMR spectra and compared to the data obtained from the integration of the correlating  $^{13}\text{C}$  NMR spectra. It is important to note that no  $^1\text{H}$  NMR spectra of 1,5-hexadiene polymers have been fully documented in literature.

##### 4.2.2.1 Homopolymers

An example of a  $^1\text{H}$  NMR spectrum, that of poly(1,5-hexadiene), is shown in

Figure 4-23.

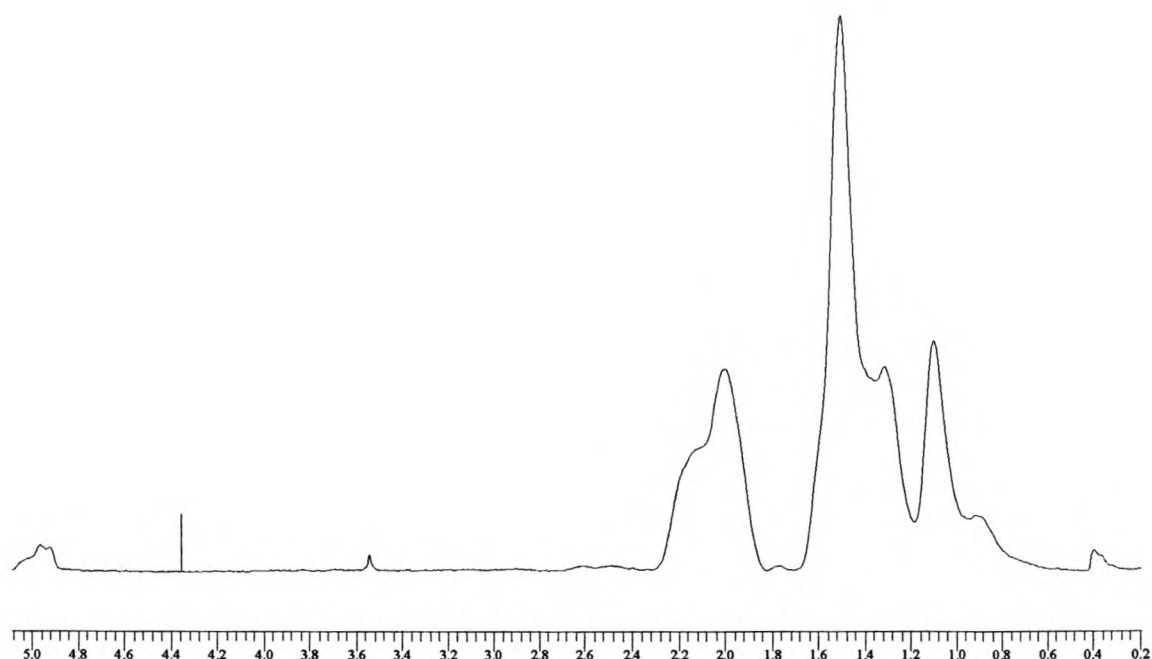


**Figure 4-23**  $^1\text{H}$  NMR spectrum of poly(1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  at room temperature.

The relaxation peaks resulting from *trans*-vinyl double bonds<sup>[3]</sup> were observed at 4.82ppm. Integration of the remaining peaks led us to believe that the relaxation peak at 2.22ppm represents the hydrogens attached to  $\text{C}_{10}$ , another indication of the presence of linear branching. The protons from  $-\text{CH}_2-$  repeat units in the backbone of the polymer chain is represented by the relaxation peak between 1.2ppm and 1.0ppm. The chemical shift between 1.6ppm and 1.2ppm is most likely due to the methine protons,  $\text{C}_{1,3}$ . The relaxation peaks observed between 2.1ppm and 1.6ppm is proposed to represent the hydrogens attached to  $\text{C}_{4,5}$ . The  $-\text{CH}_3$  protons are observed below 1.00ppm. These peaks represent chain end groups. Due to the variety of structures possible after termination, more than one relaxation peak is expected.

#### 4.2.2.2 Copolymers

In Figure 4-24, the  $^1\text{H}$  NMR spectrum of poly(hexene-co-1,5-hexadiene) is shown. As severe overlap of the carbon backbone signals is evident here, quantitative determination of cyclisation is very difficult. Cyclisation was thus determined with reference to the presence of the vinyl double bond relaxation peaks in the spectra.



**Figure 4-24**  $^1\text{H}$  NMR spectra of poly(hexene-co-1,5-hexadiene) synthesised in the presence of  $\text{Cp}_2\text{ZrCl}_2$  at room temperature.

#### 4.2.2.3 Results

The amount of cyclisation of 1,5-hexadiene is an important consideration, as it will influence crystallinity, the amount of cross-linking, functionalisation of the polymer chains and grafting possibilities. In the case where oligomers are synthesised, low amounts of cyclisation will promote the application of the oligomers as a macromonomers. It can thus be seen that this factor has a major

influence on the versatility of the product. Table 4-15 tabulates the values calculated for the amount of cyclisation of the diene in the polymeric materials synthesised.

**Table 4-15** Amount of cyclization of dienes, as determined by integration of  $^{13}\text{C}$  and  $^1\text{H}$  NMR relaxation peaks.

| HOMOPOLYMERS |                              |                      |                         |
|--------------|------------------------------|----------------------|-------------------------|
| NMR nr       |                              | $^1\text{H}$ NMR (%) | $^{13}\text{C}$ NMR (%) |
| 001          | 1,5-Hexadiene (n)            | 100                  | 100                     |
| 013          | 1,5-Hexadiene (74°C)         | 100                  | 100                     |
| 057          | 1,5-Hexadiene (b)            | 100 <sup>a</sup>     | 100                     |
| 014          | 2-Methyl-1,5-Hexadiene (b)   | 100                  | 83.40                   |
| 015          | 2-Methyl-1,5-Hexadiene (n)   | 100                  | 100                     |
| COPOLYMERS   |                              |                      |                         |
| NMR nr       |                              | $^1\text{H}$ NMR (%) | $^{13}\text{C}$ NMR (%) |
| 009          | Ethylene (n)_1               | 100                  | 100                     |
| 054          | Ethylene (n)_2               | 100                  | 100                     |
| 052          | Ethylene (b)_1               | None                 | None                    |
| 056          | Propylene (n)                | 100                  | 100                     |
| 018          | Propylene (b)                | 100                  | 100                     |
| 012          | 1-Pentene (b)                | 100                  | 100                     |
| 055          | 1-Pentene (n)                | 100                  | 100                     |
| 010          | 1-Hexene (b)                 | 100                  | 100                     |
| 008          | 1-Hexene (n)                 | 100                  | 100                     |
| 017          | 2-Methyl-1,5-Hexadiene (1:3) | 100 (HD) 100 (MHD)   | 100 (HD) 100 (MHD)      |
| 016          | 2-Methyl-1,5-Hexadiene (1:1) | 100 (HD) 100 (MHD)   | 100 (HD) 100 (MHD)      |

<sup>a</sup>Only a quintet was observed in the region of 4.00ppm - most likely a solvent effect

It is important to note that the reaction conditions (Table 3-1) for all the polymers, mainly resulted in the full cyclisation of the incorporated 1,5-hexadiene. In the case of the steric hindered 1,5-hexadiene (2-methyl-1,5-hexadiene), catalysed with the isospecific *ansa* metallocene, full cyclisation was not obtained, according to  $^{13}\text{C}$  NMR spectrum (Figure 4-22)).

## 4.2.3 Stereoregularity

The influence of the choice of catalyst precursor for the synthesis of the various oligomers, is illustrated in the isomerism characteristics of C<sub>1,3</sub> and C<sub>4,5</sub>, as numbered in Section 4.2. The results are tabulated in Table 4-16.

**Table 4-16** *Isomerism of 1,5-hexadiene monomeric unit in polymers, as observed from <sup>13</sup>C NMR spectra.*

| HOMOPOLYMERS |                              |                              |                             |
|--------------|------------------------------|------------------------------|-----------------------------|
| NMR nr       |                              | cis:trans - C <sub>4,5</sub> | cis:trans -C <sub>1,3</sub> |
| 001          | 1,5-Hexadiene (n)            | 1: 2.05                      | 1: 1.51                     |
| 013          | 1,5-Hexadiene (74°C)         | 1: 2.27                      | 1: 1.22                     |
| 057          | 1,5-Hexadiene (b)            | 1: 1.15                      | 1:1.58                      |
| 014          | 2-Methyl-1,5-Hexadiene (b)   | -                            | -                           |
| 015          | 2-Methyl-1,5-Hexadiene (n)   | -                            | -                           |
| COPOLYMERS   |                              |                              |                             |
| NMR nr       |                              | cis:trans - C <sub>4,5</sub> | cis:trans -C <sub>1,3</sub> |
| 009          | Ethylene (n)_1               | -                            | 1: 4.30                     |
| 054          | Ethylene (n)_2               | -                            | only cis                    |
| 052          | Ethylene (b)_3               | -                            | 1: 2.60                     |
| 056          | Propylene (n)                | 1: 2.28                      | 1: 1.58                     |
| 018          | Propylene (b)                | 1: 1.23                      | 1: 1.31                     |
| 012          | 1-Pentene (b)                | 1: 1.30                      | 1: 1.17                     |
| 055          | 1-Pentene (n)                | 1: 0.66                      | 1: 2.64                     |
| 010          | 1-Hexene (b)                 | 1:1.00                       | 1: 0.67                     |
| 008          | 1-Hexene (n)                 | 1 : 1.80                     | 1 : 3.50                    |
| 017          | 2-Methyl-1,5-Hexadiene (1:3) | 1: 2.33                      | 1: 1.41                     |
| 016          | 2-Methyl-1,5-Hexadiene (1:1) | 1: 1.50                      | 1: 1.69                     |

The isomerism phenomena present in the homopolymers have already been discussed in Section 4.2.1.1. Unfortunately there is no literature available on the <sup>13</sup>C NMR chemical shift assignments relating to tacticity for poly(2-methyl-1,5-hexadiene), although spectra obtained clearly show the presence thereof (Figures 4-11 and 4-12).

The greatest effect of choice of metallocene catalyst, on isomerism of the



copolymers, is clearly illustrated by consideration of the stereoregularity observed for C<sub>4,5</sub>. It is also interesting to note that *cis*-isomerism (C<sub>1,3</sub>) is obtained in the ethylene copolymer synthesised with the least amount of 1,5-hexadiene monomer. The highest *trans*-selectivity for C<sub>1,3</sub> was in the remaining ethylene copolymers, synthesised with both catalysts, and the hexene copolymer, synthesised with zirconocene dichloride. This might be explained by the fact that ethylene is a very small, although reactive, monomer. Also note that the longer the carbon chain of the monomer, the less reactive it will be with reference to copolymerisations.

#### 4.2.4 Monomer Incorporation

In using <sup>13</sup>C NMR spectra for quantitative measurements, it must be kept in mind that relaxation times of carbons play a significant role in the various peak areas/ -intensities. To obtain accurate integration values for calculation, relaxation times are dependent on the mobility of the polymer chain, it is important to consider carbons with low mobility. The backbone carbons, C<sub>6</sub> and C<sub>8</sub>/ C<sub>7</sub>, were used to calculate the amount of monomer incorporated in the copolymers. The calculated values are tabulated in Table 4-17.

**Table 4-17** Amount of comonomer incorporated in the 1,5-hexadiene copolymers, determined by integration of <sup>13</sup>C NMR relaxation peaks.

| COPOLYMERS |                            |                          |
|------------|----------------------------|--------------------------|
| NMR nr     | Comonomer                  | % Comonomer incorporated |
| 009        | Ethylene (n_1)             | 94.50                    |
| 054        | Ethylene (n_2)             | 100.00                   |
| 052        | Ethylene                   | 91.60                    |
| 056        | Propylene (n)              | <87.00                   |
| 018        | Propylene                  | <86.00                   |
| 012        | 1-Pentene                  | 28.00                    |
| 055        | 1-Pentene (n)              | 55.00                    |
| 010        | 1-Hexene                   | 50.00                    |
| 008        | 1-Hexene (n)               | 59.00                    |
| 017        | 2-Methyl-1,5-Hexadiene (n) | 11.86                    |
| 016        | 2-Methyl-1,5-Hexadiene (n) | 1.10                     |

The data in Table 4-17 confirms the incorporation of the comonomers in question. It is seen that more comonomer were incorporated where zirconocene dichloride (n) was used as the catalytic system. The more reactive comonomers (eg ethylene) were more easily incorporated than the less active comonomers (ie 1-hexene). The amount of 2-methyl-1,5-hexadiene incorporated is dependant on the amount of 1,5-hexadiene (HD) used in the polymerisation reaction. An increase in the HD concentration result in a decrease in the amount of HD incorporated. (Table 3-1 shows that the NMR sample labeled 017 was synthesised with triple the amount of HD than used for the synthesis of the NMR sample 016.)

#### 4.2.5 Number-average molecular weight

Peaks representing the backbone and end group relaxations in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were integrated. The end groups detected in the spectra were commonly  $\text{CH}_3$ -groups, detected between 20ppm and 22ppm in the  $^{13}\text{C}$  NMR spectra and below 1ppm in the  $^1\text{H}$  NMR spectra. These values were then used for the determination of the number-average molecular weight of the polymers/oligomers in the following way:

$$Mn = \frac{(I_{C6}Mw_{HD}) + (I_{7/8}MW_{cm})}{I_{endgroups}} \text{ for } ^{13}\text{C NMR}$$

**Equation 4-2**

$$Mn = \frac{(I_{C6}Mw_{HD})/n_{protons} + (I_{7/8}MW_{cm})/n_{protons}}{I_{endgroups}/n_{protons}} \text{ for } ^1\text{H NMR}$$

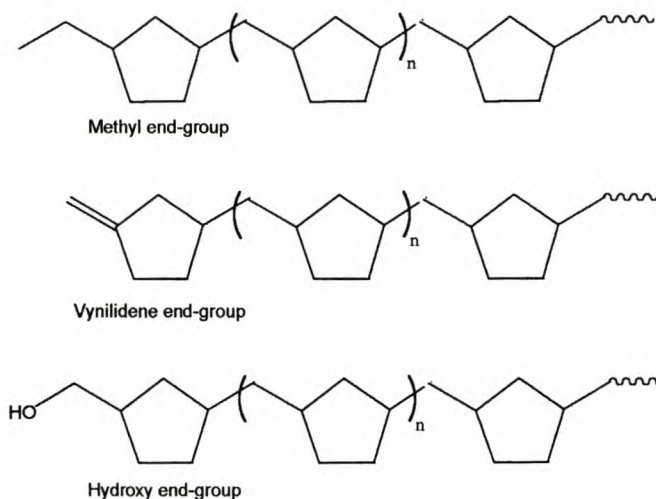
**Equation 4-3**

Where

Mn =           Number—average molecular weight  
I =             Integrated value from NMR spectra

- $MW_{CM}$  = Molecular weight of comonomer repeat unit  
 $MW_{HD}$  = Molecular weight of the repeat unit of 1,5-hexadiene  
 $N$  = Number of protons

Chain termination possibilities are discussed in Section 2.1.6, as well as in Section 2.2.2. The following end groups were detected:



**Figure 4-25** End groups for cyclic repeat units in 1,5-hexadiene polymers, detected via  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra.

Tables 4-18 and 4-19 tabulates the end-groups, as observed in both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and number-average molecular weight of the polymers in question as calculated with equations 4-2 and 4-3.

**Table 4-18** Number-average molecular weight, as determined by the integration of relaxation peaks in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, for the homopolymers.

| HOMOPOLYMERS |                            |                  |                              |                     |                                 |
|--------------|----------------------------|------------------|------------------------------|---------------------|---------------------------------|
| NMR nr       |                            | $^1\text{H}$ NMR | Detected End groups          | $^{13}\text{C}$ NMR | Detected End groups             |
| 001          | 1,5-Hexadiene (n)          | 7 557.8          | -CH <sub>3</sub>             | 7 468.18            | -CH <sub>3</sub>                |
| 013          | 1,5-Hexadiene (74°C)       |                  | Vinylidene, -CH <sub>3</sub> | 1 579.18            | -CH <sub>3</sub>                |
| 057          | 1,5-Hexadiene (b)          |                  | -CH <sub>3</sub>             | 247.44              | -CH <sub>3</sub>                |
| 014          | 2-Methyl-1,5-Hexadiene (b) |                  | Vinylidene, -CH <sub>3</sub> | >385.59             | -CH <sub>3</sub>                |
| 015          | 2-Methyl-1,5-Hexadiene (n) |                  | -CH <sub>3</sub>             | >471.50             | C <sub>6</sub> -OH <sup>b</sup> |

**Table 4-19** Number-average molecular weight, as determined by the integration of relaxation peaks in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, for the copolymers.

| COPOLYMERS |                        |                  |                                      |                     |                                       |
|------------|------------------------|------------------|--------------------------------------|---------------------|---------------------------------------|
| NMR nr     |                        | $^1\text{H}$ NMR | Detected End groups                  | $^{13}\text{C}$ NMR | Detected End groups                   |
| 009        | Ethylene (n_1)         |                  | -CH <sub>3</sub>                     | 6 972.56            | C <sub>6</sub> -OH                    |
| 054        | Ethylene (n_2)         |                  | Vinylidene, -CH <sub>3</sub>         | 2 074.01            | C <sub>6</sub> -OH                    |
| 052        | Ethylene (b_1)         |                  | Vinylidene, -CH <sub>3</sub>         | 3 788.85            | C <sub>6</sub> -OH                    |
| 056        | Propylene (n)          |                  | C <sub>6</sub> -OH, -CH <sub>3</sub> | 627.96              | -CH <sub>3</sub>                      |
| 018        | Propylene (b)          |                  | -CH <sub>3</sub>                     | 715.83              | -CH <sub>3</sub> , C <sub>6</sub> -OH |
| 012        | 1-Pentene (b)          |                  | Vinylidene, -CH <sub>3</sub>         |                     | Nd <sup>a</sup>                       |
| 055        | 1-Pentene (n)          |                  | Vinylidene, -CH <sub>3</sub>         | 538.74              | -CH <sub>3</sub>                      |
| 010        | 1-Hexene (b)           |                  | -CH <sub>3</sub>                     |                     | Nd                                    |
| 008        | 1-Hexene (n)           |                  | C <sub>6</sub> -OH, -CH <sub>3</sub> | 522.24              | -CH <sub>3</sub>                      |
| 017        | 2-Methyl-1,5-Hexadiene |                  | -CH <sub>3</sub>                     | 2 138.50            | C <sub>6</sub> -OH                    |
| 016        | 2-Methyl-1,5-Hexadiene |                  | Vinylidene, -CH <sub>3</sub>         | 6 150.20            | -CH <sub>3</sub>                      |

<sup>a</sup>Nd (not detected)

<sup>b</sup>C<sub>6</sub> is defined in all the NMR spectra as the CH<sub>2</sub> neighbour of the 5 membered ring in the carbon backbone of the polymers, resulting from the cyclisation of 1,5-hexadiene. (See Section 4.2)

Good correlation between the calculated number-average molecular weight from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained for the homopolymer synthesised at room temperature in the presence of zirconocene dichloride. It is evident from the results obtained in Tables 4-18 and 4-19 that all materials are oligomeric. It must be noted that, in the case of the insoluble materials, significantly higher molecular weights were probably obtained, but these could not be determined.

#### 4.2.6 Functionalisation

Single relaxation peaks, representing the presence of *trans*-vinyl double bonds, were detected by  $^1\text{H}$  NMR spectra (4.5ppm-5.0ppm). These double bonds were

observed for poly(1,5-hexadiene), poly(propylene-co-HD); poly(hexene-co-HD) and poly(MHD-co-HD) synthesised with zirconocene dichloride as catalyst. This is unique and creates the opportunity for functionalisation of these chains for use in their present state, or grafting that would allow the incorporation of polar groups into hydrocarbon polymer chains. Figure 4-26 shows the structure of these double bonds in the chains, as proposed by Pietikäinen *et al.* [3]



Figure 4-26 *Trans-vinyl double bonds for functionalisation as proposed by Pietikäinen et al [3].*

### 4.3 Characterisation done by THERMAL ANALYSIS

The influence of the catalytic system used for the synthesis of the homopolymers can clearly be seen by the  $T_g$  values obtained for reactions 1 and 15. A much more crystalline polymeric material is expected for the polymer synthesised with the isospecific catalyst, as supported by the results in Table 4-20.

Table 4-20 *Melting- and glass transition temperatures, obtained via DMA or DSC analysis, for the polymers synthesised, for the homopolymers.*

| HOMOPOLYMERS |             |                            |                 |               |
|--------------|-------------|----------------------------|-----------------|---------------|
| NMR          | Reaction nr |                            | $T_g$ (°C)      | $T_{m1}$ (°C) |
| 001          | 1           | 1,5-Hexadiene (n)          | -27.42          | 69.03         |
| 057          | 15          | 1,5-Hexadiene              | 10.21           |               |
|              | 30          | 1,5-Hexadiene              | Nd <sup>a</sup> | 94.87         |
| 014          | 29          | 2-Methyl-1,5-Hexadiene     | Nd <sup>a</sup> | 98.70         |
| 015          | 26          | 2-Methyl-1,5-Hexadiene (n) | Nd <sup>a</sup> | 90.82         |

<sup>a</sup>Not detected

**Table 4-21** Melting- and glass transition temperatures, obtained via DMA or DSC analysis, for the polymers synthesised, for the copolymers.

| COPOLYMERS |             |                        |                     |                      |                      |                      |         |
|------------|-------------|------------------------|---------------------|----------------------|----------------------|----------------------|---------|
| NMR        | Reaction nr |                        | T <sub>g</sub> (°C) | T <sub>m1</sub> (°C) | T <sub>m2</sub> (°C) | T <sub>m3</sub> (°C) | CP (°C) |
| 009        | 5           | Ethylene (n_1)         | Nd <sup>a</sup>     | 69.35                | 108.73               | 121.97               | -       |
| 054        | 6           | Ethylene (n_2)         | Nd <sup>a</sup>     | 97.28                | 108.10               | 124.50               | 111.59  |
| 054        | 32          | Ethylene               | Nd <sup>a</sup>     | -                    | -                    | 127.41               | 112.63  |
| 018        | 23          | Propylene              | -15.16              | -                    | -                    | -                    | -       |
| 012        | 21          | 1-Pentene              | -35.34              | 11.169               | -                    | -                    | -       |
| 055        | 16          | 1-Pentene (n)          | -44.46              | -                    | -                    | -                    | -       |
| 010        | 20          | 1-Hexene               | -44.94              | -                    | -                    | -                    | -       |
|            | 31          | Carbon monoxide        | Nd <sup>a</sup>     | 123.19               | -                    | -                    | -       |
| 017        | 28          | 2-Methyl-1,5-Hexadiene | -37.62              | 93.28                | -                    | -                    | -       |
| 016        | 27          | 2-Methyl-1,5-Hexadiene | -34.55              | -                    | -                    | -                    | -       |

It can be seen that the larger the comonomer, the lower the T<sub>g</sub> values. The catalyst precursor *rac*-MeSi<sub>2</sub>(2-Me-Benz(e)Ind)<sub>2</sub>ZrCl<sub>2</sub> (used in reaction 30 and 31) synthesised polymeric materials with very high crystallinity, the results obtained is in support of this theory. Three melting peaks for the ethylene copolymers were observed. The first melting peak in the first ethylene copolymer correlates well to that of the homopolymer (reaction 1). This specific value for the second ethylene copolymer, correlates well to that of the homopolymer in reaction 30 which indicates a similarity in structure. The second and third melting temperatures observed for both these copolymers correlate well to the T<sub>m</sub> values for linear low density polyethylene (LLDPE) and low density polyethylene (LDPE). The fact that we only observe one melting temperature for the third copolymer, synthesised with the *ansa* metallocene, shows a definite difference in the structure of the polymeric material observed, compared to the other two copolymers. Reaction 31 was carried out with a highly isospecific catalyst. This is an excellent example of a very crystalline material that is difficult to process or analyse due to the fact that it degrades before it melts. This will also explain why we could not dissolve this polymeric material for NMR analysis. It must also be

noted that the infrared analysis of poly(1,5-hexadiene-co-carbomonoxyde) showed no presence of  $-C=O$  groups. The mechanism of the polymerisation and the microstructure of this polymer are thus unknown.

The amount of crystallinity in the ethylene copolymers was also considered by comparing results obtained by DSC and WAXS analysis. These results are tabulated in Table 4-22.

**Table 4-22** Amount of crystallisation determined for the ethylene copolymers.

| NMR | Reaction nr |                | DSC    | WAXS   |
|-----|-------------|----------------|--------|--------|
| 009 | 5           | Ethylene (n)_1 | 64.48% | 93.47% |
| 054 | 6           | Ethylene (n)_2 | 45.86% | 78.76% |
| 054 | 32          | Ethylene _3    | 58.28% | 75.19% |

The data obtained from WAXS analysis are unrealistically high, although the trend seems realistic. The large difference between the data obtained from the two methods, is most probably due to the fact that the crystallisation and melting peaks in the DSC spectra compete with each other, as they are observed in the same vicinity. The result is inaccurate heat flow data and thus difficulty in determination of true crystallinity values via DSC analysis. It can be noted that the values obtained by DSC analysis, although not correct, is in the expected temperature range. The high amount of crystallinity shown for the first ethylene copolymer (with low HD incorporation – see Section 4.1.1.2 (a)) is expected. It is commonly known that if two monomers (of which the homopolymers are very crystalline) are copolymerised, the resulting polymer will show much lower crystallinity. This can be seen with the higher HD incorporation observed for the second and third ethylene copolymers.

#### 4.4 REFERENCES

- [1] Cheng, HN; Khasat, NP; *J Appl Polym Sci* **1988**, Vol 35, 825-829
- [2] Grant, DM; Paul, EG; *J Am Chem Soc* **1964**, Vol 86, 2984-2990

- [3] Pietikäinen, P.; Väänänen, T.; Seppälä, J. V.; *J Polym Sci: Part A: Polym Chem* **1999**, *35*, 1047-1055



## CHAPTER 5 Conclusions and Recommendations

### 5.1 GENERAL CONCLUSIONS

- Reaction conditions were determined for the successful synthesis of homopolymers, as well as ethylene-, propylene-, 1-pentene-, 1-hexene- and 2-methyl-1,5-hexadiene copolymers.  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  and *rac*- $\text{et}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$  were used as catalytic systems to investigate the effect on the stereoregularity and tacticity of the materials obtained.
- Detailed  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR chemical shift assignments, not published before, were given in this research project. NMR spectroscopy ( $^{13}\text{C}$ ,  $^1\text{H}$  and APT) was successfully used to comment on the microstructure of the oligomers, with reference to cyclisation, stereoregularity, monomer incorporation, number-average molecular weight and functional groups present in the products. Full cyclisation of 1,5-hexadiene in both the homo- and copolymers were observed. Melting temperatures as high as  $123.19^\circ\text{C}$  were observed, while a trend in the  $T_g$  values of the copolymers were also observed. It was shown that one is able to synthesise oligomers with predetermined stereoregularity through control of the catalytic system. We were able to synthesis materials of low  $M_n$  (247.44 – 7 468.18g/mole) with functional groups ( $-\text{CH}_2\text{OH}$ ). Vinyl groups in the polymer chains were also observed, thus creating an opportunity for grafting. Vinylidene end-groups observed create an opportunity for the use of these products as macromonomers.

### 5.2 RECOMMENDATIONS

The following recommendations for future study in this field:

- Feasibility study on the use of the vinylidene oligomers as macromonomers in the synthesis of various copolymers.
- Functionalisation of the vinylidene terminated oligomers.

- Further study on the influence of other reaction conditions on stereoregularity and determination of the reaction conditions allowing one to control the amount of cyclisation in various copolymers.

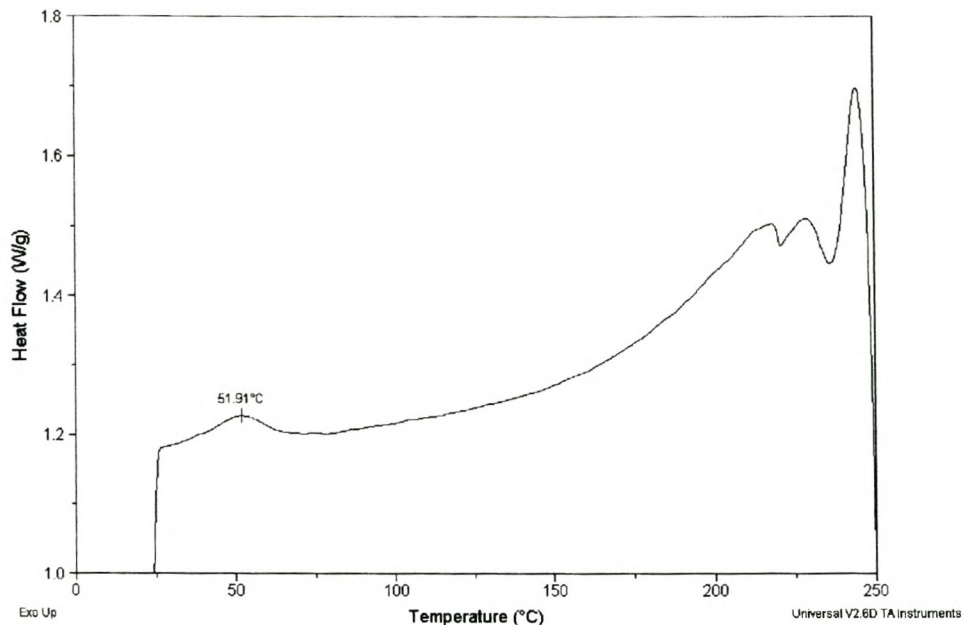
# **A D D E N D A**

## DIFFERENTIAL SCANNING CALOMETRIC SPECTRA

Sample: HOMOPOLMZ ONDEBRUGDE KAT  
Size: 3.5000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

File: C:\...Madr10.001  
Operator: Bob  
Run Date: 8-Aug-01 09:23

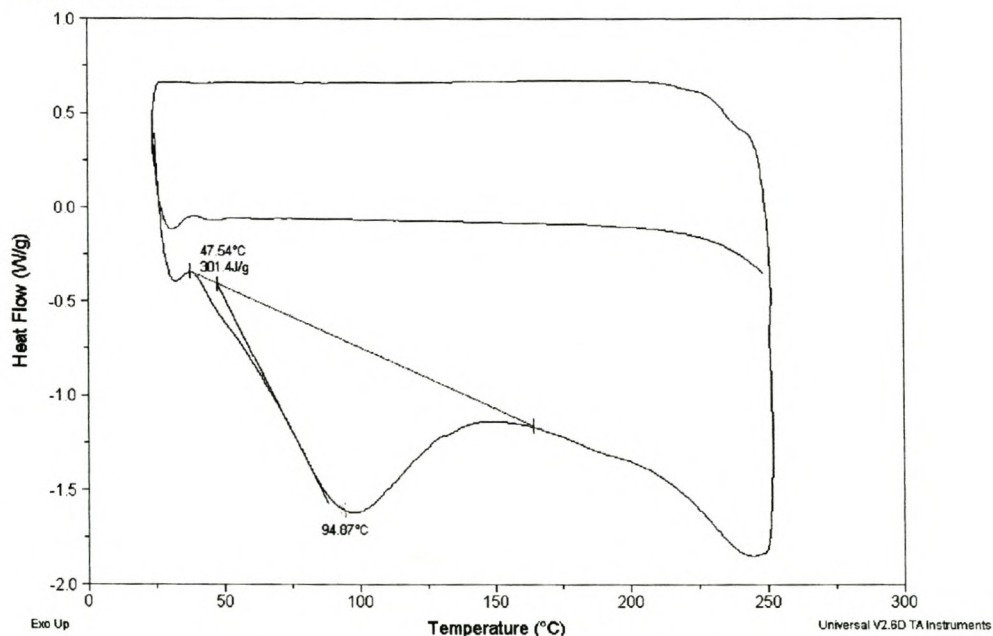


Reaction nr 15: Poly(1,5-hexadiene)

Sample: HOMOPOLY 15HD MESI2  
Size: 4.3000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

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Operator: Bob  
Run Date: 6-Aug-01 09:58

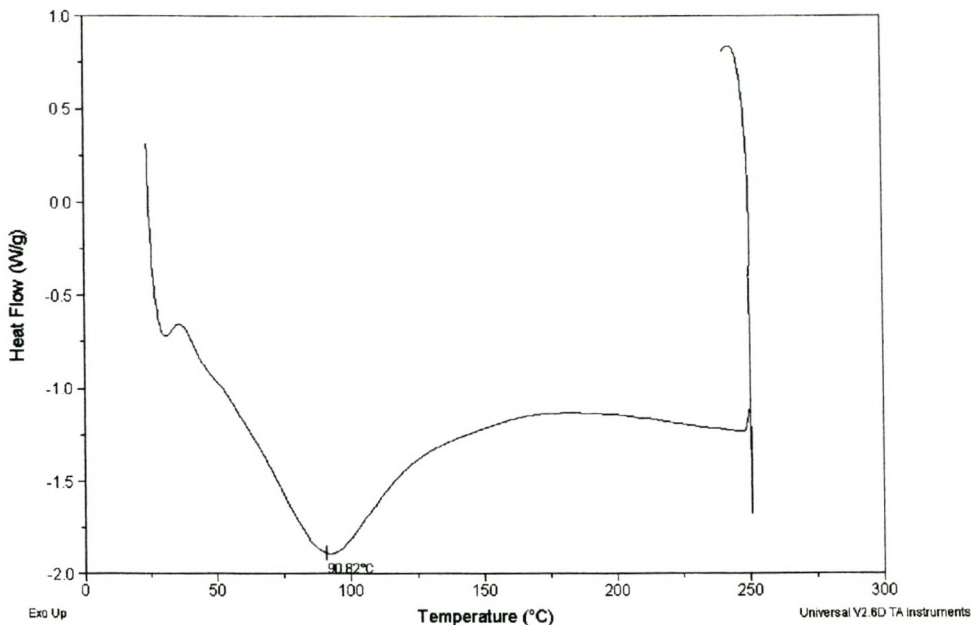


Reaction nr 30: Poly(1,5-hexadiene)

Sample: HOMOPOLMZ NON BRIDGED 7 METHYL  
 Size: 4.0000 mg  
 Method: polymer heat/cool/heat  
 Comment: MADRI SMIT

DSC

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 Operator: Bob  
 Run Date: 8-Aug-01 12:19

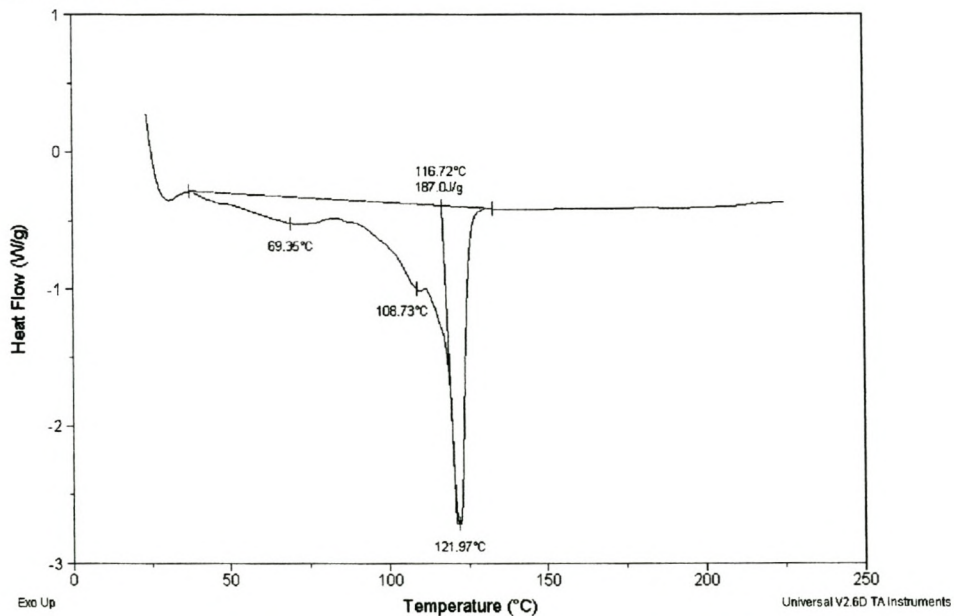


**Reaction nr 26: Poly(2-methyl-1,5-hexadiene)**

Sample: ETHYLENE COPLMR  
 Size: 5.0000 mg  
 Method: polymer heat/cool/heat  
 Comment: MADRI SMIT

DSC

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 Operator: Bob  
 Run Date: 7-Aug-01 09:30

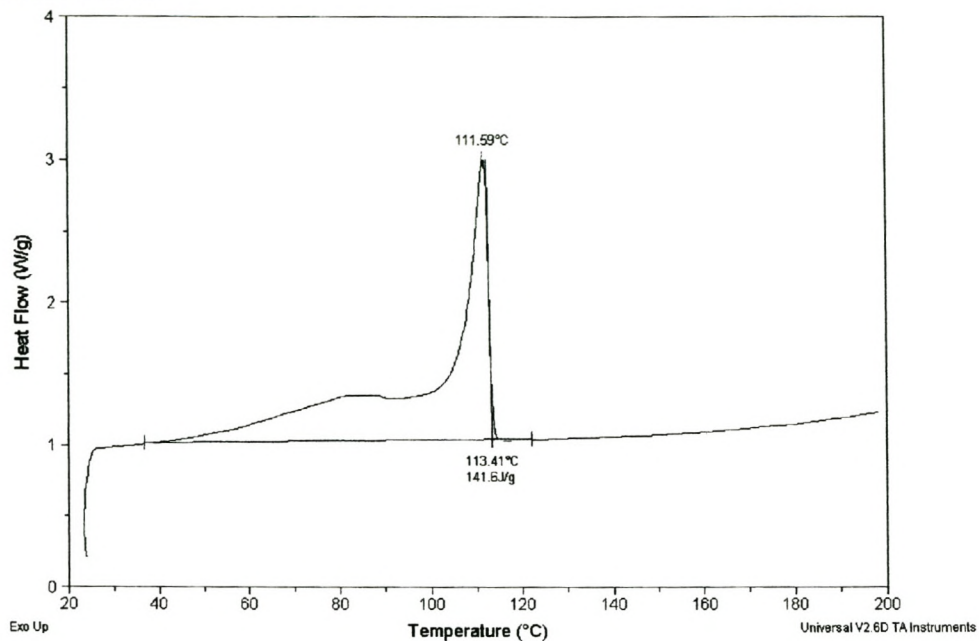


**Reaction nr 05: Poly(ethylene-co-1,5-hexadiene)**

Sample: ETHYLENE COPOLYMER  
Size: 4.0000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

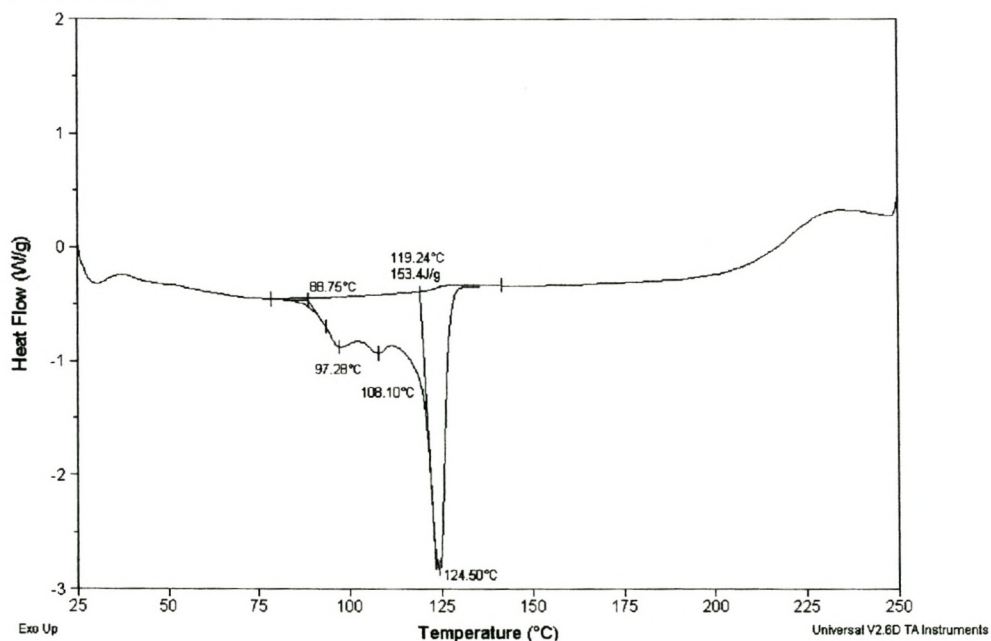
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Operator: Bob  
Run Date: 23-Jul-01 11:45



Sample: ETHYLENE COPOLYMER  
Size: 4.0000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

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Operator: Bob  
Run Date: 23-Jul-01 11:45

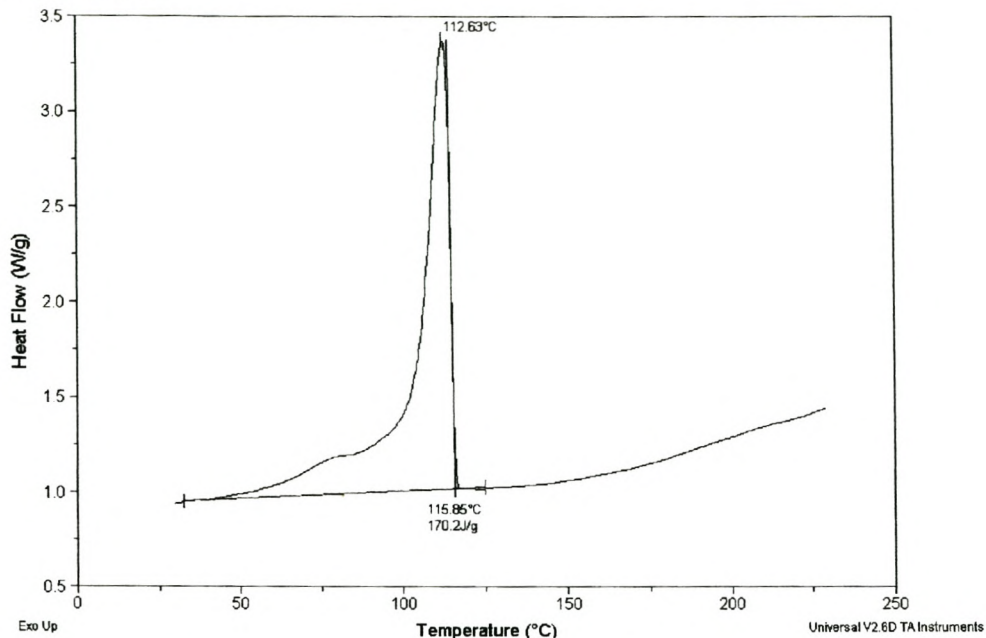


Reaction nr 06: Poly(ethylene-co-1,5-hexadiene)

Sample: ETHYLENE CO15 HD  
Size: 4.0000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

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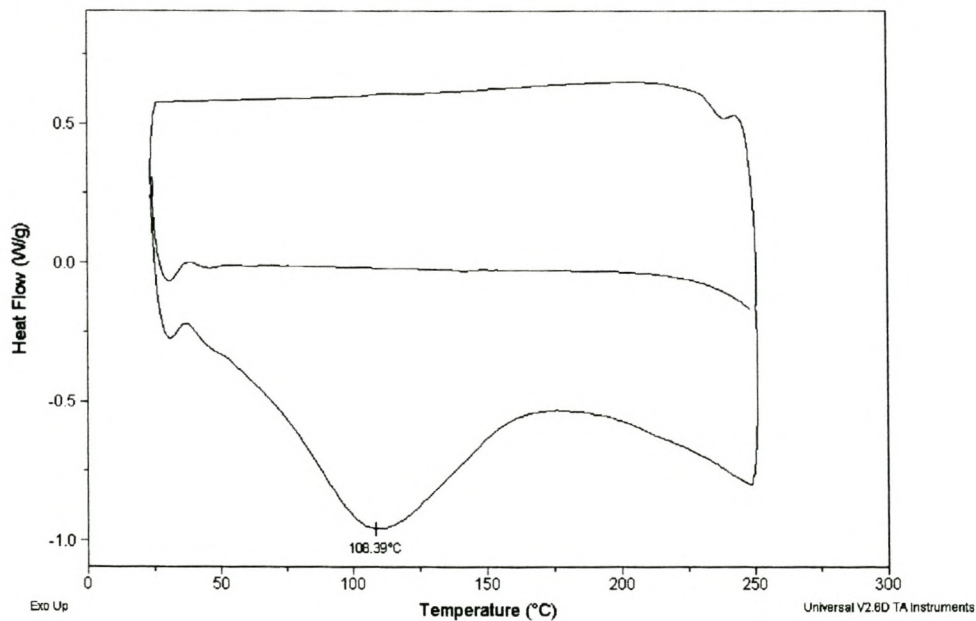


Reaction nr 32: Poly(ethylene-co-1,5-hexadiene)

Sample: 1-HEXENE-CO-HD, (SO-MAR)  
Size: 5.0000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

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Operator: Bob  
Run Date: 7-Aug-01 13:02



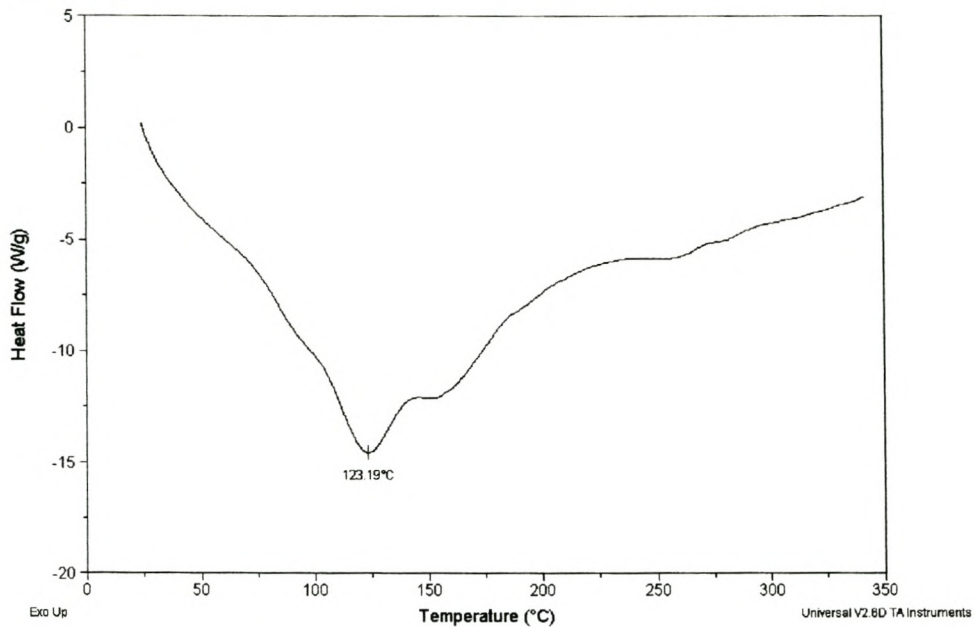
Reaction nr 20: Poly(hexene-co-1,5-hexadiene)

Sample: COPOLY 1,5HD AND CO  
Size: 5.0000 mg

DSC

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Operator: Bob  
Run Date: 18-Jul-01 12:59

Comment: MADRI SMIT

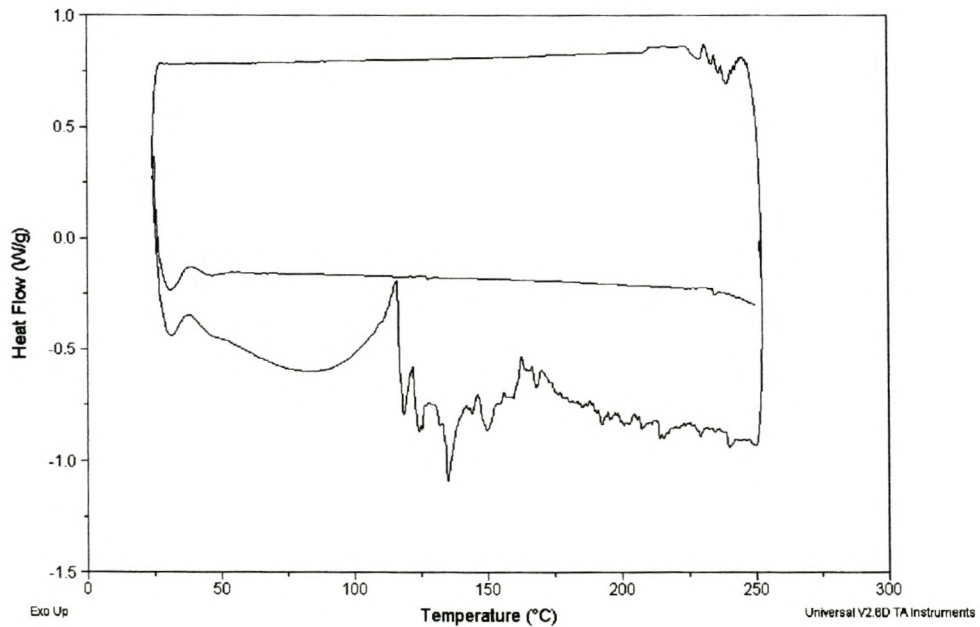


**Reaction nr 31: Poly(carbon monoxide-co-1,5-hexadiene)**

Sample: POLY(2M-1,5HD-CO-1,5HD) -#1  
Size: 4.5000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

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Operator: Bob  
Run Date: 18-Jul-01 11:34



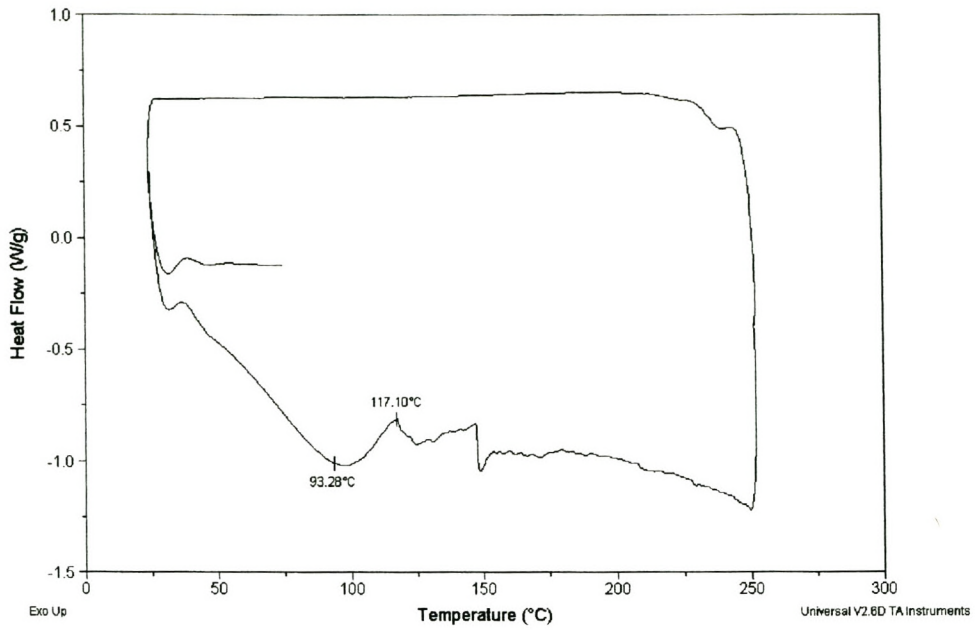
**Reaction nr 27: Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)**



Sample: POLY(2-M-1,5HD-CO-1,5H)  
Size: 5.0000 mg  
Method: polymer heat/cool/heat  
Comment: MADRI SMIT

DSC

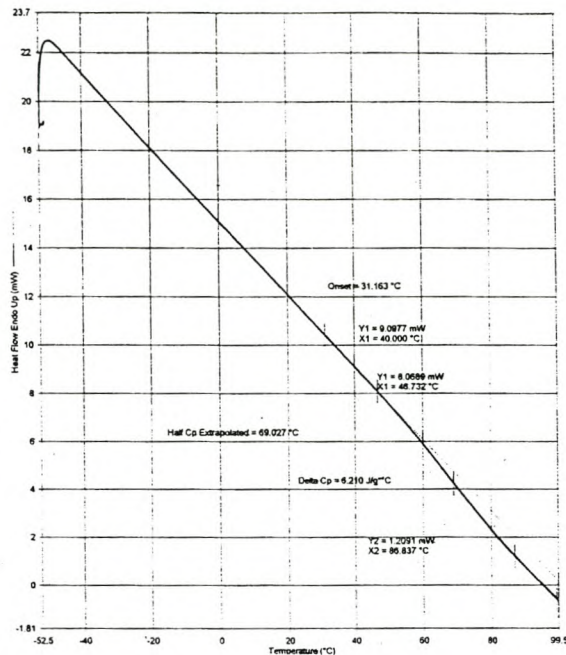
File: C:\...Madri6 001  
Operator: Bob  
Run Date: 6-Aug-01 14:47



Reaction nr 28: Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)

## DYNAMIC MECHANICAL ANALYSIS

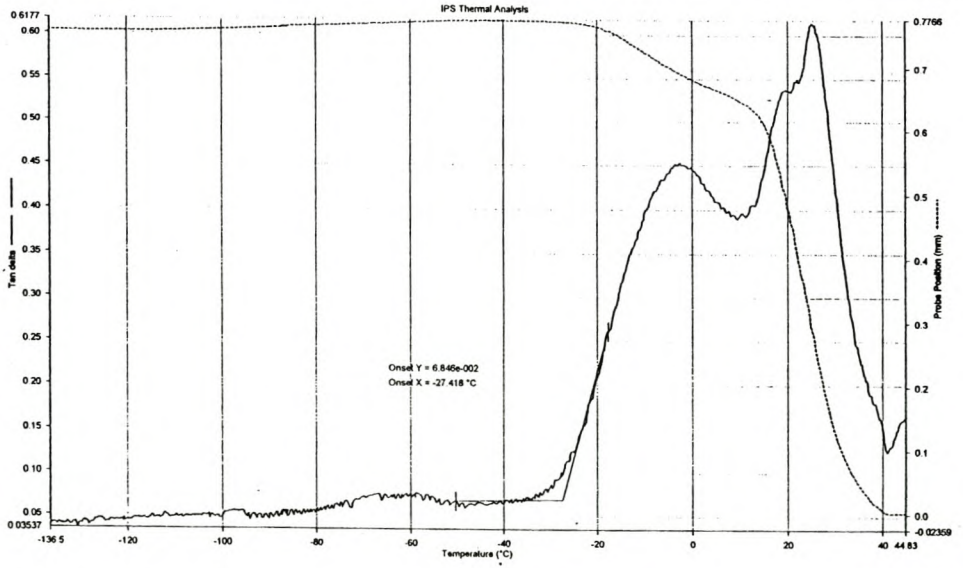
Path: C:\PE\PE\DATA\General\data  
 Operator ID: com  
 Sample ID: 1  
 Sample Weight: 1.000 mg  
 Comment: 1,5 hexadiene with pyrocarbon dichloride Gal



1) Hold for 2.0 min at -55.00°C  
 2) Heat from -55.00°C to 100.00°C at 10.00°C/min  
 3) Cool from 100.00°C to -55.00°C at 10.00°C/min  
 4) Heat from -55.00°C to 100.00°C at 10.00°C/min  
 5) Cool from 100.00°C to 25.00°C at 50.00°C/min 99/07/28 05:07:31

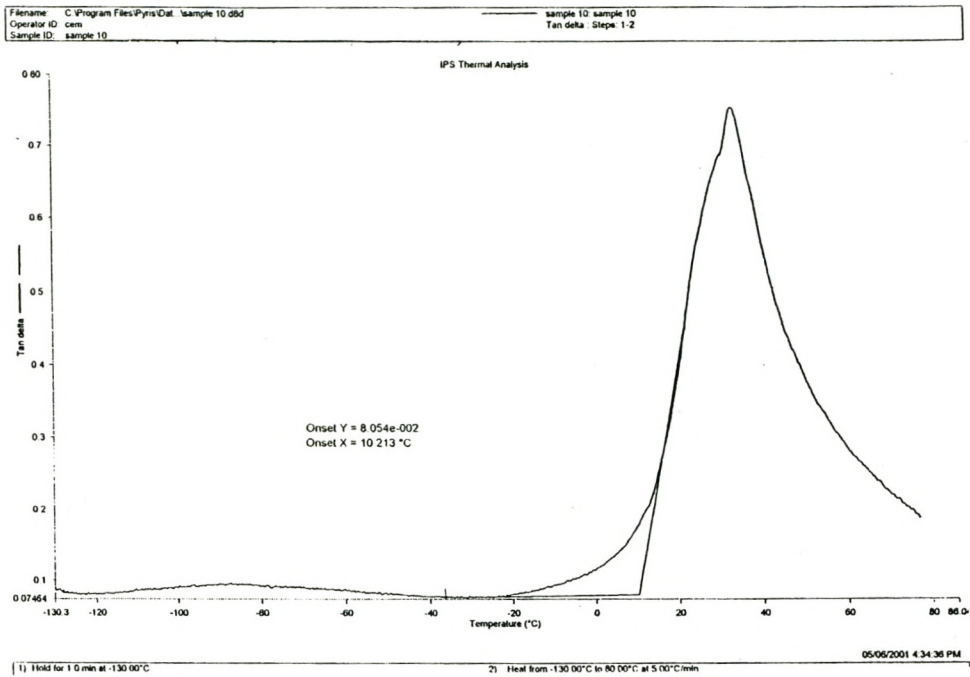
Reaction nr 01: Poly(1,5-hexadiene)

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 Operator ID: com  
 Sample ID: poly hexadiene (C<sub>8</sub>H<sub>14</sub>)  
 poly hexadiene: sample 4  
 Tan delta: Steps: 1-2  
 poly hexadiene: sample 4  
 Probe Position (mm): Steps: 1-2

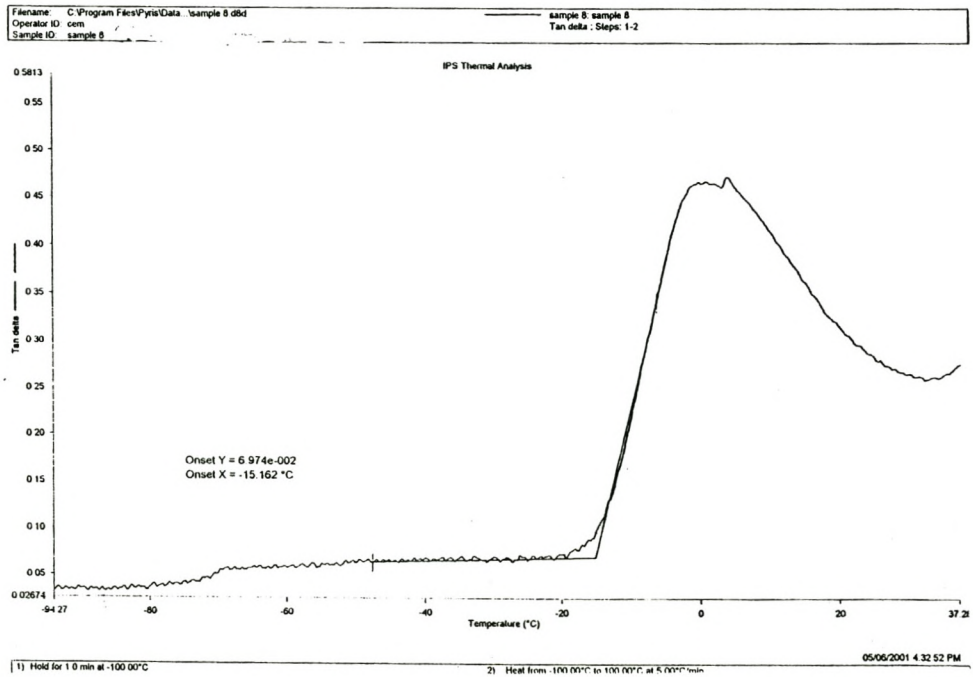


1) Hold for 1.0 min at -140.00°C  
 2) Heat from -140.00°C to 60.00°C at 5.00°C/min  
 07/05/2001 4:45:00 PM

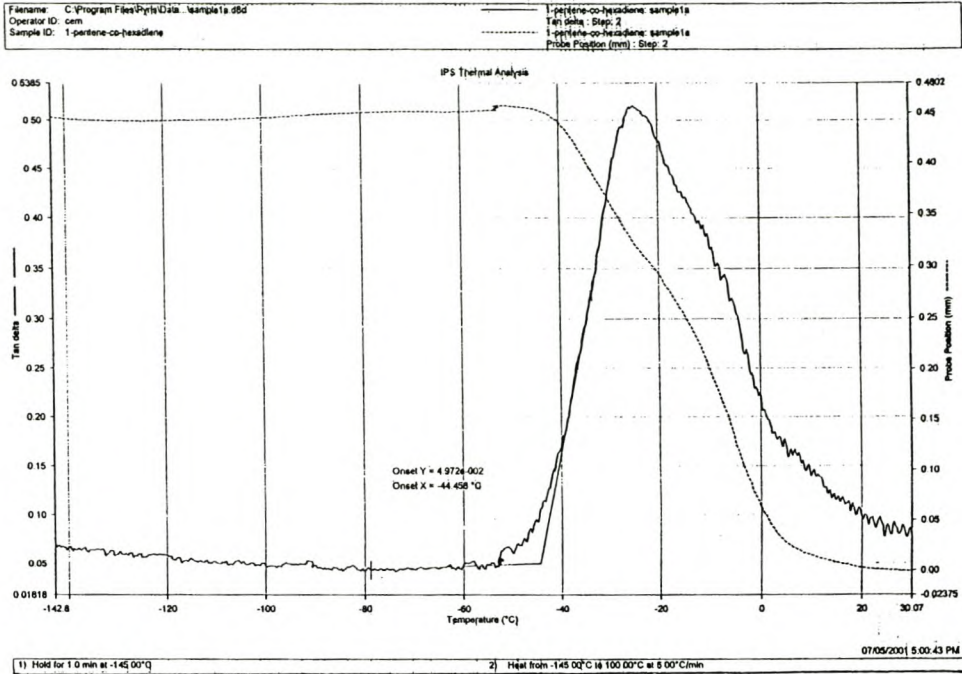
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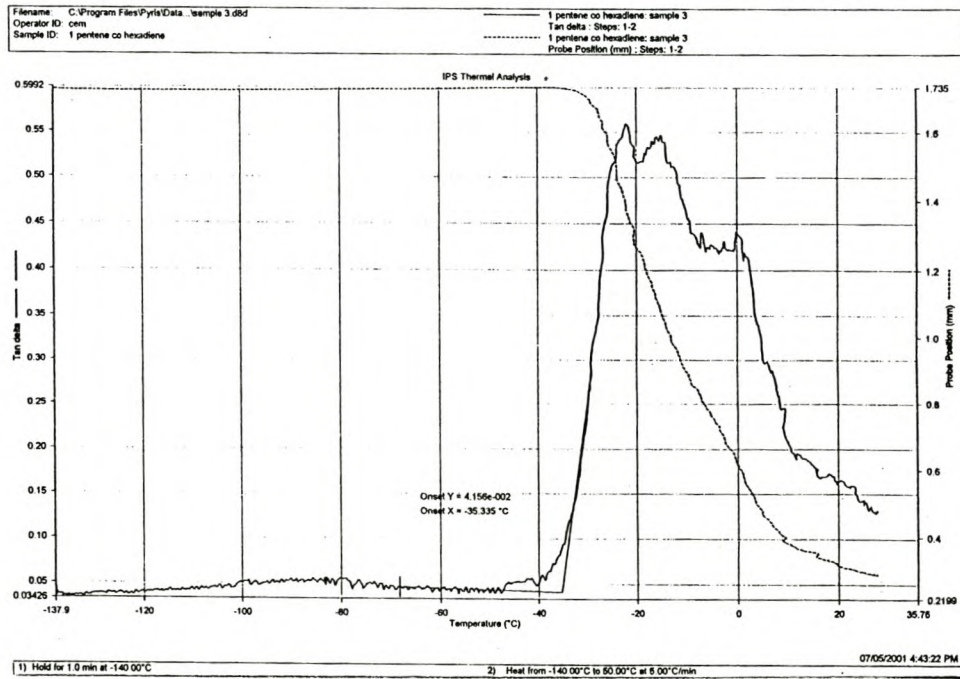
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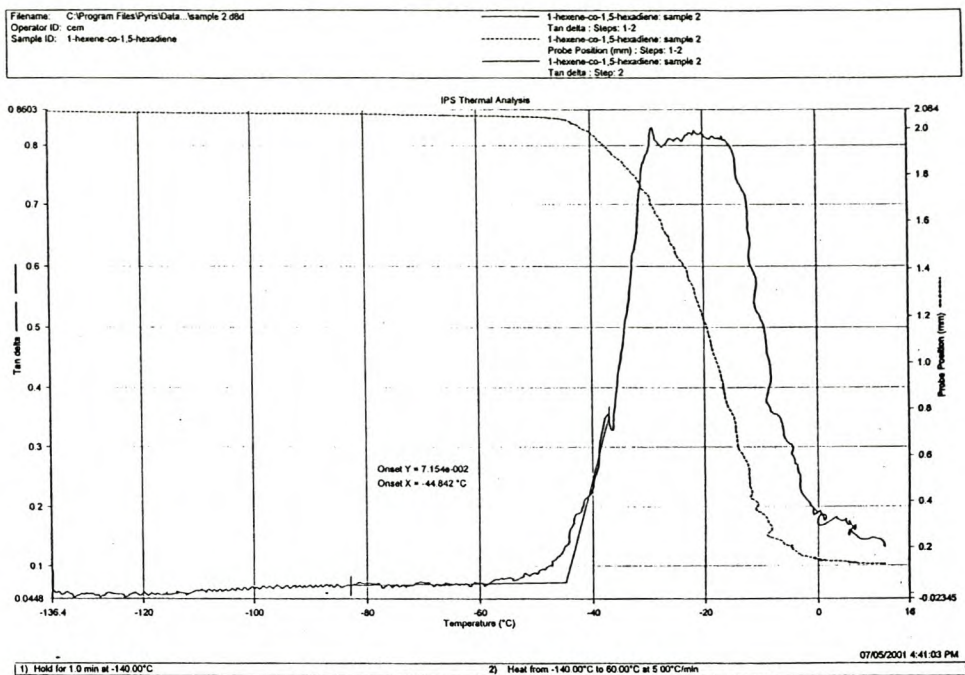
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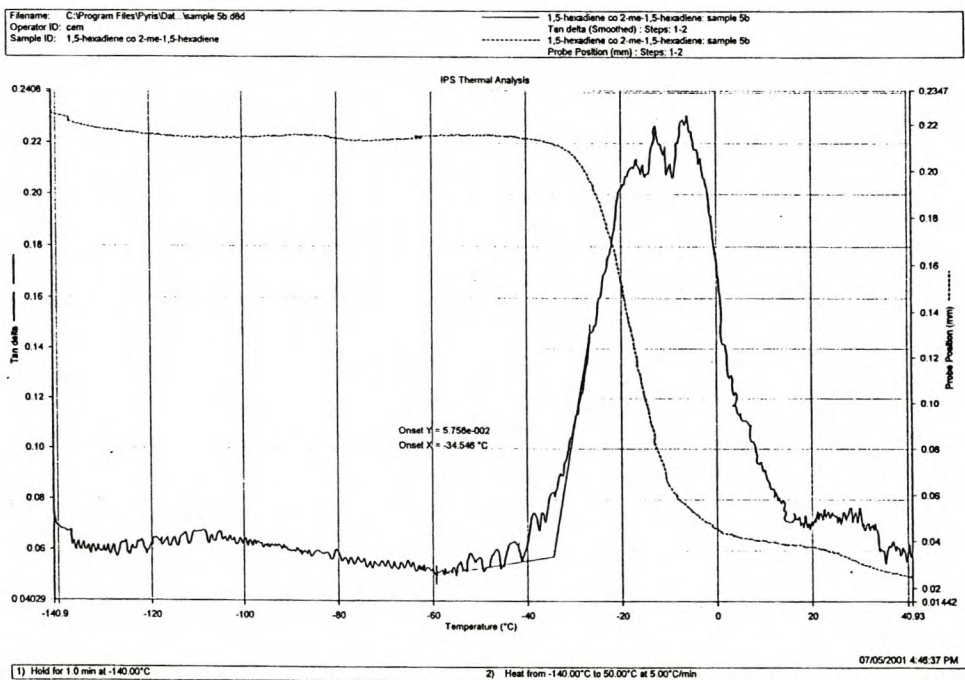
Reaction nr 16: Poly(pentene-co-1,5-hexadiene)



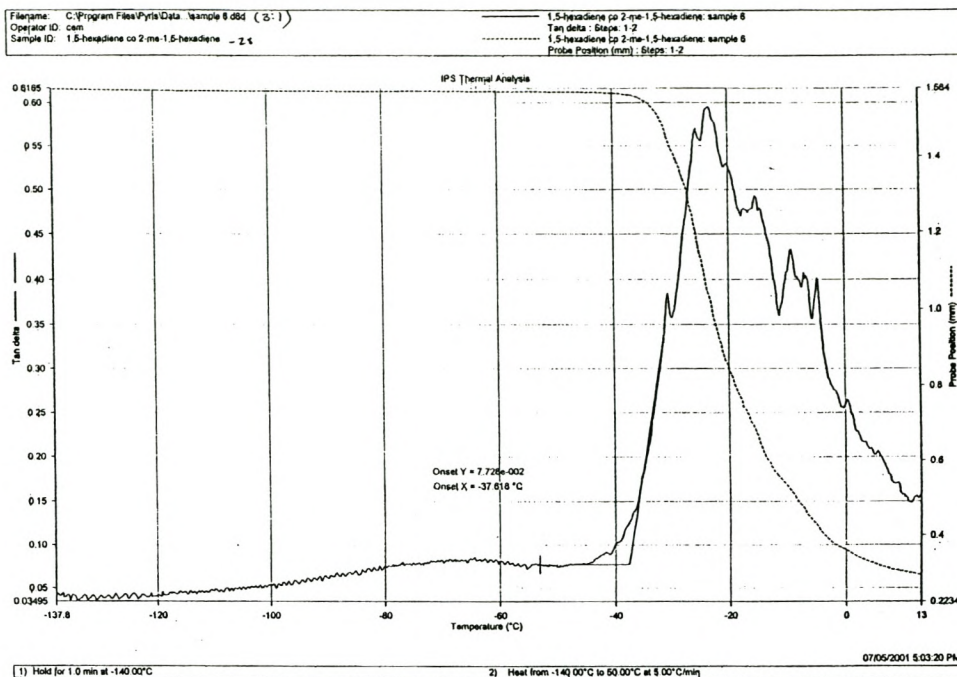
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Reaction nr 20: Poly(hexene-co-1,5-hexadiene)

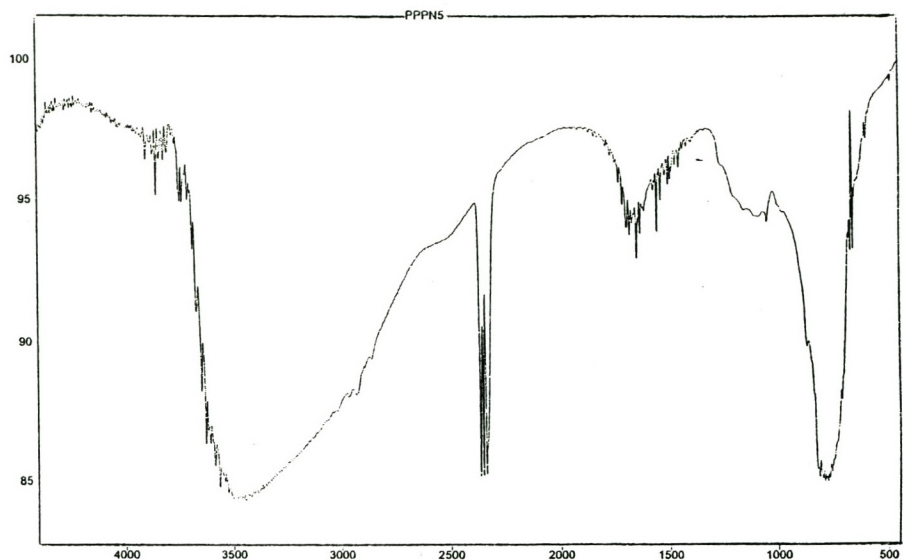


Reaction nr 27: Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)



Reaction nr 28: Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)

## INFRARED SPECTRA



Transmittance / Wavenumber (cm-1)

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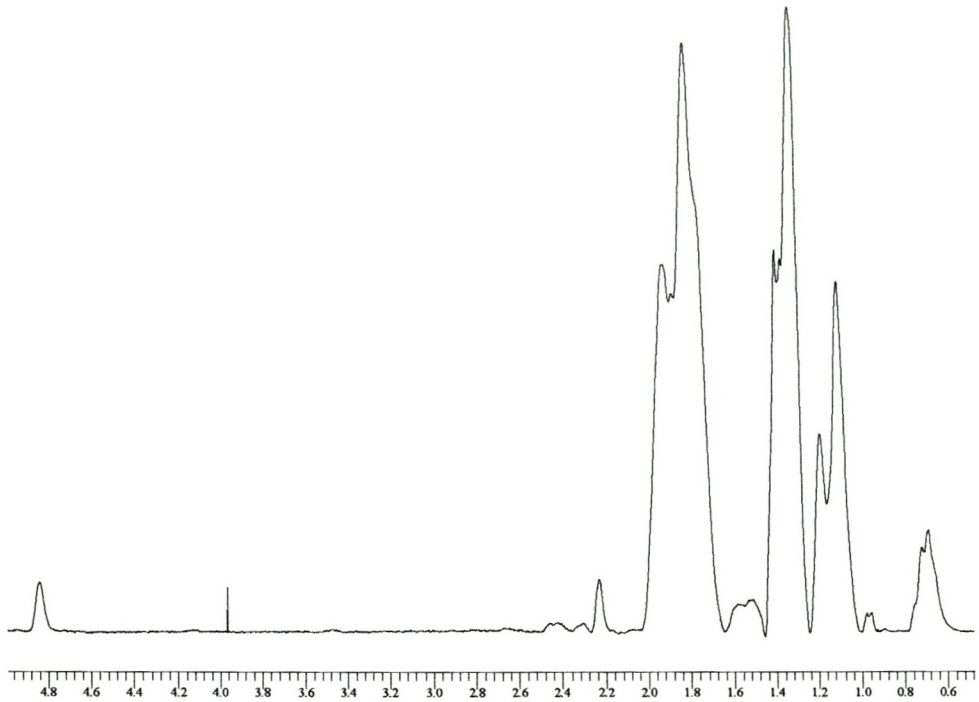
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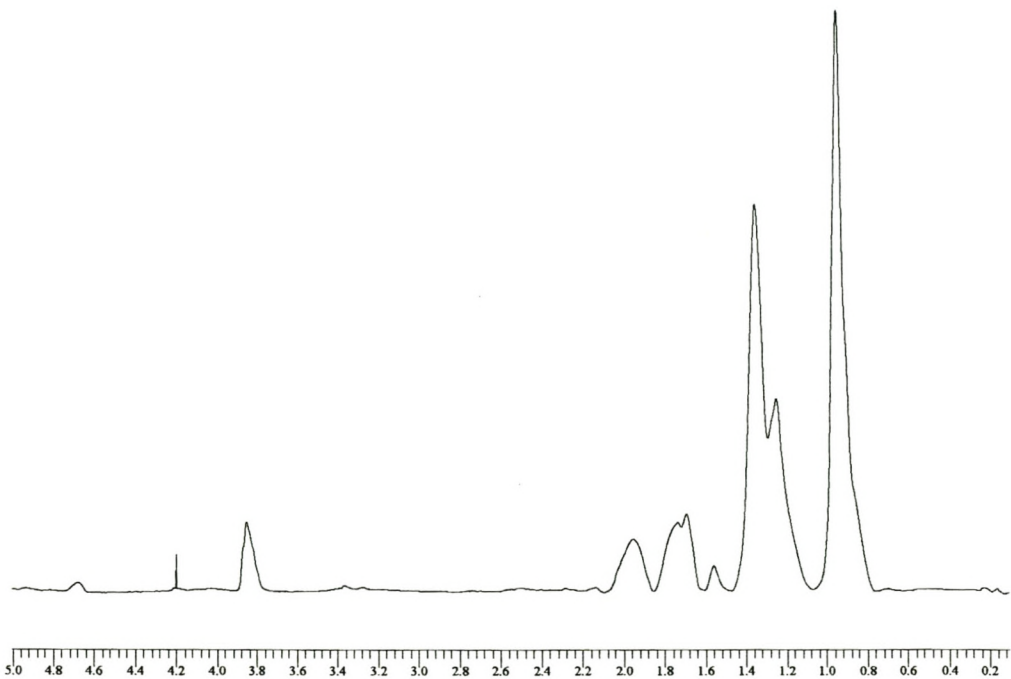
Madri Sample MA 054 white

**Reaction nr 31: Poly(carbon monoxide-co-1,5-hexadiene)**

## NUCLEAR MAGNETIC RESONANCE SPECTRA ( $^1\text{H}$ SPECTRA)

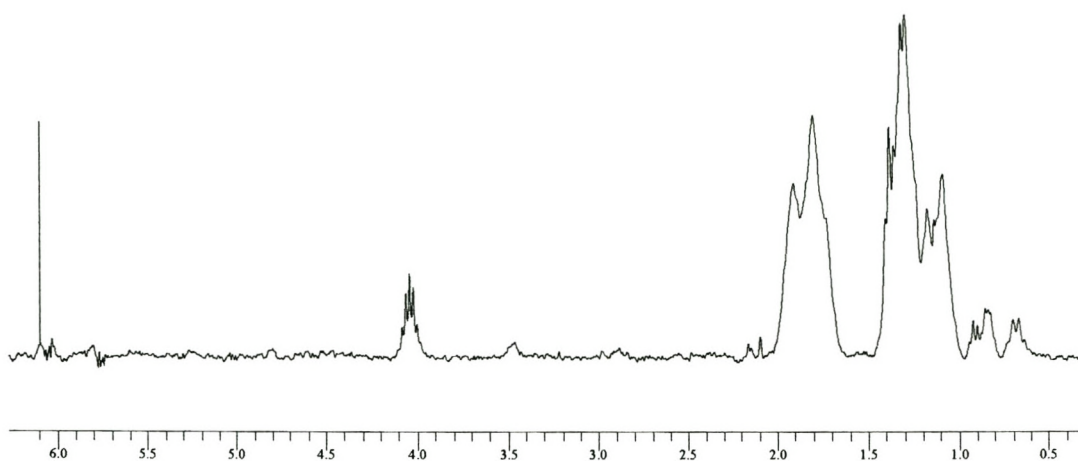


NMR 001 Poly(1,5-hexadiene)

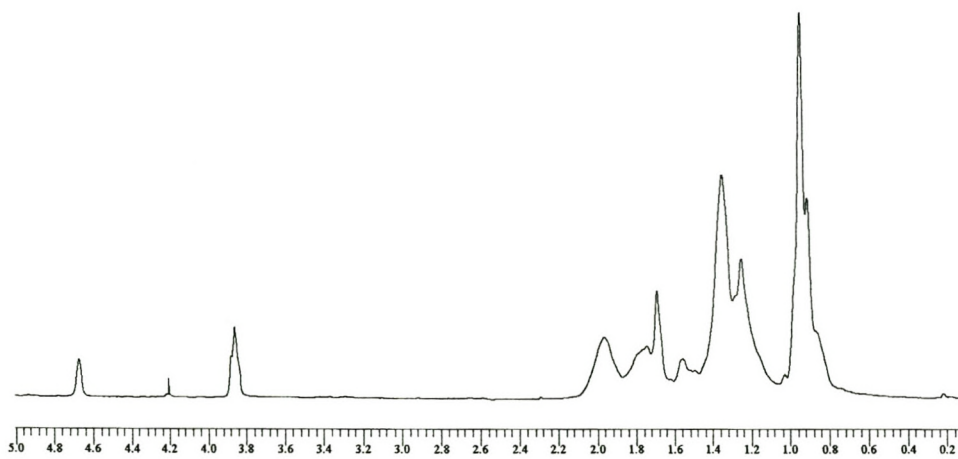


NMR 015 Poly(1,5-hexadiene)

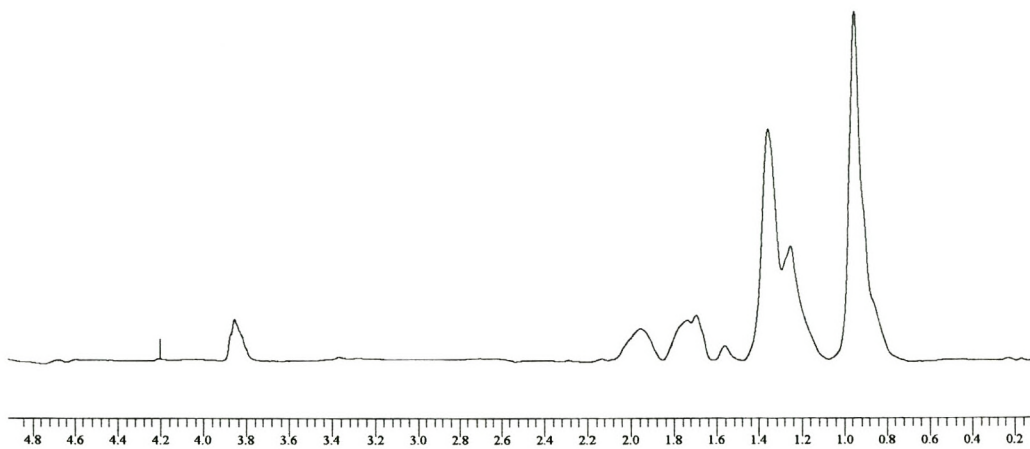




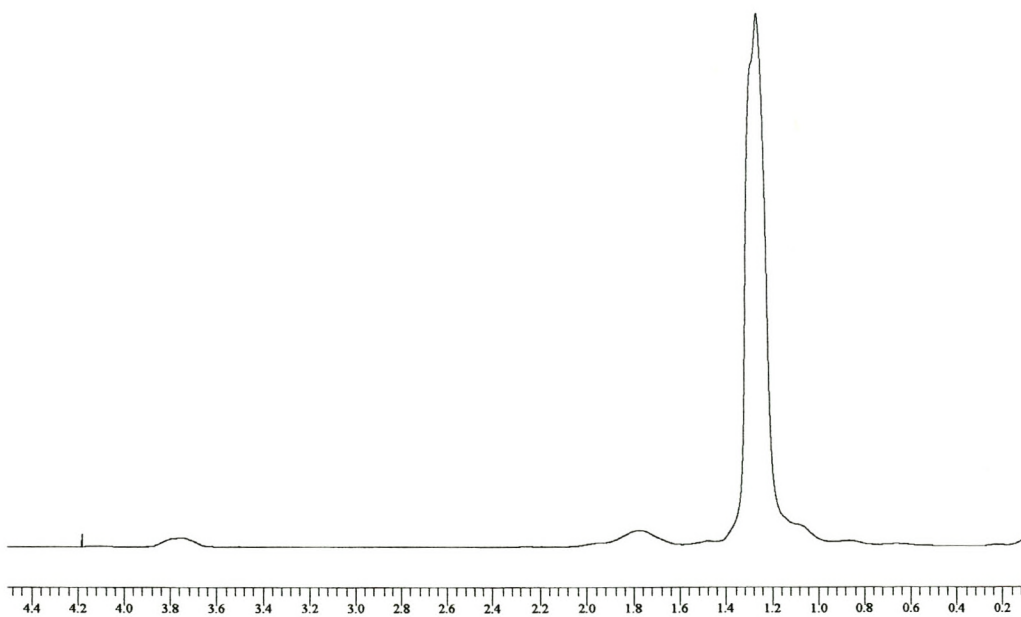
**NMR 057** Poly(1,5-hexadiene)



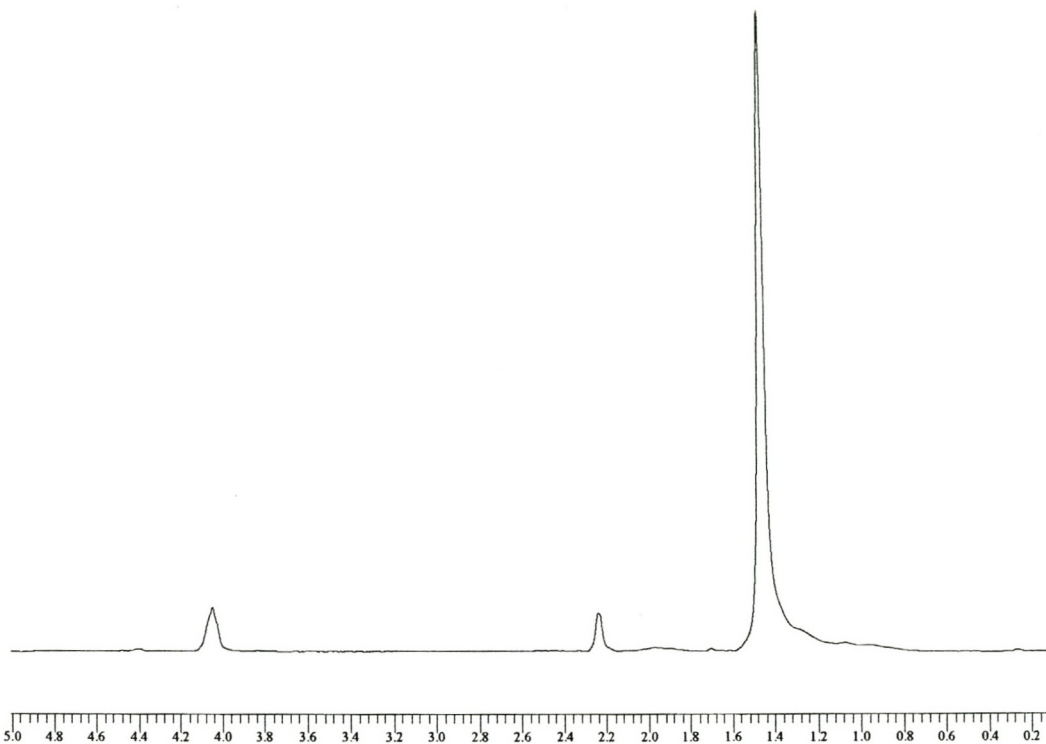
**NMR 014** Poly(2-methyl-1,5-hexadiene)



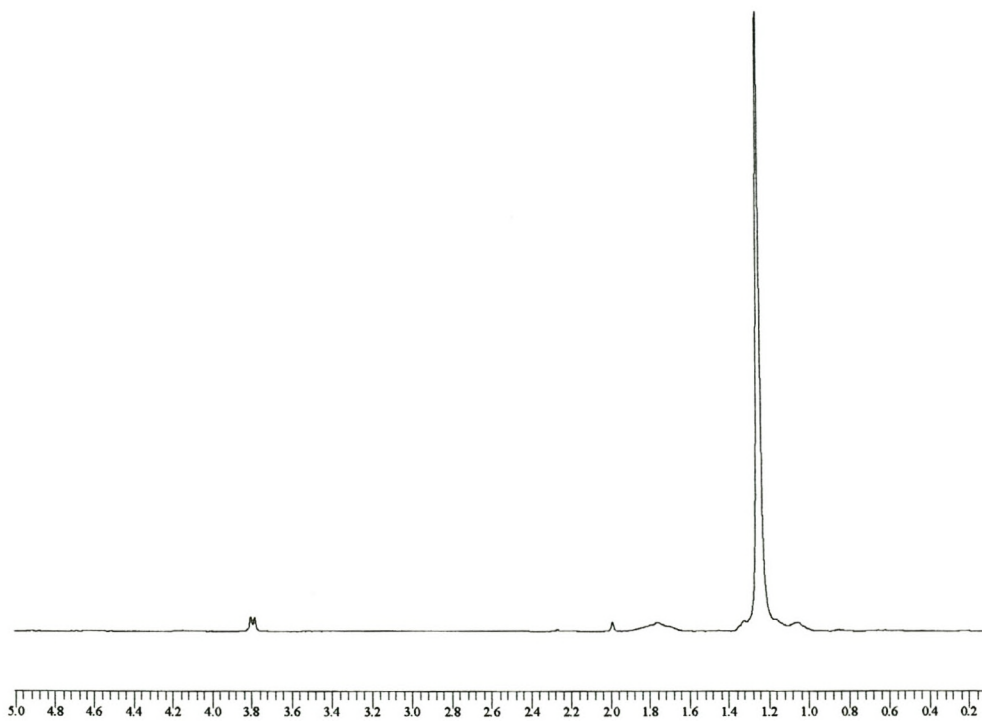
**NMR 015** Poly(2-methyl-1,5-hexadiene)



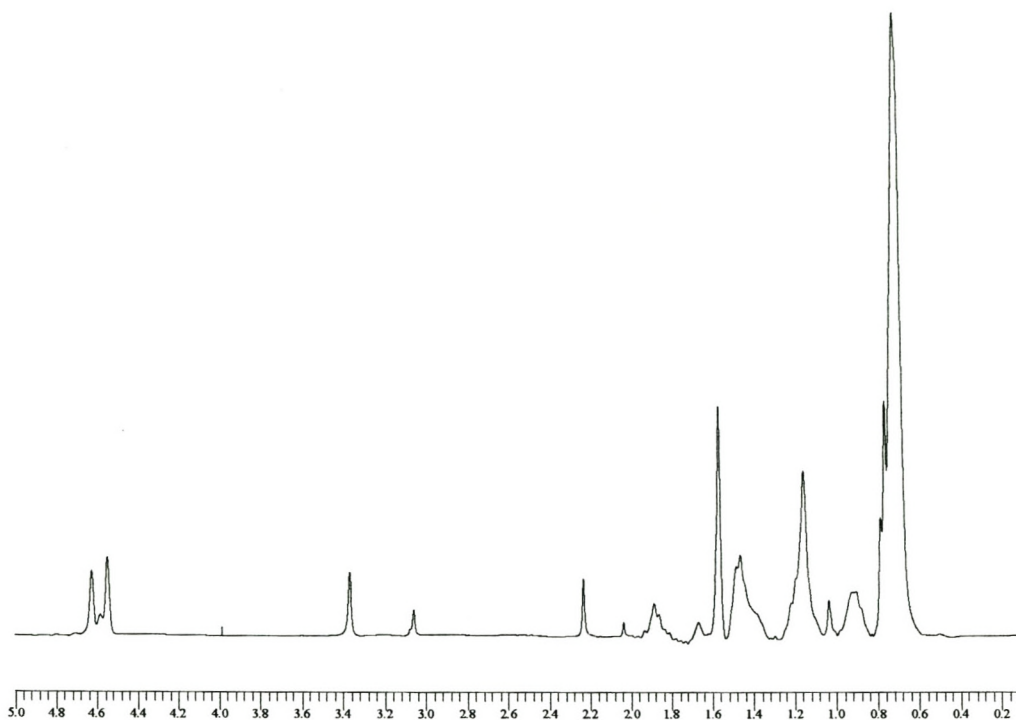
**NMR 009** Poly(ethylene-co-1,5-hexadiene)



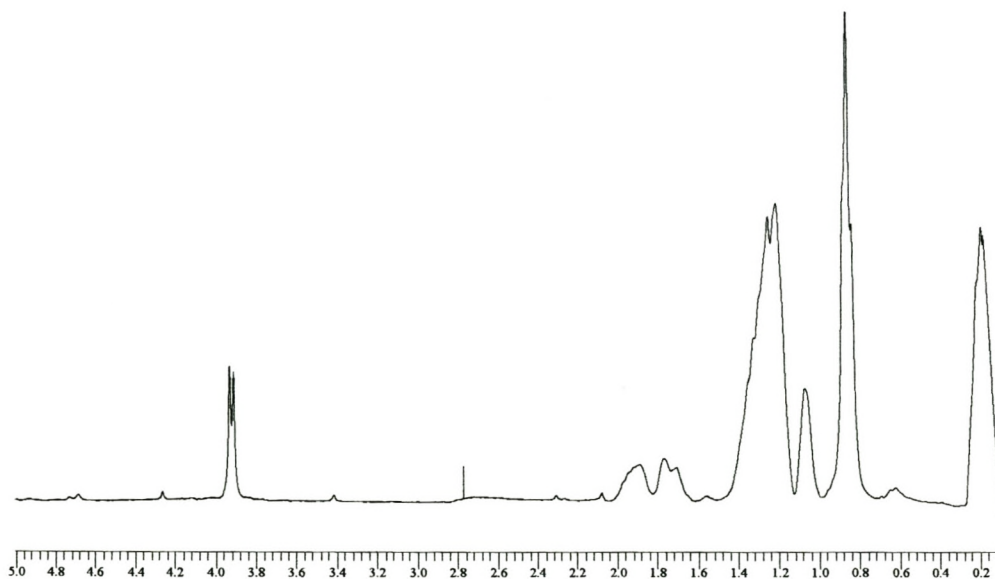
**NMR 054** Poly(ethylene-co-1,5-hexadiene)



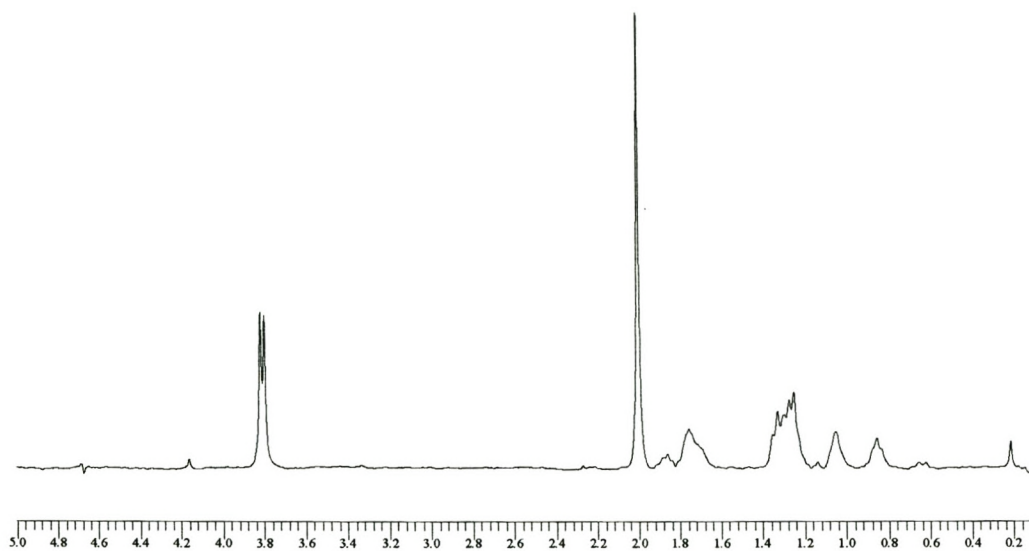
**NMR 052** Poly(ethylene-co-1,5-hexadiene)



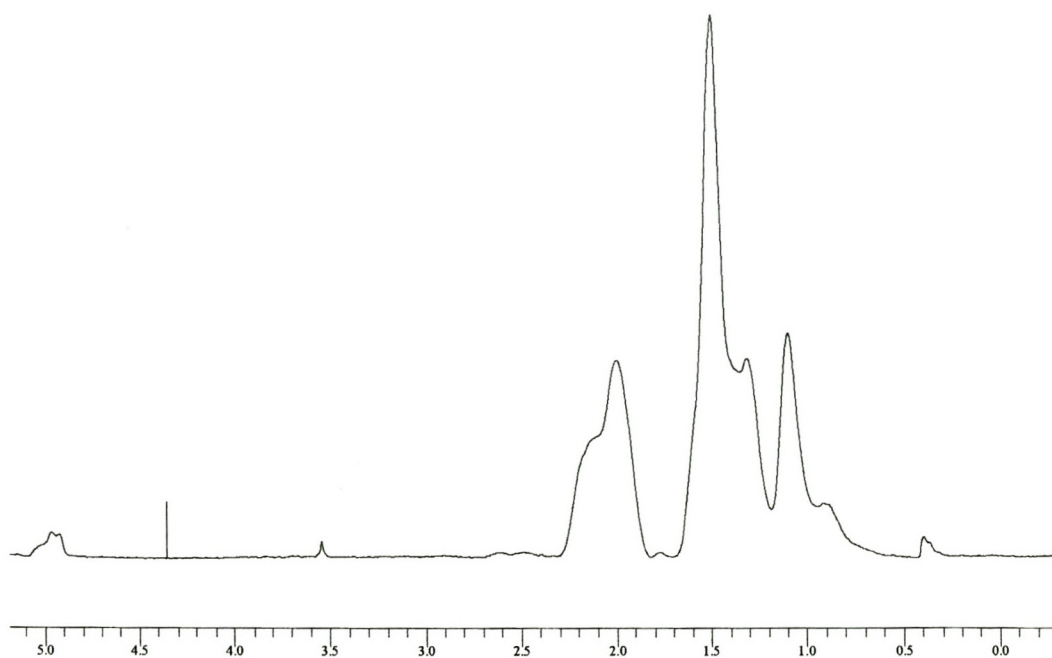
**NMR 056** Poly(propylene-co-1,5-hexadiene)



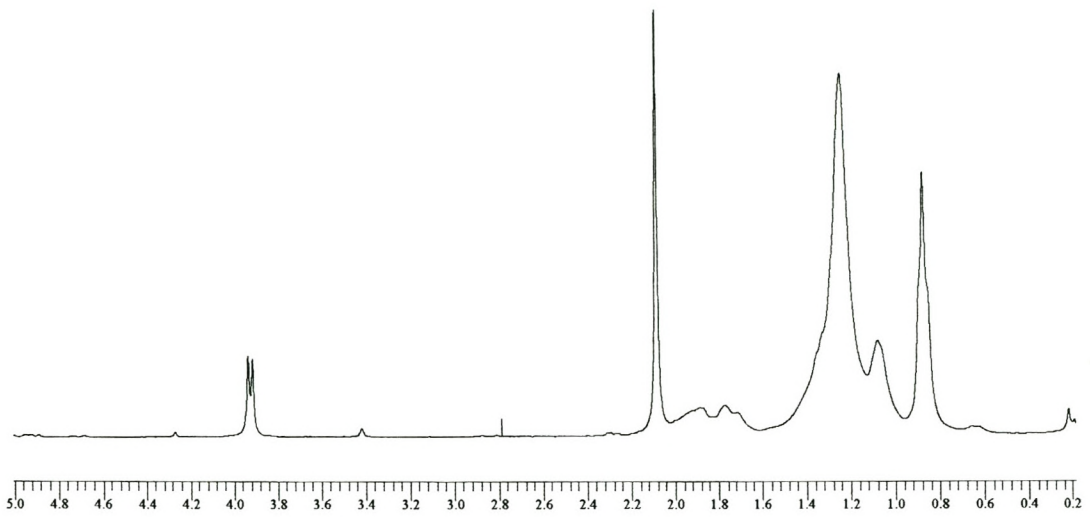
**NMR 12** Poly(pentene-co-1,5-hexadiene)



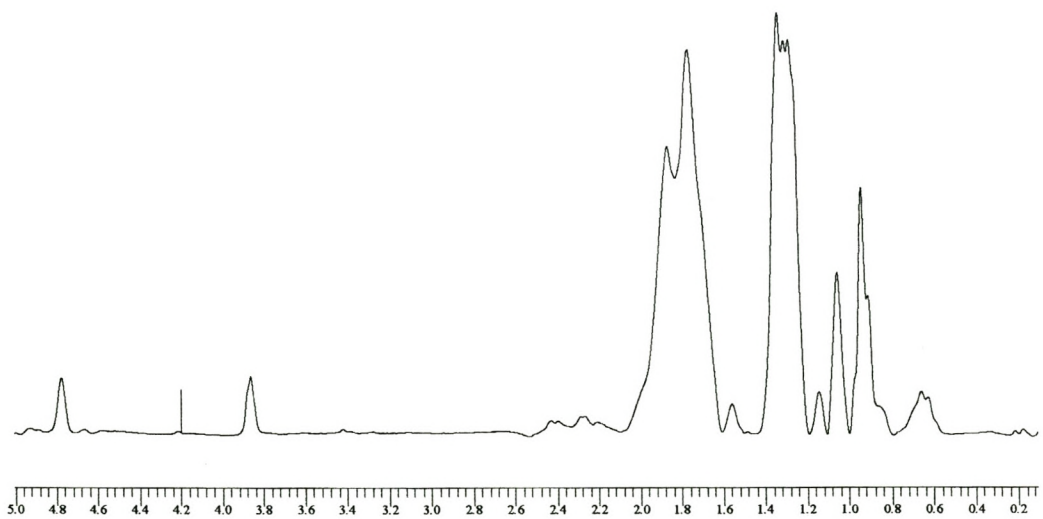
**NMR 055** Poly(pentene-co-1,5-hexadiene)



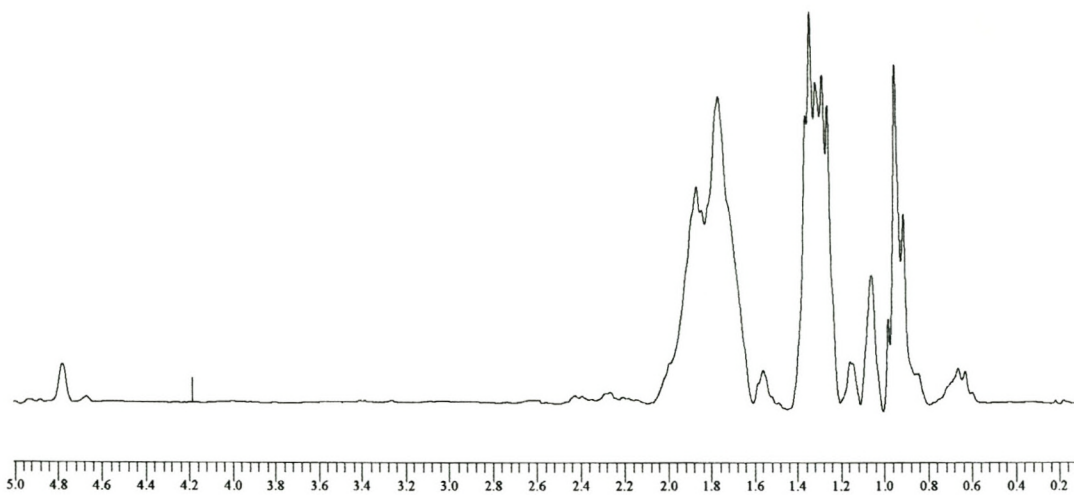
**NMR 008** Poly(hexane-co-1,5-hexadiene)



**NMR 010** Poly(hexane-co-1,5-hexadiene)

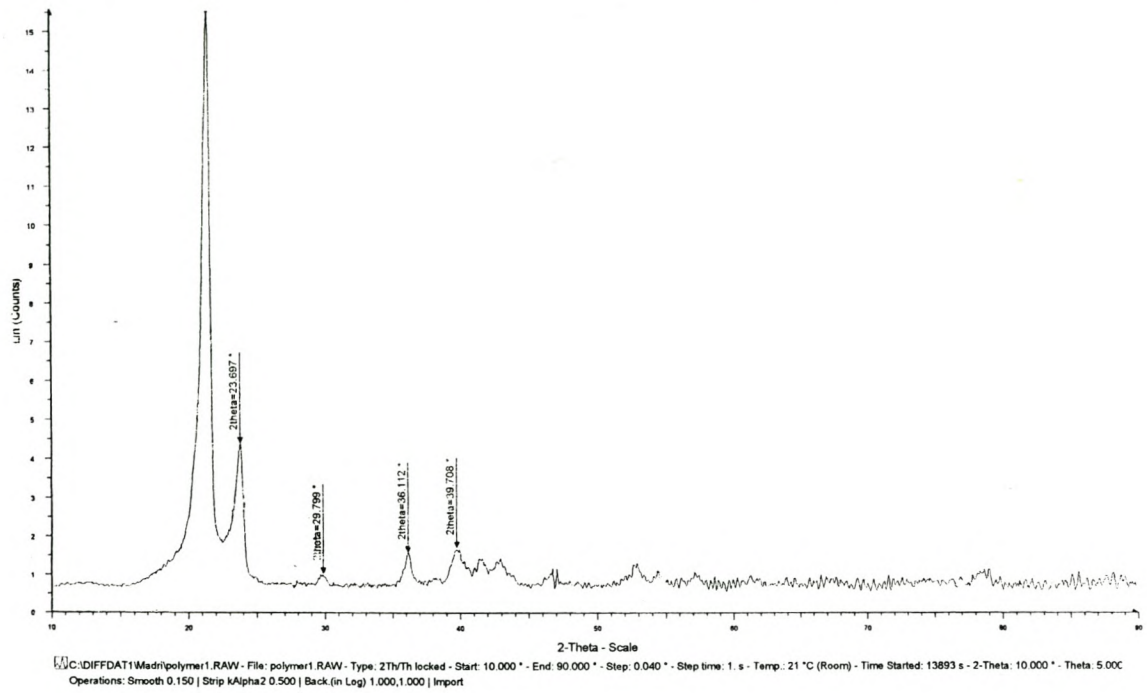


**NMR 016** Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)



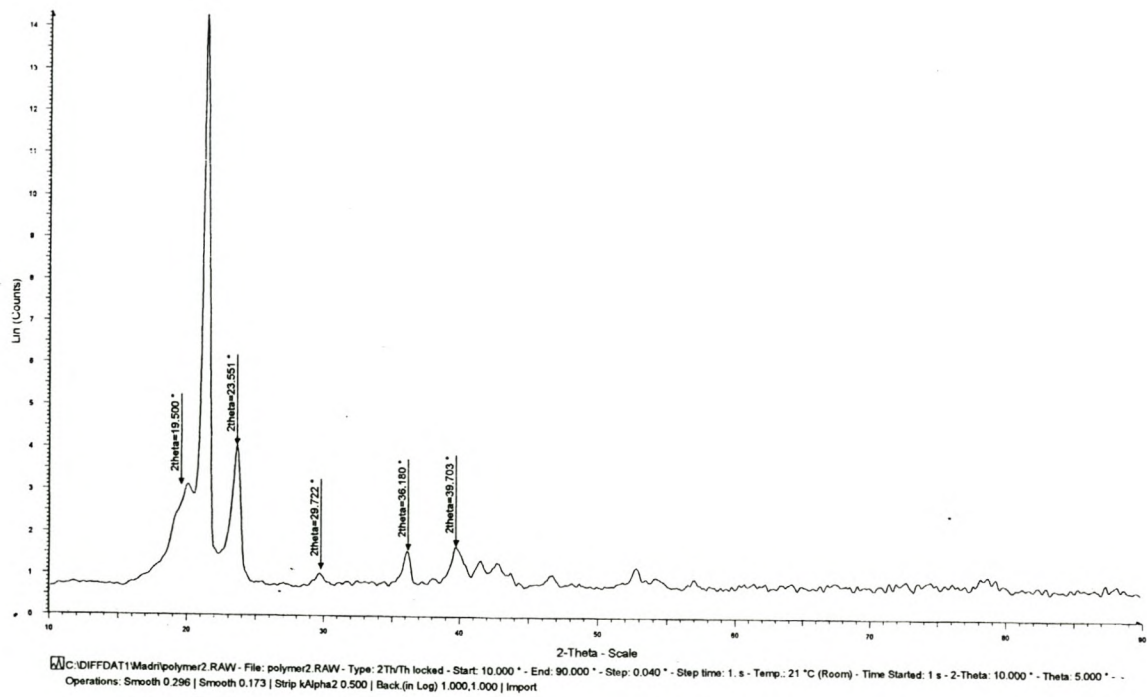
**NMR 017** Poly(2-methyl-1,5-hexadiene-co-1,5-hexadiene)

## WIDE-ANGLE X-RAY SCATTERING



Reaction nr 5

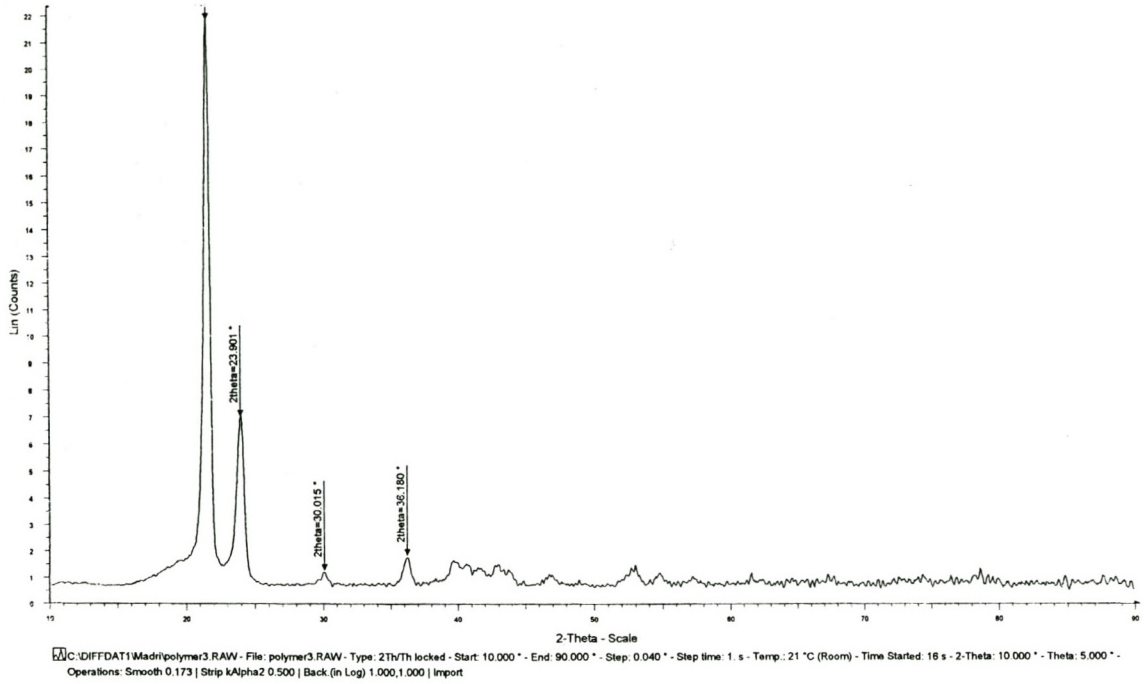
Poly(ethylene-co-1,5-hexadiene)



Reaction nr 6

Poly(ethylene-co-1,5-hexadiene)





Reaction nr 32

Poly(ethylene-co-1,5-hexadiene)