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Olefin Polymerisation Using Titanium Phosphinimide Catalysts

by

Steven N. Clemens

A Thesis

Submitted to the Faculty of Graduate Studies and Research

through the Department of Chemistry and Biochemistry

in Partial Fulfillment of the Requirements for

the Degree of Master of Science at the

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Abstract

Homopolymers of 1-hexene, random copolymers of 1-hexene and 1,5-hexadiene, and block copolymers of ethylene and 1-hexene have been prepared at sub-ambient temperatures using $\text{Cp}(\text{}^i\text{Bu}_3\text{PN})\text{TiMe}_2$ (**34**) and studied. In addition, the polymerisation of 1-hexene by (**34**) has been investigated for its potential as a living polymerisation system.

Analysis of the poly(1-hexene) produced by (**34**) via ^{13}C NMR spectroscopy reveals that the polymer contains an unusually high degree of 2,1 enchainments, with approximately one in five insertions being reversed relative to the previous one. This suggests that the coordination sphere in (**34**) is more open than in metallocene catalysts. However, despite the increased openness and ability to insert α -olefins in a 2,1 fashion, the internal olefins cyclopentene and *cis*-2-pentene could not be polymerised to an appreciable extent using (**34**).

A series of copolymers of 1-hexene and 1,5-hexadiene were prepared using (**34**), with varying amounts of 1,5-hexadiene in the monomer feedstock. Samples with a diene content of 50% were elastomeric materials, suggesting that crosslinking of inserted diene units is occurring. ^{13}C NMR analyses of the random copolymers reveals that the proportion of 1,5-hexadiene enchainment in the polymer is directly related to its proportion in the feedstock, indicating no preference for insertion of either a 1-hexene *vs.* a 1,5-hexadiene monomer. Analysis of the resonances in the ^{13}C NMR spectrum shows that the inserted 1,5-hexadiene units can be enchainment as cyclic structures, crosslinks, or pendant olefins. Integration of the ^{13}C and ^1H NMR spectra shows that approximately one in five inserted dienes remain as pendant olefins in the polymer.

Block copolymers of 1-hexene and ethylene were prepared using (34). It was observed that the properties of the block copolymers are unlike those of either of the homopolymers of which they are comprised. This shows that, although (34) is not a strictly living α -olefin polymerisation catalyst, its behaviour approaches that of a living catalyst, and can be used to produce block copolymers.

Dedication

*This work is dedicated to all of the
people who have made a difference in my life.*

Acknowledgements

I would like to thank a number of people who have, whether directly or indirectly, made this work possible and enhanced my life in the past few years. First and foremost, I would like to thank my supervisor, Doug Stephan. His support and friendship over the past few years have made my stay in Windsor enjoyable, whether over a piece of chalk and a chemistry talk, or a good laugh over potables at the local establishment.

I would also like to thank the members of the Stephan group with whom I have worked most closely during the time I have spent here: Chad Beddie, Emily Hollink, Sarah Hawkeswood, Katie Chan, Lourisa Cabrera, Jason Masuda, Jenny McCahill, Liam Spencer, Ramadan Altwer, Todd Graham, Pingrong Wei, and Denise Walsh. We've had a good group dynamic which made this an enjoyable experience both in and out of the lab. And, of course, the denizens of the Loeb group (a.k.a. the "Loebies"), our neighbours down the hall, ensuring nobody forgets the lighter side of life.

Special thanks go to Dr. James Gauld, Dr. Todd Graham, and Chad Beddie for all of their helpful suggestions and advice in proofreading my thesis (or, in certain cases, "dissin' the bro"!). I would also like to thank the members of my committee, Dr. Barb Zielinski, Dr. Steve Loeb, and Dr. Jim Green for helpful advice and tips. Thanks also to Mike Fuerth (our resident NMR guru), Sharon Horne, and the staff of the Chemistry office and the CCC. NOVA Chemicals Corporation is acknowledged for financial support, performing some of the NMR and GPC analyses, and for the opportunity for a summer work experience at their research facility in Calgary.

I would also like to acknowledge the housemates I've had over the past few years: "Goodlife" Greg Davidson (a.k.a. "Quadzilla", the only guy I know who can self-apply nicknames like these!), Liam Spencer, "Dennis the Chemist" Hoffart, and Joe "Dino" DiMartino. We came, we saw, we conquered.

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List of Abbreviations and Symbols

Å	Angstrom
Ar	Aryl
Bn	benzyl (CH ₂ Ph)
^t Bu	<i>tert</i> -Butyl (C(CH ₃) ₃)
°C	degrees Celsius
<i>ca.</i>	circa
Cp	cyclopentadienyl (η^5 -C ₅ H ₅)
CGC	constrained geometry catalyst
Cy	cyclohexyl (C ₆ H ₁₁)
DEAC	diethyl aluminum chloride
DEPT	Distortionless Enhancement by Proton Transfer
Et	ethyl (CH ₂ CH ₃)
FI	phenoxyimine catalyst
g	grams
GPC	Gel Permeation Chromatography
h	hours
L	litre
M	moles per litre
<i>m</i>	meso
MAO	methylaluminoxane
Me	methyl (CH ₃)
mes	mesityl (2,4,6-Me ₃ Ph)
MHz	megahertz
min	minutes

mL	millilitre
mm	millimetre
mol	mole
M_n	number average molecular weight
M_w	weight average molecular weight
MWD	molecular weight distribution
mw	molecular weight
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect
PDI	polydispersity index
ppm	parts per million
psi	pounds per square inch
Ph	phenyl
r	racemo
s	seconds
SEC	size exclusion chromatography
t	time
T_1	spin-lattice relaxation time
THF	tetrahydrofuran
trityl	triphenylmethyl (Ph_3C)
v	volume
w	weight
°	degree
η	hapto
μ	micro

Chapter 1 Introduction

Polymeric materials are omnipresent, being found in every living cell. Furthermore, both natural and synthetic polymers have found widespread applications throughout modern society. Consequently, substantial scientific effort is being undertaken to gain a greater understanding of the chemistry and properties of such compounds and materials. Such an understanding also enables the synthesis of new polymeric materials with unique properties.

Polyolefins are one class of synthetic polymers that has found particularly widespread use in modern society. The simplest member is polyethylene, and is one of the largest volume commodity chemical compounds on the market today. Billions of pounds of this material are produced every year in North America alone.^[1] The reason that this material is produced in such exorbitant quantities is its sheer usefulness. The lifestyle of each and every person in any developed nation on earth is affected by these materials and objects made from them.

1.1 History of Catalytic Olefin Polymerisation

In 1937, Imperial Chemical Industries (ICI) reported the synthesis of polyethylene.^[2] The material was made by subjecting very high pressures of ethylene gas (14000 - 40000 psi) and to high temperatures (100 - 400°C). Though the resultant material was of relatively low molecular weight (~ 60000 g/mol),^[3] the usefulness of the

material was quickly recognised, and was being produced commercially by the late 1930's. This discovery also realised a new area of chemistry, and before long there were other research groups investigating methods of synthesising this material.

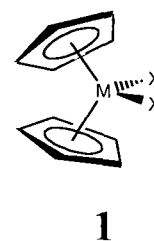
A significant discovery was made in the early 1950's by German chemist Karl Ziegler. His research group was investigating the synthesis of polyolefins in a stepwise fashion by inserting olefins into the C-Li bond of alkyllithium reagents. This method worked well in making oligomers of ethylene, however, the temperatures required to make longer chain polymers resulted in the decomposition of the alkyllithium reagent rather than the desired chain reaction of ethylene insertion. At this time, lithium aluminum hydride (LiAlH_4) had recently been discovered,^[4] and it was found that when used as the lithium source, an appreciable amount of polymer was formed. It was later deduced that the crucial component of the LiAlH_4 was not lithium but aluminum, however, further experiments showed that a fortuitous trace of metallic nickel was also at play. Experimentation with other substances that had effects "somewhat similar to those of nickel" led them to develop a system using TiCl_4 and an organoaluminum reagent which allowed them to polymerise ethylene even at atmospheric pressure.^[5, 6] This was a significant breakthrough in olefin polymerisation science, since now not only could ethylene be polymerised under mild conditions, but the resultant "low pressure polyethylene" was a more rigid material than the "high pressure polyethylene" made by ICI, and hence was a considerably more useful material.

This work earned Ziegler the Nobel Prize in Chemistry in 1963 (shared with Italian chemist Giulio Natta for contributions concerning the microstructure of polypropylene). This technology, now known as "Ziegler-Natta Polymerisation", is still in practice today for the production of many polyethylene resins.

1.2 Metallocene Catalysed Olefin Polymerisation

Further research into transition metal catalysed olefin polymerisation prompted Natta^[7] and Breslow^[8] to independently explore the use of Cp_2TiCl_2 (titanocene dichloride, **1**), $\text{M} = \text{Ti}$ $\text{X} = \text{Cl}$), activated with triethylaluminum (AlEt_3) and diethylaluminum chloride (AlEt_2Cl), respectively, for the polymerisation of ethylene. Breslow noted that when the polymerisation reaction was performed under strictly anaerobic conditions, this catalyst system produces little or no polyethylene. However, when small amounts of air were allowed into the system, it became as active as the Ziegler-Natta system, and produced a more linear polymer.^[8] Moreover, this was the first known example of a soluble chemical compound effecting the polymerisation of ethylene, which opened a door to the understanding of the details of the polymerisation reaction.

Since this discovery, a major focus of the research performed in the field of olefin polymerisation has been devoted to the use of metallocenes, particularly titanocenes (**1**, $\text{M} = \text{Ti}$) and zirconocenes (**1**, $\text{M} = \text{Zr}$). This is due in part to the fact that, especially when activated with MAO (methylaluminoxane), they produce exceptionally active catalysts.^[9] MAO is an ill defined mixture of the general chemical formula $[\text{Al}(\text{CH}_3)\text{O}]_x$, which is obtained by the partial hydrolysis of trimethylaluminum.^[10] The role of MAO is three-fold: 1) to scrub the reaction mixture of traces of water; 2) to alkylate the metallocene dichloride catalyst precursor; and 3) to abstract an alkide from the resultant metallocene dialkide species to form an electronically and coordinatively unsaturated organometallic species.^[11] It is generally agreed that this species is the active catalyst.^[12]



A further avenue for research concerning polymerisation using metallocene catalysts is related to the ancillary ligands. The cyclopentadienyl fragment can be easily altered with a wide range of substituents to control the steric and electronic properties of the catalyst precursor. Figure 1.1 shows some representative examples of such compounds, where the substitution of the cyclopentadienyl fragment can be alkyl substitution (**2**), an annulated aryl ring (indenyl) (**3**, **4**), two annulated rings (fluorenyl) (**5**, **6**), and the family of *ansa*-metallocenes, which are two cyclopentadienoid fragments bridged by a suitable group (**7** - **12**). As one would expect, there is a myriad of possible substitution patterns based on these general structures, which have been reviewed elsewhere.^[13] Through control of the ligand substitution pattern, one can control the activity of the polymerisation catalyst as well as the subtle properties of the resultant polymer, particularly when using members of the *ansa*-metallocene family. Certain substituted complexes of the type **9**, owing to their C_2 symmetry, produce highly isotactic polypropylenes, while other substituted complexes of the type **10**, owing to their C_1 symmetry, produce highly syndiotactic polypropylenes^[14] (*vide infra*). As a result, significant effort has been put into the development of this family of compounds for olefin polymerisation.

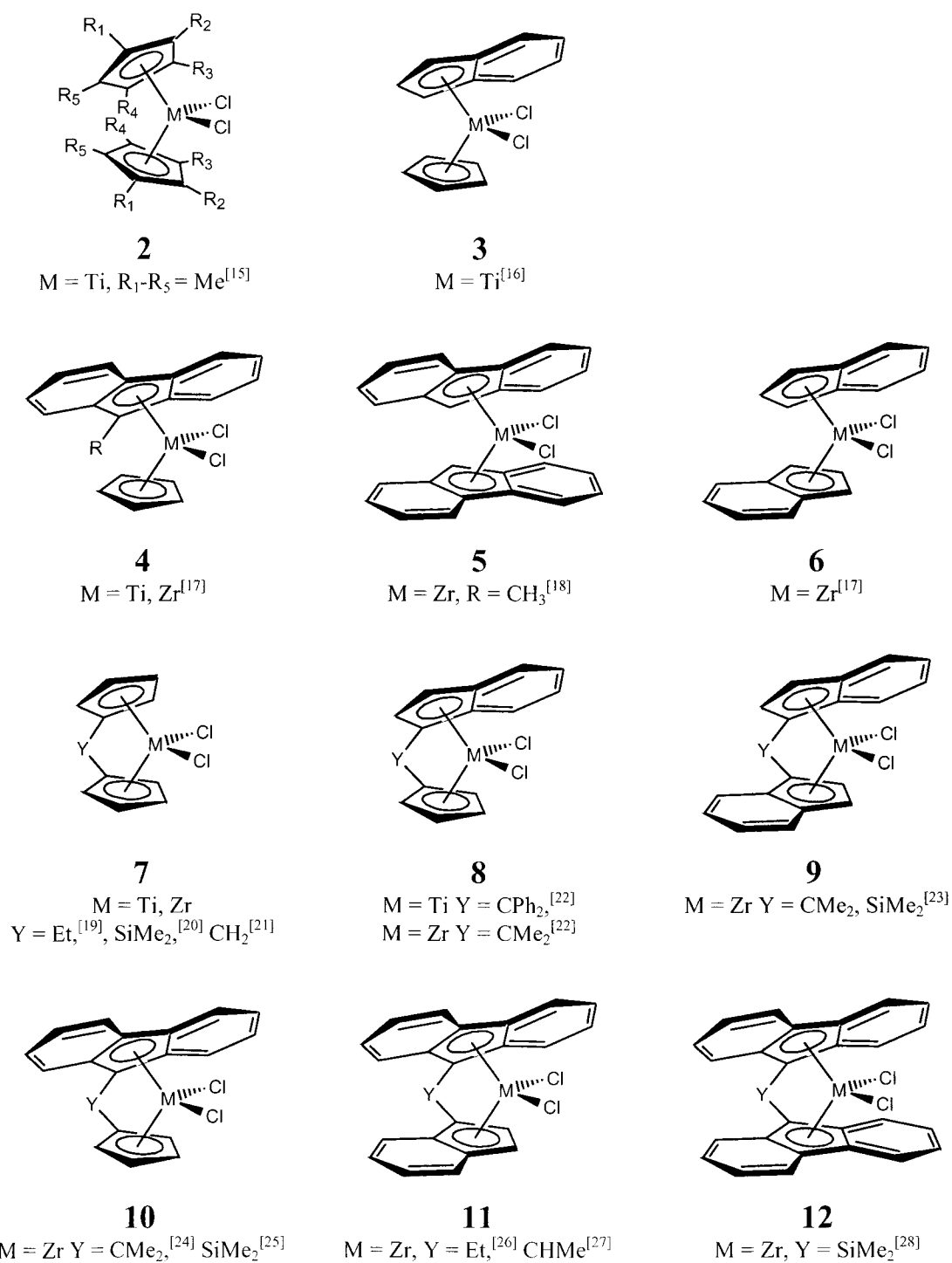
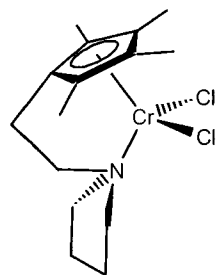
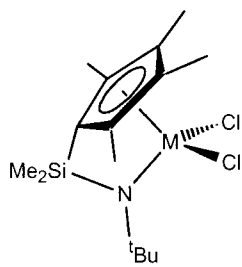


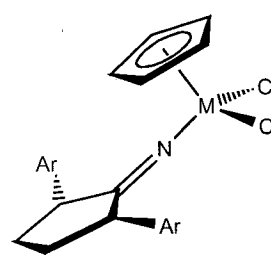
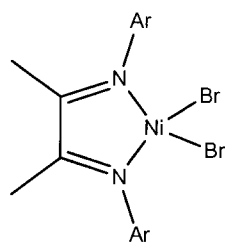
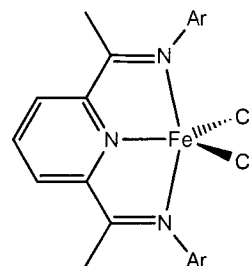
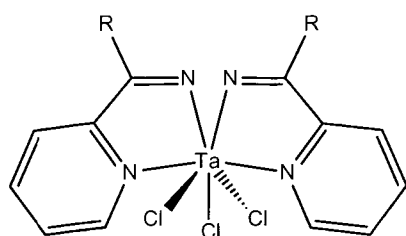
Figure 1.1. Group IV Metallocene Catalysts.

1.3 Alternatives to Metallocene Catalysts

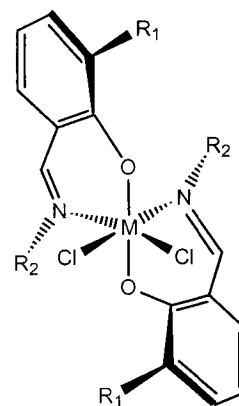
In spite of the high activity and exceptional utility of metallocene based catalysts for olefin polymerisation, much effort has been directed toward the search for alternative catalysts. This is due in part to circumvent existing patents for olefin polymerisation using metallocene catalysts, and can also develop polymers with novel chemical and physical properties. Figure 1.2 shows diagrams of a selection of some of the more active examples which are based on a wide variety of transition metals. It should be noted that, although there are isolated examples of active catalysts based on many metals across the transition row, the majority of those which are very active catalysts are complexes based on titanium and zirconium. Two excellent reviews^[29, 30] have been published which systematically categorise a wide variety of nonmetallocene olefin polymerisation catalysts, and correct many of the reported activity values for pressure. Although many of these catalysts have reported activities which rival or surpass Cp_2ZrCl_2 , only a few of them (**14**, **16**, **19**) have been exploited for commercial use.^[31-34] It is interesting to note that these three cases are all based on exceptionally different catalysts (one based on nickel, one based on tetrahedral titanium or zirconium, and one based on octahedral titanium or zirconium), and suggest different reasons for the high activity. In the case of Brookhart's nickel diimine catalyst (**16**), chain termination processes are presumed to occur through axial approach of olefins. The bulky substituted aryl groups on the imine functionalities restrict the approach of olefins to the equatorial plane, thereby producing long lived catalysts.^[35] The high activity of Mitsui's family of phenoxyimine (FI) catalysts (**19**), as well as the "constrained geometry catalysts" (CGC) (**14**) has been attributed to greater exposure of the transition metal centre, thereby providing more space for olefin binding.^[36, 37]

**13****14**

M = Ti, Zr

**15**M = Ti, Zr;
Ar = Ph, 2,6-Me₂Ph**16**Ar = 2,6-(ⁱPr)₂C₆H₃^[35]**17**Ar = 2,6-(ⁱPr)₂C₆H₃, 2,6-(ⁱPr)₂-4-MeC₆H₂**18**

R = Bz, Ph

**19**M = Ti, Zr
R₁, R₂ = alkyl, aryl
Most active: R₁=Cy, R₂=C(Me)(Ph)₂**Figure 1.2.** Alternatives to Metallocene Catalysts.

1.3.1 Phosphinimide as Ancillary Ligand

Another example of a family of highly active olefin polymerisation catalysts system are those based on the use of the phosphinimide (R_3PN) functionality, developed in the Stephan group. Compounds such as that shown in Figure 1.3 have been demonstrated to be remarkably active olefin polymerisation catalysts, with activities comparable to or better than metallocene or constrained geometry catalysts.^[38, 39] For this reason, this family of catalysts are currently under study for commercial exploitation by NOVA Chemicals Corporation.

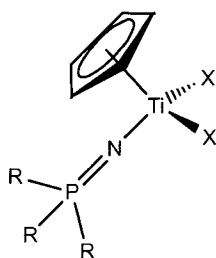


Figure 1.3. Phosphinimide Catalyst.

As in the case of the CGC and Mitsui FI catalysts, the remarkable olefin polymerisation activity of this family of compounds can be attributed, at least in part, to a more open metal centre for olefin complexation. In addition, the ease of modification of the substituents on the parent phosphines allows for systematic variation of the steric and electronic properties of the phosphinimide ligand. As a result, a wide variety of complexes based on this theme have been synthesised, characterised, and tested for their activity in olefin polymerisation.^[40]

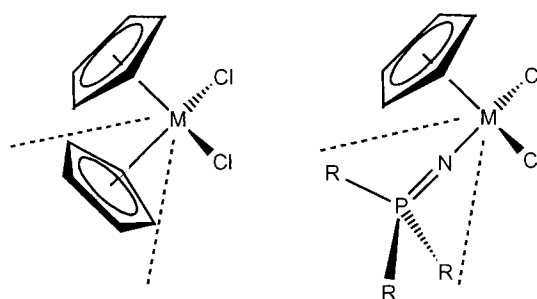


Figure 1.4. Cone Angle Comparison.

When compared to a metal bound cyclopentadienyl ligand, the phosphinimide moiety shows a remarkable similarity in the cone angle subtended at the metal centre. However, the bulk of the phosphinimide ligand is situated further from the metal centre, thereby opening up the coordination sphere (Figure 1.4).^[40, 41] From an electronic point of view, a metal phosphinimide complex can be drawn as one of a number of canonical structures, shown in Figure 1.5. These structures correspond to 2-, 4-, and 6-electron donor structures. The 6-electron donor structure is isoelectronic with the cyclopentadienyl anion, and has been suggested to be the dominant bonding mode in transition metals with empty *d*-orbitals, such as Ti(IV).^[42] Based on computational studies, the 4-electron donor has been suggested by Sundermann *et al.* to be the most accurate representation.^[43] X-ray crystallography has shown that many transition metal phosphinimide complexes are linear or nearly linear about the nitrogen atom, and that the N-M bonds are shorter than in corresponding transition metal amides (*c.f.* Ti-N distance of 1.938Å (average) in $\text{Ti}(\text{NPh}_2)_4$ ^[44] to Ti-N distance of 1.719Å in $(\text{Ph}_3\text{PN})\text{TiCl}_3$ ^[42]). These two facts suggest that structures **A**, **B**, and **D** are unlikely, due to the fact that they would be expected to be bent, while structures **C** and **E** would be expected to possess the shorter M-N bond lengths which are experimentally observed. The best description is probably a combination of these modes, depending on the electronic properties of the other ligands on the metal centre. This shows that the

phosphinimide functionality is electronically flexible, an advantage for stabilising the various electronically diverse intermediates which are presumed to be a part of the olefin polymerisation mechanism (*vide infra*).

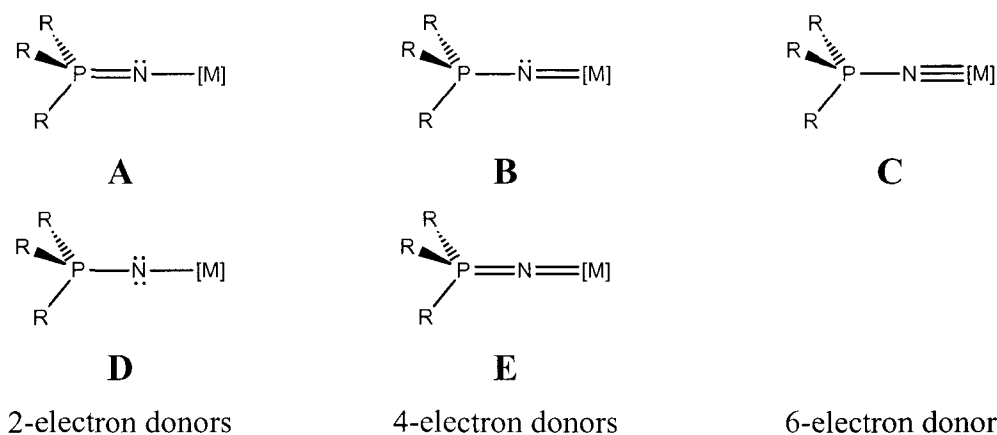


Figure 1.5. Electronic Structures of Phosphinimide Ligands.

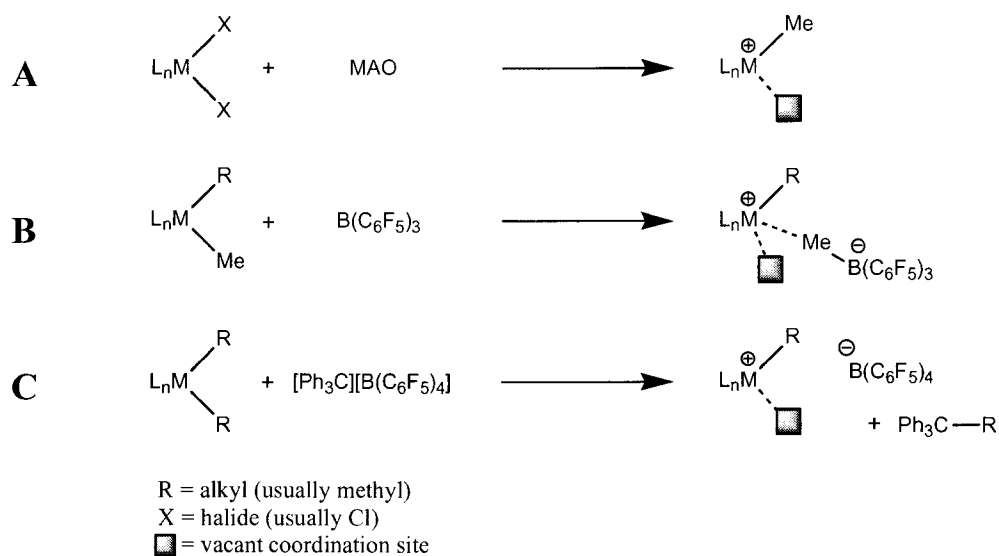
1.4 Mechanism

The mechanism for the polymerisation of olefins by group IV transition metals is based on the original, and still widely accepted, mechanism proposed by Cossee in 1964.^[45]

1.4.1 Catalyst Activation

Catalysts based on group IV transition metals typically require a cocatalyst to create the active catalytic species (technically the original ‘catalyst’ is called a *precatalyst*). The prerequisites for an effective activator are that it be sufficiently Lewis basic to abstract an alkylidene ligand from the precatalyst, and sufficiently non-nucleophilic to allow for separation of the resultant ion pair. This is typically done using either MAO (beginning

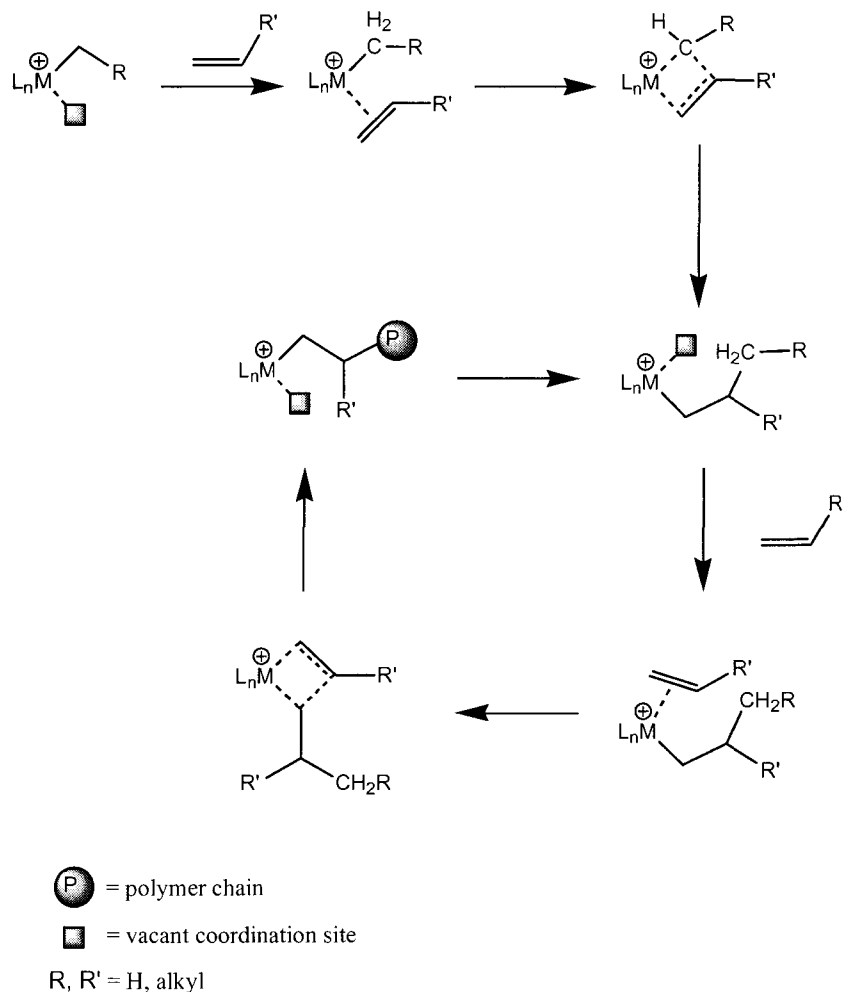
with a metal dichloride precatalyst) as shown in Scheme 1.1 path **A**, or by using a boron based reagent bearing bulky perfluoroaryl groups (beginning with a metal dialkide precatalyst), as shown in Scheme 1.1 path **B** (using a borane to generate a zwitterionic complex) and **C** (using an ionic trityl borate salt to abstract a methyl group and form an ion pair).



Scheme 1.1. Catalyst Activation.

1.4.2 Propagation

The mechanism of propagation is shown in Scheme 1.2. The electronically and coordinatively unsaturated active catalyst forms a π -complex with an available olefin monomer. This complex then proceeds through a 4-membered metallacyclobutene intermediate, and finally inserts into metal-carbon bond. The complex formed consists of an alkyl chain (two carbons longer) bound to the metal centre in place of the vacant coordination site, and a new vacant site in place of the previously bound alkyl chain. Thus, a polymer chain is generated, two carbon atoms at a time, with successive

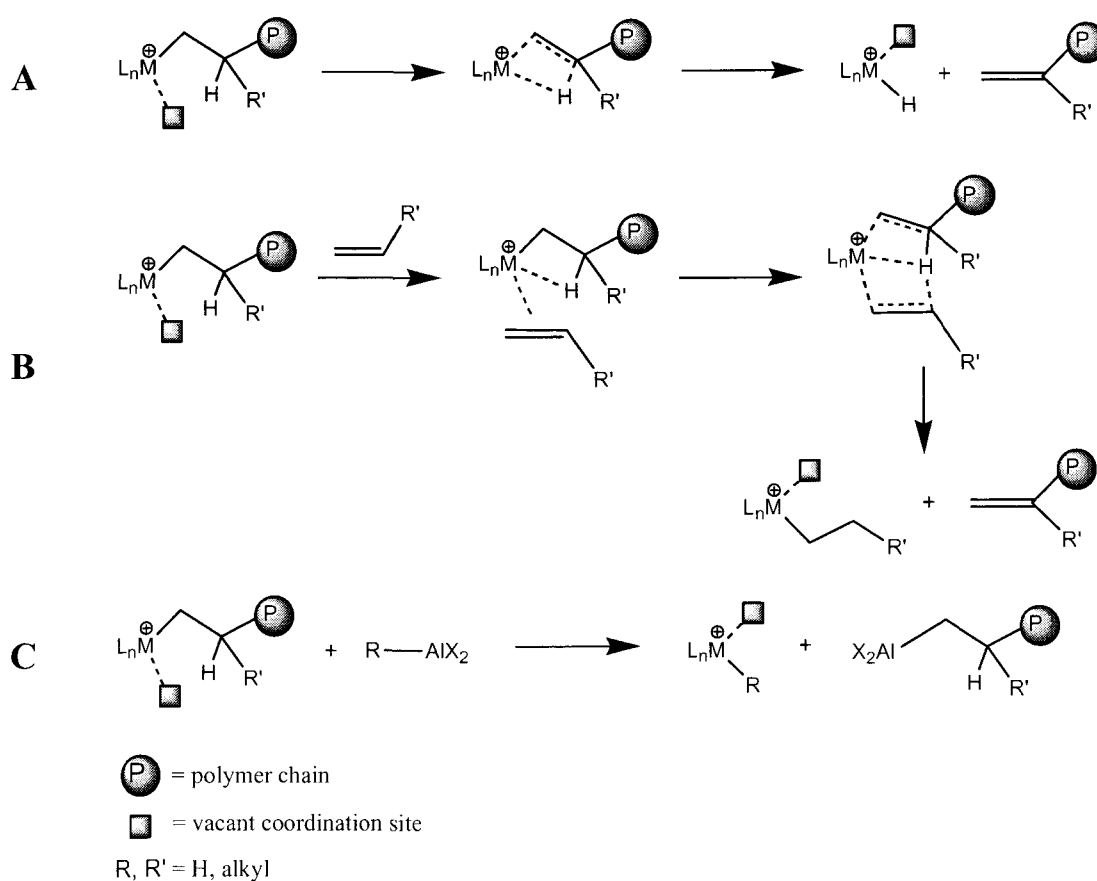


Scheme 1.2. Propagation.

insertions alternating between the two catalytic sites. If the two catalytic sites are sterically equivalent, each insertion of olefin will proceed in an equivalent manner. If, through ancillary ligand design, the two catalytic sites are sterically different, there is the possibility of having differing preference for insertion of monomers, which can lead to polymers with defined stereochemistry or copolymers with defined regiochemical microstructure. This entire process takes place on the femtosecond timescale.^[12]

1.4.3 Termination

The most common chain termination pathway is via β -hydride transfer. This mechanism is essentially the reverse of the polymerisation mechanism, proceeding through a 4-membered metallacyclobutene transition state to yield a polymer with an unsaturated vinyl end and a catalytically active cationic metal hydride species (Scheme 1.3, path **A**). Other possible termination pathways involve transfer of a β -hydride to an incoming monomer (Scheme 1.3, path **B**), or transfer of the polymer chain to an aluminum atom of the cocatalyst, generating an aluminum capped polymer species and a cationic metal alkide (Scheme 1.3, path **C**).



Scheme 1.3. Termination Pathways.

1.5 Living Polymerisation

1.5.1 Definition

In order to have an effective polymerisation system, the rate of the propagation process (k_p) must be much greater than the rate of the termination process (k_t). If the rates are comparable to one another ($k_p \approx k_t$), dimers or short chain oligomers result. In contrast, if the rate of propagation is much greater than the rate of termination ($k_p \gg k_t$), then k_t is effectively negligible, and the insertion of monomer units will continue to propagate indefinitely, or until it is stopped by some external factor. The latter situation is known as ‘Living Polymerisation’. The major advantage of living polymerisation is that it allows for exceptional control over the chemical properties of the resultant polymer, which are directly related to its physical properties. Through this, polymers of defined molecular weight and narrow polydispersity as well as novel copolymers can be synthesised.

1.5.2 Implications

For a polymerisation process to be truly living, there should be no termination of the growing polymer chains or deactivation of the catalyst. Thus, each activated catalytic site will produce one polymer chain. In addition, assuming that all of the catalytic sites are the same (a reasonable assumption for a ‘single site’ catalyst), k_p will be identical for each site. This will lead to the same number of insertions at each catalytic site in a given amount of time. Therefore, all of the polymer chains will be comprised of the same

number of monomer units, and the molecular weight of each polymer chain will be identical. This is said to be a *monodisperse* polymer (*vide infra*).

There are a number of ways one can demonstrate the living nature of a polymerisation. Since each catalytic site produces one polymer chain, and propagates at the same rate, a linear relationship will exist between polymer molecular weight and polymerisation time; a plot of molecular weight *vs.* time will yield a straight line. Another method of demonstrating a living polymerisation is to perform a series of experiments where the amount of monomer available to the system is varied, and the amount of catalyst is kept constant. If sufficient time is given to allow the catalyst to consume all of the monomer available, then a linear relationship will exist between amount of monomer and polymer molecular weight; a plot of molecular weight *vs.* amount of monomer will yield a straight line. An experiment which proves that a catalyst has consumed all of the monomer available to it and continues to propagate upon addition of more monomer is a further approach to demonstrate living polymerisation.^[46]

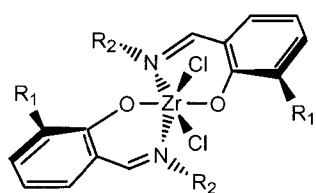
1.5.3 Examples of Living Olefin Polymerisation Catalysts

Despite the fact that active single site olefin polymerisation catalysts have been known for decades, the discovery of their living polymerisations is relatively recent.^[47]

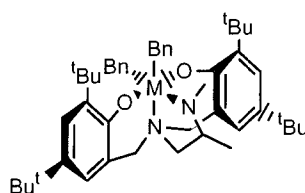
The first example of living insertion polymerisation using a transition metal complex was by Doi *et al.* in 1979. The catalyst employed was vanadium *tris*-(acetylacetonate), activated with diethylaluminum chloride (DEAC) at -65°C . The polymerisation of propene at various time intervals showed a linear relationship between molecular weight and time, indicative of a living process. The maximum molecular weight obtained in

this experiment was 91000 g/mol (after 15 hours of polymerisation time), and a polydispersity index (PDI, *vide infra*) of 1.4. Though the PDI is slightly higher than ideal (an ideal PDI for a living system is 1.0), it showed that living polymerisation was not restricted to anionic polymerisation.

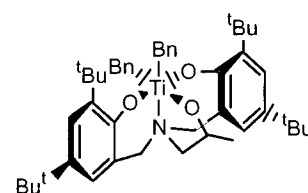
After a period of dormancy, it was not until the mid 1990's that this field experienced a resurgence of interest. Since then, a variety of living polymerisation systems have been reported based on a wide range of transition metals, however, *most* of the reports use catalysts based on group IV metals (Ti, Zr, Hf), and group X (Ni, Pd) catalysts using the bulky α -diimine ligand system developed by Brookhart *et al.* Figure 1.6 shows compounds which have been reported to effect the living polymerisation of α -olefins, with the polymerisation conditions (temperature, activator, monomer) used to effect the living polymerisation also listed.

**19**

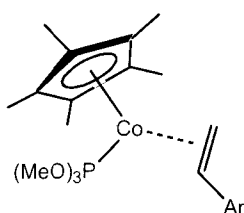
Ar^f = C₆F₅, 2,6-C₆F₂H₃, 2,4,6-C₆F₃H₂, 2-C₆FH₄
 R₁ = ^tBu, C(Me)₂(Ph)
 T = 50°C, 15 min^{a,i,ii[48]}

**20**

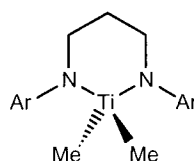
M = Ti, Zr
 T = 25°C, 30 min^{b,iii[49, 50]}

**21**

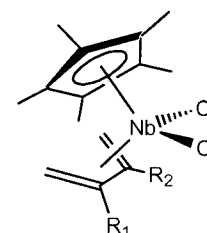
T = 25°C, 30 hours^{b,iii[51]}

**22**

Ar = halogenated aryl
 T = 25°C^{c,i,ii[52]}

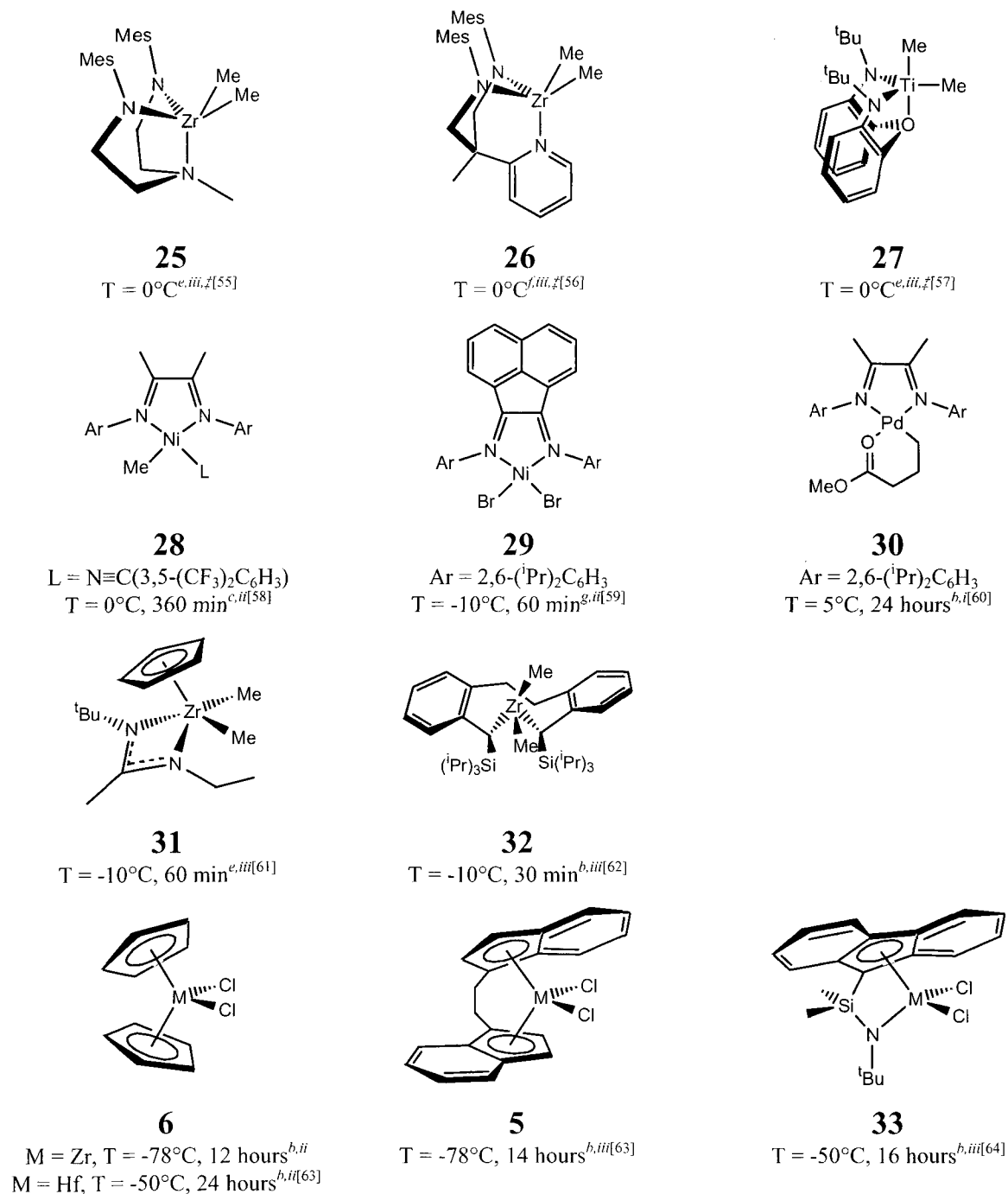
**23**

Ar = 2,6-(ⁱPr)₂C₆H₃
 T = 0°C, 25 min^{d,ii[53]}

**24**

R₁, R₂ = H, Me T = 0°C^{a,i,ii[54]}

(Figure continued on following page)



^a MAO ^b B(C₆F₅)₃ ^c No activator ^d dried MMAO ^e [PhNHMe₂][B(C₆F₅)₄] ^f [Ph₃C][B(C₆F₅)₄] ^g Ethylene ^h Propene ⁱⁱⁱ 1-Hexene [‡] No molecular weight correlation, ‘living’ nature claimed based on narrow PDI. [‡] Based on correlation of M_n to equivalents of monomer added.

Figure 1.6. Living Polymerisation Catalysts.

From this table of structures, a number of general trends can be seen:

1. Nearly all of the catalyst structures reported to effect living polymerisation have chelating ligands bound by nitrogen and oxygen donor atoms.
2. Most living polymerisations are done using bulky fluoroarylborane activators, to eliminate chain transfer reactions to an aluminum centre (*vide supra*).
3. Living polymerisations performed at high temperatures (25°C and up) are nearly always done using group IV catalysts with octahedral geometries, while living polymerisations using tetrahedral group IV catalyst must be performed at very low temperatures (-50°C and lower).
4. Cyclopentadienyl fragments are highly uncommon in living polymerisations compared to their propensity in non living systems.

These observations show that the structure of the ligand system is extremely important in creating a rigid metal centre with a precise geometry. Mitani *et al.* have shown, by systematic substitution studies, that the ancillary ligands may assume a more active role in controlling the conformation of the growing polymer chain.^[48]

1.6 Copolymerisation

One of the major advantages of using well defined, modifiable single site catalysts for polymerisation is their ability to make polymers which, in addition to the main monomeric unit, incorporate various amounts of a second monomer unit, i.e. a *comonomer*. The degree of incorporation and type of comonomer can have a profound effect on the properties of the resultant polymer. The copolymerisation of ethylene with small amounts (< 5%) of higher α -olefins (C₄ - C₂₀) yields linear polymers with desirable processability properties. These polymers, termed linear low density

polyethylene (LLDPE) account for about 1/3 of all polyethylene production,^[1] and continue to be the subject of considerable research.^[65] Similarly, elastomeric copolymers can be made using ethylene, propylene, and low amounts of a diene (EPDM rubbers), and extremely crystalline, high melting polymers can be made by incorporation of cyclic olefins to give cycloolefin copolymers (COC's).^[9]

The above copolymers are examples of random copolymers, that is, copolymers where there is no regular sequence of monomer incorporation (**A**, Figure 1.7). One of the most useful features of a living polymerisation catalyst system is the ability to create block copolymers (**B**, Figure 1.7)^[47] by adding the different monomers sequentially. Thus, a polymer can be produced which can be considered as two or more homopolymers linked together covalently.

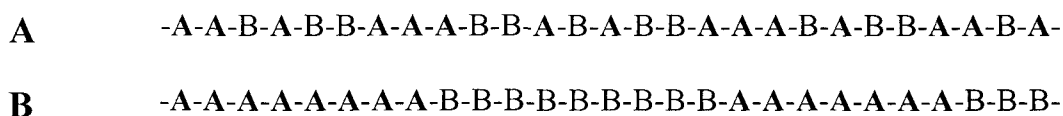


Figure 1.7. Random (**A**) and Block (**B**) Copolymers.

1.7 Analytical Techniques

The bulk properties of a polymeric material are greatly dependent on the molecular features of the polymer chains of which it is comprised. In the case of strictly hydrocarbon polymers, the properties which influence this the most are the molecular weight, molecular weight distribution, and branch features. Thus, the most common analytical techniques used for identifying this class of polymers are those which give information concerning these features.

1.7.1 NMR Spectroscopy

NMR spectroscopy is one of the most powerful analytical tools available for the characterisation of polymers.^[66] This is due to the ability of the technique to provide valuable information concerning the microstructure of the polymer chain in a quantitative manner. Since NMR chemical shifts are highly sensitive to the unique chemical environment in which a given nucleus resides, information can be obtained through examination of the chemical shifts of the peaks in an NMR spectrum. Additionally, with careful experimental design, the area beneath a given peak (its integral) is directly proportional to the relative number of nuclei giving rise to the peak in question.

In the case of hydrocarbon polymers, the two NMR-active nuclei present are hydrogen (^1H) and carbon (^{13}C). The most common form of spectroscopy for nearly all chemical analyses is ^1H -NMR spectroscopy. This is because the natural abundance of the ^1H isotope of hydrogen is high (>99%) and has a high gyromagnetic ratio, making it a quite sensitive nucleus for study by NMR spectroscopy. The ^{13}C isotope of carbon, on the other hand, has a natural abundance of only 1.1%, and is less magnetically sensitive than ^1H .^[67] Both of these reasons make observation of ^{13}C nuclei more of an experimental challenge. However, because of the information that can be gleaned from the study of ^{13}C nuclei, the field is highly developed.

Because the ^1H resonances for aliphatic protons all occur between 1 - 2 ppm, there is considerable overlap of the peaks in the spectrum. Thus, carbon-13 is the most widely studied nucleus for polymer analysis.^[66] Polymer samples are generally prepared at high

concentration, and a spectrum can conceivably be obtained using but a few scans. For instance, a ^{13}C spectrum of polyethylene prepared at 30% (w/w) would yield a spectrum consisting of a single peak at 30 ppm, arising from the many methylene (CH_2) units which comprise the bulk of polymer backbone in less than 10 scans. However, upon acquisition of many more scans, more peaks would emerge. These would arise from the methine (CH) carbons at the points where branches occur, the methyl (CH_3) units from the branch ends and the ends of the polymer chain, and slightly different peaks arising from the methylene carbons in the backbone in close proximity to the branchpoints. These are shown schematically in Figure 1.8. It is these subtle peaks which provide the most information about the microstructure of the polymer and, consequently, are of the

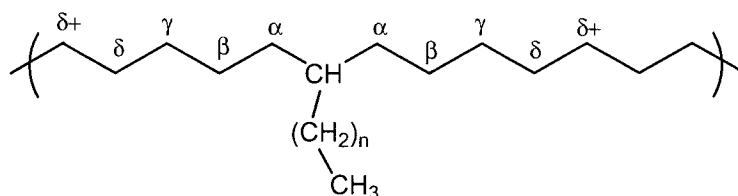


Figure 1.8. Polyethylene Branch.

most interest. In polymers of higher α -olefins, particularly propylene, the peak shifts in the NMR spectrum are highly sensitive not only to the presence of branches, but also to the stereochemistry of the branches relative to each other. Through analysis of the slight chemical shifts of the peaks due to carbons directly attached to backbone, the stereochemistry of polypropylene has been elucidated to the hexad level (that is, sequences of six insertion events) (Figure 1.9).^[68]

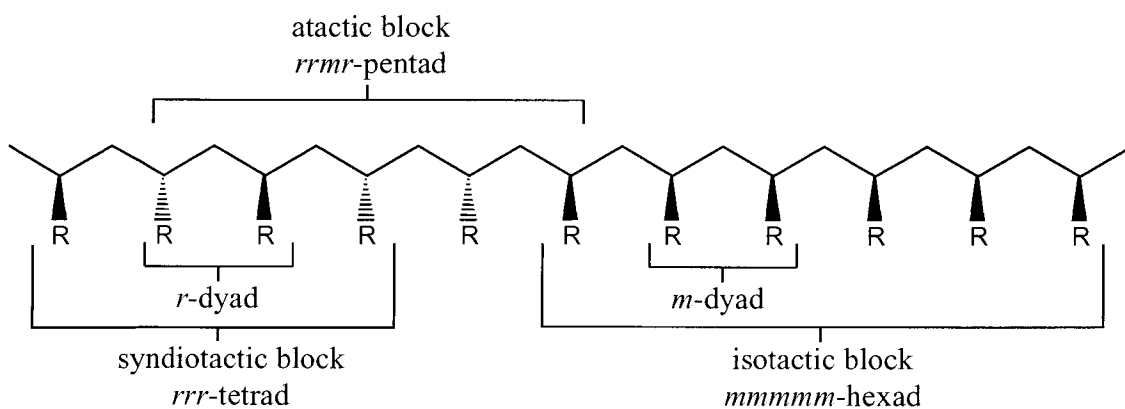


Figure 1.9. Stereochemistry of poly(α -olefin).

In order to obtain reliable information from the peak integrals, one must pay special attention to the experimental details. Integration of the peaks in the NMR spectrum requires that all nuclei have completely relaxed to their equilibrium state of alignment with the external magnetic field. Nuclei which have not completely relaxed back to the equilibrium state will give rise to less intense signals than those which have fully relaxed. It is therefore of utmost importance to ensure that all nuclei which are to be integrated have been given sufficient time to completely relax, otherwise the integrals will be skewed relative to each other. ^{13}C NMR relaxation times for aliphatic carbons in polymer samples are typically ~ 2 s, and relatively long delays (5 - 10 s) are typically used to ensure complete relaxation of all nuclei. This is further complicated in cases where unsaturations exist, as some of these carbons have relaxation times on the order of minutes.^[69]

1.7.2 Gel Permeation Chromatography

Many of the physical properties of a polymer are related to its molecular weight. Unlike small molecules, which have defined molecular weights, most polymer samples are comprised of a mixture of polymer chains of various molecular weights. Notable exceptions to this are dendrimers and proteins, which have defined chemical structures and precise molecular weights.^[70] Thus, the molecular weight of a polymer sample is an average of the molecular weights of the polymer chains of which it is comprised.

The average molecular weight of a polymer sample can be calculated in a number of different ways. The simplest of these, the mass of the polymer sample divided by the number of chains yields the *number average molecular weight*, M_n . This is shown mathematically in Equation 1.1. This method of calculating the average molecular weight gives each polymer chain equal consideration, regardless of its size. In reality, the larger polymer chains contribute more to the total mass of the sample than the smaller ones, thus a weighted average is often used to calculate the average molecular weight. This method gives a more accurate representation of the molecular weight of the ‘average’ polymer chain in the sample, and is the *weight average molecular weight*, M_w (Equation 1.2).

$$M_n = \frac{\sum_{i=1}^{\infty} n_i M_i}{\sum_{i=1}^{\infty} n_i} \quad \text{Equation 1.1}$$

$$M_w = \frac{\sum_{i=1}^{\infty} n_i M_i^2}{\sum_{i=1}^{\infty} n_i M_i} \quad \text{Equation 1.2}$$

Another property of molecular weight which is of particular importance is the range of molecular weights which comprise the average molecular weight. This is called the *polydispersity index* (PDI), or *molecular weight distribution* (MWD). It is calculated by dividing the number average molecular weight by the weight average molecular weight (Equation 1.3). In the case of monodisperse polymers where all of the polymer chains are identical, the ‘average’ molecular weight will be the molecular weight of the polymer. Thus $M_w = M_n$, and $PDI = 1$. This is true in the case of the examples mentioned above, as well as for polymers produced under living conditions.^[71] Most polymers, on the other hand, have polydispersities greater than 1.

$$PDI = \frac{M_w}{M_n} \qquad \text{Equation 1.3}$$

Gel Permeation Chromatography (GPC) is an analytical method used to determine the molecular weight and PDI of polymer samples. It is also known as Size Exclusion Chromatography (SEC). GPC is a type of liquid chromatography where the sample is passed through a porous gel at a constant solvent flow rate. The gel contains pores of various sizes, thus allowing different sized polymer molecules to permeate them. Molecules which are larger than the pores of the gel cannot permeate it and, therefore, elute through the gel at the rate of the solvent flow. As the molecules become smaller, their ability to enter the pores of the gel becomes greater, and as a result they require longer amounts of time to pass through the gel. Detection using a differential refractive index detector produces a chromatogram that relates concentration of solute to the retention time. By comparing these data to those of a standard curve generated by running a set of standards of known molecular weight, one can obtain information concerning the molecular weight (most notably M_n and M_w), and consequently the PDI.^[70, 72]

1.8 Scope of This Work

Research in the Stephan group has shown that complexes of titanium bearing a cyclopentadienyl ligand and an alkyl phosphinimide ligand are, when activated with a suitable cocatalyst, highly active ethylene polymerisation catalysts. The most active examples are those bearing the bulky ^tBu₃PN ligand.^[40] This family of compounds has also been demonstrated to be effective catalysts for the polymerisation of α -olefins and non-conjugated α,ω -dienes at ambient temperature.^[73] These polymerisations have also been shown to proceed, in some cases, to give polymers with relatively narrow molecular weight distributions. To this end, studies were conducted to determine if, under controlled polymerisation conditions, living polymerisations could be carried out using 1-hexene as the monomer. NMR investigations were performed to elucidate the microstructural properties of the polymer produced.

The copolymerisation of 1-hexene and 1,5-hexadiene, and 1-hexene and ethylene, by Cp(^tBu₃PN)TiMe₂ (**34**) was also investigated. NMR spectroscopy was used to probe the characteristics of the resulting random copolymers of 1-hexene/1,5-hexadiene. Block copolymers of ethylene and 1-hexene were also prepared and characterised using GPC.

Chapter 2 Polymerisation of 1-Hexene: Reaction Characteristics and Polymer Properties

2.1 Introduction

A polymerisation operating under living conditions is a highly controlled reaction, producing polymers with well defined properties. For example, by controlling the polymerisation time, polymers can be prepared with specific molecular weights and narrow molecular weight distributions. Since the properties of the bulk polymer are highly dependent upon the molecular weight, they can be modified with relative ease simply by altering the polymerisation time. However, not all catalyst systems can polymerise olefins under living conditions, or require conditions which render the system commercially unviable. Thus, there is considerable interest in developing living polymerisation systems capable of producing olefin polymers, operating under more practical conditions.

In this chapter, the polymerisation of 1-hexene with **(34)** is discussed. In particular, the aim of this investigation was to determine if there exists a set of conditions for which **(34)** polymerises olefins under living conditions, and to determine the kinetics of the reaction. Poly(1-hexene) has been used as it is typically quite soluble in common organic solvents, allowing for facile analysis using standard solution techniques (NMR, GPC). Furthermore, due to its physical properties, monomeric 1-hexene is convenient to purify and handle. The microstructural properties of poly(1-hexene) produced by **(34)** is also discussed.

2.2 Experimental Methods

2.2.1 General Considerations

Unless noted otherwise, all reactions were performed under an inert atmosphere of dry N₂ using an Innovative Technologies glove box and standard Schlenk techniques. Solvents used for polymerisations (toluene, pentanes) were dried by refluxing overnight over sodium-benzophenone ketyl and were used within 24 hours of distillation. 1-hexene (Aldrich), cyclopentene (Aldrich), and *cis*-2-pentene (Aldrich) were dried by refluxing over sodium-benzophenone ketyl overnight followed by vacuum transfer. Polymerisations were performed within 24 hours of purification. Solvents used for syntheses (Et₂O, pentanes) were purified by passage through Grubbs' type solvent purification columns manufactured by Innovative Technologies. Cp(^tBu₃PN)TiCl₂, [Ph₃C][B(C₆F₅)₄], and B(C₆F₅)₃ were obtained from NOVA Chemicals Ltd. and used without further purification. Sub-ambient reaction temperatures were controlled via solvent baths composed of mixtures of either nitromethane/liquid nitrogen (CH₃NO₂/N_{2(l)}, -31°C) or acetone/dry ice ((CH₃)₂CO/CO₂, -78°C).

2.2.2 Synthesis of Cp(^tBu₃PN)TiMe₂ (**34**)

This compound was synthesised by a slightly modified literature procedure.^[40] In the glovebox, 300 mg (0.75 mmol) of Cp(^tBu₃PN)TiCl₂ and 12 mL of Et₂O were put in a scintillation vial containing a magnetic stir bar. Three equivalents of MeMgBr (0.75 mL of a 3.0M solution in Et₂O) were then added at once and the reaction was allowed to stir overnight. The Et₂O was then removed *in vacuo*, and the product redissolved in

pentanes (10 mL). This solution was filtered through celite to remove excess MeMgBr and MgX₂ (X = Br, Cl) and the solvent was removed *in vacuo* to yield 215 mg of a pale yellow solid (80%). Spectral data were consistent with values reported in the literature.^[40]

2.2.3 Polymerisation Procedures

2.2.3.1 Procedure 2.A: Small Scale Polymerisation

A 50 mL Schlenk flask was equipped with a magnetic stir bar. 2.0 mL of 1-hexene (16 mmol), 4.5 mL of toluene, and cocatalyst ([Ph₃C][B(C₆F₅)₄] or B(C₆F₅)₃) were added and the flask was sealed with a septum and attached to the Schlenk line. The flask was then immersed in a bath of desired temperature, and stirred for 10 - 15 minutes at the polymerisation temperature. A syringe containing **(34)** dissolved in 0.5 mL of toluene was then brought out of the glovebox and its contents injected into the flask. This was taken to be time zero. After a desired time interval, polymerisations were quenched by injection of 1 mL of MeOH. The amounts of **(34)** and cocatalyst used are indicated in the text.

2.2.3.2 Procedure 2.B: Large Scale Polymerisation

A 250 mL Schlenk flask was equipped with a magnetic stir bar. 10.0 mL of 1-hexene (80.0 mmol), 24.0 mL of toluene, and cocatalyst ([Ph₃C][B(C₆F₅)₄] or B(C₆F₅)₃) were added and the flask was sealed with a septum and attached to the Schlenk line. The flask was then immersed in a bath of desired temperature, and stirred for 10 - 15 minutes at the polymerisation temperature. A syringe containing **(34)** dissolved in 1.0 mL of

toluene was then brought out of the glovebox and its contents injected into the flask. This was taken to be time zero. After a desired time interval, polymerisations were quenched by injection of 5 mL of MeOH. The amounts of **(34)** and cocatalyst used are indicated in the text.

2.2.3.3 Procedure 2.C: Reaction Monitoring via Aliquot Removal

A 250 mL Schlenk flask was equipped with a magnetic stir bar. 10.0 mL of 1-hexene (80.0 mmol), 24.0 mL of toluene, and cocatalyst ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ or $\text{B}(\text{C}_6\text{F}_5)_3$) were added and the flask was sealed with a septum and attached to the Schlenk line. The flask was then immersed in a bath of desired temperature, and stirred for 10 - 15 minutes at the polymerisation temperature. A syringe containing **(34)** dissolved in 1.0 mL of toluene was then brought out of the glovebox and its contents injected into the flask. This was taken to be time zero. Aliquots (1 - 2 mL) were removed at the desired times via syringe and immediately injected into a vial containing 0.5 mL MeOH to halt the polymerisation. The amounts of **(34)** and cocatalyst used are indicated in the text.

2.2.3.4 Polymer Workup Procedure

Following polymerisation, all volatiles were allowed to evaporate from the polymer samples. The sample was then redissolved in pentanes and transferred to a weighed vial. Catalyst residues were extracted with portions of acidified methanol (10:90 conc. HCl:MeOH) at least three times, or until the alcoholic layer was colourless. The resulting polymer was then dried *in vacuo* to constant mass.

2.2.4 NMR Spectroscopy

$^{13}\text{C}\{^1\text{H}\}$ NMR analyses of 1-hexene homopolymers were carried out at 25°C on a Bruker DPX300 spectrometer operating at 75 MHz. Samples were prepared as 25% - 30%w/w solutions in C_6D_6 in 5 mm NMR sample tubes. Chemical shifts were referenced to the central carbon resonance of C_6D_6 (128.4 ppm). The spectra were acquired using broadband decoupling with a 10 s delay between scans.

2.2.5 Molecular Weight Determination

Molecular weights and molecular weight distributions of 1-hexene homopolymers were performed using a Waters Breeze system GPC using THF as eluent. The detector used was a Waters model 410 refractive index detector at 35°C, and molecular weights were calibrated using narrow polystyrene standards (Polymer Laboratories Inc.). The samples were prepared by dissolving the analyte in THF (0.1% w/v) then filtering through a 0.45 μm filter.

2.3 Design of the Polymerisation Experiment

Initially, the polymerisation method employed was the approach previously undertaken in the Stephan group for the polymerisation of α -olefins.^[74] This consisted of mixing the monomer, solvent, and cocatalyst in a vial in the glovebox, and adding the catalyst to initiate the polymerisation. However, when this procedure was followed, it was noted that the solution became heated, in some cases causing the monomer to boil. Thus, a polymerisation intended to be performed at room temperature was in fact occurring at a significantly higher temperature. In addition, it was found, by ^{13}C NMR spectroscopy, that the THF being used as a quenching agent undergoes ring opening polymerisation with excess activator, further compromising the reliability of the mass and GPC analyses of the resultant polymer mixture.

Consequently, reactions were carried out in a 50 mL Schlenk flask on a Schlenk line, scaling each component up proportionally. In this manner, the temperature could be controlled by immersing the flask in a bath at the desired temperature, and quenching of the polymerisation could be done using MeOH. These conditions were further scaled up by a factor of five, and the reaction was performed in a 250 mL Schlenk flask. Thus, the reaction was performed as outlined in polymerisation procedure II, using 40 mg of **(34)** as the catalyst and 2 equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ as the cocatalyst.

2.4 Activity of (34) For 1-Hexene Polymerisation

Activity values for the polymerisation of 1-hexene using (34) are given in Table 2.1. The activities based on M_n are calculated by dividing the M_n by the polymerisation time. Hence, runs with comparable M_n :time ratios will yield the same value for the activity. This activity value is independent of errors associated with polymer recovery, as well as catalyst concentration. It is only dependent upon the conditions of the polymerisation and the monomer concentration, and assumes that each catalyst site produces one polymer chain. Activities calculated based on the recovered polymer mass are much more sensitive to other errors inherent in the experiment, most notably initial catalyst concentration, efficiency of activation, reversible and irreversible termination pathways, and mechanical losses during polymer recovery.

Table 2.1. Properties of poly(1-hexene) Produced by (34).^[a]

mmol of Catalyst	Cocatalyst ^[b]	Eq. of cocatalyst	Polymer yield (g)	Activity ^[c]	M_n (g/mol)	PDI	Activity ^[d]
0.111	B	2	0.85	45	11000	1.27	61
0.056	B	2	0.22	24	7500	1.29	45
0.111	TB	2	1.79	97	21500	1.58	129
0.111	TB	1	1.19	64	20800	1.42	124
0.056	TB	1	0.48	51	19300	1.37	116

^[a] 10 minute polymerisation times, -31°C using Procedure 2.B.

^[b] B = B(C₆F₅)₃, TB = [Ph₃C][B(C₆F₅)₄].

^[c] g·mmol⁻¹·h⁻¹ (based on mass of polymer recovered).

^[d] g·mmol⁻¹·h⁻¹ (based on M_n).

It can be seen that when the amount of catalyst is halved, there is approximately a two-fold decrease in the yield based activity, with a concomitant decrease in M_n when activated by B(C₆F₅)₃. When [Ph₃C][B(C₆F₅)₄] is employed as the activator, the

discrepancies in the relative activities between the different catalyst concentrations are reduced. However, the activity based on M_n is higher than the activity based on the mass of recovered polymer in all cases, and when $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ is used as the activator, is comparable regardless of the catalyst concentration or the catalyst:cocatalyst ratio.

The fact that the activity values calculated using the mass of recovered polymer are always lower than the values calculated from the M_n value is a good indication that, despite efforts to minimise these effects, termination pathways and lower than expected active catalyst concentrations are competing. In addition, lower catalyst concentrations result in decreased reproducibility, and runs done using 0.028 mmol of catalyst yielded no polymer. This is consistent with a report made by Brookhart *et al.* who noted problems with reproducibility when lower catalyst concentrations are used due to hydrolysis of the catalyst by impurities in the solvent.^[75] Any impurities in the solvent or monomer can have a deleterious effect on the polymerisation. If the impurities deactivate a constant amount of the potential catalyst sites faster than polymerisation takes place, using less catalyst will exaggerate this effect since a relatively higher proportion of the catalyst sites will be affected. A technique to reduce errors due to solvent impurities is to add a scavenger (i.e. triisobutylaluminum) to the polymerisation mixture, and is indeed used in many cases for this purpose.^[75] However, since the aim of this investigation is to determine if the catalyst system is able to polymerise 1-hexene under living conditions, addition of an aluminum based scrubber was intentionally avoided to prevent molecular weight broadening through termination by chain transfer to aluminum (*vide supra*).

2.5 Kinetics

As described in the introduction, a system which is polymerising under living conditions will exhibit a linear dependency of molecular weight on polymerisation time. Thus, studies were undertaken to determine if this is the case.

To avoid errors associated with comparing data from different polymerisation runs (as outlined above), experiments were conducted in which aliquots were removed from one run at various times ranging from 5 minutes to 2 hours (Procedure 2.C), and the resulting aliquots were analysed by GPC. Figure 2.1 and Figure 2.2 show plots of the molecular weights vs. time. Looking only at the initial 75 minutes of polymerisation time, an approximately linear relationship appears to exist. However, the linear line of best fit does not intersect at $M_n = 0$, instead intersecting at $M_n = 5000$ or higher, clearly nonsensical (Figure 2.1). When the entire reaction is considered (Figure 2.2), a model which considers decreasing catalyst activity forms a better description of the data. To this end, factors which could cause decreasing catalyst activity were considered.

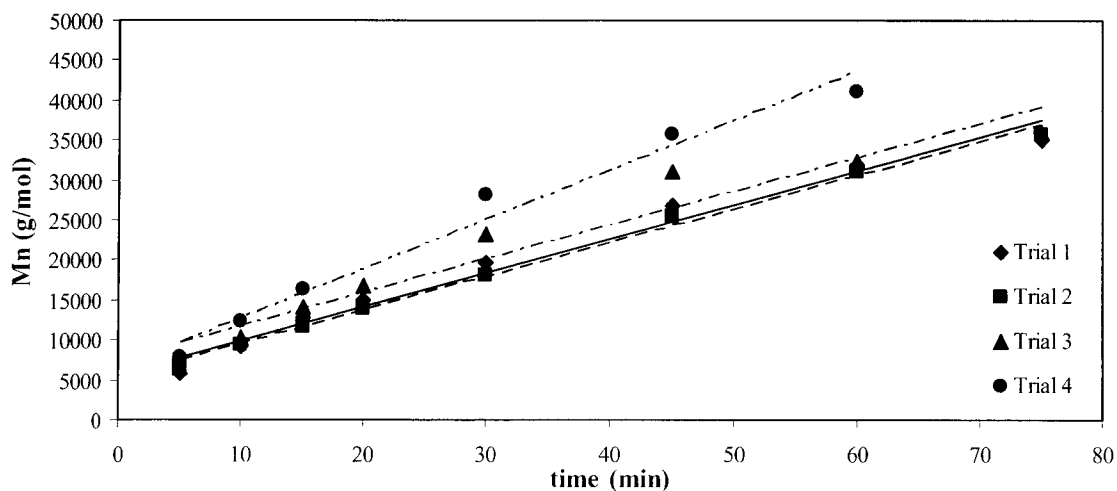


Figure 2.1. M_n vs. time for poly(1-hexene) 0 to 75 Minutes.

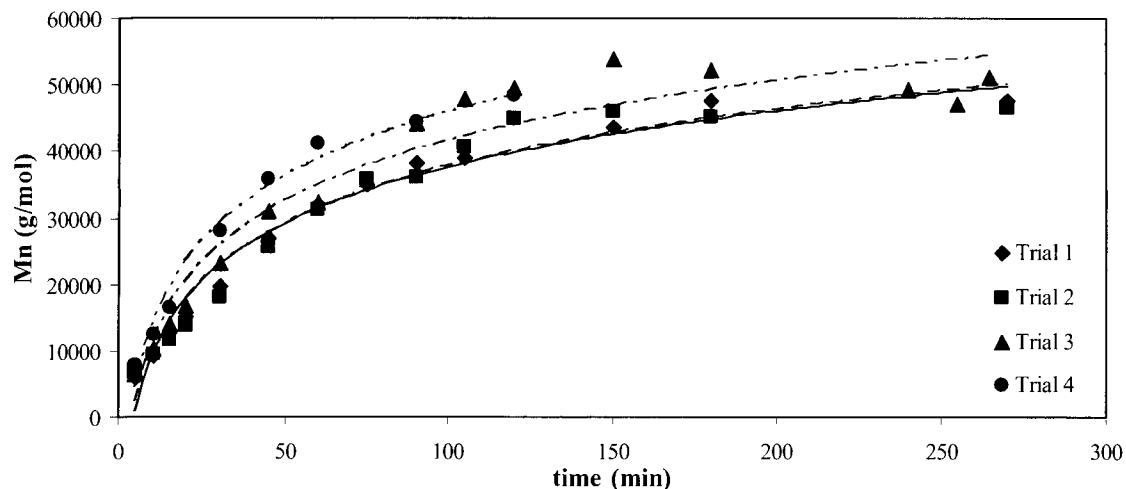


Figure 2.2. M_n vs. time for poly(1-hexene) 0 to 270 Minutes.

The liquid monomer employed is not replenished throughout the run, i.e. a finite amount of monomer is available and as the polymerisation proceeds, the concentration of free monomer decreases.

The rate of polymerisation by Ziegler-Natta catalysts is described mathematically in **Equation 2.1**.^[70] This shows a first order dependence of the rate on the initial monomer concentration. As the polymerisation proceeds, the monomer concentration decreases, and by this equation, one would expect the rate of polymerisation to decrease over time. Rearranging **Equation 2.1** gives **Equation 2.2**, which shows that the monomer concentration at time t , $[M_t]$, decreases exponentially with time as the polymerisation proceeds. Hence, at some time t , the number of moles of monomer ($mol_{mon,t}$) is equal to the number of moles of monomer initially present ($mol_{mon,0}$) minus the number of moles already polymerised. In the case of living polymerisation, each catalyst site produces one polymer chain, thus, the moles of polymer chains will equal the moles of catalyst present initially ($mol_{cat,0}$). Substituting these into **Equation 2.2** gives **Equation 2.3**, which relates the molecular weight of the polymer at time t ($mw_{p,t}$) to the amounts of

monomer and catalyst present initially. Derivation of these equations is given in Appendix A.

$$-\frac{d[M]}{dt} = k_p[cat][M_0] \quad \text{Equation 2.1}$$

$$[M_t] = [M_0]e^{-k_p[cat]t} \quad \text{Equation 2.2}$$

$$mw_{p,t} = \left(\frac{m_{mon,0}}{mol_{cat,0}} \right) \{ 1 - e^{-k_p[cat]t} \} \quad \text{Equation 2.3}$$

A plot of **Equation 2.3** with empirical data from an experiment is shown in Figure 2.3, substituting the actual experimental parameters where necessary. At each point on the model line, the increased molecular weight was calculated according to k_p , and the $[M_t]$ was adjusted each time to reflect the amount of monomer which had already been polymerised. It can be seen that, although this model is a more accurate representation of the experimental data than a linear fit, the experimental data still indicate that there is decay with respect to time.

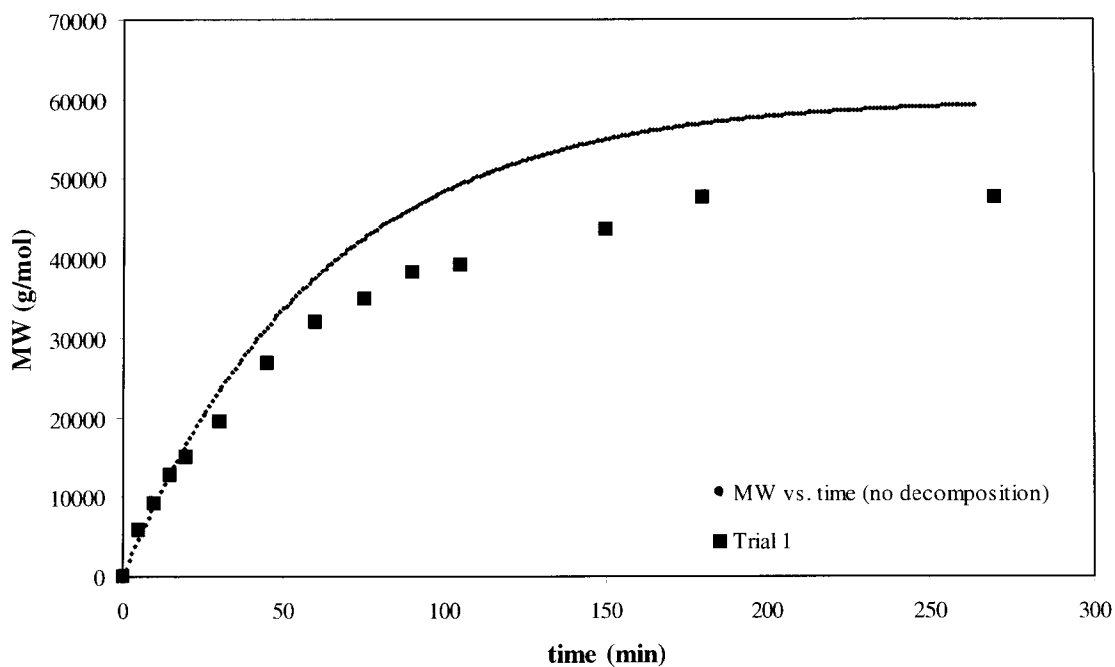


Figure 2.3. Molecular weight vs. time Plot of Trial 1 with Model Line.

A further source of decreasing catalyst activity is that of catalyst deactivation by reaction with trace impurities in the system or via thermal decomposition. Thus, inclusion of a term to account for deactivation of active catalyst sites gives **Equation 2.4**. Rearranging **Equation 2.4** gives **Equation 2.5**, and substitution of **Equation 2.5**, which describes the catalyst concentration at some time t , for $[cat]$ in **Equation 2.3** gives **Equation 2.6**.

$$-\frac{d[cat]}{dt} = k_d [cat_0] \quad \text{Equation 2.4}$$

$$[cat_t] = [cat_0] e^{-k_d t} \quad \text{Equation 2.5}$$

$$mw_{p,t} = \left(\frac{m_{mon,0}}{mol_{cat,0}} \right) \left\{ 1 - e^{-k_p \{ [cat_0] e^{-k_d t} \} t} \right\} \quad \text{Equation 2.6}$$

The results of adding a plot of **Equation 2.6** to the graph shown in Figure 2.3 is shown in Figure 2.4. It is readily apparent that this is a much better model of the experimental data, and furthermore, that this is not a living process at -30°C . As mentioned in **Chapter 1**, Cp-based catalysts are uncommon in living olefin polymerisation. The most relevant examples to this study are compounds **5**, **6**, **29**, and **31**. With the exception of compound **29**, all of the reports of living polymerisation use extremely cold temperatures (-50°C to -78°C) and $\text{B}(\text{C}_6\text{F}_5)_3$ as the activator. With this in mind, polymerisation reactions were performed at -78°C , taking aliquots at various intervals

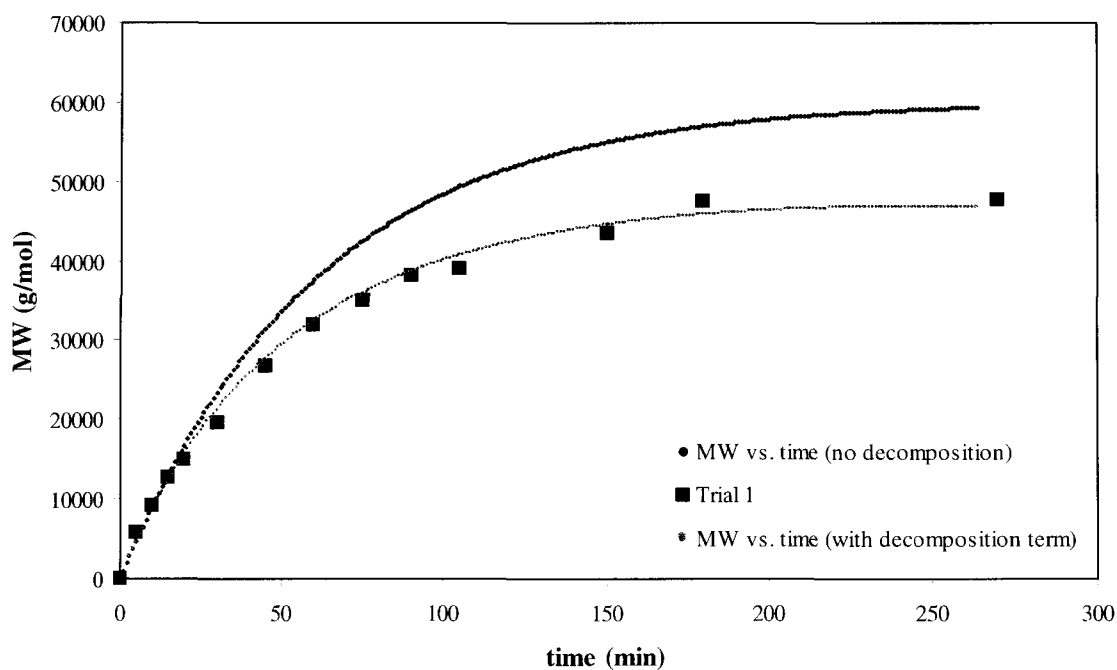


Figure 2.4. Molecular weight vs. time plot of Trial 1 with Model Line Accounting for Catalyst Decomposition.

ranging from 15 minutes to 7 hours. However, upon analysis by GPC, all of the traces show multiple peaks and very broad molecular weight distributions, and were nearly superimposable regardless of the polymerisation time. This suggests that little to no polymerisation was occurring while at -78°C in the flask, and all of the polymerisation

took place as the aliquots were drawn into the syringe (which was at ambient temperature) and injected into the quenching agent. Attempts to determine living polymerisation by running a series of polymerisation experiments at -78°C with increasing reaction times yielded little to no polymer even after six hours.

It is clearly evident that (34) is not a living polymerisation catalyst at -30°C . However, the resultant polymers produced at this temperature display moderately narrow molecular weight distributions and controllable molecular weights. Therefore investigations were undertaken to determine the details of the properties of the α -olefin polymers obtained using (34).

2.6 Properties of 1-Hexene Homopolymers

2.6.1 Physical Properties

All of the 1-hexene homopolymers prepared in this study are sticky, semi-liquid oily materials. The polymers are readily soluble in a variety of organic solvents, most notably aliphatic hydrocarbon solvents (i.e. pentanes or hexanes), aromatic hydrocarbon solvents (i.e. toluene or benzene), and THF. This is in agreement with literature reports which have shown that poly(1-hexene) remains soluble with molecular weights as high as 10^6 to 10^7 .^[76] Although this property limits its commercial utility, it is advantageous from an academic point of view, as it allows for easy analysis using standard solution techniques such as GPC and NMR spectroscopy.

2.6.2 NMR Analysis of 1-Hexene Homopolymers

Exploiting the favourable solubility properties of the polymers, NMR experiments were conducted on samples prepared at 25 - 30% w/w solutions in C_6D_6 in 5 mm sample tubes.

The importance of ^{13}C NMR spectroscopy in polymer analysis is paramount. Useful information can be obtained via integration of the signals from a carefully designed experiment. In order to gain reliable information, it is of utmost importance to ensure that all nuclei giving rise to the signals which are to be integrated have been given sufficient time to relax to their equilibrium state. In the case of polymer NMR spectroscopy, the factor which governs this is the *spin-lattice* relaxation time, T_1 . T_1 relaxation times were measured using the inversion recovery experiment. In this experiment, the sample is subjected to a pulse sufficient to tip the net magnetisation vector antiparallel to the external magnetic field (180° pulse). It is then allowed to relax for a period of time, τ , after which it is subjected to a 90° pulse and the spectrum is acquired. In this manner, a series of spectra are acquired with varying values of τ . Since the intensity of the NMR signal is related to the x -component of the magnetisation vector, the value of T_1 can be determined by deducing the value of τ which leads to a null signal. Figure 2.5 shows a stacked plot of a series of spectra of the region between 0 and 50 ppm for a sample of poly(1-hexene), with τ values ranging from 0.001 seconds to 15 seconds. Analysis of this data reveals that the T_1 values for the aliphatic carbons in this representative sample range from 0.1 seconds up to ~ 2 seconds. To ensure reliable quantitative results, the delay between scans is typically set to five times the longest T_1 value,^[66] hence, 10 second delay times were used.

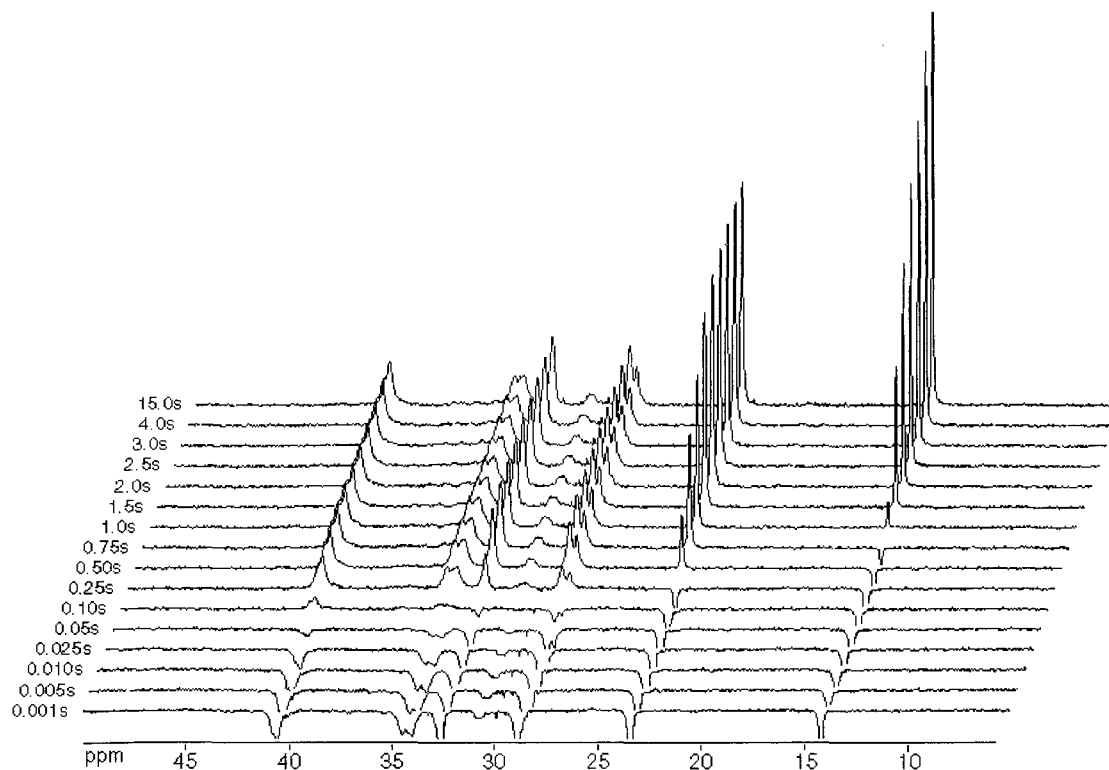


Figure 2.5. Stacked Plot of T_1 Data.

An ideal sample of poly(1-hexene) would consist of identical head-to-tail insertions, giving rise to a polymer which is uniform along the length of the chain. This is shown pictorially in Figure 2.6. Such a polymer would give rise to a spectrum containing six

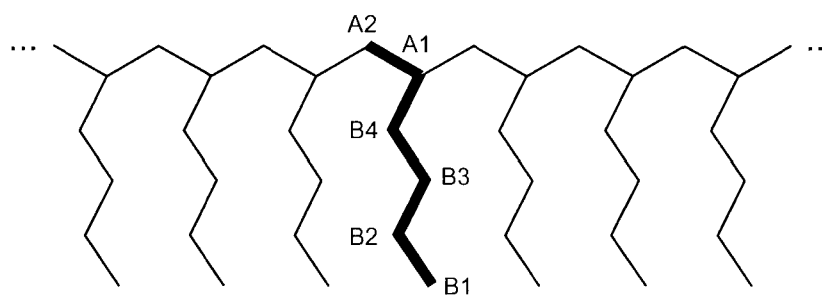


Figure 2.6. Regioregular poly(1-hexene) Showing Numbering Scheme.

large peaks of equal intensity, arising from the four carbons in the branches, the CH carbon of the branchpoint, and the CH_2 carbons in the ‘backbone’ of the polymer. A

simulated spectrum is shown in Figure 2.7. In addition to this, smaller peaks due to the endgroups on the polymer may be observed, if the molecular weight of the polymer is low enough (i.e. the concentration of endgroups in the NMR sample is high enough). There are a number of reports in the literature which display spectra that correspond to the above situation.^[61, 63, 64, 77-79] In some of these cases, the poly(1-hexene) is highly tactic, and gives rise to very narrow signals in the NMR spectrum.

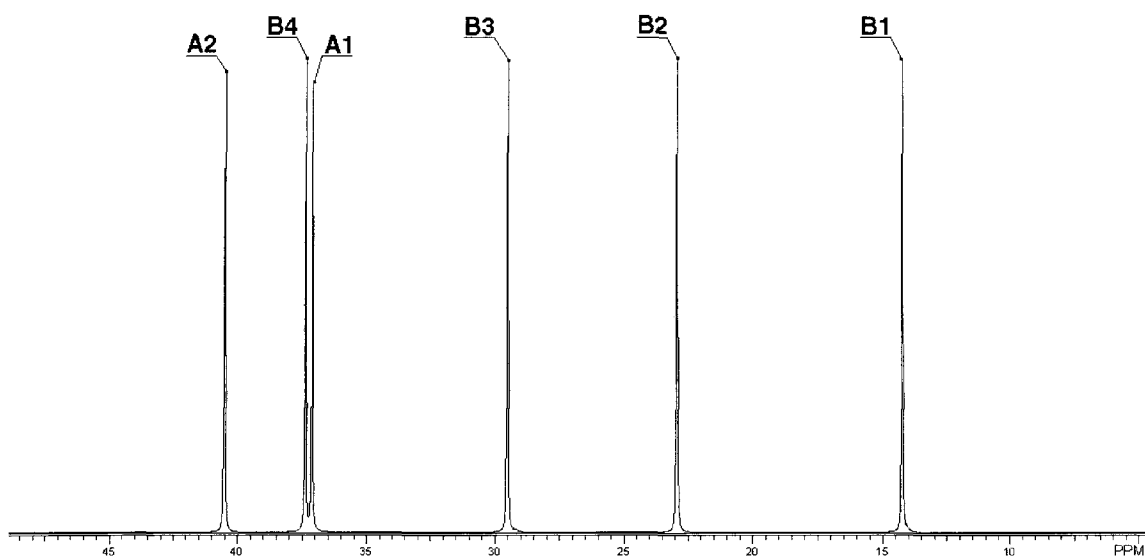


Figure 2.7. Simulated Spectrum of Regioregular poly(1-hexene). See **Figure 2.6** for diagram.

A representative NMR spectrum of poly(1-hexene) prepared with **(34)** is shown in Figure 2.8, the peak shifts and relative integrals are shown in Table 2.2. As expected, there are six large peaks which dominate the spectrum. These are assigned to the six carbons which would arise following regular head-to-tail insertions of 1-hexene as shown in Figure 2.6. The resonances due to the B1 and B2 carbons appear as sharp single peaks, however, the resonances due to the B3, B4, A1, and A2 carbons are quite broad, and show multiple peaks; indicative of a completely atactic polymer, as expected

from a C_s symmetric catalyst, since both sites of insertion are equivalent and there is no reason for preference of one insertion conformation over the other.

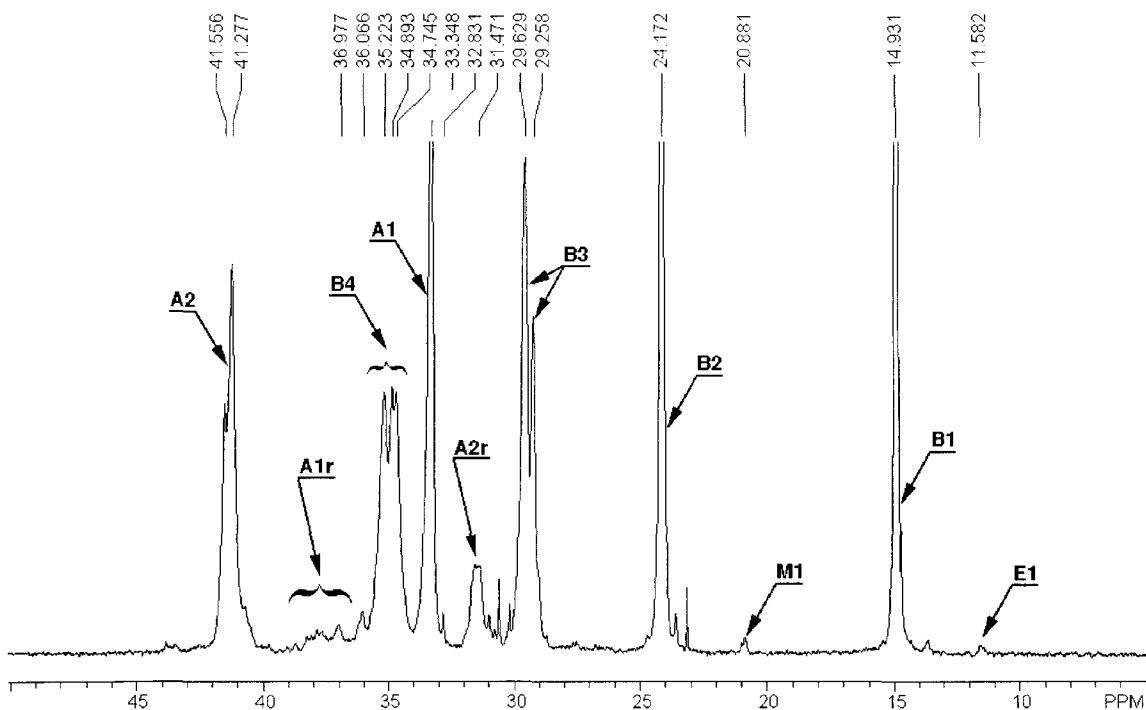


Figure 2.8. Actual Spectrum of poly(1-hexene) Prepared with (34). See **Figure 2.6** and **Figure 2.9** for diagrams.

A trend of decreasing integral can be seen moving closer to the chain backbone upon examination of the relative integrals of the six main peaks, shown in Table 2.2. In addition, the spectrum in Figure 2.8 contains broad resonances other than the six main resonances discussed above. Most notable of these are the resonances occurring at 30.4 - 32.5 ppm and 35.8 - 38.5 ppm. DEPT-135 and DEPT-90 analyses show that the resonances in the region 30.4 - 32.5 ppm arise from methylene (CH_2) carbon atoms, and the resonances in the region 35.8 - 38.5 ppm arise from methine (CH) carbon atoms. If the integral values from the resonances in the region 30.4 - 32.5 ppm and the A2 resonance (41.3 & 41.6 ppm) are added together, the sum is close to the expected value

for the backbone carbons. Similarly, the sum of the integrals from the resonances at 35.8 - 38.5 ppm and 33.3 ppm are in reasonable agreement with the expected value for the carbons in the backbone of the chain.

Table 2.2. ^{13}C NMR Spectral Data for Spectrum Shown in **Figure 2.8**.

Shift (ppm) ^[a]	Integral ^[b]	Type of Carbon ^[c]	Assignment ^[d]
14.9	1096	CH ₃	B1
24.2	1000	CH ₂	B2
29.3 & 29.6	805	CH ₂	B3
30.4 – 32.5	205	CH ₂	A2r
33.3	640	CH	A1
34.8 & 35.2	1020	CH ₂	B4
35.8 – 38.5	120	CH	A1r
41.2 & 41.6	620	CH ₂	A2

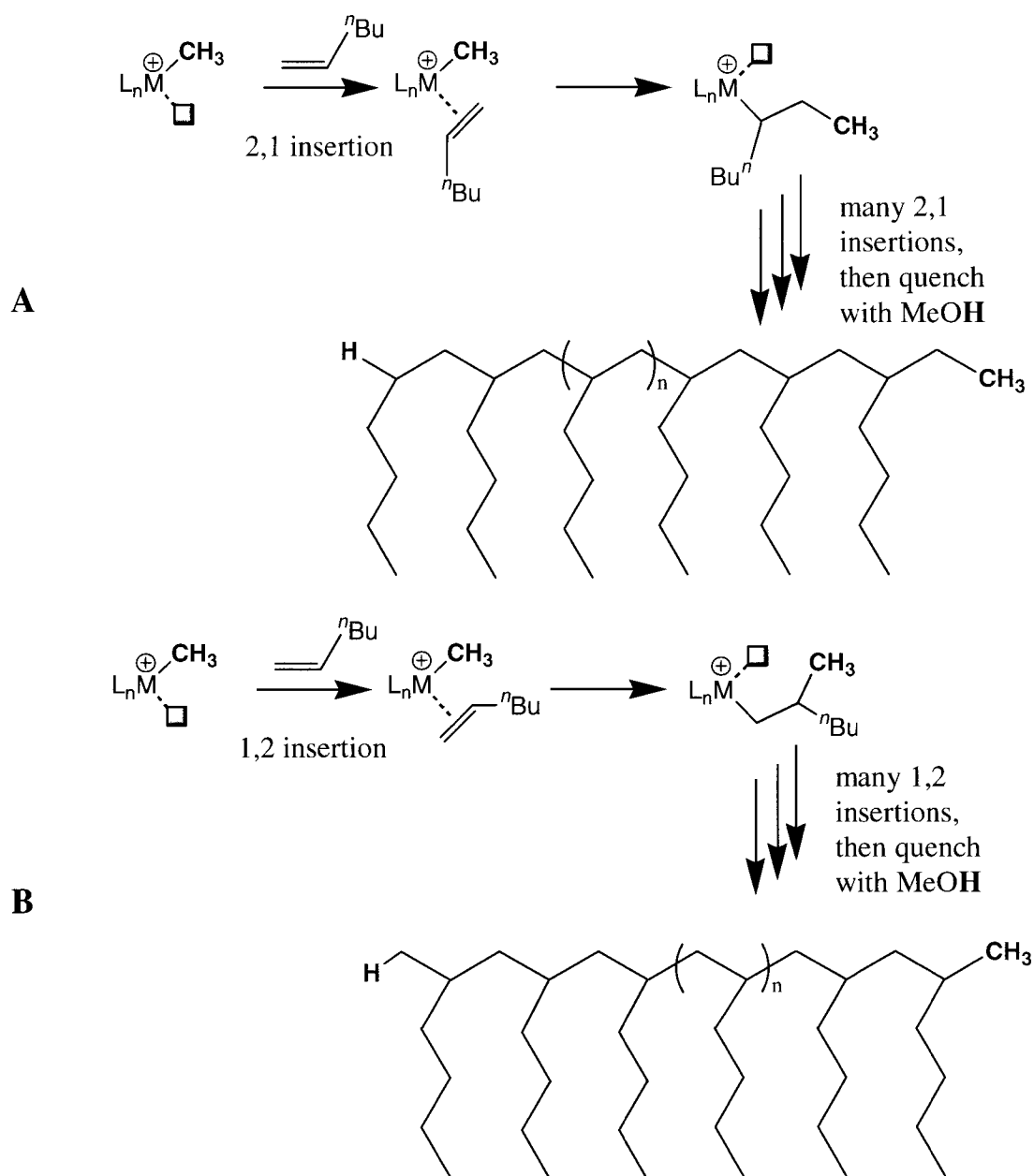
^[a] Relative to central resonance of C₆D₆ (128.4ppm).

^[b] Resonance at 24.2 defined as 1000.

^[c] From DEPT results.

^[d] Refer to diagram in **Figure 2.6**.

The extra unexpected resonances in the spectrum at 30.4 – 32.5 ppm and 35.8 – 38.5 ppm can be attributed to secondary (2,1) insertions of 1-hexene in the polymer. This is further supported by the presence of a resonance at 11.6 ppm, which would arise from an ethyl branch on the main chain.^[66] This type of branch would form if the initial insertion of 1-hexene into a metal-methyl bond was 2,1 as shown in Scheme 2.1 path A. If the initial insertion of 1-hexene is a primary (1,2) insertion (as shown in Scheme 2.1 path B), a methyl branch would result, and its shift is expected at 20.1 ppm. The resonance at 20.9 ppm in the spectrum in Figure 2.8 can be attributed to an initial 1,2 insertion of 1-hexene.



Scheme 2.1. Polymer Chain Growth via 2,1 (**A**) vs. 1,2 (**B**) Olefin Insertion.

Since the first insertion can occur in a 1,2 or 2,1 fashion, it follows that any insertion into the growing chain can also occur in a 1,2 or a 2,1 fashion. Figure 2.9 schematically shows a polymer chain with both modes of insertion in the backbone. Chemical shift

predictions using ChemDraw^[80] show that pairs of adjacent methylene carbons in the backbone resulting from 1-hexene units in a tail-to-tail relationship are expected to occur in the region 30 - 33 ppm, and pairs of adjacent methine carbons resulting from head-to-head insertions are expected to occur in the region 35 - 38 ppm. By dividing the integral of the peaks due to pairs of similar carbons in the backbone by the total integral sum of the backbone carbons, it is estimated that approximately one in five insertions is reversed relative to the previous one.

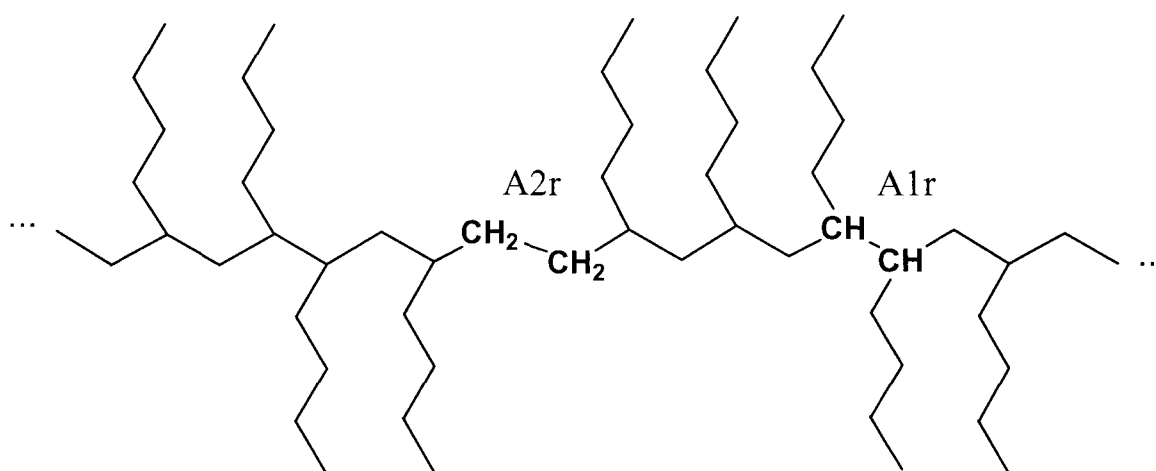


Figure 2.9. Regioregular poly(1-hexene).

Such a high degree of 2,1 insertion of α -olefins is a quite unusual feature in polymers derived from single site catalysts based on group IV transition metals. NMR spectroscopy studies on polypropylene samples prepared with group IV metallocene catalysts show regioerrors occurring at a rate of < 1% of all insertions,^[81] and Landis *et al.* observed “a complete lack of enchaind regioerrors”^[82] (by ¹³C NMR spectroscopy) in poly(1-hexene) produced by the *ansa* metallocene catalyst (9), even when using [1-¹³C]-1-hexene. The only two group IV catalyst systems reported to

polymerise 1-hexene with considerable 2,1 insertions are $\text{CpTiCl}_3/\text{B}(\text{C}_6\text{F}_5)_3$ ^[83] and a member of the *bis*(phenoxyimine)titanium catalysts **(19)**.^[84, 85]

It is reasoned that polymers typically do not possess enchainment 2,1 insertions in part because the bulky secondary metal-alkyl species formed following a 2,1 insertion increases the barrier to insertion of another olefin, and makes chain elimination processes more competitive.^[86]

2.7 Internal Olefin Polymerisation

Since **(34)** has the ability to produce poly(1-hexene) with considerable 2,1 enchainments, experiments were performed to test if internal olefins could be polymerised using **(34)**. When polymerisations of cyclopentene and *cis*-2-pentene were tested at 0°C and 25°C the catalyst system produced no discernable polymer. However, when tested at elevated temperature (45°C) with cyclopentene, a very small amount of material (< 20 mg) was recovered. During the workup, a portion of the material was soluble in pentanes. GPC analysis of the soluble fraction revealed a chromatogram with a very broad peak with $M_n = 1500$ g/mol, corresponding to *ca.* 22 cyclopentene units. The insoluble fraction was, at least partially, taken up in THF and also analysed by GPC. The resultant chromatogram consisted of a fairly sharp peak with $M_n = 3000$ g/mol, corresponding to *ca.* 44 monomer units. It has been reported in the literature that homopolymerisation of cyclopentene can be carried out using *ansa*-zirconocene catalysts to yield a polymer consisting of linked cyclopentane rings.^[87] Using NMR spectroscopy, Collins *et al.*^[88] have determined the molecular weight of such samples prepared by ethylenebis(η^5 -tetrahydroindenyl)zirconium dichloride over 24 hours,

however, the samples, which had molecular weights of up to 1400 g/mol, were only soluble in hot toluene or hot 1,2,4-trichlorobenzene. Therefore, the samples described herein, being soluble in THF and/or pentanes at room temperature with molecular weights of 1500 and 3000 g/mol, are not likely the chains of cyclopentane rings produced by Collins *et al.*^[88] However, the extremely low yield of the materials precluded further study of these polymers.

2.8 Summary

It has been shown that activated versions of **(34)** are effective catalysts for the polymerisation of α -olefins. The polymerisation reaction, though not technically living, remains controllable at sub-ambient temperatures. NMR investigations show that **(34)** polymerises α -olefins with a considerable amount of 2,1 insertions in the polymer. This is a highly uncommon mode of polymerisation, particularly for group IV transition metal based catalysts. This observation further supports the argument that the phosphinimide ligand fosters a more open metal centre for olefin coordination (*vide supra*).

Chapter 3 Random and Block Copolymerisations

3.1 Introduction

As outlined in the previous chapter, $\text{Cp}(\text{}^t\text{Bu}_3\text{PN})\text{TiMe}_2$ (**34**) has demonstrated efficacy for the homopolymerisation of 1-hexene at subambient temperatures, producing polymers with properties unlike those attained when using traditional metallocene catalysts. Early work performed in the Stephan group using (**34**) for the homopolymerisation of 1,5-hexadiene and 1,7-octadiene produced highly insoluble materials which precluded their characterisation.^[89] This insolubility was presumably due to extensive crosslinking of the polymer chains.

The focus of this investigation is to probe the details of the polymerisation of non-conjugated dienes by copolymerising them with a long chain α -olefin in order to enhance the solubility of the resultant polymers. To this end, a detailed study of the copolymerisation of 1-hexene with 1,5-hexadiene was performed, and the microstructural details of the resultant polymers were investigated using ^1H and ^{13}C NMR spectroscopy.

3.2 Experimental Methods

3.2.1 General Considerations

Unless noted otherwise, all reactions were performed under an inert atmosphere of dry N_2 using an Innovative Technologies glove box and standard Schlenk techniques. Toluene used for polymerisations was dried by refluxing overnight over sodium-benzophenone ketyl and used within 24 hours of distillation. 1-Hexene (Aldrich) and 1,5-hexadiene (Aldrich) were dried by refluxing over sodium-benzophenone ketyl overnight followed by vacuum transfer. Polymerisations were performed within 24 hours of purification. $Cp(^tBu_3PN)TiCl_2$ and $B(C_6F_5)_3$ were obtained from NOVA Chemicals Ltd. and used without further purification. $Cp(^tBu_3PN)TiMe_2$ (**34**) was synthesised in the manner outlined in **Chapter 2**. Sub-ambient reaction temperatures ($-31^\circ C$) were controlled via a solvent bath made using a $(CH_3NO_2)/N_{2(l)}$ mixture.

3.2.2 Copolymerisation Procedures

3.2.2.1 Procedure 3.A: 1-Hexene/1,5-Hexadiene Random Copolymerisations

A 250 mL Schlenk flask was equipped with a magnetic stirring bar. 80.0 mmol of monomer (a mixture of 1-hexene and 1,5-hexadiene), cocatalyst (2 mol equivalents of $B(C_6F_5)_3$, per mol of (**34**)), and toluene to make the total volume of solution equal to 34.0 mL were added to the flask, which was then sealed with a septum and attached to the Schlenk line. The flask was then immersed in a cooling bath of $CH_3NO_2/N_{2(l)}$ and

stirred for 10 - 15 minutes at the polymerisation temperature. A syringe containing **(34)** dissolved in 1.0 mL of toluene was then brought out of the glovebox and its contents injected into the flask. This was taken to be time zero. Polymerisations were quenched after 10.0 min by injection of 5 mL of MeOH. The amounts of **(34)** and cocatalyst used are indicated in the text.

3.2.2.2 Procedure 3.B: Ethylene/1-Hexene Block Copolymerisations

A 250 mL Schlenk flask was equipped with a magnetic stir bar. 24.0 mL of toluene and 2 mol equivalents of $B(C_6F_5)_3$ were added, the flask was sealed with a septum and attached to a Schlenk line equipped to deliver N_2 and C_2H_4 . The flask was opened to N_2 , immersed in $CH_3NO_2/N_2(l)$ and stirred for 10-15 minutes at the polymerisation temperature. A syringe containing **(34)** dissolved in 1.0 mL of toluene was then brought out of the glovebox and its contents injected into the flask. This was taken to be time zero. The active catalyst was allowed to pre-activate for 3 minutes. The flask was then subjected to vacuum until the solvent began to boil, and then backfilled and kept under a purge of C_2H_4 for a period of time (the polymerisation time). Following this, the flask was again subjected to vacuum until the solvent began to boil, and then backfilled with N_2 and allowed to stir an additional 3 minutes to allow removal of excess C_2H_4 . 1-Hexene (pre-cooled to $-16^\circ C$) was then added to the flask via syringe, and allowed to react for a period of time. The polymerisation was quenched by the addition of 5 mL of MeOH. The amounts of **(34)** and cocatalyst used are indicated in the text.

3.2.2.3 1-Hexene/1,5-Hexadiene Random Copolymer Workup Procedure

Following polymerisation, all volatiles were allowed to evaporate from the polymer sample. The sample was then redissolved or suspended in pentanes and transferred to a weighed vial. Catalyst residues were extracted with portions of acidified methanol (10:90 conc. HCl:MeOH) at least three times, or until the alcoholic layer was colourless. The resulting polymer was then dried *in vacuo* to constant mass.

3.2.2.4 Ethylene/1-Hexene Block Copolymer Workup Procedure

Following polymerisation, all volatiles were allowed to evaporate from the polymer sample. The sample was then transferred to a weighed vial, and pentanes was added. Catalyst residues were extracted with portions of acidified methanol (10:90 conc. HCl:MeOH) at least three times, or until the alcoholic layer was colourless. The resulting polymer was then dried *in vacuo* to constant mass.

3.2.3 NMR Spectroscopy

$^{13}\text{C}\{^1\text{H}\}$ NMR analyses of random copolymers containing less than or equal to 25% 1,5-hexadiene were carried out at 25°C on a Bruker DPX300 spectrometer operating at 75 MHz. Samples were prepared as 25% - 30% w/w solutions in C_6D_6 in 5 mm NMR sample tubes. Chemical shifts were referenced to the central carbon resonance of C_6D_6 (128.4 ppm). The spectra were acquired using broadband decoupling with a 10 s delay between scans.

$^{13}\text{C}\{^1\text{H}\}$ NMR analyses of ethylene/1-hexene copolymers and random copolymers containing 50% 1,5-hexadiene were carried out by NOVA Chemicals Ltd. Analytical and Product Characterisation Team. Spectra were acquired using a Bruker DPX300 spectrometer operating at 75MHz at 125°C using a 10 s delay between scans. The samples were prepared as 10% w/w solutions in 1,2,4-trichlorobenzene in 10 mm NMR sample tubes.

3.2.4 Molecular Weight Determination

Molecular weights and molecular weight distributions of copolymers containing up to 25% 1,5-hexadiene were performed using a Waters Breeze system GPC using THF as the eluent. The detector used was a Waters model 410 refractive index detector at 35°C, and molecular weights were calibrated using narrow polystyrene standards (Polymer Laboratories Inc.). The samples were prepared by dissolving the analyte in THF (0.1% w/v) and then filtering through a 0.45 μm filter.

Molecular weights and molecular weight distributions of ethylene/1-hexene block copolymers and random copolymers containing 50% 1,5-hexadiene were carried out by NOVA Chemicals Ltd. Analytical and Product Characterisation Team. The instrument used was a Waters 150C GPC using 1,2,4-trichlorobenzene as the eluent at 140°C. The samples were prepared by dissolving the polymer in 1,2,4-trichlorobenzene (0.1% w/v) and were run without filtration.

3.3 Random Copolymers of 1-Hexene and 1,5-Hexadiene

3.3.1 Copolymer Properties

Polymerisation reactions were performed in a manner similar to the homopolymerisations outlined in **Chapter 2**, substituting varying molar amounts of the 1-hexene monomer with 1,5-hexadiene comonomer. Table 3.1 shows data for a series of copolymers with diene contents ranging from 5% - 50% (molar ratio) in the feedstock using two different catalyst concentrations.

Table 3.1. GPC Data for a Series of poly(1-hexene)-*co*-(1,5-hexadiene) Copolymers with Varying 1,5-Hexadiene Content.

Entry	(34) (mmol)	% 1,5-hexadiene in Feedstock ^[c]	M_n (g/mol)	PDI
1 ^[a]	0.111	0	11900	1.20
2 ^[b]	0.111	5	9900	1.36
3 ^[b]	0.111	10	12300	1.26
4 ^[b]	0.111	20	12000	1.44
5 ^[b]	0.111	25	13500	1.51
6 ^[b]	0.111	50	16000	5.48
7 ^[a]	0.056	0	7500	1.29
8 ^[b]	0.056	5	6300	1.40
9 ^[b]	0.056	10	7900	1.43
10 ^[b]	0.056	20	6700	1.38
11 ^[b]	0.056	25	11600	1.34

^[a] Polymerisation carried out using Procedure **2.B** using 10 min reaction time.

^[b] Polymerisation carried out using Procedure **3.A** using 10 min reaction time.

^[c] mol % of total monomer.

The properties of the copolymers prepared with 0% - 25% 1,5-hexadiene in the monomer feedstock are quite similar to the homopolymers described in **Chapter 2**,

being oily materials which are readily soluble at ambient temperature in a variety of solvents. However, the polymer prepared with 50% 1,5-hexadiene is an elastomeric material which is insoluble in standard organic solvents at ambient temperature.

The molecular weights and polydispersities (PDI) of copolymers were determined by GPC analysis. The PDI values of the copolymers prepared with up to 25% 1,5-hexadiene in the feedstock are similar to those for the 1-hexene homopolymers. All of them remain below 1.51, and are comparable at all diene concentrations regardless of the catalyst concentration. This indicates that for both catalyst concentrations, copolymers with narrow molecular weight distributions can be produced.

The number average molecular weights (M_n) of the copolymers show a general trend of increasing M_n as the concentration of diene in the feedstock increases (Figure 3.1). Since each molecule of 1,5-hexadiene contains two double bonds whereas a molecule of 1-hexene contains only one, substituting 1,5-hexadiene for 1-hexene in solution will result in an increase in the number of *double bonds* in solution, even though the concentration of *monomer* remains constant. Since the polymerisations are run for a set amount of time and then quenched, not all of the monomer in solution is being consumed. The rate of polymerisation is dependent upon the concentration of olefin in solution, and the M_n is dependent upon the rate of polymerisation. Thus, the M_n is indirectly dependent upon the olefin concentration, and would be expected to increase slightly when the monomer feedstock contains more 1,5-hexadiene, as there would be more double bonds in solution compared to a strictly 1-hexene feedstock. When the increase in double bonds in solution is compared with the M_n for the series of copolymers, the M_n rises faster than the number of double bonds in solution (Figure 3.2). The greater increase in M_n implies that the relative number of double bonds in solution is

not the sole source of increasing M_n ; a reasonable explanation for this is an increase due to crosslinking of polymer chains.

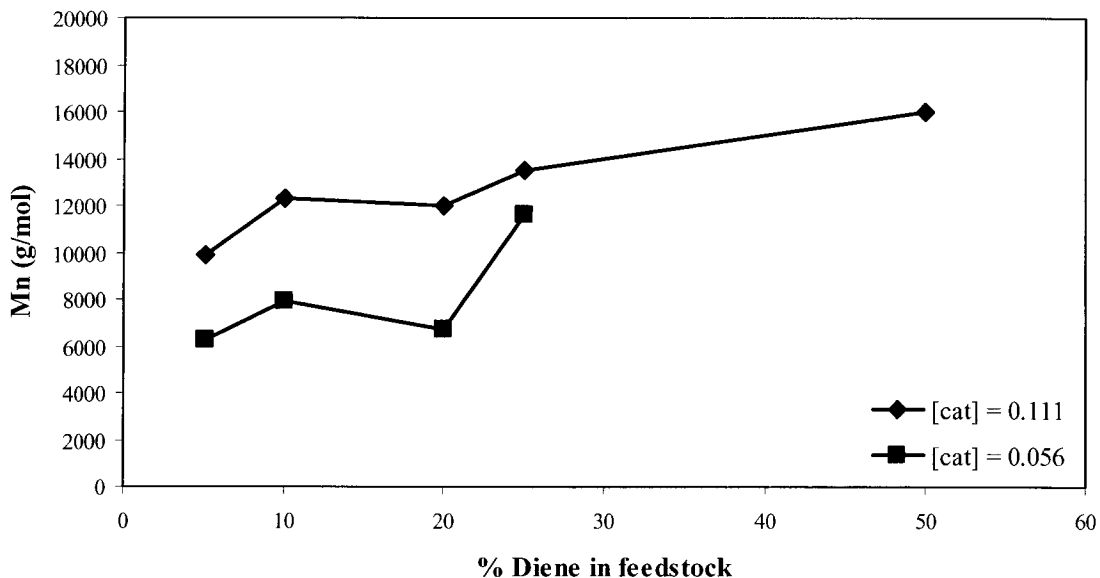


Figure 3.1. M_n vs. 1,5-Hexadiene Content for a Series of poly(1-hexene)-*co*-(1,5-hexadiene) Copolymers.

The polymers produced using higher catalyst concentrations have, for all 1,5-hexadiene concentrations, a higher M_n than those produced using the same diene concentration and a reduced amount of catalyst. This is in contrast to the expected trend of increasing M_n with decreasing catalyst concentration, since there would be proportionally more monomer available to each catalyst site. This suggests that there is increased catalyst deactivation at the lower concentration, consistent with the issues of reproducibility when a lower catalyst concentration is used (as outlined in **Chapter 2**).

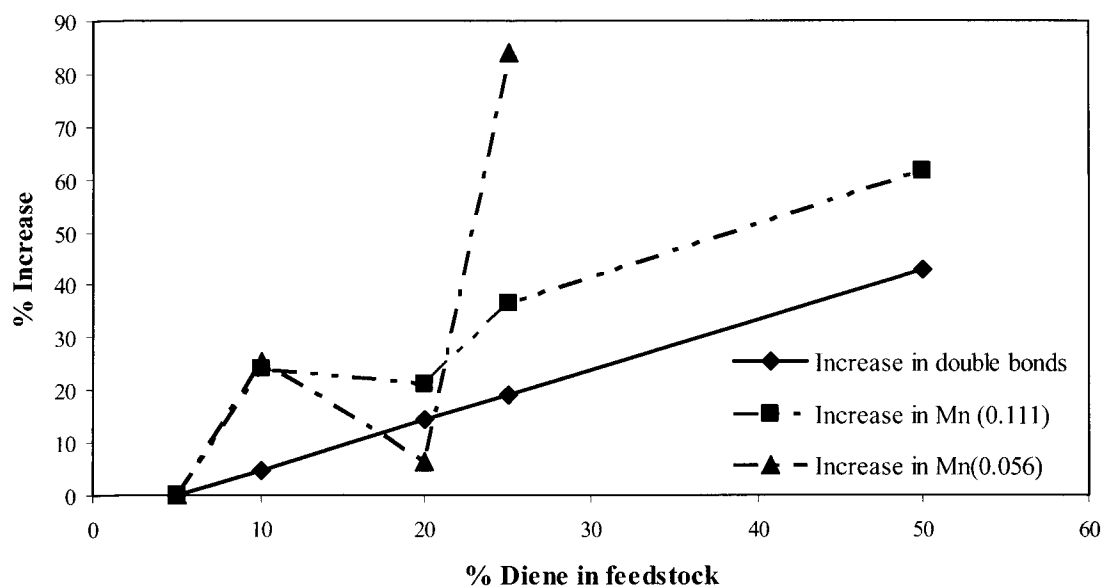


Figure 3.2. Increase in M_n and Double Bond Content in Feedstock vs. 1,5-Hexadiene Content for a series of poly(1-hexene)-*co*-(1,5-hexadiene) Copolymers.

3.3.2 NMR Analysis of Copolymers

In order to gain insight into the microstructure of the 1-hexene/1,5-hexadiene copolymers prepared with (34), a series was analysed using ^{13}C and ^1H NMR spectroscopy. A representative ^{13}C NMR spectrum is shown in Figure 3.3. DEPT-135 and DEPT-90 experiments were conducted to determine the type of carbons responsible for each of the resonances. A stacked plot of the ^{13}C NMR spectra for a series of 1-hexene/1,5-hexadiene copolymers is shown in Figure 3.4. The relative integrals of the unique peaks in the 1-hexene/1,5-hexadiene copolymers for a series of copolymers with 1,5-hexadiene contents ranging from 0% (1-hexene homopolymer) - 50% are shown in Table 3.2, and a plot of peak integral vs. 1,5-hexadiene concentration in the feedstock is shown in Figure 3.5.

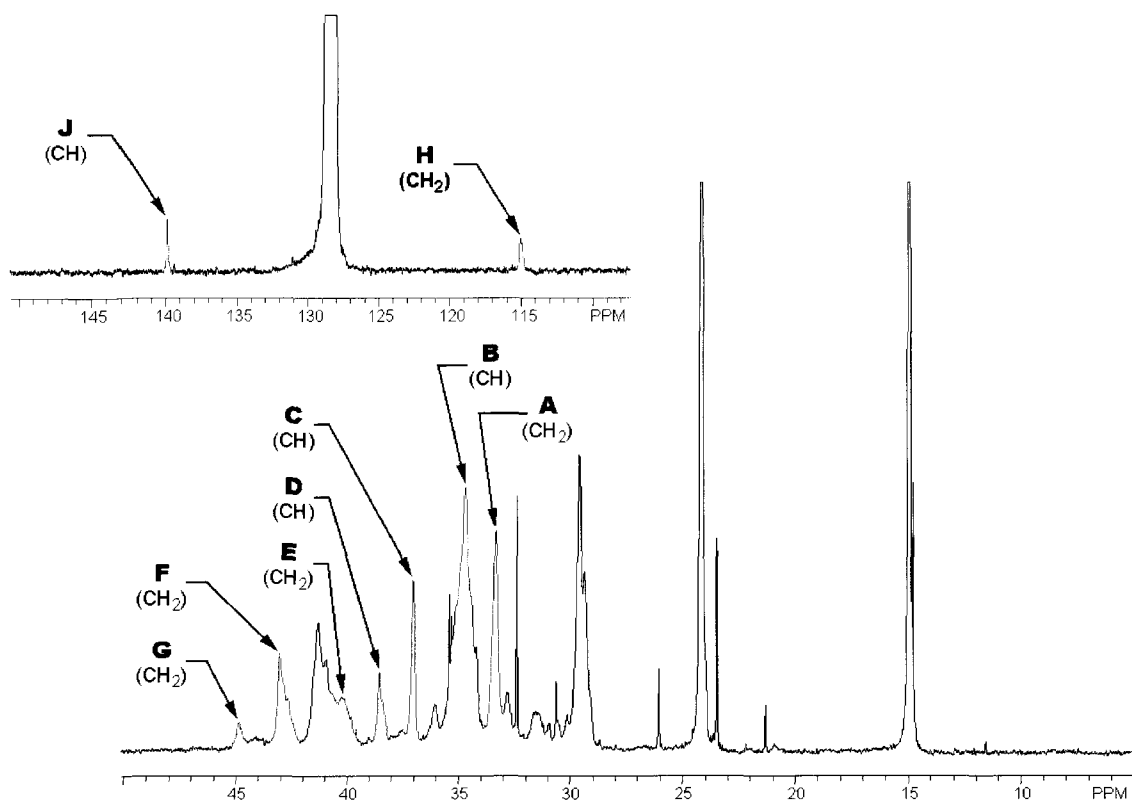


Figure 3.3. Representative ^{13}C NMR Spectrum of a poly(1-hexene)-*co*-(1,5-hexadiene) Copolymer (20% 1,5-hexadiene) Showing Peaks Related to 1,5-Hexadiene Incorporation. Letters Refer to Resonances outlined in **Table 3.2**.

^{13}C NMR spectra of the copolymers of 1-hexene/1,5-hexadiene prepared with (34) contain resonances which are not observed in the corresponding 1-hexene homopolymers. These resonances increase in size proportional to the amount of 1,5-hexadiene in the feedstock, though not necessarily at equal rates. This is shown pictorially in Figure 3.4 as a stacked plot, and graphically in Figure 3.5. This suggests that there is no preference for insertion of a 1-hexene monomer or a 1,5-hexadiene monomer, which is not surprising, considering that these two monomers have very similar physical and structural properties.

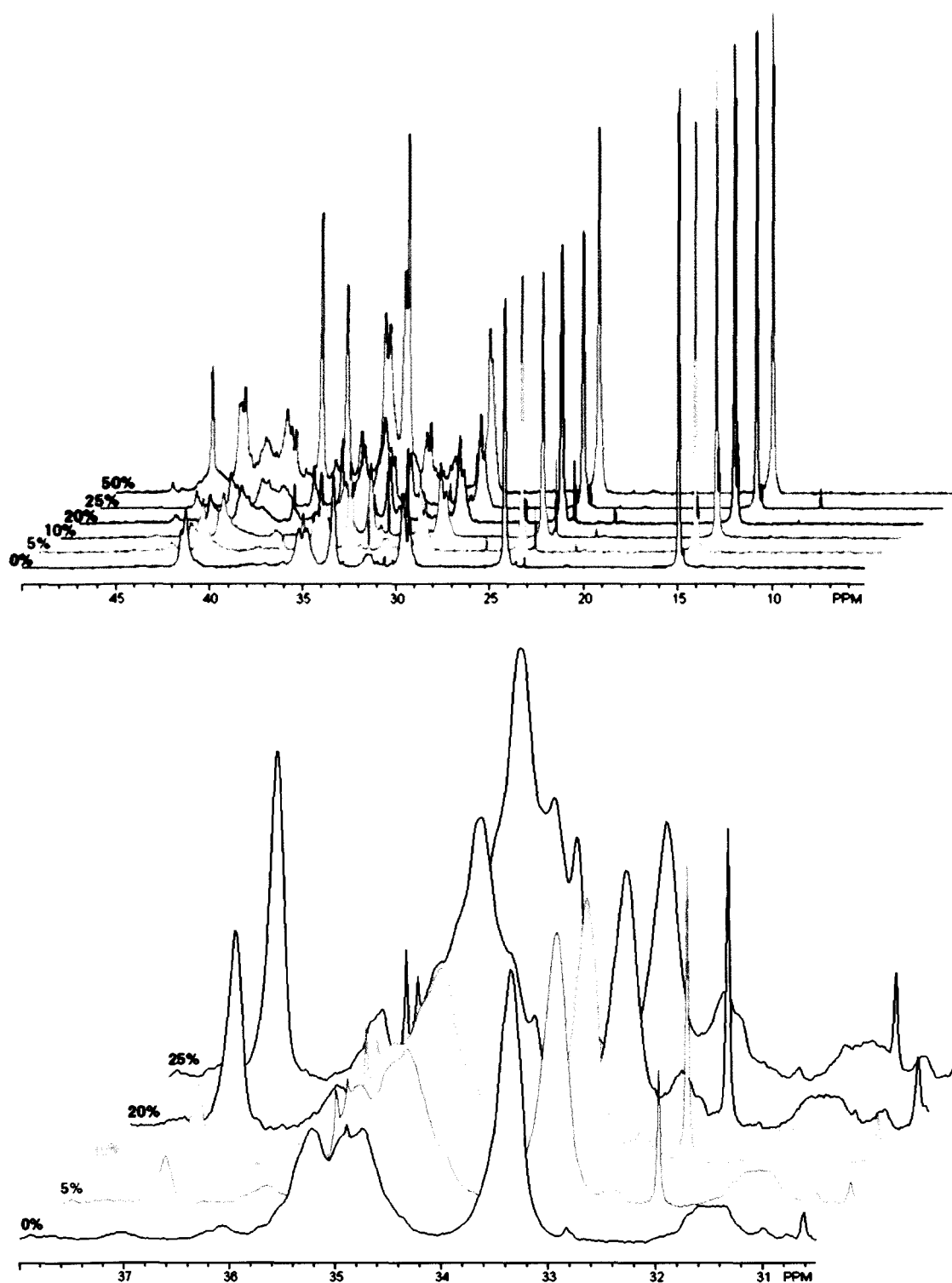


Figure 3.4. Stacked Plots of ^{13}C NMR Spectra of a Series of poly(1-hexene)-*co*-(1,5-hexadiene) Copolymers (Top: Full Spectrum of Aliphatic Region; Bottom: Expansion of 30.5 – 38.0 ppm Region).

Table 3.2. Relative Integrals for a Series of poly(1-hexene)-*co*-(1,5-hexadiene) Copolymers with Varying 1,5-Hexadiene Content.

% 1,5-hexadiene in feedstock	A 32.8	B 34.7 ^[a]	C 37.0 ^[b]	D 38.5	E 40.2	F 42.2- 43.4	G 44.9	H 115.0	J 140.0
0	0	0 (390)	50	0	0	0	0	0	0
5	44	512 (122)	50	55	53	88	38	23	17
10	72	578 (188)	88	90	118	178	31	46	30
20	138	769 (379)	186	170	230	351	75	71	56
25	184	875 (485)	260	245	300	443	103	58	50
50	213	1550 (ND)	700	725	670	945	410	164	152

^[a] Value shown in brackets is integral of region 34.4 - 35.0 ppm, value integrated in 0% 1,5-hexadiene sample subtracted from actual integral. Shifts are slightly different in 50% entry.

^[b] Integral of 0% entry subtracted from each other entry.

Waymouth *et al.* has performed extensive studies on the microstructure of poly(1,5-hexadiene) prepared with various zirconocene derivatives.^[90-92] In these studies, the 1,5-hexadiene was almost entirely cyclopolymerised to give a polymer consisting of methylene separated cyclopentane rings (Figure 3.6). Recently, Coates *et al.*^[93] have undertaken investigations on poly(1,5-hexadiene) and copolymers of propylene and 1,5-hexadiene prepared with **(19)**, a catalyst system known to polymerise olefins with a high degree of 2,1 insertions, and included ¹³C NMR analysis of the resulting polymers.

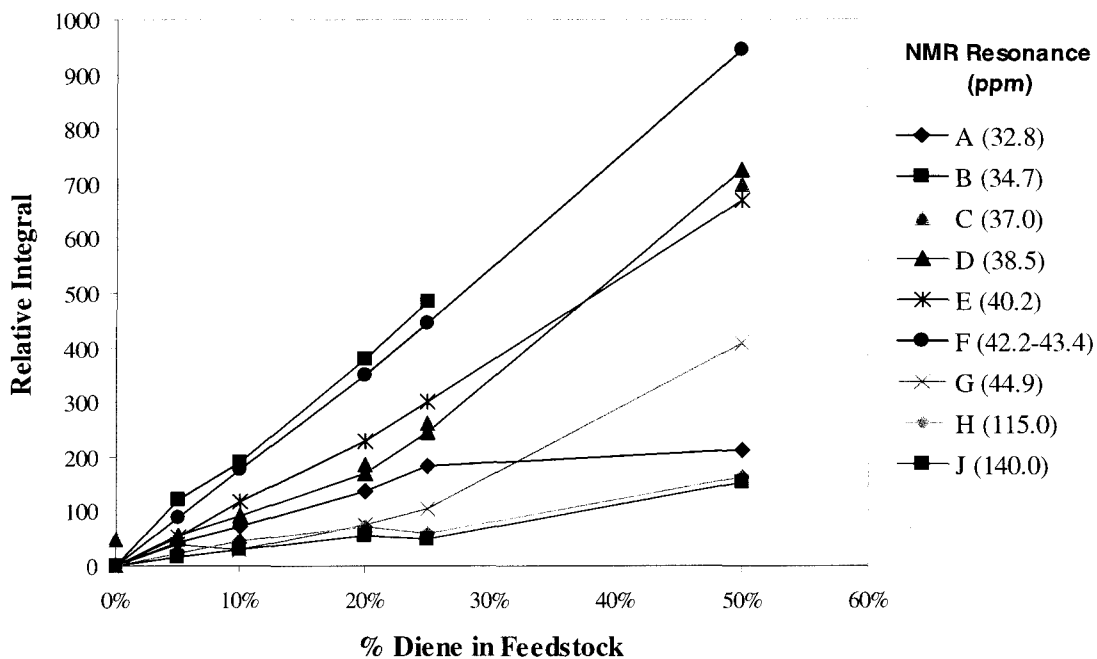


Figure 3.5. Plot of Relative Integral vs. 1,5-Hexadiene Content for Diene-related ^{13}C NMR Resonances in a Series of poly(1-hexene)-*co*-(1,5-hexadiene) Copolymers.

Based on the chemical shifts and integrals in the ^{13}C NMR spectrum, as well as correlation with the shift assignments of Coates^[93] and Waymouth,^[90] an attempt was made to assign the new resonances in the ^{13}C NMR spectrum to structural units related to 1,5-hexadiene insertions into the polymer chain.

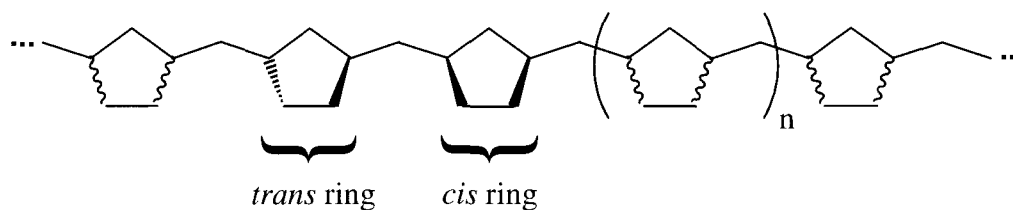


Figure 3.6. Poly(methylenecyclopentane) Polymer Showing Stereochemistry of Cyclopentane Rings.

Since Waymouth *et al.*^[90] observe nearly quantitative cyclisation of inserted diene in the homopolymerisation of 1,5-hexadiene using zirconocene complexes, it is likely that

cyclic units are easily formed following an initial 1,2 insertion. Coates *et al.*^[93] also report a high degree of cyclisation when using (19) as the catalyst. Due to the symmetry of (34), the cycles can assume a *cis* or *trans* conformation, both of which exhibit different ¹³C chemical shifts. The resonances at 37.0 and 38.5 ppm were assigned to the CH carbons of *trans* and *cis* cyclic units, respectively, and the resonance at 32.8 ppm was assigned to the two adjacent CH₂ carbons in a *cis* ring. The resonance for the corresponding CH₂ carbons of the *trans* rings could not be assigned, it is most likely overwhelmed by the resonance arising from the backbone CH carbons at 33.3 ppm (based on the shifts reported by Coates *et al.*).^[93] One or both of the resonances at 40.2 and 42.2 - 43.4 ppm is likely due in part to the CH₂ ‘backbone’ carbon of the *cis* and *trans* cyclic structures based on Coates’ assignments.^[93] However the relative integrals of each of these peaks are greater than expected from this carbon. It is possible that, in addition to the carbon from the cyclic structures, they are also due to the CH₂ carbons involved in crosslinking units. The resonance at 44.9 ppm is directly comparable to observations by Coates^[93] as well as Waymouth,^[90] and has been attributed to the backbone CH₂ between two cyclopentane rings. The downfield resonances at 115.0 and 140.0 ppm have been assigned to the olefinic CH₂ and CH carbons which would arise from a pendant olefin on an inserted diene. The resonance at 34.7 ppm, arising from a CH carbon (from DEPT), is possibly due to CH carbons at the attachment points of a crosslink. However, since it occurs directly on top of the broad resonance from 34.6 - 35.6 ppm, its integral is unreliable and therefore not assigned. A diagram of a model polymer illustrating the different diene structural units is shown in Figure 3.7.

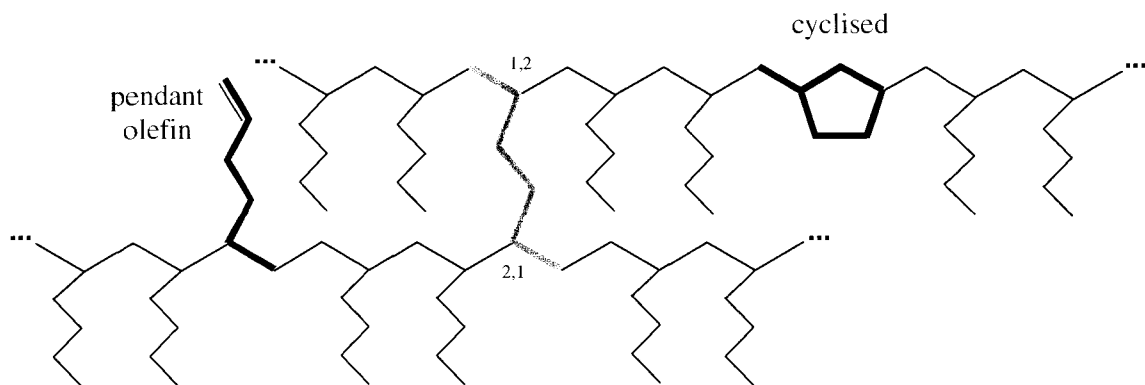


Figure 3.7. Diagram of a Model poly(1-hexene)-*co*-(1,5-hexadiene) Copolymer Showing Cyclic, Pendant, and Crosslinked 1,5-Hexadiene Units.

To assess the proportion of dienes that remain as pendant olefin units in the polymer, the integrals of the peaks at 37.0, 38.5, 115.0, and 140.0 ppm were used. Since the resonance at 37.0 ppm arises from the CH carbons of a *trans* cyclic unit, its relative integral represents the proportion of *trans* cyclic units in the polymer. The same reasoning follows for the resonance at 38.5 ppm for *cis* cyclic units. The resonances at 115.0 and 140.0 ppm are each due to one of the carbons in a pendant olefin unit, therefore the average of the two integrals was taken to be representative of the number of pendant olefin units in the polymer. The proportion of dienes which remain as pendant olefin units was determined by dividing the number of pendant olefins by the sum of all three structural units. This is shown in Table 3.3.

An alternative method of assessing the amount of olefinic units in the polymer is to use ^1H NMR spectroscopy. As mentioned in **Chapter 1**, the utility of ^1H NMR spectroscopy in polymer analysis is limited, due to the considerable overlap of the resonances. However, the resonances arising from protons attached to olefinic carbons appear in a distinct area of the spectrum, separated from the protons attached to saturated carbon atoms. To assess the proportion of dienes which remain pendant, the ratio of the total number of protons attached to saturated carbon atoms to the total number of

protons attached to olefinic carbons was determined for copolymers with a specific diene content, assuming that all inserted dienes are enchainned as pendant olefins. By obtaining the actual ratio of protons and comparing this to the theoretical ratio, an assessment of the dienes which remain pendant can be obtained. The results of this analysis are shown in Table 3.3, and an example calculation is given in **Appendix B**.

Table 3.3 also shows that, in all cases, analysis by ^1H NMR spectroscopy suggests a higher value than ^{13}C NMR analysis for the proportion of inserted dienes which remain pendant. Since the T_1 relaxation times for olefinic carbons are much longer than that of saturated carbons (~ 10 s), the 10 s delay used in the ^{13}C NMR experiments may have been insufficient to allow for complete relaxation of the magnetisation vectors from these carbons, which would lead to lower than expected integrals. In an effort to circumvent this issue, an NMR spectrum was acquired using a much longer delay time of 50 s, and one was also acquired using inverse gated decoupling, which suppresses NOE effects. However, neither of these alternatives resolved the issue when used separately, and using the two techniques simultaneously is not feasible due to the drastically increased spectrometer time which would be necessary to acquire the spectra. Despite the slight difference in absolute values, both the ^{13}C and ^1H NMR integral analyses show a general trend of decreasing pendant olefin content with increasing diene content. This can be reasoned as being evidence for an elevated degree of crosslinking in the polymer chain as the diene content is increased.

Table 3.3. Analysis of Pendant Olefin Content for a Series of poly(1-hexene)-*co*-(1,5-hexadiene) Copolymers with Varying 1,5-Hexadiene Content by ^1H and ^{13}C NMR Spectroscopy.

% 1,5-hexadiene in feedstock	^{13}C Analysis			^1H Analysis		
	Sum ^[a]	Olefin ^[b]	Proportion (%)	Expected ^[c] (%)	Actual ^[d] (%)	Proportion (%)
5	125	20	16	1.26	0.28	22
10	216	38	18	2.54	0.47	20
20	420	64	15	5.17	1.01	19
25	559	54	10	6.52	1.32	20
50	1583	158	10			

^[a] Sum of integrals of resonances at 37.0 and 38.5 ppm, plus average of 115.0 and 140.0 ppm.

^[b] Average of integrals of resonances at 115.0 and 140.0 ppm.

^[c] Expected proportion of olefinic protons to protons from saturated carbon atoms.

^[d] Actual proportion determined by ^1H NMR integration.

3.4 Block Copolymers

As mentioned earlier, a polymerisation operating under living conditions is a highly controlled reaction. Living conditions allow for the ability to produce polymers with defined molecular weights and narrow molecular weight distributions simply by controlling the polymerisation time. A further utility of living polymerisation systems is the ability to produce block copolymers. Block copolymers can be thought of as two or more homopolymers which are covalently linked. Since the copolymer is made up of domains of different polymers, its properties are unlike those of either of the homopolymer blocks. This feature can be exploited to combine the desirable properties of the constituent homopolymers as required. These block copolymers can also be used to promote miscibility between the components of a polymer blend (a compatibiliser).^[70]

Block copolymers are typically produced by sequentially adding the different monomers to the reaction mixture in the desired order. In this study, block copolymers of ethylene and 1-hexene were produced. In order to produce copolymers which are comprised of homopolymer blocks (as opposed to random copolymer blocks), it is important that the reaction vessel be devoid of the first monomer prior to addition of the second.^[58] Thus, ethylene was used as the first block, since it can easily be removed under reduced pressure before the second monomer (1-hexene) is introduced.

GPC data for three block copolymers of ethylene and 1-hexene produced with **(34)** are shown in Table 3.4. The molecular weights of each of the block copolymers clearly rises with the introduction of each new monomer, with the rate of incorporation of ethylene being 25 - 30 times more rapid than incorporation of 1-hexene. Entries 1 and 2 are examples of diblock copolymers, where the order of addition of monomers is ethylene – 1-hexene, while Entry 3 is a triblock copolymer where the order of addition of monomers is ethylene – 1-hexene – ethylene. The molecular weights of the ethylene block and 1-hexene block in Entry 3 are very similar to that of the diblock copolymer in Entry 1. Although the copolymer has been labelled an E-H-E triblock copolymer, due to incomplete polymerisation of 1-hexene, the final ethylene block is more likely a random copolymer of ethylene and 1-hexene. However, since the rate of incorporation of ethylene is much faster than that of 1-hexene, this block will primarily consist of ethylene units.

The superficial physical properties of these block copolymers are unlike those of either polyethylene or poly(1-hexene). Polyethylene, prior to processing, is a flaky white solid which is insoluble in common organic solvents at ambient temperature, while poly(1-hexene) is a sticky, oily substance, and is highly soluble in many organic

solvents. In contrast, the block copolymers prepared in this study are waxy solids. Particularly for the E-H diblock copolymers, when a solvent such as pentanes is added, the polymer does not dissolve, instead it disperses in the solvent, forming a mixture with a milky appearance. This could be a result of the formation of colloidal particles due to the lyophilicity of the poly(1-hexene) block and the lyophobicity of the polyethylene block.

Table 3.4. GPC Data for Block Copolymers of Ethylene and 1-Hexene.

Entry	Copolymer	Block	M_n	M_w	PDI
1	E-H ^[a]	E (1.5 min)	12000	22900	1.91
		E-H (30 min)	21500	34000	1.58
2	E-H ^[b]	E (1.5 min)	13300	29100	2.19
		E-H (30 min)	22400	41100	1.83
3	E-H-E	E (1.5 min)	12000	22900	1.91
		E-H (30 min)	21900	43500	1.99
		E-H-E (1.5 min)	26700	52100	1.95 ^[c]

^[a] 0.5 mL (4.0 mmol) of 1-hexene added.

^[b] 2.0 mL (16.0 mmol) of 1-hexene added.

^[c] Two distinct peak tops, one corresponding to E-H block.

3.5 Summary

The random copolymerisation of 1-hexene with 1,5-hexadiene using **(34)** has been herein described. The polymers were shown to incorporate the two monomers in direct proportion to the relative amounts of them in the monomer feedstock, thus indicating no preference for insertion of one over the other. NMR analysis revealed that the enchainment of 1,5-hexadiene units can exist as pendant olefins, cyclic structures, or as crosslinks in the polymer.

Despite the fact that the catalyst is not strictly living, its behaviour approaches that of a living catalyst. Thus, the reaction can be controlled and used to produce block copolymers. These block copolymers possess physical and solubility properties which are unlike either of the homopolymers of which they are comprised.

Chapter 4 Summary

The original impetus for the study of cyclopentadienyl-phosphinimide based transition metal compounds as catalysts for olefin polymerisation stemmed from the presumed steric and electronic similarity of the phosphinimide ligand to the η^5 -cyclopentadienide ligand. The research described in the preceding two chapters provides further experimental evidence for the unique nature of this family of compounds.

Chapter 2 describes research performed to probe the reaction of **(34)** for the polymerisation of 1-hexene, with a view to elucidating conditions which would lead to a living polymerisation. In the course of these studies, it was determined that the polymerisation does not operate in a living manner, and evaluation of the kinetics of the reaction shows that irreversible catalyst deactivation pathways are present.

^{13}C NMR analysis of the poly(1-hexene) produced by **(34)** revealed that the polymerisation produces atactic polymers, which is expected for a C_s symmetric catalyst. Quite unexpectedly, however, these polymers possess an extraordinarily high degree of enchainment of 2,1 insertions in the backbone. Very few other group IV transition metal-based catalysts are known to produce similar polymers, notable exceptions being the sterically unencumbered piano-stool compound Cp^*TiMe_3 ,^[83] and the octahedral titanium *bis*(phenoxyimine)titanium catalysts (FI) developed by Mitsui.^[36]

In **Chapter 3**, the details of olefin copolymerisations using **(34)** are described. 1-Hexene was copolymerised with the non-conjugated diene 1,5-hexadiene in a random fashion. Analysis of the NMR spectra of these polymers revealed that the degree of

enchainment of the 1,5-hexadiene was directly proportional to its relative quantity in the feedstock, indicating that there is no preference for insertion of a 1-hexene monomer over a 1,5-hexadiene monomer. By comparison of the NMR spectra of the random copolymers with similar polymers produced by others, it was determined that the 1,5-hexadiene units in the polymer can be enchainment as cyclised methylenecyclopentane units, crosslinks, or pendant olefin units. The latter of these could provide a launching point for the synthesis of functional polymers, since they contain a reactive group (alkene) enchainment in the polymer.

Though the polymerisation of α -olefins using **(34)** is not a truly living process, it was demonstrated that the reaction is controllable. This was shown through the synthesis of block copolymers of ethylene and 1-hexene, a process typically reserved for living polymerisation systems.

In conclusion, this work has shown that **(34)**, when activated with a suitable cocatalyst, polymerises α -olefins in a manner quite unlike conventional metallocene catalysts. Consequently, this unusual polymerisation process provides an avenue for the preparation of materials with unique properties.

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Appendix A Derivation of the Rate Equation

A.1 Rate Equation for a Living Polymerisation

The rate equation for complex coordinative polymerisation is

$$-\frac{d[M]}{dt} = k_p[cat][M] \quad \text{Equation A.1}$$

Where $[M]$ = monomer concentration (mol/L), $[cat]$ = catalyst concentration, t = time (h), and k_p = rate constant of polymerisation.

Equation A.1 can be rearranged to give

$$\begin{aligned} -\frac{d[M]}{[M_0]} &= k_p[cat]dt \\ \ln \frac{[M]}{[M_0]} &= -k_p[cat]t \\ \frac{[M]}{[M_0]} &= e^{-k_p[cat]t} \\ [M_t] &= [M_0]e^{-k_p[cat]t} \end{aligned} \quad \text{Equation A.2}$$

Where $[M_0]$ = monomer concentration at time 0 and $[M_t]$ = monomer concentration at time t .

In a polymerisation where there is a fixed initial amount of monomer, the moles of monomer at any time t equals the initial moles of monomer minus the moles of monomer that have already been polymerised. This can be written as

$$mol_{mon,t} = mol_{mon,0} - mol_{mon\ consumed,t}$$

and

$$[M_t] = \frac{mol_{mon,t}}{V} \quad \text{Equation A.3}$$

Where $mol_{mon,0}$ = initial moles of monomer, $mol_{mon,t}$ = moles of monomer at time t , $mol_{mon\ consumed,t}$ = moles of monomer consumed by polymerisation reaction at time t , and V = volume of solution (L).

$$\text{Now, } mol_{mon\ consumed,t} = \frac{m_{mon\ consumed,t}}{mw_{mon}} \text{ and } m_{mon\ consumed,t} = m_{p,t}$$

Where $m_{p,t}$ = mass of polymer at time t (g) and mw_{mon} = molecular weight of the monomer (g/mol).

Thus, the moles of monomer at some time t can be rewritten as

$$mol_{mon,t} = mol_{mon,0} - \left(\frac{m_{p,t}}{mw_{mon}} \right)$$

and substitution into Equation A.3 gives

$$[M_t] = \frac{\left\{ mol_{mon,0} - \left(\frac{m_{p,t}}{mw_{mon}} \right) \right\}}{V} \quad \text{Equation A.4}$$

Substituting Equation A.2 into Equation A.4 and rearranging then gives

$$mol_{mon,0} - \left(\frac{m_{p,t}}{mw_{mon}} \right) = V[M_0]e^{-k_p[cat]t} \quad \text{Equation A.5}$$

We know that the mass of the polymer is equal to the number of moles multiplied by its molecular weight, thus, substituting

$$m_p = (mol_{p,t})(mw_{p,t}) \text{ and } [M_0] = \frac{mol_{mon,0}}{V}$$

into Equation A.5 gives

$$mol_{mon,0} - \left(\frac{(mol_{p,t})(mw_{p,t})}{mw_{mon}} \right) = V \left(\frac{mol_{mon,0}}{V} \right) e^{-k_p[cat]t} \quad \text{Equation A.6}$$

Where $mol_{p,t}$ = moles of polymer at time t and $mw_{p,t}$ = molecular weight of polymer at time t (g/mol).

Simplifying Equation A.6 leads to

$$1 - \left(\frac{(mol_{p,t})(mw_{p,t})}{(mw_{mon})(mol_{mon,0})} \right) = e^{-k_p[cat]t} \quad \text{Equation A.7}$$

and substituting $(mw_{mon})(mol_{mon,0}) = m_{mon,0}$ into Equation A.7 and rearranging gives

$$1 - \left(\frac{(mol_{p,t})(mw_{p,t})}{(m_{mon,0})} \right) = e^{-k_p[cat]t}$$

$$\frac{(mol_{p,t})(mw_{p,t})}{(m_{mon,0})} = 1 - e^{-k_p[cat]t} \quad \text{Equation A.8}$$

In a living polymerisation, each catalyst site produces one polymer chain. Thus, the moles of polymer remains constant, and is equal to the moles of catalyst, i.e.,

$$mol_{p,t} = mol_{cat,0} \quad \text{Equation A.9}$$

and substituting $mol_{p,t}$ for $mol_{cat,0}$ in Equation A.8 gives

$$mw_{p,t} = \left(\frac{m_{mon,0}}{mol_{cat,0}} \right) \{1 - e^{-k_p[cat]t}\} \quad \text{Equation A.10}$$

This equation now relates k_p to the experimental quantities, assuming that $[cat]$ (and consequently $mol_{cat,0}$) remain constant throughout the polymerisation, i.e., no irreversible deactivation. This is the general equation for a living polymerisation.

A.2 Adding a Term for Catalyst Decomposition

The exponential decay of catalyst deactivation is given by

$$\frac{-d[cat]}{dt} = k_d[cat_0] \quad \text{Equation A.11}$$

Rearrangement of Equation A.11 gives

$$\frac{-d[cat]}{[cat_0]} = k_d dt$$

$$\ln\left(\frac{[cat_t]}{[cat_0]}\right) = -k_d dt$$

$$[cat_t] = [cat_0]e^{-k_d t} \quad \text{Equation A.12}$$

Where k_d = rate constant of decomposition, $[cat_0]$ = initial catalyst concentration, and $[cat_t]$ = catalyst concentration at time t .

Substituting Equation A.12 for $[cat]$ in Equation A.10 gives

$$mw_{p,t} = \left(\frac{m_{mon,0}}{mol_{cat,0}} \right) \left\{ 1 - e^{-k_p \{ [cat_0] e^{-k_d t} \} t} \right\} \quad \text{Equation A.13}$$

This equation now relates k_p and k_d to experimentally determined quantities.

A.3 Determination of Rate Constants in Equation A.13

Rearranging Equation A.10 gives

$$1 - \left(\frac{(mw_{p,t})(mol_{cat,0})}{m_{mon,0}} \right) = e^{-k_p [cat] t}$$

$$\ln \left(1 - \left(\frac{(mw_{p,t})(mol_{cat,0})}{m_{mon,0}} \right) \right) = -k_p [cat] t$$

$$k_p = - \left[\frac{\ln \left(1 - \left(\frac{(mw_{p,t})(mol_{cat,0})}{m_{mon,0}} \right) \right)}{[cat] \bullet t} \right] \quad \text{Equation A.14}$$

Where the value for $[cat]$ is the initial catalyst concentration.

Substitution of experimental data into Equation A.14 gives an *apparent* k_p value, which encompasses the *real* k_p as well as k_d . Thus,

$$k_{p,apparent} [cat_0] = k_{p,real} [cat_0] e^{-k_d t} \quad \text{Equation A.15}$$

Rearrangement of Equation A.15 gives

$$\frac{k_{p,apparent}}{k_{p,real}} = e^{-k_d t}$$

$$\ln\left(\frac{k_{p,apparent}}{k_{p,real}}\right) = -k_d t \quad \text{Equation A.16}$$

Equation A.16 is an expression relating the k_p ($k_{p,real}$) and k_d to an *apparent* k_p ($k_{p,apparent}$), which is the instantaneous rate constant at a particular time t .

Rearranging Equation A.16 leads to

$$\begin{aligned} \ln(k_{p,apparent}) - \ln(k_{p,real}) &= -k_d t \\ \ln(k_{p,apparent}) &= -k_d t + \ln(k_{p,real}) \end{aligned} \quad \text{Equation A.17}$$

Equation A.17 is in the form $y = mx + b$, and values for $k_{p,real}$ and k_d can be determined from experimental data via a simple plot of $\ln(k_{p,apparent})$ vs. t .

Appendix B Interpretation of ^1H NMR Integration

In **Chapter 3**, ^1H NMR spectroscopy was used as a tool to estimate the content of pendant olefins in the polymer. This appendix describes the process of using the integration of the resonances in the spectrum for this purpose.

This procedure is most clearly illustrated by considering a simple example. The ^1H NMR spectrum of random poly(1-hexene)-*co*-(1,5-hexadiene) contains five very broad resonances in the 0.5 – 2.5 ppm range, arising from all of the protons attached to saturated (sp^3) carbon atoms. There are also two smaller resonances at 5.1 and 5.9 ppm, which correspond to protons attached to olefinic (sp^2) carbon atoms.

Supposing that all monomers, regardless of whether it is a 1-hexene or a 1,5-hexadiene insert once, every 1,5-hexadiene insertion would remain as a pendant olefin. ^{13}C NMR analysis shows that the proportion of 1,5-hexadiene incorporation in the polymer is equal to the proportion of 1,5-hexadiene in the feedstock. For a copolymer with 20% 1,5-hexadiene, one out of every five insertions would be expected to have a pendant olefin. Table A.1 shows the expected number of each type of proton in this hypothetical polymer.

Table A.1. Expected Number of Protons in a poly(1-hexene)-*co*-(1,5-hexadiene) Polymer with 20% 1,5-Hexadiene.

Proton Type	1-hexene			1,5-hexadiene			Total Protons
	Protons per Unit	Units	Total Protons	Protons per Unit	Units	Total Protons	
CH ₃	3	4	12	0	1	0	12
CH ₂	8	4	32	6	1	6	38
CH	1	4	4	1	1	1	5
olefinic	0	4	0	3	1	3	3

The expected ratio of olefinic to aliphatic protons in this sample is

$$\text{ratio} = \frac{\sum \text{olefinic protons}}{\sum \text{aliphatic protons}} = \frac{(3)}{(12 + 38 + 5)} = 0.052$$

A pendant olefin which is inserted either as a cycle or as a crosslink will no longer have three olefinic protons, and will have 10 aliphatic protons (compared to 11 for a 1-hexene). However, for the purposes of this argument, it will be taken as being equivalent to a 1-hexene unit.

The ratio of olefinic to aliphatic protons for the example copolymer with 20% 1,5-hexadiene (as determined by ¹H NMR spectroscopy) is 0.010. Dividing the actual ratio by the expected ratio gives the proportion of 1,5-hexadiene units which remain pendant

$$\text{pendant olefins} = \frac{\text{actual ratio}}{\text{expected ratio}} = \frac{0.010}{0.052} = 0.19$$

Therefore, in this example, it is estimated that 19% of the inserted 1,5-hexadiene units remain pendant.

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