The synthesis of 1-butene oligomers with vinyl endgroups and their use in further reactions

by

Ahmed Al-Aeeb

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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.

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Ahmed Al-Aeeb

Abstract

This study comprises the synthesis, functionalization, and characterization of 1-butene oligomers, as well as the synthesis of oligobutene-based macro-RAFT agent.

The directed oligomerization of 1-butene was carried out with a Cp_2ZrCl_2 as a catalyst, activated with MAO as a co-catalyst (10% in toluene), in the ratio Al/Zr =1000/1. Oligomers possessing vinylidene double bonds, with low molecular weight (M_w), ranging between 800 and 2000 $g.mol^{-1}$ as confirmed by gel permeation chromatography, were obtained. The oligomers were successfully functionalized by adding hydroxyl functionality to the vinylidene double bond using oxymercuration-demercuration reaction, and as a result hydroxy-terminated oligobutenes were obtained.
Characterization techniques such as ^{1}H NMR, ^{13}C NMR, GC-MS and FTIR confirmed the successful synthesis and functionalization of 1-butene oligomers.

The hydroxy-terminated oligobutenes were used to prepare an oligobutene-based macro-RAFT agent. The synthesis of the macro-RAFT agent was carried out with an esterification reaction between the hydroxy-terminated oligobutenes and an acid functionalized RAFT agent. The successful synthesis of the macro-RAFT agent was confirmed by ^{1}H NMR, ^{13}C NMR, FTIR, and UV spectroscopy. The chain transfer ability of the macro-RAFT agent to induce living characteristics in free radical styrene polymerization was investigated with respect to molecular weight control and kinetic behaviour. The macro-RAFT agent was identified as suitable RAFT agent, yielding polystyrene-b-oligobutnes with low polydispersities and molecular weight ranging from 3000 to 40000 g/mol.

Online 2D chromatography was used to investigate the chemical composition distribution as well as the molecular weight distributions of PS-b-oligobutenes prepared by free radical polymerization mediated with the macro-RAFT agent. The 2D chromatography analysis confirmed the incorporation of the oligomers into the structure of the macro-RAFT agent as well as into the polystyrene obtained.

DSC analysis was used to investigate the effect on thermal properties caused by the incorporation of the oligobutenes segments into the PS structure. T_g values obtained for two samples with different molecular weights suggested that the incorporation of the oligobutenes into a polystyrene structure has no major effect, especially on the T_g.

Opsomming

Hierdie studie het die sintese, funksionalisering en karakterisering van 1-buteen oligomere behels, sowel as die sintese van oligobuteen-gebaseerde makro-RAFT-verbindings.

Die oligomerisasie van 1-buteen is uitgevoer deur gebruik te maak van Cp_2ZrCl_2 as katalis en MAO as kokatalis (10% in tolueen), en wel in die verhouding Al/Zr:1000/1. Oligomere met vinilideen dubbelbindings, lae molekulêre massa ($\overline{M}_w$), te wete tussen 800 en 2 000 g.mol^{-1} is verkry. Die oligomere is suksesvol gefunksionaliseer deur ’n hidroksielgroep deur middel van ’n addisie-reaksie aan die vinilideen dubbelbinding te voeg m.b.v ’n oksimerkurering-demerkureringsreaksie. Karakteriseringstegnieke soos ^{1}H KMR, ^{13}C KMR, GC-MS en FTIR spektroskopie is gebruik om die suksesvolle sintese, en funksionalisering van 1-buteenoligomere te bevestig.

Die hidroksi-getermineerde oligobutene is as uitgangstof gebruik vir die sintese van ’n oligobuteen-gebaseerde makro-RAFT verbinding. Hierdie sintese is via ’n esterifikasie-reaksie uitgevoer, waar die hidroksi-oligobuteen en ’n karboksielsuur-bevattende RAFT-verbinding betrokke was. Suksesvolle sintese van die makro-RAFT-verbinding is deur ^{1}H KMR, ^{13}C KMR, FTIR, en UV spektroskopie bevestig. Die vermoë van die makro-RAFT-verbinding om deur kettingoordrag lewende vryradikaalpolimerisasie van stireen teweeg te bring is ondersoek. Sodoende is polistireen-b-oligobuteen verkry met lae polidispersiteit en molekulêre massa, wat gewissel het van polimeer to polimeer, tussen 3000 en 40 000 g.mol^{-1}.

Twee-dimensionele (2D) chromatografie is gebruik om die verspreiding in chemiese samestelling sowel as molekulêre massa van PS-b-oligobuteen polimere, berei deur makro-RAFT gemedieerde vryradikaalpolimerisasie te ondersoek.

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Finally I would like to thank all the Libyan students for their encouragement and help, and for making life more enjoyable.

Dedication

I dedicate this work to my parents and family.

Contents

List of figures

List of schemes

List of tables

List of Symbols

a	alpha
λ	Absorbance
I	Initiator
$\mathbf{I}^{\bullet}$	Initiator
[I]	Initiator concentration
[I]o	Initial concentration of initiator
kd	Decomposition rate coefficient
LnM-R	Metal alkyl complex
M	Monomer
$M^{\bullet}$	Propagating active radical
P•	Active species
P_n	Polymeric chain of n-degree of polymerisation
$\mathbf{P_n^{\bullet}}$	Propagating radical of n-degree of polymerisation
R_p	Propagation rate of oligomerization
R_t	Termination rate of oligomerization
R	RAFT agent leaving group
R•	RAFT agent leaving group radical
R-X	Alkyl halide
Z	RAFT agent stabilizing group
$\overline{M}_n$	Number average molar mass
$\overline{M}_w$	Weight average molar mass
$[M]_o$	Initial concentration of monomer
$[RAFT]_o$	Initial concentration of RAFT agent
$\overline{M}_{n\ theory}$	Theoretical number average molar mass
$MW_{monomer}$	Molecular weight of monomer

MW_{RAFT}	Molecular weight of RAFT agent
[RAFT]	RAFT agent concentration
$\overline{X}_{n0}$	Degree of polymerization in the absence of a transfer agent
$\overline{X}_{n}$	Degree of polymerization
C_T	Transfer constant
k_s	Transfer rate coefficient
K_{tr}	Transfer rate coefficient
K_p	Propagation rate coefficient
K_t	Termination constant
ν_p	Rate of propagation
ν_t	Rate of termination
ν_i	Rate of initiation
f	Radical efficiency
t	Time
T_g	Glass transition temperature

List of Acronyms

AIBN	2,2'-azobis(isobutyronitrile)
[Al/Zr]	Molar ratio of methylalumoxane to zirconocene
ATRP	Atom transfer radical polymerisation
CCD	Chemical composition distribution
CSIRO	Commonwealth Scientific & Industrial Research Organization
^{13}C NMR	Carbon-13 Nuclear magnetic resonance
$C_nH_{2n+1}O^+$	Oxonium ion
2D	Online two-dimensional chromatography
DSC	Differential scanning calorimetry
EI^+	Positive electron impact ionization
FT-IR	Fourier-transform infrared spectroscopy (FT-IR)
GPC	Gel permeation chromatography
GC	Gas chromatography
GC-MS	Gas chromatography coupled with mass spectroscopy
^1H NMR	Proton nuclear magnetic resonance
HPLC	High performance liquid chromatograph
IR	Infrared
IUPAC	International Union of Pure and Applied Chemistry
LAC	Liquid adsorption chromatograph
LCCC	Liquid chromatograph at critical conditions
M	Molar (mol/L)
MMD	Molar mass distribution
MAO	Methylalumoxane
NMR	Nuclear magnetic resonance
NMP	Nitroxide mediated polymerisation
PDI	Polydispersity index
Ph	Phenyl ring
ppm	Parts per million

PS	Polystyrene
RAFT	Reversible addition-fragmentation chain transfer
RI	Refractive index
SEC	Size exclusion chromatography
THF	Tetrahydrofuran
UV	Ultraviolet

Chapter1 Introduction and objectives

1.1 Introduction

The increasing demands on polymeric products, together with the rapid development of polymer science in the last few decades, has led to the increasing use of materials such as oligomers in efforts to obtain better understanding of polymer chemistry. Synthetic oligomers are useful as reference substances for analytical purposes, and for physical and physiochemical investigations[1]. They can be used as models and intermediate macromonomers to study polymerization mechanisms and kinetics. Moreover, the functionality of the chain end groups of many oligomers is the key to obtaining materials for numerous and varied applications[2-4]

Research in the field of catalytic oligomerization is generally focussed on olefin oligomers, as these materials are intermediates for specialty chemicals. The use of zirconocene dichloride/MAO catalyst systems provide a significant approach to direct oligomerization of higher α-olefins such as 1-butene. The high regioselectivity in the coordination sphere of the zirconium centre and the chain-termination reaction, which generally proceeds via β-hydrogen elimination, give oligomers with double-bond end groups, mostly of the vinylidene type[5-8]. Such double bonds can easily be functionalized. Besides the possibility of preparing novel copolymers containing short olefin side chains, α-olefin oligomers or their derivatives may be utilized as (macro) monomeric building blocks for novel graft copolymers containing oligo-olefin side chains[3,9-14].

Free radical polymerization is the most commonly practised method of addition polymerization and is used almost exclusively for the preparation of polymers from olefinic monomers. Although free radical polymerization offers several advantages, these are still overshadowed by the disadvantages which include loss of control over molecular weight, molecular weight distribution and chain architecture during the polymerization. The emergence of "living" free radical polymerization techniques overcame these limitations. RAFT polymerization[15-17] allows the synthesis of star-, comb- or block copolymers with good control over molecular weight and molecular weight distribution. This technique is applicable to a large range of monomers, and does not require stringent

reaction conditions. RAFT "agents" are compounds such as thioesters, thiocarbonates, dithiocarbamates or xanthates. One of the significant methods to prepare polymers with complex architecture via RAFT is to use mono- or multi-functional RAFT agents with the RAFT group being connected to a central, mono- or multifunctional linker. This linker can act as: one of the building blocks of a copolymer, the core of a star polymer or the backbone of a comb polymer. In this study, as a macro-RAFT agent comprised 1-butene oligomers was prepared and used in RAFT polymerization to obtain polymers with narrow molecular weight distributions and short hydrocarbon chains at the ends of the molecules.

1.2 Objectives

The objectives of this study were as follows:

1. To use a zirconocene/MAO catalyst system to prepare vinylidene-terminated oligobutenes of varying molecular weight.
2. To functionalize the oligobutenes by adding a hydroxyl functionality to the vinylidene end-groups via oxymercuration-demercuration reaction, and obtain, as a result, hydroxy-terminated oligobutenes.
3. To use a couple of powerful techniques such as ^{1}H NMR, ^{13}C NMR, SEC, GC-MS, and FTIR spectroscopy, to confirm the synthesis and functionalization of 1-butene oligomers.
4. To synthesize oligobutene-based macro-RAFT agents in the form of S=C(Z)-S-R via an esterification reaction, where Z is the oligobutene in the final product, and attached to the RAFT agent via an ester group.
5. To investigate the chain transfer ability of the macro-RAFT agent to induce living characteristics in free radical styrene polymerization with respect to molar mass control and kinetic behaviour. Also, to prepare styrene copolymer (PS-b-oligobutenes) containing short olefin side chains as a result of using the macro-RAFT agent in living radical polymerization by the RAFT process.
6. To use critical and online two-dimensional chromatography to investigate the chemical composition distribution as well as the molar mass distributions of PS prepared by free radical polymerization mediated with macro-RAFT agent.

7. To investigate the effect of the presence of oligobutenes segments on the thermal properties, e.g glass transition temperature T_g, of the PS.

1.3 Layout of the thesis

Chapter 1 Introduction and objectives

A brief introduction to the major topics relevant to this study, which includes oligomerization of α-olefins and controlled/living radical polymerization. The objectives of the study are also included in this chapter.

Chapter 2 Historical and theoretical background

This chapter reviews the historical and theoretical aspects related to the study. Included are important studies related to this research that have been done by other researchers to date.

Chapter 3 Synthesis, functionalization and characterization of 1-butene oligomers

This chapter discuss the synthesis, functionalization and characterization of 1-butene oligomers.

Chapter 4 Synthesis and Characterization of Oligobutene-based macro-RAFT agent

This chapter covers the synthesis and characterization of oligobutenes-based macro-RAFT agent.

Chapter 5 Polymerisation of styrene mediated by macro-RAFT agents.

In this chapter the polymerisation of styrene mediated by RAFT agents is investigated. Molar mass control and kinetic behaviour are examined. Included in this chapter is the analysis of the polystyrene mediated with macro-RAFT agent by different

chromatographic techniques such as SEC, liquid chromatography under critical conditions, and two-dimensional chromatography.

Chapter 6 Conclusion and recommendations

General conclusion to the study, achievement, and recommendations for future work are given.

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Chapter 2 Historical and theoretical background

2.1. Oligomerization of α-Olefins

2.1.1 Introduction

Oligomers are known as low molecular weight members of a homologous series of the higher molecular weight polymers[1]. According to IUPAC, an oligomer is "a substance composed of molecules containing one or more species of atoms or groups of atoms (constitutional units) repetitively linked to each other"[2]. In analogy to polymerization, the formation of dimers, trimers and oligomers is called oligomerization, regardless of the mechanism of reaction[1]. Oligomerization is defined as "the conversion of a monomer or mixture of monomers into an oligomer"[2]. Oligomers can be prepared by applying suitable synthetic methods and isolated via modern fractionating techniques. The synthesis of oligomers may be carried out either in a stepwise manner, i.e., by adding one base unit at a time, or by the combination of fragments comprising lower oligomers to form the higher oligomers desired. A few oligomers have also been prepared by depolymerization procedures[1].

2.1.2 General aspects

The oligomerization ofα-olefin can be achieved via different methods, using a variety of catalyst systems, with different reaction mechanisms. The oligomers obtained depend very much on the type of catalyst system, the activity, and the stereo-selectivity of these catalysts. These catalysts are generally transition metal complexes in heterogeneous and homogenous systems, organoaluminum compounds and inorganic salts and oxides[2,3].

During the addition reaction involving α-olefins (and ethylene) the reaction is classified according to the number of molecules that partake in the reaction. This reaction basically proceeds in the presence of a transition metal catalyst and involves two key steps[2,3]. The first is the chain propagation step, which occurs at the catalyst active centre:

$$Cat{-}R + H_2C{=}CH_2 \xrightarrow{R_p} Cat{-}H_2C{-}CH_2{-}R \qquad (2.1)$$

where Cat stands for catalyst; R is alkyl or hydrogen; R_p is the rate of propagation.

The second step (equation 2.2) is the elimination of the hydrogen from the β-carbon to the catalytic center:

$$Cat{-}H_2C{-}CH_2{-}R \xrightarrow{R_t} Cat{-}H + H_2C{=}CH{-}R \qquad (2.2)$$

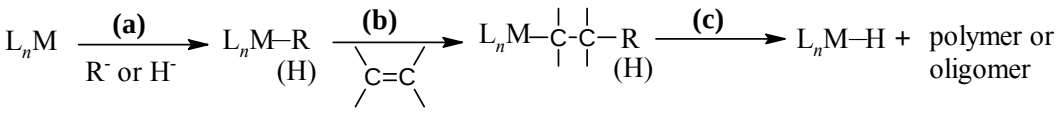
where R_t is the rate of chain transfer.

The elimination of the β-hydrogen is highly dependent on the catalyst system used. The relative reaction rates, R_p and R_t respectively, determine the molecular weight of the obtained product. If the rate of propagation is greater than the rate of chain transfer, many propagation steps proceed before the β-hydrogen elimination occurs, which leads to high molecular weight polymer. When $R_t > R_p$, dimers are obtained, and when $R_t \approx R_p$, oligomers are obtained[2]. The ratio of the propagation rate to chain transfer rate is determined and influenced by many factors[3], such as:

- the type of metal and its activation state,
- electronic properties and steric volume of ligands attached to the metal,
- the reaction conditions such as temperature and pressure,
- the nature of solvent used, and
- molecular weight moderators.

2.1.3 Mechanism of metal-catalyzed polymerization/oligomerization of olefins

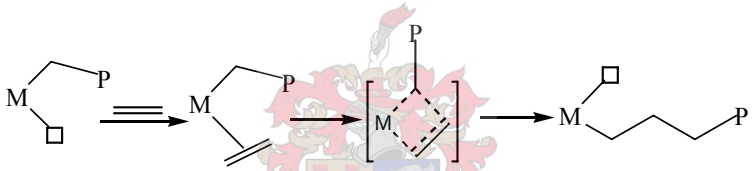
Since the time when transition metal catalysts for olefin polymerization were discovered, a large amount of research has been aimed at understanding the basic mechanistic steps involved in the catalytic process[4-7]. The polymerization or oligomerization with transition metal catalysts basically involves three steps: (a) initiation, (b) propagation, and (c) termination (Scheme 2.1). These reactions occur at the catalytically active centre of a transition metal alkyl complex L_nM-R.



Scheme 2.1 Polymerization/oligomerization reactions with transition metal catalyst systems.

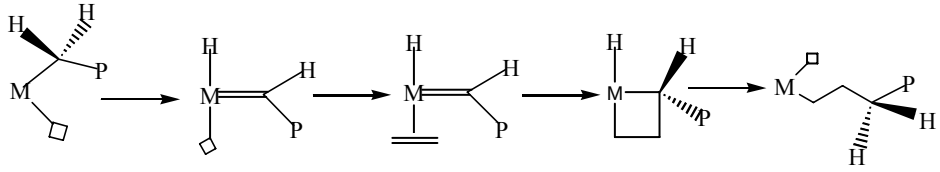
The metal alkyl complex is generated in the initiations step (a), normally by a reaction between a transition metal halide and an electropositive alkyl such as AlR_3.

The focus has been on the insertion of the monomer into the polymer chain (step (b)), which is generally accepted to occur through olefin co-ordination and followed by insertion into a metal-carbon bond. Three common mechanistic proposals for this type of insertion are known for the early transition metal catalysts. The first is alkyl migration to the coordinated olefin, and is known as the Cossee-Arlman mechanism[4] (Scheme 2.2).



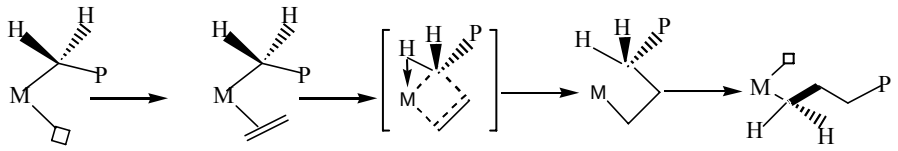
Scheme 2.2 Cossee-Arlman mechanism (direct insertion).

The second type, introduced by Rooney and Green[5], involves an oxidative 1,2 hydride shift from the α-carbon of the polymer chain, forming a metal–alkylidene hydride. This is followed by olefin coordination to give a metallacyclobutane, and reductive elimination to complete chain propagation (Scheme 2.3).



Scheme 2.3 Green-Rooney mechanism (hydride shift).

The third approach is the olefin insertion, where the α-hydrogen interacts with the metal centre only during the transition state of the C-C bond formation (Scheme 2.4). This model is known as a hybrid of the Cossee-Arlman or modified Green-Rooney mechanisms[6].



Scheme 2.4 Transition state agostic mechanism.

The chain termination step (c) occurs in several ways, mostly by chain transfer reactions, including transfer to: monomer, metal, and to a transfer agent. It always involves the elimination of a hydrogen atom from the β-carbon. In some other cases when the hydrogen is used as a transfer agent to control the molecular weight of the polymer, this can cause the chain propagation to be terminated, and a polymer chain with saturated end group to be liberated. Moreover, chain transfer with β-methyl elimination has only been identified for propylene polymerization with metallocene catalysts[8-12].

2.1.4 Oligomerization with various types of catalyst systems

The oligomerization and dimerization of α-olefins with various types of catalyst systems, the oligomerization behaviour and the influences of various factors and conditions on the oligomerization reactions are discussed in detail in the literature[2,3,13-34]. As mentioned previously, the most popular catalyst systems used for α-olefins, especially for ethylene and propylene, are titanium, zirconium, and nickel complexes in heterogeneous and homogeneous systems, heterogeneous and homogeneous Lewis and Brönsted acids, and inorganic oxides.

The most important catalyst systems that have been widely used for the oligomerization of olefins are those prepared from a transition metal component and an aluminium alkyl. The metal components include titanium, zirconium, cobalt and nickel. These catalysts, particularly Ni(II) and Ni(I) complexes display the highest activity and selectivity in olefin oligomerization[35,36]. Performance of the catalysts depends on the electronic and steric factors of the central metal ion. Acceptor ligands increase the positive charge on the central metal ion, causing an increase in the catalyst's activity but a decrease in the molecular weight of the oligomers produced. On the other hand, donor ligands make

olefin insertion into the metal-carbon bond much easier, resulting in an increase in the oligomer length and linearity. Large, bulky ligands favour the formation of intermediates from which the β-hydrogen elimination becomes more difficult, and therefore higher oligomers with a fairly high linearity are obtained[3].

A major drawback of using titanium and zirconium complexes in the oligomerization of ethylene is the formation of polyethylene and branched oligomers as side products. Nickel complexes, particularly halides, are most selective and active in ethylene oligomerization to higher linear α-olefins and have been applied industrially in the Shell Higher Olefin Process (SHOP). $AlCl_3$, metal oxides, zeolites and inorganic acids are generally used for the oligomerization of olefins possessing three or more carbons in the chain. These catalysts are less selective toward olefins and, at higher temperatures, highly branched oligomers and products resulting from alkylation, cracking, aromatization and isomerization reactions are obtained[3,35].

The oligomerization of higher α-olefins can be achieved using catalytic systems similar to those for the oligomerization of ethylene and propylene. For higher α-olefins it is much more complicated than for lower α-olefins, in terms of the sensitivity of the catalyst system being used and the reactivity of the olefin itself. Olefin reactivity in this type of reaction decreases in the following order: ethylene > propylene > 1-butene > 1-hexene > 1-octene > 1-decene[3]. The nature of the higher α-olefins allows for the formation of a greater amount of isomers than in the case of ethylene and propylene, due to the lower selectivity of the catalysts towards higher α-olefins. It is always more desirable producing linear oligomers (dimers and trimers) but with some catalytic systems, when using higher α-olefins, there is a very efficient double bond isomerization, producing internal, almost unreactive isomers, which in this case is an undesirable product[3,32].

2.1.5 Metallocene catalysts

Metallocene catalysts have long been researched and applied for olefin polymerization and oligomerization. Containing only one type of active site, these catalysts produce

polymers with narrow molecular weight distribution (polydispersity < 2) and their structures can easily be changed. These single-site catalysts typically represent the bent metallocenes of the Group-IV transition metals titanium, zirconium and hafnium[37-46]. Due to the lack of stability of titanocene catalysts at conventional polymerization temperatures and the high costs involving hafnium systems, more attention from both academics and industry has been paid to the zirconocene complexes. These metallocenes are soluble in hydrocarbons or liquid propene. By manipulating their structure and careful selection of the appropriate reaction conditions, one can accurately predict the properties of the resulting polyolefins and control the resulting molecular weight and molecular weight distribution, tacticity and comonomer content. In addition, the catalytic activity of these catalysts is 10-100 times higher than that of the classical Ziegler-Natta systems[45].

2.1.5.1 Historical development of metallocenes

The transition metal based catalysts used for α-olefins polymerization and co-polymerization reactions can be divided into two groups. The first group is known as "Ziegler-Natta catalysts" and members of the second group are commonly called "metallocene pre-catalysts".

Metallocene catalysts for olefin polymerization were discovered by Breslow[47] and Natta[48] soon after the original discovery of Ziegler-Natta catalysts. The actual structure of the metallocene pre-catalysts, in which a π-bonded metal atom is located between two aromatic ring systems, is shown in Figure 2.1. This structure was first elucidated by Wilkinson and Birmingham[49], in particular for ferrocene. They were both awarded the Nobel Prize for chemistry in 1973 for this achievement.

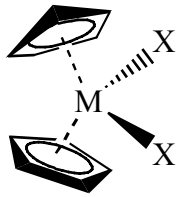


Figure 2.1 General structure of a metallocene dichloride catalyst.

These early metallocene catalysts had relatively low activity and were regarded as suitable mainly for academic research[45]. It was only with the discovery and application of methylalumoxane (MAO) as cocatalyst by German scientists Walter Kaminsky and Hansjorg Sinn in Hamburg in 1977, that it became possible to enhance the activity by a factor of 10,000[50-52]. The first type of Kaminsky catalysts included common metallocene complexes of zirconium (zirconocenes), such as biscyclopentadienylzirconium dichloride.

Polyolefins with different microstructures and characteristics can be prepared, by varying the ligands of the metallocene (Figure 2.2). The discovery of metallocene catalysts meant that for the first time the possibility existed to produce polyethelenes, polypropenes and copolymers with narrow molecular weight distributions[50], syndiotactic polypropylene[53], and syndiotactic polystyrene[54]. It became possible to produce cyclopolymers of 1,5-hexadiene[55], while cycloolefin copolymers could be made with a much higher activity than was ever possible with the so called Ziegler-Natta catalysts[56]. The synthesis of optically active oligomers became possible[57,58], as did composite materials of powdered metals with polyolefins[59]. Organic or inorganic particles (starch, cellulose, quartz sand, or powdered metal) can be coated with a hydrocarbon-soluble metallocene catalyst and, in turn, after polymerization, with a polyolefin film of variable thickness[59].

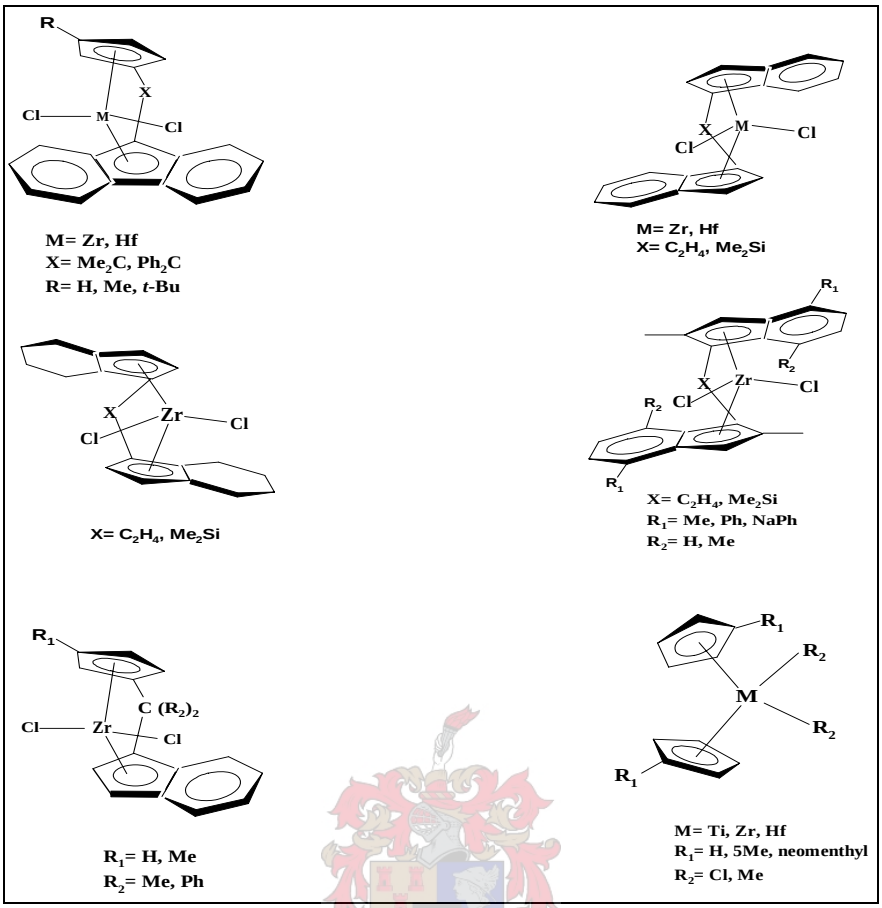


Figure 2.2 Some classes of metallocene catalysts used for olefin polymerization[60].

2.1.5.2 The role of the co-catalyst

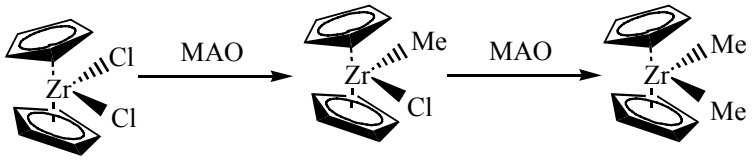
As mentioned earlier, the combination of metallocenes and alumoxane as co-catalyst results in extremely high polymerization activities. One of the popular, if not the most popular, co-catalyst, is methylalumoxane (MAO), which is prepared by careful treatment of trimethylaluminum with water[60]:

$$nH_2O + (n+1)Al(CH_3)_3 \longrightarrow (H_3C)_2Al - [O\text{-}Al - CH_3]_n - CH_3 + 2nCH_4$$

In spite of the intensive studies that have been carried out, the actual structure and function of MAO is still not fully understood. However, there has been an agreement that the basic structure of MAO consists of linear or cyclic structures of the basic unit [CH_3-Al-O], composed of alternating three-coordinate aluminium and two-coordinate oxygen atoms, and methyl substituents saturate the free valences[61-63]. These structures have

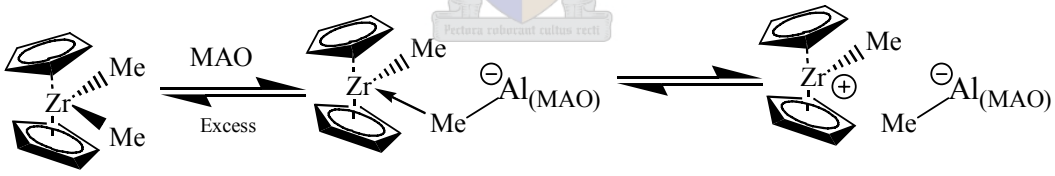
molecular weights from 1200 to 1600 g.mol^{-1} and are soluble in hydrocarbons. Of the co-catalysts available, methylalumoxane is much more effective than ethylaluminoxane or isobutylaluminoxane[45].

One of the functions of MAO is to form the catalytic active centre, which proceeds in two steps. In the first step, the metallocene alkylated, by replacing the dichloride ligands with methyl groups, giving the methyl and dimethyl metallocene compounds (Scheme 2.5).



Scheme 2.5 Alkylation of metallocene by MAO.

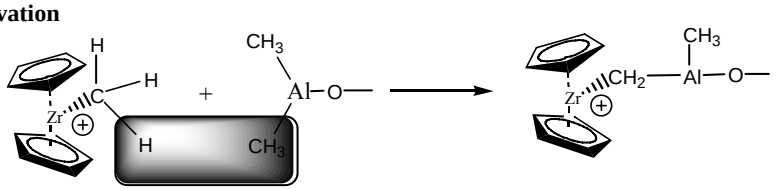
The second step involves the formation of a metallocene cation and MAO anions, by the abstraction of either Cl^- or CH_3^- from the metallocene compound by an Al-centre in MAO (Scheme2.6) [64,65]. These cationic species are the active centres in the olefin polymerization, as was confirmed by ^{13}C NMR and X-ray measurements[66-68].



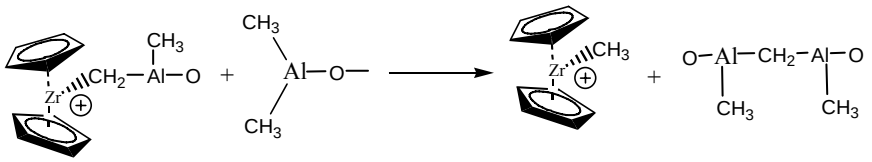
Scheme 2.6 Formation of the alkylated metallocene cation.

Another function of MAO is the reactivation of inactive complexes [M-CH_2-Al], formed by α-hydrogen transfer due to the presence of MAO in the solution after a fast complexation and methylation[43,60].

Deactivation



Reactivation



Scheme 2.7 Reactivation reaction with MAO[60].

2.1.6 Zirconocene dichloride/MAO catalyst systems for α-olefin dimerization and oligomerization

Since the introduction of metallocene dichloride/MAO catalysts to the industry as a new generation of Ziegler-Natta catalysts for α-olefin polymerization, numerous studies have been documented. Studies have shown that one of the most important modern classes of these catalysts is bis-cyclopentadienylzirconium dichloride (zirconocene) complexes. The zirconocene dichloride/MAO based systems showed very high activity for the polymerization of olefins, particularly ethylene, propylene and butene[37-39,42,51,69-72]. In many of the studies, however the formation of low molecular weight oligomers was regarded as undesirable; they were considered as impurities and by-products[51,70,73].

It is now recognized that oligomers obtained with metallocenes can be effectively applied as models and intermediates in preparative polymer chemistry. The homogeneity of the reaction mixture and the low mass of the oligomers allows the study of mechanistic aspects and reaction mechanisms of metallocene polymerization reactions[11,12,58,74-76]. Moreover, such catalysts with high regioselectivity and activity towards α-olefins produce oligomers with unsaturated double bond end groups, predominantly of the vinylidene type. Research into the chemistry of chain-ended functional oligomers has led to a large number of potential applications[14].

2.1.6.1 Factors that affect the oligomerization and dirmerization with metallocenes

It is generally understood that the degree of polymerization and the molecular weight of a polymer are dependent on the ratio of the rate of propagation (R_p) to the rate of termination (R_t) during polymerization. The correlation between the molecular weight (or average degree of polymerization $\overline{P_n}$) and the reaction rates can be expressed mathematically in equation 2.1[11].

$$\bar{P}_n = \frac{\sum R_p}{\sum R_t} \qquad (2.1)$$

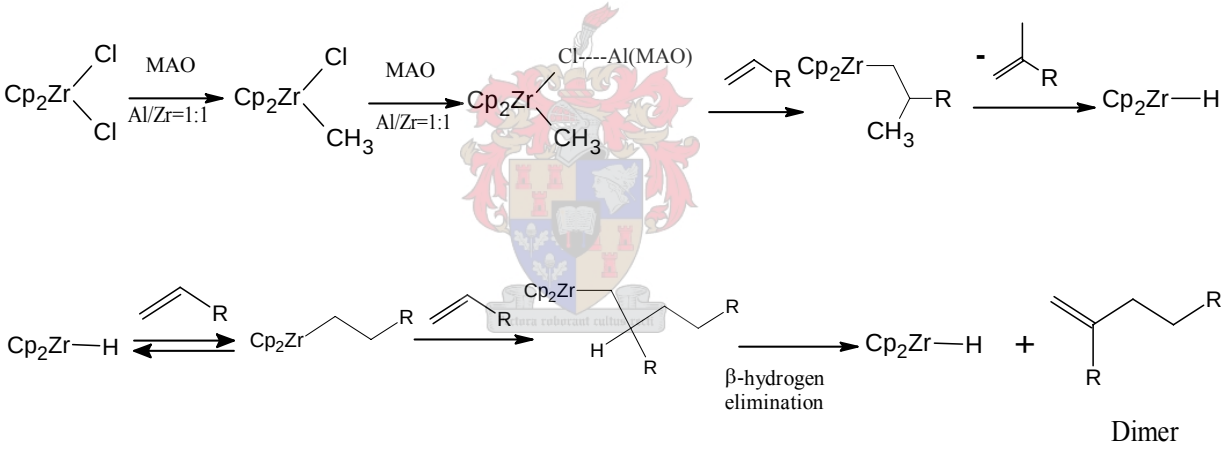
Thus the molecular weight is proportional to the rate of propagation R_p and inversely proportional to the rate of termination R_t. This suggests that reducing the rate of propagation versus the rate of termination is the key to obtaining low molecular weight oligomers. The influence of both the catalyst structure and polymerization conditions (polymerization temperature, monomer concentration, catalyst/co-catalyst ratio) on the termination reaction (also called chain transfer reaction), and consequently on the molecular weight, is well documented[11,12,76-80].

Resconi *et al.*[11] and Janiak *et al.*[79] have shown that the molecular weight is strongly dependent on the structure and steric effect of the π-cyclopentadinyl ligands. Brintzinger *et al.*[77] observed that the molecular weight of polypropylene is strongly decreased by reducing the concentration of propylene monomer. Teuben *et al.*[76], Brintzinger *et al.*[81] and Resconi *et al.*[46] investigated the influence of the reaction temperature on the oligomerization of propylene. They concluded that the oligomer distribution strongly depends on the reaction temperature; molecular weight decreases as the temperature increases.

Janiak *et al.*[79] and Mülhaupt *et al.*[80] studied the influence of the concentration of the catalyst and the molar ratio of methylalumoxane to zirconocene [Al/Zr] on the catalyst activity and the molecular weight of the polymer. The activity of the catalyst increased

steadily with increasing [AI]/[Zr] molar ratio. A molar ratio of Al/Zr ranging from 500:1 up to 10,000:1 is needed for the polymerization process.

In a study by Bergman *et al.*[34] a molar ratio of 1:1 of Al:Zr was applied to activate the zirconocene dichloride. Selective dimerization for different alkenes and α-olefins (1-butene, 1-pentene, 1-hexene, and 1-heptene) was achieved. The authors investigated the possible mechanism of the reaction. They suggested that the reason for the chemoselective dimerization is the incomplete alkylation of the catalyst and the chloro ligands remaining in the coordination sphere of the zirconium, resulting in the formation of a zirconium-hydro species after the first insertion. After two monomer units have inserted to these active hydro species, *β*-hydrogen elimination proceeds and the formed dimer is released from the coordination centre (Scheme 2.8).

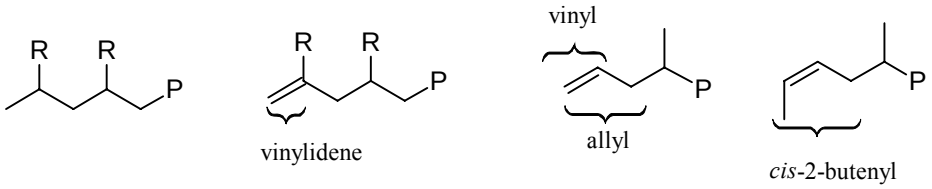


Scheme 2.8 Selective dimerization of α-olefins with zirconocene dichloride.

2.1.6.2 End group functionality

The nature of metallocenes as single-site catalysts allows directing the insertion of the olefin monomers to form regioregular and stereoregular polyolefins, with exceptional selectivity. Chain transfer reactions with metallocenes also have a significant influence on the structure and the properties of the polymer or oligomer obtained, in particular on the type of the end group at the end of the chains. Extensive mechanistic studies have shown that with metallocenes five main chain transfer reactions are expected: *β*-hydrogen transfer to the metal[10,82-84], *β*-hydrogen transfer to monomer[85,86], *β*-methyl transfer to the

metal[8,10,83], chain transfer to the aluminum co-catalyst[87,88], and chain transfer to a transfer agent such as silanes and hydrogen [75,89-92]. Accordingly, polymers or oligomers possessing four different types of end groups are obtained; vinylidene double bond (predominant), vinyl/allyl double bond or 2-butenyl group (in case of propylene), and saturated end groups (Figure 2.3) [11].



P= continuing polymr/ oligomer chain

Figure 2.3 End group functionalities obtained with metallocene catalysts[11].

It should be p`ointed out that *β*-alkyl elimination is not a general transfer mechanism in α-olefin polymerization with metallocenes. Resconi *et al*.[12] investigated, besides propylene, the polymerization of 1-butene, 4-methyl-1-pentene, and allyltrimethylsilane. Results showed that while the *β*-methyl transfer is observed in some cases for propylene, *β*-alkyl transfer, e.g. *β*-ethyl for 1-butene, appears to be inaccessible for these catalyst systems; only unsaturated vinylidene or saturated end groups were observed.

The functionalization of such double bonds, particularly the vinylidene type, has become a very interesting area of study, since a large number of applications are possible. Oligomers, in particular oligoethylene and oligopropylene, have been used as monomers to produce polymers. Quijada *et al*.[93] and his workers obtained a new type of branched polyethylene from ethylene by tandem action of two single site metallocene catalysts activated with MAO. Using the same concept, Bazan *et al*.[94] synthesized butene-ethylene and hexene-butene-ethylene copolymers from ethylene monomers. Moreover, Pellecchia *et al*.[27] investigated the co-oligomerization of ethylene and styrene to produce polyethylene with 4-aryl-1-butyl branches. Ethylene and styrene were first co-oligomerized to phenylhexenes, which were then copolymerized with the ethylene to form the final product.

One of the most attractive features of the double bond end groups is their ability to be converted into various other polar functional groups using a range of simple and conventional organic reactions. Extensive studies by Mülhaupt and coworkers[95-97] on the functionalization of vinylidene-terminated oligopropenes have shown that the vinylidene double bond can be readily functionalized to yield a broad range of monofunctional oligopropenes with one polar end group. Oligopropenes with hydroxy-, thiol-, carboxy-, amino-, ester- and succinic anhydride- terminated functional groups were prepared. Derivatives from these monofunctional oligopropenes were used to prepare block copolymers of AB and ABA as well as graft copolymers, where A is equivalent to oligopropenes. Esterification of the hydroxyl-terminated oligopropenes with methacrylic acid was carried out to prepare macromonomers, to produce the novel class of oligopropenes with a polymerizable acrylic end group. Such monofunctional oligopropenes and copolymers are attractive intermediates in polymer synthesis and useful in applications such as adhesives, blend compatibilizers, and emulsifiers. Figure 2.4 (adapted from Janiak[14]) shows some applications and functionalization reactions for oligopropenes and oligo-olefins in general.

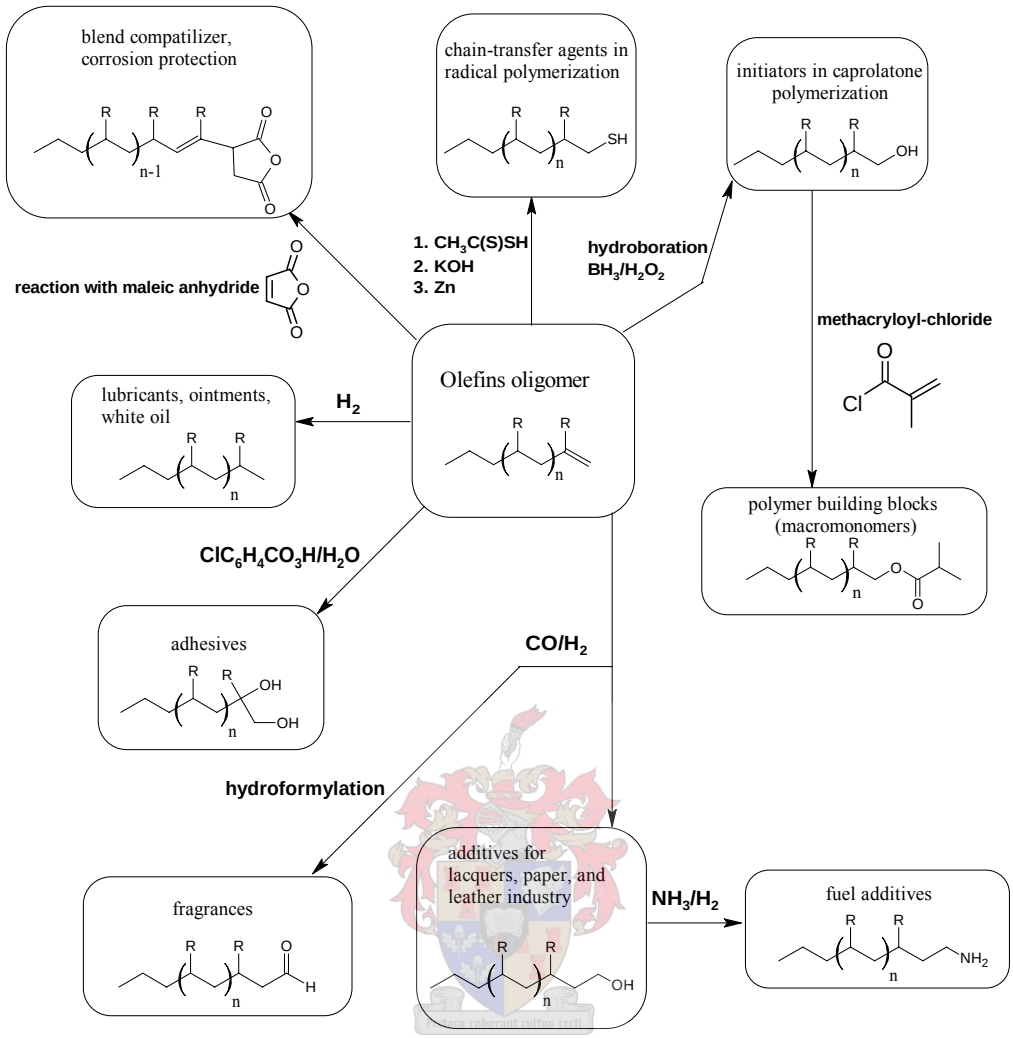


Figure 2.4 Variety of functionalization reactions for oligo-olefins with possible applications of the products[14].

2.2 Radical Polymerization

Free radical polymerization occurs via chain-growth polymerization, whereby chains propagate by adding one monomer molecule at a time to a growing chain. The rapid addition of monomer molecules to the reactive end group of a growing chain is controlled by a propagating rate until chains terminate and become unreactive. In most cases the monomers used are olefinic, although in group transfer processes and the polymerization of cyclic monomers, this type of unit is not required[98].

Due to the random nature of the initiation and termination processes present in radical polymerization, polymers produced usually contain a broad range of molecular sizes.

Conventional free radical polymerization is the method of choice for approximately 50% of all polymers produced commercially[99,100]. The advantages include its compatibility with a wide range of monomers, the use of predictable reaction conditions and tolerance of trace amounts of water and impurities. Disadvantages include the presence of chain transfer and termination of the propagating radicals. These reactions lead to a loss of control over molar mass, chain architecture and the broadening of molar mass distribution. The biggest problem is that termination of radicals allows no re-initiation at a later stage[101-103].

2.2.1 Reactivity of monomers

The monomers are commonly monosubstituted ethylenes (CH_2=CHX) or unsymmetrically 1,1-disubstituted ethylenes (CH_2=CXY). The substituents X and Y determine the reactivity of the propagating radicals and monomers, which influences the properties of the final polymer; e.g. reaction of substituents with propagating radical species introduces structural complexities into the polymer (branching and cross-linking), and the net result of that complicates the kinetic course of the polymerization[98].

There are many factors that can influence the reactivity of both the monomer and the radical. Tedder[99] suggested a set of guide-lines to predict the activity of the monomer and its radical:

(a) For mono- or 1,1-di-substituted olefins, the addition of the monomer will preferentially be to the unsubstituted (tail) end of the double bond.

(b) Substituents with π-orbitals (CH=CH_2, -Ph) which can offer resonance stabilization to the double bond, may enhance the rate of addition of monomer to the propagating species at the remote end of the double bond, whilst the substituents with non-bonding pairs of electrons (-F, -Cl, -OR), that have only a very small resonance stabilization effect, reduce the rate of the addition of monomer.

(c) Electron withdrawing substituents will enhance the addition of nucleophilic radicals, while electron donating substituents will enhance the addition of electrophilic radicals.

(d) In the case of polysubstituted olefins the regioselectivity of addition is controlled by the degree of steric compression with forming the new bond.

In conclusion, the resonance stabilization provided by the substituent groups is a determining factor in reactivity[104,105]. Thus for a CH=CX monomer the reactivity of adding monomer and stabilization of radical can be illustrated as follows:

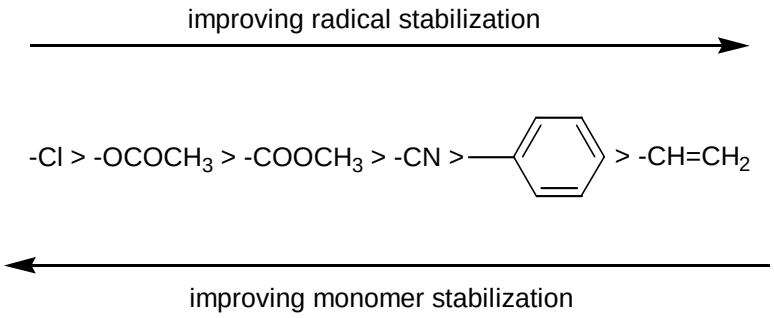
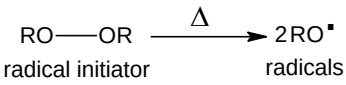


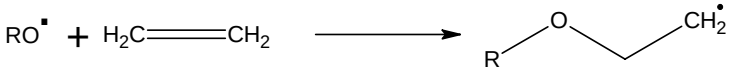
Figure 2.5 The monomer reactivity.

2.2. 2. The mechanism of polymerization

Free Radical polymerization can be divided to three individual stages: initiation, propagation and termination. During initiation, the initiator undergoes homolytic cleavage to give two radicals, which will each add to an alkene monomer, converting it into a radical. The newly formed radical reacts with another monomer, adds a new subunit and signifies the start of chain propagation.

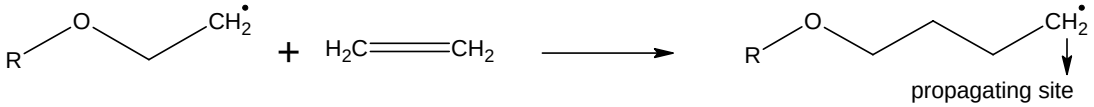
Chain-initiating steps:





Scheme 2.9 An initiation reaction.

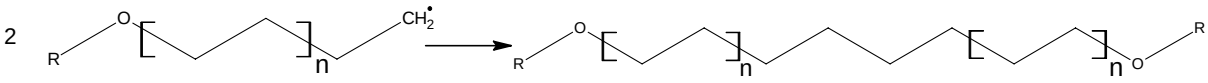
Chain-propagating step:



Scheme 2.10 A propagation reaction.

The process is repeated until termination occurs by one of three methods: chain coupling, disproportionation and reaction with an impurity.

Chain coupling:



Scheme 2.11 A combination reaction.

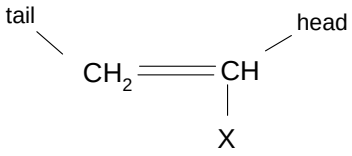
Disproportionation:

Scheme 2.12 A disproportionation reaction.

Reaction with an impurity:

Scheme 2.13 Termination by reaction with an impurity.

Chain-growth polymerization of substituted ethylenes shows a preference for head-to-tail addition, where the head of one monomer is attached to the tail of another (Figure 2.6).



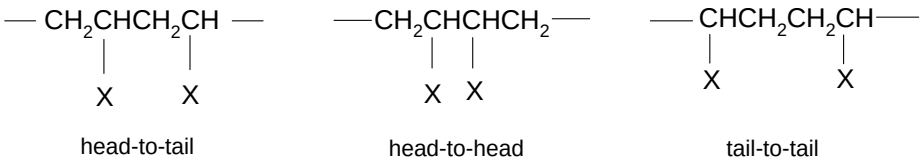


Figure 2.6 Different types of addition of monomer.

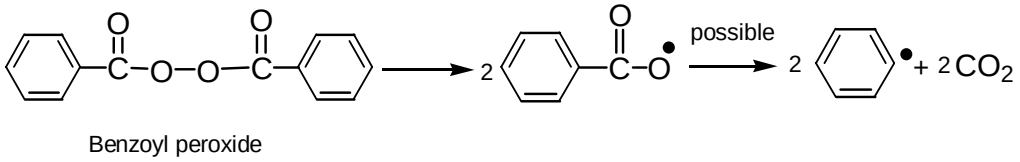
The propagating site preferentially attacks the sterically less hindered carbon of the alkene. Groups stabilizing adjacent radicals also favour head-to-tail addition.

2.2. 3. Initiators

The initiator is the source of the radicals that react with monomers and initiate the polymerization. The radicals can be generated in different ways, such as thermal or photochemical intramolecular bond cleavage, redox reactions, and photochemical hydrogen abstraction[98,106].

Thermal initiators, specifically, involve intramolecular bond cleavage. Two very important factors should be considered when it comes to the choice of initiator for polymerizations. The first factor is the solubility of the initiator, and the second is the temperature at which the reactions will be carried out.

Peroxides and azo compounds are the two types of thermal initiators that well-known and commonly used. The peroxides include hydrogen peroxide, benzoyl peroxides, acyl peroxides, alkyl Peroxides, and peresters. They are thermally sensitive and decompose by homolytic cleavage of the O-O bond to produce two free radicals[98]. For example, the decomposition of benzoyl peroxide proceeds id shown in Schem 2.14:



Scheme 2.14 Decomposition of benzoyl peroxide.

Note that the possibility of producing two different radicals: a Ph-CO–O$^{\bullet}$ radical or a Ph$^{\bullet}$ radical, which will lead to two different end groups in the polymer.

Most of the azo compounds have the general formula as presented below:

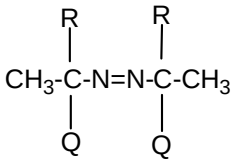
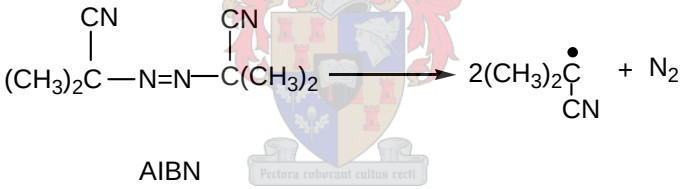


Figure 2.7 General formula of azo compounds.

where R= alkyl and Q= carboxylic acid or a derivative.

AIBN is commonly regarded as the most suitable initiator for radical polymerizations in non-aqueous media at temperatures between 45 and 65°C. The dissociation is as follows:



Scheme 2.15 Decomposition of AIBN.

In the case of aqueous solutions, potassium persulfate is employed as initiator.

2.2.4 Kinetics of vinyl radical polymerization

2.2.4.1 Initiation:

Initially, radicals (**R**$^{\bullet}$) must be generated. This occurs by decomposition of chemical compounds called initiators, or by the monomer it self through the use of an energy source such as light, heat or radiation.

Decomposition: $I \xrightarrow{k_d} 2R^{\bullet}$

The radicals initiate polymerization by addition of monomer, forming $M_1^{\bullet}$, which is now a growing polymer chain with one monomer and becomes the active radical species that can propagate by the sequential addition of monomers.

Addition: $$R^{\bullet} + M \xrightarrow{k_a} M_1^{\bullet}$$

The rate of initiation, v_i can be described by equation 2.2

$$v_i = -\frac{[dM^{\bullet}]}{dt} = 2fk_d[I] \qquad (2.2)$$

where k_d is the coefficient decomposition rate and f is the fraction of radicals which successfully initiate chains. From this it can be predicted that at a certain time t the initiator concentration will be given by equation 2.3:

$$[I] = [I]_0 e^{-k_d \cdot t} \qquad (2.3)$$

where $[I]_0$ is the initiator concentration at time t = 0.

2.2.4.2 Propagation:

The active radical chain formed during the initiation step is now capable of undergoing propagation which comprises over a sequence of radical additions to carbon-carbon double bonds. The reaction is typically as follows:

Propagation: $$M_x^{\bullet} + M \xrightarrow{k_p} M^{\bullet}_{x+1}$$

The rate coefficient of propagation step is k_p and the rate of propagation, v_p, can be described by equation 2.4

$$\upsilon_p = -\frac{d[M]}{dt} = k_p[M^\bullet][M] \qquad (2.4)$$

$M^\bullet$ is a growing chain with a radical end group and M is monomer.

2.2.4.3 Termination:

Termination is the final reaction that occurs between two chain radicals and terminates the reaction, producing a polymer chain. This step involve coupling or disproportionation

Coupling: $M_x^\bullet + M_y^\bullet \xrightarrow{k_{tc}} M_{x+y}$

Disproportionation: $M_x^\bullet + M_y^\bullet \xrightarrow{k_{td}} M_x + M_y$

The termination rate constant is denoted as k_t unless it is necessary to distinguish between the two mechanisms. The rate of termination is

$$\upsilon_t = -\frac{d[M^\bullet]}{dt} = 2k_t[M^\bullet]^2 \qquad (2.5)$$

where $k_t = k_{tc} + k_{td}$

In many cases the concentration of free radicals $[M^\bullet]$ becomes essentially constant very early during polymerization and radicals are formed and destroyed at identical rates. The rate of initiation is therefore equal to the rate of termination and $\upsilon_i = \upsilon_t$. In this *steady-state* condition

$$2fk_d[I] = 2k_t[M^\bullet]^2 \qquad (2.6)$$

and then

$$[M^\bullet] = \left(\frac{fk_d[I]}{k_t}\right)^{1/2} \qquad (2.7)$$

Substitution of equation 2.7 in equation 2.4 provides the rate of a thermal free radical polymerization:

$$-\frac{d[M]}{dt} = k_p\left(\frac{fk_d}{k_t}\right)^{1/2}[M][I]^{1/2} \qquad (2.8)$$

2.2.4.4 Chain transfer:

In general terms, when there is an exchange of radical activity between molecules, by which the active centre of polymerization is transferred from a growing chain to another molecule, chain transfer occurs. The reaction is thereby not terminated but chain growth is interrupted and the molecular mass limited. This type of reaction can take place with any molecular species present during polymerization: initiator, monomer, polymer, solvent and any other chain transfer agent (or regulator) purposely added, or accidentally present in the reaction mixture.

The chain transfer takes place in two steps; a propagating chain reacts with a transfer agent to terminate one polymer chain and produces a new radical, and initiates a new chain.

$$P_i^{\bullet} + T \xrightarrow{k_{tr}} P_i + T^{\bullet}$$

$$T^{\bullet} + M \xrightarrow{k_s} P_1^{\bullet}$$

k_{tr} and k_s are the rate constants for transferring and reinitiating respectively.

Transfer agents are usually used to achieve many goals: control the molecular weight, control the polymerization rate, control the gel or Trommsdorff effect, and control the nature of the polymer end groups. The influence of chain transfer on the rate of the degree of polymerization is expressed simply by the Mayo equation, which is derived by dividing the rate of propagating of the monomer by the rate of formation of polymer molecule (the overall rate of termination):

$$\frac{1}{\overline{X}_n} = \frac{1}{\overline{X}_{n0}} + C_T\frac{[T]}{[M]} \qquad (2.9)$$

where $\overline{X}_n$ is the degree of the polymerization and $\overline{X}_{n0}$ is the degree of polymerization in the absence of a transfer agent, and C_T is the transfer constant which is the ratio $\frac{k_t}{k_p}$.

2.3 Living Radical Polymerization

With the emergence of techniques allowing "living" radical polymerization the limitations of conventional free radical polymerization was overcome. The synthesis of polymers with pre-defined molecular weights based on monomer and initiator concentrations, narrow polydispersity indexes and end-group functionality can now be achieved by Atom Transfer Radical Polymerization(ATRP)[107,108], Nitroxide Mediated Polymerization (NMP)[109] and Reversible-Addition Fragmentation Transfer (RAFT), which are the main techniques constituting living radical polymerization. The production of polymers with complex architectures[110-112] by means of free-radical techniques is of considerable interest because of the ease and versatility of free-radical polymerization. Although the research field largely involves ATRP and NMP, both of these techniques have limitations.

2.3.1 Reversible Addition-Fragmentation Transfer (RAFT)

The RAFT process was discovered in Australia by the Commonwealth Scientific & Industrial Research Organization (CSIRO) team[113-115]. RAFT polymerization is the best example involving degenerative transfer. This means that the radical activity is transferred between two polymer chains with no effective change in the overall energy. Le *et al*.[116,117] illustrated that thiocarbonyl compounds can be used to give living character to radical polymerizations. The compounds include dithioesters[118-122], xanthates[123-126], dithiocarbamates[113,125,127,128], trithiocarbonates[123,129-133], and phosphoryl-/(thiophosphoryl)dithioformates[134,135]. The general structure of a RAFT agent is illustrated in Figure. 2.8, where Z is the stabilizing group responsible for the reactivity of the C=S toward radical addition, and R is the free radical leaving group that will be able to re-initiate the polymerization. The RAFT process is effective for a wide range of

monomers, including functional monomers, and can be performed in a wide variety of solvents, including water and under broad range of experimental conditions.

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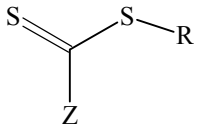


Figure 2.8 General structure of a RAFT agent.

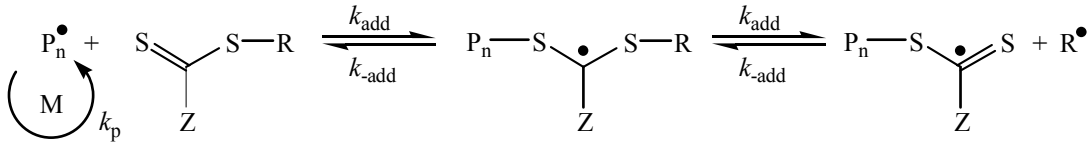
2.3.1.1 Mechanism

The basic RAFT mechanism[113] as proposed by the CSIRO group was based on the general addition-fragmentation mechanism. As in the case of conventional free radical polymerization, the initiator decomposes into primary radicals ($I^{\bullet}$), which can either propagate with monomer to form oligomeric chains of n degree of polymerization ($P_n^{\bullet}$) or react with the RAFT agent through its thiocarbonyl thio bond.

Initiation and Propagation:

The first rate-determining step is the reaction of the oligomeric propagating radical $P_n^{\bullet}$ with the RAFT agent, forming an intermediate radical. Fragmentation of the formed intermediate species can be either into the two original reactant species, or into a temporary dormant polymeric RAFT agent and a radical ($P^{\bullet}$) originating from the RAFT agent. This is followed by re-initiation of polymerization by the radical ($P^{\bullet}$) reacting with monomer to form a propagating radical $P_m^{\bullet}$.

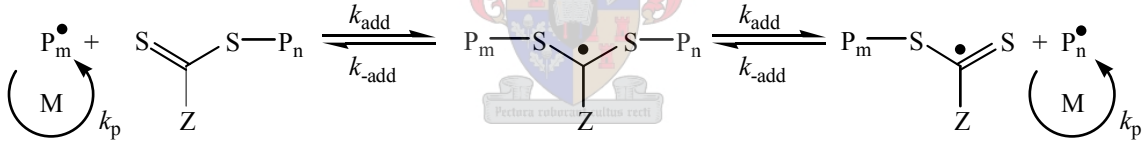
Pre-equilibrium:



Scheme 2.16 Reversible chain transfer.

The thiocarbonyl thio moiety (S=C-S) has been exchanged between the active and dormant polymer chains of the starting species. The newly formed dormant species can be reactivated. The end result is that most polymer chains are formed with thiocarbonyl thio end-groups. To ensure polymer chains with low polydispersities, the rate of addition of the propagating polymeric radicals to the dithiocarbonyl double bond must be fast compared to that of propagation, and termination must be suppressed by keeping the propagating radical concentration low.

Chain equilibrium between active and dormant species in the RAFT process:



Scheme 2.17 Chain equilibration.

In order to achieve the outcomes constituting "controlled" reactions, the transfer rate must be quite fast, at least as fast as propagation. The degree of control of the transfer agent depends on its structure[136,137]. The activation group Z determines the rate of radical addition to the thiocarbonyl double bond. To reinitiate polymerization it is important that the RAFT agent contains a good leaving group R. In addition, the initial transformation from RAFT agent to dormant polymer species needs to be rapid to allow all polymer chains to start growing at the same time. Inhibition and retardation might occur if the expelled radical $P^{\bullet}$ has difficulty in adding to monomer. Conversion of the transfer agent will be slow and a broader molecular weight distribution will be obtained. Steric factors, radical stability, and polar factors appear to be important in determining the leaving

group ability of R. The more stable, more electrophilic, more bulky radicals are better leaving groups. The leaving group ability decreases in the series where R is tertiary>>>secondary> primary.

Termination:

$$P_n^{\bullet} + P_m^{\bullet} \longrightarrow \text{Dead polymer}$$

Although the termination is limited in the RAFT process, some termination reactions still occur via coupling of two radical chains, which results in so called "dead polymer chains". However, studies have shown that the great majority of the polymer chains retained the thiocarbonyl thio moiety as the end group. This was proved by ^{1}H-NMR and UV/visible spectroscopy[127,138].

One of the unique features of the RAFT process is that the molecular weight of the polymer increases in a linear manner with monomer conversion, and it is controlled by the stoichiometry of the reaction[113,132,139]. In addition, the molar mass can be predicted theoretically, by applying the following equation[140]:

$$\overline{M}_{n,theory} = \frac{\chi[M]_0}{[RAFT]_0}(M_M) + M_{RAFT} \qquad (2.10)$$

where $[M]_0$ and $[RAFT]_0$ are the initial concentrations of the monomer and the RAFT agent, M_M and M_{RAFT} are the molar masses of the monomer and the RAFT agent respectively, x is the fractional conversion and $\overline{M}_{n,theory}$ is the theoretical number average molecular weight of the formed polymer.

Recent development in the RAFT process, particularly the preparation of block copolymers, star polymers (with block structure), and comb polymers under mild reaction conditions, was the driving force to carry out this study. Studies have shown that preparation of such polymers can be achieved by using mono- or multi-functional RAFT agents with the RAFT group being connected to a central, multifunctional linker, which acts as the core of the star polymer or the backbone of the comb. The core or the

backbone can act as either the leaving group R or the Z group, depending on the chemical linkage between the RAFT agent and the core or backbone[110,112,130,141,142].

As we reviewed and discussed earlier in this chapter, the oligomerization of α-olefins with metallocene catalyst systems provides oligomers with vinyl end-groups that can be easily functionalized. These functionalized oligomers (hydroxyl functionality as we will show later in chapter three) can be used to prepare macro-RAFT agents, with the RAFT group being connected to a mono-functional linker, which results in a copolymer with the oligomers being one of the building blocks of the copolymer or oligo-olefin side chains attached to the rest of a backbone of polymer via the RAFT linkage.

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Chapter 3 Synthesis, functionalization and characterization of 1-butene oligomers

3.1 Introduction

The use of metallocene catalyst systems in the polymerization and oligomerization of α-olefins has been widely reported in the literature. Extensive studies have been carried out on the oligomerization behaviour of different monomers, such as propene, 1-butene, 1-pentene and 1-hexene, and the effects on oligomers formation of reaction temperature, reaction time, metallocene/MAO ratios, activation time for catalyst and the catalyst concentration[1-12].

In this chapter the synthesis and functionalization of 1-butene oligomers are discussed, as well as the characterization techniques used to analyze the products. Here the aim was to utilize 1-butene oligomers in controlled free radical polymerization (RAFT) reactions, therefore 1-butene oligomers were prepared according to procedures and conditions described in the literature, without any further investigation. The functionalization of 1-butene oligomers was achieved by adding hydroxyl functionality to the vinyl end group, based on work done by Mulhaupt *et al.*[2], who synthesized hydroxy-terminated oligopropenes. Use of these hydroxyl functionalities provided a suitable approach by which to introduce the oligomers to the RAFT polymerization, as will be discussed in chapter 4.

Because of its simplicity and speed, the oxymercuration-demercuration reaction was used to achieve the hydration of vinyl end groups of oligomers chains. It has been shown that the oxymercuration of olefins in aqueous THF, followed by *in situ* reduction of the organomercurial by alkaline sodium borohydride, offers a highly convenient procedure for achieving the anti-Markovnikov hydration of double bonds, with a high yield[13-18].

The general procedure used for the synthesis of 1-butene oligomers was based on the methods used by Bergman, Kaminsky, Janiak and Wahner[4,6,10,19]. The functionalization of both butene oligomers and the trimer fraction were carried out according to the procedure described by Brown and Geoghegan[14]. In order to follow the chemistry involved in the synthesis and functionalization of 1-butene oligomers, a fraction of 1-

butene trimer (5-ethyl-3-methylene nonane) was separated from the final oligomeric mixture, and used as a model in all the syntheses and reactions investigated in this study. This allowed a good interpretation to all the results obtained by different characterization techniques. Both the 1-butene oligomers and the 5-ethyl-3-methylene nonane were characterized using nuclear magnetic resonance (NMR) spectroscopy, gas chromatography (GC), gas chromatography coupled with mass spectroscopy (GC-MS) and Fourier-transform infrared spectroscopy (FT-IR). Size exclusion chromatography (SEC)/ gel permeation chromatography (GPC) was used to determine the molecular weight of the resulting oligomers.

3.2 Chemicals

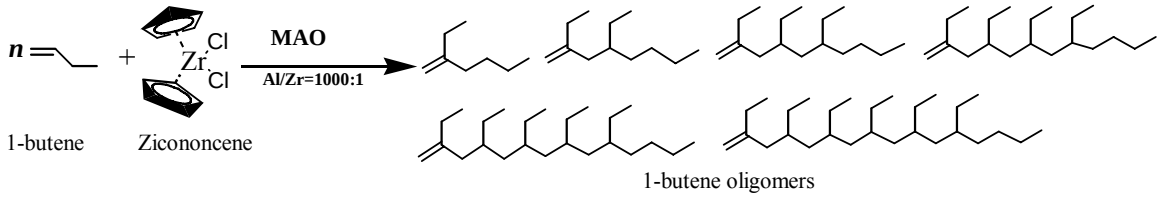
1-Butene (99.9%) was purchased from Sigma-Aldrich and used as received. Toluene (CP 99.8%) and tetrahydrofuran (THF) (99.5%) were obtained from Kimix. Diethyl ether (98%) was obtained from Merck. Sodium lumps in kerosene (99%), $CpZrCl_2$ (98%) and Methylalumoxane (MAO) as a 10 wt% toluene solution, were purchased from Aldrich and used as received. Benzophenone (99%) was obtained from Fluka. Mercury acetate (98.5%) and sodium borohydride (minimum 95%) were obtained from Saarchem and used as received. Sodium hydroxide pellets (97%) were purchased from Associated Chemical Enterprises.

3.3 General procedures

All experiments that involved air and moisture sensitive reagents, such as the preparation of the catalyst solution, activation of zirconocene with MAO, and oligomerization, were carried out under argon, with standard Schlenk techniques. Toluene, diethyl ether and THF were dried over sodium metal and sodium benzophenone ketyl, followed by distillation, and storage under argon[20].

3.4 Synthesis of 1-butene oligomers (typical)

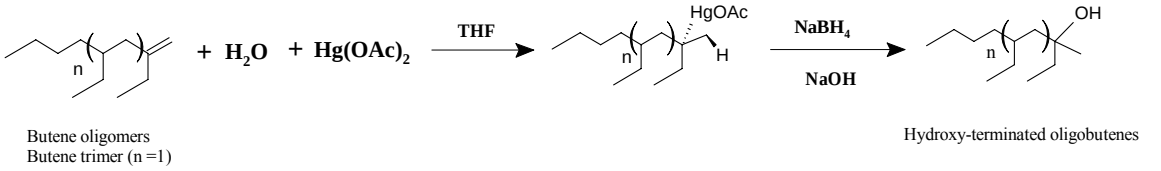
The oligomerization reaction of 1-butene was carried out with **Cp_2ZrCl_2** as a catalyst, activated with **MAO** as a co-catalyst (10% in toluene), in the ratio Al/Zr = 1,000/1.



Scheme 3.1 1-Butene oligomerization reaction and conditions.

Zirconocene dichloride (8.8 mg, 0.03 mmol) dissolved in toluene, and MAO (30 mmol, 20 ml of a 10% solution in toluene), were placed in a 100 ml Schlenk flask, and then stirred for an hour. 1-Butene (30 g, 136.7mmol) was added by condensation at - 78°C using a dry ice bath. The mixture was stirred for 1 day at room temperature. The reaction was then stopped; the catalyst was deactivated by addition of 10% HCl solution in methanol. The toluene layer was separated, extracted with 2M NaOH, water, and saturated NaCl, successively, and then dried over anhydrous $MgSO_4$. The trimer fraction (5-ethyl- 3-methylene nonane) was obtained as a colourless liquid from the oligomeric mixture by fractional distillation through a 12 cm Vigreux column at 65-68 ^oC/20 mbar, to yield 6 g product (20%).

3.5 Functionalization of 1-butene oligomers (oxymercuration-demercuration reaction)



Scheme 3.2 Oxymercuration-demercuration reaction of 1-butene oligomers.

A 1-litre flask, fitted with a magnetic follower, dropping funnel and a thermometer, was charged with mercuric acetate (31.9 g, 100 mmol) and 100 mL of water. The mixture was

stirred until the acetate was dissolved. Upon addition of THF (300 mL) an orange-yellow suspension was formed. After stirring for a further 15 minutes, 100 mmol of the olefin (5-ethyl-3-methylene nonane) or 1-butene oligomers, synthesized as described in Section 3.4, was added. The reaction mixture was then stirred at room temperature for 1 hour to ensure the completion of the oxymercuration step. With vigorous stirring, 100 mL of a 4.5 M sodium hydroxide solution was added dropwise, followed by the addition of sodium borohydride (1.9 g, 50 mmol) in a 100 mL solution of 4.5 M sodium hydroxide. The reaction temperature was kept at about 25C^{o} during the addition of both solutions, by controlling the rate of addition. The flask was chilled in an ice bath as required. Reduction occurred readily with the separation of elemental mercury. The reaction mixture was stirred for 3 hours at ambient temperature to complete the demercuration step. The elemental mercury was allowed to settle overnight in a separating funnel. The organic and aqueous layers were separated. As the aqueous layer was saturated with sodium chloride, an additional organic layer formed. The new formed organic layer was separated. The remaining aqueous layer was extracted with two 30 mL portions of ether. The ether extracts and the two organic layers were combined. Most of the organic solvent was carefully removed under reduced pressure using a rotary evaporator; the evaporation was stopped when the two phases begin to separate. Fifty mL of ether and 20 ml of water were added. The ether layer was separated, washed with four 25 ml portions of water, and dried over anhydrous calcium sulphate. Finally, the ether was removed by rotary evaporation.

In the case of 5-ethyl-3-methylene nonane, the product 5-ethyl-3-methylnonan-3-ol was distilled, and collected at 106-110 °C/23 mbar (yield 90%, as revealed by GC).

3.6 Instrumentation

3.6.1 NMR spectroscopy

Nuclear magnetic spectra were done on either a 300 MHz Varian VXR spectrometer equipped with a Varian magnet (7.0 T) and a 1 mm switchable probe, or a 400 MHz Varian Unity Inova spectrometer equipped with an Oxford magnet (14.09) and a 5 mm inverse detection PFG probe. Standard pulse sequences were used for obtaining ^{1}H and

^{13}C spectra. Samples were prepared for NMR analysis as follows; approximately 80 mg of the product was weighed into an NMR tube, followed by addition of 0.7 mL deuterated chloroform which contained TMS as internal reference standard.

3.6.2 Gas chromatography (GC)

Gas chromatography (GC) was recorded on Perkin Elmer Autosystem XL instrument, equipped with a Quedrex 007 series methyl silicone capillary column (15 m x 0.32 mm. I.D) and FID detector. Samples of 1μL were injected manually and run for 45 min at a sampling rate of 12.5 pts/s. The carrier gas was nitrogen, with a pressure of 23 kPa. The oven temperature program was set as follows; initial temperature: 80 °C, initial hold: 0.00 min, total run time: 45 min, maximum temperature: 350°C, equilibration time: 2 min, ramp 1:2/min to 100°, hold for 0.00 min, ramp 2:10/min to 250°, hold time 20 min. The injection port of the GC was set at 250 °C, and the detector was set at 300 °C.

3.6.3 Gas chromatography coupled with mass spectrometry (GC-MS)

Gas chromatography–mass spectrometry (GC–MS) was performed on a AMD 604 High Resolution Mass Spectrometer, with scan: m/z 25-500 and scan rate: 0.8 sec/decade (with 0.2 seconds inter scan delay). Samples (10 μl) were dissolved in dichloromethane (about 1 mL) and an aliquot (1 μL) injected into the gas chromatograph inlet. Gas chromatography instrument Carlo Erba GC 6000 Vega Series, transfer line temperature 250°C, equipped with TRB5ms, silanol-terminated (95%)-methyl-(5%)-phenylpolisiloxane copolymer stationary phase column (60 m x 0.25 mm I.D x 0.25 μm film thickness), was used in the inlet method. Helium gas with pressure of about 190 kPa (linear velocity: 28.6 cm/sec at 40°C), split flow: 20 ml/min (septum purge: 5 mL/min) at temperature: 250°C, was used as the carrier. The oven temperature program was set as 80-280°C at 4°C/min (hold 20 min). The electron energy of 70eV was used for positive electron impact ionization (EI^+). The source temperature was set at 200ºC.

3.6.4 Fourier-transform infrared spectroscopy (FT-IR)

Infrared spectroscopic analysis was performed on a Perkin-Elmer Paragon 1000 Fourier Transform Infrared Spectrometer. A small drop of the sample was placed on a NaCl disk,

and then the spectrum was recorded. The absorption of the sample was then deducted from the NaCl background. IR spectrum were recorded at wave length ranged from 4000 to 500 cm^{-1}, with 32 number of scans and resolution of 4.0 cm^{-1} at interval 1.0 cm^{-1}.

3.6.5 Size Exclusion Chromatography (SEC)/Gel Permeation Chromatography (GPC)

The following instrumentation was used to determine the molecular weight of 1-butene oligomers. A Waters 2690 separation module Alliance, comprising of an Alliance 2690 pump and Alliance injector, combined with a PL mixed E 3 µm column (length 30 cm, diameter 0.75 cm, temperature 30 °C), evaporative light scattering detector (ELDS) PL-ELS from Polymer Lab, UV detector Agilent 1100 Series, and PSS 246/501 interface. Fifty microlitres of samples dissolved in THF (5 mg/ml) were injected into the column using THF as an eluent at flow rate of 1.00 ml/min. UV absorption was recorded at 254 nm.

3.7 Characterization

3.7.1 SEC/GPC measurements

As expected, GPC measurements for a series of oligomers obtained from different oligomerization reactions showed that all the oligomers had low average molecular weight ($\overline{M_w}$), ranging between 800 and 2,000 $g.mol^{-1}$. The differences in the molecular weights are due only to the variation in the concentration of the monomer, as all other factors (e.g reaction temperature, catalyst concentration, etc) were kept constant. Table 3.1 shows $\overline{M_w}$ and number average molecular weight ($\overline{M_n}$) values for oligobutenes (the footnote underneath the table shows all the oligomerization conditions that applied).

Table 3.1 GPC results for 1-butene oligomerizations

Reaction	1-butene (mol)	$\overline{M_w}$ (g/mol)	$\overline{M_n}$ (g/mol)	Dispersity $\overline{M_w}/\overline{M_n}$
1	0.2317	1364	811	1.68
2	0.2852	1450	925	1.57
3	0.3209	1557	953	1.63
4	0.5169	2514	1127	2.23

Oligomerization conditions: Al:Zr =1000:1, *T* = 25 °C, reaction time = 24 h, catalyst concentration = 3 X 10^{-5} and pre-activation time for catalyst = 1h.

3.7.2 NMR spectroscopy

The following proton and carbon NMR shifts are typical for the trimer fraction. They can also be applied on the oligomeric mixture; especially those shifts assigned to the end-groups, where ^{1}H NMR and ^{13}C NMR shifts are the same for both the trimer and the oligomers.

^{1}H NMR ($CDCl_3$) 5-ethyl-3-methylene nonane: δ (ppm) = 0.787 (m, 6H, $2CH_3$), 0.964 (t, 3H, CH_3), 1.16-1.66 (m, 9H, CH, $4CH_2$), 1.92 (m, 4H, $2CH_2$), 4.66, 4.722 (d, 2H, $C=CH_2$). **^{13}C NMR ($CDCl_3$)** 5-ethyl-3-methylene nonane: δ (ppm) = 10.93, 12.57, 14.33($3CH_3$), 23.35, 26, 28.72, 29.16, 32.93, 41.39 ($6CH_2$), 37.06 (CH), 109.49, 151.24 ($C=CH_2$). **^{1}H NMR ($CDCl_3$)** 5-ethyl-3-methyl-3-nonanol: δ (ppm) = 0.82 (m, 9H, $3CH_3$), 1.13 (s, 3H, CH_3), 1.18-1.5 (m, 13H, CH, $6CH_2$). **^{13}C NMR ($CDCl_3$)** 5-ethyl-3-methyl-3-nonanol: δ (ppm) = 8.55, 11, 14.45, 27.92 ($4CH_3$), 23.42, 26.77, 29.17, 34.84, 35.4, 45.54 ($6CH_2$), 34.97 (CH), 73.83 (C-OH).

The ^{1}H NMR spectrum of the trimer fraction as well as that of the mixture of 1-butene oligomers displays two significant broad singlets at 4.67 and 4.75 ppm in the olefinic region. The appearance of these two singlets is due to the vinylidene double bond at the end of the oligomers chains. This is generally known, in the polymerization and oligomerization of 1-butene and higher α-olefins, to be a result of *β*-hydrogen transfer reactions [19,21]. Figure 3.1(a) displays all the proton chemical shifts of the trimer. The ^{1}H NMR spectrum of the oligomer mixture is shown in the Appendix (Figure1).

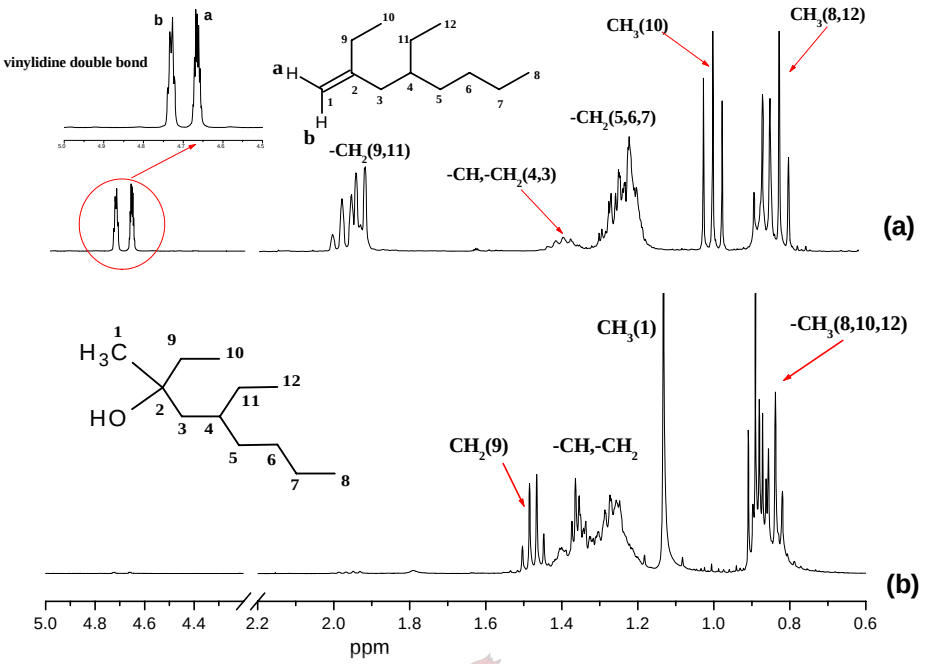


Figure 3.1 ^{1}H NMR spectra of: (a) vinylidene- and (b) hydroxy- terminated 1-butene trimer.

In addition, the ^{1}H NMR was used to confirm the conversion of the vinylidene end-group to a monofunctional hydroxyl group. The ^{1}H NMR spectrum of the hydroxy-terminated oligobutenes (Figure 3.1(b)) is characterized by; the disappearance of the two vinylidene singlets in the olefinic region as well as the triplet of the methyl group at 0.99 ppm, the appearance of a new singlet of a methyl group at 1.13 ppm, and the upfield shift of the signal of the methylene group from 1.92 to 1.45 ppm. A comparison of the proton chemical shifts of the trimer and the hydrox-terminated trimer is shown in Figure 3.1.

^{13}C NMR was used to assign the chemical shifts of the carbons of the start and the end groups of the oligomers. The characteristic patterns in both the aliphatic and olefinic regions are assigned to 2-alkyl-substituted-1-alkene. Figure 3.2(a) displays the ^{13}C NMR of the trimer fraction and shows all the chemical shifts of these groups. The ^{13}C NMR spectrum of the oligomers is shown in the Appendix (Figure 2).

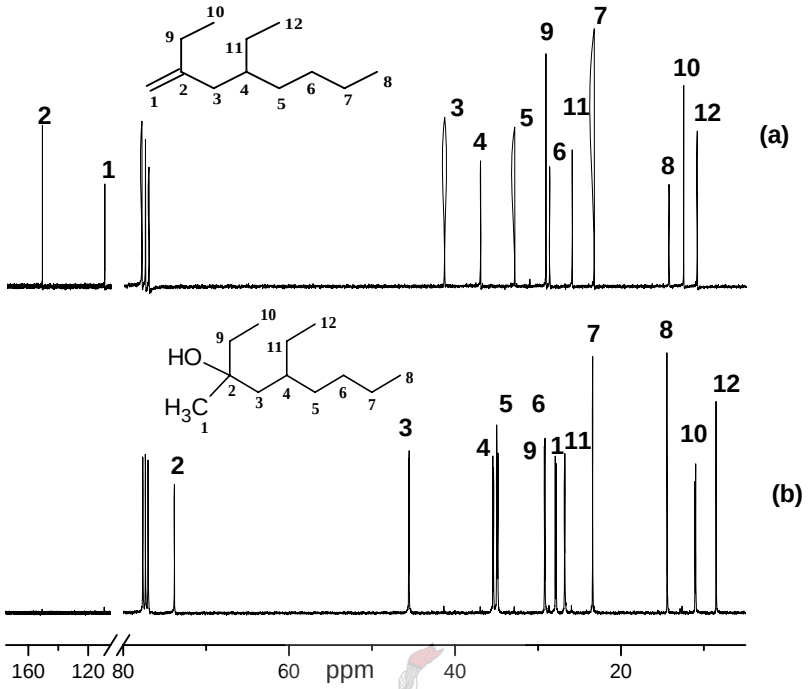


Figure 3.2 ^{13}C NMR spectra of: (a) vinylidene- and (b) hydroxy- terminated 1-butene trimer.

The ^{13}C NMR spectra confirmed the conversion of the vinylidene double bond to a hydroxyl group. Figure 3.2(b) shows, a new peak at 73.8 ppm, which is related to the tertiary carbon attached to the hydroxyl group, and the disappearance of the peaks related to the vinylidene end group at 109.5 and 151.24 ppm,.

In conclusion, the proton and carbon chemical shifts displayed in Figures 3.1 and 3.2, particularly those assigned to the vinylidene and the hydroxyl groups, confirm the successful synthesis and functionalization of 1-butene oligomers.

3.7.4 GC/MS analysis

Due to the volatility of the oligomeric fractions, GC (with flame ionization detection, FID) and GC/MS analyses were used to separate and identify the different oligomer fractions. A GC chromatogram of the 1-butene oligomers (Figure 3.3) reveals the formation of dimers to octamers of 1-butene.

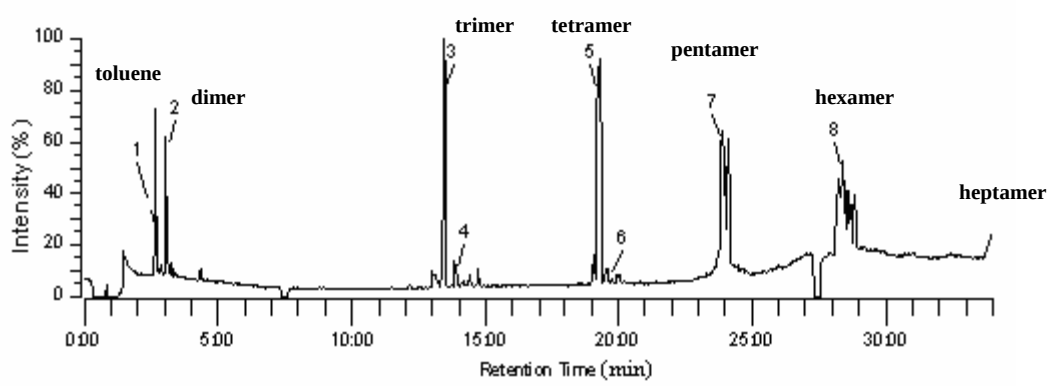


Figure 3.3 GC chromatogram of the oligomerization products of 1-butene.

As shown in Figure 3.3, the obtained oligomers were accompanied by configurational isomers as minor products, eluting ± 1 min from the main compounds. The trimer fraction, for instance, eluted at 14.5 min and consisted of less than 10% isomers (other than the main product).

Low resolution EI^+ mass spectra of the oligomeric mixture provided the identity for each oligomer component, as well as its isomer. Figures 3.4 and 3.5 show the EI^+ mass spectrum of the trimer and its isomer respectively. The mass spectrum of the other components are shown in the Appendix; Figure. 3-7.

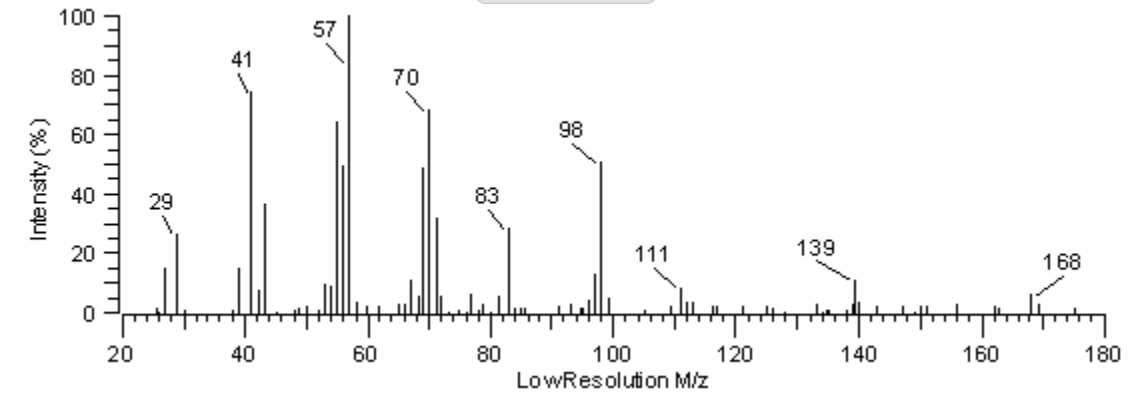


Figure 3.4 EI^+ mass spectrum of the trimer.

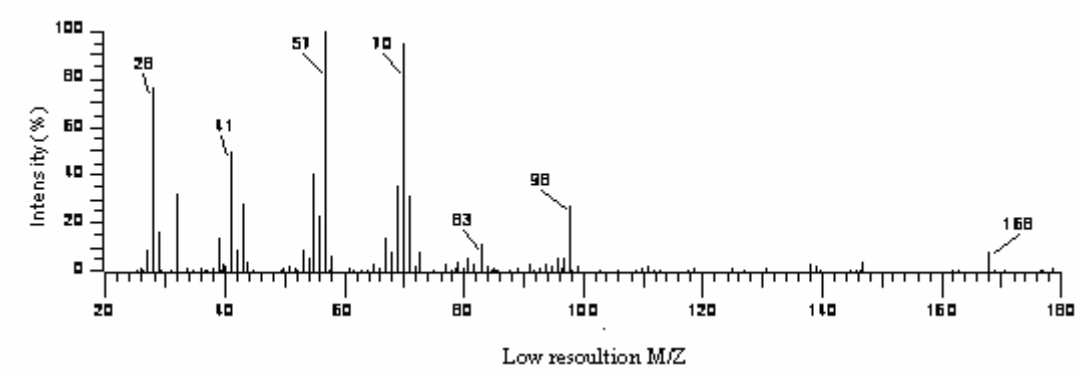


Figure 3.5 EI$^+$ mass spectrum of the trimer isomer (minor compounds eluting ± 1 min from the trimer).

The above figures display the presence of the molecular ion peak (*m*/*z* 168 = M^+) accompanied by characteristic peaks for a series of $[C_nH_{2n-1}]^+$ fragment ions (*m*/*z*; 27-29, 41-43, 55-57, 69-71, 83…) which are typical of alkenes. Particularly, the ion peak (*m*/*z* 70) is the main fragmentation product for many 2-alkyl-substiuted-1-alkenes[19,22-24].

GC/MS analysis was also applied to the functionalized oligomers. The GC chromatogram presented in Figure 3.6 shows the separation of the different hydroxy-terminated oligobutenes. It reveals that, although there are still traces of unreacted oligomers, the conversion of the vinylidene double bond to an alcohol (hydration reaction) proceeded in over 90% yield.

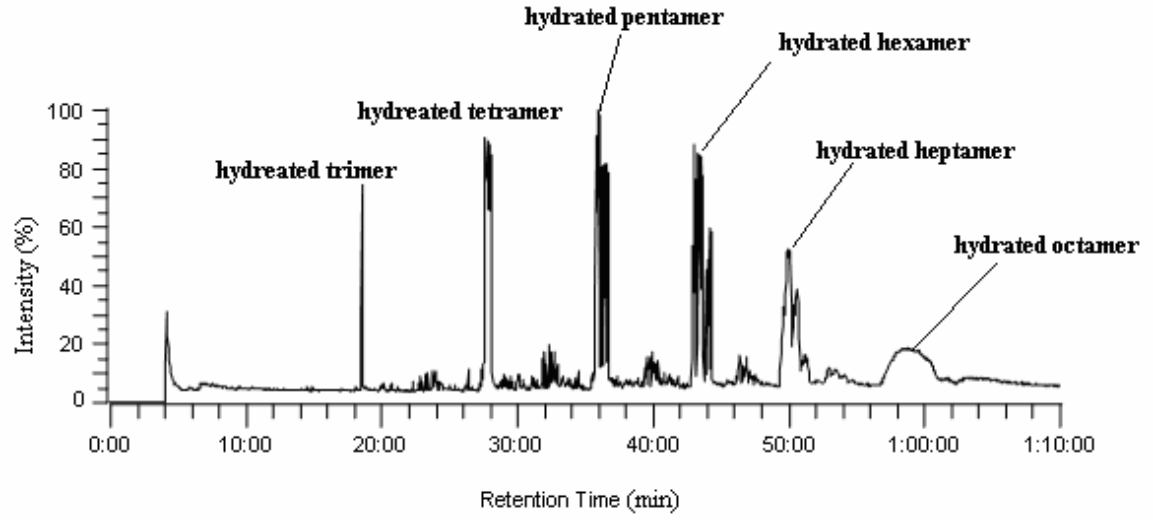


Figure 3.6 GC chromatogram of the hydroxy-terminated oligobutenes.

GC/MS analysis confirmed that the identity of each fraction to be mainly tertiary alcohols. For example, the first fraction that elutes at about 20 min, as shown in the chromatogram (Figure 3.7), was identified 5-ethyl-3-methylnonan-3-ol.

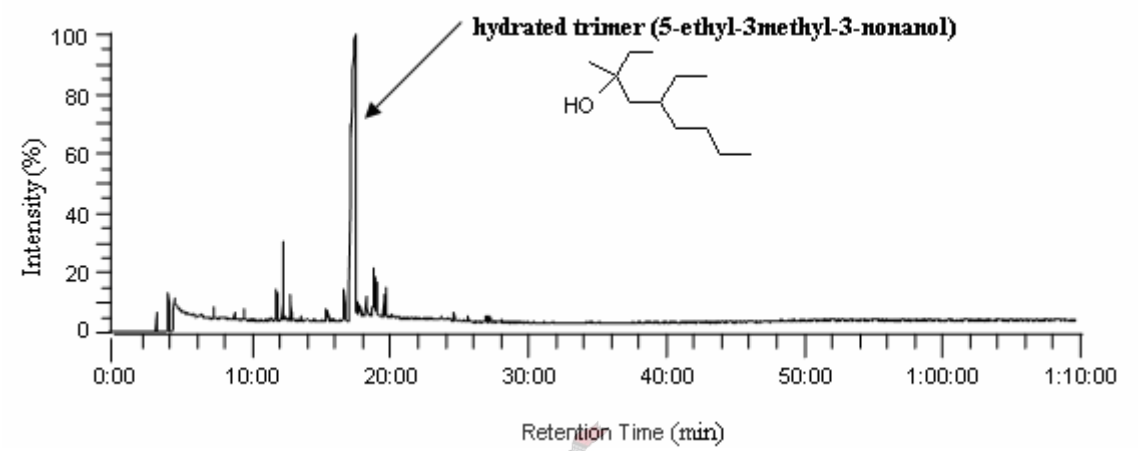
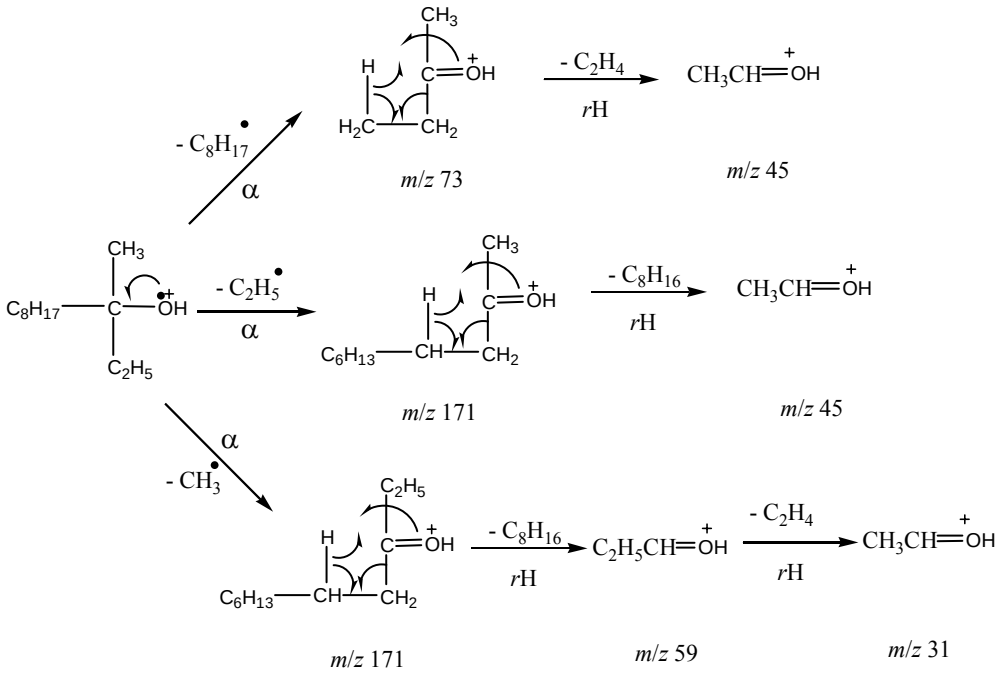


Figure 3.7 GC chromatogram of the hydroxy-terminated butene trimer.

It should be pointed out that, according to Markovnikov rule, minor compounds such as mono-alcohols are expected from this type of reactions.

It is well known that the mass spectra of alcohols in general are featured by molecular ions for oxonium ion ($C_nH_{2n+1}O^+$) as a result of a α-cleavage reaction at the α-carbon[22,24] (Scheme 3.3).



Scheme 3.3 α-cleavage and hydrogen rearrangement reactions of 5-ethyl-3-methylnonan-3-ol[22].

Accordingly, in the spectrum of 5-ethyl-3-methylnonan-3-ol (Fig. 3.8) this reaction produces the important peaks at *m/z* 73, 157 and 171. The $C_nH_{2n+1}O^+$ ion formed undergoes either rearrangement of hydrogen (*r*H), which is illustrated by the peaks at *m/z* 31, 45, and 59, or further decomposition by dehydration which results in formation of the *m/z* 55, 139, and 153 peaks. Peaks at *m/z* 29 and 43 suggest another decomposition pathway for $C_nH_{2n+1}O^+$, including the formation of CHO^+ and $C_2H_3O^+$ ions respectively[22].

The elimination of water is also one of the other major decomposition pathways possible for alcohol molecular ions. This leads to the loss of H_2O and of (H_2O + C_nH_{2n}) (n =2)[22,24].As a result, peaks at *m/z* 97 and 111 are seen on the mass spectrum of 5-ethyl-3-methylnonan-3-ol (Fig. 3.8). The rest of the spectrum corresponds to the hydrocarbon fragments which closely resemble those of the corresponding alkene.

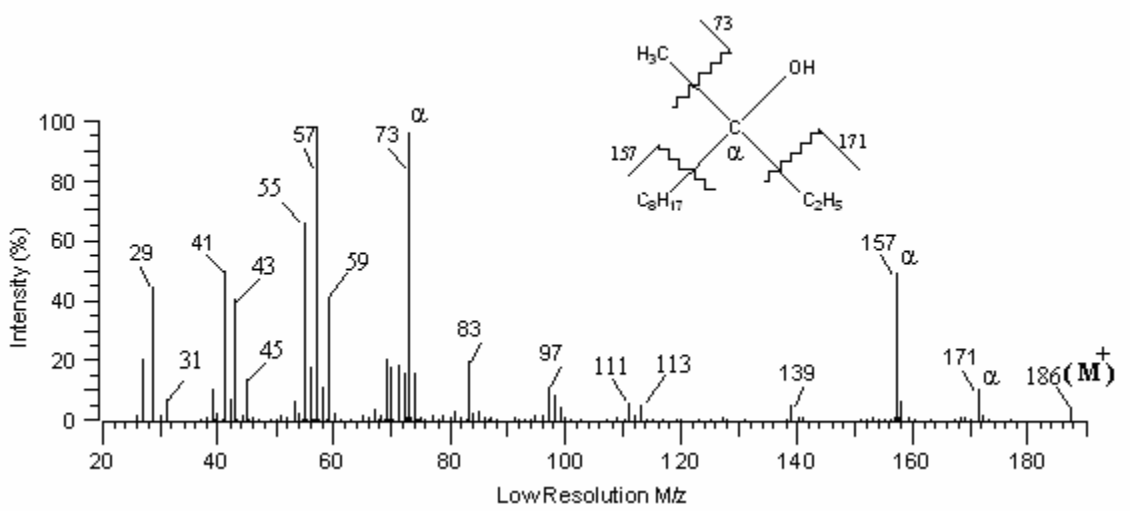


Figure 3.8 EI$^+$ mass spectrum of 5-ethyl-3-methylnonan-3-ol.

This interpretation of the mass spectrum can also be applied to all the other hydrated oligomer fractions. For the mass spectra of the other fractions see the Appendix (Figure 8-13).

3.7.5 IR spectroscopy

Infrared spectroscopy (IR) is a very powerful technique that helps to identify and determine the chemical structure of a compound, and in particular to monitor the presence of chemical functional groups. Molecular vibrations and rotations of many functional groups show characteristic absorption bands in defined regions of the IR spectrum. Thus such functional groups can be identified by their absorption bands[25].

In the case of oligobutenes, besides the conventional absorption bands of hydrocarbon groups such as methyl and methylene, three unique absorption bands corresponding to the vinylidene double bond are observed[25]. These bands appear on the IR spectrum as follows: C-H stretching vibration with medium intensity around 3075 cm^{-1}, C-H bending vibration with strong intensity at 888 cm^{-1}, and C=C stretching vibration with strong intensity around 1645 cm^{-1}.

The successful functionalization of the oligomers to prepare hydroxy-terminated oligobutenes was also confirmed by the IR spectroscopy. The complete absence of all the

bands corresponding to the vinylidine double bond, and the appearance of a new broad band corresponding to the hydroxyl group at 3435 cm^{-1}, demonstrate the successful formation and functionalization of 1-butene oligomers.

Figure 3.9 displays a comparison between the IR spectra of oligobutenes and hydroxy-terminated oligobutenes.

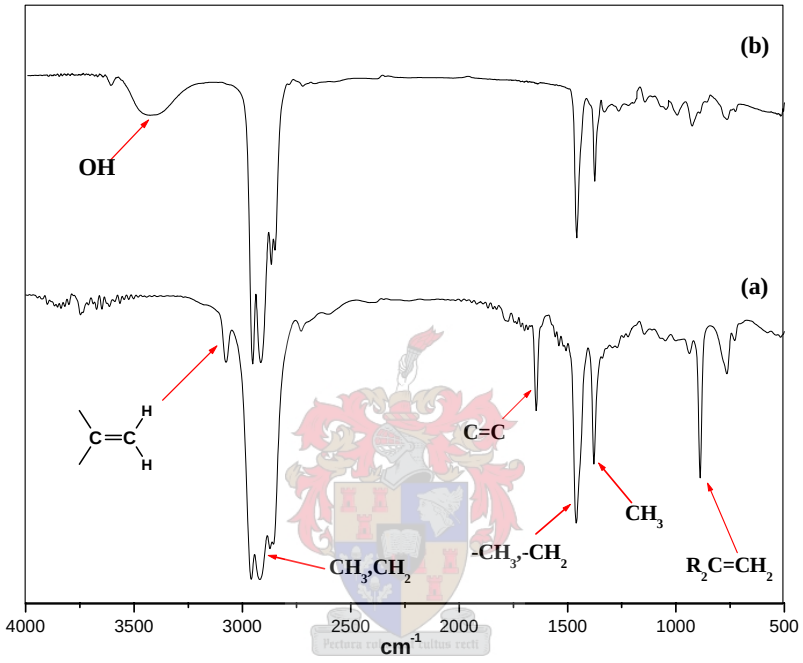


Figure 3.9 IR spectra of: (a) oligobutenes and (b) hydroxy-terminated oligobutenes.

3.8 References

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Chapter 4 Synthesis and Characterization of Oligobutene-based macro-RAFT Agents

4.1 Introduction

This chapter describes the synthesis and characterization of oligobutene-based RAFT agents, hereafter referred to as macro-RAFT agents. In order to achieve that, a reaction between the hydroxy-terminated oligobutenes and a RAFT agent possessing a suitable functional group is necessary. In a method used by Davis *et al*.[1-3] trithiocarbonate based RAFT agents with carboxylic acid groups were found to be suitable for reacting with a range of hydroxyl multifunctional compounds, such as carbohydrates, to prepare a wide variety of macro-RAFT agents. The advantage of the trithiocarbonate based RAFT agents over other thioester based RAFT agents is their ease of preparation, even in the presence of other functional groups such as carboxylic acids[1-3].

The synthesis of the macro-RAFT was carried out in three steps. The first step involved the synthesis of the carboxylic acid of the trithiocarbonate-containing RAFT agent **(1)** (3-benzylsulphanylthiocarbonylsuphanylpropionic acid). The second step involved conversion of the acid to an acid chloride **(2)**, which was used in the third step to prepare the macro-RAFT agents **(3)** and **(4)** (trimer- and oligobutene-based RAFT agents, respectively). This type of reactions is considered as an esterification reaction, where the butene oligomers in the final product are attached to the RAFT agent via an ester group. In this case the oligomeric part of the macro-RAFT agent basically functions as a Z group of the RAFT agent, while the benzyl group functions as a leaving group R (Figure 4.1).

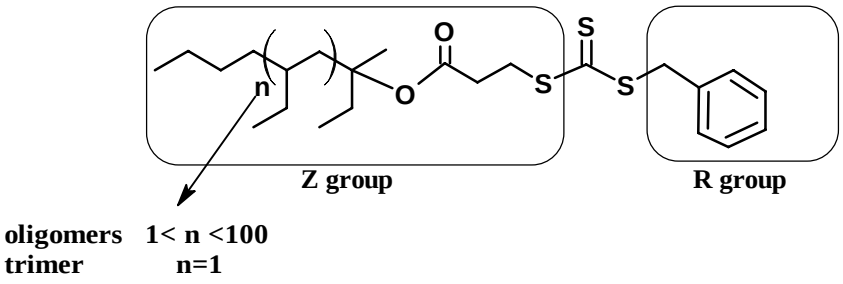


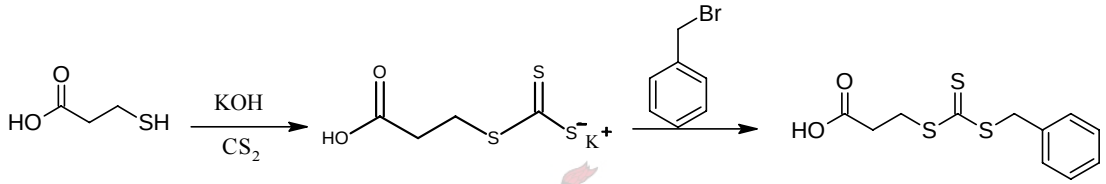
Figure 4.1 General structure of the macro-RAFT agent.

All the experimental procedures and characterizations were carried out for both the hydroxy-terminated trimer and the hydroxy-terminated oligobutenes.

4.2: Chemicals

The following chemicals were used: 3-Mercaptopropionic acid (99%, Acros Organics), carbon disulfide (99.5%, Merk), benzyl bromide (98%, Fluka), thionyl chloride (99%, Merk), pyridine (CP 99.5%, Sarchem), carbon tetrachloride (AR 99.5%, Lab Chem), potassium hydroxide (85%, R&S Scientific).

4.3 Synthesis of 3-benzylsulphanylthiocarbonylsuphanylpropionic acid (1).

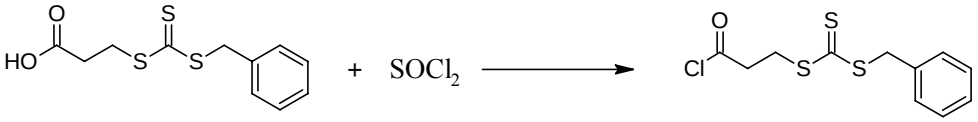


(1)

A 250 mL three-necked round-bottom flask equipped with reflux condenser and dropping funnel was charged with a solution of potassium hydroxide (13 g, 0.23 mol) in water (125 mL). 3-Mercaptopropionic acid (10 mL, 0.115 mol) was added. Carbon disulfide (15 mL, 0.115 mol) was added dropwise, and an orange solution formed immediately. The mixture was stirred for 5 hours and then heated together with benzyl bromide (19.8 g, 0.0.115 mol) for 12 h at 80 °C. The mixture was cooled down to room temperature and chloroform (150 mL) was added. The reaction mixture was acidified with hydrochloric acid (25%) until the organic layer turned yellow and a clear aqueous layer was obtained. The aqueous phase was extracted with chloroform (2 x 100 mL). The combined organic layers were dried over anhydrous magnesium sulphate. After evaporation of the solvent, the remaining product was purified by gel column chromatography, using a 3:1 hexane-ethyl acetate mixture as eluent, to yield a yellow powder **(1)** (26.24 g, 83%), T_m = 86-88 °C.

The final product was characterized by ^{1}H and ^{13}CNMR and IR spectroscopy, and the chemical structure was confirmed. Details are shown in Figures 4.2, 4.3 and 4.6.

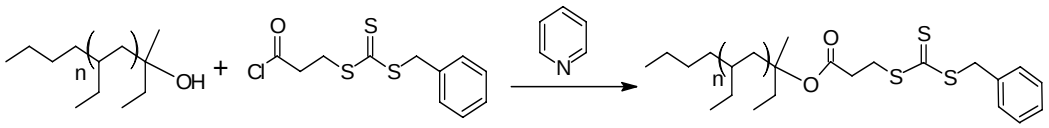
4.4 Synthesis of 3-benzylsulphanylthiocarbonylsuphanylpropionic acid chloride (2).



(2)

The acid **(1)** (10 g, 36 mmol) was dissolved in carbon tetrachloride (50 mL), in a 100 ml three-necked round-bottom flask equipped with reflux condenser and dropping funnel. After the drop-wise addition of thionyl chloride (10 mL), the mixture was then gradually warmed and refluxed until a clear solution was obtained. After refluxing for a further hour, the product was isolated by removal of the solvent under vacuum. The remaining yellow oil was dried under high vacuum. The product (10.52 g, 98.5%) was used immediately for the synthesis **(3)** and **(4)**.

4.5 Synthesis of oligobutene-based macro-RAFT agents (3) and (4)



(3) n =1

(4) 1< n <100

5-Ethyl-3-methyl-3-nonanol (8 g, 43 mmol) or hydroxy-terminated oligobutene (12 g, $\overline{M_w}$ = 2,000) (synthesized as described in Section 3.5) was dissolved in dry ether (50 mL) in a 250 ml three-necked round-bottom flask. Two equivalents of pyridine was added in one portion. After the dropwise addition of three equivalents of the acid chloride **(2)** in an ice bath, the mixture was stirred overnight at ambient temperature. HCl (30 mL, 10%) was added, then the organic layer was washed with sodium carbonate (50 mL, 10%), saturated NaCl solution (30 mL) and water (2 x 30 mL) respectively, and dried over

anhydrous magnesium sulphate. After evaporation of the solvent, the remaining product was twice purified by gel column chromatography, with a 3:1 hexane-ethyl acetate mixture, followed by 1:1 hexane- petroleum ether, as eluents to yield a very viscous yellow oil.

4.6 Characterization

4.6.1 NMR analysis

The chemical structures of the RAFT agents **(1)**, **(2)**, **(3)** and **(4)** were confirmed by ^{1}H-NMR and ^{13}C-NMR spectroscopy, as following:

RAFT agent **(1)**: **^{1}H NMR ($CDCl_3$):** 2.84 (t, 2H, CH_2-C=O, J = 7.17 Hz), 3.62 (t, 2H, CH_2-S, J = 7.17 Hz), 4.61 (s, 2H, CH_2-Ph), 7.27 (m, 5H, Ph), 10.1 (br, 1H, OH). **^{13}C NMR ($CDCl_3$):** 32.78, 30.69 (CH_2-CH_2), 41.4 (CH_2-Ph), 127.96–129.38 (Ph), 134.98 (Ph), 177.81(C=O), 223.18 (C=S).

RAFT agent **(2)**: **^{1}H NMR ($CDCl_3$):** 3.35 (t, 2H, CH_2-C=O), 3.62 (t, 2H, CH_2-S), 4.61 (s, 2H, CH_2-Ph), 7.27 (m, 5H, Ph). **^{13}C NMR ($CDCl_3$):** 45.53, 30.46 (CH_2-CH_2), 41.55 (CH_2-Ph), 128.05–129.4 (Ph), 134.76 (Ph), 172.49 (C=O), 222.6 (C=S).

RAFT agent **(3)**: **^{1}H NMR ($CDCl_3$):** 0.74 (m, 9H, $3CH_3$), 1.11-1.3 (br, 8H, CH_2), 1.35 (s, 3H, CH_3), 1.46 (q, 2H, CH_2) 1.67 (m, 2H, CH_2), 1.8 (m, 1H, CH), 2.58 (t, 2H, CH2-C=O), 3.51 (t, 2H, CH_2-S), 4.55 (s, 2H, CH_2-Ph), 7.21 (m, 5H, Ph). **^{13}C NMR ($CDCl_3$):** 7.9, 10.3, 13.9 ($3CH_3$), 23.5 (CH_3-CO), 22.9, 28.5, 31.5, 41.5, 26.8, 34 (CH_2), 33.87 (CH), 31.25 (CH_2-C=O), 34.1 (CH_2-S), 41.31 (CH_2-Ph), 86.96 (C-O), 127.9–129.4 (Ph), 135.1 (Ph), 170.7(C=O), 223.6 (C=S).

The NMR spectra presented in Figures 4.1 and 4.2 display all the proton and carbon chemical shifts expected for the RAFT agents **(1)** and **(2)**.

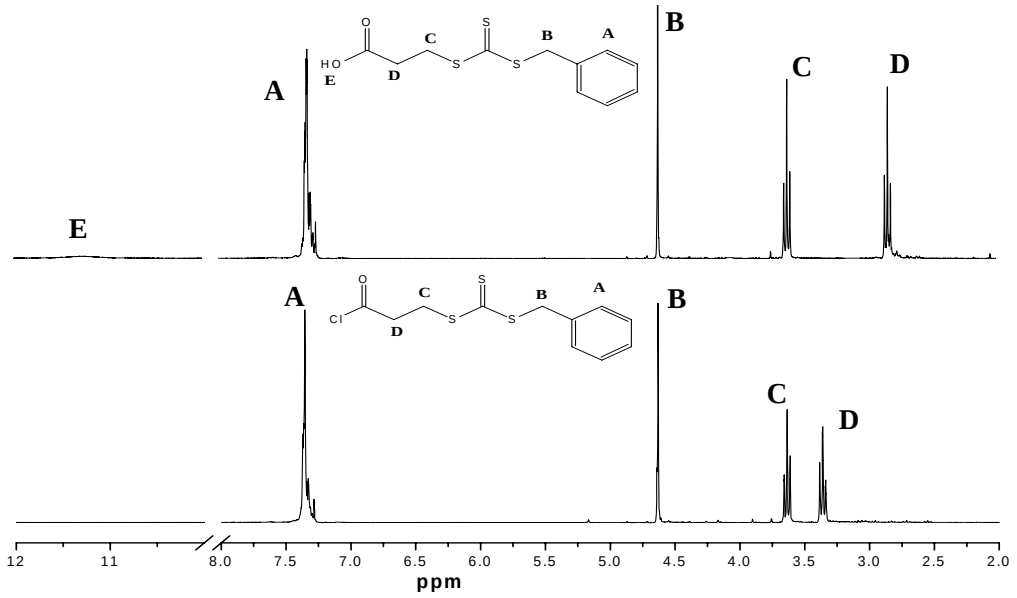


Figure 4.2 ^{1}H NMR spectra of the RAFT agents (1) (top) and (2) (bottom).

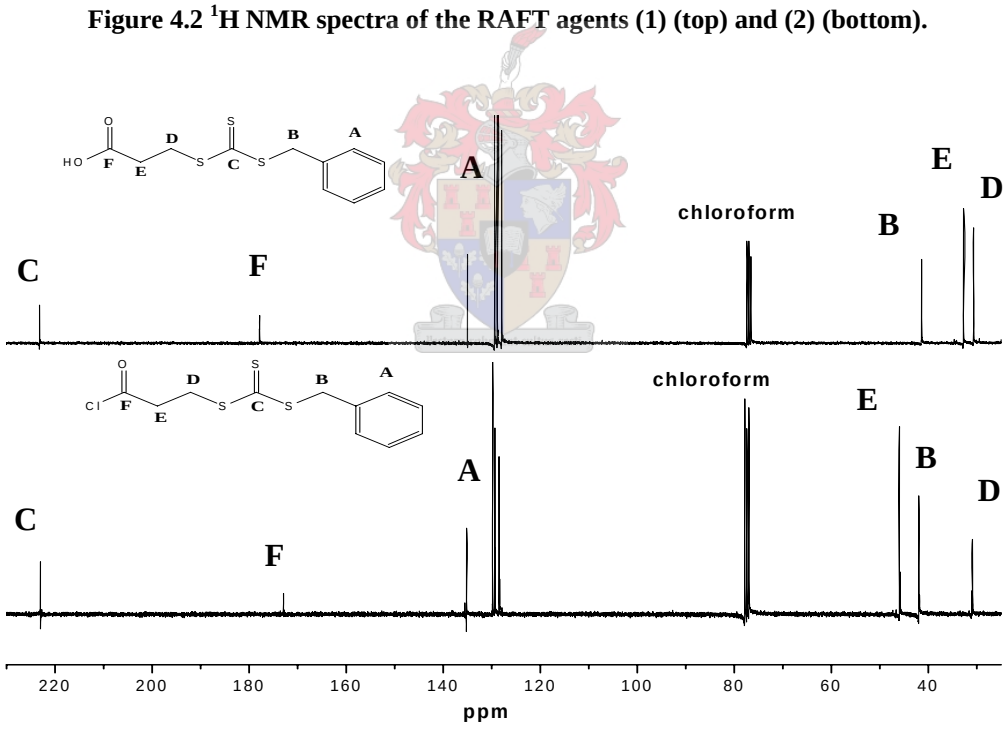


Figure 4.3 ^{13}C NMR spectra of the RAFT agents (1) (top) and (2) (bottom).

^{1}H NMR and ^{13}C NMR spectroscopy also showed the presence of all the shifts of all the functional groups expected for both macro-RAFT agents **(3)** and **(4)**. However, due to the composition of the oligomeric mixture, which is based mainly on aliphatic oligomer

chains with unequal lengths, the overlapping of peaks in the aliphatic region in the spectrum of **(4)** were expected. Therefore, in order to identify the chemical structure of the macro-RAFT **(4)**, a comparison between the two spectra (Figures 4.4 and 4.5) is needed.

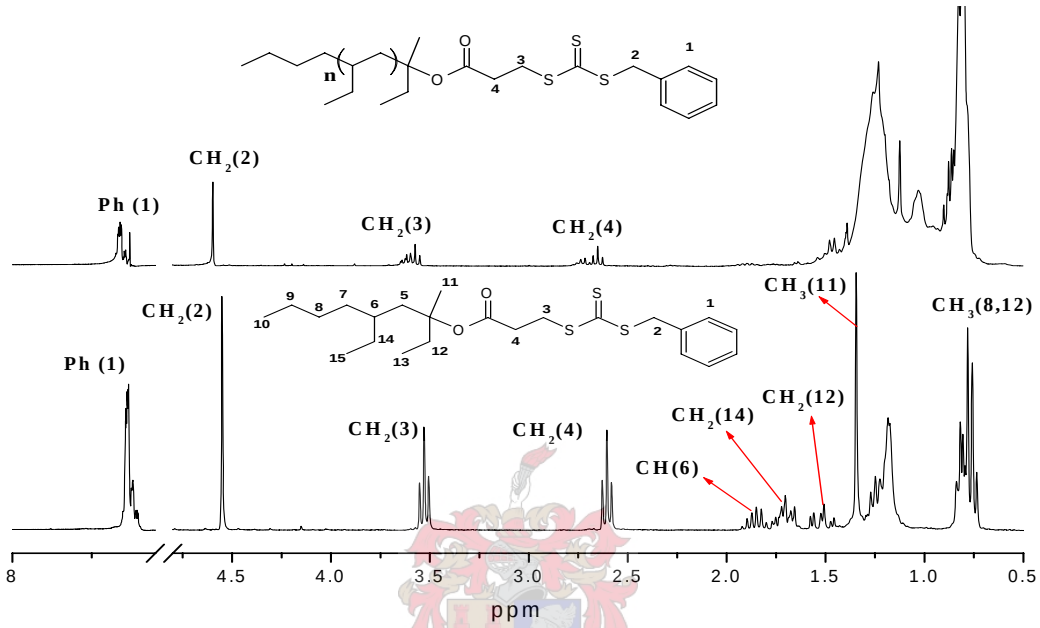


Figure 4.4 ^{1}H NMR spectra of the macro-RAFT agents (4) (top) and (3) (bottom).

As it can be seen from the ^{13}C NMR spectra (Figure 4.4), the characteristic chemical shifts for all the functional groups (such as C=O, C-O, C=S and C-S), and especially those for the ester group, confirm that the esterification reaction was achieved and that the final macro-RAFT agent was successfully synthesized.

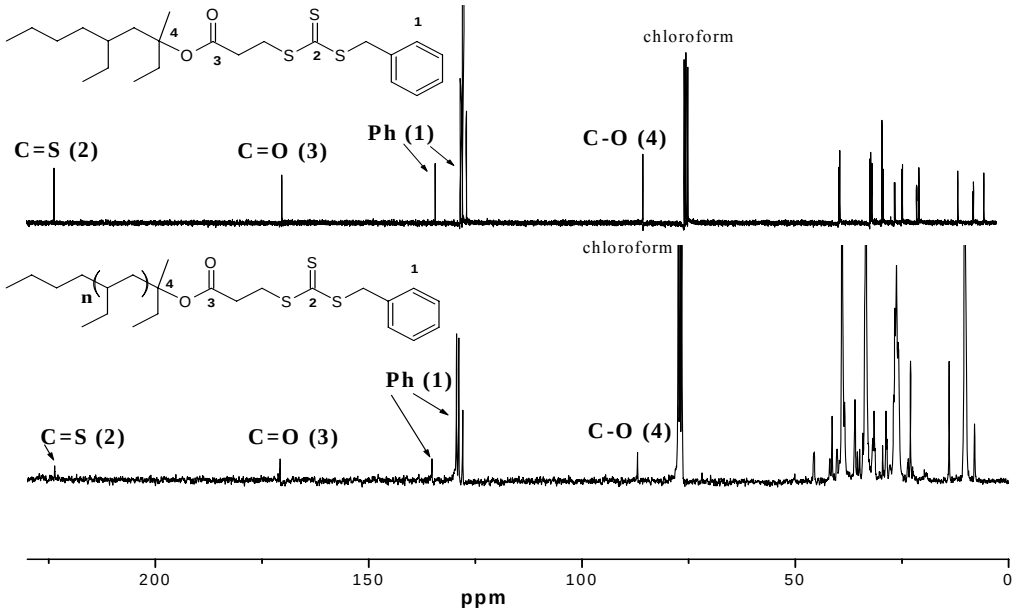


Figure 4.5 ^{13}C NMR spectra of the macro-RAFT agents (3) (top) and (4) (bottom).

4.6.2 IR spectroscopy

The characteristic absorption bands for different chemical bonds and functional groups (such as C=O, OH, C=S, C-S and other specific bonds[4]) were observed in the IR spectra for all RAFT agents **(1)**, **(2)**, **(3)** and **(4)**. Comparing the IR spectra of the starting materials with that of the final products showed and confirmed the chemical structure of the macro-RAFT agents. Figures 4.5 and 4.6 present the IR spectra of all the RAFT agents that were synthesized as described in this chapter.

RAFT agent **(1)**: **IR (NaCl)** (cm^{-1}): 3027 (Ph), 2924 (-CH_2, -CH_3), 2661(-OH), 1708 (C=O), 1064 (C=S), 803 (C-S).

RAFT agent **(2)**: **IR (NaCl)** (cm^{-1}): 3028 (Ph), 2914 (-CH_2, -CH_3), 1791 (C=O), 1065 (C=S), 805 (C-S).

RAFT agent **(3)/(4)**: **IR (NaCl)** (cm^{-1}): 3028 (Ph), 2956-2863 (-CH_2, -CH_3), 1727 (C=O), 1189 (C-O), 1067 (C=S), 806 (C-S).

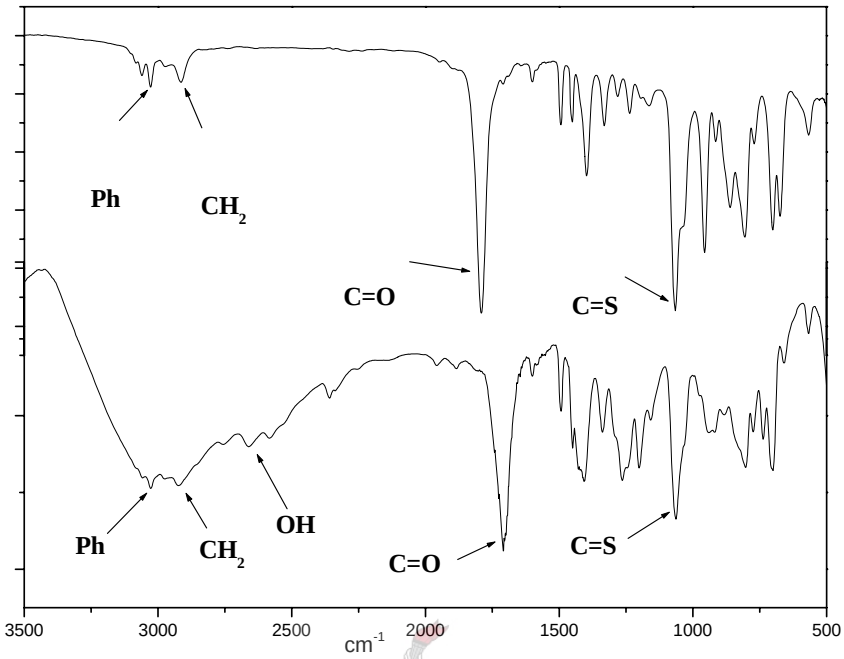


Figure 4.6 IR spectra of the macro-RAFT agents (1) (bottom) and (2) (top).

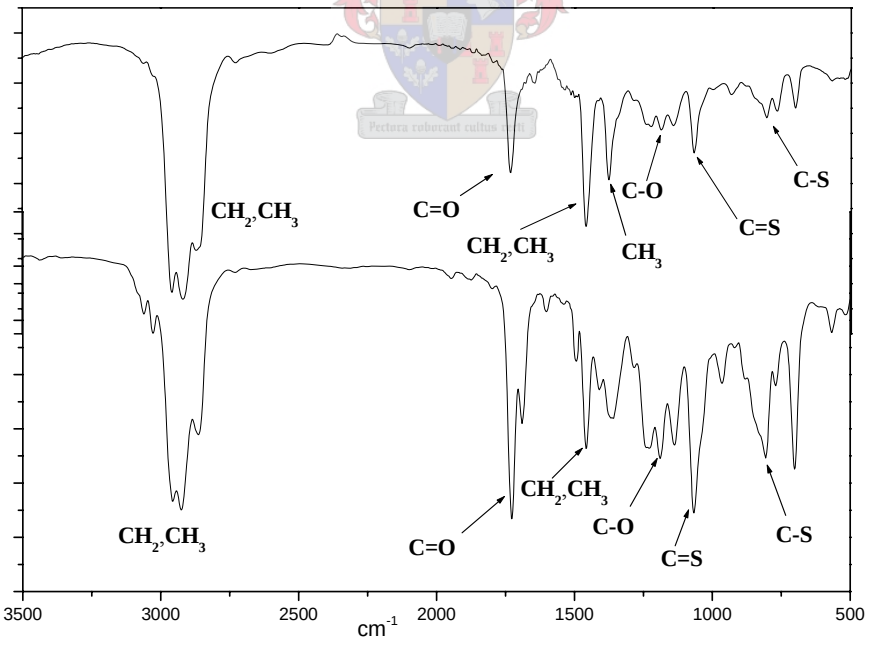


Figure 4.7 IR spectra of the macro-RAFT agent (3) (bottom) and (4) (top).

4.6.2 UV spectroscopy

UV spectroscopy is a technique used to determine the wavelength of maximum absorption (λ_{max}) of UV absorpting species. The UV/visible spectrometer operates on the double beam principle, with one beam passing through the sample and the other passing through a reference cell[5]. It is known that the thiocarbonyl moiety (C=S) has an absorption maximum at 320 nm. Therefore all the RAFT agents were expected to have an absorption maximum at this specific wavelength. This was indeed observed when the UV absorption of **(3)** and **(4)** recorded at a UV/visible spectrometer.

A Perkin Elmer UV/visible spectrometer Lambda 20 Spectrometer was used to identify the UV absorption band of the C=S bond present in the RAFT agents **(1)**, **(2)**, **(3)**, and **(4)**. The analysis of the data was done with UVWinlab v.4.2 software. Quartz cuvettes (supplied by CND Scientific) with a 10 mm path length were used. UV analysis of the RAFT agents showed the following results:

UV(C=S): ($n \longrightarrow \pi^*$, λ_{max} = 432 nm) and ($\pi \longrightarrow \pi^*$, λ = 308 nm), dichloromethane was used as a solvent.

4.7 References

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(2) Jesberger, M.; Barner, L.; Stenzel, M. H.; Malmstrom, E.; Davis, T. P.; Barner-Kowollik, C. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3847.

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(4) Hesse, M.; Meier, H.; Zeeh, B. In *Spectroscopic Methods in Organic Chemistry*; Georg Thieme Verlag: Stuttgart & New York, 1997; pp 29-70.

(5) Harwood, L. M.; Moody, C. J.; Percy, J. M. In *Experimental Organic Chemistry*, 2ed ed.; Blackwell Science Ltd, 1999; pp 356-366.

Chapter 5 Polymerization of styrene mediated by macro-RAFT agents

5.1 Introduction

It has been proven over the last few years since the discovery of the RAFT process in 1998 that the RAFT process is a simple and convenient method to obtain polymers with: living characteristics, controlled molecular weight distribution (MWD), low polydispersities, and well defined architecture and end groups. Moreover, the RAFT process is applicable to polymerization of a wide range of monomers under the same conditions that are employed in conventional free radical polymerization (initiation, solvents, and temperature)[1,2]. The RAFT process also does not need additional experimental precautions and can be applied in both homogeneous and heterogeneous polymerizations, such as emulsion[3-6] and miniemulsion[7-10] polymerizations.

In spite of all the advantages that the RAFT process has, however, there are some disadvantages:

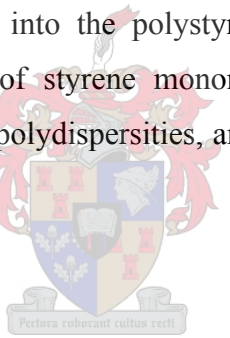
1. The RAFT agents are not easy to synthesize and purify.
2. RAFT compounds consist basically of thiocarbonyl thio compounds which have a strong and nasty smell, and the final polymers are sometimes coloured.
3. Inhibition and retardation are often observed in RAFT polymerizations[4,11-14].
4. Termination is not specifically suppressed; this is generally represented by the formation of tails in the molar mass distribution curves as a result of the formation of a small number of dead chains produced by radical-radical termination[4,15].

As in all living techniques, the termination reactions are not entirely suppressed in a RAFT system. However, the concentration of terminated products can be minimised by using very low initiator concentrations.

The RAFT process, as mentioned above, has the ability to polymerize any monomers susceptible to free-radical polymerization. Styrene has been used in the study of different polymerization systems,[16-18] such as: bulk[19], solution, emulsion[4,20,21] and miniemulsion[22] because it has proved to be successful in the preparation of homopolymers and copolymers. Styrene can be either used alone as self-initiated monomer or accompanied

with an initiator in both bulk and solution polymerization in the presence of a RAFT agent. Therefore, styrene, the most commonly studied monomer, was used in this study to investigate the reactivity and the efficiency of the macro-RAFT agent in living free radical polymerization.

This chapter discusses the use of the macro-RAFT agents **(3)** and **(4)** that were synthesized as described in Chapter 4, in living radical polymerization by the RAFT process. The living character of styrene polymerization as a function of the macro-RAFT agent is also discussed here. The polymerization of styrene was carried out in bulk, using AIBN as an initiator. Monomer conversion was determined gravimetrically, and molecular weight and molecular weight distributions of styrene polymerizations were measured by size exclusion chromatography. Two-dimensional (2D) chromatography was used to confirm the incorporation of the oligomers into the structure of the macro-RAFT agent **(4)** as well as into the polystyrene obtained. Good control was achieved over the polymerization of styrene monomer, and polymers with: narrow molecular weight distributions, low polydispersities, and short hydrocarbon chains at the ends of the molecules were obtained.



5.2 Experimental

5.2.1 Chemicals

Styrene was obtained from Plascon Research, washed with a 0.3 M potassium hydroxide solution before distillation under reduced pressure. The monomer was then stored in a refrigerator at -4 °C. azo bis(isobutyronitrile) (AIBN) was purchased from Riedel de Haen, and re-crystallized from methanol. The macro-RAFT agents **(3)** and **(4)** were prepared as described in Chapter four. For HPLC analysis, the solvents used were tetrahydrofuran (THF) HPLC grade (Biosolve), and acetonitrile (ACN) HPLC grade (Biosolve).

5.2.2 Polymerization

Bulk RAFT polymerizations of styrene mediated with macro-RAFT agents **(3)** and **(4)** were carried out in a Schlenk system at 60 °C, using AIBN as the initiator. Table 5.1 shows the quantities of reagents used in the bulk polymerization. Typically, the required concentrations of the RAFT agents, monomer, and initiator are mixed together in the reaction vessel, the vessel is sealed with a rubber septum, and purged with a stream of nitrogen gas. The reaction vessel was immersed in an oil bath and heated to 60°C. All reactions were conducted under nitrogen atmosphere and samples were withdrawn at specific time intervals by syringe. The samples were dried at ambient temperature under vacuum. The isolated polymers were then weighed for gravimetric studies.

Table 5.1 The quantities of reagents used in bulk polymerization of styrene polymerization mediated by the RAFT agents (3) and (4).

Reaction	RAFT agent	Mass of RAFT agent g	Mass of AIBN g	Mass of styrene g
1	**(3)**	0.4139	0.0222	25.55
2	**(4)**	0.75	0.0121	30

5.3 Analysis

Any polymerization system is considered as a controlled/living polymerization when there some experimental criteria exist[23], such as narrow molecular weight distribution, a linear relationship between number average molecular weight and monomer conversion, and constant concentration of active centres during the polymerization. In order to investigate some of these criteria, the polymerization kinetics of styrene was studied by the gravimetric method, whereas: molecular weight and molecular weight distributions were determined by SEC.

5.3.1 Kinetic behaviour of living polymerization

The first-order-kinetic plots displayed in Figures 5.1 and 5.2 show the monomer conversion versus time for reactions 1 and 2. Figure 5.1 shows that the conversion increases with time. After approximately 12 hours of reaction time the conversion reached 60 %.

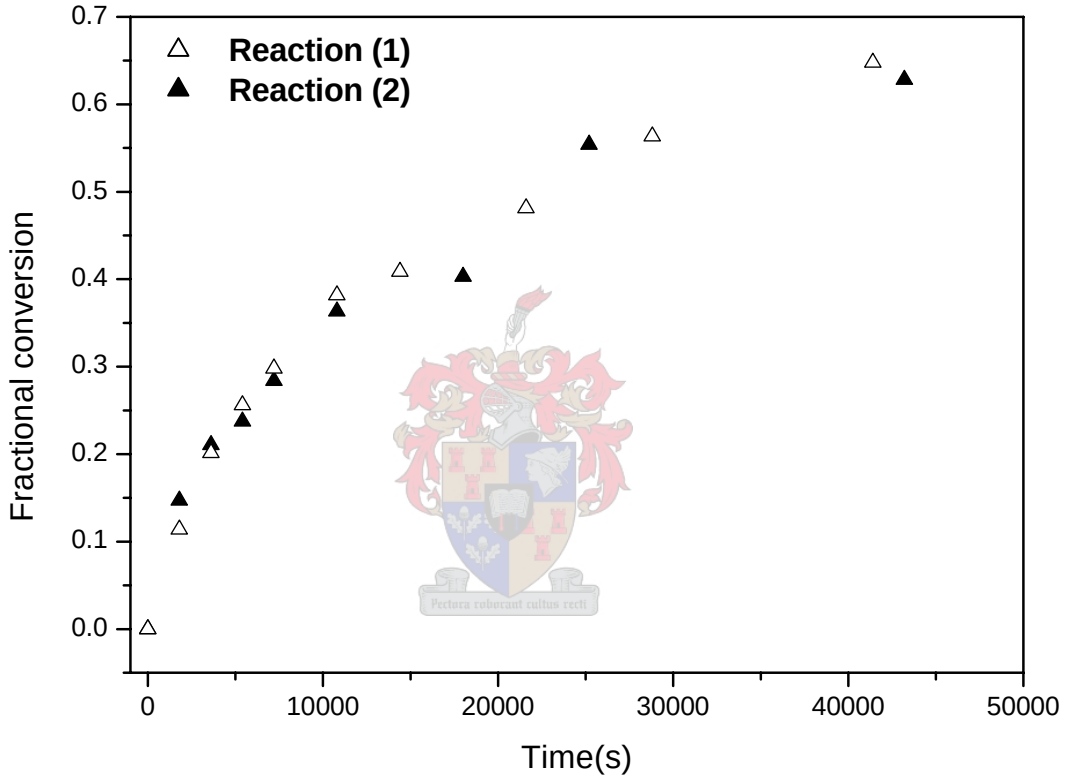


Figure 5.1 Conversion versus time for styrene polymerization mediated with RAFT agents (3) and (4).

The semi-logarithmic kinetics plot in Figure 5.2 suggests that there is a first order monomer consumption rate. It can be stated that this first order relationship presented in Figure 5.2 is due to the steady state of radical concentration, which causes the propagating radicals (growing chains) to grow constantly during the course of the polymerization.

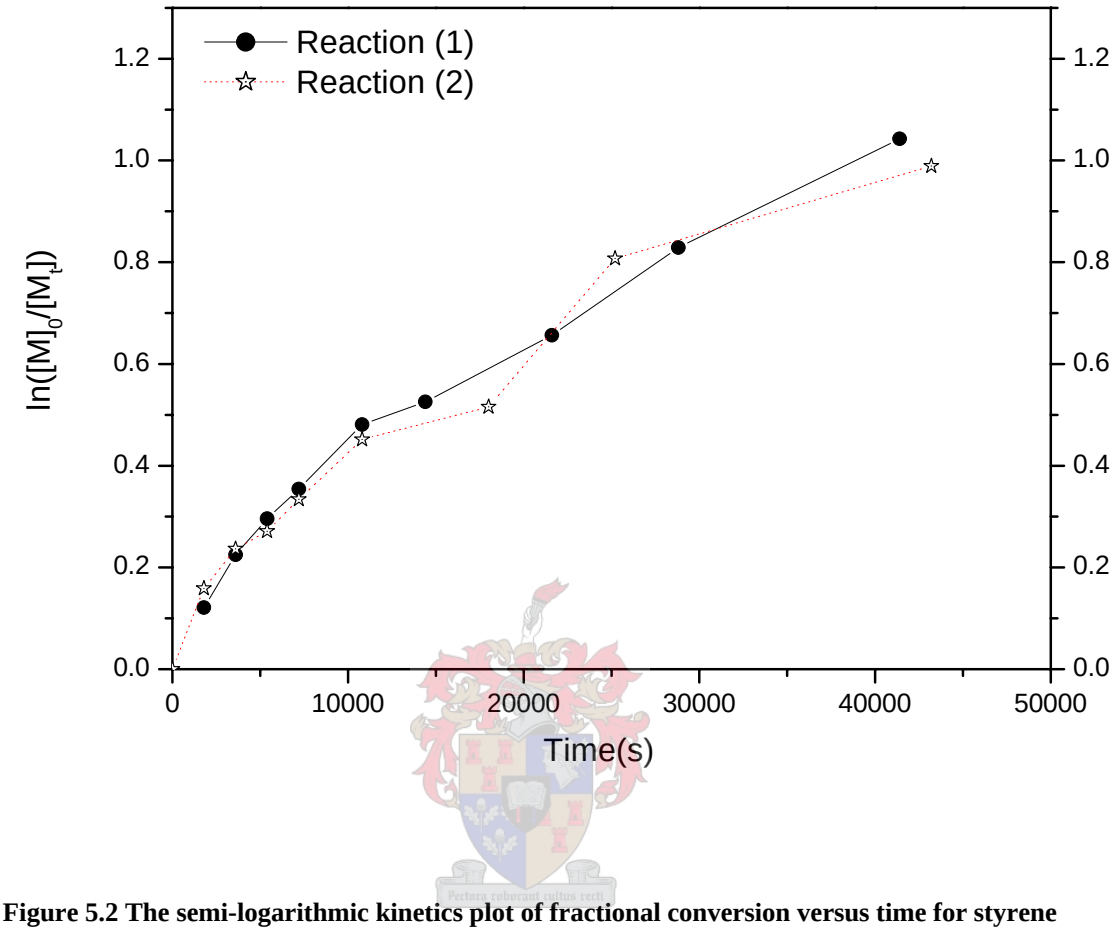


Figure 5.2 The semi-logarithmic kinetics plot of fractional conversion versus time for styrene polymerization mediated by RAFT agents (3) and (4).

In addition, an inspection of Figure 5.2 indicates that there is no obvious retardation in the early stage of the polymerization. The retardation usually exists in RAFT process as a result of one of three factors: irreversible termination[12,24], reversible termination resulting from slow fragmentation[25-27], or slow reinitiation of the leaving group[12,28]. Hence the structure of the RAFT agent is crucial in minimizing retardation phenomena. Trithiocarbonate based RAFT agents in general, including macro-RAFT agents similar to those presented in this study, show no retardation, and the polymerization rate is also found to be independent of the RAFT agent concentration[29-31]. Therefore, the absence of retardation in the early stage of the polymerization as presented in the Figure 5.2, demonstrate the effectiveness of the trithiocarbonate macro-RAFT agents **(3)** and **(4)** in controlling the polymerization of styrene.

5.3.2: Size exclusion chromatography measurements

5.3.2.1: Molecular weights and molecular weight distributions

Molecular weights and molecular weight distributions were measured SEC. Dried polystyrene samples were dissolved in THF (8 mg/mL) and filtered through a 0.45 µm nylon filter. The SEC instrument comprised a Waters 717plus Auto-sampler, Waters 600E System Controller (run by Millennium[32] V3.05 software) and a Waters 610 fluid unit. A Waters 410 differential refractometer was used at 35°C as detector. Tetrahydrofuran (HPLC grade) purged with IR-grade helium was used as eluent at flow rates of 1 mL/min. The column oven was kept at 30°C and the injection volume was 100 µml. Two PLgel 5 µml Mixed-C columns and a pre-column (PLgel 5 µml Guard) were used. Calibration was done using narrow polystyrene standards ranging from 800 to $2x10^6$ g mol^{-1}. All molecular weights were reported as polystyrene equivalents.

Some of the other established criteria for a living polymerization, such as narrow molar mass distribution and low polydispersity, can be examined by SEC analysis. The linear increase of the molar mass with conversion accompanied with decreasing in the polydispersity, are good indications for successful living polymerization. Thus, results displayed in Figures 5.3 and 5.4 show controlled living characteristics for the styrene polymerization mediated with RAFT agents **(3)** and **(4)**.

In an ideal RAFT polymerization, the molecular weight increases with the conversion according to equation (2.9). The theoretical and experimental molecular weight data for linear polystyrene match, as shown in Figure 5.3. It can be seen that $\overline{M_n}$ increases as a function of monomer conversion. This gives evidence that there is a constant number of growing chains during the polymerization. However, there are indications of slight deviations from the expected curve. In case of the polymerization mediated with RAFT agent **(4)**, $\overline{M_n}$ in the beginning of the polymerization seems to be higher than the theoretical value, whereas at high conversions, is slightly lower for both reaction 1 and 2, probably because of radical-radical termination reactions (e.g. initiator-derived

chains) [4,10,32], as well as the presence of oxygen molecules that were introduced to the reaction while sampling.

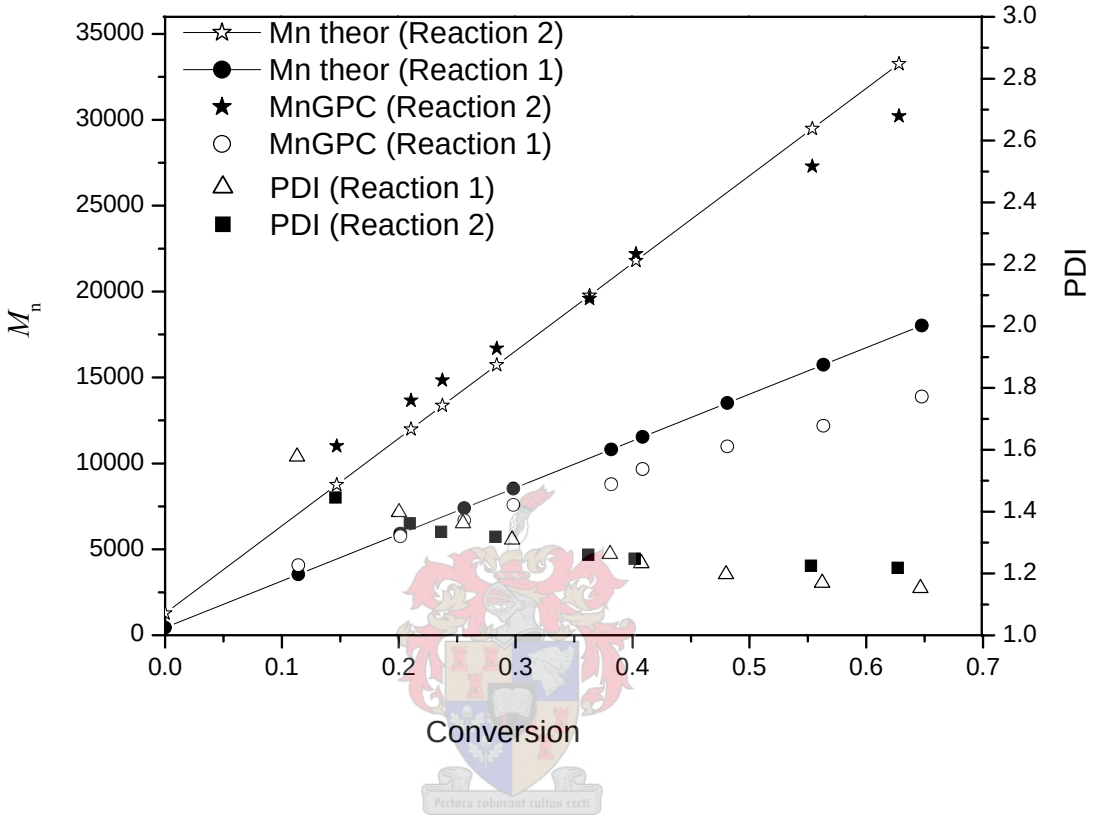


Figure 5.3 M_n and PDI evolution with the monomer conversion in the polymerization of styrene (60 °C) in the presence of RAFT agents (3) and (4).

In addition, the evolution of polydispersity with the conversion as shown in Figure 5.3, demonstrate that the living characteristic of the polymerizations. Indeed, polydispersity indices decreased as the polymerization progressed from PDI =1.5 to1.15. This indicates that most of the chains grew via the RAFT mechanism, and a control over the molecular weight was achieved[32].

The development of the experimental molecular weight and molecular weight distributions with increasing conversion of the polystyrene was also investigated by SEC analysis. Figure 5.4 shows the GPC traces of polystyrenes synthesized in reactions 1 and 2.

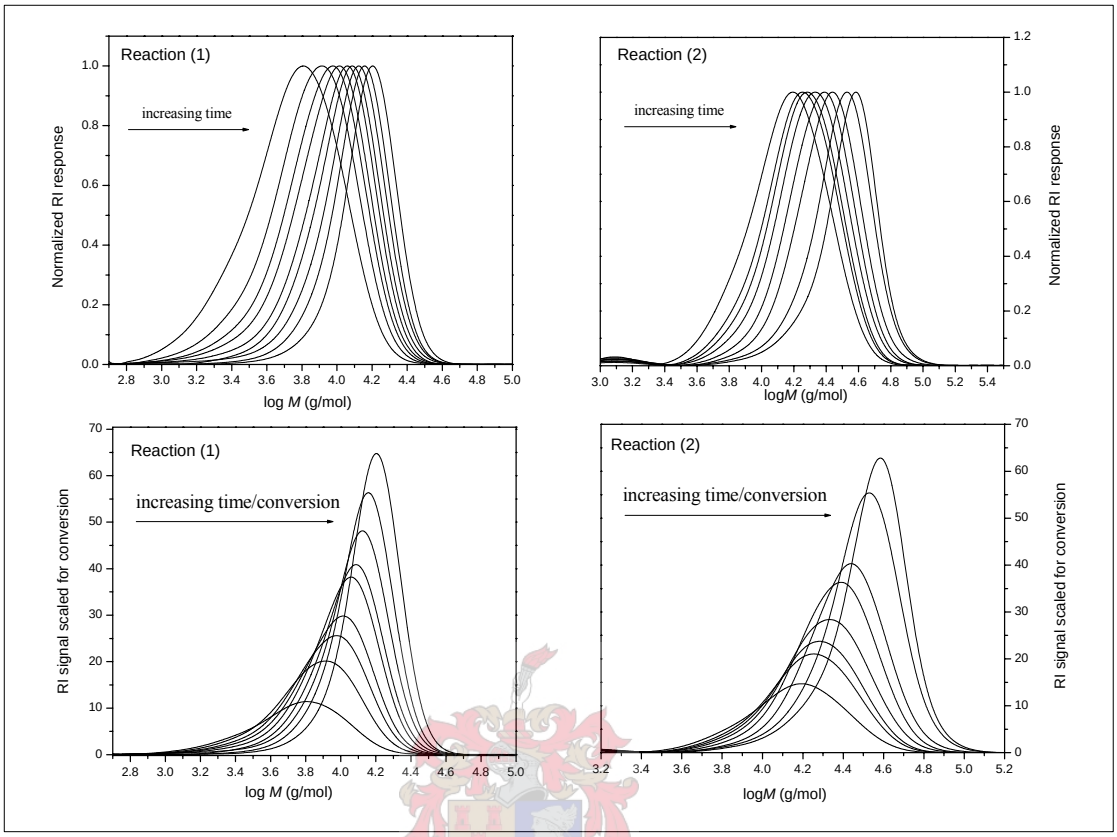


Figure 5.4 Evolution of the molar mass distributions with the monomer conversion in the polymerization of styrene (60 °C) in the presence of RAFT agents (3) and (4).

Each chromatogram presented in Figure 5.4 exhibits, besides a linear increase in molecular weight with time as well as monomer conversion, a narrow monomodal molecular weight distribution. The linearity indicates that the molecular weight was developing during the polymerizations in a living controlled manner, as a result of the presence of the RAFT agents **(3)** and **(4)**. However, it is noted that the molecular weight distribution is seen to tail to lower molecular weight. This tailing, as stated in the literature[4], is due mostly to the radical-radical termination (e.g. termination by coupling of polystyryl propagating radicals) among short chains.

5.3.2.2 UV-RI overlay analysis of polystyrene as determined by SEC

The reactivation of the polymers formed by RAFT polymerization, for chain extension or for use as precursors to produce blocks, stars or polymers of more complex architectures, is another criterion of the living polymerization by RAFT. This can be examined by the detection of active functionality, the thiocarbonylthio group(s) that is retained as end capping groups of the polymers obtained [1,2,4]. As the thiocarbonylthio group (C=S) has a strong UV absorption at 320 nm wavelength, PS polymers obtained from reaction 1 and 2 were examined by SEC using RI and UV , as dual detectors, to determine whether the polystyrene chains possess the RAFT end group or not.

An overlay comparison of the two signals, as diplayed in Figure 5.5, shows that the RAFT moiety is homogenously distributed in most of the PS chains.

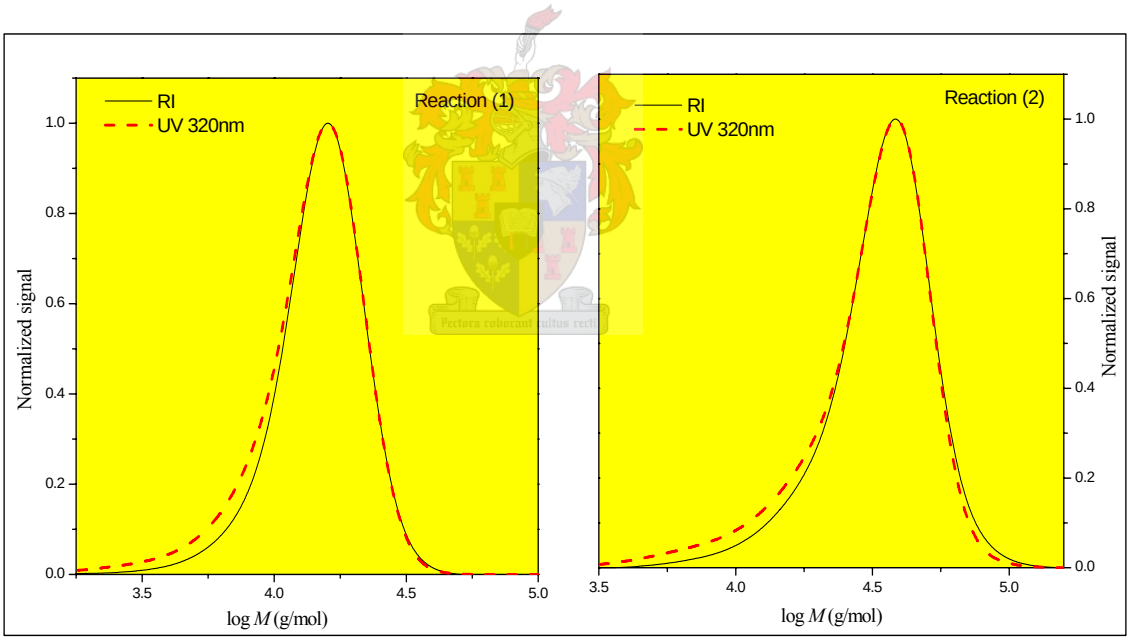


Figure 5.5 UV-RI overlays of PSs prepared from reactions 1 and 2.

An inspection of Figure 5.5 indicates that the RAFT agents **(3)** and **(4)** are incorporated in the PS chains and able to be used in further RAFT mediated living polymerization. Notably, there is a strong UV absorption at low molecular weight, which is probably due

to the fact that the chains are small at the early stage of polymerization, resulting in a high concentration of RAFT agent per mass of chain.

5.3.2: Critical and 2D chromatography

Although SEC yields true molecular weight for linear homopolymers, it provides misleading results in the case of more complex systems, such as copolymers, polymer blends, and branched or functional polymers. The major challenge that faces SEC is the overlapping molecular weight distributions of different blended components. Therefore, such complex systems are characterized by means of distributions in molecular weight (MWD) as well as chemical composition distributions (CCD). MWD are usually characterized by SEC while CCD are mostly determined by means of interaction chromatography[33]. Liquid chromatography under critical conditions (LCCC) has proved to be a useful technique to measure the CCD of individual blocks in diblock and triblock compolymers[34]. The principle of the separation under critical conditions is to compensate between the entropic exclusion effect and the enthalpic effects, thus only small differences in the chemical structure such as end groups or different blocks, will govern the retention.

It has been shown by Pasch *et al.*[34-36] that two-dimensional information on CCD and MWD can be obtained by coupling of LCCC with SEC. Using a fully automated 2D chromatographic system developed by Kilz *et al.*[37], copolymers or functional polymers can be fractionated in first dimension with LCCC through the application of suitable solvent-nonsolvent combination, to obtain the chemical composition distribution. Fractions are automatically stored in a sample loop and then transferred to the second dimension where each sample is separated according to size (hydrodynamic volume) via SEC.

In this study, online 2D chromatography was used to obtain separation of the materials (RAFT agent **(4)** and PS prepared from reaction (2)) in two dimensions to provide insight into the chemical composition distributions of the materials. The analysis of the materials was carried out using Liquid Adsorption Chromatography (LAC) coupled with Size

Exclusion Chromatography (SEC). The experimental conditions were investigated and optimized according to Pasch *et al* [34].

For analysis of RAFT agent **(4)** and PS at the critical point for PS, a LCCC system was used. A Waters 2690 separation module Alliance pump was used. The solvent mixture was 50.8% THF and 49.2% CAN by weight and was taken at the critical point of PS. The columns used for the separation were: C18 guard, Waters Symmetry C18 300 Å (average particule size 5µm, dimensions 4.6x250mm i.d), and Supelco Nucleosil Si C18 100 Å (average particule size 5µm, dimensions 250x4.6mm i.d), and the column oven temperature was set at 30°C. The detectors used were evaporative light scattering detector (ELDS) PL-ELS from Polymer Lab and UV detector Agilent 1100 Series. The flow rate was 0.5 mL/min. Data collection was done with PSS-WINGPC7 from Polymer Standards Services (PSS; Mainz, Germany).

For the on-line 2-D chromatography, the first dimension setup was the same as described fro the LCCC analysis of PS. However, for the 2D chromatography the flow rate was set at 25 µL/min. Sample fractions from the first dimension were collected in an eight-port valve system (VICI Valco EHC8W), which consisted of two loops, each having a sample capacity of 100 µL. The second dimension consisted of a Waters 515 HPLC pump delivering a flow rate of 4 µml/min. The column used was a Polymer Standard Service (PSS) SDV linearM (average particule size 5mm, dimensions 50x20 mm i.d). The same detectors were used as for the analysis in first dimension. The operation of the coupled injection valves was controlled by the software PSS Win GPC7 which was used for data collection, processing was performed by Win GPC 2D.

In order to determine the critical point of PS, where all the styrene homopolymer chains elute together without contributing to the retention, polystyrene calibration standards of molecular weights ranging from 4,000 to 30,000 g/mol had to be injected. The results showed that styrene homopolymer eluted at a retention volume of 6 mL under the conditions selected.

5.3.2.1 LCCC analysis

Figures 5.6 and 5.7 present chromatograms for the separation of RAFT agent **(4)** and PS mediated by RAFT agent **(4)**, respectively. Figure 5.6 shows the full separation of the oligomeric components that comprise the macro-RAFT agent. An overlay comparison of the RI and UV at 320 nm signals, as displayed in Figure 5.6, shows that the RAFT moiety is possessed by most of the oligomer fractions.

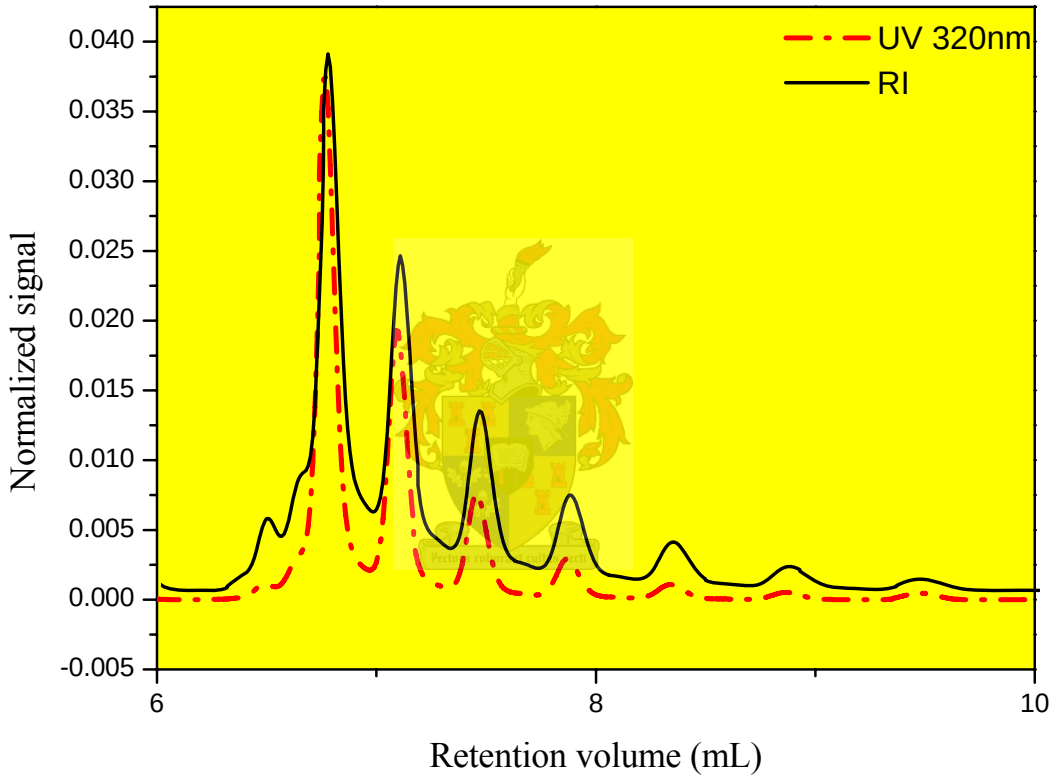


Figure 5.6 LCCC chromatogram of macro-RAFT agent (4).

In the Figure 5.7, the chromatogram for the separation of PS-block-oligobutenes under critical conditions of PS is shown. Since PS does not absorb UV at 320 nm, whereas PS-b-oligobutenes does, as a result of the presence of RAFT moieties attached to the oligomer segments, some information on the MWD and CCD can be gained by using dual RI/UV detection. Using PS for calibration, in a first approximation the overall

MWD is obtained from the RI detector tracing. Two elution peaks can be seen on the chromatogram. Based on the assumption of the elution order and comparison with the PS standards (see Appendix, Figure 14-16 for PS standards chromatograms), the first small peak that appears at 6.2 mL can be assigned to PS homopolymer, whereas the second peak is assigned to PS-b-oligobutenes. The partial separation of the two peaks indicates that the oligomer segments appear to function as functional short chains rather than block segments.

The presence of PS homopolymer, as we discussed earlier, could mostly be due to the radical-radical termination (e.g. termination by coupling of polystyryl propagating radicals) among short chains[4,34]. In addition, by UV detection, only the PS-b-oligobutene species are detected. Accordingly, the UV tracing indicates PS-b-oligobutene as the major component.

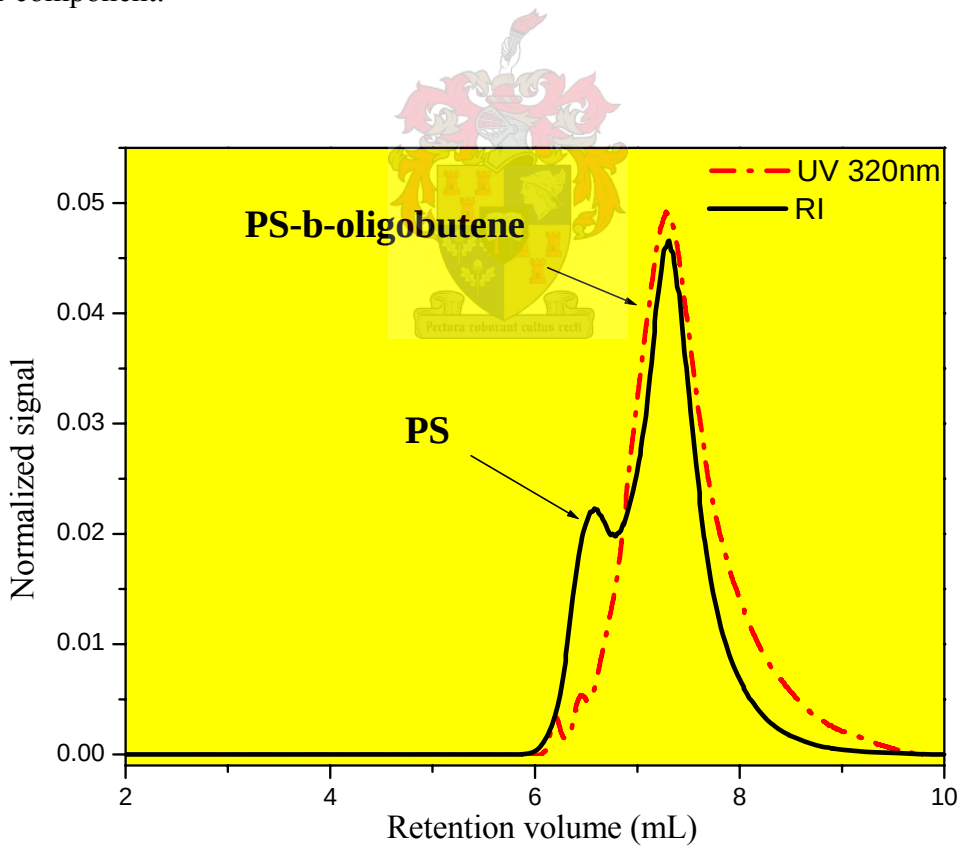


Figure 5.7 LCCC chromatogram of PS prepared from reaction 2.

5.3.2.2 Two-dimensional analysis

The coupling of LCCC with SEC obtains better separation and provides additional information on the chemical composition of these polymers in relation to the molecular weight distribution. The first dimension corresponds to LCCC condition for PS, while SEC corresponds to the second dimension.

The results of the two-dimensional separation of the macro-RAFT **(4)** as well as PS-b-oligobutenes are presented as two dimensional (2D) counter plots and a three-dimensions (3D) colour map in Figures 5.8 and 5.9 respectively. The ordinate represents the separation in the first dimension, while the abscissa indicates the SEC separation of the fractions. The 2D counter plot of the macro-RAFT **(4)**, as shown in Figure, 5.8, indicates over ten fractions which are different in chemical composition and molecular weight. It seems that the first five fractions are more concentrated than the other fractions; therefore, they are shown on the counter plot as one big peak. Comparing the 2D counter plot in Figure 5.8 with the LCCC chromatogram in Figure 5.6 it is obvious that the resolution is significantly improved, and the number of detected fractions is higher.

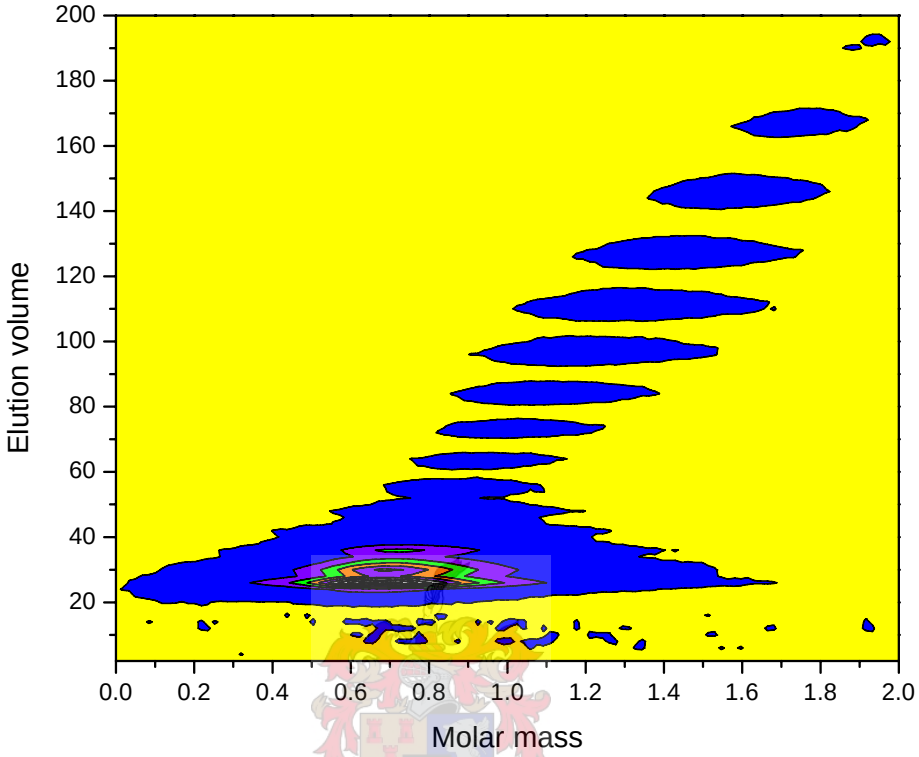


Figure 5.8 2-D contour plot of oligobutenes-based macro-RAFT agent.

The 2D and 3D plots presented in Figure 5.9 indicate two fractions which are different in chemical composition and molar mass. The assignment of the fractions is based on the critical conditions of PS indicated in LCCC.

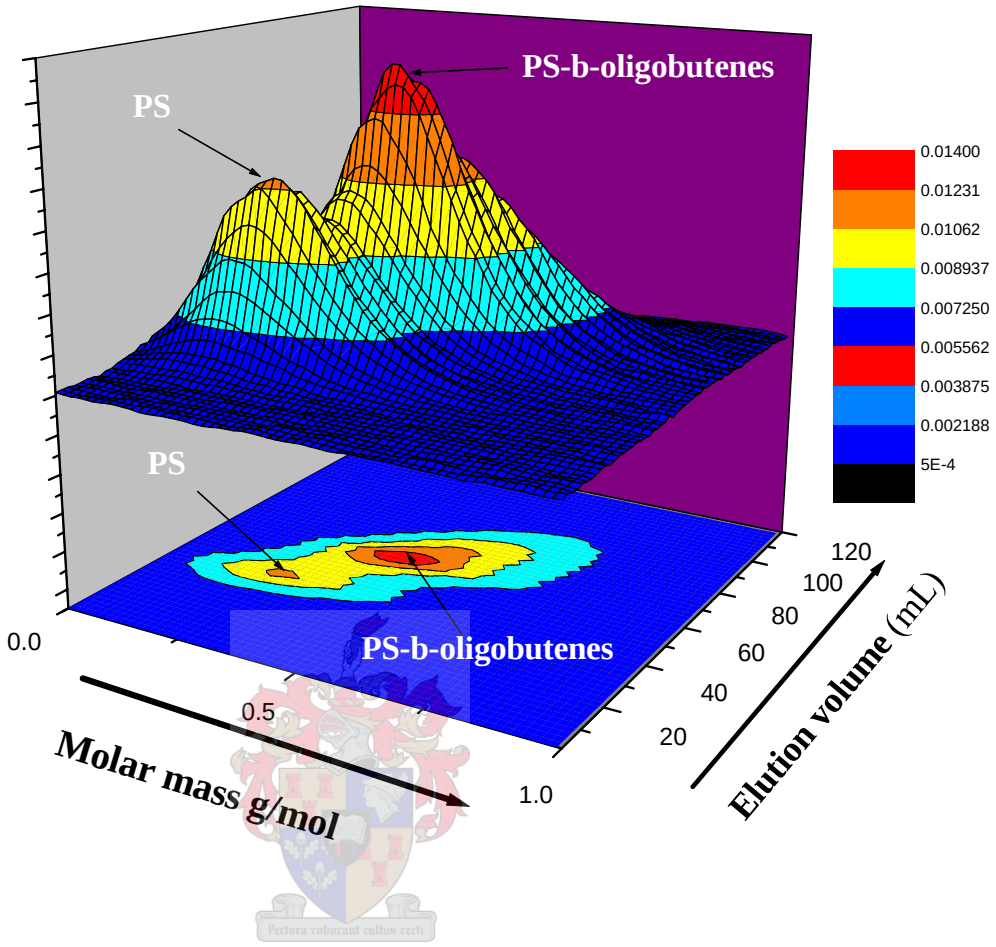


Figure 5.9 3-D colour map and 2-D contour plot of analyzed PS-block-oligobutenes.

In conclusion, by carrying out the measurements at the critical conditions of PS with a UV detector set up at 320 nm, the 2D chromatography analysis confirmed the incorporation of the oligomers into the structure of the macro-RAFT agent as well as into the polystyrene obtained.

5.3.3 Differential scanning calorimetry (DSC) analysis

DSC was used to investigate the thermal properties of the PS-b-oligobutene. The dependence of the glass transition temperature (T_g) on the structure and chemical composition of the polymer is well known[38]. Therefore, DSC analysis was carried out to study the effect of the incorporation of the oligobutene segments into the PS structure on

the T_g of a virgin homopolystyrene. It is also known that the T_g of a polymer is a function of its molecular weight, it increases with increase of molecular weight and vice versa.

The glass transition temperature was determined using a TA Instruments Q100 DSC system, calibrated with indium metal according to standard procedures. Two samples of PS-b-oligobutene with molecular weights $\overline{M_n}$ =13 656 and 30 214 g mol^{-1}, respectively, were investigated by DSC.

Table 5.2: T_g data for PS homopolymers and PS-b-oligobutenes copolymer

System/M_w	**M_n**	**T_g °C**
PS-17400 [a]	15 100	86
PS-3700 [a]	36 000	94
PS-b-oligobutene-15907	13 656	83.7
PS-b-oligobutene-36803	30 214	98

[a] adopted from Turi[205].

Table 5.2 shows a comparison between the T_gs of PS-b-oligobutene samples and T_g data for the PS homopolymer as given by Kumler *et al.*[38]. The results presented in Table 5.2 show that there is no significant change in the values of T_g, which suggests that the oligobutenes segment of PS-b-oligobutene copolymer has no major effect on the thermal properties of PS and they function only as functional side chains.

5.4 References

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Chapter 6 conclusions and recommendations

6.1 Conclusions

1. 1-Butene oligomers with vinylidene double bond end-groups were successfully synthesized. The oligomerization reaction was carried out with **Cp_2ZrCl_2** as a catalyst, activated with **MAO** as a co-catalyst (10% in toluene), in the ratio Al/Zr = 1000/1. Oligomers with low molar masses (M_w), ranging between 800 and 2000 g.mol^{-1}, was obtained as confirmed by GPC measurements. 1-Butene trimer (5-ethyl-3-methylene nonane) was separated from the final oligomeric mixture, and used as a model in all the syntheses and reactions investigated in this study.
2. Oligomer characterization was carried out by ^{1}H NMR, ^{13}C NMR, SEC (GPC), GC-MS, and FTIR spectroscopy. ^{1}H NMR and ^{13}C NMR results confirmed the presence of the vinylidene groups at the end of oligomers chains. GC-MS revealed the formation of dimers to heptamers of 1-butene. FTIR confirmed the presence of the expected functional groups of the oligomers.
3. In order to introduce the oligomers to the controlled free radical polymerization RAFT, the vinylidene end groups had to be converted to hydroxyl functionalities. The functionalization of 1-butene oligomers was achieved by the oxymercuration-demercuration reaction. Accordingly, hydroxy-terminated oligobutenes were obtained.
4. The conversion of vinylidene group and the structure of hydroxy-terminated oligobutenes were investigated by means of ^{1}H NMR, ^{13}C NMR, GC-MS, and FTIR spectroscopy. The successful functionalization of oligobutenes was confirmed by comparing the characterization results of oligobutenes with hydroxy-terminated oligobutenes.
5. The synthesis of oligobutenes-based RAFT agents **(3)** and **(4)** was investigated. The investigation involved, beside the macro-RAFT agent, the synthesis of RAFT agent **(1)** (3-benzylsulphanylthiocarbonylsuphanylpropionic acid) and RAFT agent **(2)** (3-benzylsulphanylthiocarbonylsulphanylpropionic acid chloride). An esterification reaction between the hydroxy-terminated oligobutenes and the

RAFT agent **(2)** was successfully carried out as confirmed by ^{1}H NMR, ^{13}C NMR, FTIR, and UV spectroscopy.

6. The chain transfer ability of the macro-RAFT agents **(3)** and **(4)** to induce living characteristics in free radical styrene polymerization was investigated with respect to molecular weight control and kinetic behaviour. Both RAFT agents **(3)** and **(4)** were identified as suitable RAFT agents, yielding linear polystyrene with low polydispersities and molecular weight ranging from 3000 to 40000 g/mol.
7. The styrene polymerizations mediated with macro-RAFT agents **(3)** and **(4)** did not exhibit any retardation, which agrees with the literature. The molecular weights of PS were measured using SEC calibrated with linear PS standards. Although, the molecular weight evolution of PS was in agreement with the molecular weigh predicted (calculated by equation 2.9), a small deviation was observed, as a result of radical-radical termination reactions and evaporation of the styrene monomer. Furthermore, SEC measurement showed linear increase in molecular weight with time as well as monomer conversion, indicating that the molecular weight was developing during the polymerizations in a living controlled manner, as a result of the presence of the RAFT agents **(3)** and **(4)**.
8. Online 2D chromatography was used to investigate the chemical composition distribution as well as the molecular weight distributions of PS prepared by free radical polymerization mediated with macro-RAFT agent **(4)**. The analyses of both the oligobutenes-based macro-RAFT agents and PS were carried out using SEC as well as Liquid Adsorption Chromatography (LAC) to obtain separation of the materials in two dimensions, to provide insight into the chemical composition distributions of the materials. By carrying out the measurements at the critical conditions of PS with a UV detector set up at 320 nm, the 2D chromatography analysis confirmed the incorporation of the oligomers into the structure of the macro-RAFT agent as well as into the polystyrene obtained.
9. The PS-b-oligobutenes obtained was also characterized by DSC, to investigate the effect of the presence of oligobutenes segments on the thermal properties of the PS. The T_g values obtained for two samples with different molecular weights

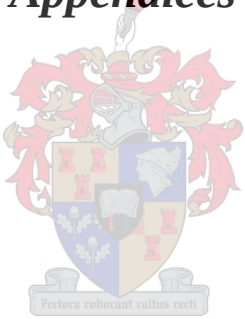
suggested that the incorporation of the oligobutenes into a polystyrene structure has no major effect, especially on the T_g.

10. The use of 1-butene trimer and a low molecular weight oligobutenes as precursors for macro-RAFT agents, and the subsequent successful formation of polystyrene-b-oligobutene indicates that this approach could be used with higher molecular weight oligobutenes or low molecular weight poly(1-butene) as well. This would lead to block copolymes.

6.2 Recommendations

1. The use of higher molecular weight poly(1-butene) as precursor for macro-RAFT agents, and the preparation of buten/styrene copolymers.
2. The utilization of the hydroxyl-terminated butene trimers and higher oligomers as side-groups in branched alkyl (meth)acrylates. These could be an interesting group of monomers for radical polymerization and copolymerization reactions

Appendices



A 1 1-Butene oligomers

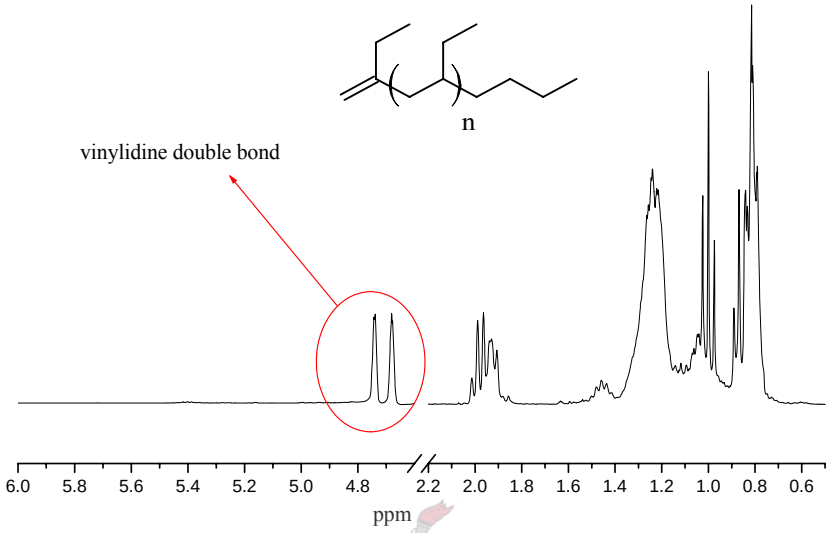


Figure A1: ^{1}H NMR spectrum of 1-butene oligomers.

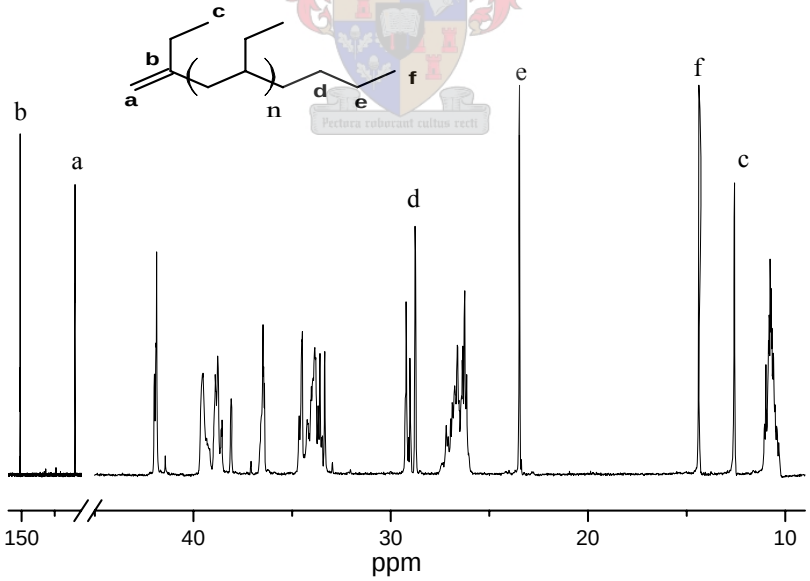


Figure A2: ^{13}C NMR spectrum of 1-butene oligomers.

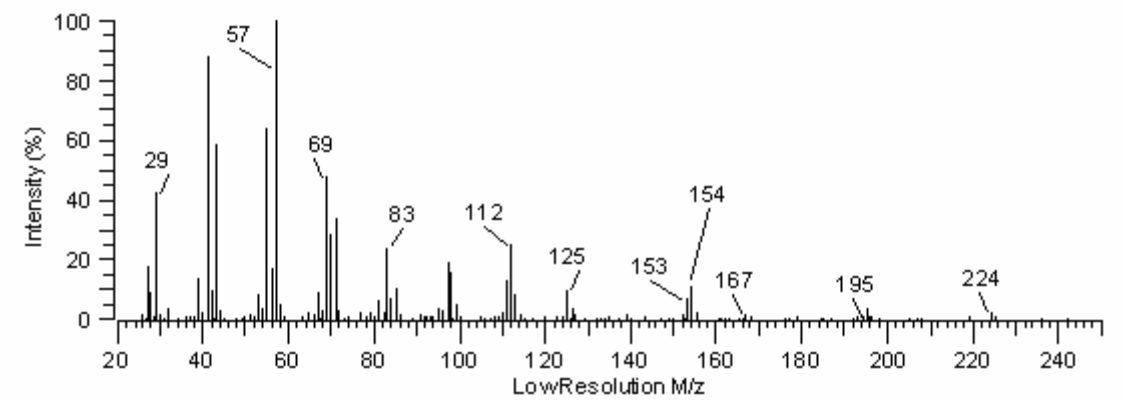


Figure A3: EI$^+$ mass spectrum of the tetramer of 1-butene oligomer.

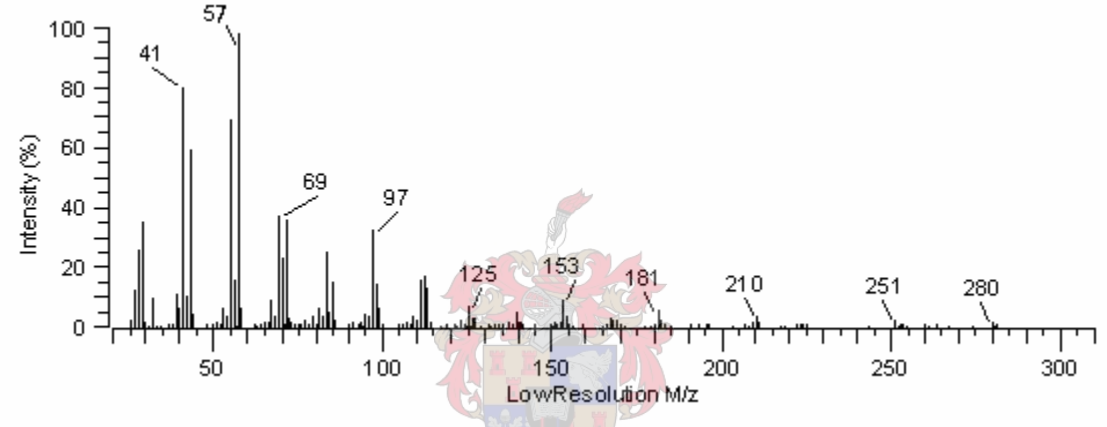


Figure A4: EI$^+$ mass spectrum of the pentamer of 1-butene.oligomer.

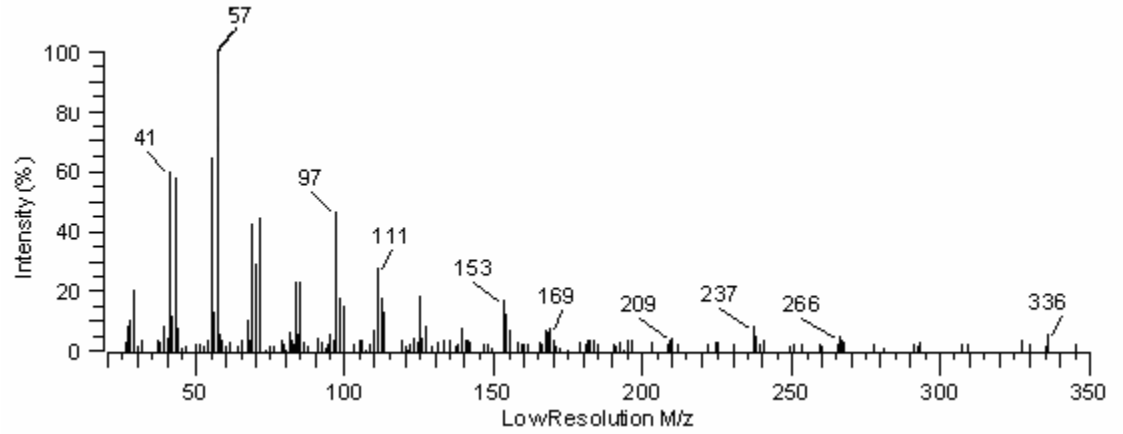


Figure A5: EI$^+$ mass spectrum of the hexamer of 1-butene oligomers.

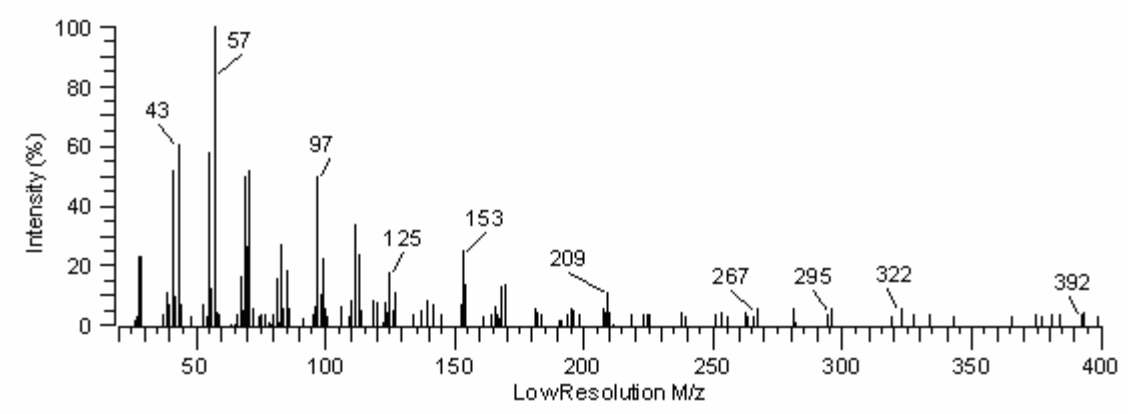


Figure A6: EI$^+$ mass spectrum of the heptamer of 1-butene.

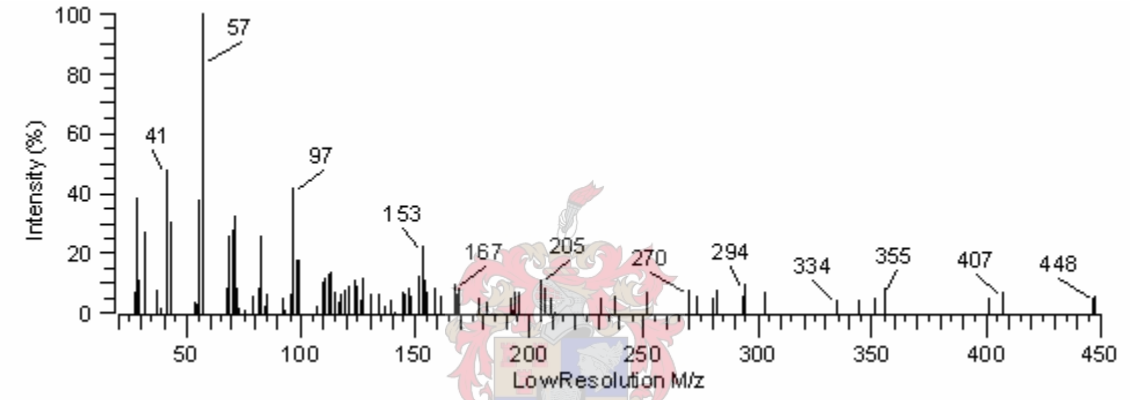


Figure A7: EI$^+$ mass spectrum of the octamer of 1-butene.

A 2 Hydroxy-terminated oligobutenes

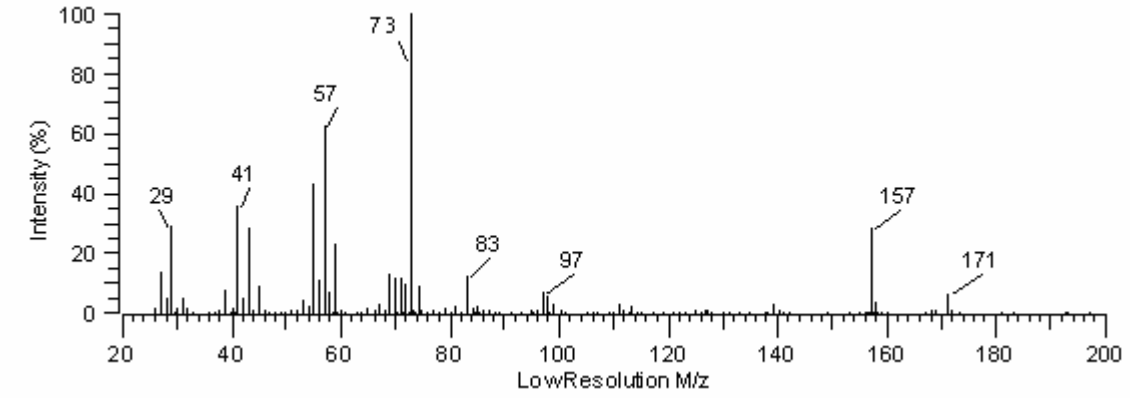


Figure A8: EI$^+$ mass spectrum of the hydroxy-terminated 1-butene trimer.

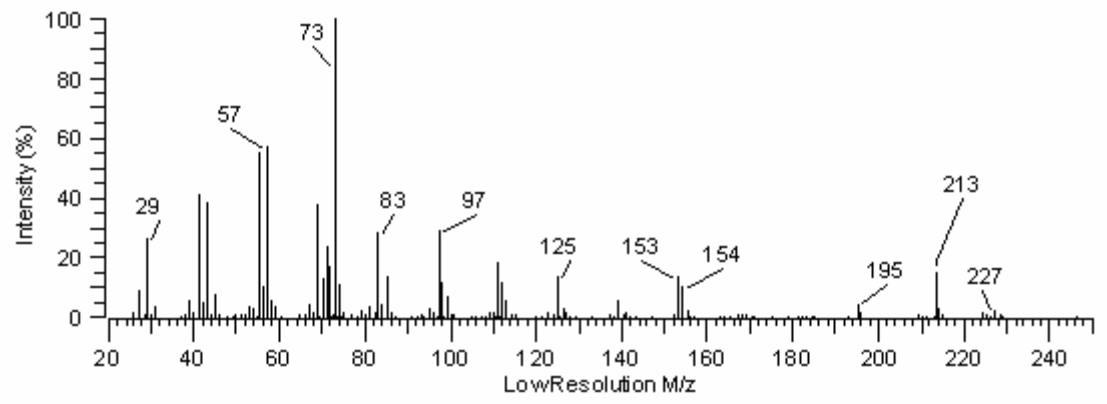


Figure A9: EI^+ mass spectrum of the hydroxy-terminated 1-butene tetramer.

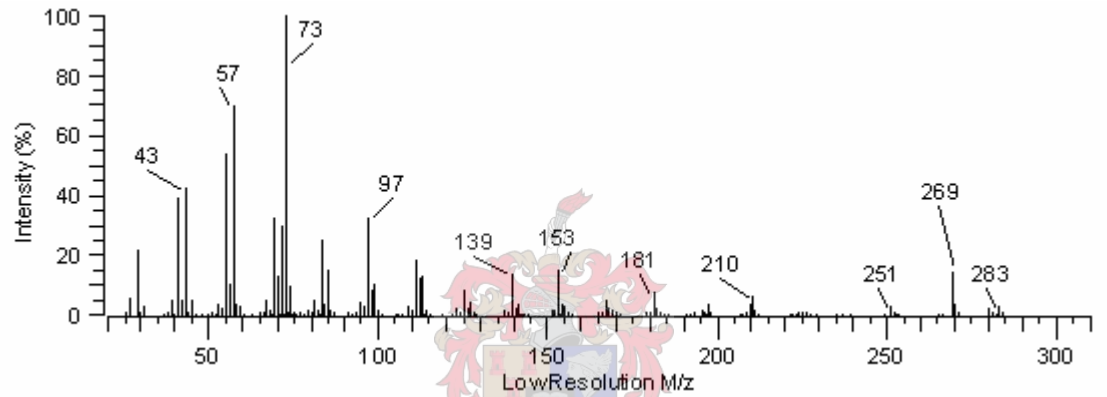


Figure A10: EI^+ mass spectrum of the hydroxy-terminated 1-butene pentamer.

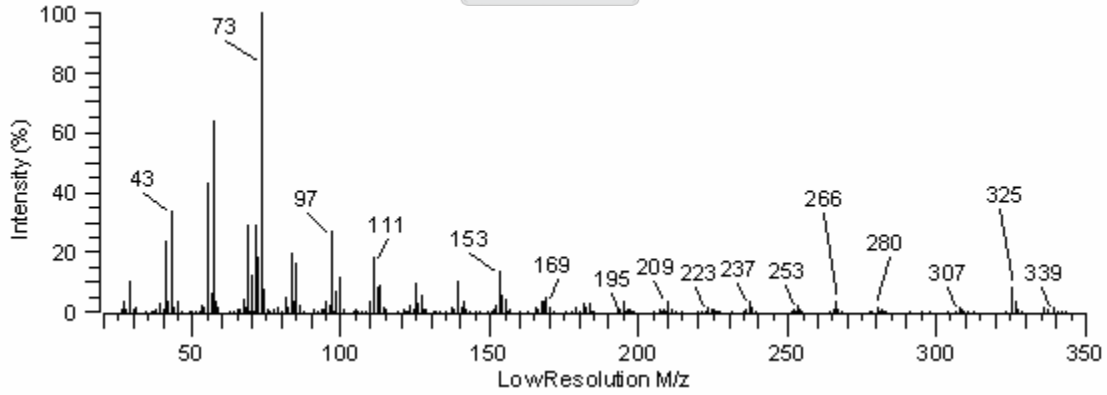


Figure A11: EI^+ mass spectrum of the hydroxy-terminated 1-butene hexamer.

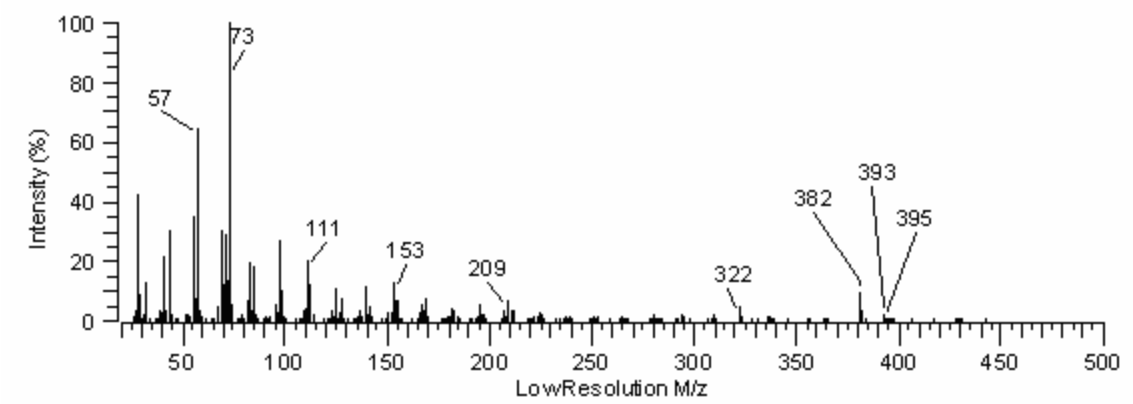


Figure A12: EI^+ mass spectrum of the hydroxy-terminated 1-butene heptamer.

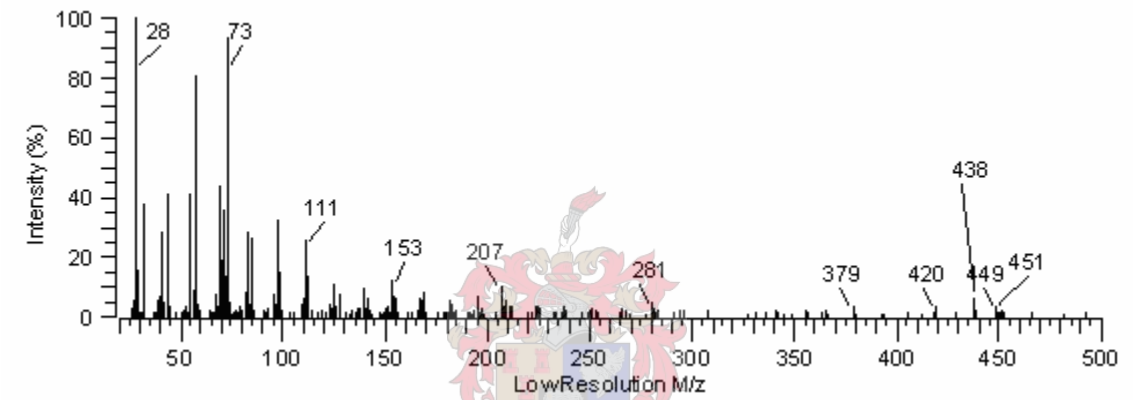


Figure A13: EI^+ mass spectrum of the hydroxy-terminated 1-butene octamer.

A 3 Standard polystyrene chromatograms under critical conditions

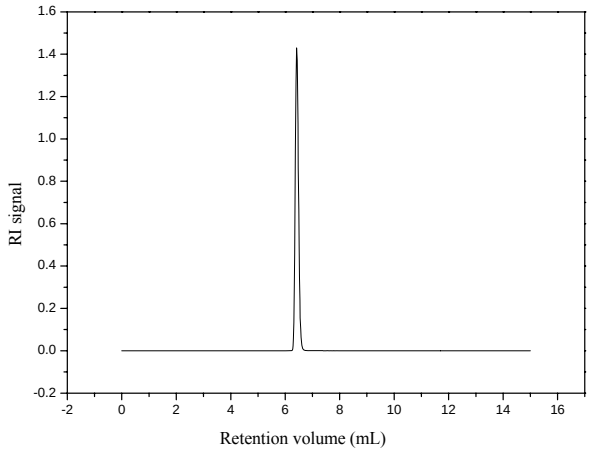


Figure A14: chromatogram of PS standard with molar mass 4000 g/mol.

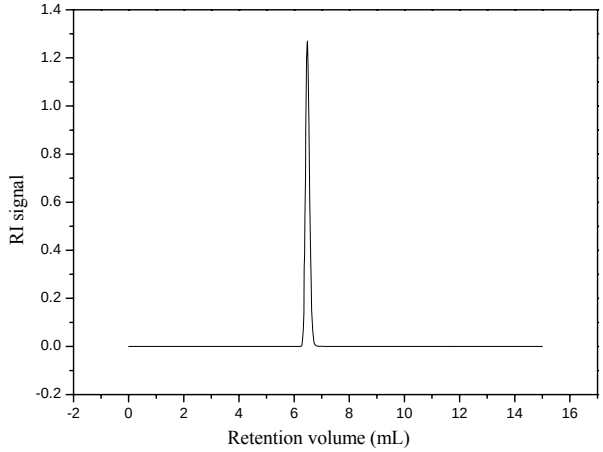


Figure A15: chromatogram of PS standard with molar mass 16700 g/mol.

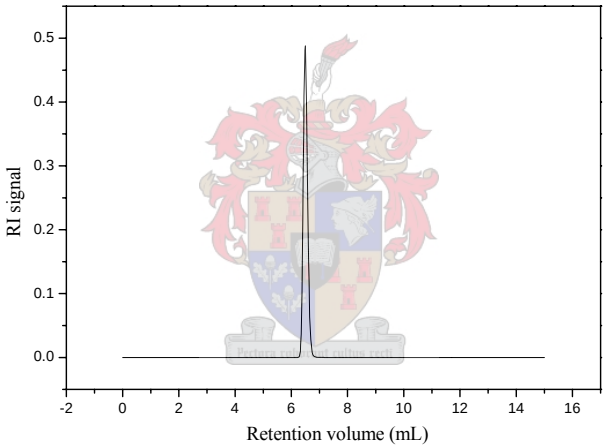


Figure A16: chromatogram of PS standard with molar mass 30,000 g/mol.