The use of adamantane-containing compounds in polymer chemistry.

By

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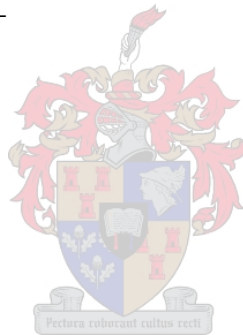
Dr AJ Van Reenen

Study Leader

December 2005

DECLARATION

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

Signature:_____

Date:_____

Abstract

The primary focus of the research was the use of adamantane-containing molecules in polymer science.

The research is divided into 2 parts, the first involving the syntheses of a new ligand for use in a metallocene catalyst system. The second part involved the synthesis of new monomers for the use in free radical polymerization systems,

In the first part of the research, the synthesis of the ligand, 2-dimethyladamantylethylcyclopentadiene was attempted. This was done via the starting materials adamantylethylbromide and dimethylfulvene. In the first step the adamantylethylbromide was prepared via the tosylation reaction of admantaneethanol. Further, the use of either a Grignard or Barbier reaction to insert the 6,6 dimethylfulvene to yield the final product was attempted. The isolation of the final product could not successfully be completed, even though spectroscopic evidence suggested that the synthesis had been partially succssful.

In the second part of the reasearch, the monomers 4-(1-adamantyl)phenolmethacrylate, adamantylmethylacrylate and admantylethylacrylate were synthesized. These monomers were homo-and copolymerized using a controlled radical reaction mechanism (RAFT).

Opsomming

Die primere fokus van die navorsing het die gebruik van adamantaan-bevattende verbindings in polimeerchemie behels.

Die navorsing is in2 hoofareas verdeel, die eerste het die sintese van 'n nuwe ligand vir gebruik in 'n matalloseen katalissisteem behels, en de tweede die sintese van nuwe monomere vir gebruik in radikaal polimerisasiereaksies.

In die eerste gedeelte van die navorsing is die sintese van die ligand 2-dimetieladamntieletielsiklopentadieen aangepak. Dit is gedoen via die uitgangsmateriale adamtieletielbromied en dimetielfulveen. As eerste stap is die adamantieletielbromied berei via die tosileringsreaksie van adamantaanatanol. Voorts is of 'n Grignard-tipe of Barbier-tipe reaksie gebruik om die 6,6 dimetielfulveen in te voeg om sodoende die finale produk te verkry. Alhoewel die finale produk wel berei is, was die isolasie en suiwering daarvan onmoontlik.

In die tweede gedeelte van die navorsing is die monomere 4-(1-adamantiel)metakrilaat, adamantielakrilaat en adamantieletielakrilaat suksesvol gesintetiseer. Hierdie monomere is gehomopolimeriseer sowel as gekopolimeriseer deru gebruik te maak van 'n beheerde radikaalpolimeriasie (RAFT).
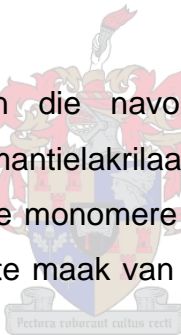
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This thesis is dedicated to my late mother

Mayindza Moundzeo Honorine (✝)

1957 /01/ 01   -   2003 /04/ 03

History is not to be erased, but to be preserved, only when we learn from our history are we able to avoid repeating mistakes. H P Yoba N'goma

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CHAPTER 1

Introduction and research objectives.

1.1   Introduction

Adamantane as a compound represents the smallest unit of the diamond lattice, and consists of three fused cyclohexane rings [1] in the "chair" configuration. It has long been considered a strain-free molecule because the structural features are thought to be "ideal". This molecule has numerous representations, as depicted in Figure 1.1

a = Adamantane   b and c = Other representations
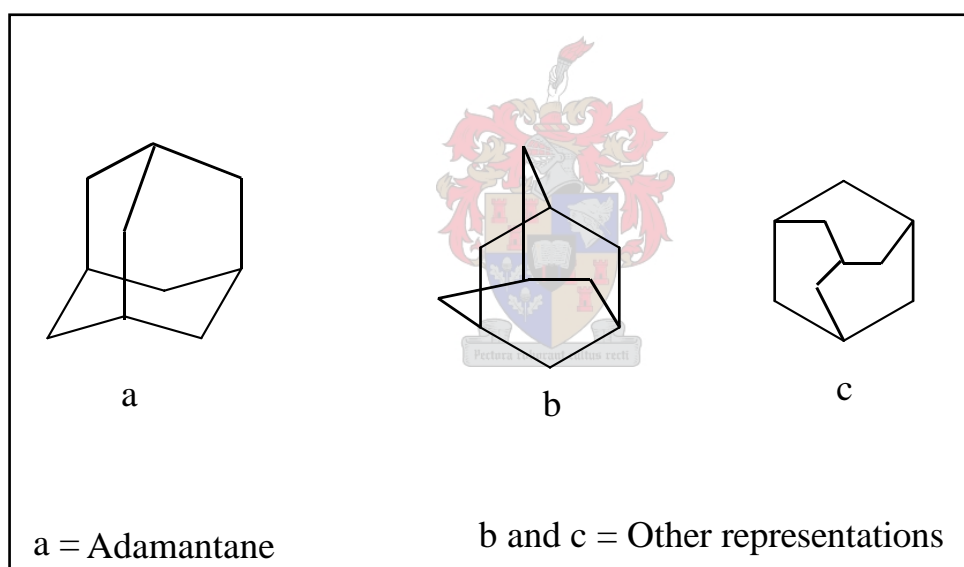
Figure 1.1: Different structures of the Adamantane Molecule

1.2   Why Adamantane?

The synthesis and characterization of adamantane derivatives continue to be an interesting area of exploration in the pursuit of structure–property relationships in chemistry. Adamantane has attracted great interest especially because of its exceptional qualities.

In this molecule, all carbon –carbon and carbon –hydrogen bond lengths are equal, while all tertiary carbons are similar. Tertiary carbons are more reactive than secondary carbons, and form carbocations more easily. The reactions involving adamantane, however, need more strict conditions compared to those that are used with non-bridgehead compounds (linear chain and simple aromatic rings). The introduction of a double bond to, and elimination reactions from adamantane is almost impossible. The substitution reactions using the tertiary carbons are always easy and usually produce considerable yields of the end product due to the absence of other side reactions.

Nowadays, chemists have found both inspiration and fascination in the adamantane molecule. The symmetrical fusion of the cyclohexyl units of adamantane not only results in a virtually strain-free molecule [2], but this configuration also affords a uniquely beautiful and conceptually pleasing structural motif. Indeed, the first convenient synthesis of adamantane by Schleyer [3] in 1957 remains a significant accomplishment. Although the adamantyl ligand (Ad*) has found some utility in organometallic compounds of phosphorus [4] silicon, germanium, and tin [5], it is surprising that it has not been more widely embraced as a viable ligand in chemistry.

Adamantane containing polymers for instance has generated a great deal of interest nowadays due to the fact that pendant adamantane groups improve physical properties such as stiffness, glass transition temperature and solubility, as well as decreasing or eliminating [6-8]. Also, adamantane has been incorporated into the backbone of many polymers, like poly(esters), poly(imides) and poly(benzyl ethers) [9-10].

1.3   Research objectives

Transition metal catalyzed olefin polymerization is one of the most fascinating areas in modern chemistry [12]. The field is still expanding rapidly and has shown to be highly attracting both in scientific breakthroughs and in proven commercial importance [13]. The development of new types of catalysts in catalytic olefin polymerization very clearly illustrates the enormous potential organometallic chemistry has for catalysis.

The initial interest of this research project was to synthesize different types of compounds containing adamantane, which have relevance to polymer chemistry.

The catalyst system developed by Coates and Waymouth [Figure 1.2] for producing elastomeric polypropylenes prompted the idea of using adamantyl substituents on a cyclopentadienyl ligand to produce unbridged metallocene catalysts with limited rotating ability [14].
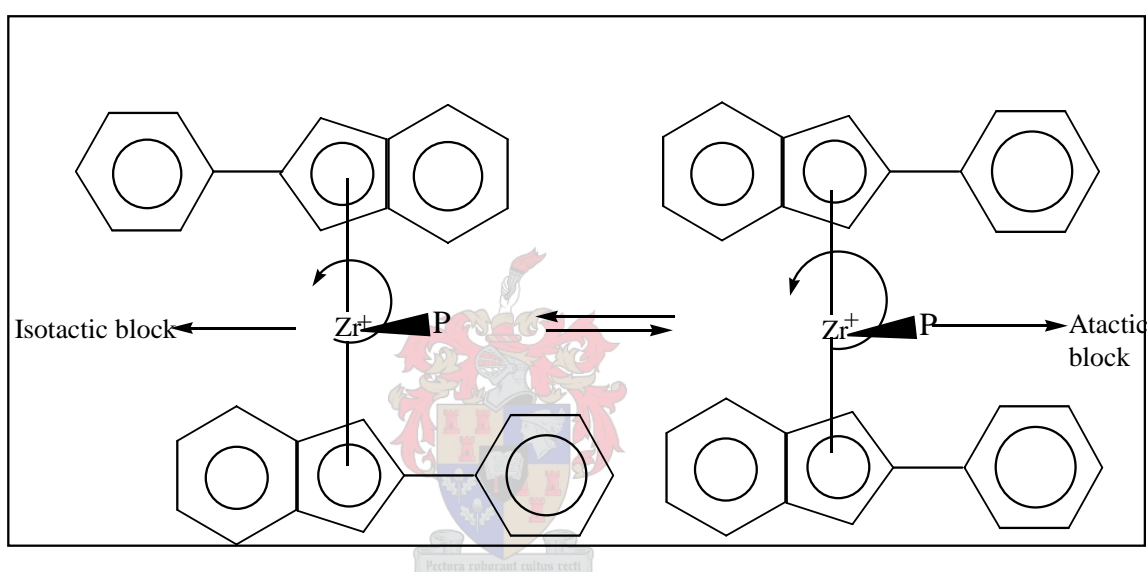
Figure 1.2. Catalyst for the production of stereoblock polymers.

A convincing argument for the behavior of the catalyst system depicted in Figure 1.2 and the exact details of the reaction mechanism are still missing and are currently the topic of intense research and debate. It was felt that some of these issues could be addressed in this study.

Thus, the aim was to synthesize a new type of a catalyst; bis(2-dimethyladamantylethylcyclopentadienyl) zirconium dichloride, (2-DAdECp)$_2$ZrCl$_2$ (Figure 1.3) by introducing an adamantyl (Ad∗) group, which is bigger than phenyl to the cyclopentadienyl (Cp∗). The catalyst could, due to the influence of adamantyl group spend considerable time in C$_2$ symmetry position during the polymerization which is not the case when Waymouth catalyst is used. The temperature of reaction should also play a role.

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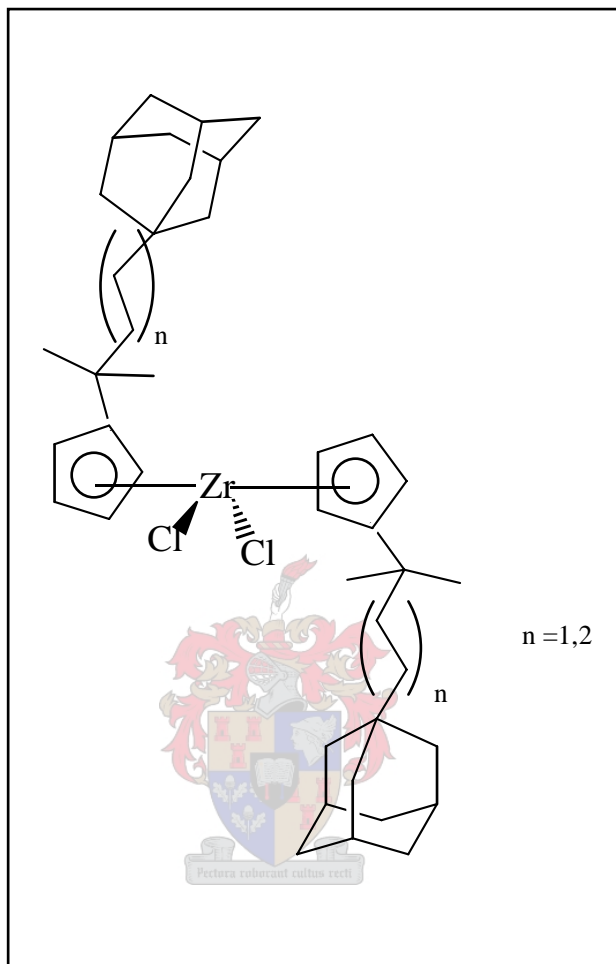
Figure1.3. Bis (2-dimethyladamantylethylcyclopentadienyl) zirconium dichloride, (2-DAdECp)$_2$ZrCl$_2$

The primary goal of the **first part** of the research was to synthesize the above catalyst ligand. Upon successful synthesis, the secondary goals would be:

1. The initial evaluation of the catalyst in terms of activity for ethylene polymerization.

2. The evaluation of polymer microstructure as function of reaction condition for selected 1-alkenes (1-butene, 1-pentene, 1-hexene, 1-octene).

In the **second part** of the research, the primary goal was to synthesize and characterize three different monomers containing adamantyl group, homo and copolymerize them with butyl acrylate using a RAFT agent.

For sake the of simplicity it should be pointed out that by using RAFT the purpose of this work was not to examine the reactions kinetics, but simply to attempt to make new compounds and study their thermal properties.

In this part we attempting to:

1.   Synthesize monomers

- 4-(1-adamantyl)phenylmethacylate (AdPhMA)
- 1-adamantylmethyl acrylate (AdMA)
- 1-adamantylethyl acrylate (AdEA)

2.   Homo and copolymerize (with butyl acrylate) monomers mentioned under point 1.

3.   Characterize the formed polymers by:

- Nuclear Magnetic Resonance (NMR) and Infrared (IR) spectroscopy to determine composition.
- Gel Permeation Chromatography (GPC) to determine the molecular weights.
- Thermogravimetric Analyses (TGA) to evaluate thermal stability

4.   Establish a comparison between free radical and controlled free radical homopolymerization (NMR).
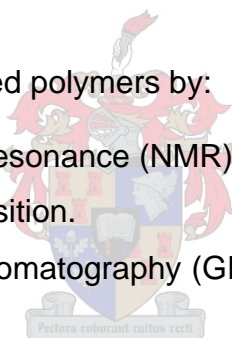
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CHAPTER 2

Historical review and theoretical background

This chapter deals specifically with the historical review and theoretical background of:

   I. Metallocene catalysts and the process of polymerization of olefins with these catalysts

   II. The synthesis and use of adamantane containing monomers and

   III. Brief sight in Living polymerization techniques

METALLOCENE CATALYSTS

2.1 Introduction

In the last few years a remarkable new class of catalysts has received lot of interest in the production of polyolefins. Transition metal catalysts have been widely used in the polyolefin industry since the early 1960's, with the heterogeneous type of catalyst being prevalent. In the 1990's a new type of homogeneous catalyst was introduced on a commercial scale. The difference with the homogeneous catalysts w.r.t the heterogeneous catalysts are generally described in terms of the "multi-sitedness" of the heterogeneous catalysts, and the single-centered nature of the metallocene catalysts. In the latter type, the single active centre can be "tuned" by altering the ligand sphere of the central metal. With the use of these "single site" or "single center" catalysts, it is now possible to obtain uniform polymers with well controlled properties.

2.1.1 Basic concepts and early history.

The discovery and elucidation of the structure of metallocene compounds is considered a landmark in the history of organometallic chemistry. Bis(cyclopentadienyl) iron or ferrocene were first synthesized independently in the early fifties by Kealy and Pauson [1] and Miller *et al* [2].The correct bond structure of ferrocene was described in 1952 by Wilkinson *et al* [3] . These discoveries greatly stimulated research in organometallic chemistry.

Wilkinson and Fischer were awarded the Nobel Prize in 1973 for their scientific contribution to organometallic chemistry [4].
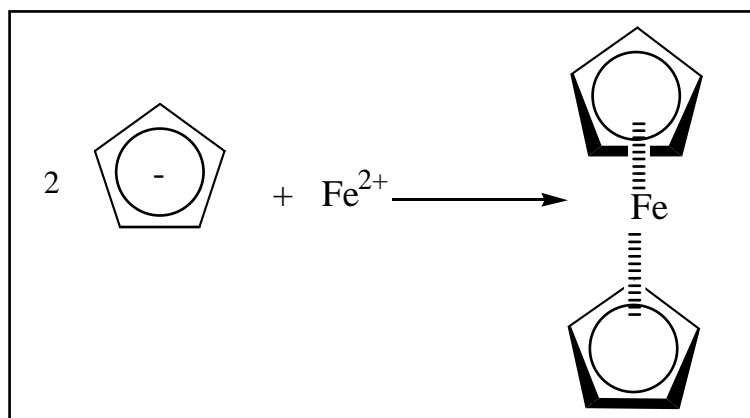
2.1.2 More recent developments.

Metallocene catalysts are organometallic coordination compounds in which one or two cyclopentadienyl rings or substituted cyclopentadienyl rings are π-bonded to a central transition metal atom. The most remarkable feature of these catalysts is that their molecular structure can be designed to create active center types to produce polymers with entirely novel properties.

Currently, there are a number of review articles published in the literature on metallocene catalysts, covering different aspects of metallocene catalyst synthesis, nature of sites, polymerization mechanisms, metallocene catalyst patents and polymerization reaction engineering [5 - 10].

In the present thesis we will highlight some of the particular features of metallocene catalysts that make them attractive.

To really understand the importance of catalysts in general and metallocene "single –site" catalysts in particular, it is necessary to briefly look at the difference between these catalysts and "multi-sited" Ziegler- Natta type catalysts.

Most polyolefin manufacturing processes today utilize conventional heterogeneous transition metal (Ziegler – Natta) catalysts. Several types of

these Ziegler- Natta catalysts are stereospecific, i.e. the insertion of prochiral monomers into the growing polymer chain in an orientation is favored over all other possible orientations, leading to the production of isotactic and syndiotactic polymers. Because these catalysts have more than one type of active site, they produce polymers with broad molecular weight distribution (MWD) and limited control of stereoregularity (generally either isotactic or atactic polymers are produced). In contrast, metallocenes can be synthesized as single-site type catalysts to produce polymers with narrow MWD (with the theoretically predicted polydispersity index of two) and controlled stereoregularity (isotacticity can be varied from 60 to 95% by changing catalyst structure).

Most exciting, while it is very difficult to control the nature of the site types on conventional heterogeneous Ziegler- Natta catalysts, metallocene catalysts can be designed to synthesize polypropylene (PP) with different chain microstructures. Atactic, isotactic, isotactic- stereoblock, atactic-stereoblock and hemiisotactic configurations can be produced with metallocene catalysts. It is also possible to synthesize PP chains that have optical activity by using only one of the enantiomeric forms of the catalyst. Additionally, copolymers of propylene, ethylene and higher α olefins made with metallocene catalysts have random comonomer incorporation and narrow chemical composition distribution (CCD). The evolution of the metallocene catalyst structures for olefin polymerization is shown in Table 2.1 [11].

Table 2.1   **Timetable of the chronological development in this area since the initial discovery of ferrocene.**

1952	Development of the structure of metallocene (ferrocene) by Fischer and Wilkinson	Ref. 14
1955	Metallocene as compenent of Ziegler- Natta catalyst, low activity with common aluminium alkyls.	Ref. 15
1973	Addition of small amount of water to increase the activity (Al:H_2O=1:0.05 up to 1:0.3) (Reichert, Meyer and Breslow)	Ref. 16, Ref. 17
1975	Unusual increase in activity by adding water at the ratio Al:H_2O=1:2 (Kaminsky, Sinn and Motweiler)	Ref. 19
1977	Using separately prepared methylalumoxane (MAO) as cocatalyst for olefin polymerization.(Kaminsky and Sinn)	Ref. 20
1982	Synthesis of *ansa* metallocene with C_2 symmetry (Brintzinger)	Ref. 21
1984	Polymerization of propylene using a *rac/meso* mixture of *ansa* titanocenes lead to partially isotactic polypropylene. (Even)	Ref. 22
1984	Chiral ansa zirconocenes produce highly istactic polypropylene (Kaminsky and Brintzinger)	Ref. 23

Metallocene catalysts result from the reaction of metallocenes and a cocatalyst, which is generally an organoaluminium compound. The exact definition of the class of soluble organometallic complexes (usually referred to

as "metallocene catalysts") are group 4 (titanium, zirconium or hafnium) metallocenes. Among the three metals, Zr is the most commonly used [14].

Breslow and Newburg were the first to identify that a solution of bis(cyclopentadienyl) titanium(IV) chloride in presence of alkylaluminums exists as a homogeneous clear solution [15] capable of polymerizing ethylene to reasonably high molecular weight products. Later studies by Natta *et al.* [16], Chien *et al.* [18,19], Patat [20], Patat and Sinn [21], Shilov *et al.* [22], Adema [23], Clauss and Bestian [24], Dyachkovski [25], Henrici-Olivé and Olivé [26], Reichert [27], Kaminsky [28], Waters and Mortimer [29], and Mejlik [30], have contributed to our significant understanding of olefin polymerization using homogeneous transition metal catalyst systems by suitably modifying the catalyst and co-catalyst components.

Additionally a number of attempts were made to improve these catalysts. Reichert and Meyer were the first to demonstrate an enhancement in the polymerization activity upon addition of water to the $Cp_2TiEtCl/AlEtCl_2$ catalysts system [27, 32]. Breslow and Long obtained considerable increase in activity and molecular weight for ethylene polymerization with the catalyst system $Cp_2TiCl/AlMe_2Cl$ by increasing the amount of water to ratios of 3/1 (H_2O/Al) and 2.5 (H_2O/Al) [33]. Sinn and Kaminsky observed a large increase in activity, up to 500,000g PE/g Ti, when a halogen-free soluble catalyst system, Cp_2TiMe_2, was added to two equivalents of trimethylaluminum (TMA) or triethylaluminum (TEAL) previously treated with one equivalent of water [34]. Mejlik and co-workers also reported that the soluble catalyst $Cp_2TiEtCl/AlEtCl_2$ revealed an increase in activity when water is added to the system [30, 35]. Sinn and Kaminsky extensively studied the reaction between AlR_3 and water to understand the high polymerization activity of metallocene catalysts in presence of H_2O/AlR_3. In the course of these studies, they observed that an oligomeric aluminoxane was formed by the reaction of TMA and water [36] (Equation 1),

$$n\ Al(CH_3)_3 + n\ H_2O \rightarrow (\ [Al(CH_3)\ O]_n + 2nCH_4 \qquad (1)$$

which was responsible for high polymerization activities. The subsequent synthesis of methylalumoxane (MAO) in 1977 by Sinn and Kaminsky has

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provided organometallic and polymer chemists with a potent cocatalyst able to activate group 4 metallocenes to the polymerization of olefins [37].

In the early 1980s Brintzinger *et al* synthesized racemic ethylene- bridged bis(indenyl)zirconium dichloride , $Et(Ind)_2ZrCl_2$, and racemic ethylene-bridged bis(4,5,6,7-tetra-hydroindenyl) zirconium dichloride, $Et(H_4Ind)_2ZrCl_2$ [38] as well as their titanium analogues $Et(Ind)_2TiCl_2$ and $Et(H_4Ind)_2TiCl_2$ [39] which have both meso and racemic configurations. The *ansa* metallocenes, $Et(Ind)_2ZrCl_2$ and $Et(H_4Ind)_2ZrCl_2$ which were activated by methylalumoxane (or methylaluminoxane, MAO) allowed stereospecific polymerization of propylene for the first time. Ewen synthesized a C_S symmetric zirconocene ($[Me_2C(Flu)(C_P)]ZrCl_2$) in 1988, which allowed for the production of syndiotactic polypropylene in high quantities [40]. Since 1985 a rapid worldwide industrial and academic development began in the field of metallocene catalysts which is still continuing.

2.1.3 Elastomeric polypropylenes and catalysts for these polymers.

The first elastomeric polypropylene (ePP) was generated by a C_1-symmetric bridge titanocene and was described Gauthier *et al.* [41a]. In 1995 Waymouth and Coates [41b] described a class of metallocenes, where the block structure of polypropylene can be controlled by the ligands of the metallocene. The (2-phenylindenyl)zirconium dichloride complex oscillates between a chiral and an achiral form. The chiral form produces isotactic polypropylene and the achiral isomer forms atactic polymer. Since these isomers can be transformed into each other the resulting polypropylene is an atactic – isotactic – stereoblock polymer with elastomeric properties [42 - 44]. The ratio of atactic and isotactic blocks is determined by the interconversion of the different forms into each other and therefore depends on the temperature. Polymers of this type can however only be accessible via metallocene catalysts (Figure 2.2)**.**
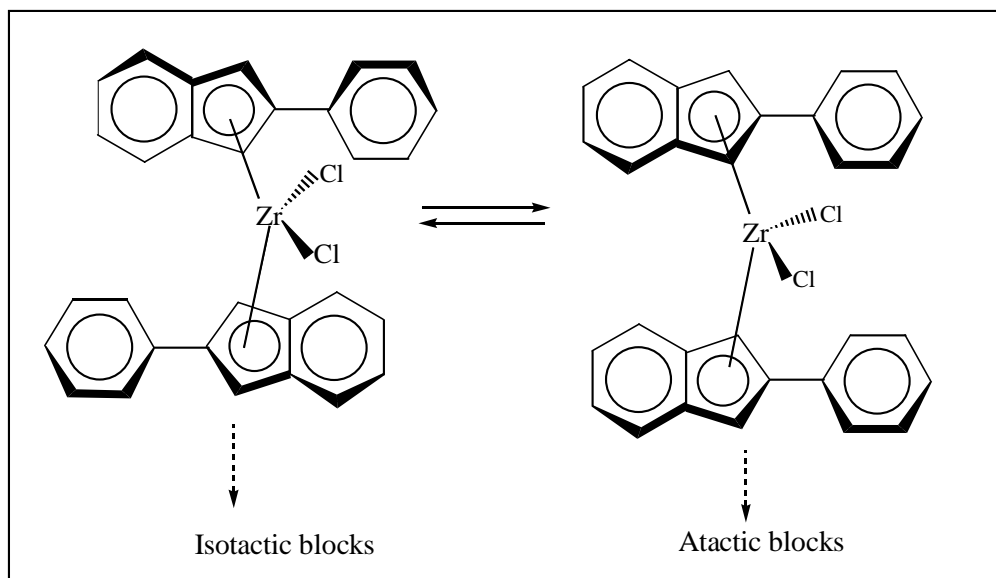
Figure 2.2   **Catalysts which yield a highly stretchable atactic-isotactic stereoblock polypropylene with elastomeric properties.**

2.2 Theoretical background

2.2.1 Activation of metallocene catalysts

Group 4 metallocene catalyst complexes need to be activated before being used in olefin polymerization [51]. The activator should be capable to alkylate the metallocene. One of the prerequisites accepted for the activator is that it should be able to take one of the methyl groups and act as an only weakly coordinating counterion, so that it does not hinder the olefin coordination to the cationic metal centre. Further, the activator should be capable of reactivating deactivated species (Scheme 2.1). MAO fulfils all the preceding requirements and is the most commonly used activator for metallocene catalysts. In addition, MAO acts as a scavenger of catalyst poisons by reacting with impurities such as water and oxygen that may be present in the catalytic system. Though intensively investigated, the structure of MAO is only partly resolved. It is generally assumed that MAO consists of oligomeric – Al(CH$_3$)-O- structural units and complexed trimethylaluminium residues forming cage structures that are in dynamic equilibrium with each other [52 - 56]. MAO is needed in large excess; [Al]/[M] ratio of 200-5 000 are often used

for metallocene activation. The reason for required excess is still not fully clarified and is currently the topic of intense research and debate.

It is well documented that group 4 metallocene cations are responsible for the catalyst activity in olefin polymerization.

The presence of cationic metallocene species has also been verified by the use of weakly co-ordinating anions such as $(C_6H_5)_4B^-$ and $(C_6F_5)_4B^-$, as counterions for alkylated metallocene cations [60].

Deactivation of zirconocene catalyst in a pure zirconocene/MAO system occurs via methane abstraction through formation of a $Zr-CH_2-Al$ bimetallic species. Fortunately, the deactivated bimetallic species can be reactivated by MAO through ligand exchange. Likewise catalyst deactivation can also occur if a Lewis basic compound such as water or oxygen is present.

2.2.2   The role of the cocatalyst: MAO

The cocatalysts are the key to the activity of the metallocenes. Methylaluminoxane (MAO) is mostly used during the polymerization as the cocatalyst. Some crucial functions for MAO have been postulated.

The first important function of the MAO is the alkylation of the halogenated metallocene complex and abstraction of a methyl group that leads to the formation of the active complex [61 - 64] (Figure 2.3).
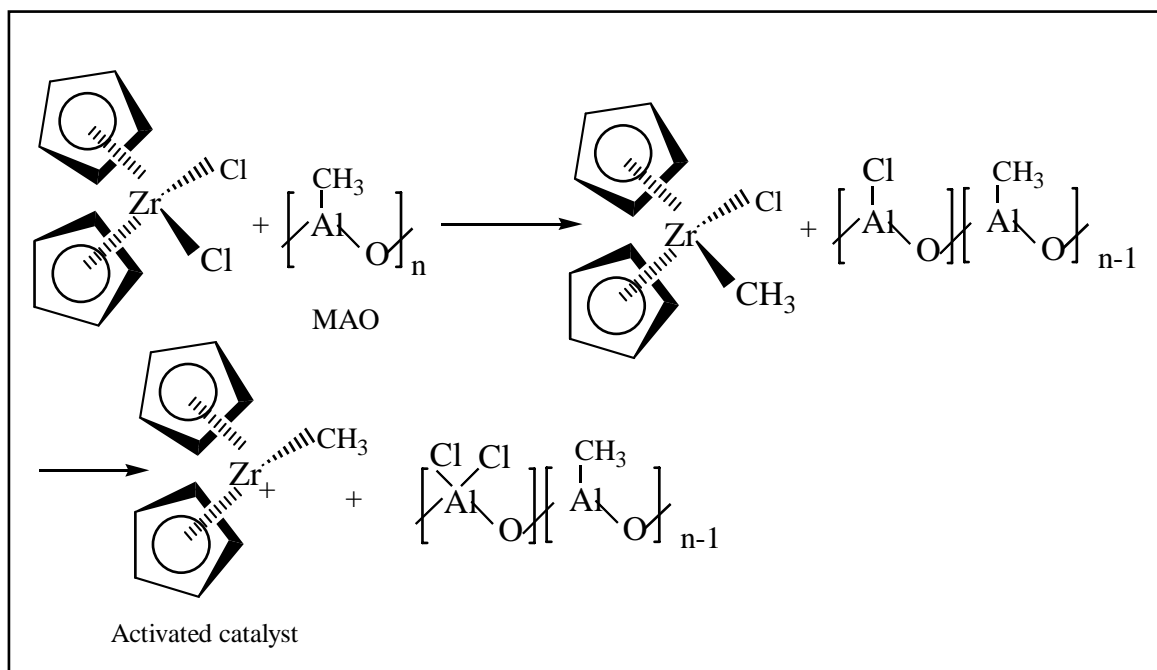
Figure 2.3. **MAO activation of metallocene catalyst precursors for polymerization [66].**

Second, MAO scavenges polar compounds in the vicinity of the catalyst. Transition metals would easily react with these compounds, resulting in the deactivation of the catalytic system [65].

Third, MAO as cocatalyst reactivates inactive species formed by hydrogen transfer reactions. This could also explain the high catalyst-cocatalyst mole ratio required (eg 1: 1000) for metallocene polymerization with MAO as cocatalyst [65].

While the structure of MAO is complex, it is generally accepted that it is a oligomeric compound with a molecular weight between 1 000 and 1 500g/mol, obtained by the controlled hydrolysis of trimethylaluminum (AlMe$_3$) [65].

The exact structure of MAO is not yet known. Some plausible structures have been listed. Initially it was thought to be a mixture of linear **(a)** and cyclic **(b)** structures as shown in Figure 2.4**.**
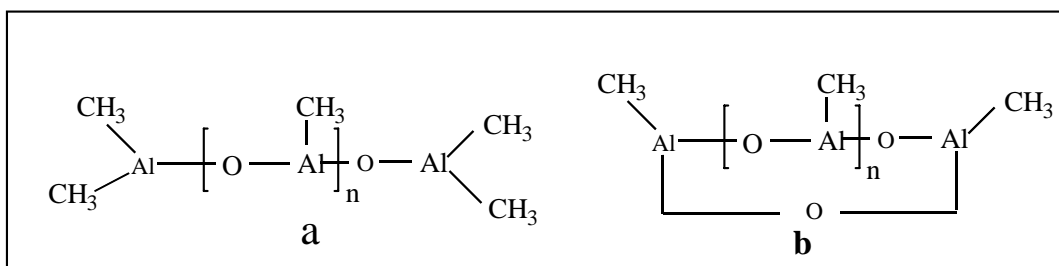
Figure 2.4 Plausible structure for methylaluminoxane as proposed by Kaminsky *et al:* (a) linear and (b) cyclic [67].

Presently the most accepted structure of MAO looks like clusters and cages (c) and (d) with trimethylaluminium dispersed within the complex (Figure 2.5).
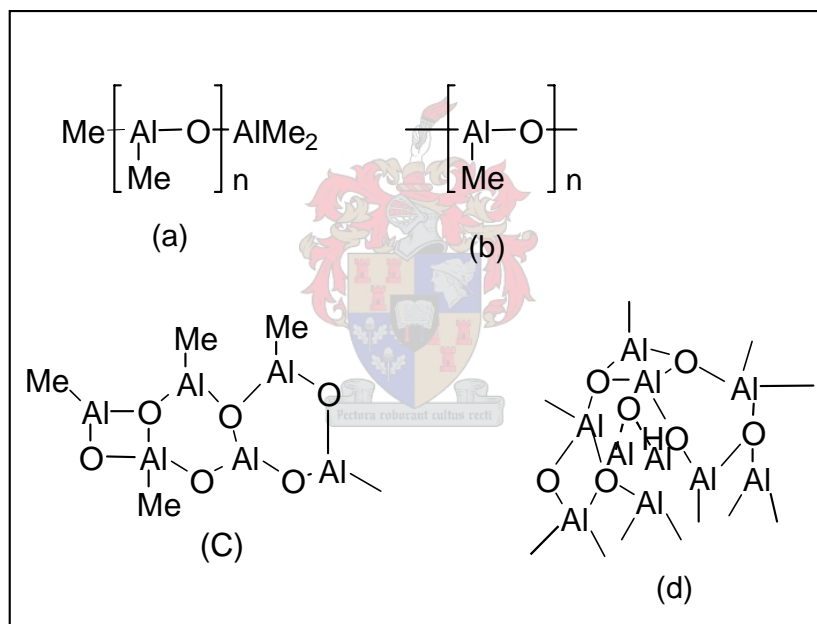
Figure 2.5 Suggested structure for MAO

2.2.3 Mechanisms of olefin polymerization and active species

It is well established now that the two key steps in metallocene catalyzed polymerization mechanism are the complexation between the monomer and the active centre, followed by insertion into the growing polymer chain. Polymer growth takes place via insertion of monomer into the transition metal-carbon bond. So far two main mechanistic schemes have been proposed for olefin polymerization .The direct insertion mechanism, proposed by Cossee

and Arlman, and the metathesis mechanism proposed by Green and Rooney [76].
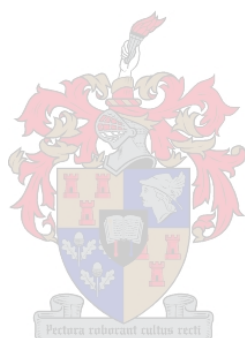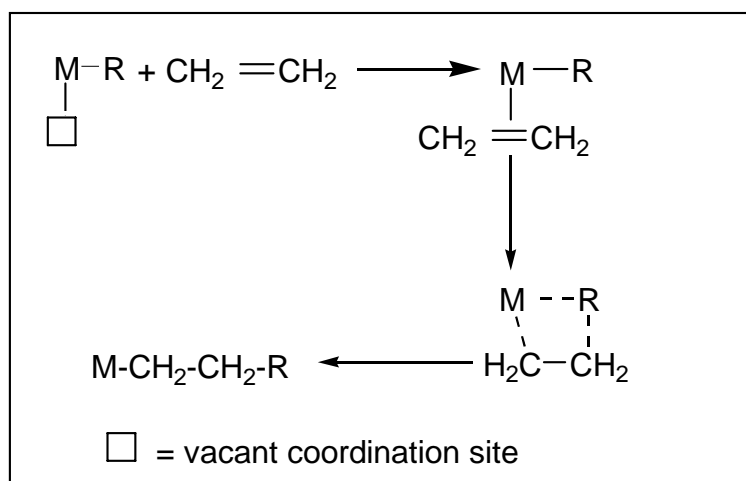
Figure 2.6   **Direct – insertion mechanism proposed by Cossee - Arlman**
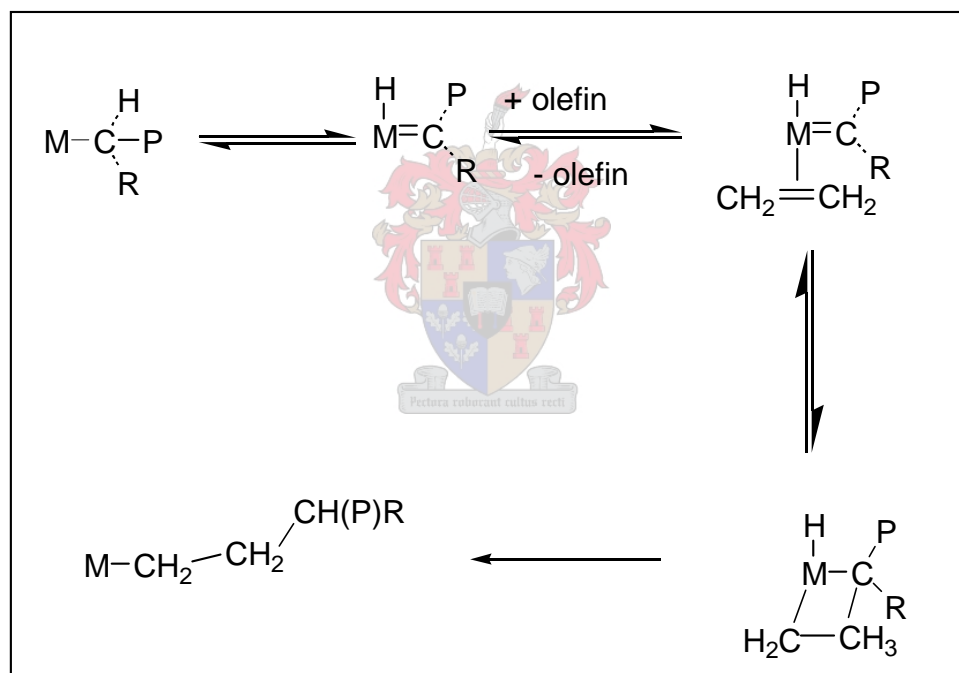
Figure 2.7   **Metathesis mechanism proposed by Green and Rooney**

2.2.4   Control of stereo- and regioselectively during polymerization of α-olefins

2.2.4.1   Stereoselectivity
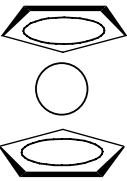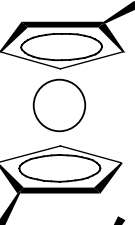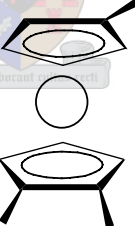
With zirconocenes it is possible to polymerize propylene and higher α-olefins. [70]. Initially the stereoselectivity of the standard Ziegler /Natta system could not be achieved, but recent advances have changed that [71, 73, 74].

These new *ansa*- metallocenes (or bridged metallocenes) consists of two indenyl ligands (Cp-ligands with a fused benzene ring) that are covalently linked by a bridge. This means the ligands can be fixed in a certain geometry providing, *inter alia,* a chiral metal centre.

Propylene polymerization, for example, with catalysts of this type yields highly isotactic polymers. These advances led to the question which mechanism controls stereochemistry of the polymer growth and what influence the different metallocenes have on tacticity and other properties of the polymers obtained with them. Ewen [76] developed a set of symmetry rules to describe the catalysts and the polymers they would produce during polymerization of α-olefins. Figure 2.8 shows how various metallocenes can lead to different polymers.
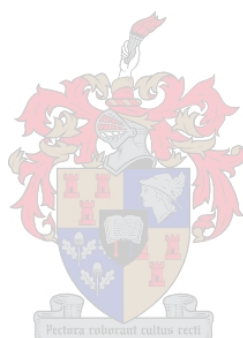
Symmetry	Structure	Type of polymer
C_2V Achiral		Atactic
C_2 Chiral		Isotactic
C_s Achiral		Atactic
C_S Prochiral		Syndiotactic
C_1 Chiral		Hemi-isotactic to isotactic

Figure 2.8   **Catalyst symmetries [76].**

There are two types of stereo-errors that may be caused by two types of control mechanisms acting on the growing chain.

The first type of stereoerror, originating from the chain end itself (chain end control), results in the switching of the side group from the one side to the other side of the chain. (Figure 2.10)

This can happen if the placement of the next monomer unit is controlled by the chirality (propylene is prochiral) of the last inserted monomer. If the last inserted monomer was erroneously placed (by some unspecified mechanism)

with its side-group on the opposite side of the chain, placement of subsequent monomer units continue with this trend.

The other, more likely possibility is that the stereoregulation is controlled by the catalyst complex, so-called enantiomorphic site control (Figure 2.10) and the mechanism is illustrated in Figure 2.9 [87]
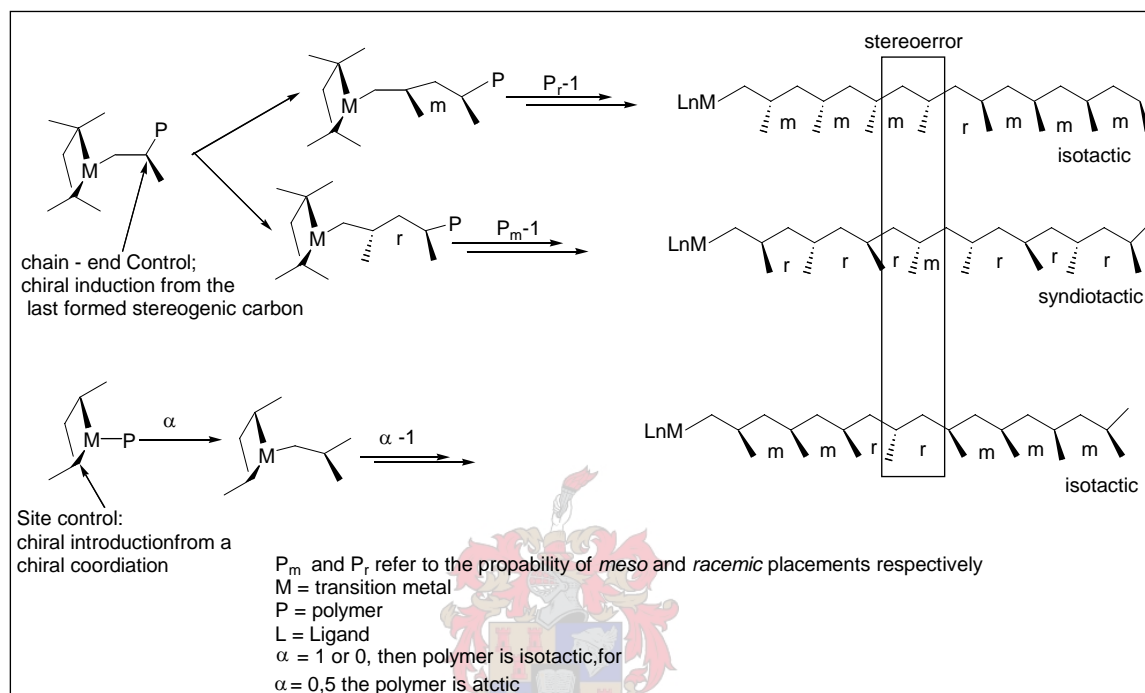
Figure 2.9   Chain – end and Enantiomorphic Site Mechanism of Stereocontrol [87]
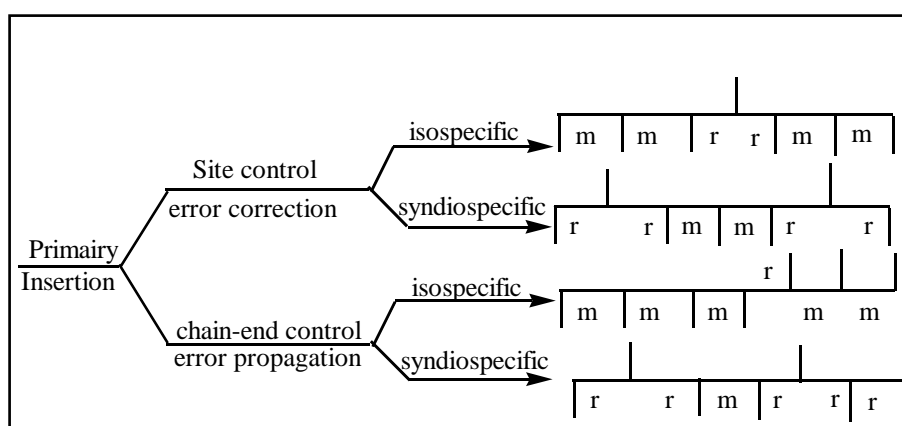
Figure 2.10   **Types of stereoerrors**

2.2.4.2   Regioselectivity

In addition to the stereoselectivity the structure of the ligands also influences the regioselectivity. A propylene molecule can be inserted into the growing polymer chain by three ways:

1. 1-2 or head to tail, insertion, the "normal" insertion mechanism

2. 2-1 or head to head insertion mechanism and

3. 1-3 or tail to tail insertion.

This is illustrated in Figure 2.11.
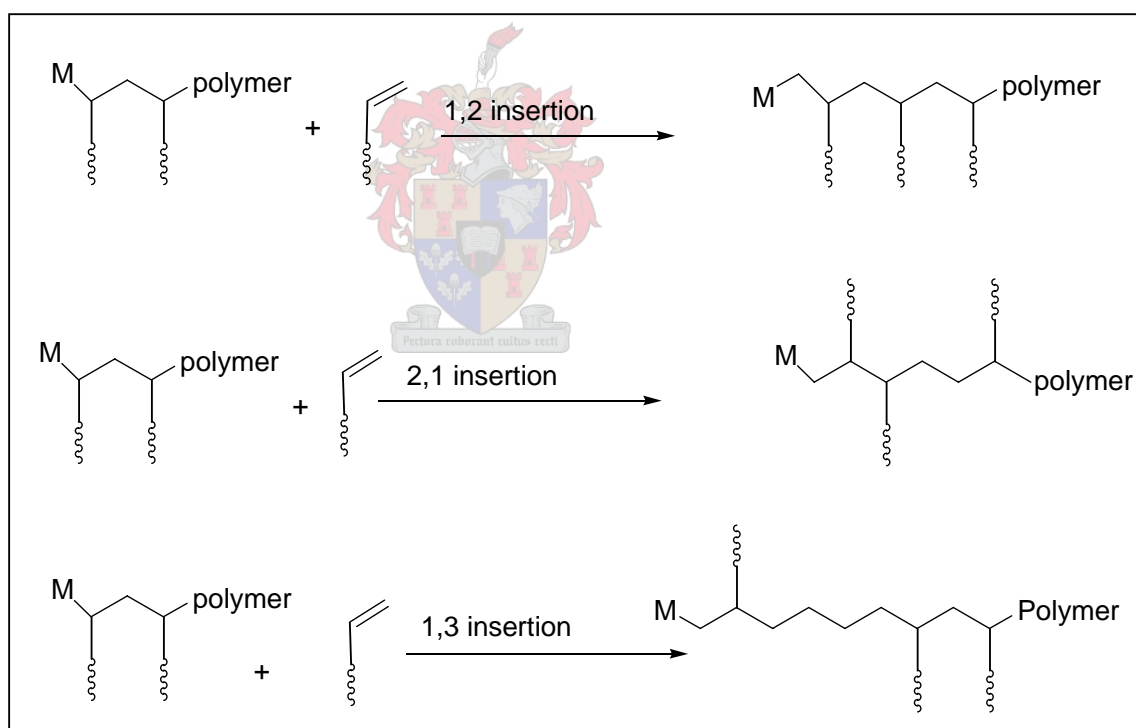
Figure 2.11   **Control of regioselectivity**

2.3. Advantages and disadvantages of using metallocene catalysts

Metallocene catalysts have several advantages [84] but the most important are:

- high catalyst activity,

- low catalyst requirements,

- ability to polymerize a wide variety of monomers by suitably tuning the ligands around the transition metal,

- narrow molecular weight distribution approaching the theoretical value of 2.0 as predicted by the Schultz- Flory mechanism,

- ability to polymerize α-olefins with almost any desired stereospecificity.

Despite their advantages, they present some disadvantages [84] which are:

- decay-type kinetics with ethylene/higher α-olefin mixtures,

- high Al/Zr ratios for obtaining high catalyst activity and relatively stable kinetic profile,

- high cost of MAO,

- inability to adopt the catalyst to processes operating in slurry or gas phase,

- poor control over polymer morphology.

2.4 Conclusion: Metallocenes

The discovery of metallocene catalysts has led to the dramatic changes in the polyolefin industry. A class of polymers is available with properties never thought possible before in the polyolefin business. The unique possibility to tailor the catalyst according to need makes metallocene catalyst a versatile and very valuable tool in the hands of chemists and product developers. Moreover, the impact of metallocene catalyst extends beyond simple olefin polymerization. It has opened the doors to new classes of polyolefin

inaccessible by classical Ziegler-Natta polymerization. It promotes the interest to explore further possible applications of metallocenes in general and it is encouraging the search for other single-site catalysts in place of heterogeneous catalysts.

Metallocene catalysts for the polymerization of ethylene, propylene and other α-olefins are the focus of intense current interest. The tacticity of polypropylene varies predictably with the structure of the metallocene catalyst: C_{2V} symmetric metallocenes generally afford atactic polypropylene; C_2 symmetric metallocenes produce highly isotactic polypropylene; C_1 metallocenes also produce isotactic polypropylene, but generally with less stereospecificity. Whereas the types of isospecific metallocene catalysts are structurally highly variable, syndiotactic and atatic polypropylene has been produced using essentially a single type of *Cs* symmetric *ans*a-metallocene.

The polymerization behavior of Waymouth catalyst (2-PhInd)$_2$ZrCl$_2$ leading to an alternation in catalyst structure between achiral (C_2 symmetric) and chiral (*Cs* symmetric) coordination geometries. The question here is what did we learn? We have to confess that we still do not understand all details in order to be able to explain this behavior and the full mechanism details, clearly. This is one of the biggest reasons why this study was in correlation with Waymounth catalyst, to attempt to better understand why the (2-PhInd)$_2$ZrCl$_2$ complex oscillates between a chiral and achiral form when consecutive insertions take place as well as chain migratory insertion reaction.

MONOMERS: ADAMANTANE-CONTAINING POLYMERS.

2.5 Introduction: Monomers.

The use of adamantane for both academic and medical purposes has been reported so far. The incorporation of adamantane groups into polyacrylate, polyester, polycarbonate, and acetylenic polymers has resulted in increased thermal stability and glass transition temperature [88-90]. Adamantane compounds has been used in medical applications, particularly as antiviral compounds [91-93].

2.5.1. Bulky adamantane group: use and effects

Adamantyl groups have been incorporated in a wide variety of well defined polymer as part of the main chain and as side groups [81 - 83]. Incorporation of the bulkiness of adamantane as a pendant group leads to the properties modification such as the decrease of crystallinity, the increase of solubility, reduced chain mobility and significantly raised glass temperature (Tg) of the parent polymer. Different types of chain-growth polymers based on ester derivatives of ethyl α- hydroxymethylacrylate were synthesized showing adamantane effect.

A series of new monomers with adamantane as a pendant group have been synthesized and used in polymerization. The 4-(1-adamantyl) phenolacrylate is a typical example of these monomers which were synthesized by alkylation of phenol or halo (Cl, Br) benzenes with 1-bromoadamantane [82, 94].

Adamantane – based derivatives have been used in the syntheses of various styrenic and (meth) acrylic star polymers. These star polymers are noteworthy for the rigid tetrahedral disposition of their chain origin because of the geometry disposition of the adamantane core [81, 88].

Scheme 2.1 illustrates a synthetic route of star polymers from a tetrafunctional initiator. These star polymers have glass transition temperatures similar to those known for high-molecular linear polymers [84]. These initiators are totally soluble in solvents such as: chloroform, benzene and toluene.

Methods for making star polymers fall into two broads classes. In the arm approach, monofunctional living linear macromolecules are synthesized initially, while in the second strategy for synthesizing star polymers is the core-first approach. To date most star polymers have been synthesized by an ionic process.
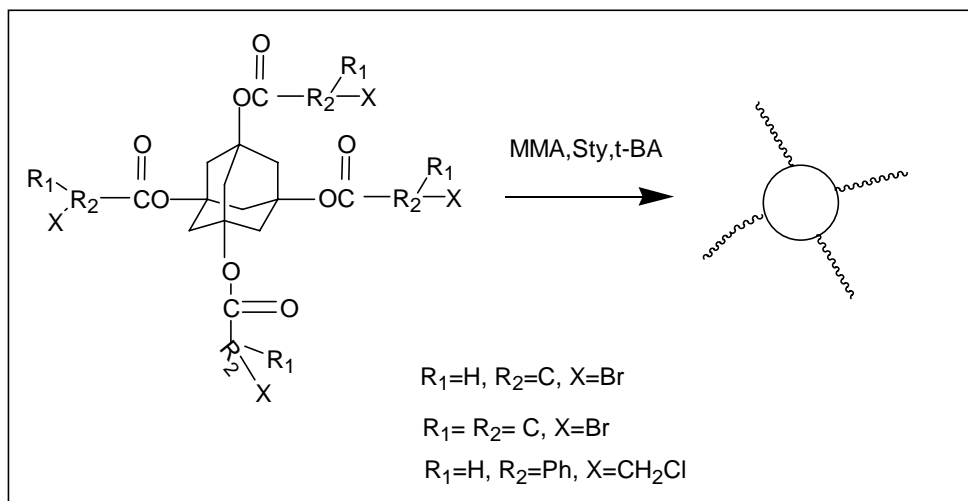
Scheme 2.1   Synthetic route of star polymer from an initiator

The earliest synthetic procedure for the preparation polyadamantane was made by utilizing 3, 3 dibromo-1,1-biadamantane via the Wurtz type reaction. When an alkyl halide is treated with sodium, the main product is the paraffin hydrocarbon. The reaction is called Wurtz reaction as depicted below:

$$2R.X + 2Na \quad ====> \quad R.R + 2NaX$$

Polyadamantane was also synthesized by the polycondensation of polybromoadamantane under the influence of sodium metal.
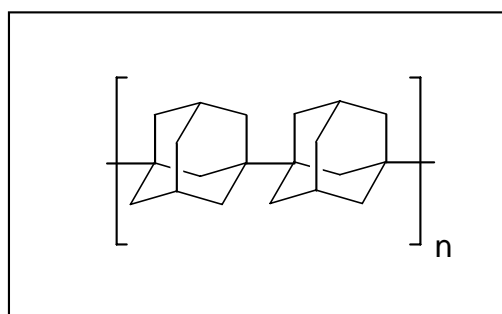
Scheme 2.2   Polyadamantane structure

Incorporation of benzene to adamantane led to a copolymer which is well known as another type of polyadamantane.
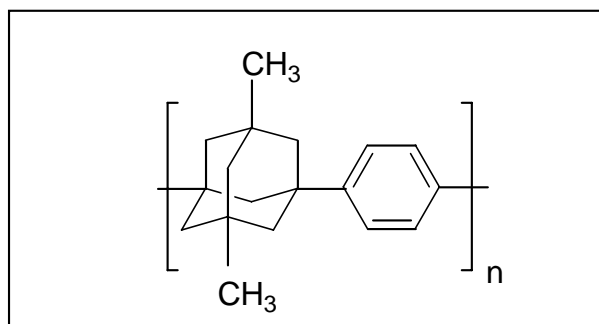
Scheme 2.3.   Aadamantyl-benzene copolymer

Although adamantane has been investigated for many years, only a few examples related to its biological activity of some of its functional derivatives are known. But it is interesting to note that some of the copolymers have been documented, most of which have no particular functional group with established biological activity. Copolymers having potential antiviral activity are depicted below.
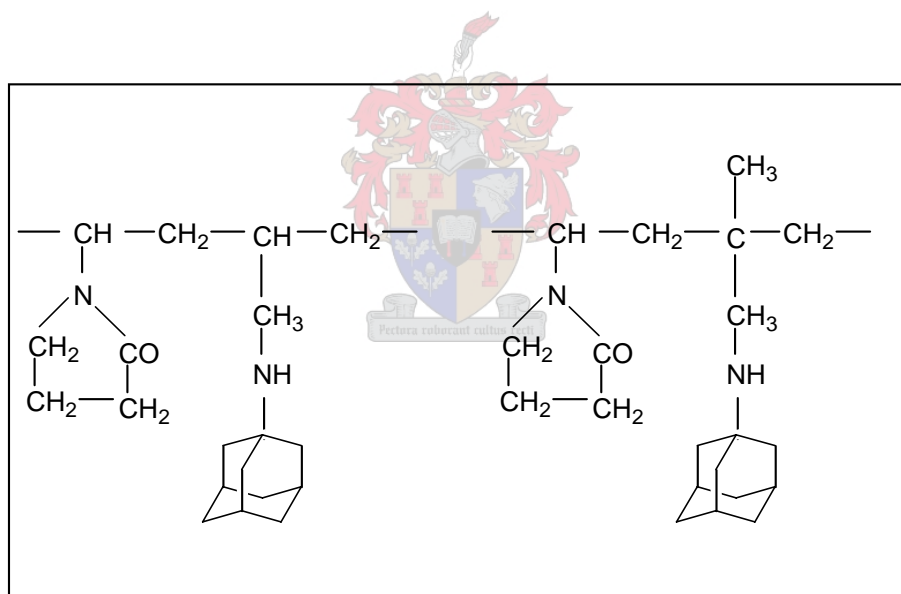
Figure 2.12   Copolymers with antiviral activity.

It must be pointed out that various new derivatives of adamantane such as halides, alcohols, ketones, carboxylic acids, esters, amides, nitriles have been found to be active as antiviral agents [85].

Adamantyl acrylates and methacrylates polymerize under the influence either of free-radical and anionic catalysts. The result of a kinetic study of free-radical polymerization showed that the adamantane derivatives are very

reactive and the bulky adamantyl group does not jeopardize polymerization. The exceptional properties of such polymers are enhanced T_g s, decreased crystallinity and increased rigidity of the polymer chains.

Solutions of poly (adamantyl acrylates) are very viscous and are used as thickening agents for lubricating oils. Copolymerization with adamantyl acrylates leads to an increase in glass transition temperatures and the hardness of the copolymers.

2.6   Conclusion: Monomers.

The glass transition temperature (T_g) is known to increase with substituent size in the case of rigid, inflexible substituents. Bulky and inflexible substituents lead to steric constraints that couple appreciably with the backbone to increase the dynamics constraints imposed on local segmental motion. It also known that positioning the center of mass of the substituent closer to the backbone and increasing the bulkiness of the substituent are important to increase the T_g

Adamantane for instance has been incorporated into the backbone of some polymers such as polyesters [86].The polymers show enhanced properties such as hydrolytic and thermo-oxidative stability .Moreover, when adamantane is incorporated as a pendant group on the polymer backbone, the result is property modifications including decreased crystallinity, increased solubility and enhanced T_g and thermal stability [86].

LIVING POLYMERIZATION TECHNIQUES

2.7   Stable free radical polymerization

Stable free radical polymerization (SFRP) belongs to the group of reversible free radical termination. A radical polymerization is conducted, for example, in the presence of nitroxide, which reversibly caps the propagating radical chain. This results in a controlled living system and gives polymers with low polydispersity.

The success of SFRP as a living mediating technique depends on the nature of the stabilized radicals, which range from (arylazo)oxy [102], substituted triphenyls [103] and triazolnyl [104] to nitroxides and their associated alkylated

derivatives. The latter is the most widely studied and certainly most successful class of nitroxide compounds. The compounds depicted in Scheme 2.4 have been successfully developed and used for different applications in the filed if the free radical polymerization.

SFRP is a process that does not only tolerate a number of functional groups[105] but also does not require stringent starting material purification.

| 2,2,6,6,-tetramethyl-1-piperidinyoloxy (TEMPO) | di-tert-butylnitroxide (DNB) | n-tert-butyl-N-(1-diethylphosphono-2,2-dimetylpropyl) nitroxide(DEPN) |
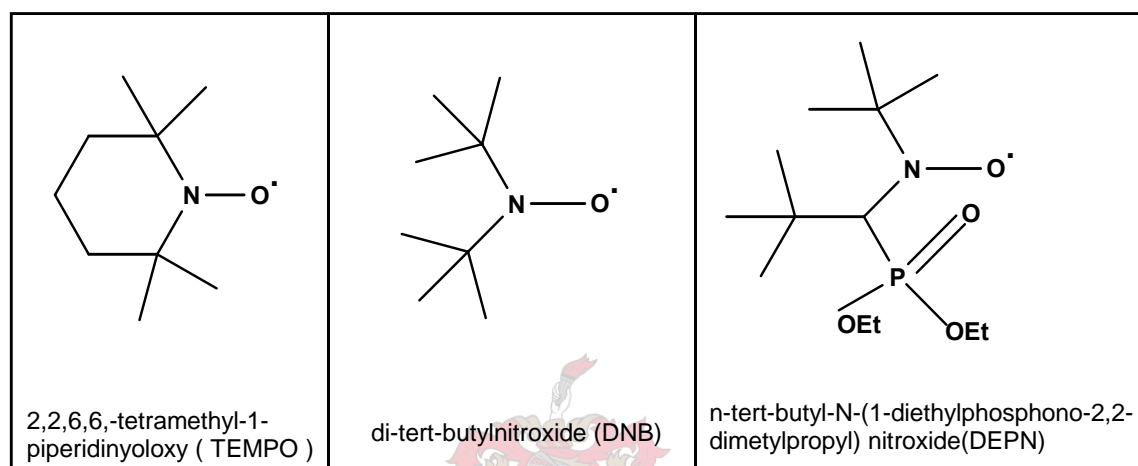
Scheme 2.4   Examples of nitroxide mediators

2.8   Atom transfer radical polymerization

Atom transfer radical polymerization (ATRP) [107] is a simple, inexpensive polymerization technique used more in research laboratories than in industry. ATRPis mediated by a variety of the metal complexes.This living technique, discovered independently by Sawamoto [108] and Matyjaszewski [107] in the 1990s, provides an opportunity to emphasize the concept of living radical polymerization by minimizing unwanted side reaction often occur in polymerization techniques.

ATRPcombines certain advantages of radical polymerization, including the ability to polymerize a variety of monomers [107,109] for the preparation of efficient block copolymers and the synthesis of polymers with low polydispersities. As, SFRP, ATRP does not require stringent reaction conditions [110].The preparation of polymeric materials through the use of ATRP is possible in different media, such as emulsion system [111].

2.9 RAFT: Reversible addition – fragmentation chain transfer polymerization

2.9.1 Introduction

The recent progress of controlled/"living" radical polymerization methods has offered new and robust synthetic routes to well-defined, low-polydispersity polymers through the use of ATRP or SFRP is possible. The choice of monomer remains the key problem to overcome when those mentioned methods are used in the synthesis of polymers. It has been proven that methacrylate and vinyl acetate monomers cannot be polymerized by the use of NMP and ATRP techniques respectively [95]. More recently, a specific technology that has the distinction of being applicable to a wide range of monomers has been developed. This new process is called RAFT polymerization and is mediated by the use of thiocarbonyl thio compounds.

The reversible addition-fragmentation chain transfer (RAFT) is widely used in living radical controlled polymerization due to its several advantages:

The RAFT process does not need additional experimental precaution compared to conventional radical polymerization.

For a chosen monomer, the chain transfer activity of a RAFT agent is a function of substituents Z and R.

The RAFT technique can be applied in both homogeneous and heterogeneous polymerization reactions, such as emulsion [96 - 98] and miniemulsion [99 - 103] polymerization.

The RAFT technique can be combined with other living techniques, such as ATRP, to produce polymers

Although RAFT has advantages, however, they are some disadvantages :

The synthesis and the purification of thiocarbonyl thio compounds are not too easy, they are time-consuming

Thiocarbonyl thio compounds have a strong smell and the final products are sometimes coloured and viscous.

Inhibition and retardation are often observed in RAFT polymerization

Termination is not specifically suppressed; this is generally represented by the formation of tails in the molar mass distribution.

The RAFT technique is mainly driven by the presence of a reactive double bond species S=C(Z)SR. This dormant species allows the formation of growing chains when active species are added in the reaction. Even if the RAFT Mechanism is not fully understood yet [102] Rizzardo *et al.* [112] have proposed a mechanism that is generally accepted which is showed in the Scheme 2.5 .
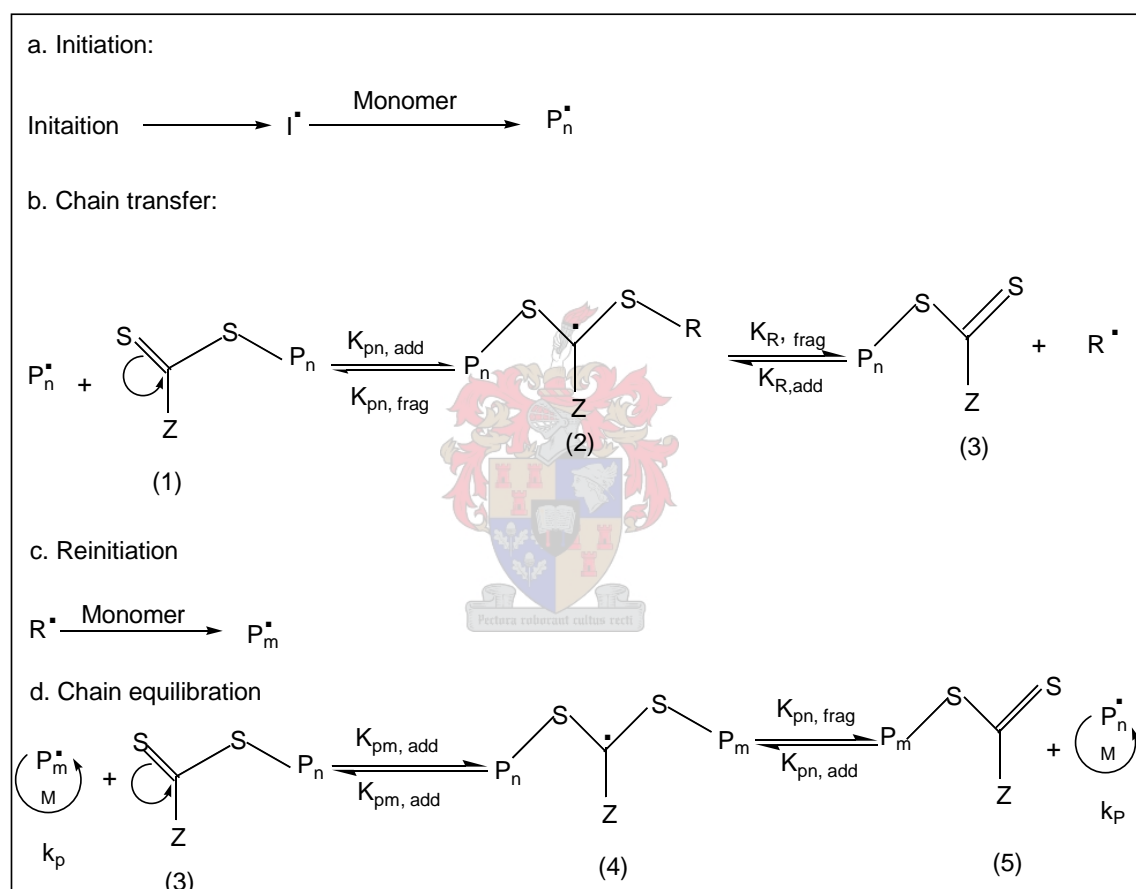
Scheme 2.5   The RAFT process, as proposed by Rizzardo.

2.10 *Conclusion: Living polymerization techniques.*

Twentieth century had seen the improvement of old preparation methods, the discovery of new techniques for the preparation of complex polymers. These polymeric techniques include SFRP, ATRP and RAFT. Moreover, each technique has the ability to yield polymers with specific functionalities.

It should be pointed out that the RAFT process is only six years old and possesses almost the same advantages as SFRP and ATRP techniques. This

can explain why this new technology is currently regarded as one of the most promising techniques.

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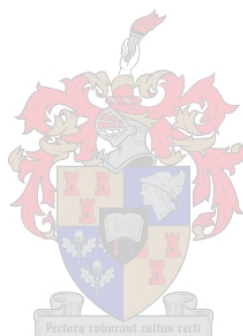
CHAPTER 3

Catalyst synthesis: The synthesis of bis(dimethyladamantyl ethylcyclopentadienyl)zirconium dichloride.

In this chapter, the attempt to synthesize the Bis- (dimethyladamantylethyl-cyclopentadienyl) Zirconium dichloride is reported. Unfortunately, due to the complexity of some reactions we could not reach our goal. Thus, we are going to discuss the different approaches as well as the difficulties involved in the synthesis of this compound.

3.1   Introduction

The discovery of Kaminsky and Sinn in 1980 lead to metallocene complexes that can be activated by methylalumoxane (MAO), and used as a principal catalyst in organometallic to polymerize α- olefins. These catalysts led to high activities, narrow molecular weight distribution polymers and good stereochemical control are some of the major achievements in recent years .It is such outstanding merits that led to a significant increase in research intensity in metallocenes themselves and their various derivatives as a new kind of catalyst, to produce polymers with the uniformity of the molecular weight distribution.

In recent years there has some considerable interest in the use of adamantane as ligand in the development of novel homogeneous catalyst systems.   Recently a variety of metallocene complexes which contain admantane or 6, 6-dimethylfulvene have been reported [1-8].

It was thought that the introduction of an adamantyl group into a ligand used for the synthesis of an unbridged metallocene catalyst would allow us to gain some insight into the effect of such a bulky substituent on the preferred symmetry of the formed catalyst. The so-called Waymouth catalyst [bis (2-phenylindene)zirconium dichloride] produces elastomeric polypropylene, and

thus is explained a terms of the hindered rotation of the ligands around the central metal atom due to the presence of the bulky phenyl group. In the case of an adamantyl substituted ligand, ligand rotation should be hindered even more.

Scheme 3.1 represents the new type of metallocene catalyst envisaged in this study.
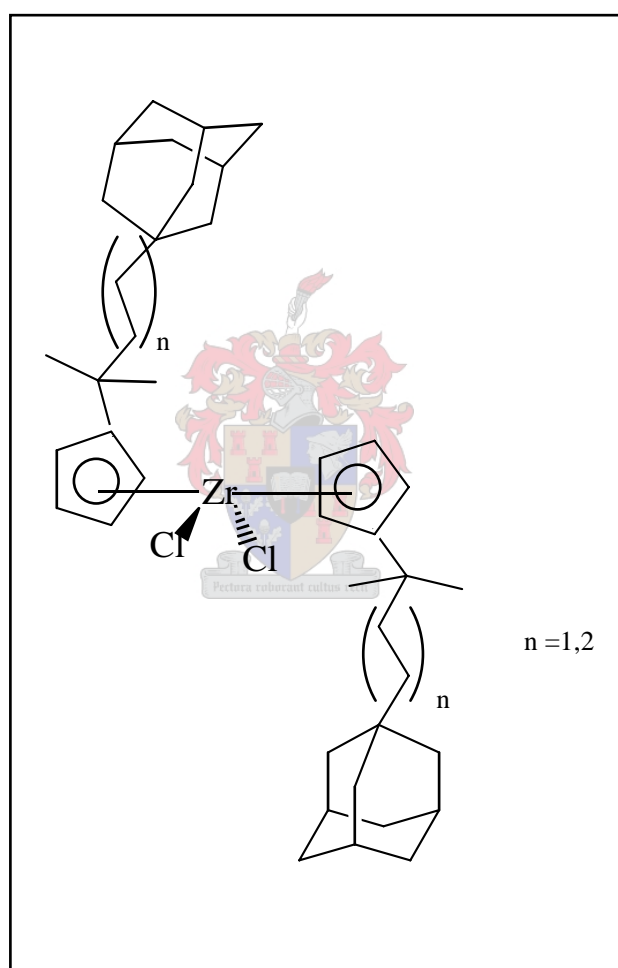
Scheme 3.1.   Metallocene catalyst envisaged

To the best of our knowledge this type of metallocene complex has not been reported as a polymerization catalyst. This is one of the most exciting reasons why we wanted to synthesize and examine the characteristics of these types of catalysts. It should be interesting to see how the metallocene in Scheme

3.1 should operate during polymerization at low and high temperature as well as to compare the results to those of Bis (2-phenylindenyl) zirconium dichloride, (2-PhInd)$_2$ ZrCl$_2$ as a catalyst.

In this Chapter we describe the preparation of different compounds supposed to allow us to synthesize metallocene in Scheme 3.1.

In general the synthesis of metallocene in Scheme 3.1 can be summarized in four principal steps, namely:

1. Tosylation of primary alcohol end- group via a S$_N$2 reaction.

2. Bromo substitution of tosylates via S$_N$2 reaction.

3. Insertion of 6,6 dimethylfulvene via Grignard and Barbier one-step reaction.

4. Formation of metallocene.

3.2. The synthesis of bis(dimethyladamantylethyl cyclopentadienyl)zirconium dichloride

3.2.1. Theoretical background.

The direct synthesis of Bis (dimethyladamantylethyl cyclopentadienyl) zirconium dichloride has not been reported, but some strategic stages used to synthesize the aimed product (catalyst) are well documented [2, 9].

The Scheme 3.2 is a summary of one approach with four synthetic steps that were followed to synthesize the aimed product.

3.2.2. Approach to the preparation of Bis (dimethyladamantylethyl cyclopentadienyl)zirconene dichloride.
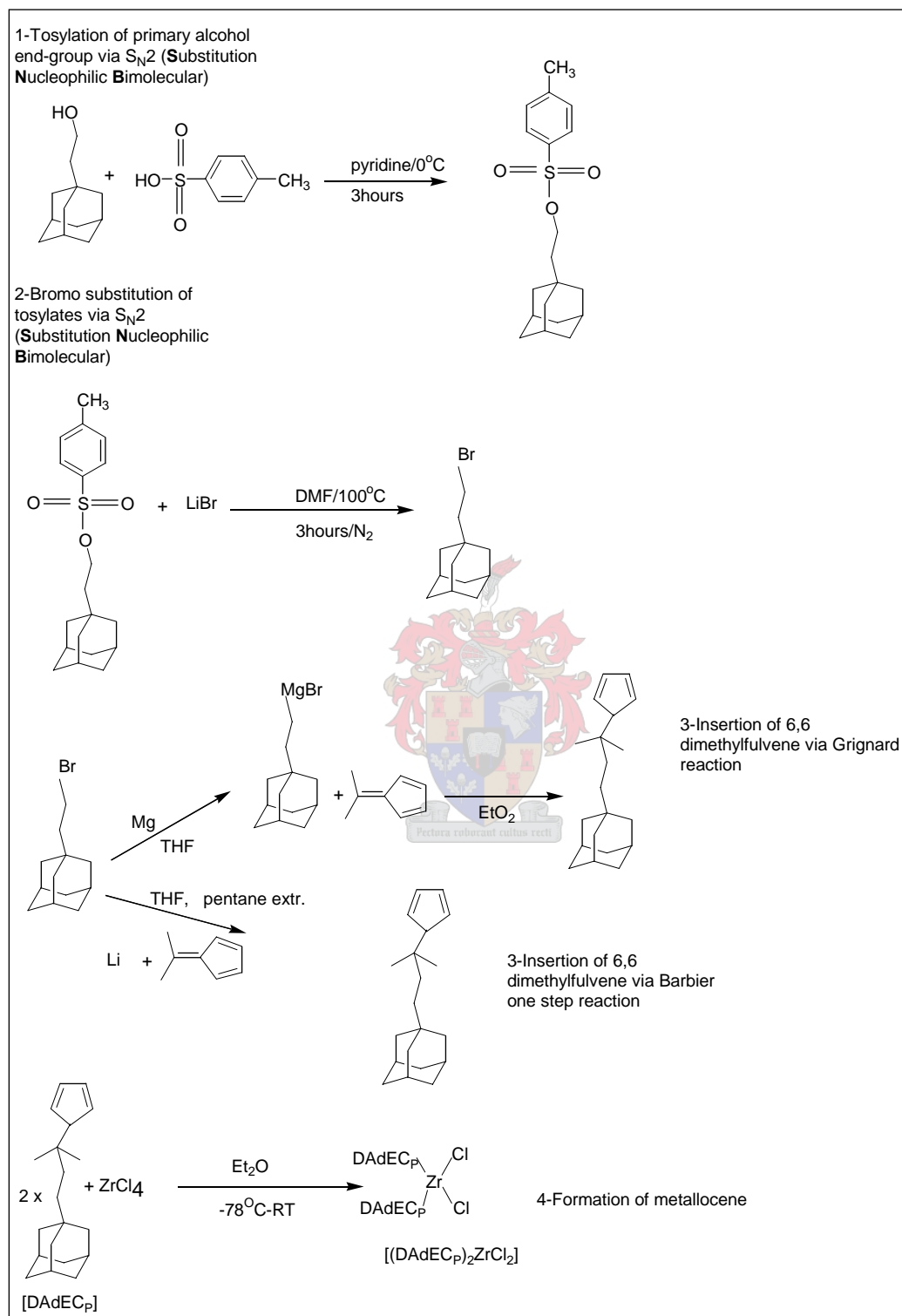
Scheme 3.2   Summary of one approach with four synthetic steps followed to synthesize (DAdEC$_P$)$_2$ZrCl$_2$

In this approach, the step 3 above (the insertion of 6,6 dimetylfulvene from Grignard and Barbier derivative) has not yet been published to the best our

knowledge, whereas the tosylation of primary alcohol end group and the bromo substitution of tosylates on the so –called S_N2 reaction are well known.

- The tosylation of the primary alcohol end-group.

In this the type of reaction, we replace H in HO^- with more electronegative groups while increasing the leaving group ability. When H is replaced with RS $(O)_2$, we obtain a very important class of leaving groups, the sulfonate esters. The common sulfonates (tosylates and mesyaltes) are easily made from alcohols and tosyl chloride (TsCl) or mesyl chloride (MsCl).

- Bromo substitution of tosylates.

Nucleophilic substitutions occurs with molecules that have an sp^3 carbon bonded to a leaving group (- halogen, - OH_2^+, -OTos). There are two fundamental events in these substitutions reactions:

- ✓ formation of the new bond to the nucleophile, and

- ✓ breaking of the bond to the leaving group.

Depending on the relative timing of these events, the reaction can occur via two distinct mechanisms:

- ▪ bond breaking to form a carbocation proceeds the formation of the new bond: SN_1 reaction, and

- ▪ simultaneous bond formation and bond breaking (SN_2 reaction).

The synthesis of dimethyl-(1-adamantanyl) cyclopentadiene was one of the difficulties encountered in this study. The latter has been impossible to obtain by direct synthesis. The two approaches used, that is the Grignard and Lithium metal reaction, for some obscure reason, failed completely, and this made us believe that this compound might not be possible to synthesize using 6,6 Dimethylfulvene. Although the carbocation chemistry of the adamantane system has been extensively studied, the chemistry of adamantyl bridgehead anions is less well-documented [24]. Moreover, the available literature of this bridgehead anion is complicated by problems related to reproducibility of experimental protocols. Ashby and co-workers report that stirring a two phrase mixture of bromoadamantane and magnesium actually decreased the yield of Grignard reagent [24]. Dubois also reported that the use of activated

magnesium preparation developed did not afford to form magnesium intermediate [24]. However, knowing that chemistry is a large field, with plenty of methods, we guess that there might be other routes in which this compound could be synthesized. But, being confined with our objective which was to use dimethylfulvene, and using this approach (Scheme 3.2) we have drawn the conclusion that the target compound was unsynthesizable.

3.3 Experimental part

3.3.1 Materials and methods

All experiment involving air –and moisture sensitive compounds were performed under a nitrogen atmosphere, working in a notrogen dry box. Glassware was dried overnight at 120^0 C before use.

3.3.2 Reagents

All the chemicals used were obtained from Aldrich

Adamantaneethanol

Adamantaneethanol was used as received

Pyridine

Pyridine was carefully dried over KOH.

Toluenesulphonyl chloride

Used as received

Diethyl Ether

Because of the moisture sensitivity of the magnesium turnings used in the Grignard reactions, the ether had to be carefully dried. Diethyl ether was dried over sodium under reflux.

Dichloromethane
Used as received.

6,6 Dimetylfulvene.

Used as received.

Toluene

Toluene was obtained from Saarchem.

Toluene (500mL) was dried over sodium pieces and boiled under reflux with a small amount of benzophenone, until the toluene had a dark blue color. Benzophenone was used as indicator to indicate when the toluene was dry. Toluene was then stored onto 4 A° Molecular sieve.

DMF

DMF was obtained from Saarchem.

Before used DMF (1L) was dried over 100 mg of ninhydria and boiled under vacuum.

3.3.3   Equipment

Apparatus for the preparation of all compounds comprised:

A 250mL three-necked flask, condenser, syringes, dropping funnel, rubber septum, separating funnel, nitrogen inlet

3.3.4   Laboratory Safety

Toluenesulphonyl chloride which is highly toxic was handled with care. Safety procedures for the use of Grignard reagent were taken into consideration.

3.3.5   Analytical methods

3.3.5.1   Nuclear Magnetic Resonance Spectroscopy (NMR)

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 Spectrometer at temperature (25^0 C), at 300MHz and 75MHz respectively. $CDCl_3$ was used as sample solvent.

3.3.5.2   Infrared Spectroscopy (IR)

The IR spectra of the compounds were recorded on a Pekin Elmer 1 600 Fourier Infrared Transform Spectroscopy (FTIR). Pellets of the substance diluted in KBr (KBr discs) were used to record the infrared spectra in transmission mode over the MID-IR range 4000-400cm^{-1} at a standard resolution of 4 cm^{-1} representing data point spacing of just 2 cm^{-1}.The

spectrometer equipped with a Ge-on-KBr beam splitter and DTGS/CsI detector, was continuously purged with UHP nitrogen gas from AFROX. The operating and data manipulation software was performed with the basic OMNIC package for spectroscopy.

3.4   Preparation of Adamantylethyl tosylate

[1]
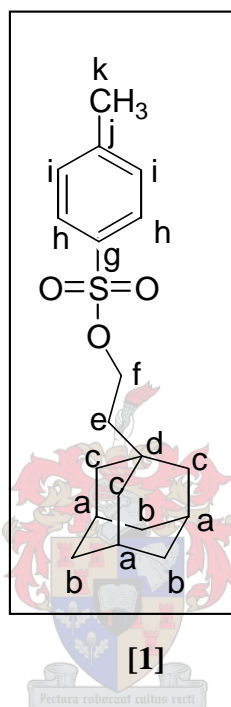
Adamantaneethanol (7g, 0.04mol) and dry pyridine (15mL) were placed in 250 mL three neck round flask fitted with a stirrer and toluenesulphonyl chloride (7.4g, 0.04 mol) was added .Mixture was cooled to 0 ^{o} C and vigorously stirred for 3 hours. The reaction was monitored by T.L.C analysis using hexane: ethyl acetate, 9:1 as solvent. When the reaction was completed, the mixture poured into a small amount of water to dissolve the precipitated pyridine hydrochloride, and then extracted with 100mL of dichloromethane. The organic phase was transferred to a separating funnel and washed with 50mL of dilute hydrochloric acid and then repeatedly with water, until a neutral solution was observed. The organic layer was dried over magnesium sulphate and filtered. The solvent was removed on a rotary evaporator and the product then dried under vacuum. A white solid **(1)** was obtained; yield 8.56g, 66 %.

3.4.1 Characterization of Adamantylethyl tosylate

Table 3.1   **^{1}H NMR Chemical Shifts (δ) of [1] in CDCl$_3$**

Shift (ppm)	Multiplicity	N° of protons	J (Hz)	Assignment
1.31-1.87	Multiplet	17	-	H_a-H_e
2.41	Singlet	3	-	H_k
4.2	Triplet	3	7.2	H_f
7.34	Doublet	2	8.3	H_i
7.79	Doublet	2	8	H_h

Table 3.2   **^{13}C NMR Chemical Shifts (δ) of [1] in CDCl$_3$**

Shift (ppm)	Assignment
21.8	C_k
29	C_a
31.5	C_d
36.8	C_b
42.5	C_c
42.6	C_e
67.5	C_f
128	C_h
130	C_i
133.5	C_j
144.7	C_g

FTIR spectra of the adamantylethtyltosylate showed two sharp intense peak at 2844 and 2904 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. Adamantylethtyltosylate spectra showed also peaks at 1599, 1354 and 964

cm^{-1} due to the aromatic C=C, S=O and S-O stretching vibrations respectively. The FTIR was done to confirm the proposed structure of adamantylethyltosylate.

3.5 Preparation of Adamantylethyl bromide
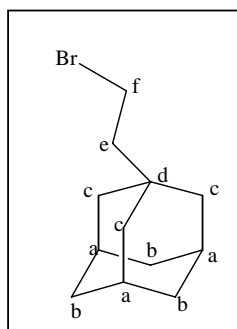
[2]

In 250mL three neck round bottom flask with a stirrer unit and a reflux condenser are placed the foregoing adamantylethyltosylate (7g, 0.02mol) and lithium bromide (4.33g, 0.02mol) in DMF (20mL).The reaction mixture was stirred vigorously and heated to 100 ^{o} C under nitrogen atmosphere for three hours and then cool down at room temperature. The reaction mixture was treated two times with hydrochloric acid (3M, 50mL),then extracted with diethyl ether (3✕ 50mL), the organic layer separated was dried with magnesium sulphate and the solvent was evaporated on a rotary evaporator to give Adamantylethyl bromide, yield 4.88g, and 92%

3.5.1   Characterization of Adamantylethyl bromide

Table 3.3: ^{1}**H NMR Chemical Shifts (δ) of [2] in CDCl$_3$**

Shift (ppm)	Multiplicity	N^o of protons	J(Hz)	Assignment
1.4-1.82	Multiple	17	-	H$_a$-H$_e$
3.4	Triplet	2	8.1	H$_f$

Table 3.4 ^{13}C NMR Chemical Shifts (δ) of [2] in CDCl$_3$

Shift (ppm)	Assignment.
28.33	C$_a$
29	C$_e$
34	C$_d$
37	C$_b$
42	C$_c$
48	C$_f$

FTIR spectra of the adamantylethtylbromide showed two sharp intense peaks at 2844 and 2902 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group, and the peaks at 560 and 1452 cm^{-1} corresponding to the C-Br (stretch) and CH$_2$-Br (bend) respectively.

3.6   *Preparation of dimethyladamantylethyl cyclopentadiene*

3.6.1   First approach: Grignard type reaction

3.6.1.1 Preparation of Adamantylethyl Magnesium Bromide

First attempt

A solution of adamantylethyl magnesium bromide **[3]** (Grignard reagent) was prepared from magnesium turnings (0.049g, 0,002 mol) and adamantylethyl bromide **[2]** (0.5g, 0.002 mol in 10mL of THF) in 15ml of THF. The magnesium turnings were introduced into the 250ml three –neck round bottom flask with 15mL of dry THF and a stirrer and then boiled under reflux. Adamantylethyl bromide was added progressively dropwise over a period of 30 minutes. After all of the adamantylethyl bromide had been added, the mixture was left under reflux for about 45 minutes.

A solution of 6,6-dimethylfulvene (0.5mL, 0.004 mol) in THF (10mL) was added dropwise at 0° C to the Grignard reagent over the period of 30 minutes. The reaction mixture was allowed to warm to room temperature (r.t) and stirred for twelve hours. The reaction mixture was hydrolyzed with 25mL of saturated aqueous ammonium chloride (0.21g, 0.004 mol) and then extracted with 3x 25mL of diethyl ether. The solvent was removed from the organic layer and the ethereal layer brown yellow oil was dissolved in pentane, dried over sodium sulfate and filtered through Celite. The solvent was removed from rotary evaporator to yield a yellowish oil 0.37g.

Second attempt

A solution of adamantylethyl magnesium bromide **[3]** (Grignard reagent) was prepared from magnesium turnings (0.049g, 0,002 mol) and adamantylethyl bromide **[2]** (0.5g, 0.002 mol in 10mL of dry THF) in 15mL of dry THF. The magnesium turnings were introduced into the 250mL three–neck round bottom flask with 15mL of dry THF and a stirrer and then boiled under reflux. Adamantylethyl bromide was added dropwise over a period of thirty minutes, then reflux for thirty minutes, and stirred over night. Solution was then filtered by using glass wool to remove the excess magnesium turnings.

Addition of 6,6 dimethylfulvene to Adamantanylethyl magnesium bromide

A solution of 6,6-dimethylfulvene (0.7ml, 0.004 mol) was added dropwise at 0° ^{C} to the Grignard reagent over a period of thirty minutes.The reaction mixture was refluxed for one more hour, cooled to room temperature (r.t) and stirred over night. The reaction mixture was hydrolyzed with 25 mL of saturated aqueous ammonium chloride (0.21g, 0,004 mol) and then extracted with 3x 25 mL of diethyl ether. The solvent was removed from the organic layer and the ethereal layer brown yellow oil was dissolved in pentane, dried over sodium sulfate and filtered through Celite. The solvent was removed from rotary evaporator to produce 0.52g, of yellow oil.

3.6.1.2   Second approach: A one step alternative to the Grignard Reaction

Into a three – neck round bottom flask equipped with an additional dropping funnel, was introduced lithium slices (0.043g, 0.006mol) under nitrogen atmosphere and dry THF (20mL) .A small portion of the reagent mixture of 6,6-dimethylfulvene and adamantylethyl bromide were dropped into the flask. After a certain period of induction, the reaction begins. This was noticed by a change in the appearance of the lithium surface from a dull matt appearance to a golden silvery sheen. When this appearance is clearly marked, the addition of the reagents [adamantylethyl bromide (1 g, 0.004 mol) and 6,6-dimethylfulvene(1mL, 0,008 mol)] was continued dropwise over a period of approximately 30 min.The reaction was completed after a return of the lithium surface to a dull colour. The mixture was treated with NH_4Cl (0.3 g, 0.006 mol) and allowed to stir for fourteen hours.The THF was removed by evaporation after the excess of lithium was filtered off. The reaction mixture was then extracted with pentane (2 x 20 mL) and dried with $MgSO_4$.The pentane was removed to give yellow product, which was immediately purified by chromatography on silica gel (petroleum ether/Et_2O.5:1) to give 0.41g**,** 75% of byproduct .The byproducts could be adamantylpropane or fulvene derivative because the reaction might leads entirely to the product of proton transfer as the reaction is showed in Scheme 3.3
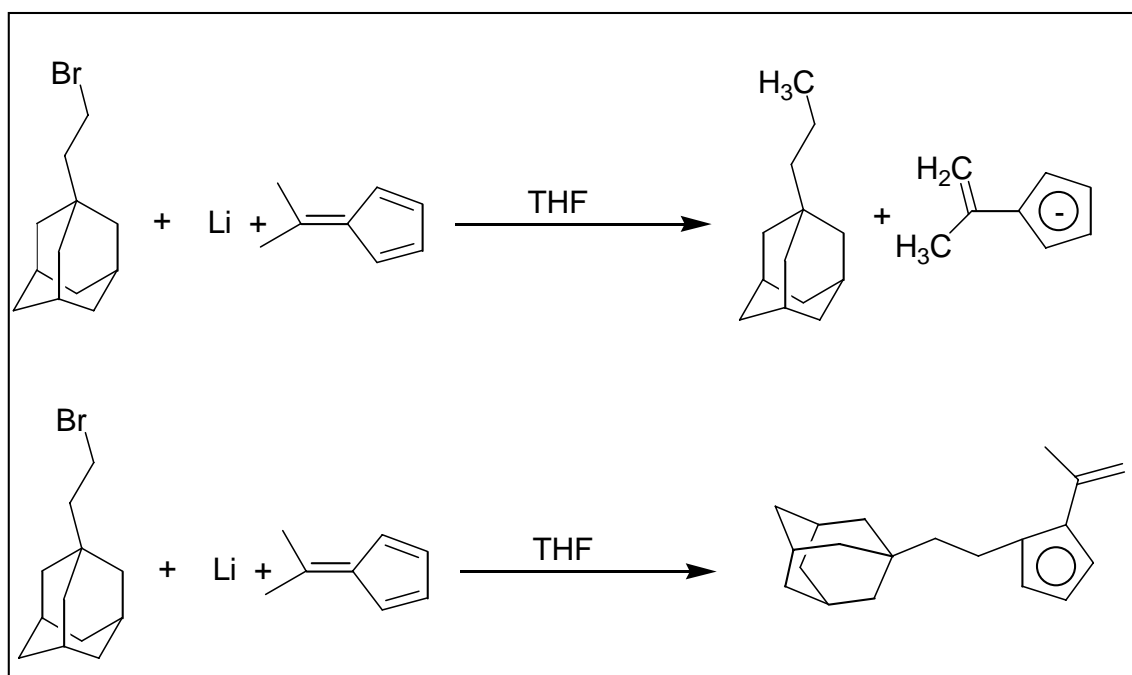
Scheme 3.3   Proton transfer reaction

3.6.2 Results and discussion.

Despite repeated efforts we were unable to synthesize the dimethyl (1-adamantylethyl) cyclopentadiene. NMR analyses of unknown obtained product revealed a range of reaction products in both attempts used. Column chromatography was used for purification but failed. This clearly showed that byproduct was quite difficult to separate from the main product. NMR results showed that the purification was unsuccessful, because we were unable to obtain the wanted product. Thus, the byproducts could be biadamantane or unreacted starting material. The low yield of the Grignard reaction and multiple possible sites of reaction on the 6,6-dimethylfulvene are possible reasons for the impurities present in the intended product.

From these results, it was evident that the approach of using Grignard and lithium reaction to prepare the required compound was not effective enough to give the targeted product.

3.7   Conclusions

In this chapter we reported the attempted synthesis of new type of metallocene catalyst by using specifically the 6,6-dimethylfulvene to form the cyclopentadiene on the catalyst. Thus, in light of the above results, we can therefore say without any doubt that **(1)** and **(2)** were readily synthesized and provided high yield. Whilst the two approaches used for incorporation of 6,6-dimethylfulvene to form cyclopentadiene were unsuccessful. The use of chromatography proved to be unsuccessful. Nevertheless, we do believe that these results opened new possibilities and can serve as a guideline for future study of similar investigation.
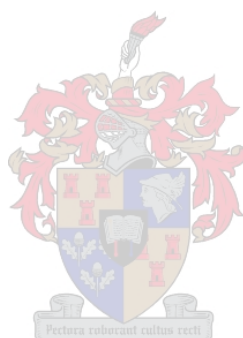
3.8   References

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CHAPTER 4

Synthesis of ester monomers containing the bulky adamantyl group

4.1   Introduction

The synthetic study of new types of adamantane derivatives containing methacrylate or acrylate esters has been the objective of a considerable amount of scientific work. These efforts have been achieved by providing suitable knowledge and the most common and successful preparative methods for them have been developed and published [1-2].

The main focus of the work described in this chapter was to synthesize three different monomers of adamantane containing acrylate and methacrylate esters with different variations in length and rigidity, ethylene, methylene and phenylene, between the adamantane and the polymer backbone. These monomers were later used in a series of homo and copolymerization reactions using RAFT process. (See Chapter 5).

4.2   Theoretical background

4.2.1 Preparation methods.

A number of synthetic routes have been documented [3] on the preparation of various new derivatives of adamantane such as halide, alcohols, ketones, carboxylic acids, amides, nitriles and esters. The procedure followed for the synthesis of these monomers with acrylate and methacrylate was described in literature [1-2] for similar reactions and proved to be successful.

Scheme 4.1 shows schematically the three approaches that were followed to synthesize these monomers.
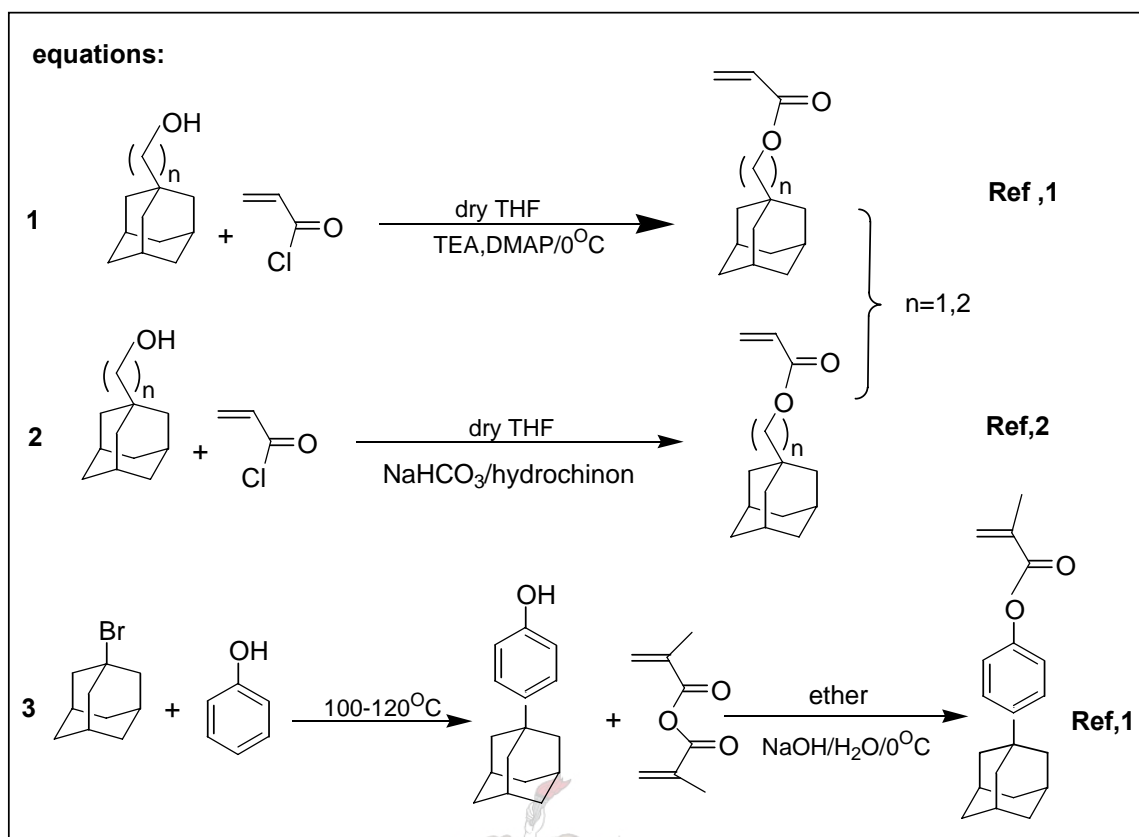
Scheme 4.1   Synthetic route for monomers

4.3   Experimental section.

4.3.1 Materials and methods.

All experiment involving air and moisture sensitive compounds were conducted under nitrogen. Glassware was dried overnight at 120 ^{o}C before use, and experiments were conducted in a nitrogen atmosphere.

4.3.2 Reagents.

All the chemicals used were obtained from Aldrich and Saarchem. Solvents used were dried under nitrogen before use.

Adamantanemethanol, adamantaneethanol, 1-bromoadamantane, phenol, triethylamine (TEA), 4-(N,N-dimethylamino)pyridine (DMAP) were purchased from Aldrich and used as received.

Hydroquinone, sodium carbonate (Na_2CO_3), sodium hydrogen carbonate ($NaHCO_3$), acryloyl chloride and methacrylic anhydride were purchased from Saarchem and used as received

4-(1-Adamantyl) phenol was synthesized by reaction of 1-bromoadamantane and phenol using a literature method [3].

Tetrahydrofuran, (THF) and diethylether were dried over sodium pieces and boiled under reflux with a small amount of benzophenone, until the toluene had dark blue color. Benzophenone was used as an indicator to indicate when the toluene was dry by showing the dark blue color. Toluene was then stored on 4Å molecular sieve.

4.3.1 Analytical methods.

4.3.1.1   Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 Spectrometer at temperature (25° C) at 300 MHz and 75 MHz respectively. $CDCl_3$ was used as sample solvent throughout.

4.3.1.2   Infrared (IR) spectroscopy

The IR spectra of the compounds were recorded on a Pekin Elmer 1 600 Fourier Transform Infrared Spectroscopy (FTIR). Pellets of the substance diluted in KBr (KBr discs) were used to record the infrared spectra in transmission mode over the MID-IR range 4000-400cm^{-1}at a standard resolution of 4 cm^{-1} representing data point spacing of just 2 cm^{-1}.The spectrometer equipped with a Ge-on-KBr beam splitter and DTGS/CsI detector, was continuously purged with UHP nitrogen gas from AFROX. The operating and data manipulation software was performed with the basic OMNIC package for spectroscopy.

4.4 Monomer synthesis.

4.4.1 Preparation of 1-Adamantylethyl Acrylate (AdEA,1).
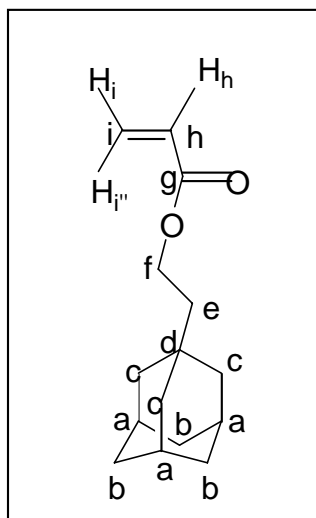
(AdEA)

In a 250 mL three – neck round bottomed flask, a mixture of 1-adamantaneethanol (5g, 0.027 mol), sodium hydrogen carbonate ($NaHCO_3$) (3.4g 0.04 mol) and a small amount of hydrochinon was dissolved in dry THF (20 mL) under nitrogen. Solution was brought to 0 ^{0}C, and a fresh solution of Acryloyl chloride (3.3 mL, 0.04 mol) in THF was added dropwise from the dropping funnel. Immediately, the mixture took a yellow colour. Thereafter, the reaction was stirred to ambient temperature overnight. The solvent was evaporated and the remaining product was extracted with ether. The organic phase was collected   and then washed with water (3 x 15 mL), sodium carbonate [Na_2CO_3 (4%)], again with water until the pH became neutral, and then with saturated NaCl solution. The ethereal layer was then dried with $MgSO_4$, which gave yellow oil (3.55g, 56%) after evaporation.

4.4.1.1 Characterization of Adamantylethyl acrylate (AdEA).

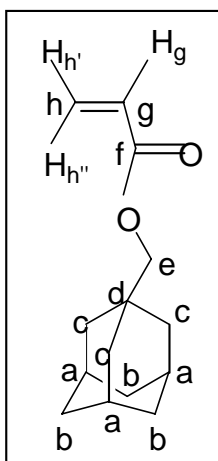**Table 4.1** ^{1}H NMR Chemical Shifts (δ) of [AdEA] in $CDCl_3$

Shift (ppm)	Multiplicity	N^o of protons	J (Hz)	Assignment
1.4-1.9	Multiple	17	-	H_a-H_e
4.2	Triplet	2	15	H_f
5.7	Doublet-doublet	1	12	H_i
6.1	Doublet-doublet	1	28	H_h
6.3	Doublet-doublet	1	19	$H_{i''}$

Table 4.2 ^{13}C NMR Chemical Shifts (δ) of [AdEA] in $CDCl_3$

Shift(ppm)	29	36.8	42.5	31.5	42	61	166.5	130.5	129
Assignment	C_a	C_b	C_C	C_d	C_e	C_f	C_g	C_h	C_i

FTIR spectra of the adamantylethyl acrylate showed two sharp intense peak at 2844 and 2904 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectrum of Adamantylethyl acrylate are the strong C=O, which appeared at 1727 cm^{-1}, and C-O stretching absorptions, which was seen at 1197cm^{-1}.

4.4.2 Preparation of 1-Adamantylmethyl Acrylate (AdMA, 2).

(AdMA)

The procedure used was the same as above for **(AdEA).** The final product was a yellowish oil (3.75g, 67%).

4.4.2.1 Characterization of 1-Adamantylmethyl Acrylate.

Table 4.3 ^{1}H NMR Chemical Shifts (δ) of [AdMA] in CDCl$_3$

Shift (ppm)	Multiplicity	N° of protons	J (Hz)	Assignment
2-2.5	Multiple	15	-	H_a-H_c
4.29	Triplet	2	-	H_e
5.7	Doublet-doublet	1	12	$H_i(H_h^{'})$
6.1	Doublet-doublet	1	28	H_g
6.3	Doublet-doublet	1	19	$H_{h"}$

Table 4.4 ^{13}C NMR Chemical Shifts (δ) of [AdMA] in CDCl$_3$

Shift (ppm)	27.9	36.7	39	33	73.9	166.6	130.3	128.7
Assignment	C$_a$	C$_b$	C$_c$	C$_d$	C$_e$	C$_f$	C$_g$	C$_h$

FTIR spectra of the adamantylmethtyl acrylate showed two sharp intense peak at 2847 and 2901 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectrum of adamantylmethyl acrylate are the strong C=O, which appeared at 1726 cm^{-1}, and C-O stretching absorptions, which was seen at 1195cm^{-1}.

4.4.3 Preparation of 4-(1-Adamantyl) phenyl Acrylate (AdPhMA3).

4.4.3.1   Synthesis of (1-adamantyl) phenol (4).
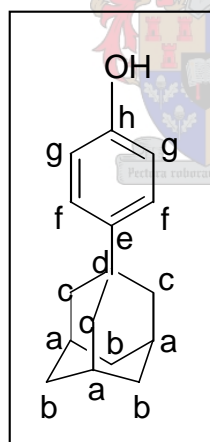
(AdPh)

A three – neck 250mL round – bottom flask fitted with a magnetic stirrer unit and the reflux condenser are placed the foregoing 1-bromoadamantane (25.58g, 0.12 mol) and phenol (13.6g, 0.12 mol). A solution was stirred at 100°C for one hour thirty minutes; the solid obtained was then heated at 120°C for two hours to complete the reaction. After being cooled, the reaction mixture was dissolved in 200 mL of ether and extracted with 200 mL of a 10% sodium hydroxide solution. The aqueous layer was collected, mixed with 100 mL of

water and then acidified with 200 mL of a 5% hydrochloric acid to form write solution, which after separation by filtration produced write precipitates, dried under vacuum pump to give 50g (86% yields).

4.4.3.2 Characterization of 4-(1-Adamantyl) phenol)(AdPh).

Table 4.5 ^{1}H NMR Chemical Shifts (δ) of [AdPh] in CDCl$_3$

Shift (ppm)	Multiplicity	N° of protons	J (Hz)	Assignment
1.7-2.1	multiple	15	-	H$_a$-H$_b$
6.6	Doublet	2	8.5	H$_f$
7.1	doublet	2	8.5	H$_g$

Table 4.6 ^{13}C NMR Chemical Shifts (δ) of [AdPh] in CDCl$_3$

| Shift (ppm)	28.5	35.5	43	36.5	144	115	126	153
Assignment	C$_a$	C$_b$	C$_c$	C$_d$	C$_e$	C$_g$	C$_f$	C$_h$

FTIR spectra of the 4-(1-adamantyl) phenol) showed two sharp intense peak at 2847 and 2905 cm^{-1} which can be attributed to C-H stretching vibrations both symmetrical and asymmetrical respectively on adamantyl group. The broad peak at 3260 cm^{-1} is due to O-H band. The peaks at 1514 and 1247 cm^{-1}due to C=C (aromatic ring) and C-O stretching which are characteristic for Phenols.

The compound **(4)** was readily synthesized via Friedel-crafts alkylation of phenol with 1-bromoadamantane. The Friedel-crafts reaction is known to be an important method of introducing alkyl and acyl groups into aromatic compounds. Aluminum chloride, in general, is the most widely used catalyst for this reaction, but it is not easily recovered.

The NMR spectrum of **(4)** proved that there was no evidence of adamantyl incorporation at the *ortho* position. The ^{13}C NMR spectra depicted eight peaks as expected, four signals are attributed to adamantyl and other four corresponded to phenyl ring signals.

Furthermore, NMR analysis of compound **(4)** revealed that the straight alkylation of phenol and 1-bromoadamantane used to synthesize **(4)** was a very efficient method; the main product obtained was not subjected to a further purification and produced a very good yield.

4.4.3.3   Formation of 4-(1-Adamantyl) phenyl acrylate (AdPhMA, (3)).
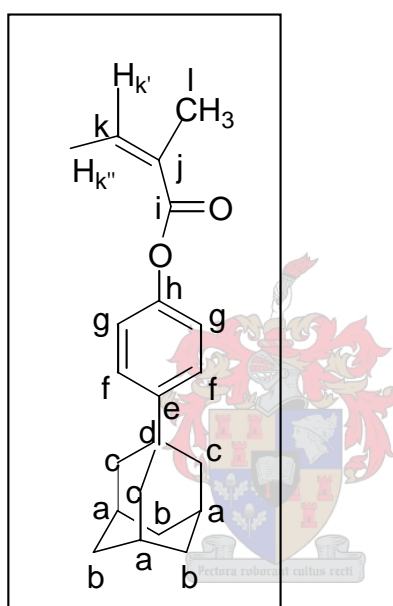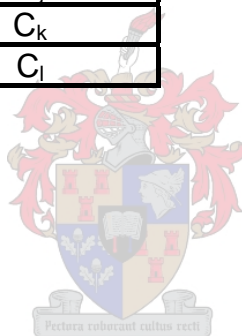

(AdPhMA)

A three – neck 250 mL round –bottom flask equipped with a magnetic stirrer and a dropping funnel was charged with a mixture (10g, 0.043 mol) of 4-(1-Adamantyl) phenol and methacrylic anhydride (8.75mL, 0.065 mol).The contents were dissolved in 15 mL of ether and placed in an ice bath .The aqueous solution of NaOH (3.44g in 10mL of water) was added drop wise for about 20 minutes and then was allowed to stir overnight. A reaction mixture was washed repeatedly with water until a neutral pH was obtained, then with saturated NaCl solution. The ethereal layer was dried over anhydrous sodium sulfate and removed on a rotary evaporator to give a write crude product (7.82g) which was immediately recrystallized from absolute ethanol to give write crystals, yield (6.74g ,52%).

4.4.3.4 Characterization of 4-(1-Adamantyl) phenyl methacrylate (AdPMA (3))

Table 4.7 ^{13}**C NMR Chemical Shifts (δ) of [AdPhMA] in CDCl$_3$**

Shift (ppm)	Assignment
28.5	C_a
36	C_b
43	C_c
35	C_d
137	C_e
126	C_f
121	C_g
149	C_h
167	C_i
148.5	C_j
127	C_k
18	C_l

Table 4.8 ^{1}H NMR Chemical Shifts (δ) of [AdPhMA] in CDCl$_3$

Shift(ppm)	Multiplicity	N^{O}of protons	J(Hz)	Assignment
2.07	singlet	3	-	H$_l$
2.03-1.7	multiple	15	-	H$_{a-c}$
5.7	singlet	1	-	H$_{k'}$
6.3	singlet	1	-	H$_{k''}$
7.05	doublet	2	8.6	H$_g$
7.4	doublet	2	8.8	H$_f$

FTIR spectra of the 4-(1-Adamantyl) phenyl methacrylate showed two sharp intense peak at 2850 and 2910 cm-1 which can be attributed to C-H stretching vibrations both symmetrical and asymmetrical respectively on adamantyl group. A characteristic peak at 1720 cm^{-1} belonging to the carbonyl group and the most intense band at 1130 cm^{-1} belongs to ester group (C-O).

4.5   Conclusions.

Three monomers were synthesized. The synthetic methods have been reported to be successful for similar reactions and we have confirmed this. They proved to be very effective because no further purification was needed and all monomers were produced with very good yields. According to the characteristics methods (NMR and FTIR), the monomers were pure enough to be polymerized or incorporated into polymers.

4.6 References

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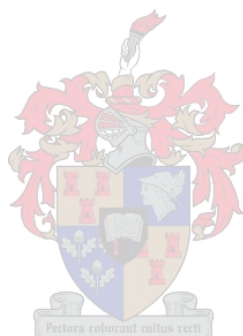
CHAPTER 5

Homo and random copolymerization of Adamantane-containing acrylates using the RAFT process

5.1   Introduction

While the free radical polymerization of acrylates is of course well-known, and some groups have reported on the polymerization of adamantyl acrylates, only a limited number of articles exclusively focused on acrylate RAFT polymerization [2-5], while no papers have been reported the RAFT-mediated polymerization of adamantyl acrylates. All these articles reported very similar characteristics as far as polymerization kinetics were concerned. In general, with most RAFT agents used, polymerizations led to well – controlled homopolymers with predictable molar mass and narrow molar mass distribution due to very large chain transfer constants.

In this chapter, a similar series of homo and copolymers were synthesized with different variations in length and rigidity of the spacer (ethylene, methylene and phenylene), between the adamantyl group and the acrylate group on the polymer backbone. Homo- and copolymerization reactions were conducted by control polymerization technique via the RAFT process .The thermal properties were investigated and compared between them. The incorporation of the bulky pendant group like the adamantyl group has been shown to significantly affect the glass transition temperature (T_g) of polymers.[6-7] .Adamantyl groups can be incorporated in polymers as part of the main chain and as side group [8-10]. The incorporation of adamantane groups into acrylate, ester, carbonate, and urethane polymers has been reported to result in increased thermal stability and glass transition temperatures [18].

5.2   Experimental section

5.2.1 Materials.

All experiments with air – and moisture sensitive compound were conducted in a nitrogen atmosphere using three-neck round bottom flask for copolymerization and Schlenk tube for homopolymerization.

Glassware as well as the reactors used were dried overnight at 120^0 C before use.

Toluene was dried over sodium pieces and boiled under reflux with a small amount of benzophenone, until the toluene had dark blue color. Toluene was then distilled, and stored onto $4A^0$ molecular sieve.

Acetone, Methanol and Dichloromethane were obtained from Saarchem and used without further purification.

The   RAFT   agent   S-1-dodecyl-S'-(R,R'-dimethyl-R-acetic-acid) trithiocarbonate (DITBC) was synthesized in-house.

The initiator 2, 2'-azobis(isobutyronitrile) (AIBN) was obtained from Saarchem.

Monomers: All monomers used, were synthesized as described in Chapter 4 except butyl acrylate which was obtained from PLASCON and used as received.

5.3   Analytical Methods and Instrumentation.

5.3.1 GPC analysis.

Molecular weight and molecular weight distributions were obtained using size exclusion Chromatography (SEC) with THF as a solvent.

GPC analysis was carried out using a Waters model 610 pump, a model 410 refractive index detector (at 30°C) and a waters model 486 UV detector (at 320 nm) in series. Injections were done by a Waters model WISP 712 autoinjector, using an injection volume of 100 µL. The columns used were a PLgel guard (5 µm particles) 50x7.5 mm column, followed by two PLgel mixed-C (5 µm particles) 300x7.5 mm columns at 30°C in series.

Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL min^{-1}. Calibration has been done using polystyrene standard (Polymer Laboratories). Data acquisition and processing were performed using Waters Millennium32 (v3.2 or 4.0) software. Before injection, the samples were filtered over a 13 mm a x 0.2 µm nylon filter.

5.3.2 Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyses (TGA).

TGA analyses were performed using a SDT simultaneous DTA-TGA (TA Instrument). Samples of the polymers were heated under a nitrogen atmosphere at the rate of 20°C/min from the temperature 45°C to 900°C .Glass transition temperature and melting points were determined by DSC. Samples were run on a TA Instrument Q100 DSC system calibrated with indium metal according to standard procedure. Heating and cooling rates were maintained at a standard 10°C/minute. All samples are maintained at 50°C for 1 minute to remove thermal history. The samples were cooled from 50°C to -70°C and the heating cycle was recorded during the second heating scan from -70°C to 50°C.

5.3.3 Nuclear Magnetic Resonance Spectroscopy (NMR).

^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 Spectrometer at temperature (25° C) at 300 MHz and 75 MHz respectively. CDCl$_3$ was used as sample solvent throughout.

5.3.4 Infrared (IR) spectroscopy.

The IR spectra of the compounds were recorded on a Pekin Elmer 1 600 Fourier Transform Infrared Spectroscopy (FTIR). Pellets of the substance diluted in KBr were used to record the infrared spectra in transmission mode over the MID-IR range 4000-400cm^{-1}at a standard resolution of 4 cm^{-1} representing data point spacing of just 2 cm^{-1}.The spectrometer equipped with a Ge-on-KBr beam splitter and DTGS/CsI detector, was continuously purged with UHP nitrogen gas from AFROX. The operating and data manipulation software was performed with the basic OMNIC package for spectroscopy.

5.4   Synthesis of polymers.

5.4.1 Precautions taken.

All polymerization reactions carry some element of danger. During the polymerization reactions, safety precautions are required. All experiments of the air – and moisture sensitive compounds were conducted in a nitrogen atmosphere.

5.4.2 General homopolymer synthesis.

A mixture of the monomer (80 mg) initiator, (AIBN, 2.6mg), RAFT (DITBC) (15mg) and toluene (20 mL) was charged to a dried 50ml Schlenk tube fitted with a magnetic stirring bar. The system was degassed by freeze-evacuate-thaw cycle three times followed by a purge with nitrogen. The tube was then placed in an oil bath and heated at 70°C. The reaction was held in the oil bath at 70°C for two days. The polymerization reaction was stopped and the solution was precipitated into methanol and then dissolved into dichloromethane before being precipitated into methanol to give yellow crystal. The obtained polymer was analyzed by NMR and IR to determine composition, by SEC to determine the molecular weights and polydispersity, thermogravimetric analyses (TGA) to evaluate thermal stability and DSC to determine T_g.

Homopolymers synthesized were: poly(1-adamantylmethyl acrylate) (poly(AdMA), poly(1-adamantylethyl acrylate) (poly(AdEA), and poly(4-(1-adamantyl) phenyl methacrylate) (poly(AdPhMA).

5.5   Copolymer synthesis.

5.5.1 General copolymer synthesis.

Butyl acrylate (4g), comonomer (1g), AIBN (initiator) (0.01g), DITBC (RAFT agent) (0.073g) and toluene (5g) were accurately weighed and then transferred to a 250 mL three-necked round-bottom flask equipped with a condensor and stirred at 300 rpm using a magnetic stirrer. The homogeneous mixture was purged with nitrogen for 30 minutes to eliminate oxygen, and then the reaction flask was immersed in an oil bath and heated to 80°C. The

reaction mixture was carried out under nitrogen at a constant temperature 80°C. After three hours, the reaction was completed and was dried under reduced pressure at 60°C for 24 hours.

It must be pointed out here that due to limited solubility of the methylated phenol monomers the corresponding copolymer was precipitated into hot methanol, and then dissolved into dichloromethane before being reprecipitated into methanol. Despite repeated efforts, we were unable to remove all impurities in AdPhMA copolymer.

All copolymers were analyzed by NMR and IR to determine composition, by SEC to determine the molecular weights and polydispersity and TGA to evaluate thermal stability.

Copolymers synthesized were: poly(1-adamantylethyl acrylate-co-BA) (poly(1-AdEA-co- BA), .poly(1-adamantylmethyl acrylate-co-BA) (poly(1-AdMA-co-BA), poly[4-(1-adamantyl) phenyl methacrylate-co-BA)] (poly [4-(1-AdPhMA-co-BA)]).

5.6 Results and discussion.

5.6.1 Homopolymer synthesis.

The homopolymerization reactions proceeded to very good yields (see Table 5.1). The final yellow product was soluble in most of organic solvent. Due to steric hindrance and sites for chain transfer to monomer, the reaction time of polymerization was very slow. The successful homopolymerization was observed by the disappearance of vinyl protons and carbon and the appearance methylene backbone on both ^{1}H and ^{13}C spectra. The reaction mixture used in the homopolymerization done with the different monomers and their yields are summarized in table 5.1

Table 5.1   Hopolymerization reaction and their yields

| Polymer	monomer (mg)	AIBN(mg)	RAFT(mg)	Temp(^{o}C)	Yield(%)
Poly(AdMA)	AdMA(80)	2.6	15	80	61%
Poly(AdEA)	AdEA(80)	2.6	15	80	57%
Poly(AdPhMA)	AdPhMA(80)	2.6	15	80	65%

5.6.2 Characterization

5.6.2.1   NMR and FTIR.

Structures of all homopolymers were confirmed by ^{1}H, ^{13}C and FTIR In particular ^{13}C spectra of monomer and polymer were used to establish the comparison of the chemical shift values. In addition, FTIR analysis comes to support all information provided by NMR results.

Poly (1-adamantylethyl acrylate)

The structure of poly (1-adamantylethyl acrylate) is shown in Figure 5.3 and chemical shift values are given in Table 5.2.
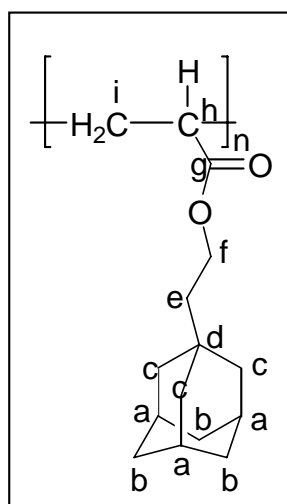
Figure 5.1   The structure of poly (1-adamantylethyl acrylate) .

Table 5.2. Comparison of ^{13}C NMR Chemical Shifts of poly (1-adamantylethyl acrylate) and 1-adamantylethyl acrylate

Carbon	Monomer	Polymer
a	29	29
b	36.8	36.8
c	42.5	42
d	31.5	31.5
e	42	41.2
f	61	61
g	166.5	174.8
h	130.5	-
i	129	-

From this comparison we can see the ideal similarity of the chemical shifts between those of the monomer and polymer. In the case of carbons **h** and **i** it is very difficult to observe the peaks from the ^{13}C NMR spectrum as the spot in which these peak are expected to be depicted are hidden under the large peak **c** at 42 ppm. ^{1}H and ^{13}C NMR analysis showed disappearance of vinyl protons and carbons at 5.7 – 6.3 and 129 – 130.5 ppm, respectively, and the appearance of backbone methylene proton and carbon 3.4 at 42 ppm in the ^{1}H and ^{13}C NMR spectrum. The spectrum (1H and ^{13}C NMR) were consistent with the polymer structure.

FTIR spectrum of the poly (1-adamantylethyl acrylate) showed two sharp intense peak at 2848 and 2904 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectrum of poly(1-adamantylethyl acrylate) are the strong C=O, which appeared at 1736 cm^{-1}, and C-O stretching absorptions at 1162 cm^{-1}.

Poly (1-adamantylmethyl acrylate)

The structure of poly (1-adamantylmethyl acrylate) is shown in Figure 5.4 and chemical shift values are given in Table 5.3.
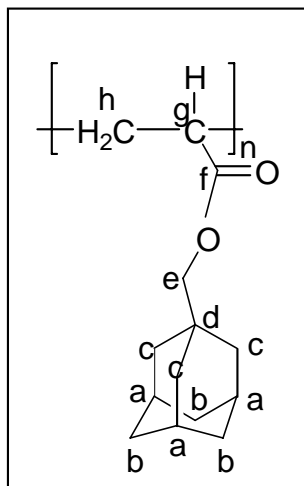
Figure 5.2 **The structure of poly (1-adamantylmethyl acrylate)**

Table 5.3 **Comparison of ^{13}C NMR Chemical Shifts of poly (1-adamantylmethyl acrylate) and adamantylmethyl acrylate**

Carbon	Monomer	Polymer
a	27.9	28.4
b	36.7	36.8
c	39	39.1
d	33	32.9
e	73.9	74.1
f	166.6	175.1
g	130.3	42.5
h	128.7	46.6

From Table 5.3 we can see the similarity of the chemical shifts between those of the monomer and polymer. All eight peaks expected were seen on the polymer ^{13}C spectrum. The polymerization was confirmed by the disappearance of vinyl protons and carbons at 5.7 – 6.3 and 129 – 130 ppm,

respectively, and the appearance of backbone methylene proton and carbon 2.7 at 46.6 ppm in the ^{1}H and ^{13}C NMR spectrum. The spectrum is consistent with the polymer structure.

An important point must be kept in mind is that the homopolymerization of AdMA without [11-12] and with RAFT showed identical NMR results.

FTIR spectrum of the poly (1-adamantylethyl acrylate) showed two sharp intense peak at 2848 and 2904 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectrum of poly(1-adamantylethyl acrylate) are the strong C=O, which appeared at 1736 cm^{-1}, and C-O stretching absorptions at 1162 cm^{-1}.

Poly [(4-(1-adamantyl) phenyl methacrylate)], (Poly(AdPhMA)

The structure of poly [(4-(1-adamantyl) phenyl methacrylate)] is shown in Figure 5.5 and chemical shifts values are given in Table 5.4
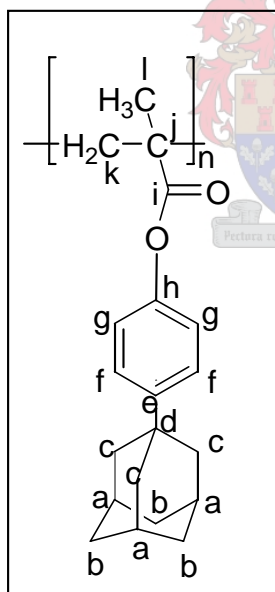
Figure 5.3   **Structure of poly (4-(1-adamantyl) phenyl methacrylate)**

Table 5.4 Comparison of [13] C NMR Chemical Shifts of poly [(4-(1-adamantyl) phenyl methacrylate)] and [(4-(1-adamantyl) phenyl methacrylate)].

Carbon	Monomer	Polymer
a	28.5	28.7
b	36	36.5
c	43	43.1
d	35	35.7
e	137	149
f	126	120.6
g	121	125.9
h	149	149
j	167	53.3
i	148.5	175.2
k	127	45.6
l	18	17.6

From Table 5.4 we can see a good comparison of the chemical shifts for similar hydrocarbon between the monomer and the polymer from the ^{13}C NMR spectrum. The peaks at 28.7 ppm, 36.5 ppm and 43.1 ppm represent the three adamantane peaks of carbon **a, b** and **c**. The signals downfield at 120.6 ppm, 125.9 ppm and 175.2 ppm are attributed to the four phenyl ring signals of carbon **f, g h** and **e** respectively. These peaks were not supposed to appear. There is no convincing argument to explain the presence of these peaks.

The polymerization was confirmed by the disappearance of vinyl protons and carbons at 5.7 – 6.3 and 127 – 148.5 ppm, respectively, and the appearance of backbone methylene proton and carbon 3.4 at 45.6 ppm in the ^{1}H and ^{13}C NMR spectrum. The spectrum is consistent with the polymer structure.

Most importantly to keep in mind is that the homopolymerization of AdPhMA without [11-12] and with RAFT showed identical NMR results.

FTIR spectra of the poly [(4-(1-adamantyl) phenyl methacrylate)] showed two sharp intense peak at 2 843 and 2 903 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectrum of poly [(4-(1-adamantyl) phenyl methacrylate)] are the strong C=O, which appeared at 1 750 cm^{-1}, and C-O stretching absorptions at 1 170 cm^{-1}.

5.6.2.2   GPC Analyses

The homopolymers synthesized were analysed by GPC to determine the molecular weight (MW) and polydispersity index (PDI). GPC results are given in Table 5.5

Table 5.5   **Molecular weight and polydispersities of poly(1-adamantylethyl acrylate), poly(1-adamantylmethyl acrylate) and poly [4-(1-adamantyl) phenyl methacrylate)]**

Polymer	Molecular Weight (g.mol^{-1})	Polydispersity
Poly(AdEA)	3 400	1.3
Poly(AdMA)	6 200	1.4
Poly(AdPhMA)	18 812	1.4

The GPC analysis of the homopolymers shows that it oligomers were formed referring to the low molecular weight. The polydispersities of the resulting polymers were quite constantly slightly narrow with values from 1.3 to 1.4 (see Table 5.5). This provides evidence that good control was obtained (PDI < 1.5) during the polymerization.

5.6.2.3   Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis is a thermal analysis technique used to measure changes in the weight (mass) of a sample as a function of temperature and/or time. TGA was used to determine polymer degradation temperatures.
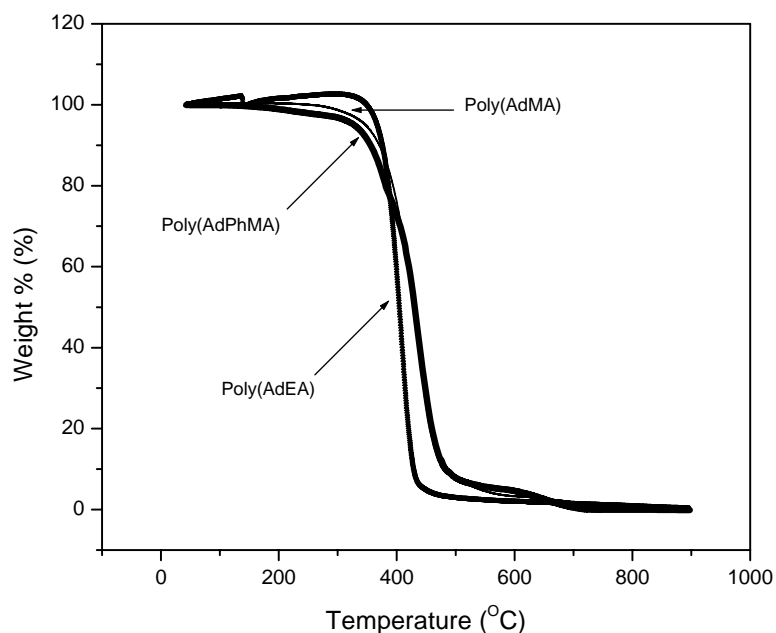
Figure 5.4   TGA traces of poly(1-adamantylethyl acrylate), poly(1-adamantylmethyl acrylate) and poly [4-(1-adamantyl) phenyl methacrylate)]

Depicted above are the TGA curves of the homopolymers. As expected, the samples masses decreases with rising temperature because polymers are being degraded at higher temperatures. TGA thermogram of Poly(AdEA) and Poly(AdMA) showed only one weight loss at 379.3 and 386°C, respectively. While TGA thermogram of Poly(AdPhMA) showed double weight loss patterns at about 243 and 408°C respectively. The first weight loss might have been due to the removal of water on the polymer and the second weight loss is attributed to the decomposition of the polymer. These curves provided information concerning the thermal stability of the initial polymers, intermediate compounds that may be formed. The TGA trace analysis revealed that the Poly[4-(1-Adamantyl) phenyl methacrylate)] exhibited a higher heat resistance which indicates to be more stable, followed by Poly(1-Adamantylmethyl acrylate) and then Poly(1-Adamantylethyl acrylate). The degradation temperature of polymer are given in Table 5.6

Table 5.6   Degradation temperature of poly(1-adamantylethyl acrylate), poly(1-adamantylmethyl acrylate) and poly [4-(1-adamantyl) phenyl methacrylate)]

Polymer	Temperature (°C)
Poly(AdPhMA)	408
Poly(AdMA)	386
Poly(AdEA)	379

5.6.3. Copolymer synthesis.

1-Adamantylethyl acrylate, 1-Adamantylmethyl acrylate, and 4-(1-Adamantyl) phenyl methacrylate) were successfully copolymerized with butyl acrylate. The successful living copolymerization was observed by the disappearance of vinyl protons and carbon and the appearance methylene backbone on both ^{1}H and ^{13}C spectra. The copolymerization reactions proceeded to a very good yield. The final yellow viscous product was soluble in most of organic solvent. The reaction mixture used in the copolymerization done with the different monomers and their yields are summarized in Table 5.7

Table 5.7   Copolymerization reaction and their yields

Polymer	Monomer(g)	Butyl acrylate(g)	AIBN(g)	RAFT(g)	Temp(°C)	Yield(%)
Poly(1-Adamantylmethyl acrylate-co-BA)	AdMA(1)	4	0.01	0.073	80	61
Poly(1-Adamantylethyl acrylate-co-BA)	AdEA(1)	4	0.01	0.073	80	51
Poly[4-(1-Adamantyl) phenyl methacrylate)-co-BA]	AdPhMA(1)	4	0.01	0.073	80	68

5.6.4 Characterization.

5.6.4.1 NMR and FTIR

Structures of all copolymers were confirmed by using NMR (^{1}H and ^{13}C) and FTIR .The ^{13}C spectra was used to determine the chemical shift values of the expected and observed peaks in both spectra monomer and polymer. FTIR analysis comes to support all information provided by NMR results.

Poly (1-Adamantylethyl acrylate-co-Butyl acrylate)

The ^{13}C NMR spectra of the copolymer of 1-adamantylethyl acrylate and butyl acrylate is shown in Figure 5.8.The spectra of 1-adamantylethyl acrylate and butyl were used to identify the peaks in the spectra of Poly(1-Adamantylethyl acrylate-co-butyl acrylate). Peak assignments for copolymer are given in Table 5.8

Table 5.8 Comparison of ^{13}C NMR Chemical Shifts of Poly(1-Adamantylethyl acrylate-co-Butyl acrylate) and 1-Adamantylethyl acrylate - Butyl acrylate

Carbon	Monomer[††,†††]	Polymer
a	29 [††]	28.8
b	36.8 [††]	36.9
c	42.5 [††]	42.6
d	31.5 [††]	n/d
e	42 [††]	n/d
f	61 [††]	n/d
g	166.5 [††,†††]	174.8
h	130.5[2††]	n/d
i	129[††]	n/d
j	64.2[†††]	n/d
k	30.3[†††]	64.3
l	18.8[†††]	18.8
m	13.3[†††]	13.4
i	-	41.2

[††]Based on monomer (AdEA) spectra, [†††]Based on the spectra of B.A

From Table 5.8 we can easily see a good comparison of the chemical shifts of the monomer[†††,††] for similar hydrocarbon polymers and the chemical shifts of

the polymer from the ^{13}C NMR spectra. As expected, the polymer to be predominantly poly(acrylate) with a small amount of 1-adamantylethyl acrylate incorporated. The peaks at 29 ppm, 36.8 ppm and 42 ppm represent the three adamantane signals of carbons **a, b**, and **c.** The intensity of the peaks that represent the adamantane carbons are very small compared to the intensity of the butyl acrylate peaks. The peak **r** at 41.2 ppm with small intensity represents the backbone of the polymer. In the case of carbons **d, e, f,** and **h** it is very difficult to observe their peaks from ^{13}C NMR spectrum as the spot in which these signals are expected to be depicted are hidden under larger peaks. The four tallest signals presented on the spectrum are from B.A. This provides confirmation that only a small amount of 1-adamantylethyl acrylate was incorporated into the final copolymer.

The copolymerization was confirmed by the disappearance of vinyl protons and carbons respectively, and the appearance of backbone methylene proton and carbon in the ^{1}H and ^{13}C NMR spectrum.

It should be note that comonomer incorporation was difficult to determine in both spectrum (^{1}H and ^{13}C NMR), because the necessary peaks were weak and difficult to differentiate from the baseline.
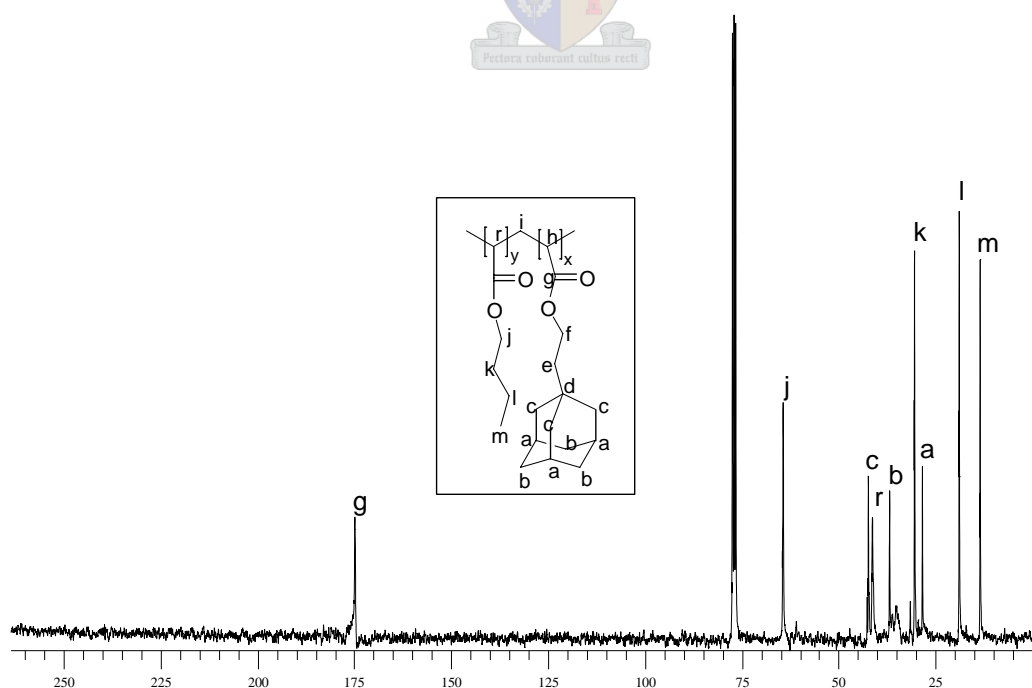
Figure 5.7 ^{13}**C NMR spectrum of Poly (1-Adamantylethyl acrylate-co-Butyl acrylate) in CDCl$_3$**

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FTIR spectra of the Poly (1-Adamantylethyl acrylate-co-butyl acrylate) showed two sharp intense peak at 2874 and 2959 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectra of Poly(1-Adamantylethyl acrylate-co-butyl acrylate) are the strong C=O, which appeared at 1732 cm^{-1}, and C-O stretching absorptions at 1164 cm^{-1}. A medium intensity peak at 1451 cm^{-1} corresponding to the bending C-C=O.
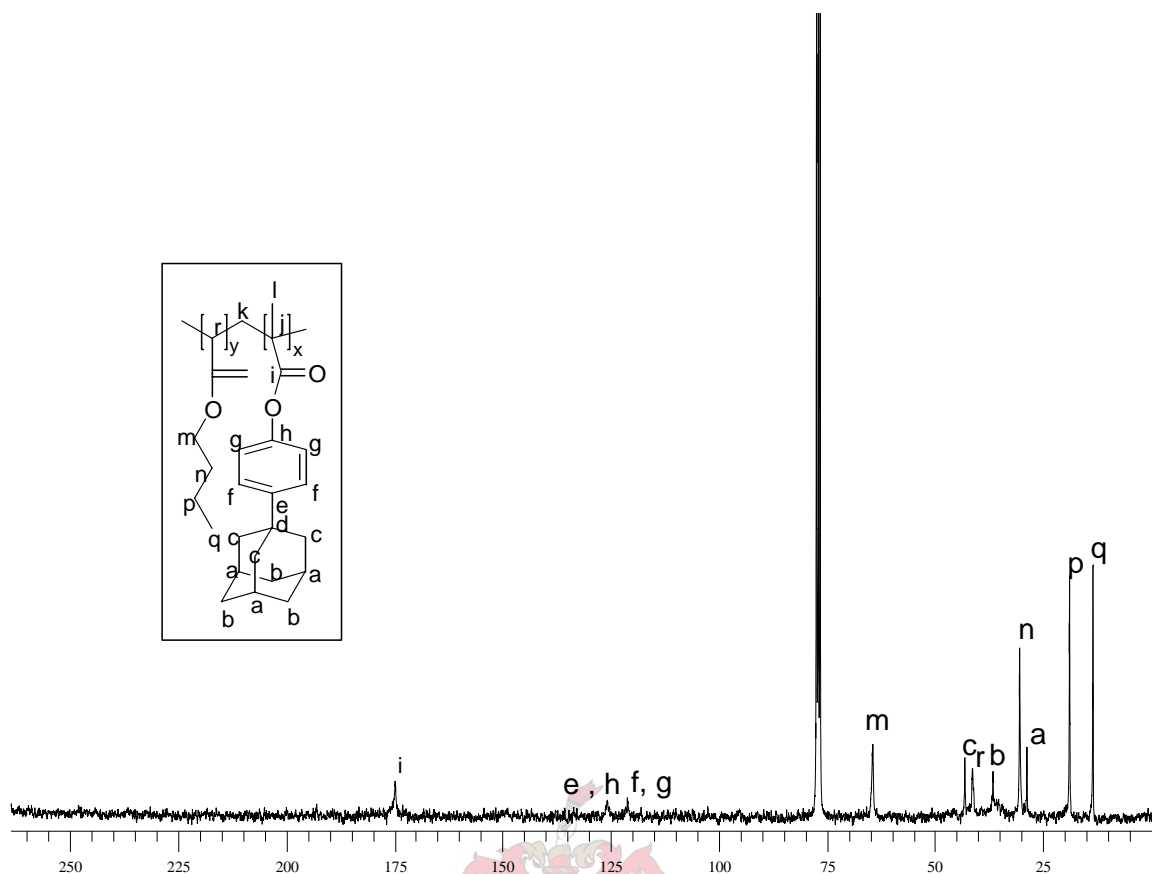
Poly(1-Adamantylmethyl acrylate-co-Butyl acrylate)

The ^{13}C NMR specta of the copolymer of 1-adamantylmethyl acrylate and butyl acrylate is shown in Figure 5.8.The spectra of 1-adamantylethyl acrylate and butyl were used to identify the peaks in the spectra of Poly(1-Adamantylmethyl acrylate-co-butyl acrylate). Peak assignments for copolymer are given in Table 5.9**.**
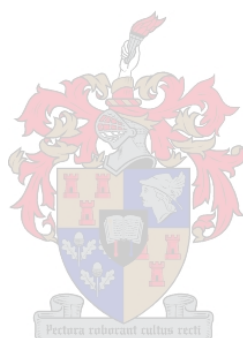
Table 5.9 Comparison of ^{13}C NMR Chemical Shifts of Poly(1-Adamantylmethyl acrylate-co-Butyl acrylate) and 1-Adamantylmethyl acrylate - Butyl acrylate

Carbon	Monomer[††,†††]	Polymer
a	27.7[††]	27.8
b	36.7[††]	36.8
c	39[††]	41.3
d	33[††]	-
e	73.6[††]	74.1
f	166.6[††]	174.7
g	130[††]	-
h	128.7[††]	-
i	64.2[†††]	64.3
j	30.3[†††]	30.4
k	18.8[†††]	18.9
l	13.3[†††]	13.4
r	-	39.1

[††]Based on monomer (AdMA) spectra, [†††]Based on the spectra of B.A

From Table 5.9 we can easily see a good comparison of the chemical shifts of the monomer[†††, ††] for similar hydrocarbon polymers and the chemical shifts of the polymer from the ^{13}C NMR spectrum. As expected, the polymer to be predominantly poly(acrylate) with a small amount of 1-adamantylethyl acrylate incorporated. The peaks at 27.8 ppm, 36.8 ppm and 41.3 ppm represent the three adamantane signals of carbons **a, b**, and **c.** The intensity of the peaks that represent the adamantane carbons are very small compared to the intensity of the butyl acrylate peaks. The peak **r** at 39.1 ppm with small intensity represents the backbone of the polymer. In the case of carbons **d** and **g** it is very difficult to observe their peaks from ^{13}C NMR spectrum as the spot in which these signals are expected to be seen is hidden under larger peaks. Another vital factor that can prevent us to see those peaks from the spectra can be due to the steric hindrance from the adamantyl group on the polymer chain. The four tallest signals presented on the spectrum are from B.A. This provides confirmation that only a small amount of 1-adamantylmethyl acrylate was incorporated into the final copolymer.

The copolymerization was confirmed by the disappearance of vinyl protons and carbons respectively, and the appearance of backbone methylene proton and carbon in the ^1H and ^{13}C NMR spectrum.

It should be note that comonomer incorporation was difficult to determine in both spectrum (^1H and ^{13}C NMR), because the necessary peaks were weak and difficult to differentiate from the baseline.
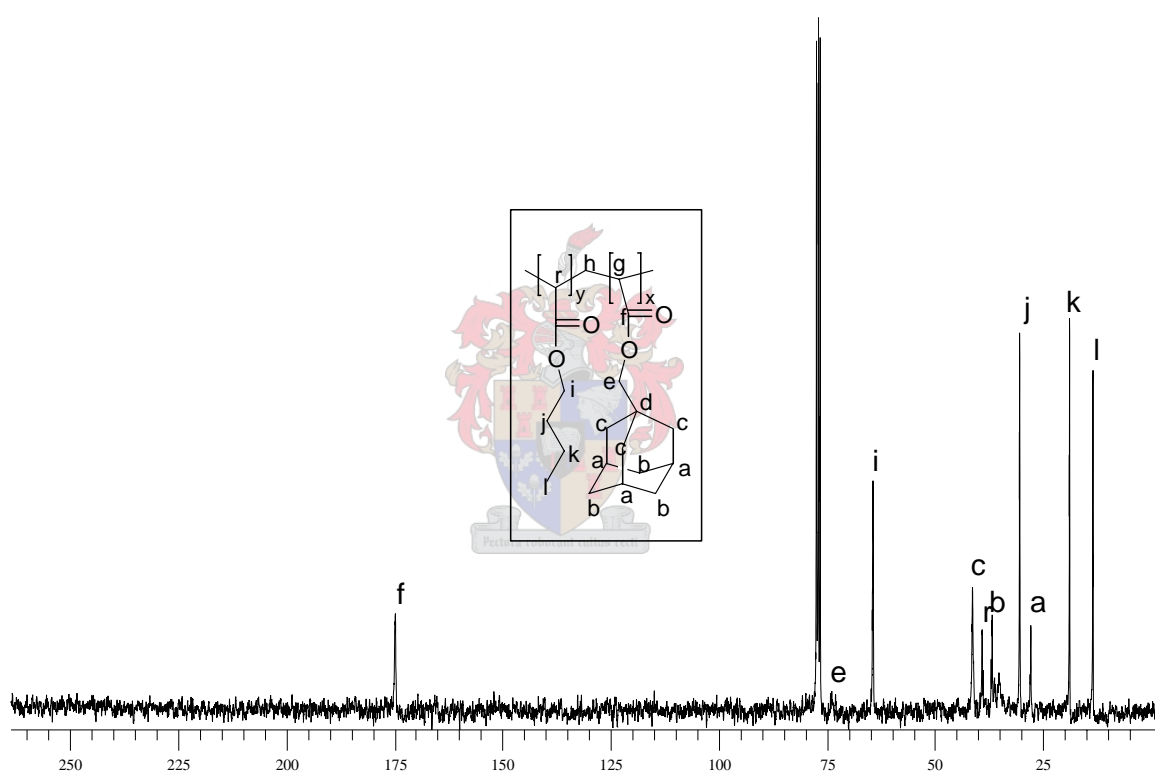
Figure 5.6 ^{13}C NMR spectra of Poly (1-Adamantylmethyl acrylate-co-Butyl acrylate) in CDCl$_3$

FTIR spectra of the Poly (1-Adamantylmethyl acrylate-co-butyl acrylate) showed four medium at 2849, 2874, 2933 and 2959 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectra of Poly(1-Adamantylmethyl acrylate-co-butyl acrylate) are the strong C=O, which

appeared at 1735 cm^{-1}, and C-O stretching absorptions at 1164 cm^{-1}. A weak intensity peak at 1452 cm^{-1} corresponding to the bending C-C=O.
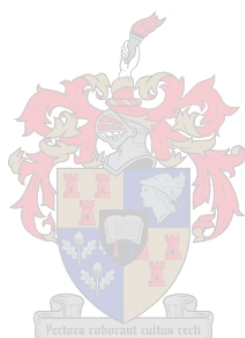
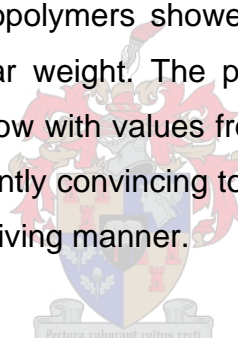## Poly [4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrylate)]

The ^{13}C NMR spectra of the copolymer of [4-(1-adamantyl)phenyl methacrylate)] and butyl acrylate is shown in Figure 5.9.The spectra of [4-(1-adamantyl)phenyl methacrylate)] and butyl acrylate were used to identify the peaks in the spectra of Poly [4-(1-adamantyl) phenyl methacrylate-co-butyl acrylate)]. Peak assignments for copolymer are given in Table 5.10

Table 5.10 **Comparison of ^{13}C NMR Chemical Shifts of Poly [4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrylate)].and [4-(1-Adamantyl) phenyl methacrylate - Butyl acrylate**

Carbon	Monomer[††,†††]	Polymer
A	28.5[††]	28.7
B	36[††]	36.6
C	43[†††]	43.1
D	35[††]	n/d
E	137[††]	126
F	126[††]	121.1
G	121[††]	121.1
H	149[††]	126
I	167[††]	174
J	148.5[††]	-
K	127[††]	-
L	18[††]	-
M	64.2[†††]	64.3
N	30.3[†††]	30.4
P	18.8[†††]	18.9
Q	13.3[†††]	13.4
R	-	41.3

[††]Based on monomer (AdPhMA) spectra, [†††]Based on the spectra of B.A

Figure 5.7   13C NMR spectrum of poly 4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrylate) in CDCl₃

From Table 5.10 we can easily see a good comparison of the chemical shifts of the monomer[†††,††] for similar hydrocarbon polymers and the chemical shifts of the polymer from the 13C NMR spectrum. As expected, the polymer to be predominantly poly(butylacrylate) with a small amount of [4-(1-adamantyl)phenyl methacrylate)] incorporated. The peaks at 27.8 ppm, 36.6 ppm and 43.1 ppm represent the three adamantane signals of carbons **a, b**, and **c.** The intensity of the peaks that represent the adamantane carbons are very small compared to the intensity of the butyl acrylate peaks. The peak **r** at 41.3 ppm with small intensity is due to the branching in the poly(methyl acrylate) backbone. In the case of carbons **j,** and **l** it is very difficult to observe their peaks from 13C NMR spectrum as the spot in which these signals are expected to be depicted are hidden under larger peaks. Another vital factor that can prevent the sight those peaks from the 13C spectrum can be due to the steric hindrance from the adamantyl group on the polymer chain. The

signals at 121.1 ppm and 126 ppm represent the four phenyl ring signals of carbons **f, g, e** and **h**. These peaks were not supposed to appear. There is no convincing argument to explain the presence of these peaks.

The four tallest signals presented on the spectrum are from B.A. This provides confirmation that only a small amount of [4-(1-adamantyl) phenyl methacrylate)] was incorporated into the final copolymer. However, comonomer incorporation was difficult to determine in both spectrum (^{1}H and ^{13}C NMR), because the necessary peaks were weak and difficult to differentiate from the baseline.

FTIR spectra of the Poly[(4-(1-adamantyl) phenyl methacrylate)]-co-butyl acrylate) showed four peaks at 2 849, 2 874, 2 931 and 2 959 cm^{-1} due to the presence of C-H stretch vibration symmetrical and asymmetrical respectively on adamantyl group. The two most characteristic features in the spectra of Poly[(4-(1-adamantyl) phenyl methacrylate)]-co-butyl acrylate) are the strong C=O, which appeared at 1735 cm^{-1}, and C-O stretching absorptions at 1164 cm^{-1}. A weak intensity peak at 1451 cm^{-1} corresponding to the bending C-C=O.

5.6.4.2   GPC Analyses

The copolymers synthesized were analysed by GPC to determine the molecular weight (MW) and polydispersity index (PDI). GPC results are given in Table 5.11.

Table 5.11 **Molecular weight and polydispersities of Poly (1-Adamantylethyl acrylate-co-Butyl acrylate), Poly (1-Adamantylmethyl acrylate-co-Butyl acrylate) and Poly [4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrylate)].**

Polymer	Molecular Weight	Polydispersity
Poly(1-Adamantylethyl acrylate-co-BA)	21 906	1.5
Poly(1-Adamantylmethyl acrylate-co-BA)	34 113	1.4
Poly[4-(1-Adamantyl) phenyl methacrylate)-co-BA]	22 707	1.2

The GPC analyses of the copolymers showed that oligomers were formed referring to the low molecular weight. The polydispersities of the resulting polymers were not really narrow with values from 1.2 to 1.5 (see Table 5.11), but these values were sufficiently convincing to conclude that copolymer were produced in a well-controlled living manner.

5.6.4.3   Thermogravimetric Analysis (TGA)
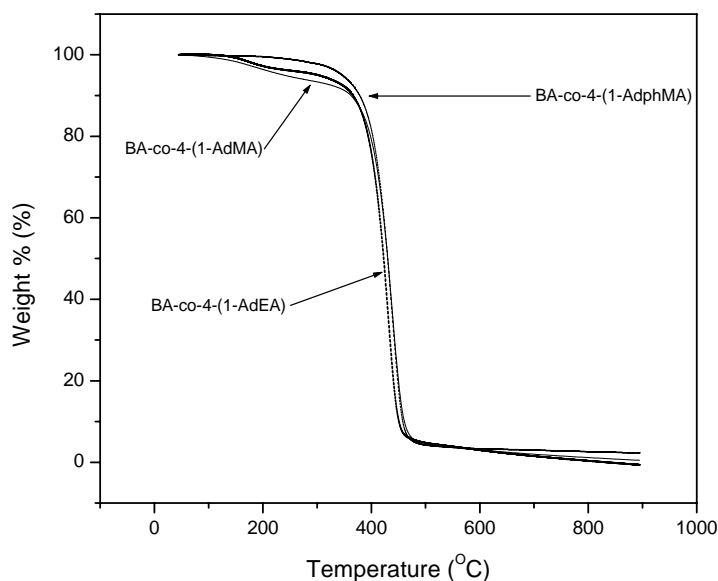
Figure 5.8   **TGA traces of Poly (1-Adamantylethyl acrylate-co-Butyl acrylate), Poly (1-Adamantylmethyl acrylate-co-Butyl acrylate) and Poly [4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrylate)].**

Depicted above are TGA curve of copolymer. As expected, the sample masses decrease with rising temperature because polymers are being degraded at higher temperatures. TGA thermogram of Poly(1-adamantylmethyl acrylate-co-BA) showed only one weight loss at 401.2 corresponding to the decomposition of the polymer. Whilst the TGA thermograms of Poly(1-adamantylethyl acrylate-co-BA) and Poly[4-(1-Adamantyl) phenyl methacrylate)-co-BA] showed double weight loss patterns at about 133 and 397.7^{o}C for Poly(1-adamantylethyl acrylate-co-BA) and 130.9 and 404.2^{o}C for the Poly[4-(1-adamantyl) phenyl methacrylate)-co-BA], respectively. The first weight loss might due to the removal of the butyl acrylate from the copolymer. The second weight loss at 404.2^{o}C might be responsible for the decomposition of the copolymer. These curves provided information concerning the thermal stability of the initial polymers, intermediate compounds that may be formed. The TGA temperatures of all copolymers are slightly different. The TGA traces analyses revealed that the Poly[4-(1-adamantyl) phenyl methacrylate)-co-BA] exhibited a higher heat resistance which indicating to be most stable, followed by Poly(1-

adamantylmethyl acrylate-co-BA) and then Poly(1-adamantylethyl acrylate-co-BA). The degradation temperature of copolymer are given in Table 5.12.
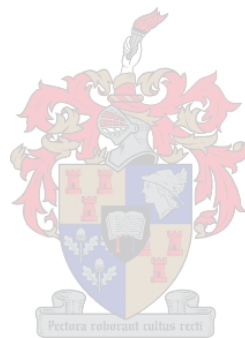
Table 5.12   **Degradation temperature of Poly (1-Adamantylethyl acrylate-co-Butyl acrylate), Poly (1-Adamantylmethyl acrylate-co-Butyl acrylate) and Poly [4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrylate)].**

Polymer	Temperature(^{o}C)
Poly(1-Adamantylethyl acrylate-co-BA)	398
Poly(1-Adamantylmethyl acrylate-co-BA)	401
Poly[4-(1-Adamantyl) phenyl methacrylate)-co-BA]	404

5.10 Conclusions

The homopolymerization was successfully achieved by using the RAFT process. It can therefore be concluded that the poly (AdMA) and poly (AdPhMA) prepared without and with RAFT have shown the same NMR results. The synthesis of the homopolymers without RAFT was published by Acar *et al* [12].

Butyl acrylate was successfully copolymerized with Adamantylethyl acrylate, 1-Adamantylmethyl acrylate, and 4-(1-Adamantyl) phenyl methacrylate) in solution using RAFT process.

AIBN and DITBC have been proven to be effective for homo- and copolymerization of adamantylethyl acrylate, 1-adamantylmethyl acrylate, and 4-(1-adamantyl) phenyl methacrylate) with BA to give polymers with narrow polydispersities. The living radical is also useful method for preparation of copolymers.

FTIR and ^{13}C NMR were effective methods in determining the homo-and copolymer structures.

From GPC analysis, we have demonstrated that the RAFT polymerization procedure is applicable to the preparation of a wide variety of well-defined random copolymers with low polydispersities indicating that the polymerization took place in well-controlled living manner.

5.11 References

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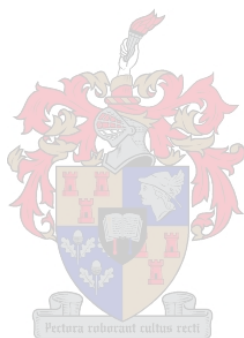
CHAPTER 6

Conclusions

6.1   Introduction

The general conclusion in this study can be drawn from the work carried out on the synthesis of a catalyst Bis (2-Dimethyladamantylethylcycloppentadienyl) zirconium dichloride, synthesis of monomers containing the bulky adamantyl group and the homo-and copolymerization of this monomer with butyl acrylate using the RAFT process.

6.2   Synthesis of a catalyst Bis (2-Dimethyladamantylethyl cyclopentadienyl) zirconium dichloride.

Intermediate compounds namely adamantylethyl tosylate and adamantylethyl bromide were readily synthesized and provided very good yield (see Chapter 3)

From the results obtained by NMR analysis, it was clear that the two approaches used to synthesize dimethyladamantylethyl cyclopentadiene, Grignard type reaction and Barbier one step reaction were not suitable. It resulted in a mixture of unknown products. The use of chromatography method for purification of the crude product was not successful.

6.3   Synthesis of monomer.

Different methods used to synthesize 1-adamantylmethyl acrylate, 1-adamantylethyl acrylate, and [(4-(1-adamantyl) phenyl methacrylate)] proved to be very effective because no further purification was needed and all monomers were produced with very good yields.

6.4   Homo-and Copolymerization

The homopolymerization was successfully achieved by using the RAFT process.

Butyl acrylate was successfully copolymerized with 1-adamantylethyl acrylate, 1-adamantylmethyl acrylate, and [4-(1-adamantyl) phenyl methacrylate)] in solution using the RAFT process.

AIBN and DITBC have been proven to be effective for homo- and copolymerization of adamantylethyl acrylate), 1-adamantylmethyl acrylate), and [4-(1-adamantyl) phenyl methacrylate)] with B.A.

^{13}C NMR method clearly revealed that only a very small amount of adamantylethyl acrylate), 1-adamantylmethyl acrylate, and [4-(1-adamantyl) phenyl methacrylate was incorporated during the copolymerization reactions referring to the intensities of different peaks in the copolymer.

FTIR spectroscopy was also successfully used to confirm the structure of the polymer.

From data obtained from GPC analysis, we have demonstrated that the RAFT living free- radical polymerization procedure is applicable to the preparation of a wide variety of well defined copolymer with polydispersities <1.5 providing the evidence that the polymerization was controlled.

The TGA traces analyses revealed that the Poly[4-(1-Adamantyl) phenyl methacrylate)-co-BA] exhibited a higher heat resistance which indicated to be most stable, followed by Poly(1-Adamantylmethyl acrylate-co-BA) and then Poly(1-Adamantylethyl acrylate-co-BA).

In the case of poly(1-adamantylmethyl acrylate-co-BA) and poly(1-adamantylethyl acrylate-co-BA), the temperatures of decomposition values are slightly higher compared to those of the corresponding homopolymer. While poly [4-(1-adamantyl) phenyl methacrylate)-co-BA] showed lower decomposition temperature than its corresponding homopolymer.

APPENDIX A

NMR SPECTRA
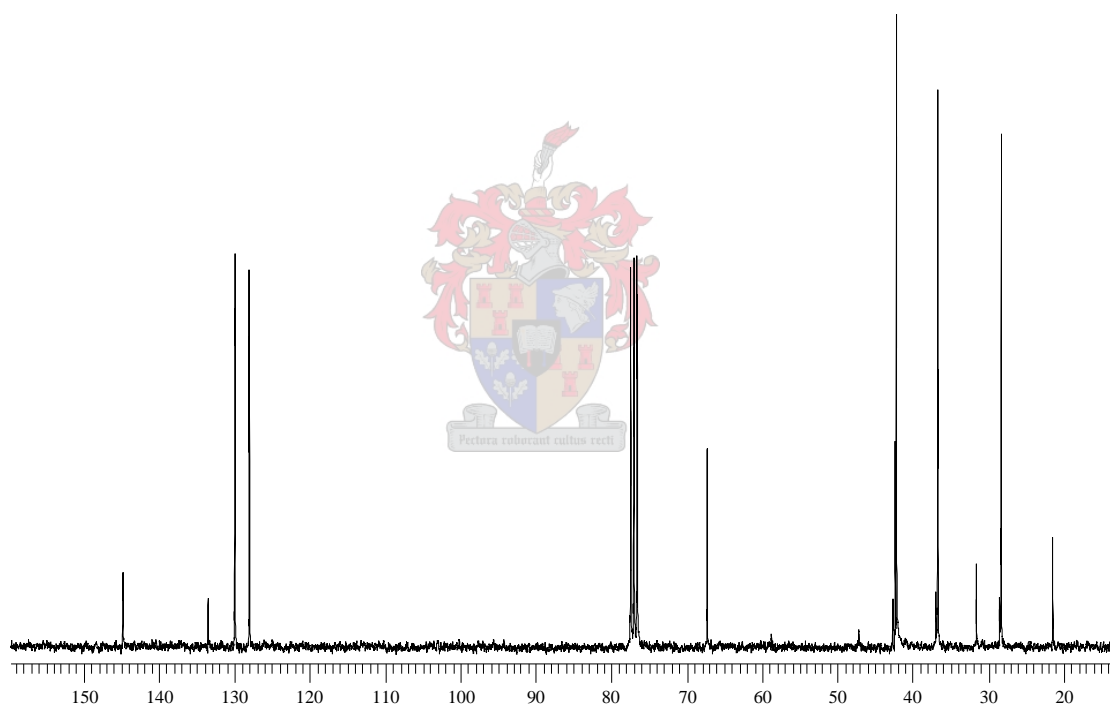
Fig A.1   ¹³C NMR spectra of Adamantylethyl tosylate in CDCl₃
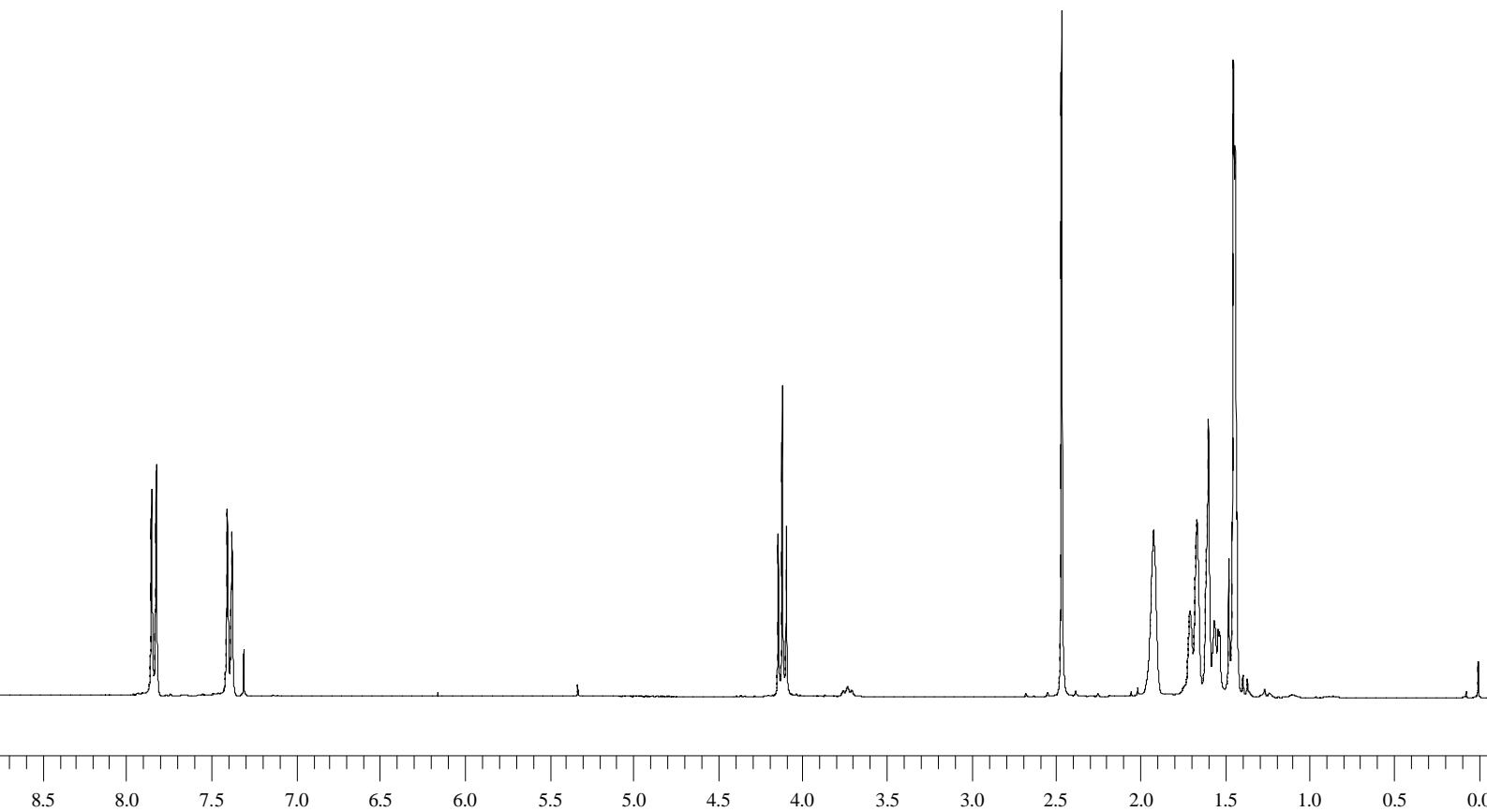
Fig A.2 ^{1}H NMR spectra of Adamantylethyl tosylate in CDCl$_3$
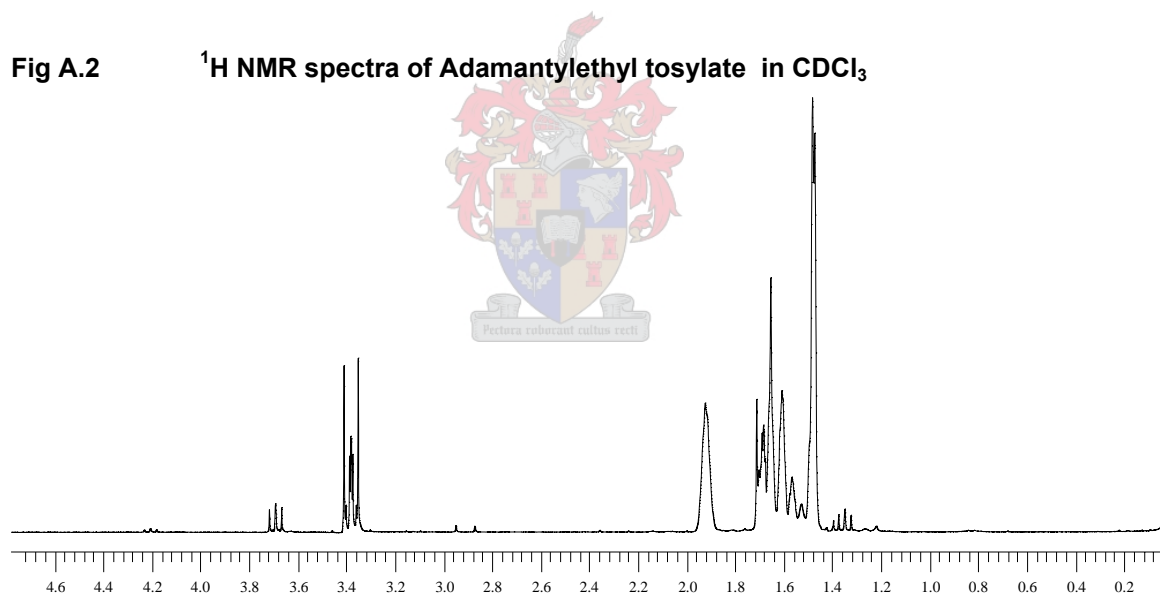
Fig A.3 ^{1}H spectra of Adamantylethyl bromide in CDCl$_3$

Fig A.4 **¹³C spectrum of Adamantylethyl bromide in CDCl₃**

Figure A.5 **¹³C NMR spectra of AdEA in CDCl₃ in CDCl₃**

Fig A.6 ^{1}H NMR spectra of Adamantylethyl acrylate in CDCl$_3$

Figure A.7 ^{13}C NMR spectra of 1-Adamantylmethyl Acrylate in CDCl$_3$

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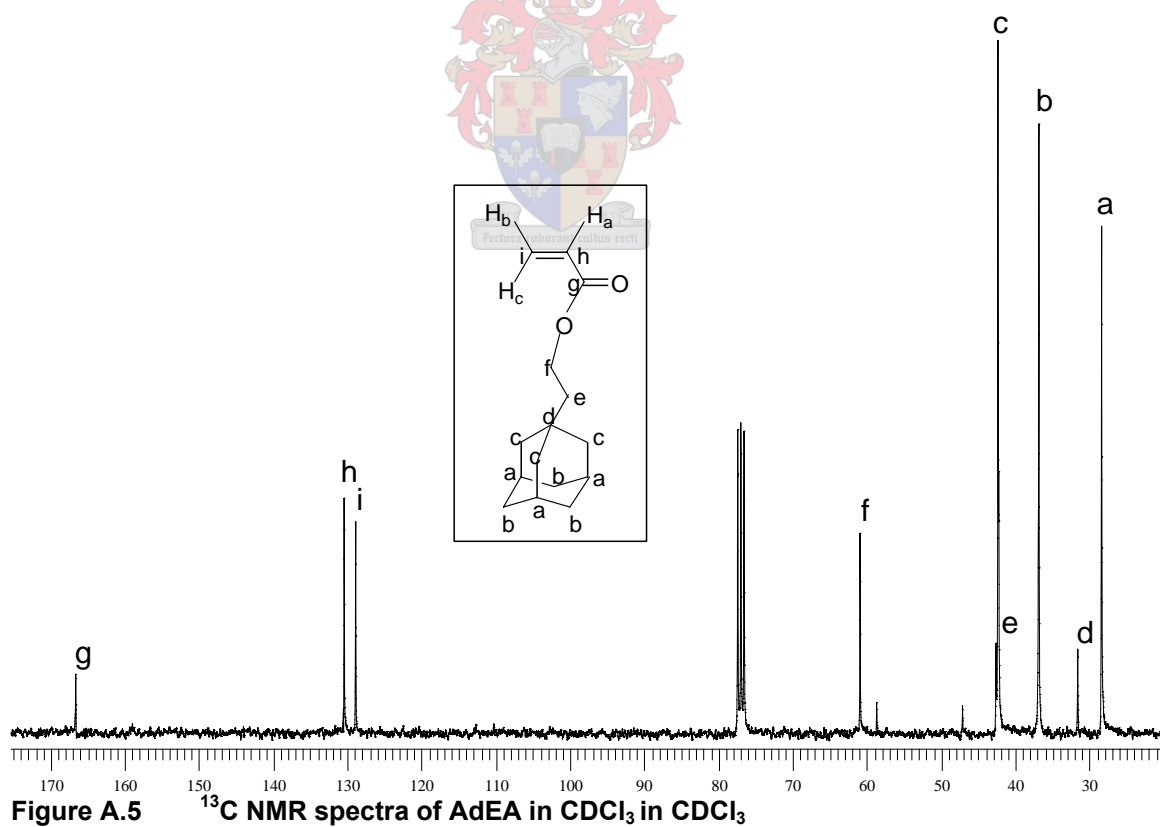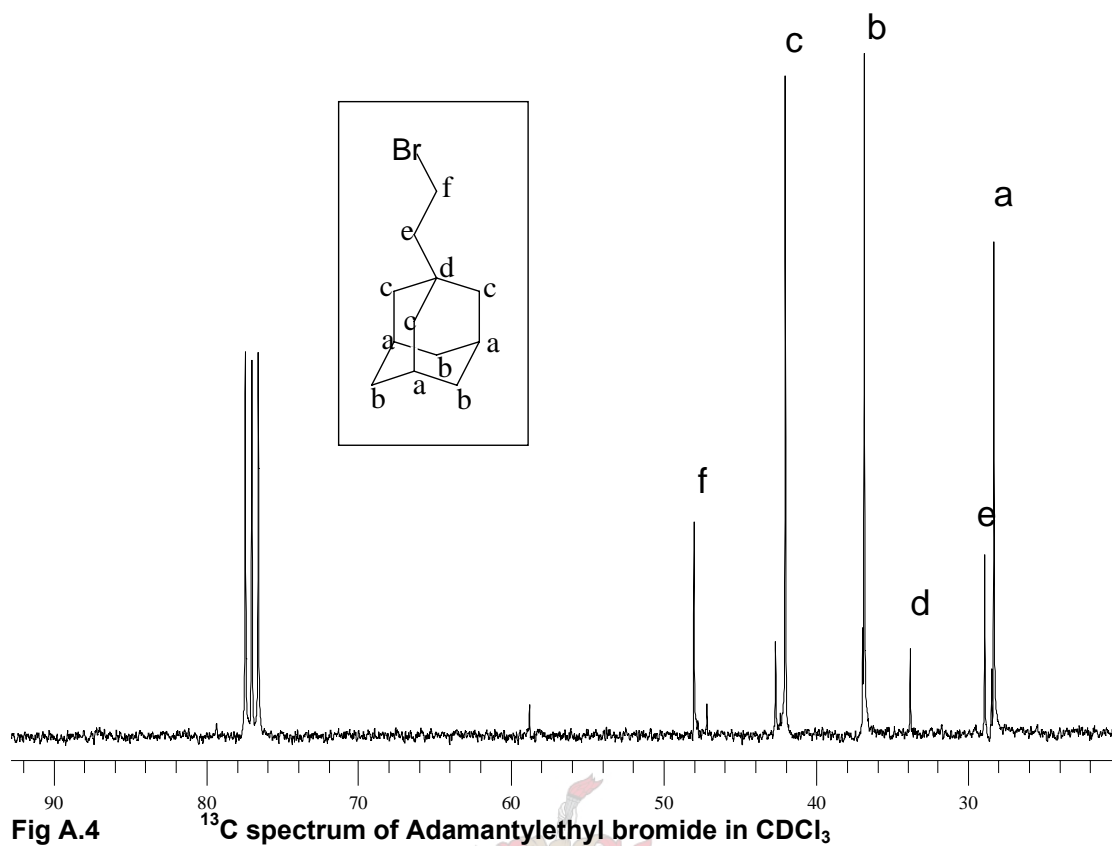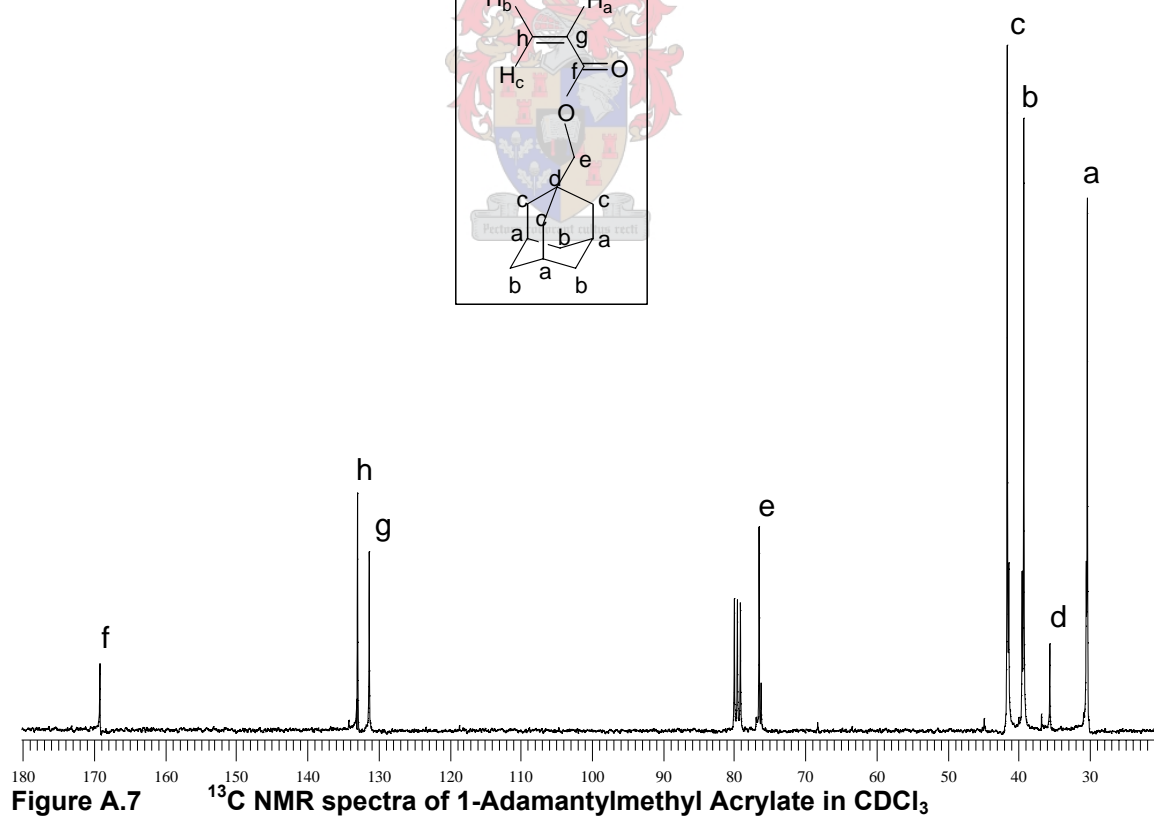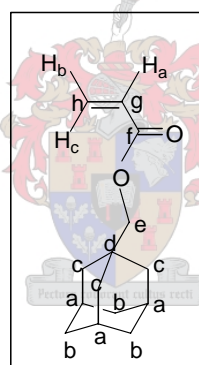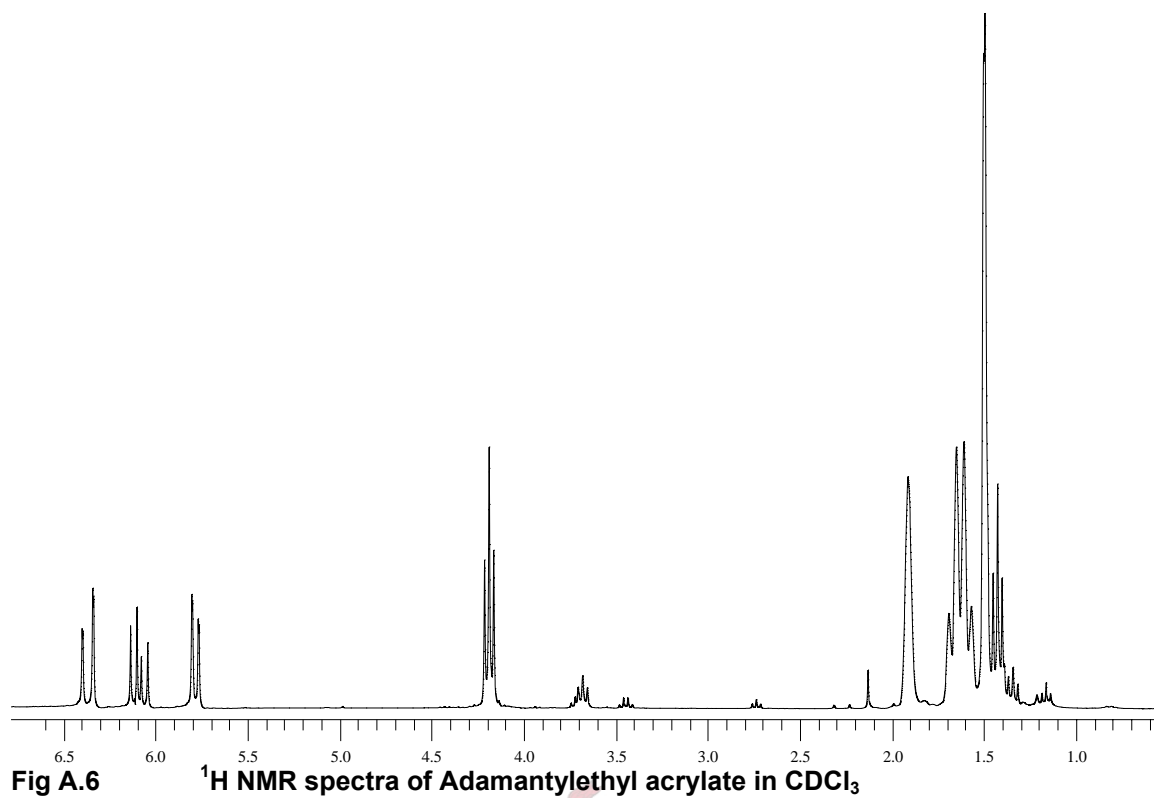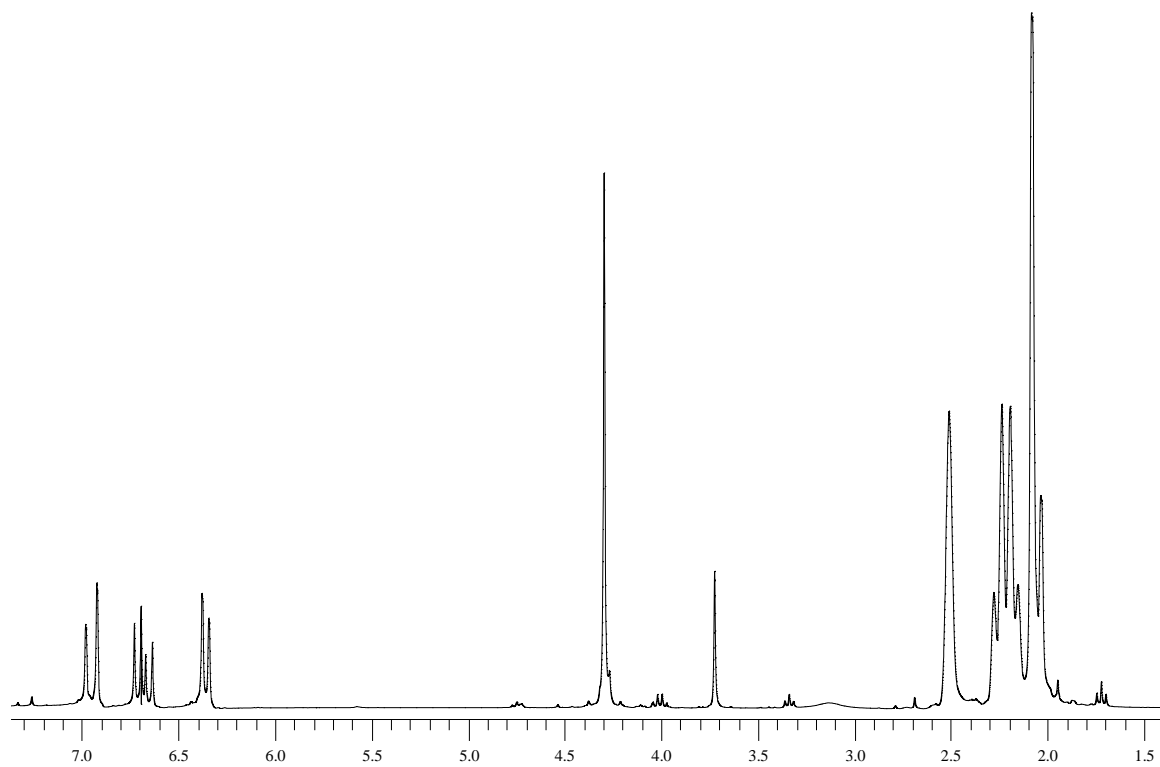
Fig A.8 ¹H NMR spectrum of Adamantylmethyl acrylate in CDCl₃
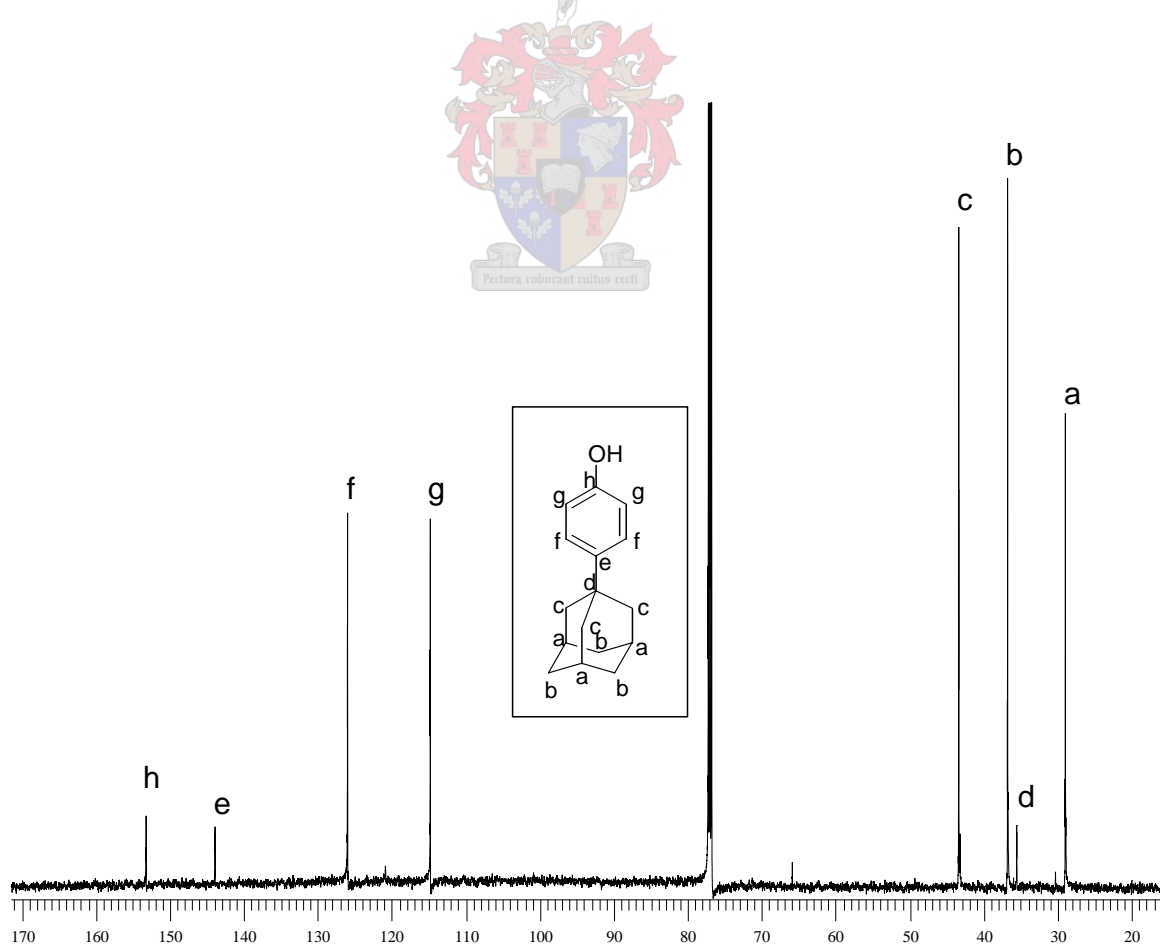
Figure A.9 ¹³C NMR Spectra of 4-(1-Adamantyl) phenol (4) in CDCl₃

103
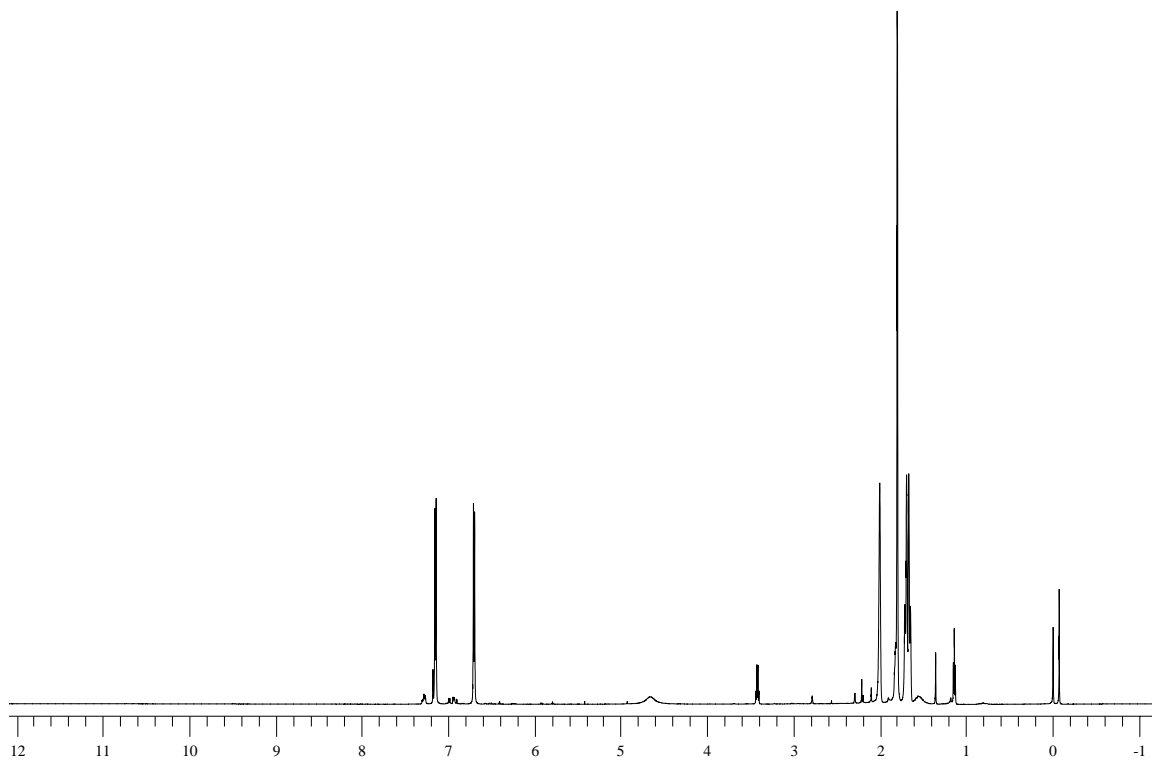
Fig A.10 ^{1}H NMR spectra of 4-(1-Adamantyl) phenol in CDCl$_3$
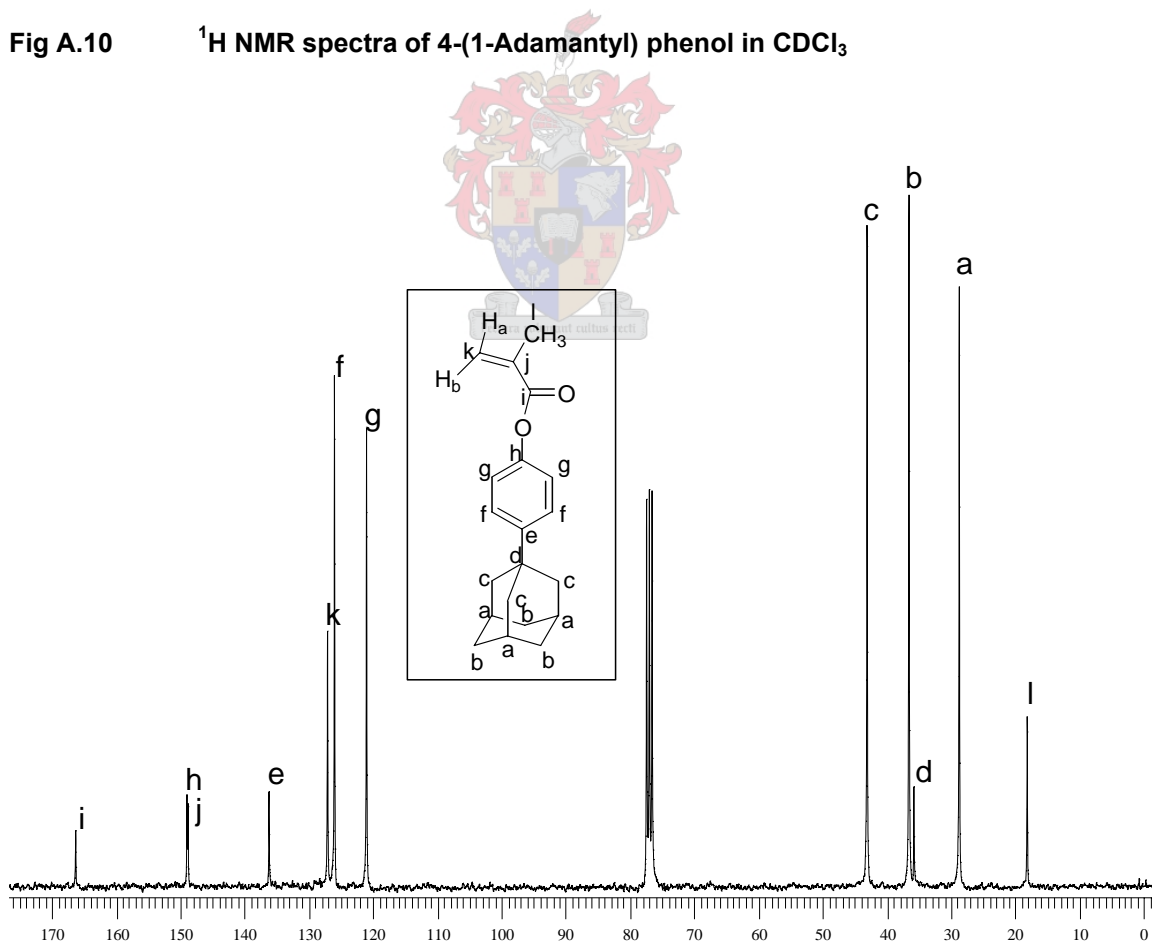
Figure A.11 ^{13}C NMR Spectra of 4-(1-Adamantyl) phenyl Methacrylate (AdPhMA,3) in CDCl$_3$

104
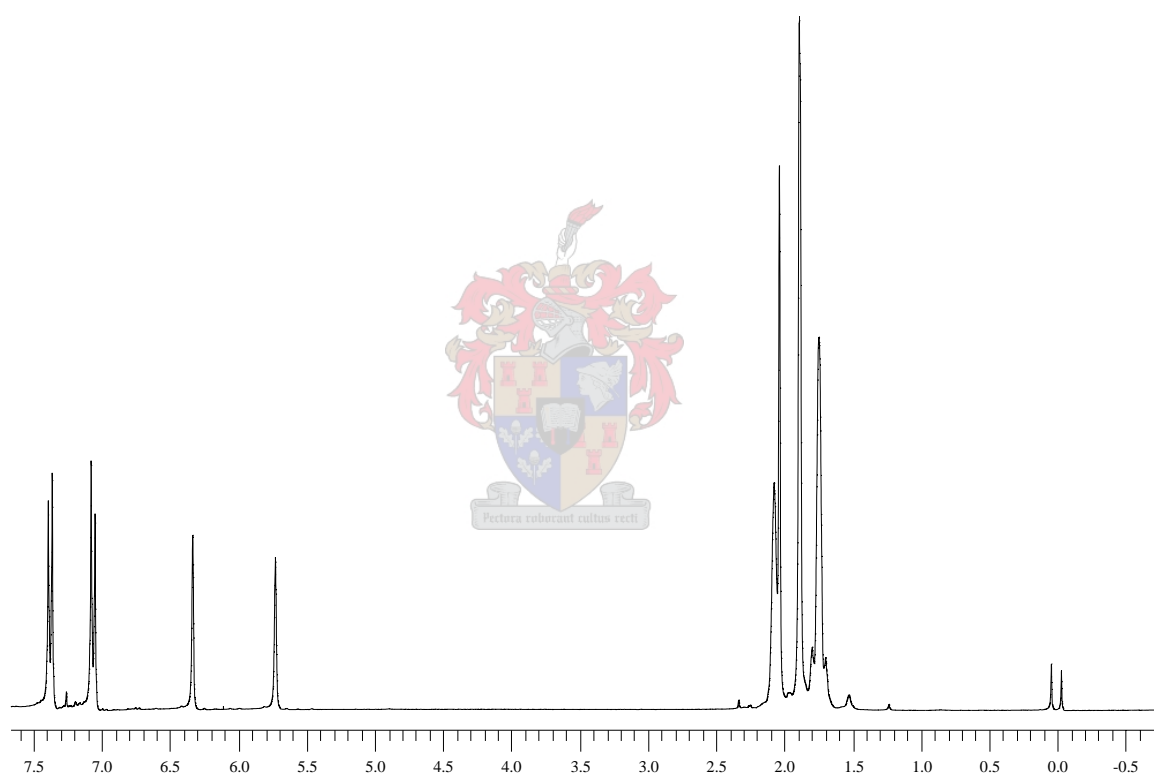
Fig A.12 ^{1}H NMR spectra of 4-(1-Adamantyl) phenylmethacrylate in CDCl$_3$
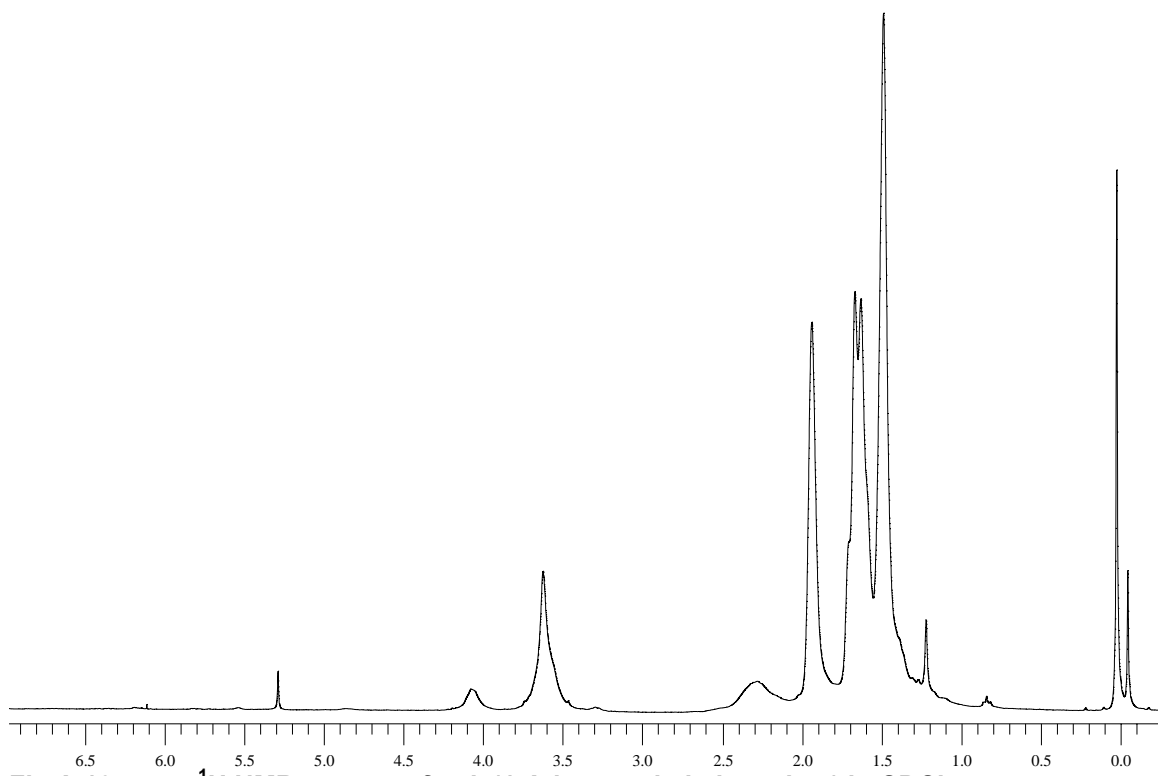
Fig A.13 ^{1}H NMR spectra of poly(1-Adamantylethyl acrylate) in CDCl$_3$
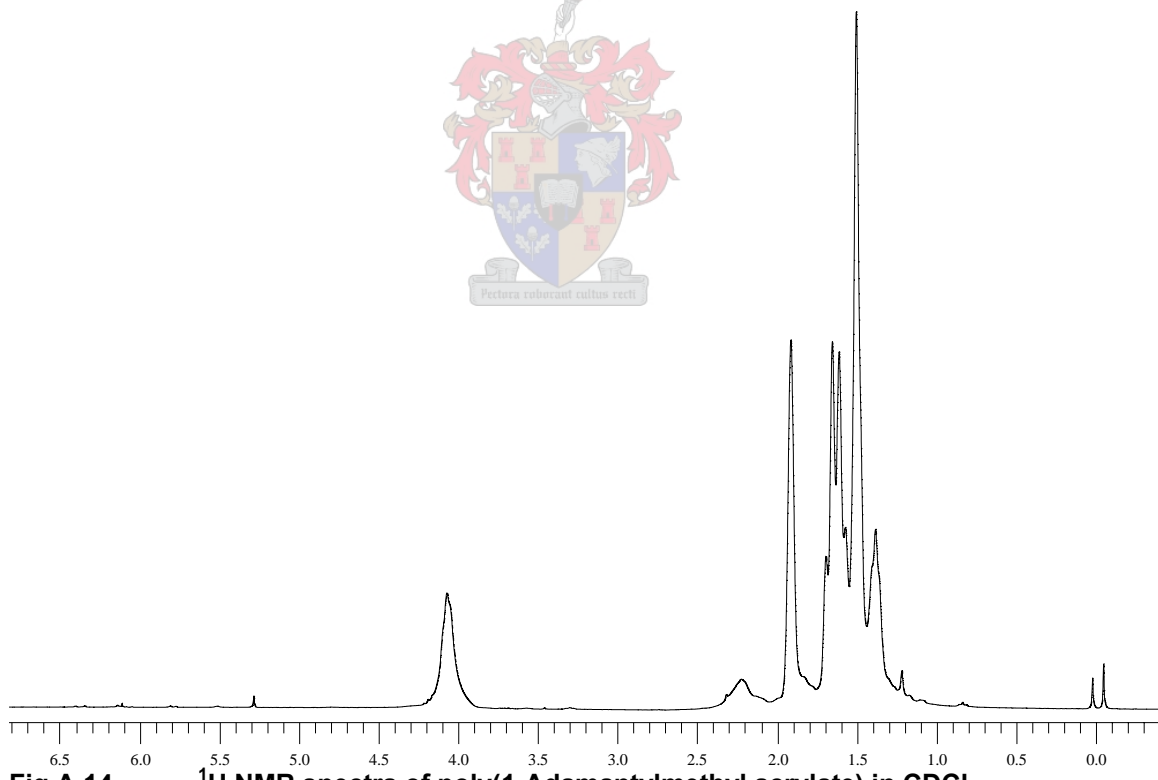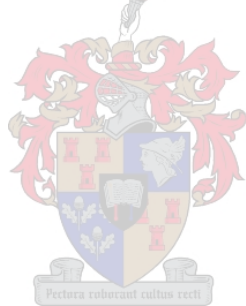
Fig A.14 ^{1}H NMR spectra of poly(1-Adamantylmethyl acrylate) in CDCl$_3$

106
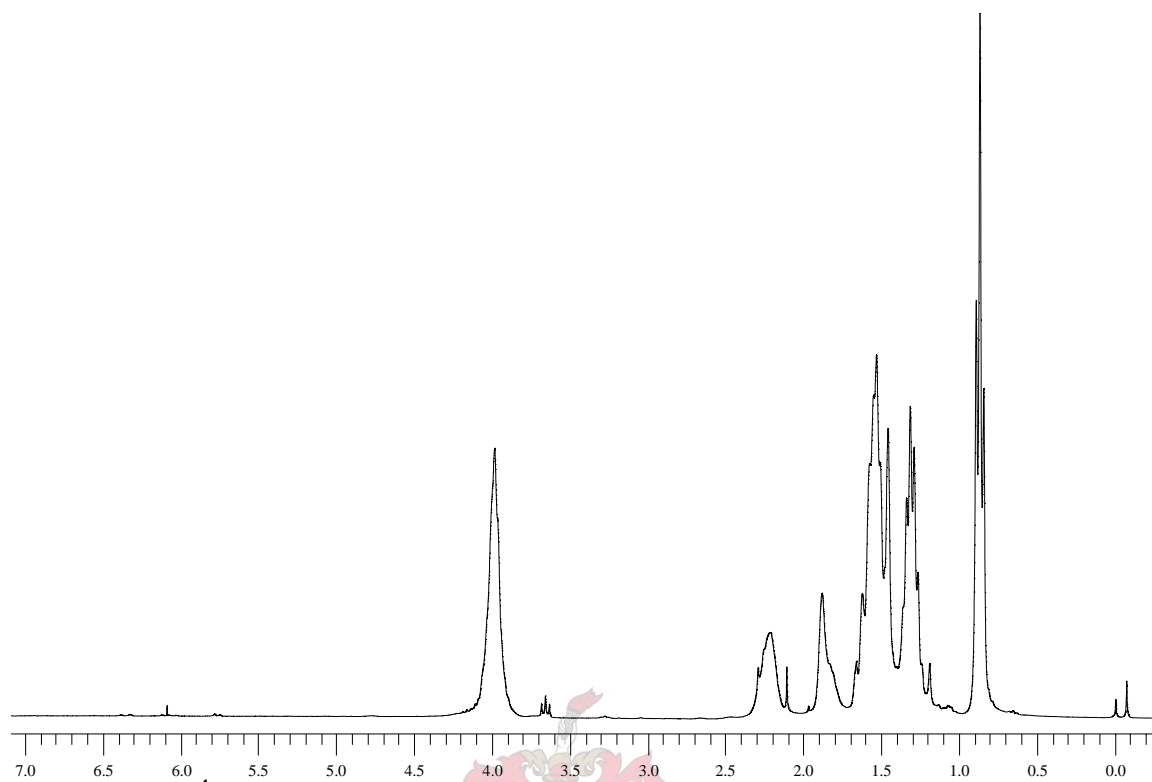
Fig A.15 ^{1}H NMR spectra of poly (1-Adamantylethyl acrylate-co-Butyl acrylate) in CDCl$_3$
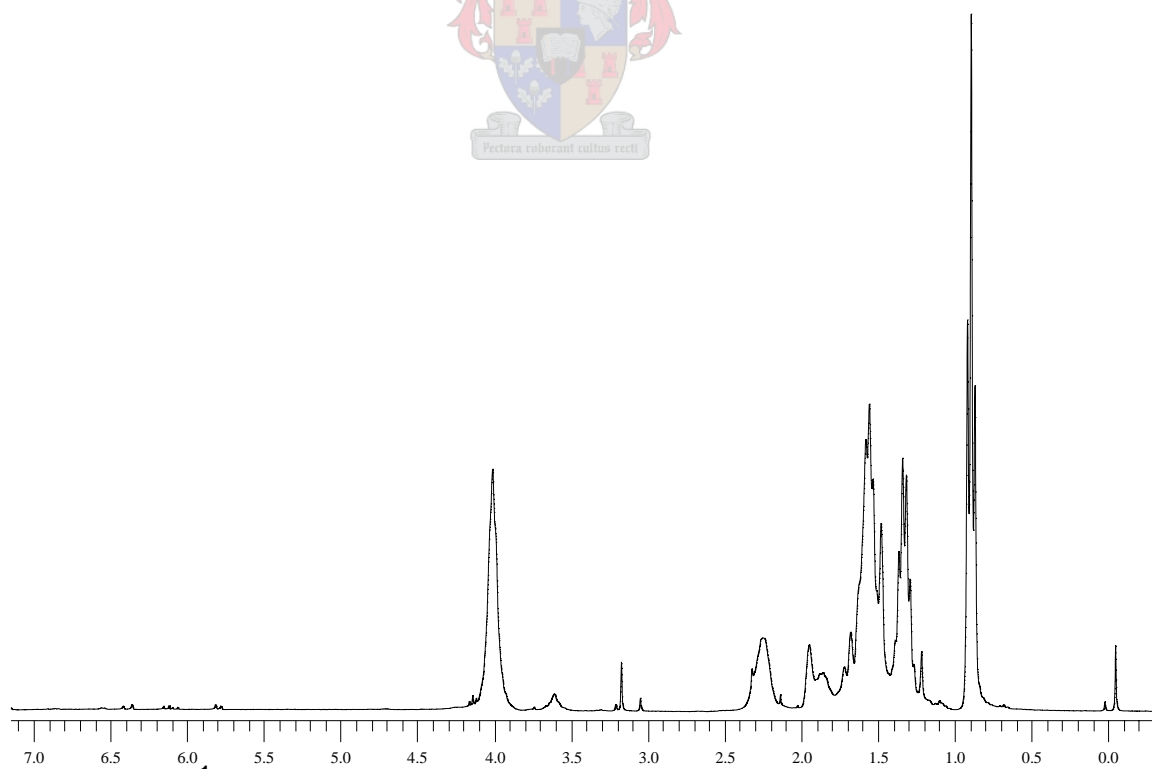
Fig A.16 ^{1}H NMR spectra of poly (1-Adamantylmethyl acrylate-co-Butyl acrylate) in CDCl$_3$
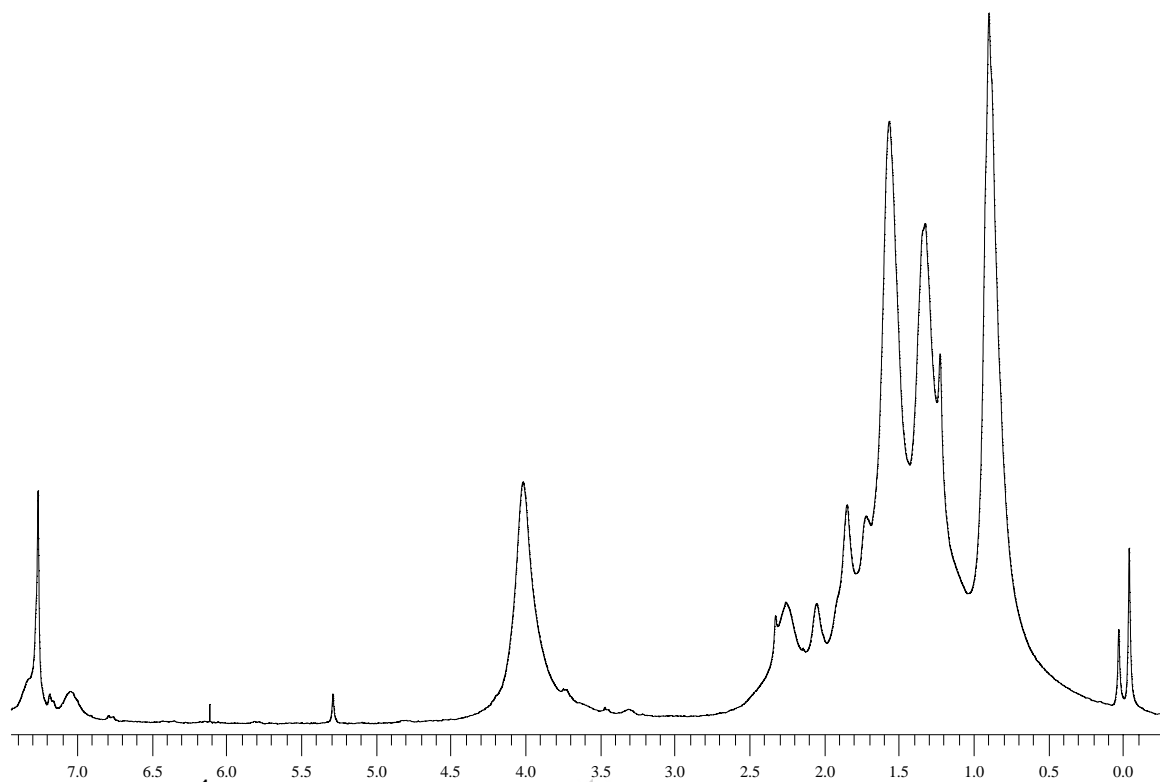
Fig A.17 ^{1}H NMR spectrum of poly 4-(1-Adamantyl)phenyl methacrylate-co-Butyl acrylate) in CDCl$_3$
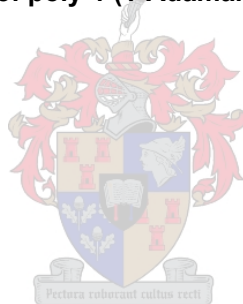
APPPENDIX B

FTIR SPECTRA
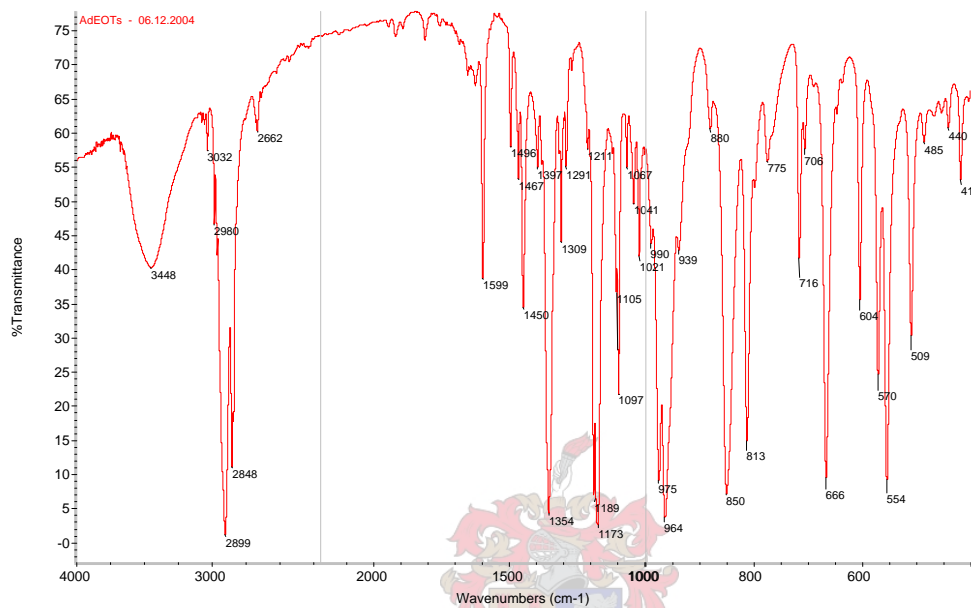
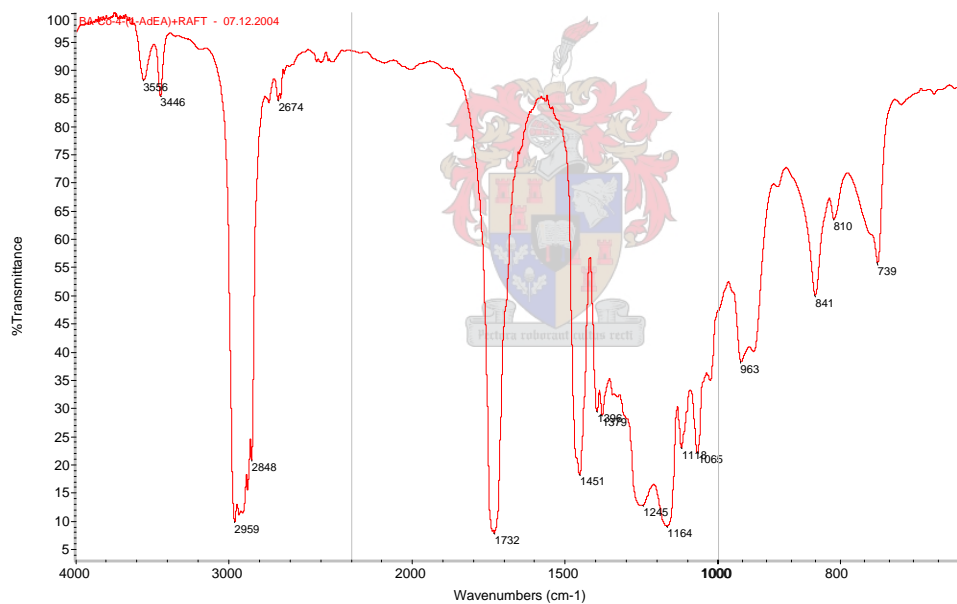**Fig B.1**   **The infrared spectra of adamantylethyltosylate (KBr plates)**
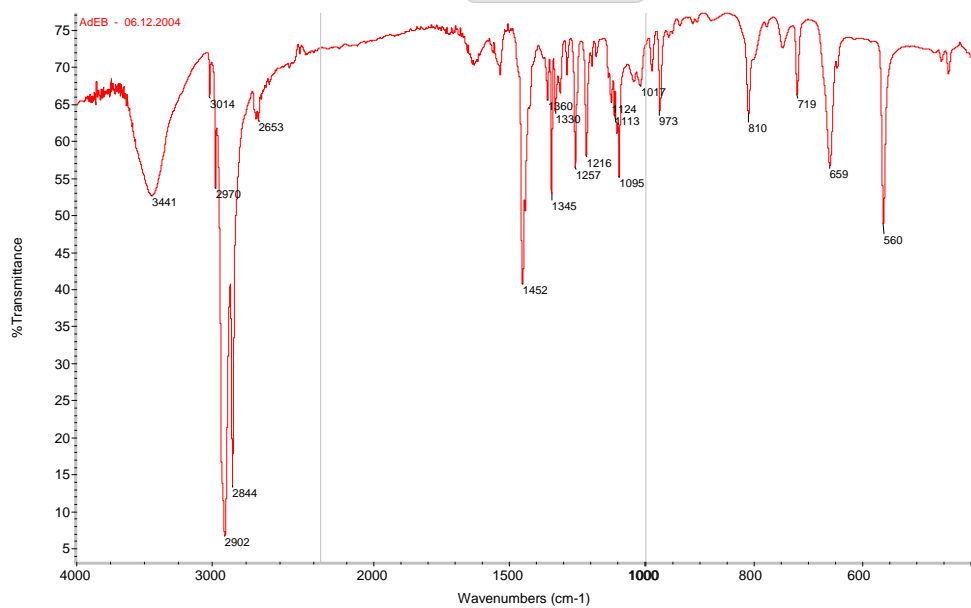
Fig B.2   **The infrared spectra of adamantylethylbromide (KBr plates)**
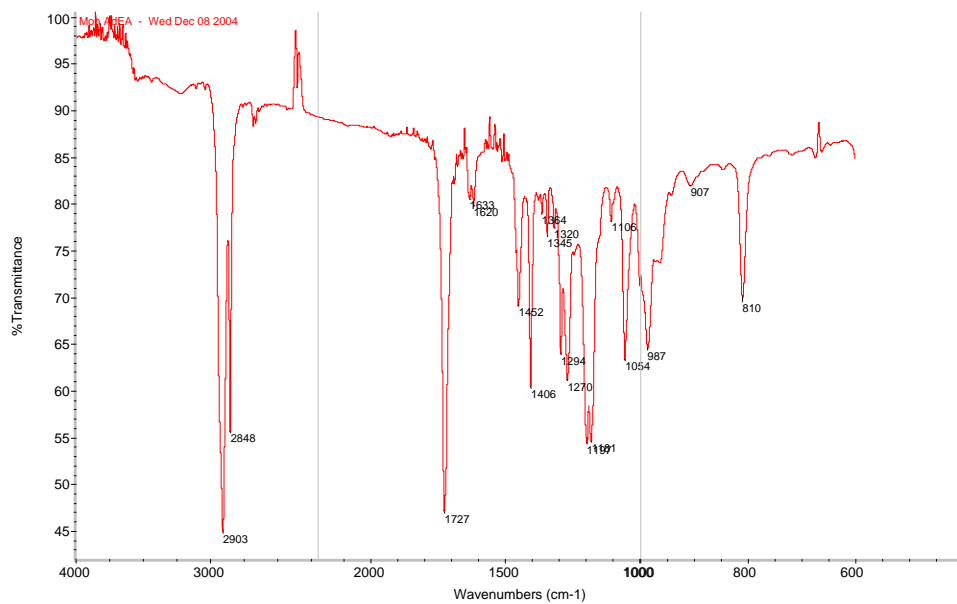
Fig B.3   **The infrared spectra of 1-Adamantylethyl acrylate (KBr plates)**
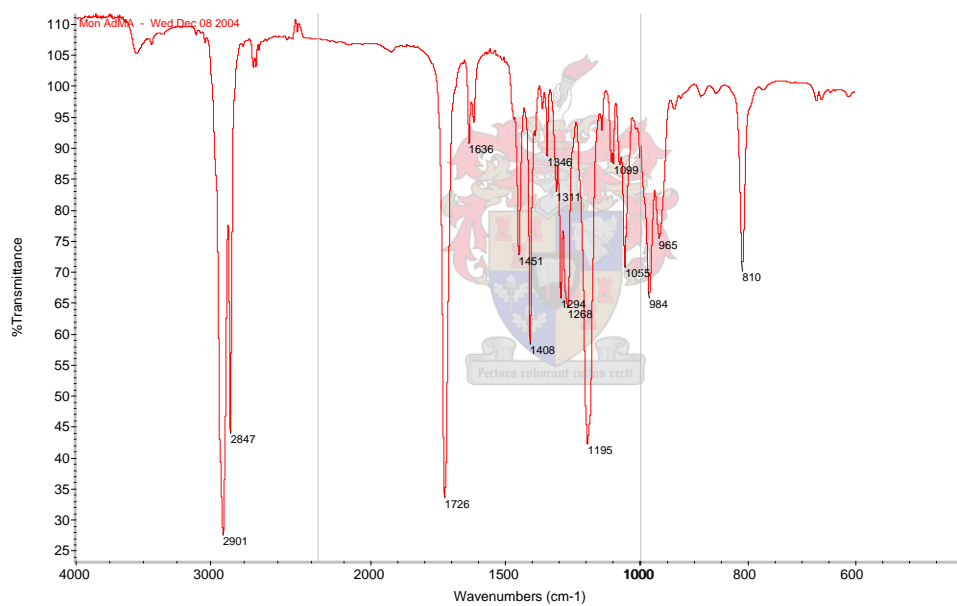
Fig B.4   **The infrared spectra of 1-Adamantylmethyl acrylate (KBr plates)**
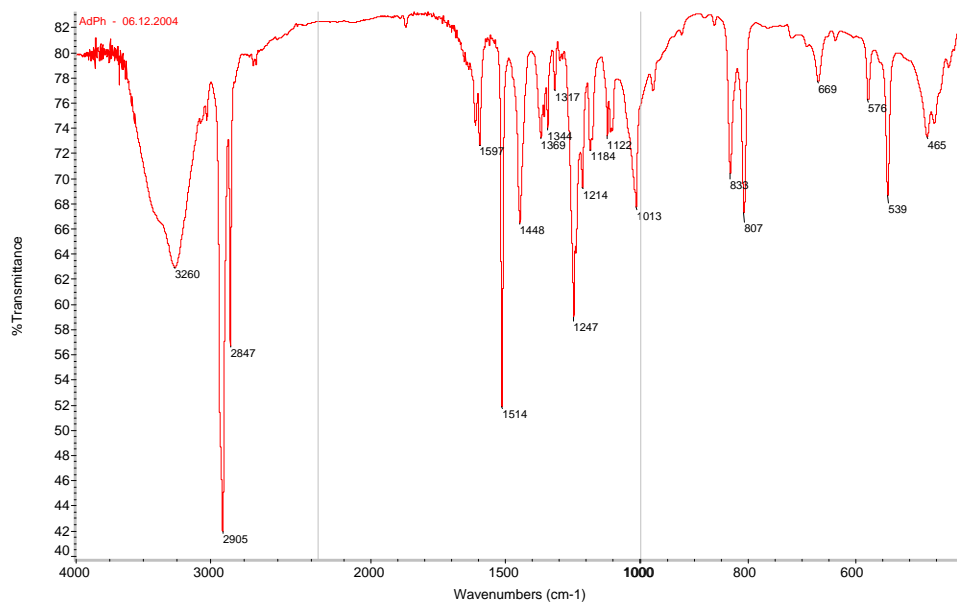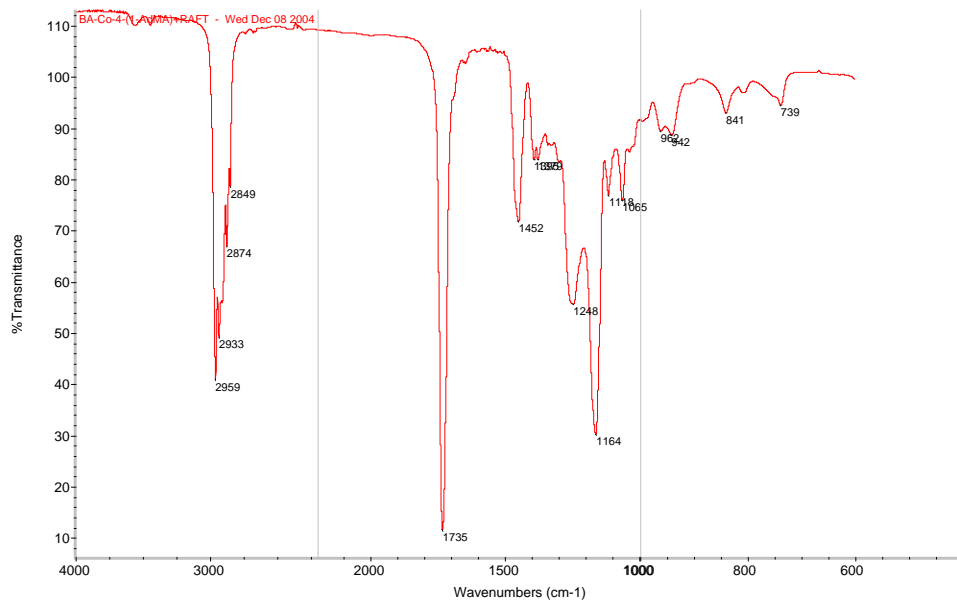
Fig B.5   The infrared spectra of 4-(1-Adamantyl) phenol (KBr plates)
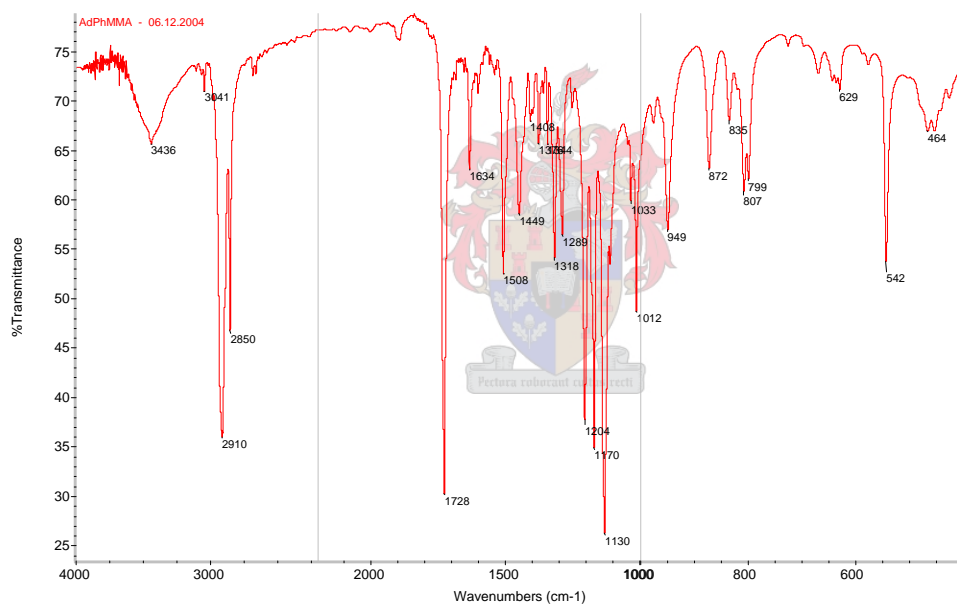
Fig B.6   The infrared spectra of 4-(1-Adamantyl) phenyl methacrylate (KBr plates)
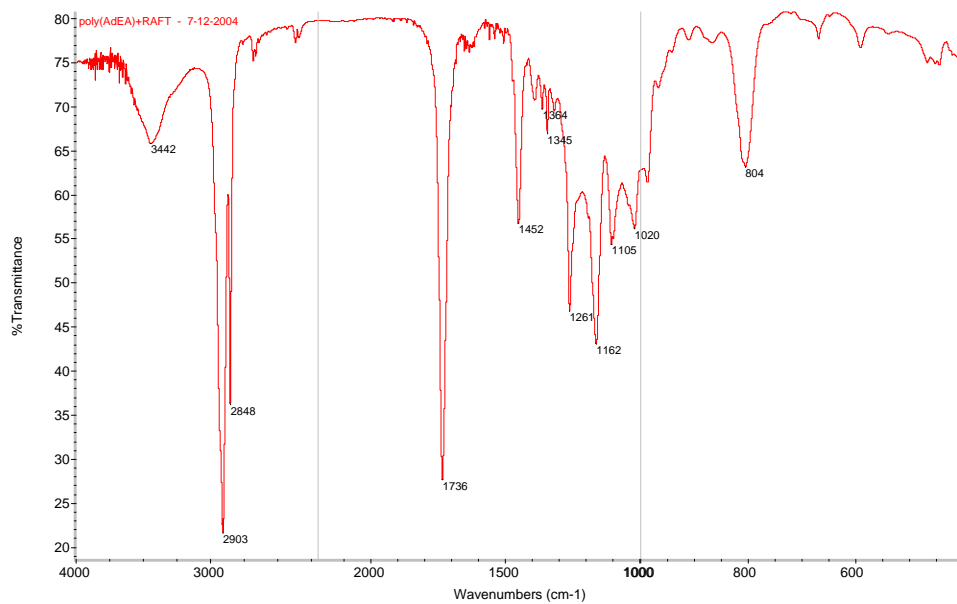
Fig B.7 **The infrared spectra of poly (1-Adamantylethyl acrylate) (KBr plates)**
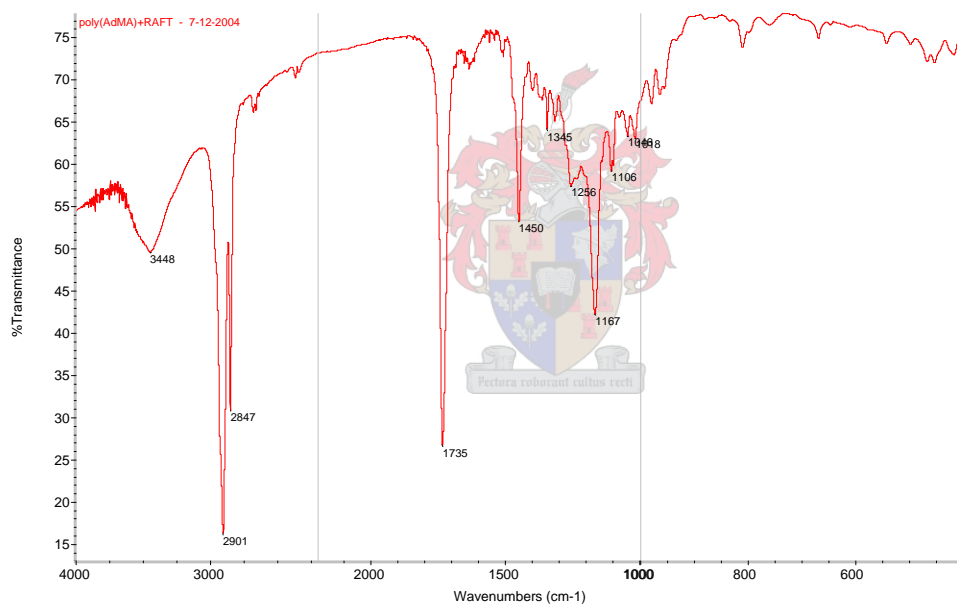
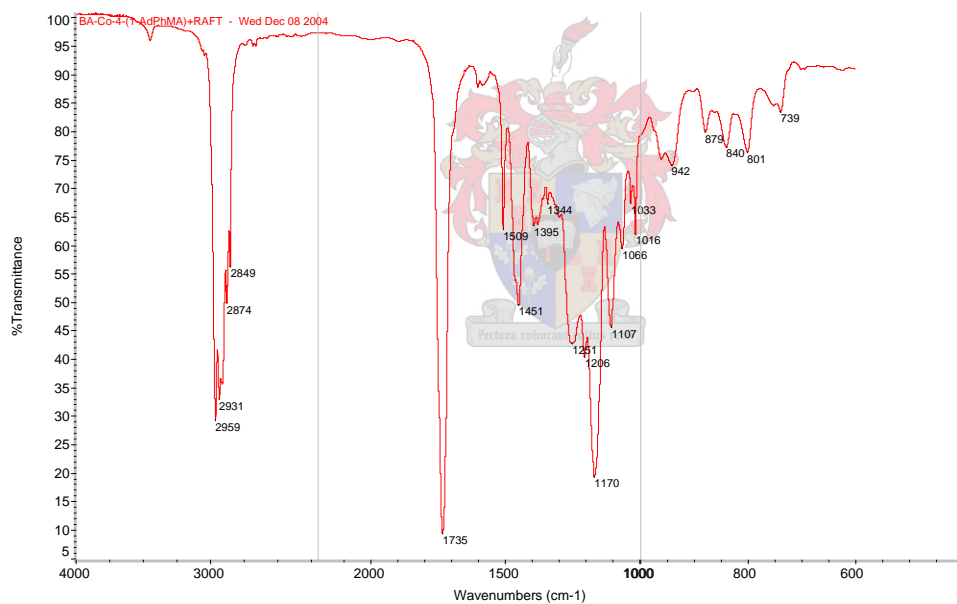**Fig B.8** **The infrared spectra of poly (1-Adamantylmethyl acrylate) (KBr plates)**
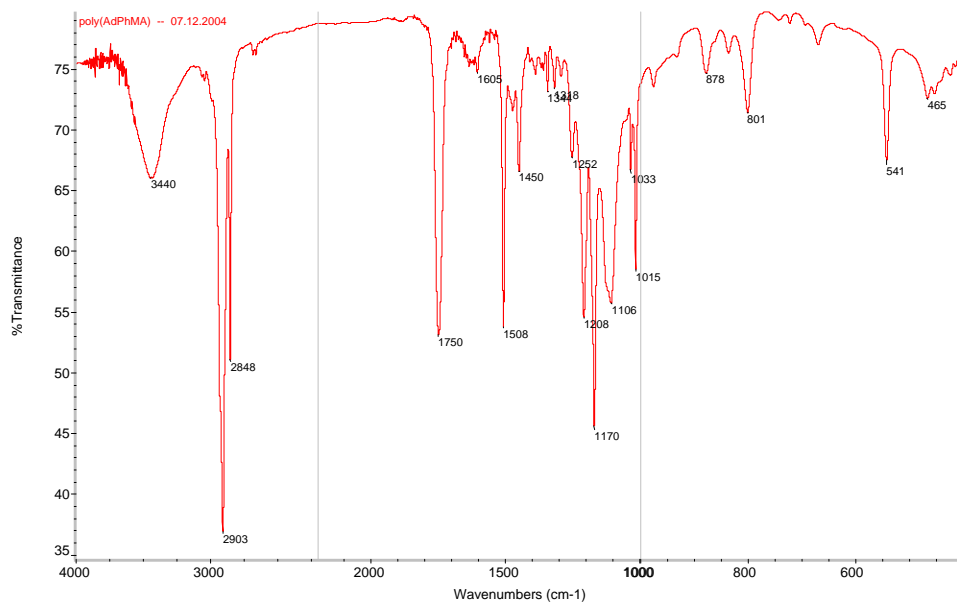
Fig B.9   **The infrared spectrum of poly 4-(1-Adamantyl) phenyl methacrylate (KBr plates)**

Fig B.10   **The infrared spectra of poly (1-Adamantylethyl acrylate-co-Butyl acrylate) (KBr plates)**
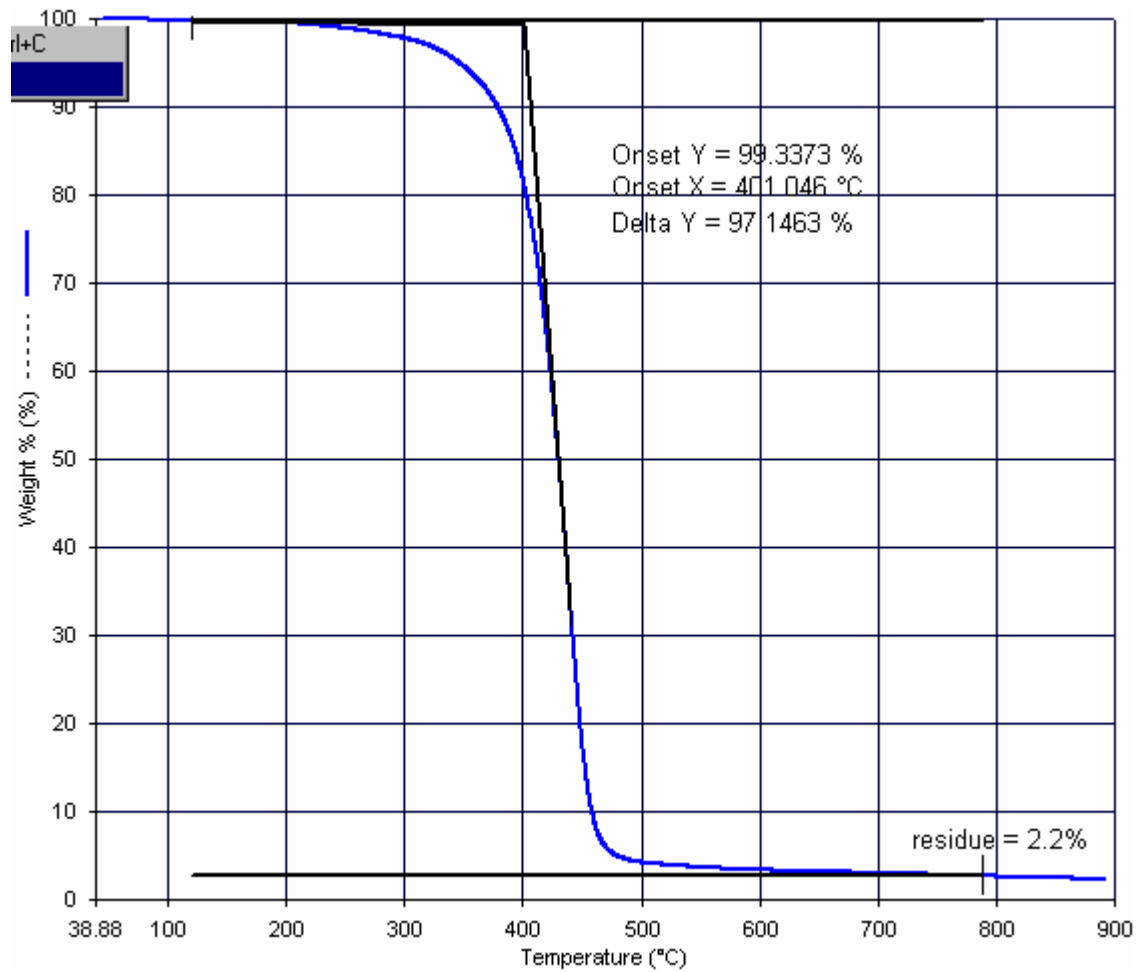
Fig B.11 **The infrared spectrum of poly (1-Adamantylmethyl acrylate-co-Butyl acrylate) (KBr plates)**

Fig B.12 **The infrared spectrum of poly [4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrlate] (KBr)**
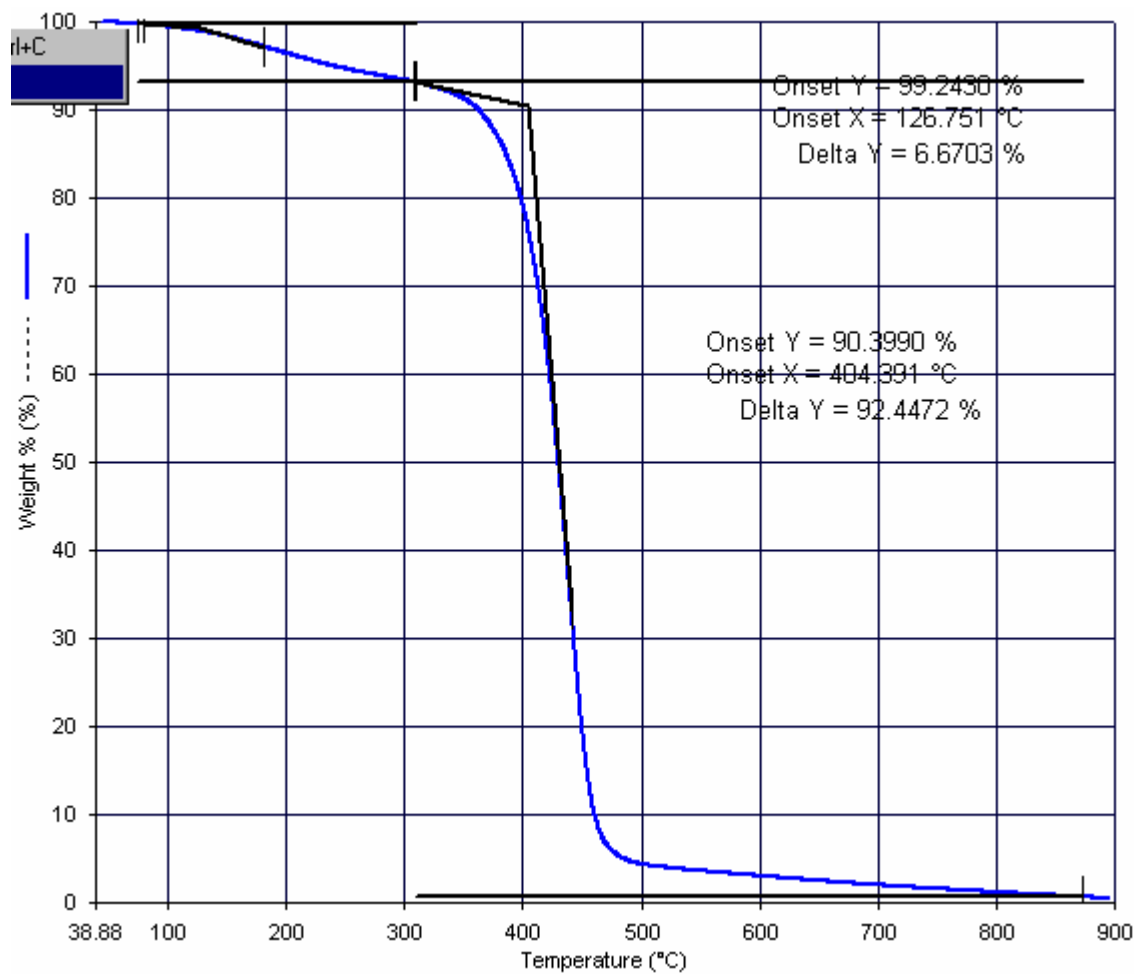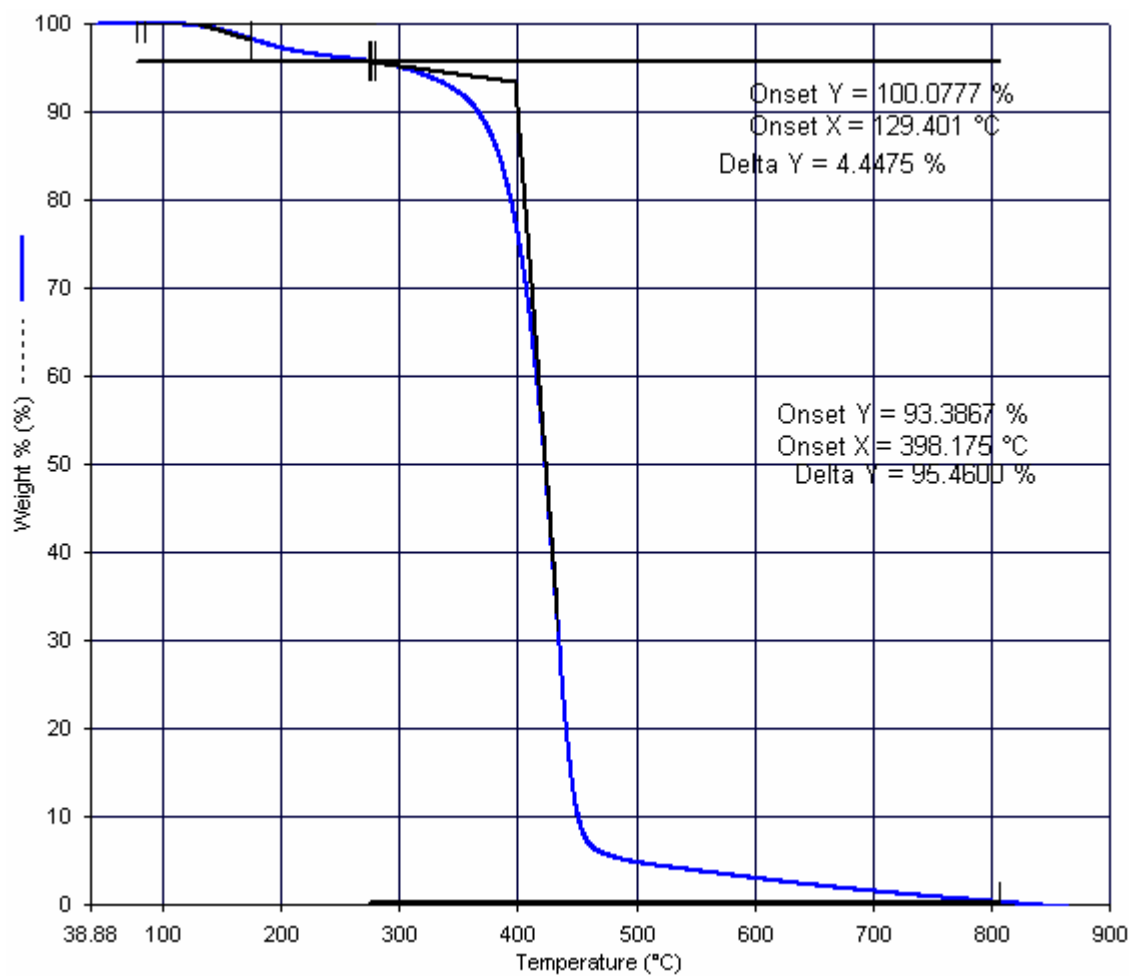
APPPENDIX C

TGA TRACES

Onset Y = 99.3373 %
Onset X = 401.046 °C
Delta Y = 97.1463 %

residue = 2.2%

Fig C.1   TheThermal Analysis of poly [4-(1-Adamantyl) phenyl methacrylate-co-Butyl acrlate]

Onset Y = 99.2430 %
Onset X = 126.751 °C
Delta Y = 6.6703 %

Onset Y = 90.3990 %
Onset X = 404.391 °C
Delta Y = 92.4472 %

Fig C.2   The Thermal Analysis of poly (1-Adamantylmethyl acrylate-co-Butyl acrylate)

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Onset Y = 100.0777 %
Onset X = 129.401 ℃
Delta Y = 4.4475 %

Onset Y = 93.3867 %
Onset X = 398.175 ℃
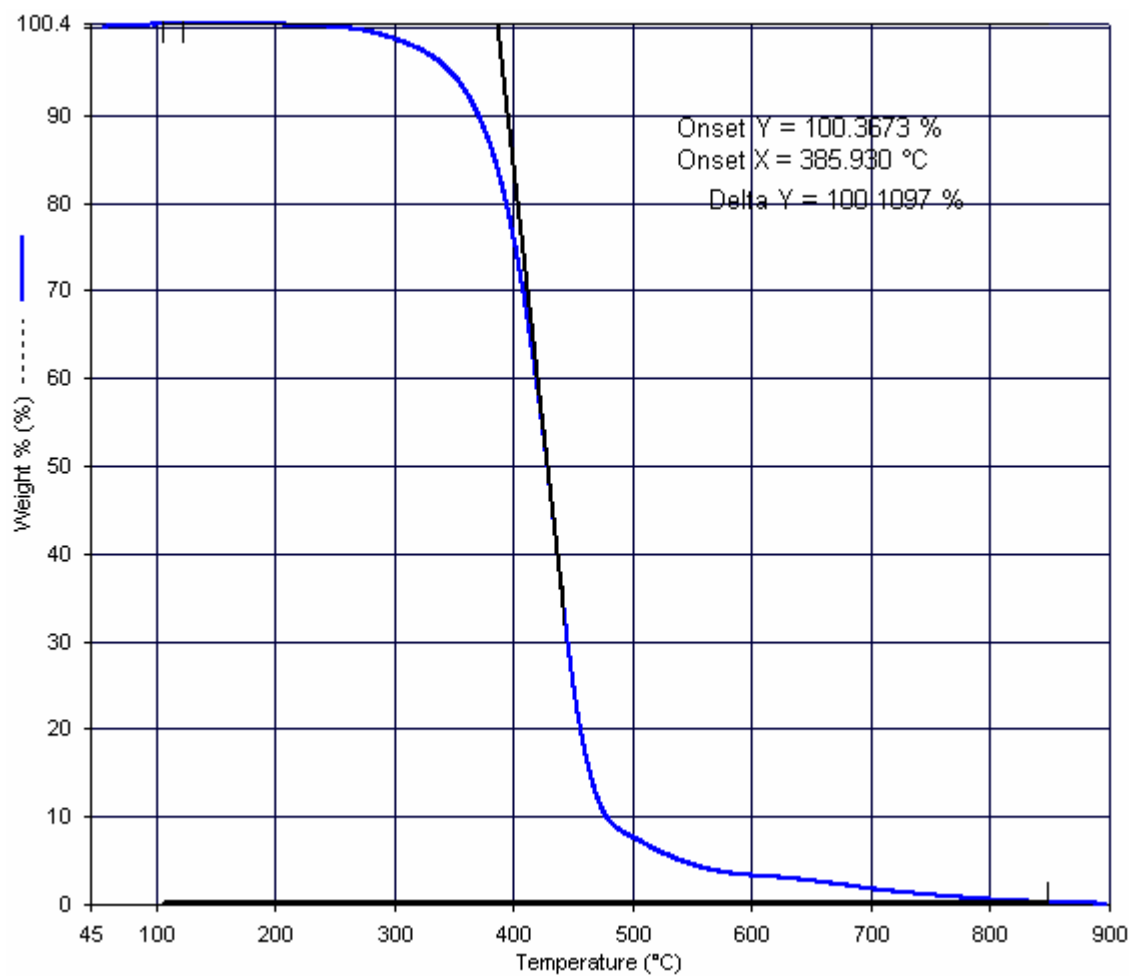Delta Y = 95.4600 %

Fig C.3   The Thermal Analysis of poly (1-Adamantylethyl acrylate-co-Butyl acrylate)

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Fig C.4   **TheThermal Analysis of poly 4-(1-Adamantyl) phenyl methacrylate**

Onset Y = 100.3673 %
Onset X = 385.930 °C
Delta Y = 100.1097 %
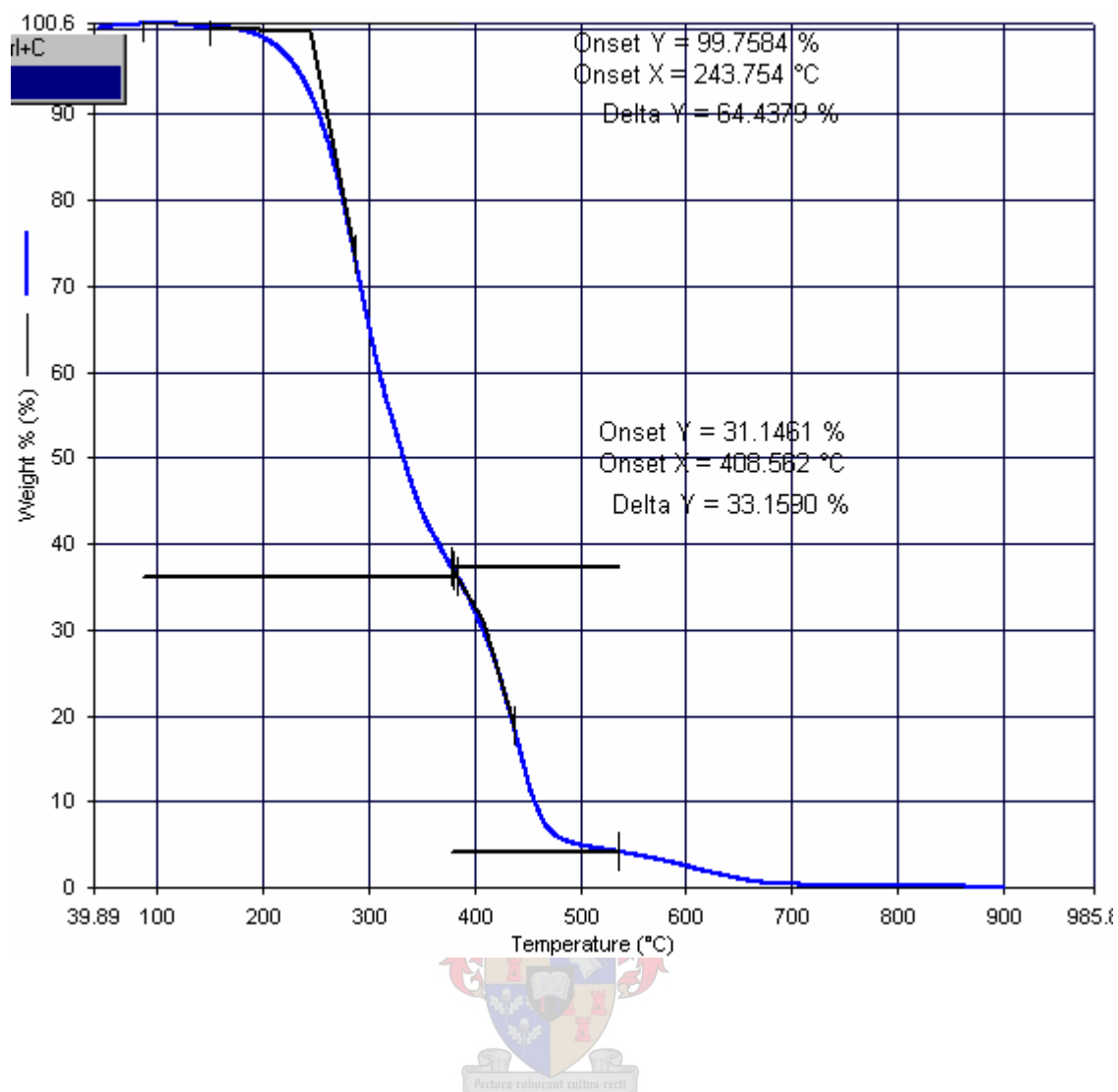
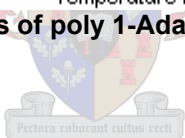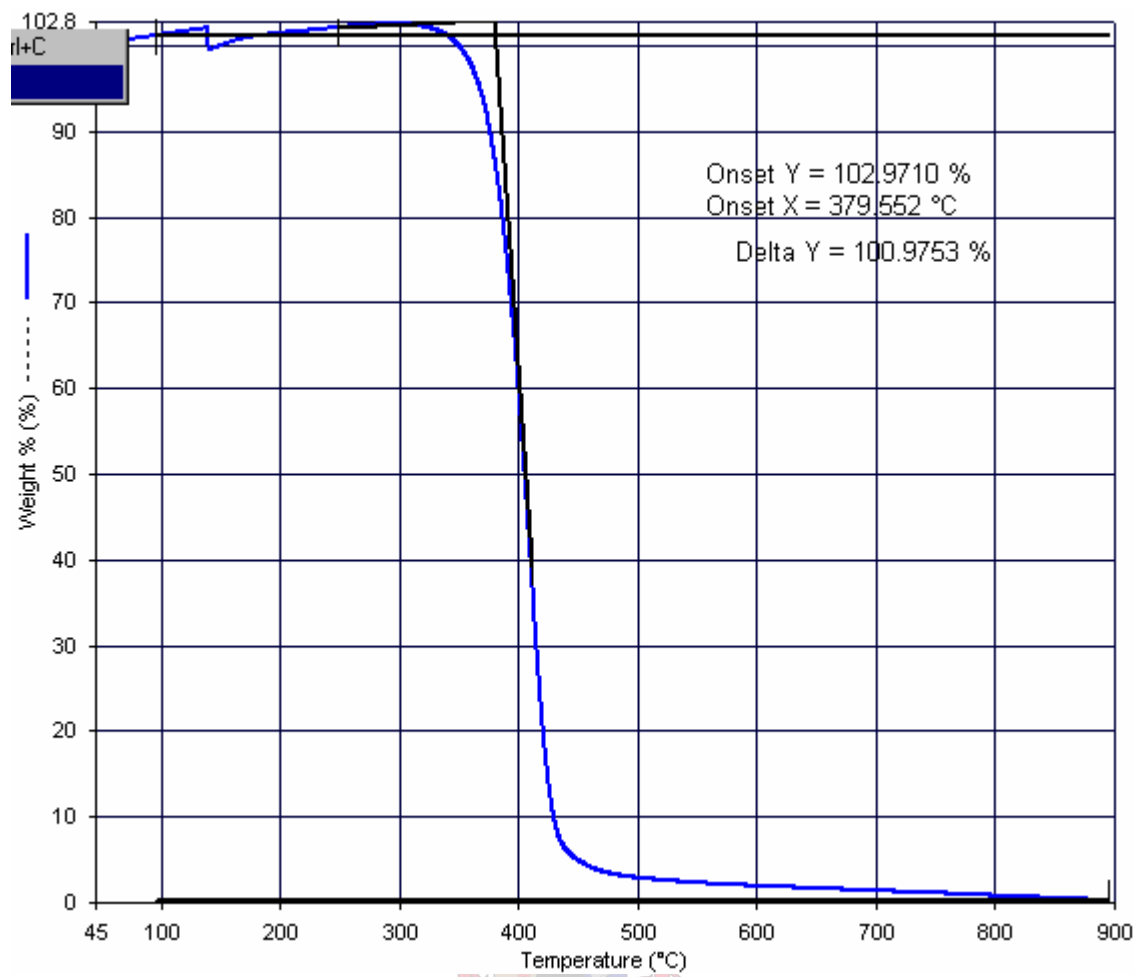**Fig C.5   The Thermal Analysis of poly 1-Adamantylethyl acrylate**

FigC.6   **The Thermal Analysis of poly (1-Adamantylmethyl acrylate)**