

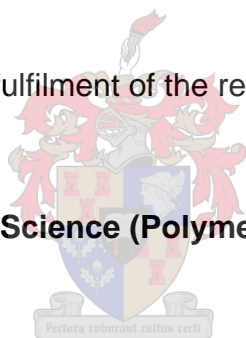
**DESIGN, SYNTHESIS AND CHARACTERIZATION OF  
NOVEL RAFT AGENTS**

by

**Achille Mayelle BIVIGOU KOUMBA**

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at the

**University of Stellenbosch**

Study leader: Prof R D Sanderson

Co-study leader: Prof Bert Klumperman

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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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A. M BIVIGOU KOUMBA

July 2005

Stellenbosch



## Abstract

This thesis begins with the description of the preparation of thirteen dithioesters (of the form Z-(C=S)-S-R) which were characterized via Fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR) and ultraviolet spectroscopy (UV). The dithioesters were then used as reversible addition-fragmentation chain transfer (RAFT) mediating agents in the bulk polymerization of styrene, in order to observe differences in the kinetic behaviour of the polymerizations and, as a result, the efficiencies of the dithioesters in mediating the polymerizations.

The similarities and differences in the reactivities of the RAFT agents were determined by rate studies, via gravimetry and by size exclusion chromatography (SEC). The first living characteristic observed in the polymerizations mediated by the thirteen RAFT agents was that there were linear relationships between the semi-logarithmic plots of fractional conversion versus time. Secondly, the number average molar mass ( $M_n$ ) of the formed polymers increased linearly as a function of monomer conversion and narrow distributions, PDI (<1.5) were obtained in most cases. These characteristics indicated that the RAFT agents used were indeed effective mediating agents for the thermally initiated polymerisation of styrene.

In order to study the influence of the respective Z and R groups of the RAFT agents on the activities of the thirteen dithiobenzoates that were synthesised, the agents were grouped into seven different series (A through G). Series A through D were used to study the role of the Z groups and Series E through G were used to clarify the differences in the behaviours of the R groups. It was demonstrated that:

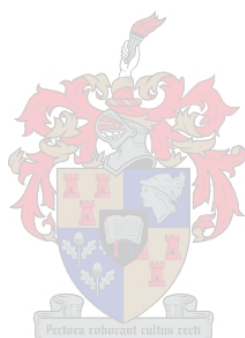
### Z group

The following Z groups were studied: phenyl, 4-methylphenyl, 4-methoxyphenyl and 4-fluorophenyl groups. Although the rates of polymerisation for the reactions investigated did show a slight dependence on the Z group, the Z groups with electron withdrawing or donating substituents did not significantly affect the activity of RAFT agents.

### R group

The following R groups were studied: cyanoisopropyl (-C(Me)<sub>2</sub>CN), cyanovaleric acid (-C(Me)(CN)(CH<sub>2</sub>)<sub>2</sub>COOH) and cumyl (-C(Me)<sub>2</sub>Ph), and a sulfur-centred radical (-S(CS)Ph). The first three R groups appeared to be more effective leaving groups in styrene polymerisation than the

benzyl thiocarbonylsulfur group. In the case of coupled chain transfer agents there was a long inhibition period due to the three radicals required to initiate polymerization (two to form RAFT agents *in situ*).



## Opsomming

Hierdie tesis begin met die beskrywing van die sintese van dertien nuwe omkeerbare addisie-fragmentasie ketting-oordragverbindings (OAFO verbindings, Eng: RAFT agents) en hulle karakterisering met behulp van Foerier Transfer Infra-Rooi (FTIR), Kern Magnetiese- Resonans (KMR) en Ultra-Violet spektroskopie (UV). Hierdie ditioesters is daarna as omkeerbare addisie-fragmentasie ketting-oordrag verbindings (OAFO) gebruik in die massapolimerisasie van stireen, ten einde verskille in die kinetiese gedrag van die polimerisasies en die doeltreffendheid van die verskillende ditioesters in die bemiddeling (Eng: mediation) van die polimerisasiereaksies te ondersoek.

Die ooreenkomste en verskille in die reaktiwiteite van die OAFO-verbindings is deur middel van tempostudies, i.e. gravimetrie en gelpermeasiechromotografie (GPC), bepaal. Die eerste tekens dat die polimerisasiereaksies met die 13 verskillende OAFO verbindings lewende eienskappe (Eng. living characteristics) het was die liniêre verwantskappe tussen die semi-logaritmiese kurwes van die gedeeltelike monomeer omskakeling (Eng: fractional conversion) met tyd. Tweedens, die nommer gemiddelde molere massa ( $M_n$ ) van die polimere wat gevorm is, het op 'n liniêre manier toegeneem as 'n funksie van monomeeromskakeling en, in die meeste gevalle, is dimere met noue molere massa distribusiers ( $<1.5$ ) gevorm. Hierdie eienskappe het daarop gewys dat die OAFO-verbindings effektief was vir die termies-geïnduseerde polimerisasie van stireen.

Ten einde die rol van beide die Z- en R-groepe in die OAFO-verbindings op die aktiwiteite van die dertien ditioensoate wat berei is te bestudeer, is hulle in sewe verskillende klasse gegroep. Reeks A tot D is gebruik om die rol van die verskillende Z-groepe te bepaal en reeks E tot G is gebruik om die verskille in die effek van die R-groepe te bepaal. Binne-in daardie sewe klasse is die volgende ondersoek:

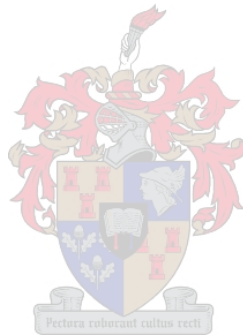
### Z-groep

Die volgende Z-groepe is bestudeer: para-metielfeniel, para-metoksifeniel en para-fluorofeniel. Alhoewel die polimerisasietempo wel effens daarvan afhanklik was, het die Z-groepe met elektron-onttrekkende en -donerende groepe geen noemenswaardige invloed op die aktiwiteite van die OAFO-verbindings gehad nie.

### R-groep

Die volgende Z-groepe is bestudeer: sianoisopropiel ( $-C(Me)_2CN$ ), sianovaleriaansuur ( $-C(Me)(CN)(CH_2)_2COOH$ ) en kumiel ( $-C(Me)_2Ph$ ), en 'n swawelgesentreerde radikaal ( $-S(CS)Ph$ ).

In die polimerisasie van stireen het dit geblyk dat die eerste drie verlatende groepe meer effektief as die bensieltiokarboniëlswawel groep (-S(CS)Ph) was. In die geval van gekoppelde kettingoordragverbindings was daar 'n lang inhibisieperiode, as gevolg van die drie radikale wat benodig is om polimerisasie aan die gang te sit (twee word benodig om OAFO-verbindings *in situ* te vorm).



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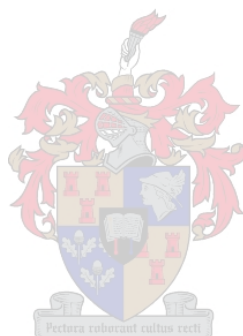
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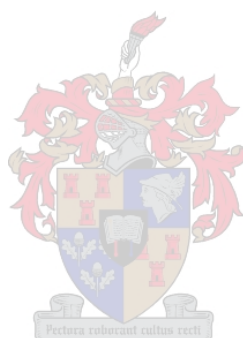
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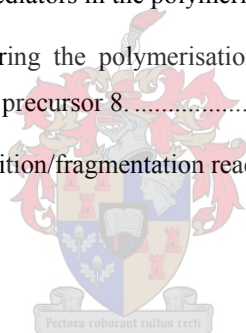


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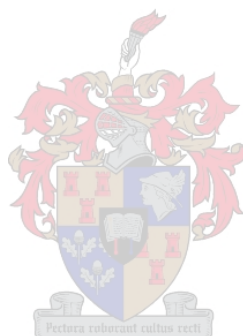
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## List of Symbols

|                |   |
|----------------|---|
| $\lambda$      | absorbance  |
| $C_{tr}$       | chain transfer constant   |
| $C_{-tr}$      | reverse chain transfer constant   |
| $DP_n$         | average degree of polymerisation  |
| I              | initiator   |
| $k_{add}$      | addition rate coefficient   |
| $k_{frag}$     | fragmentation rate coefficient  |
| $k_d$          | dissociation constant   |
| $k_j$          | reverse transfer constant   |
| $k_{tr}$       | transfer rate coefficient   |
| $k_p$          | coefficient of polymerisation   |
| M              | monomer   |
| $M_n$          | number average molar mass   |
| $M_{n,exp}$    | experimental number average molar mass                                  |
| $M_{n,th}$     | calculated number average molar mass                                    |
| Mw             | weight average molar mass   |
| MMD            | molar mass distribution   |
| $[M]_0$        | initial concentration of monomer  |
| [Monomer]      | monomer concentration   |
| $MW_{monomer}$ | molar mass of monomer   |
| $MW_{raft}$    | molar mass of RAFT agent  |
| $Mt^n/ligand$  | transition metal complex for atom transfer reaction, without the halide |
| N              | nitrogen atom   |
| O              | oxygen atom   |
| P•             | active species  |
| $P_n$          | polymeric chain of n-degree of polymerisation                           |

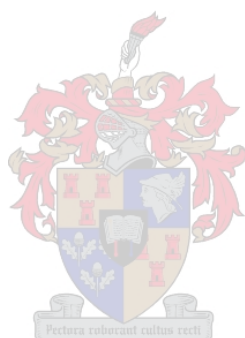
|                            |   |
|----------------------------|---|
| $P_n^\bullet$              | propagating radical of n-degree of polymerisation                   |
| $[P-X]$                    | number of dithiobenzoate end-capped chains                          |
| P-X                        | dormant species   |
| R                          | RAFT agent leaving group  |
| $R^\bullet$                | RAFT agent leaving group radical                                    |
| $[RAFT]_0$                 | initial concentration of RAFT agent                                 |
| R-X                        | alkyl halide  |
| $X-Mt^{n+1}/\text{ligand}$ | transition metal complex for atom transfer reaction with the halide |
| $Y^\bullet$                | intermediate RAFT radical   |
| Z                          | RAFT agent stabilizing group  |



## List of Acronyms

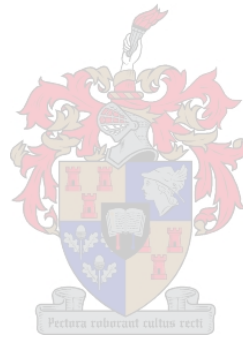
|                                 |   |
|---------------------------------|---|
| AIBN                            | 2,2'-azobis(isobutyronitrile)   |
| ATRA                            | atom transfer radical addition  |
| ATRP                            | atom transfer radical polymerisation                                    |
| C <sub>6</sub> H <sub>4</sub> R | benzene derivatives   |
| CTA                             | chain transfer agent  |
| DBN                             | di- <i>tert</i> -butylnitroxide   |
| DEPN                            | <i>n-tert</i> -butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide |
| ESR                             | electron spin resonance   |
| FRP                             | free radical polymerisation   |
| GPC                             | gradient permeation chromatography                                      |
| <sup>1</sup> H NMR              | proton nuclear magnetic resonance                                       |
| iniferter                       | initiator-transfer agent-terminator                                     |
| IR                              | infrared  |
| KOH                             | potassium hydroxide   |
| LRP                             | living radical polymerisation   |
| M                               | molar (mol/dm <sup>-3</sup> )   |
| MMA                             | methylmethacrylate  |
| NMR                             | nuclear magnetic resonance  |
| NMP                             | nitroxide mediated polymerisation                                       |
| PDI                             | polydispersity index  |
| Ph                              | phenyl ring   |
| ppm                             | parts per million   |
| PSt                             | polystyrene   |
| RAFT                            | reversible addition-fragmentation chain transfer                        |
| SEC                             | size exclusion chromatography   |
| SFRP                            | stable free radical polymerisation                                      |

|       |   |
|-------|---|
| St    | styrene   |
| TEMPO | 2,2,6,6-tetramethyl-1-piperidinyloxy free radical |
| THF   | tetrahydrofuran                                   |
| UV    | ultraviolet                                       |



*“The important thing is not to stop questioning. Curiosity has its own reason for existing” Albert Einstein.*

## *CHAPTER I: Introduction and objectives*



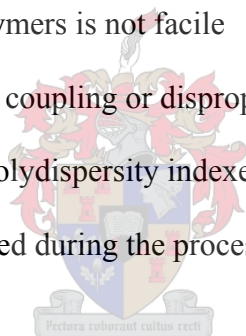
## 1.1 General introduction

Modern society has an increased demand for new materials with specific properties. To meet this need, the development of new techniques by which to prepare such materials has become necessary. Free radical polymerisation (FRP)<sup>1</sup> is one of the main techniques used industrially for the production of polymeric materials. Although this synthetic technique has allowed the preparation of advanced polymers, for use in diverse fields, it does not provide control over the architecture of the polymers being synthesized. To overcome the disadvantages of free radical polymerisation, a range of so-called living polymerisation techniques, including reversible addition-fragmentation chain transfer (RAFT), has been developed.

## 1.2 Free radical polymerisation

Free radical polymerisation is a technique that has been well exploited in both industrial and research laboratories. However, there are some disadvantages which have not yet been overcome:

- Preparation of multiblock copolymers is not facile
- Chains are terminated by radical coupling or disproportion
- Resultant polymers have large polydispersity indexes (>2)
- The free radicals that are produced during the process have high reactivity
- Several side reactions can occur
- The chain lifetimes are short; most chains are dead and have varying chain lengths
- The final properties of the products are unpredictable



This makes free radical polymerisation a difficult technique to use when control over the architecture and the molecular mass of the polymers being synthesized is required. Recent studies in the field of free radical polymerisation aim to retain the advantages that free radical polymerisation offers while improving on its deficiencies. This has resulted in a new method of polymer synthesis, namely *controlled/living radical polymerisation*.

## 1.3 Living radical polymerisation

To date, living radical polymerisation (LRP) remains mostly applied at academic and laboratory levels, for reasons of economy and other practical constraints, such as sensitivity to oxygen and purity of reagents. Living radical polymerisation allows us to overcome two major drawbacks of free radical polymerisation:

- The lack of control of the polymer molar mass
- The inability to produce block copolymers

Living radical polymerisation is based on the principle of the reversible activation of a dormant species (P-X) or reversible deactivation of the active species (P•) (see Chapter 2). The living polymerisation techniques have attracted much attention, especially over the past decade, due to the fact that it is possible to use them to prepare polymers with well-defined structures and low polydispersities. In other words, LRP has the ability to produce polymers quite accurately. Other advantages that LRP offers are:

- Easy formation of multi-block copolymers
- Products of controlled molar mass
- “Living” chains
- Precise end-group control
- Polymers with very narrow molar mass distributions
- Formation of polymers with precisely controlled molecular architectures
- Elimination of chain transfer to polymer and subsequent branching
- Termination still occurs, but is limited or reduced by living techniques

Over the past few years, the following three main techniques in the field of living radical polymerisation have received the most attention and they are essentially grouped as reversible capping and transfer techniques:

Reversible capping (deactivation):

- Nitroxide mediated polymerisation (NMP)
- Atom transfer radical polymerisation (ATRP)

Transfer techniques:

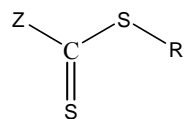
- Reversible addition-fragmentation chain transfer (RAFT)

## 1.4 Reversible addition-fragmentation chain transfer

Using the reversible addition-fragmentation chain transfer process, a robust and versatile technique, it is possible to prepare polymers with controlled architectures. This is made possible by using

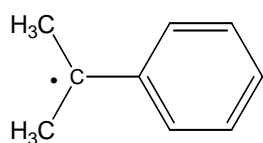


functional chain transfer agents, called RAFT agents. The effectiveness of a RAFT agent depends on the properties of the Z and R groups<sup>2-4</sup> as depicted in Scheme 1.1.

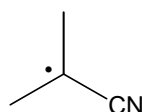


**Scheme 1.1 Reversible addition-fragmentation chain transfer agent.**

- ❖ R is a free radical homolytic leaving group (Scheme 1.2) that is capable of re-initiating the polymerisation.



Cumyl radical



Isobutyronitrile radical

**Scheme 1.2 Examples of free radical (R<sup>•</sup>) leaving groups in a RAFT agent.**

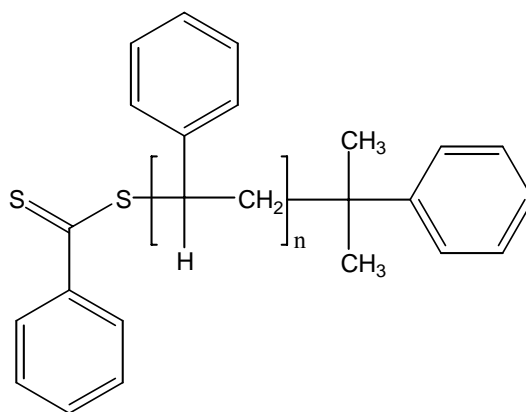
- ❖ Z is a group that governs the activity of the C=S toward radical addition.

Although the RAFT process is well known to occur using several existing chain transfer agents (Section 2.6.6), synthesizing such agents is not always simple.

## 1.5 RAFT polymerisations conducted in bulk

Since bulk polymerisation comprises few components, characterization of the transfer agents in bulk polymerisation has been one of the first challenges facing polymer chemists. In bulk polymerisation, errors are minimized because the reaction mixture consists of monomer and transfer agent in the presence or absence of initiator (see Chapter 4). This is one reason, among others, why bulk polymerisation was chosen as the polymerisation technique in this study (Section 2.11.4).

RAFT polymerisations are performed by the continual “insertion” of the monomer molecules into the chain transfer bond, leading to polymers with a chain transfer fragment at the chain end, so that the chain end remains essentially “alive”. A typical example of a RAFT polymerisation is illustrated by the polymerisation of styrene in Scheme 1.3, using 1-methyl-1-phenylethyl benzenecarbodithioate as RAFT agent.



**Scheme 1.3** RAFT mediated polymerisation of styrene using 1-methyl-1-phenylethyl benzenecarbodithioate as RAFT agent.

## 1.6 Background to this research and objectives

RAFT is a new controlled polymerisation route that permits the synthesis of well-defined macromolecules with controlled chemical composition, predictable molar mass, and narrow molar mass distribution. The ability to control polymer architecture is essential in advanced technological applications where well-defined macromolecular architectures are required. The development of the RAFT technique, which has a great future in industrial applications, is however characterized by inhibition or initialisation periods at the initial stages<sup>5</sup> and by the retardation effects that occur during the RAFT process.<sup>6</sup> These phenomena, especially the latter, have generated serious debates (Sections 2.13 and 2.14).<sup>6-10</sup> The clarification of these effects therefore remains important to the full understanding of the RAFT mechanism.

The overall objective of this work was therefore to obtain a fundamental understanding of the molecular processes involved in the RAFT technique via the use of different chain transfer agents. Initial efforts were focused upon synthesising RAFT agents with specific R and Z groups, with the aim of improving chain transfer activities. Research efforts were to be focused specifically on the RAFT polymerisation of styrene.

Three specific areas were to be investigated:

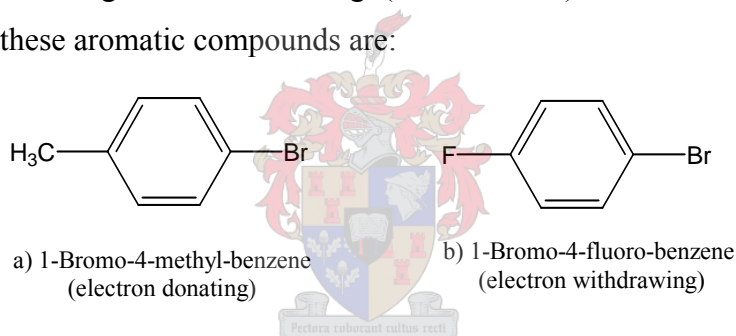
- Design and synthesis of selected RAFT agents
- Characterization of RAFT agents
- Kinetic investigation of homopolymerisation reactions utilizing the synthesised RAFT agents

### 1.6.1 Design and synthesis of selected RAFT agents

Dithioester compounds were to be prepared as the selected RAFT agents. These dithioesters give high transfer coefficients<sup>11</sup> when, for example, styrene is used in the polymerisation.<sup>11</sup> However, the R and Z substituents (Scheme 1.1) have to be chosen carefully according to the class of monomers used (see Sections 2.7 through 2.8). The main requirements of choosing RAFT agents are:

- High rate constant for the addition of the propagating radical to the thiocarbonylthio compound (Scheme 2.8, in Section 2.6.2).
- High rate constant for the fragmentation of the intermediate radical (Scheme 2.8, in Section 2.6.2).

It appears that radical stabilizing moieties with Z groups like phenyl enhance the rate of addition and improve the transfer coefficients better than methyl groups do. This scientific approach led the author to select the Z groups as aromatic compounds (see Schemes 1.3 through 1.4). These aromatic compounds vary from being electron donating (Scheme 1.4a) to withdrawing (Scheme 1.4b). Typical examples of these aromatic compounds are:



**Scheme 1.4 Electron (a) donating and (b) withdrawing compounds.**

A high rate of fragmentation of the intermediate radicals (species **2** and **4** in the RAFT mechanism, Scheme 2.8) into the polymeric thiocarbonylthio compound (species **3** and **5** in Scheme 2.8) is obtained when the R group is chosen as a good homolytic leaving group. The homolytic leaving capacity of R increases with increasing stability of the formed radical R (see Scheme 2.14 in Section 2.8), with the electrophilic character and with increasing steric hindrance of R. For example, the cumyl group (C(CH<sub>3</sub>)<sub>2</sub>Ph) is a better leaving group than benzyl ((CH<sub>2</sub>)<sub>2</sub>Ph) (see Scheme 2.14). Furthermore, the expelled radical R must be reactive enough to reinitiate the polymerisation, otherwise the RAFT agent will act only as a terminating agent. Retardation may be observed if the efficiency of the re-initiation is low. It is for these reasons that tertiary free radicals were selected as R groups in this work (Section 2.8).

The Grignard method was to be used to synthesize the intermediate compounds (Chapter 3).

## 1.6.2 Characterization of RAFT agents

The chemical structures of the above mentioned dithioester compounds were to be verified via spectroscopic methods, such as FT-IR spectroscopy, nuclear magnetic resonance spectroscopy (NMR) and ultraviolet-visible light spectroscopy (UV).

## 1.6.3 Kinetic investigation of styrene homopolymerisation reactions

The controlled radical polymerisation of styrene was to be carried out in a bulk system, using the respective dithioesters as chain transfer agents.

Special attention was to be devoted to kinetic investigations to evaluate the efficiency of these RAFT agents and to obtain an understanding of the kinetic and mechanistic details of the RAFT process. This was to be supported by the use of size exclusion chromatography, which can be considered as a reliable analytical technique.

## 1.7 Outline of the thesis

This thesis comprises of seven chapters:

### ***CHAPTER I: Introduction and objectives***

A brief introduction is given to free radical polymerisation, living radical polymerisation, and RAFT reactions conducted in a bulk styrene polymerisation. Background to the project and the objectives are also given.

### ***CHAPTER II: Historical and theoretical background***

Chapter two gives a short review of controlled/“living” radical polymerisation techniques. Similarities and differences between the three most important techniques in the field of controlled radical polymerisation, namely: nitroxide mediated polymerisation, atom transfer radical polymerisation and reversible addition-fragmentation chain transfer polymerisation are presented. A discussion on the choice of different R and Z groups, the choice of initiator, and reasons why bulk was chosen as the polymerisation technique in this study is presented.

### ***CHAPTER III: Synthesis of dithioesters***

This chapter describes the synthesis of RAFT agents. The first part of this chapter highlights the theory based on Grignard methods used to synthesize novel intermediate compounds. The second part describes the synthetic pathways leading to RAFT agents. The synthesis of disulfides, cyanoisopropyl, cyanovaleric acid and cumyl functionalized dithiobenzoates is discussed.

Preparation of the latter is feasible with the addition of  $\alpha$ -methyl styrene to intermediate benzenecarbodithioic acids synthesized using Grignard reagents.

#### ***CHAPTER IV: An examination of the living character of styrene polymerisation mediated by functionalised dithiobenzoates***

In this chapter the living character of styrene polymerisation as a function of chain transfer agents, synthesized as described in Chapter 3, is examined. The polymerisations were conducted in bulk, making use of the self-initiation of styrene at 100°C. Monomer conversion was determined gravimetrically, and molar masses and molar mass distributions of styrene polymerisations were measured by size exclusion chromatography (SEC). The different behaviours and reactivities of these RAFT agents were considered and an attempt was made to explain these differences.

#### ***CHAPTER V: The activity of the dithiobenzoates and derivatives as a function of phenyl Z group modification***

The thirteen chain transfer agents (CTAs) prepared as described in Chapter 3, were grouped in two different classes of RAFT agents.

The first class of RAFT agents comprises three series of monofunctional RAFT agents, which differ in their R groups:

- R<sub>1</sub>: cyanoisopropyl (Series A)
- R<sub>2</sub>: cyanovaleric acid (Series B)
- R<sub>3</sub>: cumyl (Series C).



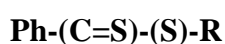
The second class of RAFT agents comprises one group of RAFT agent precursors, which represents the Series D: diphenyldithioperoxyanhydride and derivatives.

The kinetic behaviours of compounds in the above series A, B, C and D were determined by gravimetry and SEC.

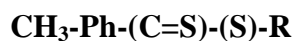
#### ***CHAPTER VI: The activity of the dithiobenzoates and derivatives as a function of R group modification***

Here the results of a study of the role of the respective R groups on the activities of 12 of the 13 dithiobenzoates studied in Chapter 5 are discussed. These compounds were grouped into three series.

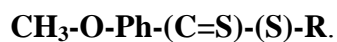
- The first series consisted of RAFT agents having phenyl as the Z group:



- In the second series the Z group was the 4-methylphenyl:



- In the last series the Z group consisted of the 4-methoxyphenyl:



## ***CHAPTER VII: Conclusions and recommendations***

General conclusions to the study are made. Knowing that the equilibrium between the intermediate  $[\text{Y}^\bullet]$  and propagating  $[\text{P}^\bullet]$  radicals are relevant factors for studying the mechanism of RAFT, ESR studies are recommended as an extension to this study.



## 1.8 References

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*“I do not feel obliged to believe that the same God who has endowed us with sense, reason, and intellect has intended us to forgo their use” Galileo Galilei.*

## *CHAPTER 2: Controlled/“Living” radical polymerisation*

Chapter 2 deals with the background to living radical polymerisation and provides a comparison of the three main living radical polymerisation techniques, which are: nitroxide mediated polymerisation (NMP), atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer polymerisation (RAFT). The relative advantages and limitations of each technique are described. It also demonstrates how crucial the choice of different R and Z groups are in designing and synthesizing RAFT agents with good efficiencies. Finally, the choice of initiator and the reasons why bulk polymerisation medium was chosen are discussed in detail in this chapter.

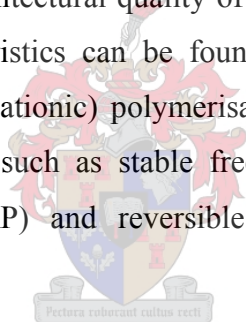




## 2.1 Introduction

The increasing academic and industrial interest in well-structured polymers has resulted in a research drive to produce macromolecules through controlled or “living” polymerisation techniques. Living polymerisation and controlled polymerisation are two concepts which have given rise to much debate in polymer science. Some researchers suggest, for example, that the concept of controlled radical polymerisation can be used “when chain-breaking reactions undoubtedly occur, like in radical polymerisation”.<sup>1</sup> Other groups stipulate that the characteristics of living polymerisation occur “whenever propagation and reversible termination are significantly faster than any process for irreversible termination”. To avoid any confusion, the author will consider both “living” and controlled radical polymerisation as processes “which allow polymers to grow whenever monomer is supplied, and such polymers can grow to a desired maximum size while their degree of termination or chain transfer is still negligible”.<sup>2,3</sup>

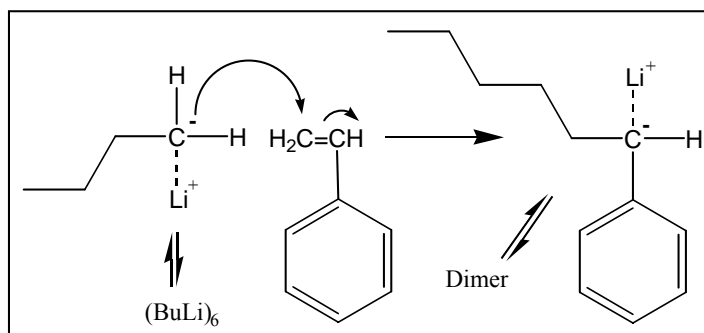
Since about the 1940s, polymerisation has seen the emergence of several techniques aimed at a common objective: to improve the architectural quality of polymers resulting from the application of these techniques.<sup>4</sup> Living characteristics can be found among the following polymerisation techniques: living ionic (anionic and cationic) polymerisations, and free radical polymerisations, which includes controlled techniques such as stable free radical polymerisation (SFRP), atom transfer radical polymerisation (ATRP) and reversible addition-fragmentation chain transfer (RAFT).



## 2.2 Background to living polymerisation techniques

### 2.2.1 Living ionic polymerisation

Living ionic polymerisation techniques were developed more than half a century ago, in the 1950s, by researchers such as Szwarc.<sup>5</sup> These techniques are mediated by anionic (R<sup>-</sup>, Li<sup>+</sup>) or cationic agents. In such polymerisation systems, chain ends stay alive unless terminating agents are added. A typical example is shown in Scheme 2.1.

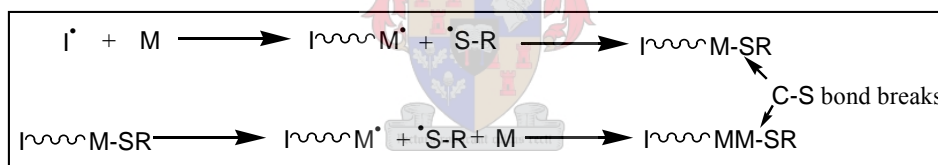


**Scheme 2.1 Example of anionic polymerisation.**

In the reaction above there is no termination unless terminating agents, such as 1,2 dichloro-ethane ( $\text{ClCH}_2\text{CH}_2\text{Cl}$ ), are added.

### 2.2.2 Living radical technique

It was not until the 1980s that Otsu<sup>6,7</sup> developed a “real” living radical technique based on “reversible termination”. This method is governed by two components (see Scheme 2.2). One conventional initiator starts a chain with a C-C bond, which is not reversible. The second component gives very stable radicals ( $\text{R-S}\cdot$ ) that “terminate” chains, with a C-S bond that breaks easily (reversible termination).



**Scheme 2.2 Reversible termination.**

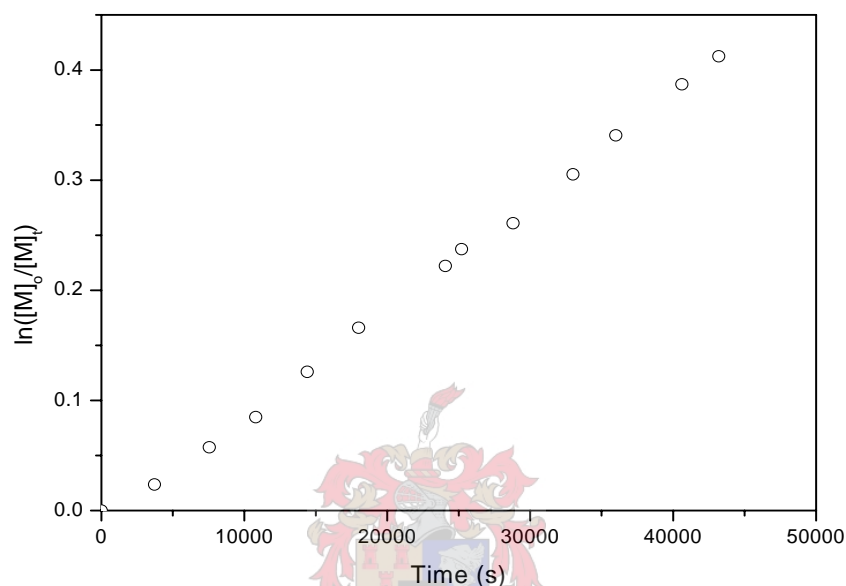
(R is an alkyl group and M is a monomer).

In this technique, monomer is added between chain end and iniferter and the resulting reversibly terminated chains are essentially still “alive”. From the mid 1980s until today, other successful approaches have been investigated in order to develop the concept of living free radical polymerisation. Use has been made of mediating agents such as nitroxides, halides or thiocarbonylthio compounds. Before giving a general overview of these techniques, it is useful to examine some features, which are required to identify the living polymerisation process. These features are divided into four groups, as described in Sections 2.3.1 through 2.3.4.

## 2.3 General features of living free radical polymerisation

### 2.3.1 Internal first-order kinetics with respect to monomer

First-order kinetics can be derived from the semi-logarithmic plots of the monomer consumption versus time (Figure 2.1). The straight line indicates a steady state (rate of initiation = rate of termination), and a resulting constant radical concentration.



**Figure 2.1** Example of a first-order kinetic plot of fractional conversion versus time for the reaction of 4-cyano-4-[[4-methoxyphenyl]carbothioyl]sulfanyl]pentanoic acid with styrene.

### 2.3.2 Linear growth of degree of polymerisation with conversion

The number average degree of polymerisation ( $DP_n$ ) is defined as the ratio of the total concentration of monomers initially present to the total number of polymer chains in the system after the polymerisation has taken place:<sup>8</sup> In this definition, residual monomer will have a negative effect on  $DP$ , which is not true for radical polymerisation but is for step-growth polymerisation (e.g. polyester synthesis).

$$DP_n = \Delta [M]/[I]_0 = [M]_0/[I]_0 \times \text{conversion}$$

where:  $[M]_0$  and  $[I]_0$  are the initial concentrations of a monomer and of initiator.

### 2.3.3 Narrow molar mass distribution

A polymer with a low polydispersity is expected to be produced from living polymerisation techniques if the following criteria are satisfied:

- Rate of initiation is greater than or equal to that of propagation
- The exchange rate of active species should be faster than propagation
- The chain termination or transfer should be negligible

### 2.3.4 Long-lived polymer chains

After complete consumption of the monomer initially present, the introduction of additional initiators, in the case of the RAFT process for instance, tends to reactivate the chain ends and, in the presence of monomers, new polymers (block copolymers) are formed.

After examining some features of living, or “controlled” free radical polymerisation, we should now understand why it has received considerable attention in recent years. Moreover, with a strong motivation to overcome the drawbacks of living ionic polymerisations (reactions conditions are not easily controllable<sup>9</sup> and they do not tolerate electrophilic functional groups), new techniques based on the utilization of radicals (as mentioned in Section 2.2.2), leading to the formation of growing chains through a mechanism of reversible deactivation, have been developed. The use of stable radicals, for example, has led to the method called: stable free radical polymerisation (SFRP).

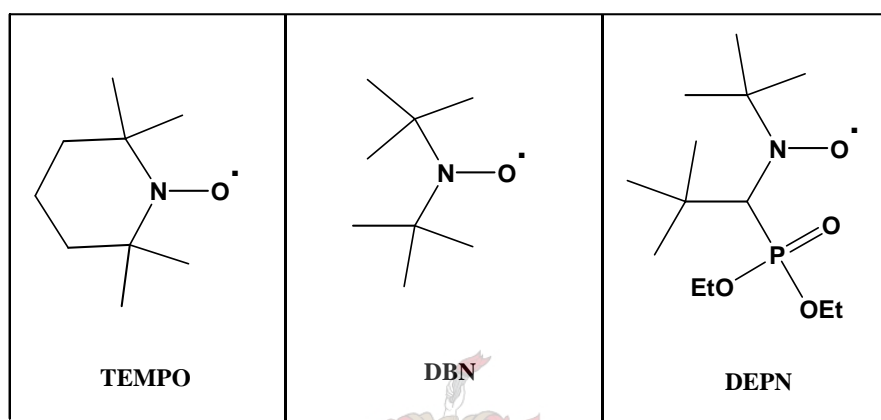
## 2.4 Stable free radical polymerisation

### 2.4.1 Introduction

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

The success of SFRP as a living mediating technique depends on the nature of the stabilized radicals, which range from (aryloxy),<sup>10</sup> substituted triphenyls<sup>11</sup> and triazoliny,<sup>12</sup> to nitroxides and their associated alkylated derivatives. The latter is the most widely studied and certainly most successful class of nitroxide compounds. These compounds have been successfully developed and used for different applications in the field of living free radical polymerisations. Typical examples

are: 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO),<sup>13-19</sup> di-tert-butyl nitroxide (DBN),<sup>20-22</sup> and n-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl) nitroxide (DEPN), (See Scheme 2.3).<sup>14,23-25</sup> The use of such mediators (DEPN for example) allows the polymerisation of a wide variety of monomers such as styrene derivatives, acrylates, acrylamides, and acrylonitrile. Thus, complex copolymers<sup>24,26,27</sup> and homopolymers, including poly-(methyl methacrylate) and polystyrene, with accurate control of molar masses, and polymers with polydispersities as low as 1.05 can be now prepared.<sup>28</sup> The versatile nature of these mediators can be used to control the preparation of random and block copolymers from a wide selection of monomer units.

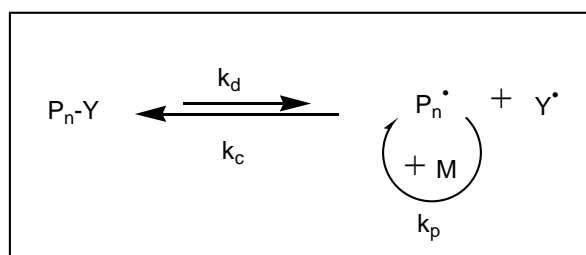


Scheme 2.3 Examples of nitroxide mediators.

SFRP is a process which does not only tolerate a number of functional groups<sup>29</sup> but also does not require stringent starting material purification as the ionic techniques do.

## 2.4.2 General mechanism of SFRP

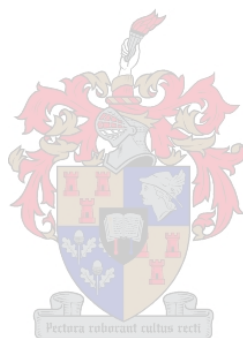
In the SFRP process a capped dormant species (alkoxyamine initiators) ( $P_n\text{-Y}$ ) is thermally labile and, on heating, decomposes to form a stable nitroxide radical ( $Y\bullet$ ) and a reactive carbon-centred radical ( $P_n\bullet$ ). The latter species ( $P_n\bullet$ ) can add a monomer ( $M$ ) before combining with a nitroxide ( $Y\bullet$ ) to give a new alkoxyamine. The mechanism is illustrated by Scheme 2.4 and by the polymerisation of styrene initiated by TEMPO species in Scheme 2.5.

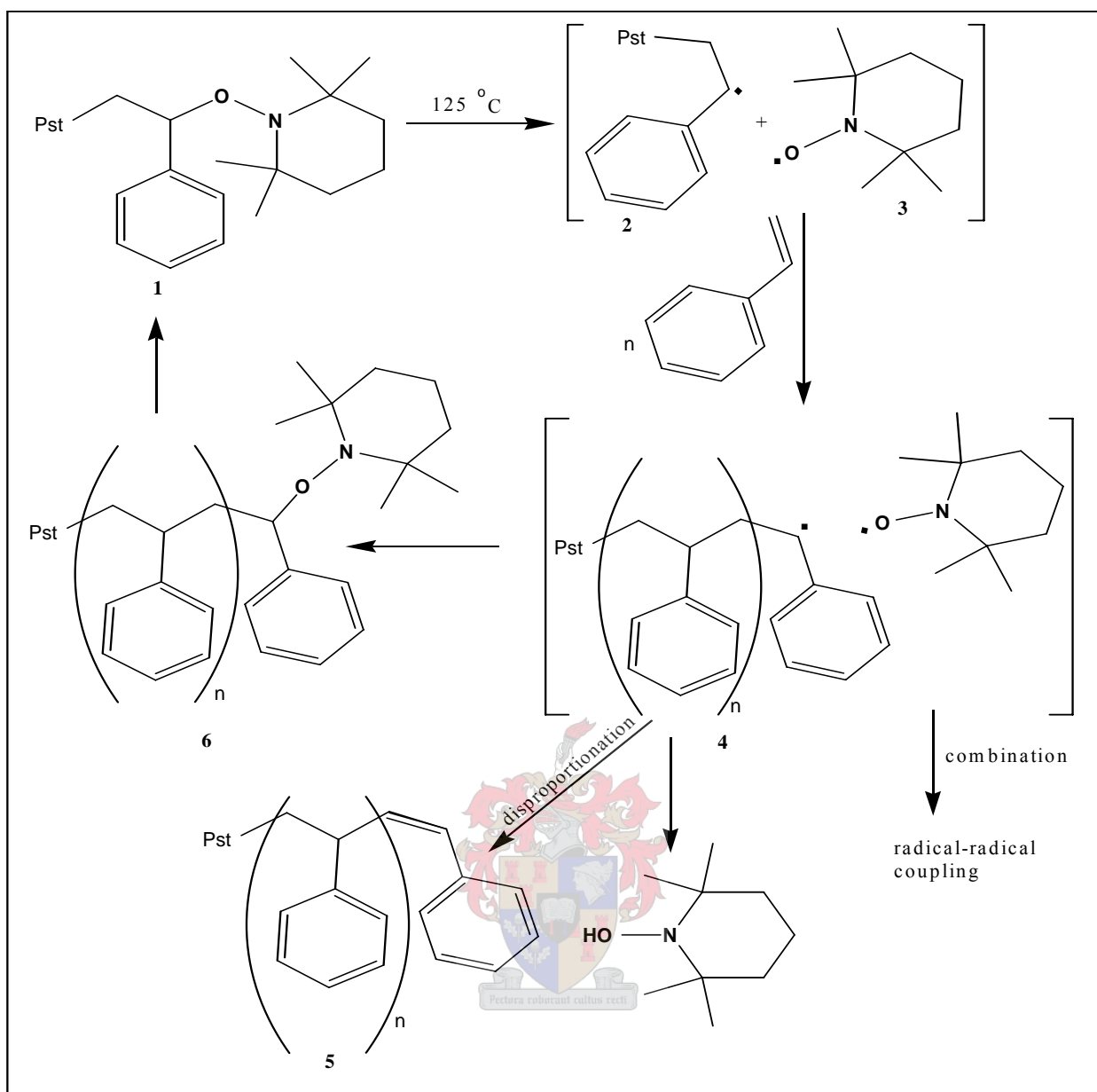


Scheme 2.4 General mechanism of SFRP.

Hawker et al.<sup>9</sup> have discussed the most important steps in nitroxide mediated radical polymerisations. They noted that the important structural feature in this technique is the carbon oxygen (–C-ON) bond of the alkoxyamine. In fact, the capping agent, the nitroxide radical (3), is generated by the thermolysis process, which causes the homolytic bond cleavage of (–C-ON) of dormant species (1) and produces the activated agent responsible for the polymerisation, namely the polymeric radical (2) (Scheme 2.5). Consequently, while the polymerisation is taking place, the polymeric radical (2) can undergo chain extension with monomer (styrene) to yield a new chain extended polymeric radical (4). Chain extension is controlled by the equilibrium between the dormant and active (freely propagating, radical) recombination of (4) with the nitroxide radical (3) gives the dormant species (6).

By adding monomers, the process laid out above can be reactivated. The activation/deactivation, which occurs during the polymerisation cycle, together with the formation of the reversible termination of the growing polymeric chain, keeps the level of radicals low, and this leads to a well-controlled polymerisation (Scheme 2.5).<sup>9</sup>





**Scheme 2.5** Polymerisation of styrene mediated by TEMPO.

It should be noted that instead of adding to a monomer, species (4) may tend to terminate via combination or disproportionate with TEMPO to give species (5).

Although SFRP has been known since the early 1980s<sup>30,31</sup> some disadvantages associated with the use of nitroxides as capping agents remain to be overcome (see Table 2.1). These include sensitivity to oxygen and the availability of the nitroxides (expensive and difficult to synthesize), even if TEMPO and some derivatives are currently readily available. Moreover, these mediating agents present a preference to undergo side reactions (disproportionation between propagating species and nitroxide).

## 2.5 Atom transfer radical polymerisation

### 2.5.1 Introduction

Atom transfer radical polymerisation (ATRP)<sup>32</sup> is a simple, inexpensive polymerisation technique, used more in research laboratories than in industry. ATRP is mediated by a variety of metal complexes. This living technique, discovered independently by Sawamoto<sup>33</sup> and Matyjaszewski<sup>32</sup> in the 1990s, provides an opportunity to emphasize the concept of living radical polymerisation by minimizing unwanted side reactions which often occur in polymerisation techniques.

Being a member of the LRP family, ATRP combines certain advantages of radical polymerisation, including the ability to polymerise a variety of monomers,<sup>32,34</sup> for the preparation of efficient block copolymers and the synthesis of polymers with low polydispersities. In addition, like SFRP, ATRP does not require stringent reaction conditions<sup>35</sup> and is applicable over a wide temperature range (Table 2.1). A direct consequence is therefore a facile use of the technique. The preparation of polymeric materials through the use of ATRP is possible in different media, such as emulsion systems.<sup>36</sup>

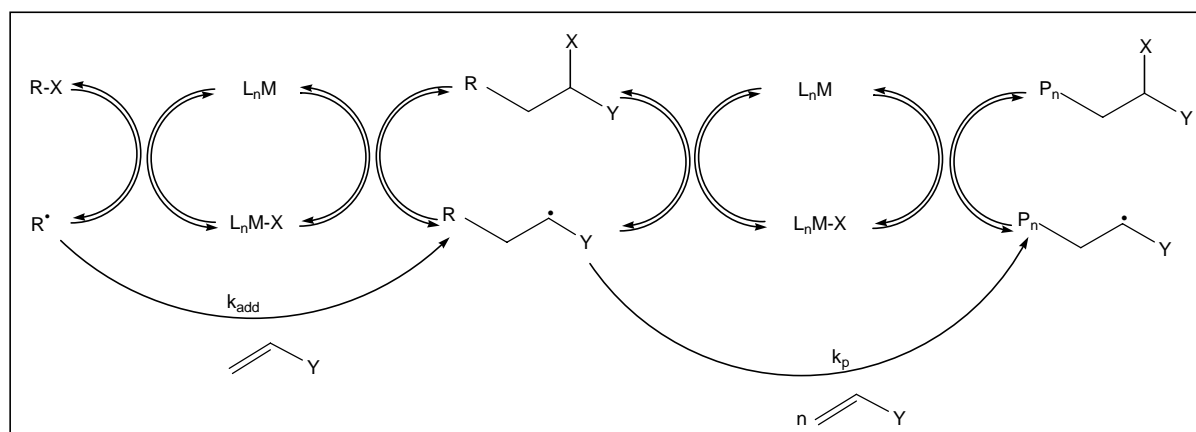
### 2.5.2 Mechanism of ATRP

Being a member of the reversible termination systems, ATRP polymerisation is based on a capping agent and halides (R-X) that are also considered as initiators, where X is usually a bromide or chloride. As in SFRP, the amount of initiator used in ATRP is very important because the determination of the final molar mass of the polymer formed after consumption of monomers is a function of the concentration of radicals produced throughout the polymerisation process.<sup>37</sup>

The mechanism of ATRP is well known (Scheme 2.7);<sup>37</sup> it originates from atom transfer radical addition (ATRA) commonly used in organic synthesis (Scheme 2.6).<sup>38-43</sup>

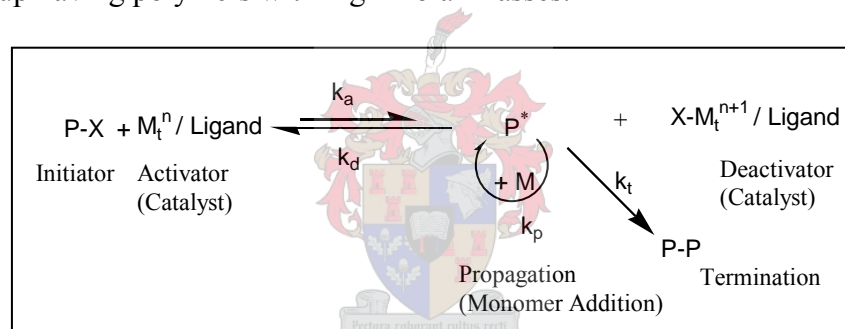
In ATRA, the mechanism starts by a transition metal complex  $M^n$  to  $M^{n+1}$  (typical metals used like Cu, Fe inter alia), due to the abstraction of a halogen atom X from an alkyl halide (R-X), which generates an alkyl radical  $R^\bullet$ . This radical propagates by adding monomer such as  $CH_2=CHY$  continually. Thus, the resulting growing chain ( $RCH_2CHY^\bullet$ ) will close the catalytic cycle due to the abstraction of the halogen from the metal with higher oxidation state  $M^{n+1}X$ , to form a stable compound ( $RCH_2CHXY$ ).





**Scheme 2.6** Catalytic cycles involved in ATRA and ATRP.

ATRP is a polymerisation technique that was developed on the basis of ATRA and it has the ability of allowing the preparation of growing chains with “active” free radical end-chains according to the ATRA mechanism (Scheme 2.7). One of the advantages of this derivative technique (ATRP) is to allow the reactivation of the polymerisation process in the presence of the additional monomers. Finally, we end up having polymers with high molar masses.<sup>44</sup>



**Scheme 2.7** ATRP and reverse ATRP mechanisms.

### 2.5.2.1 The ATRP process

ATRP is a member of the family of living radical polymerisation techniques that relies on both the choice of initiator and catalyst complex. However, in order to minimize the risk of contamination in the final product, the active catalyst selected should provide low levels of transition metal. Moreover, due to the fact that oxygen is a contaminant it leads to side reactions (oxidation of the transition metal or reaction with a carbon centred radical), care has to be taken to reduce the amount of dissolved oxygen in the system.

Although ATRP has been enormously successful in producing new polymeric materials at academic level, the commercially viable production of such polymers through the use of ATRP remains an important goal to be achieved.

## 2.6 Reversible addition-fragmentation chain transfer polymerisation

### 2.6.1 Introduction

Today, it is increasingly recognized that obtaining polymers with controlled MMD, architecture, etc. through the use of ATRP or SFRP is possible. However, the choice of monomer remains the first problem to overcome when those aforementioned methods are used in the synthesis of block copolymers and other polymeric materials. For instance, methacrylate and vinyl acetate monomers cannot be polymerised by the use of NMP and ATRP techniques respectively.<sup>45</sup> More recently, a specific technology that has the distinction of being applicable to a wide range of monomers has been developed. This new process is called RAFT polymerisation and is mediated by the use of thiocarbonylthio compounds.

The discovery of reversible addition-fragmentation chain transfer (RAFT) is a milestone in living radical controlled polymerisation due to its several advantages:

- The RAFT process does not need additional experimental precautions compared to conventional radical polymerisation
- For a given monomer, the chain transfer activity of a RAFT agent is a function of substituents *Z* and *R* (see Sections 1.4 and 2.7 through 2.8)
- The RAFT technique can be applied in both *homogeneous and heterogeneous* polymerisations, such as emulsion<sup>46-48</sup> and miniemulsion<sup>49-52</sup> polymerisations
- The RAFT technique can be combined with other living techniques, such as ATRP, to produce polymers

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

- The synthesis and the purification of thiocarbonyl thio compounds are not too easy; they are time-consuming
- Thiocarbonyl thio compounds have a strong smell and the final products are sometimes coloured
- Inhibition and retardation are often observed in RAFT polymerisations
- Termination is not specifically suppressed; this is generally represented by the formation of tails in the molar mass distribution

Table 2.1 summarizes the characteristics of the three types of living radical polymerisation techniques.<sup>4</sup>

**Table 2.1: Comparison of SFRP, ATRP and RAFT processes**

| Features       | SFRP  | ATRP  | RAFT  |
|----------------|---|---|---|
| Monomers       | Styrene, acrylate and acrylamides.<br>No methacrylate.                              | All monomers, except those poisoning the catalytic system (acrylic acid) and vinyl acetate.   | Nearly all monomers.  |
| Conditions     | Generally elevated temperatures are used (>120°C).<br>Sensitive to O <sub>2</sub> . | From high to low temperatures (-30°C to 150°C).<br>Some tolerance to O <sub>2</sub> and inhibitors with M <sub>1</sub> <sup>o</sup> . | All temperatures, but moderate are preferred.<br>Some tolerance to O <sub>2</sub> . |
| End groups     | Alkoxyamines.   | Alkyl halides.  | Thiocarbonyl thio compounds.  |
| Other features | Conventional radicals used for polymerisations.                                     | Transition metal catalyst/ligand used.<br>Should be removed and recycled.<br>Conventional radicals can also be used.                  | Conventional radicals used for polymerisations.                                     |

From Table 2.1 and observations discussed in Sections 2.4 through 2.6.1, the RAFT process appears to be one of the most useful techniques in the field of living free radical polymerisation. The RAFT technique is a sub-class of transfer-based techniques, which depend on the rapid transfer of radical activity among growing chains, where most growing chains are not in their radical form, but in a dormant state. 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 technique is mainly driven by the presence of a reactive double bond species S=C(Z)SR. This dormant species allows the formation of growing chains when active species are added in the reaction. Even if the RAFT mechanism is not entirely understood yet,<sup>53</sup> Rizzardo *et al.*<sup>54</sup> have proposed a mechanism that is generally accepted (Scheme 2.8).

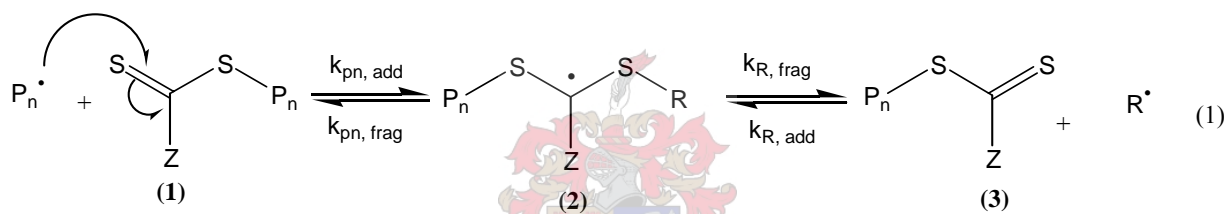
It was found that RAFT agents having high reactivity provide polymers with well-controlled molar masses and narrow molar mass distributions<sup>54,55</sup> and these polymers with low polydispersities can be influenced not only by the appropriate choice of the RAFT agent but also by the reaction conditions. Moreover, the most effective RAFT agents are those of dithioesters, trithiocarbonates, xanthates, and certain aromatic dithiocarbamates<sup>56</sup> (Section 2.6.6).

## 2.6.2 Mechanism of RAFT

a. Initiation:



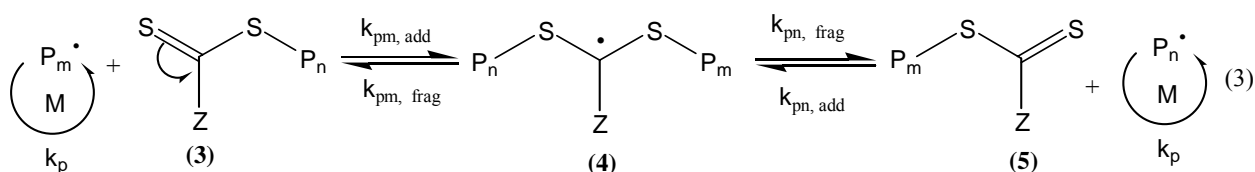
b. Chain transfer:



c. Reinitiation:



d. Chain equilibration:



Scheme 2.8 The RAFT process, as proposed by Rizzardo.<sup>54</sup>

### 2.6.2.1 The RAFT process

The RAFT process involves the chain transfer of an active species that reacts with a propagating radical  $\text{P}_n^\bullet$ , which is generated by initiator decomposition.

The mechanism proposed by Rizzardo *et al.*<sup>54</sup> (Scheme 2.8) involves a series of reversible addition-fragmentation steps, which commence with the addition of the propagating radical  $\text{P}_n^\bullet$  to the dormant chain (1). The resulting intermediate radical (2) fragments to a new polymeric thiocarbonyl thio compound (3) and a new radical  $\text{R}^\bullet$  (equilibrium (1)). It is however possible that the adduct

radical (2) fragments back to the original polymeric species ((1) and  $P_n^\bullet$ , this first sequence is a classical chain transfer reaction). In the former case, the new radical  $R^\bullet$  formed is added to a monomer  $M$ , in order to form a new propagating radical  $P_m^\bullet$ . This propagating radical  $P_m^\bullet$  plays a crucial role in the RAFT polymerisation. It allows the polymerisation to carry on when it adds to the polymeric RAFT agent (3) to form a so-called intermediate radical (species (4)), which can either undergo fragmentation to give a new dormant species (5), or fragments back to species (3) and  $P_m^\bullet$ . Once the dormant species (1) is consumed, equilibrium is set up between propagating radicals and dormant species (equilibrium (3)).

In the RAFT process, when the polymerisation is stopped, most of the polymers are polymeric thiocarbonyl thio compounds (5). This stable compound (5) acts as a polymeric RAFT agent. Therefore, the addition of a new monomer and an initiator leads to a new equilibration between the propagating radicals.

The following criteria need to be met for an effective RAFT process:

- 1) A rapid conversion of the RAFT agent into a dormant chain.

In order to minimize unwanted termination processes at the earlier stage of the RAFT process, the RAFT agent should be quickly converted into dormant chains. This is called initialisation.

- 2) A dynamic exchange of radicals among all chains.

Both the rates of addition of free polymeric radicals to the RAFT agent and fragmentation of intermediate radicals must be fast relative to the rate of propagation radicals, in order to give all chains an equal chance to add to monomer and grow at the same rate.

- 3) Minimal side reactions.

### 2.6.3 The rate of consumption of the transfer agent

Recent studies by Chiefari *et al.*<sup>57</sup> have shown that the consumption of the transfer agent is a function of the propagating radicals  $[P^\bullet]$  and the ejected radical  $[R^\bullet]$ . Thus, the consumption of initial RAFT agent (step (1)), can be expressed by the following two transfer coefficients:

$$C_{tr} = k_{tr}/k_p \quad \text{Eq. 2.1.}$$

$$C_{-tr} = k_{-tr}/k_j \quad \text{Eq. 2.2.}$$

- $C_{tr}$  stands for transfer coefficient or transfer constant, which is the ratio of the rate constant for chain transfer to the rate constant for propagation at zero conversion of a given monomer and chain transfer agent (CTA).<sup>58</sup>

- $k_{tr}$  stands for the rate constant for chain transfer
- $k_p$  is the rate constant for propagation
- $C_{tr}$ ,  $k_{-tr}$  and  $k_j$  describe the reverse transfer constants.

For a given RAFT agent, a linear increase in the number average molar mass  $M_n$  with conversion and a low polydispersity will be obtained if the ratio of the chain transfer constant ( $C_{tr} = k_{tr}/k_p$ ) is high (above 100). Moreover, it was observed that the  $C_{tr}$  varies significantly for different RAFT agents that have the same leaving group ( $R\bullet$ ) but different activating Z groups. Therefore,  $k_{tr}$  values seem to be related to the nature of the activating Z groups contrary to the leaving moiety  $R\bullet$ , which does not play a significant role on the final  $k_{tr}$  values as long as it has the ability to reinitiate the polymerisation very quickly.

#### 2.6.4 Determination of the initial transfer rate in the RAFT process

The transfer constant is defined as the ratio of the rate constant for chain transfer to the rate constant for propagation at zero conversion of monomer and RAFT agent.<sup>58</sup> The rate constant for chain transfer that occur by addition-fragmentation is defined by the following equations:<sup>59</sup>

$$k_{tr} = k_{pn, add} \times k_{R, frag} / (k_{pn, frag} + k_{R, frag}) \quad \text{Eq. 2.3.}$$

$$k_{-tr} = k_{pn, frag} \times k_{R, add} / (k_{pn, frag} + k_{R, add}) \quad \text{Eq. 2.4.}$$

where  $k_{pn, add}$  and  $k_{R, add}$  are the rate constants for addition of a polymeric radical of n degree of polymerisation and an initial RAFT agent leaving group radical, to a RAFT agent respectively (Scheme 2.8), and  $k_{pn, frag}$  and  $k_{R, frag}$  are the rate constants for fragmentation of a polymeric radical of n degree of polymerisation and an initial RAFT agent leaving group from a RAFT agent respectively (Scheme 2.8).

Studies have shown that the effectiveness of a RAFT agent in the RAFT process depends on:<sup>58</sup>

- The rate of reaction of the RAFT agent with the propagating radicals ( $k_{add}$ ), which is under the influence of (1) and (3) in Scheme 2.8
- The rate of fragmentation of the intermediate radicals between products and starting materials, is determined by the magnitude of  $k_{pn, frag}$  and  $k_{R, frag}$
- The ability of the expelled radicals,  $R\bullet$ , to reinitiate polymerisation.

In the RAFT process, the transfer constant and the polydispersity are strictly related. Therefore, the preparation of new materials with low polydispersities is achieved by the use of chain transfer agents with higher transfer constants. Aryl (as Z group) dithiobenzoate derivatives, for example, are

recommended in the polymerisation of monomers such as styrene and acrylate esters because their transfer constant values with such monomers are estimated to be larger than 20.<sup>58</sup>

The determination of the rate constants themselves is not part of this study.

### 2.6.5 Determination of molar masses

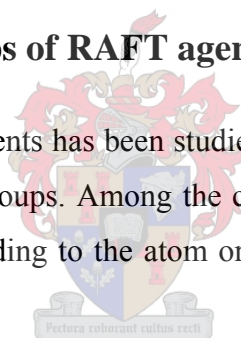
As with all living polymerisation techniques, the RAFT process is characterized by an increase of the molar mass in a linear manner with monomer conversion.<sup>58</sup> With knowledge of the monomer and RAFT agent concentrations, the evolution of  $M_n$  can be predicted as follows (Eq. 2.5):<sup>58</sup>

$$M_{n, \text{theory}} = t [M]_0/[RAFT]_0 \times MW_M + MW_{RAFT} \quad \text{Eq. 2.5.}$$

Where:  $[M]_0$  and  $[RAFT]_0$  are the initial concentrations of the monomer and the RAFT agent,  $MW_M$  and  $MW_{RAFT}$  are the molar masses of a monomer and of the RAFT agent, respectively,  $t$  is the fractional conversion, and  $M_{n, \text{theory}}$  is the theoretical number average molar mass of the formed polymer.

### 2.6.6 The most common Z groups of RAFT agents

The chain transfer activity of RAFT agents has been studied extensively and it was found that their activity is a function of the Z and R groups. Among the common Z groups of RAFT agents used, five classes have been identified according to the atom or group atom used to form the C-Z bond (S=C-Z). See Table 2.2.



**Table 2.2: Classes of RAFT agents with different Z groups**

| RAFT agents       | Z group                           |
|-------------------|-----------------------------------|
| Dithioesters      | Alkyl-, aryl-                     |
| Trithiocarbonates | Alkyl-S-                          |
| Dithiocarbamates  | R <sub>1</sub> R <sub>2</sub> -N- |
| Xanthates         | Alkyl-O-                          |
| Phosphoryl-esters | Phosphonate                       |

### 2.6.6.1 Dithioesters

Among the five classes, the dithioesters are one of the most effective and have higher transfer coefficients<sup>58</sup> than the others in the RAFT-mediated polymerisation of styrene for example, where the R group is common. See Chapter 3.

### 2.6.6.2 Trithiocarbonates

Trithiocarbonates are effective RAFT agents,<sup>58</sup> and are often characterized by high transfer coefficients.<sup>60</sup> They are relatively simple to synthesize and easier to purify than other RAFT agents, such as dithioesters for example. The role of the activating group is governed by the alkyl-S-moiety.

### 2.6.6.3 Dithiocarbamates

Dithiocarbamates (DTCs) are used in agriculture as fungicides, as well as in the rubber industry as vulcanisation accelerators and antioxidants.<sup>61</sup>

It is noteworthy that the efficiency of the dithiocarbamate groups depends on the substituents on the nitrogen.<sup>58</sup> See Table 2.2.

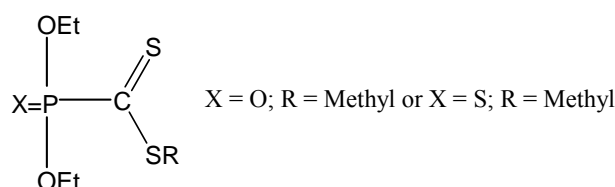
### 2.6.6.4 Xanthates

Patented by Rhodia,<sup>62</sup> xanthates are compounds that are easier to synthesize than dithioesters. Xanthates have low transfer constants in polymerisations of certain monomers such as styrene and methyl methacrylate.<sup>58</sup> They are commonly used to manufacture cellulose film.

### 2.6.6.5 Phosphoryl dithioformates as RAFT agents

The search for new and efficient trapping agents has also resulted in the use of phosphoryl moieties.<sup>63,64</sup> Here the phosphoryl group can bear different substituents. Typical examples are methyl diethoxyphosphoryl- or diethoxythiophosphoryl-dithioformates (Scheme 2.9).<sup>65</sup>

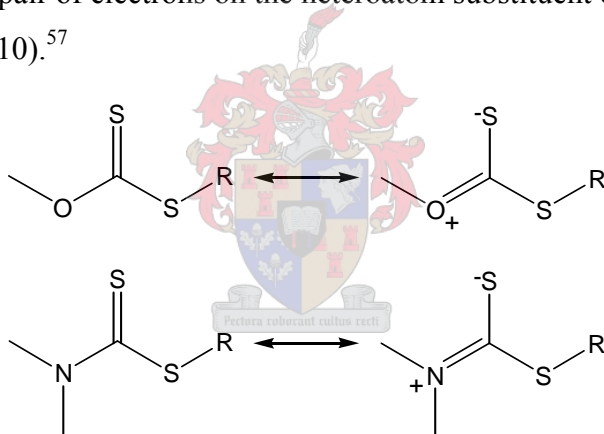




Scheme 2.9 Example of phosphoryl dithioformates.

## 2.7 Influence of the Z group on the double bond (S=C)

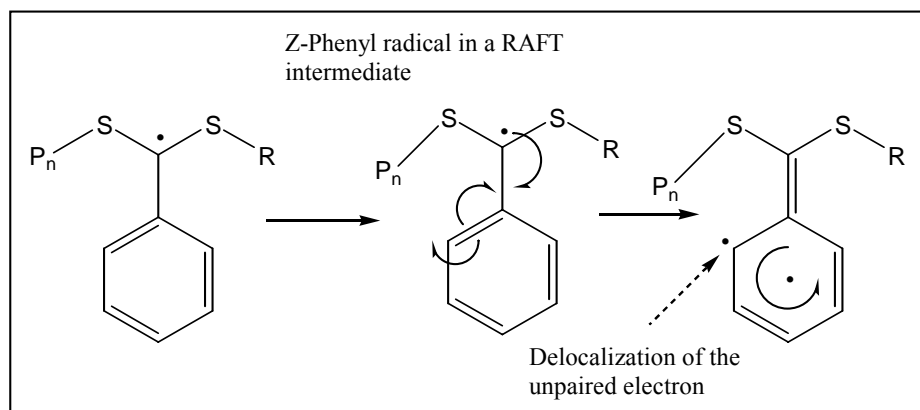
Among the five classes of RAFT agents described above, it has been suggested that within each class the differences in transfer coefficient should mainly reflect the influence of the Z group on the rate of free radical addition to the (S=C) double bond. For example, some authors<sup>57</sup> have found that the relatively low activity observed in certain cases of dithiocarbamate and xanthates derivatives contrary to dithioesters can be explained by the formation of resonance structures, which arise through interaction between the O or N lone pairs and the double bond (S=C) (Schemes 2.10 through 2.11). In other words, a lowering of the double bond character of the (S=C) bond by conjugation with the lone pair of electrons on the heteroatom substituent explains the low activity of these reagents (Scheme 2.10).<sup>57</sup>



Scheme 2.10 Resonance structures of xanthates and dithiocarbamates.

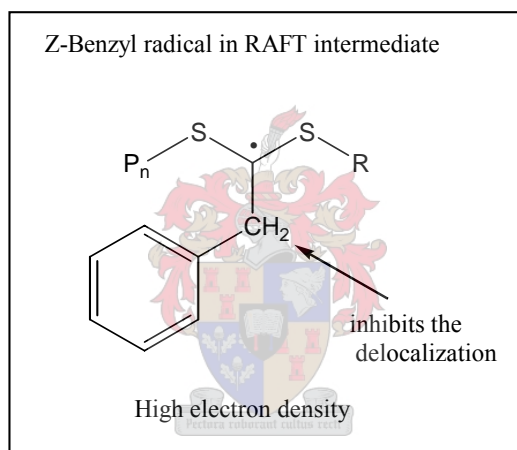
Thus, those compounds which present stabilizing effects on the intermediate radical will speed up the rate of addition of the propagating radical to the RAFT agent, and simultaneously lower the fragmentation rate of the leaving groups.

These same considerations should be taken into account with the substituents that are electron withdrawing or which are able to delocalise the lone pair as this should enhance the activity of these compounds. Thus, the efficiency of a RAFT agent should be potentially increased in the case where a Z substituent does not present a stabilizer effect on the intermediate radicals (see Schemes 2.11 and 2.12).



**Scheme 2.11 Stabilization of the intermediate radical by the phenyl Z group during the RAFT process through electron delocalization.**

In addition, Chiefari *et al.*<sup>57</sup> have demonstrated that when the Z group is taken from the following series: Ph; SCH<sub>2</sub>Ph; SMe; Me, the transfer coefficient is higher for the aromatic compounds.

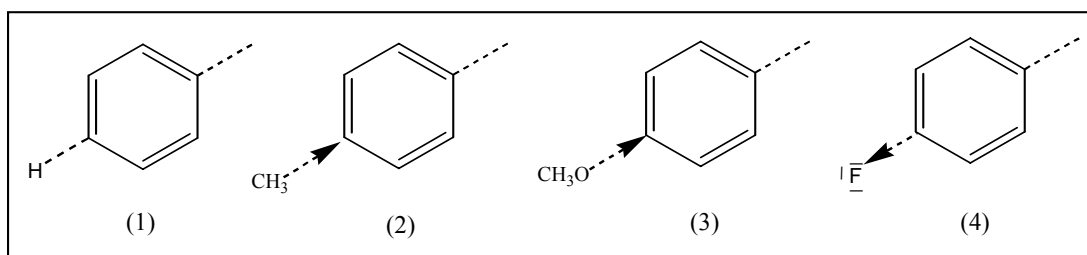


**Scheme 2.12 Intermediate radical in the benzyl group.**

By changing the Z group from a phenyl to a benzyl group, e.g. as reported by Coote *et al.*,<sup>66</sup> the radical in the RAFT intermediate is changed from being in a disulfur benzylic position to a less stable disulfur alkyl position (see Schemes 2.11 and 2.12). The destabilization along the phenyl group allows delocalisation of the unpaired electron into the aromatic ring, whereas the benzyl substituent inhibits this effect via the insulating CH<sub>2</sub> group. These electronic effects play an important role in providing a better rate of fragmentation.

In the present study, the author considers the effect that an aryl substituent group (C<sub>6</sub>H<sub>4</sub>R' taken as a Z group) has on the RAFT process. Related questions are: what is the effect of a para-substituent on the reactivity of a dithiobenzoate in RAFT mediated polymerisation? Does the substituent R', taken as hydrogen, electron donating or deactivating, significantly influence the addition or fragmentation in the RAFT process?

To answer these questions, several aryl groups were selected as Z groups (see Scheme 2.13): phenyl (1) with  $R' = H$ , 4-methylphenyl (2) ( $R' = CH_3$ ), 4-methoxyphenyl (3) ( $R' = OCH_3$ ) and 4-fluorophenyl (4) ( $R' = F$ ).



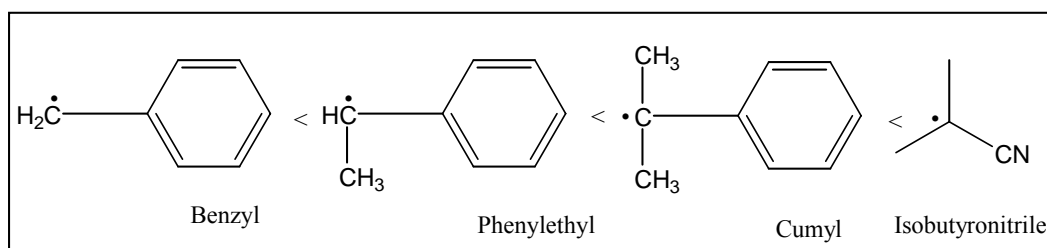
**Scheme 2.13 Phenyl Z group (1) and its derivatives: (2) 4-methylphenyl ( $C_7H_8$ ), (3) 4-methoxyphenyl ( $C_6H_5OCH_3$ ), (4) 4-fluorophenyl ( $C_6H_5F$ ).**

From electronic effects, one can expect that if the rate of addition in the RAFT process is dependant on the Z group, the order of decreasing reactivity across the series seen in Scheme 2.13 should be: 4-methoxyphenyl dithiobenzoate > 4-methylphenyl dithiobenzoate > phenyl dithiobenzoate > 4-fluorophenyl dithiobenzoate.

## 2.8 Effect of the radical leaving group ( $R\cdot$ )

The effect of R as leaving group on the fragmentation step occurring in the RAFT process is as crucially important as the Z group effect.<sup>67</sup> A high rate constant for fragmentation of the intermediate radicals (2) and (4) to polymeric thiocarbonylthio species (3) and (5) (Scheme 2.8) is achieved by selecting a R group which should behave as a good homolytic leaving group with respect to the propagating radical and it should have the ability to reinitiate polymerisation.

The homolytic leaving ability of a R group appears to increase with electronic factors, radical stability of the expelled radicals  $R\cdot$  and increasing steric bulk of the R group.<sup>67</sup> Thus, it was found that tertiary radicals  $R\cdot$  result in a larger transfer coefficient than primary or secondary radicals  $R\cdot$ , because there is a difference in stability of those radicals. Typical examples of different alkyl radicals are shown in Scheme 2.14.



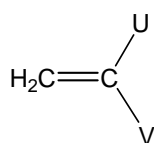
**Scheme 2.14 Examples of different alkyl radicals.**

The carbon that bears the unpaired electron is electron deficient, and thus electron-releasing alkyl groups attached to this carbon provide a stabilizing effect. The alkyl groups or electron rich groups, such as phenyl, that are attached to this carbon increase the stability of the radical formed.

Even if both the Z and R groups are important factors in the determination of the value of the transfer coefficient for a given alkyl dithioester, monomers also play an essential role during the polymerisation reactions. For example, it has been shown by Rizzardo et al.<sup>58</sup> that styrene polymerisation is efficient with dithiobenzoate CTAs, in which the Z group is Ph- and the R group is one of the following: -C(Me)<sub>2</sub>Ph, -C(Me)<sub>2</sub>CN, -C(Me)<sub>2</sub>CO<sub>2</sub>Alkyl, -C(Me)<sub>2</sub>CH<sub>2</sub>C(Me)<sub>3</sub>, -C(Me)<sub>3</sub>, -C(Me)HPh, -CH<sub>2</sub>Ph, -CH<sub>2</sub>CO<sub>2</sub>H. These CTAs are effective and give polymers with low polydispersities and good control of molar mass. Contrary, in MMA polymerisation, effectiveness decreases in the order where R is C(Me)<sub>2</sub>Ph > -C(Me)<sub>2</sub>CN > -C(Me)<sub>2</sub>CO<sub>2</sub>Alkyl > -C(Me)<sub>2</sub>CH<sub>2</sub>C(Me), -C(Me)<sub>3</sub> > -C(Me)HPh > -CH<sub>2</sub>Ph. In fact, in this series it is only the CTAs where R = -C(Me)<sub>2</sub>Ph or -C(Me)<sub>2</sub>CN that give polymers with low polydispersities and good control of molar mass. Therefore, the transfer coefficient is higher when styrene is used with alkyl dithioesters as RAFT agents and the transfer coefficient is lower for the same transfer agents in the presence of methyl methacrylate. It is for these reasons, amongst others, why in this work the R groups for styrene polymerisation were chosen from C(Me)<sub>2</sub>Ph, C(Me)<sub>2</sub>CN and C(Me)(CN)(CH<sub>2</sub>)CO<sub>2</sub>H.

## 2.9 Choice of monomers

Monomers are reactive compounds that are used as starting materials in the manufacture of useful and essential polymers. It is their chemical reactivities that make these monomers useful in polymer preparation. Examples of monomers are hydrocarbons, such as ethene or styrene. Styrene and ethene form polymers to make plastics like polystyrene and polyethylene. Therefore, the preparation of polymers with specific properties (mechanical properties, resistance to weathering and UV, resistance to moisture and chemicals, and film formation, for example) depends on the choice of monomer.<sup>58</sup> The RAFT process, as mentioned in Section 2.6.1 and Table 2.1, has the ability to polymerise any monomers susceptible to free-radical polymerisation. Such monomers are identified by the following structure presented in Scheme 2.15.<sup>58</sup>



**Scheme 2.15** Example of a monomer unit, where, for example U = H, alkyl, alkoxy groups and halogen; V = phenyl, COOR, OCOR, CN, CONH<sub>2</sub> and halogen (there are other possibilities).

## 2.9.1 Reasons for the selection of styrene as monomer in this study

Styrene monomer, or vinyl benzene, is a colourless liquid that reacts in a propagation reaction to form polystyrene. Moreover, styrene is the most common monomer used in different polymerisation systems,<sup>9,37,57</sup> such as: bulk,<sup>68</sup> solution, emulsion<sup>69,70</sup> and miniemulsion<sup>71</sup> because it has proved to be successful in the preparation of homopolymers and copolymers. Styrene used alone as monomer unit in a bulk polymerisation in the presence of a RAFT agent plays two important roles: the first is to initiate the polymerisation via the production of radicals, generated through the Mayo mechanism (see Section 4.3) and the second is to react with a radical to produce a propagating radical which is responsible for reinitiating the polymerisation (step (2) in the RAFT mechanism, see Section 2.6.2). Therefore, styrene, the most commonly studied monomer, will be used to investigate the reactivities of various selected RAFT agents.

## 2.10 Choice of initiators

Free radical initiators are molecules, which easily decompose into free radicals and serve as reactive intermediates in synthetic methodologies such as organic and polymer synthesis. There are several ways of generating radicals: thermally, photochemically or by high-energy radiation (electron beam or gamma-radiation).<sup>58</sup> Precautions should be taken when the initiating system is chosen such that there is no adverse interaction of the initiator or the initiating radicals with the transfer agent under the conditions of the experiment.<sup>58</sup> In other words, if radicals are thermally produced, the temperature required to produce them should not be unfavourable to the chain transfer agent used. Moreover, the initiator chosen should be soluble in the reaction medium or monomer mixture. Finally, a suitable choice of initiator is dependent on its half-life at the desired reaction temperature and its initiation ability relative to the monomer employed.

## 2.11 Choice of polymerisation techniques

Free radical polymerisation is a very common polymerisation process that can be carried out in many different media.

Four main polymerisation techniques are commonly used in order to prepare polymers by free radical polymerisation:

- Solution polymerisation
- Suspension or dispersion polymerisation
- Emulsion polymerisation

- Bulk polymerisation

### 2.11.1 Solution polymerisation

#### **Monomer + Initiator + Solvent**

Solution polymerisation is one of the preferred methods to use for chain-growth polymerisation. The solvent helps in heat transfer and reduces the rapid build-up of viscosity in the reaction mixture, and therefore normally eliminates the Trommsdorff effect (see Section 2.12).

The polymer may or may not be soluble in the solvent; in the latter case (e.g. styrene + methanol) the polymer precipitates from solution. However, chain-transfer to solvent can be a problem and can lead to a reduction in the average value of the viscosity. In addition, an additional (expensive) step may be required to remove the solvent at the end of the reaction.

### 2.11.2 Suspension or dispersion polymerisation

#### **Monomer + Initiator + Medium (usually water) + Stabilizer**

In this process the monomer and the initiator are both insoluble in the reaction medium (water). Thus, the monomer is dispersed as droplets (as in emulsion polymerisation), but the initiator is now present in these droplets (and not in the aqueous phase). The role of the stabilizer is purely to stabilize these droplets. There are no micelles in the aqueous phase.

This process can be used to produce particles in the size range 1 to 5  $\mu\text{m}$ . Compared to an actual bulk polymerisation, heat transfer problems are now greatly diminished, because the aqueous phase can now conduct away most of the heat generated.

### 2.11.3 Emulsion polymerisation

#### **Monomer + Initiator + Medium (usually water) + Surfactant (usually anionic e.g. sodium dodecyl sulphate)**

In emulsion polymerisation, monomer has only a very limited solubility in the medium (e.g. styrene in water). Most of the monomer is initially in dispersed droplets, hence the term “emulsion” polymerisation. One role of the (anionic) surfactant is to help stabilize these droplets, by absorbing at the droplet/water interface. However, some of the monomer is present in the water phase. Autoacceleration may (in specific cases) still occur and the isolation of the polymer can be difficult and expensive.

## 2.11.4 Bulk polymerisation

### Monomer + Initiator

Compared to the previously mentioned polymerisation techniques (Sections 2.11.1 through 2.11.3), bulk polymerisation seems to be the simplest one but it does however have many problems in up scaling. In general, bulk polymerisation is not restricted by the presence or the absence of any additional initiator compared to other techniques when, for example, styrene is used as a monomer. For example, in this research, it requires only the use of monomer and a RAFT agent.

Moreover, the risk of contamination of the product formed during bulk polymerisation can be easily minimized by controlling the parameters used during the reaction (monomer and initiator). In this homogeneous system, the polymer should be soluble in the monomer in such a way that the concentration of monomer decreases continuously and the viscosity increases continuously with increasing conversion (example: polystyrene). At very high temperatures, heat and bubble transfer will give problems, and hence the Trommsdorff effect will be strongly present.

Of the four polymerisation systems (Sections 2.11.1 through 2.11.4), it is the bulk polymerisation technique that was used in the present study, to determine the efficacy of the novel RAFT agents, synthesized as described in Chapter 3.



## 2.12 Trommsdorff effect

The "gel" or Trommsdorff effect comprises a spectacular increase in conversion rates during the latter stages of free radical polymerisation, when the increasing viscosity limits the rate of termination because of diffusional limitations. In fact, the free radicals cannot find other radicals to terminate with as easily as they can find other monomers to propagate with.

## 2.13 Inhibition in the RAFT process

Inhibition can be defined as a period in which there is no polymerisation activity. This is observed at the early stages of polymerisation. Long inhibition periods have been observed during RAFT mediated polymerisation. Several attempts have been made to explain inhibition phenomena during RAFT mediated polymerisation. Perrier *et al.*<sup>72,73</sup> have studied the origin of inhibition effects in the polymerisation of methyl acrylate at 60°C by varying the initial RAFT agent concentration (1-phenylethyl dithiobenzoate and 2-(2-cyanopropyl) dithiobenzoate). They found that a cyanoisopropyl leaving group induces less inhibition than a phenylethyl leaving group. Thus, they suggested that the slow fragmentation of the intermediate RAFT radical (species **2** in Scheme 2.8)



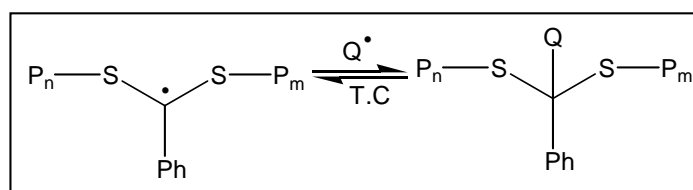
in the pre-equilibrium could explain the inhibition rather than the reinitiation ability of the leaving group.

However, Moad *et al.*<sup>74</sup> observed an inhibition period lasting up to 1 h for the styrene polymerisation mediated by 1-methyl-1-phenylethyl benzenecarbodithioate. This long period has been attributed to the slow initiation of styrene by the cumyl radical.

McLeary *et al.*<sup>75</sup> have investigated the concentration of several characteristic species involved in the first steps of the RAFT polymerisation of styrene in the presence RAFT agent 1-phenylethyl dithiobenzoate and 2-(2-cyanopropyl) dithiobenzoate at 70°C and 84°C. They demonstrated that the RAFT process starts with an initialisation period, which was defined as the period in which the starting RAFT agent is consumed. The critical process in the initialisation of the RAFT controlled polymerisation was found to be the addition of a single monomer unit to the growing chains before the addition of another monomer unit. By implication, the rate-determining step during the initialisation period is the propagation of the initial RAFT leaving groups.

## 2.14 Rate retardation in the RAFT process

The phenomenon of retardation in the RAFT process has given rise to numerous discussions. Some research groups have claimed that the retardation observed in this technique is due to the slow fragmentation of intermediate radicals. Thus, Davis *et al.*<sup>76</sup> assumed that the intermediate radical is stable enough to cause no termination with  $\mathbf{P}\cdot$  (no cross-termination), whereas on the other hand, Monteiro *et al.*<sup>77</sup> assumed that the intermediate radical undergoes cross-termination between propagating and intermediate radicals. See Scheme 2.16.<sup>67</sup>



**Scheme 2.16 Termination reactions involving the intermediate radical**

(T.C is termination by combination and  $\mathbf{Q}\cdot$  is a radical).

In both cases, a computer simulation was made, but the difference between both the  $k_{fr}$  values used by the two groups was 6 through 7 orders of magnitude, i.e.  $k_{fr}$ :  $10^{-2} \text{ s}^{-1}$  from the first group and  $k_{fr}$ :  $10^5 \text{ s}^{-1}$  for the second.<sup>14</sup> The computer simulations brought no solution to this controversy even though the rate data for the ratio styrene/dithiobenzoate system used by the two respective groups were more or less similar. However, recently Calitz *et al.*<sup>78</sup> presented ESR and NMR data on the aforementioned phenomenon; they obtained similar results to those given by Monteiro *et al.*<sup>77</sup>

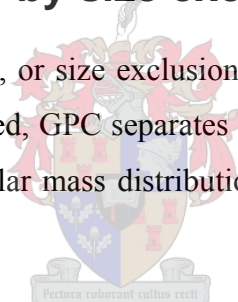


Despite numerous other studies done by other researchers to clarify this phenomenon of retardation that is surrounded by controversy, no satisfactory answer has yet been found to the debates highlighted above. Therefore, it is hoped that the current research might give us more information about this phenomenon of retardation that remains present in the RAFT process. Taking into account studies that have led to the process of retardation in the RAFT technique (Sections 2.7 and 2.8), several possible origins have been identified as sources of this retardation:<sup>58</sup>

- Z group as radical agent stabilizer for the intermediate (2)
- Slow fragmentation of the intermediate radical (2) during the polymerisation
- Inability of R group to reinitiate the polymerisation
- Slow fragmentation of the intermediate radical obtained from the polymeric RAFT agent (4)
- One of the preferences of the ejected radical ( $R\cdot$ ) might be to add to the RAFT agent rather than to monomer.

## 2.15 Analysis of polymers by size exclusion chromatography

Gel permeation chromatography (GPC), or size exclusion chromatography (SEC), is an important analytical technique for polymers. Indeed, GPC separates polymers by size, and therefore provides an indirect measure of the polymer molar mass distribution (MMD). Molar mass is related to the hydrodynamic volume.

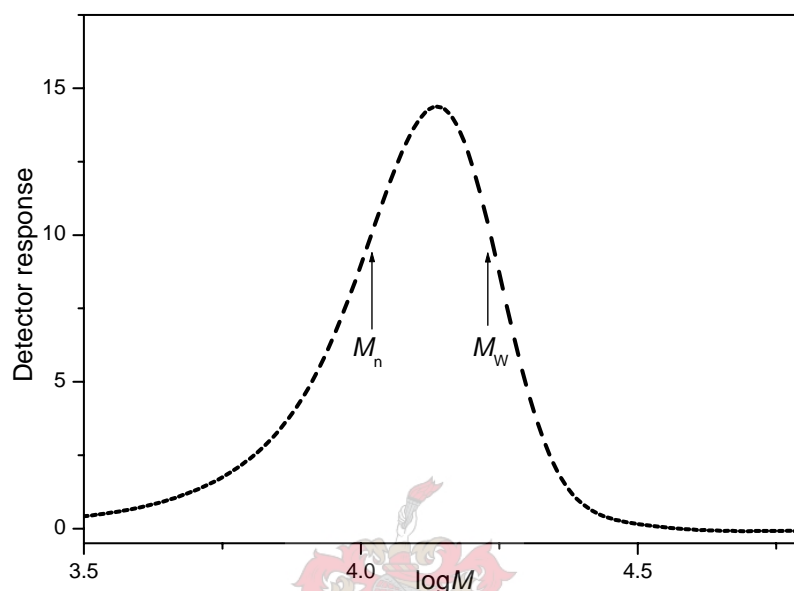


### 2.15.1 Obtaining a calibration curve

In GPC, a dilute polymer solution is injected into a solvent stream, which then flows through a series of columns packed with porous gel beads. Smaller molecules pass into and out of the pores in the beads while larger molecules are excluded. The elution volume varies according to the size of the swollen molecules (hydrodynamic volume). The fractionation occurs therefore, with the largest molecules eluting first (smallest elution volume). The hydrodynamic volume of an eluting polymer molecule varies exponentially with eluting volume. To obtain molar mass data and convert the GPC chromatogram into a molar mass distribution, the relation between molar mass and elution time (based on hydrodynamic volume) is obtained from a series of polymer standards of known molar masses.

### 2.15.2 Obtaining molar mass averages

The most common and convenient way to characterize a distribution of molar masses making up a polymer sample is by using molar mass averages, such as number average molar mass ( $M_n$ ) and weight average molar mass ( $M_w$ ), as shown in the following for a typical polymer chromatogram (Figure 2.2).



**Figure 2.2** A typical polydisperse polymer molar mass distribution showing the approximate locations of  $M_n$  and  $M_w$ .

The ratio  $M_w/M_n$  is known as the polydispersity or polydispersity index (PDI). The PDI is often used as a measure of the width of the molar mass distribution. Polymers that are monodisperse (that is all chains have the same molar mass) have a PDI of 1.

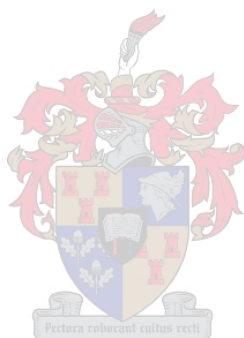
### 2.15.3 Obtaining normalized molar mass distributions

As mentioned, the PDI is often used as a measure of the breadth of the molar mass distribution. However it is often a poor substitute when compared to a graphical representation of the complete molar mass distribution curve, especially if not monomodal or skewed distribution.

## 2.16 Conclusions

The twentieth century had seen the improvement of old preparation methods and the discovery of new techniques for the preparation of complex polymers. These polymeric techniques include SFRP, ATRP and RAFT. Moreover, each technique has the ability to yield polymers with specific functionalities. Therefore, the challenge today is to determine how these future possible industrial technologies can be materialized in order to benefit society.

It should be noted that the youngest technology, the RAFT process, is only six years old and possesses almost the same advantages as its predecessors (SFRP, ATRP). This can explain why this new technology is currently regarded as one of the most promising techniques. RAFT, based on a simple structure (see Chapter 1), is a route worth using for the synthesis of new materials. Thus studies on the RAFT mechanism and RAFT agent synthesis are worth conducting for the improvement of the process efficiency, which relies directly on the choice of R and Z groups as highlighted here in Sections 2.7 and 2.8.



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*“Imagination is more important than knowledge. Knowledge is limited. Imagination encircles the world”*

*Albert Einstein.*

## *CHAPTER 3: Synthesis and characterization of RAFT agents*

This chapter describes the synthesis of RAFT agents via two different routes. In both cases Grignard reagents were used to prepare dithiocarboxylic acids. Then, as a first option, oxidation with dimethyl sulphoxide (DMSO) to diphenyldithioperoxyanhydride and its derivatives was carried out. The formation of dithioesters is possible when the coupled compounds (disulfides) are allowed to react with initiators such as 2,2'-azobisisobutyronitrile (AIBN) or 4,4'-azobis(4-cyanopentanoic acid). As a second option, the addition of olefins, specifically  $\alpha$ -methylstyrene, to dithioacids was used to yield dithioesters functionalised with a cumyl leaving group.

The synthesized RAFT agents were identified by fourier-transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR) and ultraviolet spectroscopy (UV).

### 3.1 Introduction

In Chapter 2 (Sections 2.6.6.1 through 2.6.6.5) a number of classes of RAFT agents were described. Among these, the dithioesters, especially the dithiobenzoates, are one of the most effective because of their high transfer coefficients.<sup>1</sup>

The dithiobenzoates synthesized as described in Chapter 3 are thiocarbonylthio compounds, where the Z groups are either aromatic structures with electron donating or withdrawing substituents (Section 2.7) and R groups are chosen from: C(Me)<sub>2</sub>Ph, -C(Me)<sub>2</sub>CN and (CN)(CH)<sub>2</sub>CO<sub>2</sub>H (Section 2.8).

The synthesis of efficient RAFT agents has received attention from many polymer chemists, and as a direct consequence of this there are now several different transfer agents available with different reactivities.<sup>2,3</sup> Thus, in the literature review of the synthesis of RAFT agents several pathways will be described (see Section 3.3).

### 3.2 Thiocarbonylthio moieties

Thiocarbonylthio moieties are functionalities which react readily with a large variety of reagents (nucleophiles, electrophiles and radicals) because of their weak carbon-sulfur double bond (C=S). The efficiency of dithioesters to mediate the preparation of homopolymers, gradient or block copolymers with controlled molar masses and with very low polydispersities can be attributed to the choice of Z and R groups,<sup>2,3</sup> in combination with the monomer and the polymerisation system used. For example, in homogeneous polymerisation the RAFT agent and the monomer should be soluble if one wishes to avoid slow polymerisation.<sup>1</sup>

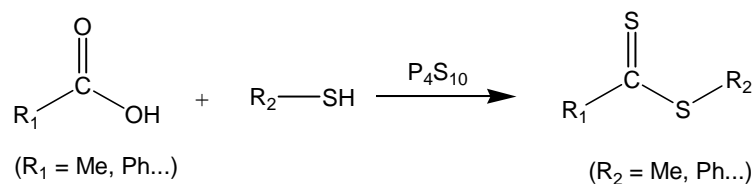
### 3.3 Synthesis of dithiocarboxylic acids and esters

The literature on dithiocarboxylic acids<sup>1,4,5</sup> and esters<sup>6,7</sup> has greatly expanded over the past few years. Among the huge variety of methods used for synthesizing dithioesters, the technique involving the intermediacy of a dithiocarboxylic acid seems to be the best one.<sup>4,7</sup> Because of its wide application in organic synthesis, this technique has been thoroughly examined according to the necessity and the availability of reagents and several methods for the preparation of dithiocarboxylic acids and esters have been fully developed such as:

1. Synthesis of dithiocarboxylic acids via organometallic reagents (Grignard reagents)<sup>4</sup> and exchange of bis(thiocarbonyl)disulfide with azo compounds.<sup>8,9</sup>

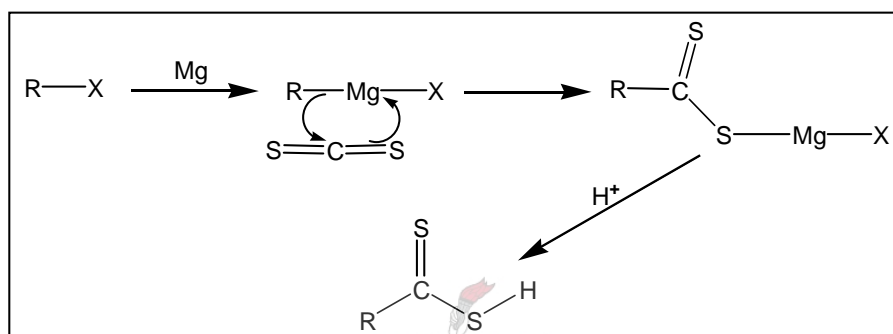


2. Preparation of dithioesters from the reaction of thiols with carboxylic acids in the presence of  $P_4S_{10}$ <sup>10,11</sup> (Scheme 3.1).



**Scheme 3.1**  $P_4S_{10}$  as versatile reagent for the synthesis of dithioesters.

3. The synthesis of dithiocarboxylic acids involving nucleophilic attack on carbon disulfide,<sup>4</sup> e.g. by a Grignard compound (See Scheme 3.2).



**Scheme 3.2** Benzenecarbodithioic acid prepared via a Grignard reagent.

Of these numerous techniques, all of which have proven to be successful for the synthesis of dithiocarboxylic acids, it is the first one that captured the author's attention for the following reasons:

- It is a relatively easy reaction
- It is cost-effective, because only a few reagents are required and the product can be oxidized to disulfides.

### 3.3.1 Grignard reagents

Since 1901, Grignard chemistry is an important and versatile route for building up the carbon skeleton of new organic compounds.<sup>12</sup> Grignard compounds are frequently used in the synthesis of hydrocarbons, alcohols, carboxylic acids, and other compounds.<sup>13,14</sup>

Air and moisture must however be excluded from the reaction vessel since Grignard reagents are very reactive.<sup>15-17</sup> Owing to this sensitivity and instability,<sup>15-17</sup> once Grignard reagents have been prepared they are often used directly, without first being isolated. The scope of the applications of organometallic reagents to organic synthesis strongly depends on the availability of functionalised carbon groups, such as C=O, S=C=S, S=O, C=N, N=O, and C=N, attached to the metal. A Grignard

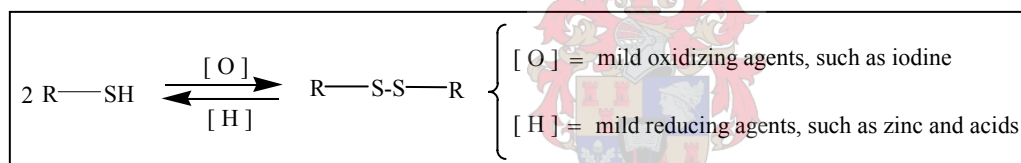
reagent has the general formula RMgX (Scheme 3.2). It consists of X as a halogen, a metal (Mg) and R as an alkyl or aryl group. The metal is positively polarized and the alkyl group reacts like a carbanion, in such way that the “carbanionic” R group attacks the electron-poor carbonyl carbon. For example, the reaction with carbon disulfide proceeds as shown in Scheme 3.2.

This is an effective pathway for making dithiocarboxylic acids by the Grignard method. In general, the Grignard reagent might be considered as a nucleophile because of the attraction between the “negative charge” of the carbon atom in the Grignard reagent and the “positive charge” of the carbon in the carbonyl compound.

### 3.4 Diphenyldithioperoxyanhydride and its derivatives

The preparation of diphenyldithioperoxyanhydride can be realized by oxidative coupling of dithioacids or their salts.

Oxidation of thiols and other sulfur compounds change the oxidation state of sulfur. A typical representation of sulfur oxidation is given in the following example, Scheme 3.3. The mild oxidation converts thiols to disulfides.



Scheme 3.3 Representation of sulfur oxidation.

Diphenyldithioperoxyanhydride and its derivatives prepared in the present study were oxidized by dimethyl sulfoxide at ambient conditions from benzenecarbodithioic acid synthesized via the Grignard reaction.

## 3.5 Experimental

### 3.5.1 Materials

The following reagents were used to prepare thirteen RAFT agents:

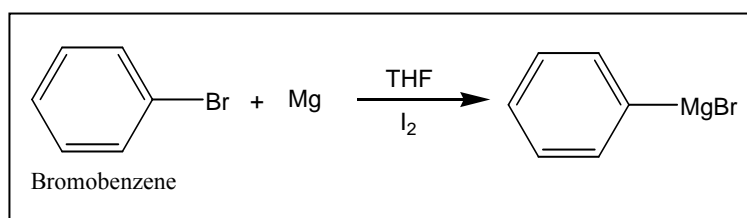
$\alpha$ -methylstyrene [98-83-9] 99% (Acros); 4,4'-azobis (4-cyanopentanoic acid) [2638-94-0] 75% (Sigma-Aldrich); 2,2'-azobisisobutyronitrile [78-67-1]; 4-bromoanisole [104-92-7] 99% (Sigma-Aldrich); 1-bromo-4-fluorobenzene [460-00-4] 99% (Sigma-Aldrich); 4-bromotoluene [106-38-7] 98% (Sigma-Aldrich); diethyl ether [60-29-7] 99.5% (Merck); HCl [7647-010] 32% (ACE); bromobenzene [108-86-1] 99% (Sigma-Aldrich); carbon disulfide (CS<sub>2</sub>) [75-15-10] 99.9%

(Aldrich); carbon tetrachloride [56-23-5] ( $\text{CCl}_4$ ) 99,9% (Aldrich), ethyl acetate [141-78-6] CP; pentane [109-66-01] CP; heptane [142-82-5] CP (ACE); THF [109-99-9], distilled from  $\text{LiAlH}_4$  [16853-85-3]; iodine [7553-56-2] 99% (Aldrich) and magnesium sulphate 98% [7439-95-4] (Aldrich).

## 3.6 The synthesis of benzenecarbodithioic acid and its derivatives

### 3.6.1 Synthesis of benzenecarbodithioic acid

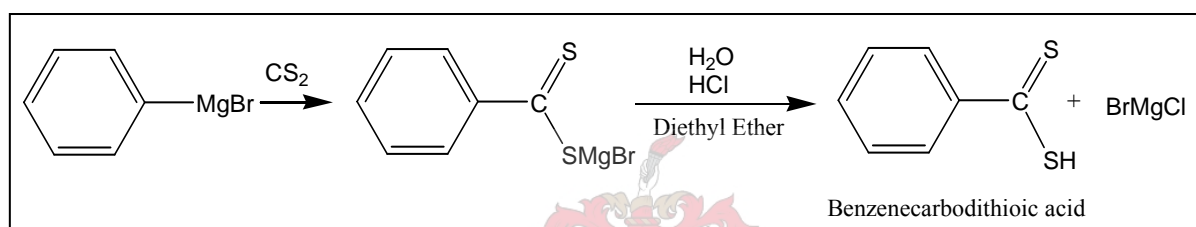
Magnesium turnings (1g, 0.04 mol), a crystal of iodine as a catalyst<sup>12</sup> and dry, distilled tetrahydrofuran (THF) (~5 to 10 mL) were placed in a 250 mL three-necked flask, fitted with two dripping funnels, containing (6.28g, 0.04 mol) bromobenzene in one and THF (30 mL) in the other, a condenser, and a magnetic stirrer, with calcium chloride guard tubes protecting the two dropping funnels. A few drops of bromobenzene were added from the dripping funnel into the three-necked flask. The content of the reaction flask was then heated gently, with stirring, until the reaction started (~5 to 20 min). The reaction starts when the yellow colour of iodine disappears and a clear white solution is formed. This step is most essential to the successful preparation of the Grignard reagent, thus care should be taken to avoid the destruction of the Grignard reagent. For this reason a cooling bath is prepared, ready to be used to reduce any excessive heat that may develop. A few drops of THF and the remainder of the total volume of bromobenzene were added from the dripping funnels, dropwise, to the mixture (white-clear solution) at such a rate that the reaction continued but that the temperature remained controlled (35°C to 40°C). The final reaction mixture was allowed to react (in the cooling bath) with stirring, for a period of 40 to 50 min, followed by continued stirring at room temperature for 10 to 15 min (to verify that the heat has ceased in the reaction flask). The resultant mixture containing the Grignard reagent was grey-brown or grey-green colour. Scheme 3.4 summarizes the preparation of a Grignard reagent.



Scheme 3.4 Preparation of the Grignard reagent.

The empty dripping funnel, which contained the bromobenzene, was refilled with 3.05 g (0.04 mol) of anhydrous carbon disulfide and the reaction mixture was again cooled in an ice bath before

adding the carbon disulfide. Then, carbon disulfide was added dropwise to the obtained Grignard agent, over a period of 15 to 25 min, while maintaining the reaction temperature at 35°C to 40°C. The addition of a few drops of THF also reduced the heat generated by the addition of the carbon disulfide. When the reaction was complete, the new Grignard reagent was gently neutralized by slowly adding 250 mL of cold water into a separating funnel into which the synthesized product had been poured. The unreacted magnesium was either filtered or neutralized during the formation of the dithioacid with 3 x 100 mL of diethyl ether and 33% fuming hydrochloric acid (0.2N, 200 mL). The extraction was completed when the colour of the solution turned purple. The combined organic extracts were washed three times with water and dried over anhydrous magnesium sulphate (MgSO<sub>4</sub>). The dried organic fractions were combined in a 250 mL round-bottom flask and the solvent (ether) removed by rotary evaporation (800 to 240 mbar, 40°C). Scheme 3.5 summarizes the preparation of benzenecarbodithioic acid.

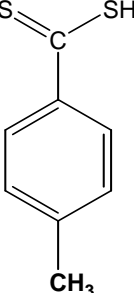
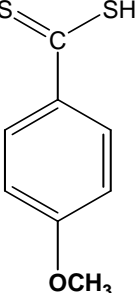
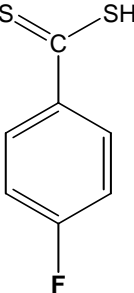


Scheme 3.5 Preparation of benzenecarbodithioic acid.

### 3.6.2 Synthesis of substituted derivatives of benzenecarbodithioic acid

Three substituted derivatives of benzenecarbodithioic acid (shown in Table 3.1) were prepared by the substitution of bromobenzene, by 4-bromotoluene, 4-bromoanisole and 1-bromo-4-fluorobenzene respectively, and using the same reaction procedure as described in Section 3.6.1. These syntheses differed from one to another in their respective “speeds” of colour formation. 4-methyl- and 4-methoxybenzenecarbodithioic acids were facile to prepare and their respective starting materials, namely 4-bromotoluene and 4-bromoanisole, required little heating time before the reactions commenced, whereas bromobenzene and 1-bromo-4-fluorobenzene needed more time than the former two. Moreover, it was found that the electron-donating derivatives such as 4-methylbenzenecarbodithioic acid and 4-methoxybenzenecarbodithioic acid were crystalline (pink-purple and orange, respectively).

**Table 3.1: Substituted derivatives of benzenecarbodithioic acid synthesized**

| 4-methylbenzenecarbodithioic acid   | 4-methoxybenzenecarbodithioic acid  | 4-fluorobenzenecarbodithioic acid   |
|---|---|---|
|  |  |  |

The following observations were made:

- 4-methylphenylmagnesium bromide was easily formed, and was identified by its pink colour.
- The same observation was made for the 4-methoxyphenylmagnesium bromide, which was identified by its orange colour.
- The 4-fluorobenzenecarbodithioic acid (pink compound) was an interesting compound because of the presence of fluorine in the para-substitution of the benzene ring, which permitted the classification of it as an electron withdrawing compound.<sup>20</sup>

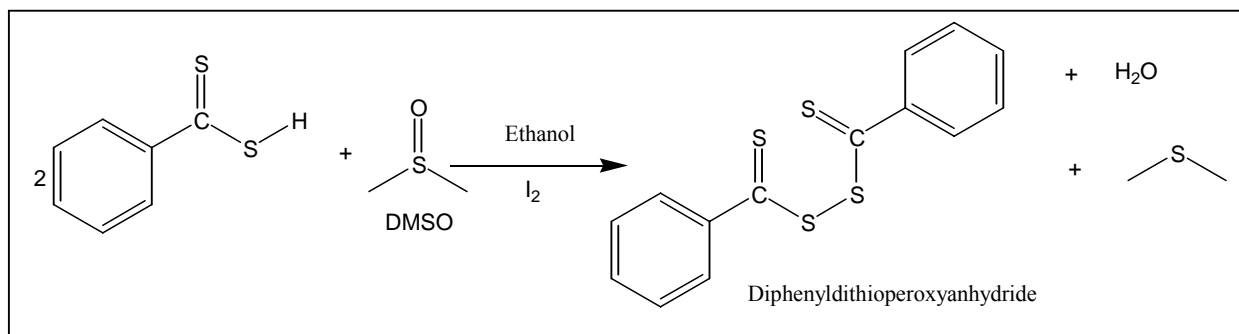
### 3.7 Diphenyldithioperoxyanhydride and its derivatives

Benzenecarbodithioic acid is an unstable compound and was therefore used immediately, in order to prevent extensive product loss. Thus, for the preparation of disulfides, the benzenecarbodithioic acid and derivatives were used directly after removal of the solvent from the reaction flasks. The preparation of diphenyldithioperoxyanhydride and its derivatives was possible using the method of *Le et al.*<sup>1</sup> The reaction of dimethyl sulfoxide and dithioacid was used to prepare the disulfides. These compounds are lovely crystals, distinguishable by their respective colours. The thioanisole dimer crystals are orange and the benzene dimer crystals are pink.

#### 3.7.1 Diphenyldithioperoxyanhydride

The preparation of diphenyldithioperoxyanhydride was carried out by the reaction of DMSO with benzenecarbodithioic acid (Scheme 3.6). A 250 mL round-bottom flask containing 6.17g (0.04 mol)

of the dithioacid previously prepared (Section 3.6.1) was charged with 6.25g (0.08 mol) of DMSO, and a crystal of iodine as catalytic reagent, in a medium of absolute ethanol (100 mL). The resulting mixture was stirred at room temperature for 40 to 50 min, using a magnetic stirrer. To speed up the crystallization, the reaction was stopped and the flask was closed hermetically with a stopper (surrounded with parafilm) and placed in a refrigerator overnight. The reaction was complete upon the formation of pink crystals. These crystals were washed with 200 mL of cold ethanol, filtered and dried for 10 to 24 hours. The yield was 10.42 g (0.034 mol) of the product (85%).



**Scheme 3.6 Preparation of diphenyldithioperoxyanhydride.**

The compound was identified by  $^1\text{H}$  NMR, FT-IR and UV. Their respective spectra are shown in the Appendix (Figures 19 through 21 and Table 7).

$^1\text{H}$  NMR spectrum: ( $\text{CDCl}_3$ )  $\delta$  (ppm): 8.09 (d, 2H, *o*-ArH); 7.62 (t, 2H, *m*-ArH); 7.44 (t, 1H, *p*-Ar - H).

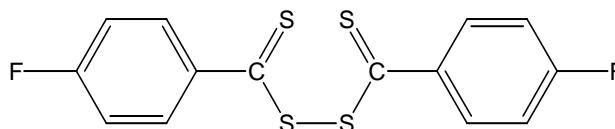
FT-IR (KBr disc.  $\text{cm}^{-1}$ ) 1428 (C=C aromatic); 1038 (C=S); 629 (C-S stretching); 565 (S-S).

UV(C=S): ( $n \rightarrow \pi^*$ ;  $\lambda = 525$  nm) and ( $\pi \rightarrow \pi^*$ ;  $\lambda = 282$  nm).

Chloroform-d was used for  $^1\text{H}$ -NMR and dichloromethane for UV analyses.

### 3.7.2 Bis(4-fluorophenyl)dithioperoxyanhydride

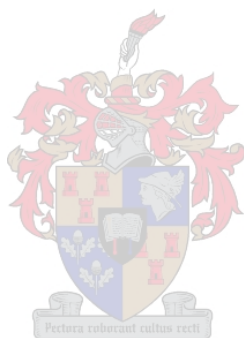
An attempt to prepare bis(4-fluorophenyl)dithioperoxyanhydride (Scheme 3.7) by the method of *Le et al.*<sup>1</sup> was discontinued as NMR results were inconclusive.



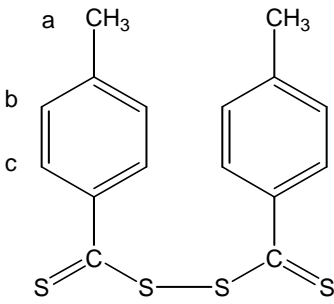
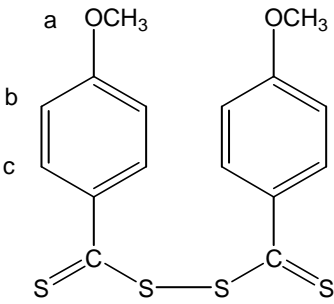
**Scheme 3.7 Structure of bis(4-fluorophenyl)dithioperoxyanhydride**

### 3.7.3 Bis(4-methylphenyl)dithioperoxyanhydride and bis(4-methoxyphenyl)dithioperoxyanhydride

The synthetic procedure depicted in Section 3.7.1 (Scheme 3.6) was extended to include the synthesis of bis(4-methylphenyl)dithioperoxyanhydride (10.70 g, 0.032 mol (80% yield)) and bis(4-methoxyphenyl)dithioperoxyanhydride (13.19 g, 0.036 mol (90% yield)). These compounds were identified by  $^1\text{H}$  NMR, FT-IR and UV. See Table 3.2.



**Table 3.2: <sup>1</sup>H NMR, FT-IR and UV analyses of bis(4-methylphenyl)dithioperoxyanhydride and bis(4-methoxyphenyl)dithioperoxyanhydride**

| bis(4-methylphenyl)dithioperoxyanhydride (1)                                      |            | bis(4-methoxyphenyl)dithioperoxyanhydride (2)                                      |            |     |
|---|------------|--|------------|-----|
|  |            |  |            |     |
| (1)   | C=C        | C=S  | C-S        | S-S |
| IR (cm <sup>-1</sup> )  | 1587       | 1051   | 561        | 479 |
| <sup>1</sup> H-NMR  | a          | b  | c          |     |
| δ (ppm)   | 2.39       | 7.27   | 8.09       |     |
| UV (nm)   | A (n → π*) |  | B (π → π*) |     |
| (C=S)   | 523        | 323  |            |     |
| (2)   | C=C        | C-O  | C=S        | C-S |
| IR (cm <sup>-1</sup> )  | 1588       | 1239   | 1166       | 591 |
| <sup>1</sup> H-NMR  | a          | b  | c          |     |
| δ (ppm)   | 3.09       | 6.48   | 8.17       |     |
| UV (nm)   | A (n → π*) |  | B (π → π*) |     |
| (C=S)   | 518        | 353  |            |     |

Benzene-d<sub>6</sub> was used for <sup>1</sup>H-NMR and dichloromethane for UV analyses.

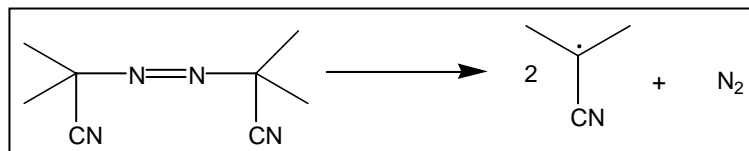
The details of the <sup>1</sup>H NMR, FT-IR and UV analyses are presented in the Appendix (Figures 22 through 24 and Table 8, for compound (1), and Figures 25 through 27 and Table 9, for compound (2)).

### 3.8 1-cyano-1-methylethyl benzenecarbodithioate and its derivatives

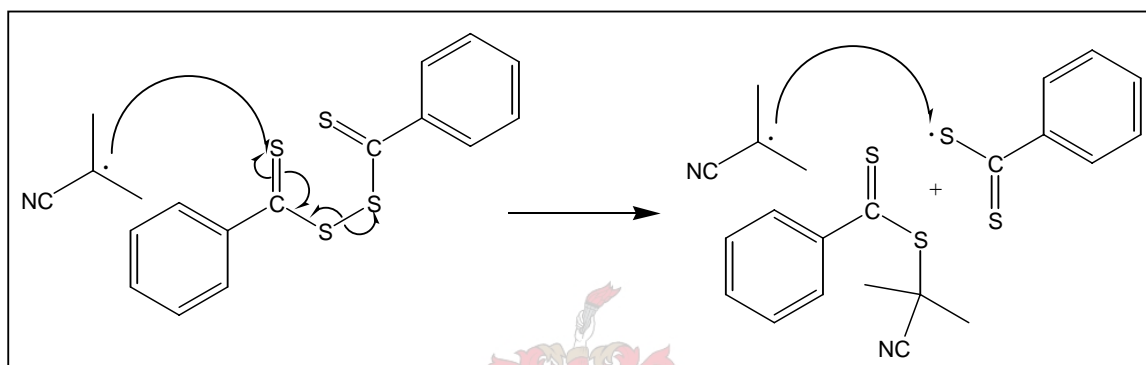
1-cyano-1-methylethyl benzenecarbodithioate, 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate and 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate rely on the generation and



the combination of free radicals under thermal homolysis (Scheme 3.8).<sup>9,21</sup> Complete reaction is only assured by the controlled generation of further radicals, using an initiation sequence such as the addition of small quantities of 2,2'-azobisisobutyronitrile. A typical example of the generation of the cyanoisopropyl radical is given in Schemes 3.8 and 3.9.



**Scheme 3.8 Decomposition of AIBN.**



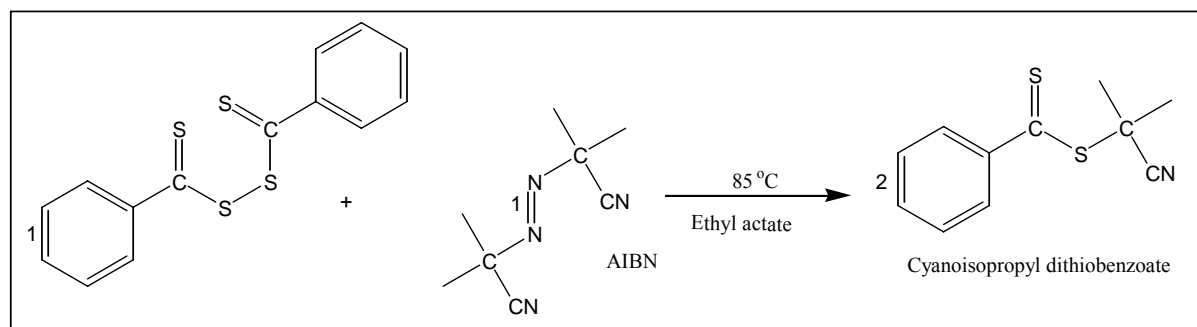
**Scheme 3.9 Mechanism of radical attack on disulfides.**

The addition of thermal initiator all in one portion is not the experimental strategy of choice since the ensuing flood of radicals can combine and disproportionate in a counter-productive way; slow addition, in solution, over a period of time is more effective.<sup>22</sup> Thus, the appropriate choice of initiator is generally determined by the reaction temperature and hence by the appropriate half-life of the decomposition. Moreover, knowing that the initiator decomposition rate is a first-order exponential decay and that the length of time required to reach a higher conversion thus increases exponentially, the reaction conditions chosen for this experiment were subsequently: temperature 85°C, ethyl acetate as solvent and 18 or 24 hours reaction time. A typical example of a reaction is described below (Section 3.8.1).

### 3.8.1 1-cyano-1-methylethyl benzenecarbodithioate

The reaction set up comprised a 250 mL three-necked round-bottom flask fitted with a reflux condenser, a stopper and a septum. The diphenyldithioperoxyanhydride (3.37 g, 0.011 mol) prepared as described (Section 3.8.1), and 3.37 g (0.02 mol) of AIBN were dissolved in ethyl acetate (100 mL). As the reaction had to be conducted in the absence of oxygen, the reaction mixture was refluxed under nitrogen gas (N<sub>2</sub>) while stirring, using a magnetic stirrer. Purging and

stirring the mixture continued overnight at 85°C. The next day, the reaction was stopped and cooled to room temperature. Then the mixture was transferred into a round-bottom flask (250 mL). Ethyl acetate was removed under vacuum. The resulting product was dissolved in a small volume of dichloromethane and subjected to column chromatography on silica gel, using pentane: heptane: ethyl acetate (1/1/2) as eluent. Removal of the eluent afforded a crude product of a red oil: 1-cyano-1-methylethyl benzenecarbodithioate<sup>23</sup> (3.41 g, 0.0154 mol (70% yield)), see Scheme 3.10. Details of the analyses are given in the Appendix (Figures 1 through 3 and Table 1).



**Scheme 3.10 1-cyano-1-methylethyl benzenecarbodithioate formation.**

<sup>1</sup>H NMR spectrum: (CDCl<sub>3</sub>) δ (ppm): 7.91 (d, 2H, *o*-ArH); 7.27 (d, 2H, *m*-ArH); 2.39 (s, 3H, *p*-Ar-CH<sub>3</sub>).

FT-IR (KBr disc. (cm<sup>-1</sup>)) 2229 (CN); 1593 (C=C aromatic); 1040 (C=S); 1442 (C-(CH<sub>3</sub>)<sub>2</sub>); 605 (C-S).

UV(C=S): (n → π\*; λ = 513 nm) and (π → π\*; λ = 304 nm).

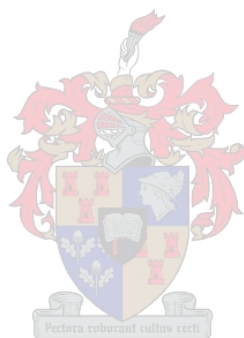
Chloroform-d was used for <sup>1</sup>H-NMR and dichloromethane for UV analyses.

### 3.8.2 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate and 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate

The following two RAFT agents were synthesized in a similar way to the 1-cyano-1-methylethyl benzenecarbodithioate (see Section 3.8.1), the only difference being that ethyl acetate and toluene were used as solvent for the reaction in the ratio of 100/50 mL. The reactions of bis(4-methylphenyl) dithioperoxyanhydride or bis(4-ethoxyphenyl) dithioperoxyanhydride with AIBN, as in the previous case, led to 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate and 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate. Yields were 3.88 g (0.0165 mol (75% yield)) and 4.42 g (0.0176 mol (80%)) respectively. It is recommended that the 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate and 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate be purified directly after their preparation because they crystallize

rapidly and they are not readily soluble, thus purifying them by column chromatography is not too easy.

These chain transfer reagents were identified by  $^1\text{H}$  NMR, FT-IR and UV. The results are reported in Table 3.3 below and in the Appendix (Figures 4 through 6 and Table 2 for the compound **(1)**, and Figures 7 through 9 and Table 3 for the compound **(2)**).



**Table 3.3: <sup>1</sup>H NMR, FT-IR and UV characterization of 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate and 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate**

| 1-cyano-1-methylethyl 4-methylbenzene-carbodithioate (1) |                       |      | 1-cyano-1-methylethyl 4-methoxybenzene-carbodithioate (2) |                 |     |
|--|-----------------------|------|---|-----------------|-----|
|  |                       |      |   |                 |     |
| (1)  | CN                    | C=C  | C=S   | CH <sub>3</sub> | C-S |
| IR (cm <sup>-1</sup> )                                   | 2231                  | 1598 | 1040  | 1446            | 569 |
| <sup>1</sup> H-NMR                                       | a                     | b    | c   | d               |     |
| δ (ppm)  | 1.92                  | 2.39 | 7.91  | 7.24            |     |
| UV (nm)  | A (n → π*) B (π → π*) |      |   |                 |     |
| (C=S)  | 513                   | 314  |   |                 |     |
| (2)  | CN                    | C=C  | C=S   | CH <sub>3</sub> | C-S |
| IR (cm <sup>-1</sup> )                                   | 2235                  | 1600 | 1048  | 1446            | 577 |
| <sup>1</sup> H-NMR                                       | a                     | b    | c   | d               |     |
| δ (ppm)  | 1.92                  | 3.85 | 7.97  | 6.86            |     |
| UV (nm)  | A (n → π*) B (π → π*) |      |   |                 |     |
| (C=S)  | 508                   | 347  |   |                 |     |

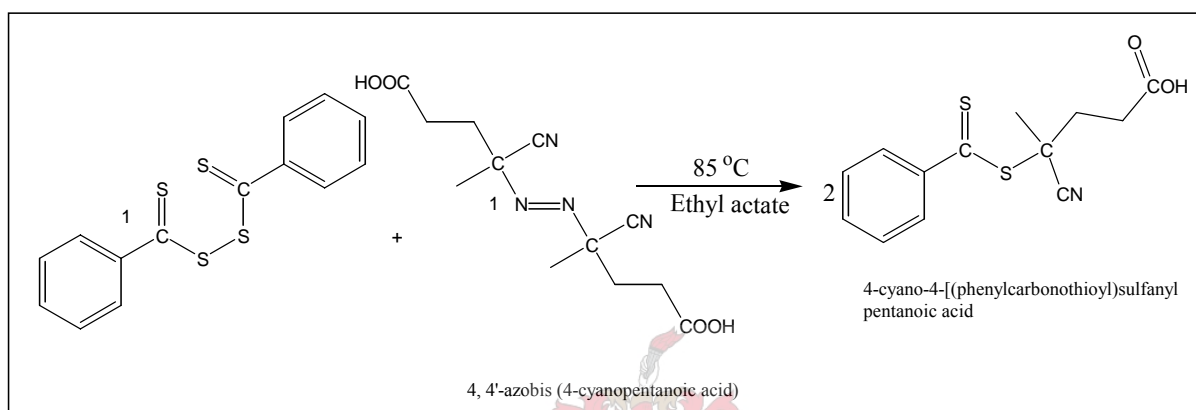
Chloroform-d was used for <sup>1</sup>H-NMR and dichloromethane for UV analyses.

### 3.9 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid and its derivatives

The syntheses of 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid and its derivatives were carried out in a similar fashion to 1-cyano-1-methylethyl benzenecarbodithioate (Sections 3.8.1 and 3.8.2) using the method of *Le et al.*<sup>1,8</sup> The AIBN was replaced by 4,4'-azobis(4-cyanopentanoic acid) as a new source of generation of radicals. The products were purified by liquid chromatography, on silica column, using a 2:2:6 ratio of pentane: heptane: ethyl acetate. The final products crystallized after removal of solvents under vacuum were analysed by <sup>1</sup>H NMR, UV and IR.

### 3.9.1 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid

Diphenyldithioperoxyanhydride (2.17 g, 0.007 mol), prepared as described in Section 3.8.1, and 4,4'-azobis(4-cyanopentanoic acid) (2.17 g, 0.0075 mol) were dissolved in 100 mL of ethyl acetate. The solution was placed in a 250 mL three-necked flask fitted with a reflux condenser, a stopper and a septum. The solution was heated overnight at 85°C while purging with nitrogen. After removing the solvent using a rotary evaporator (800 to 240 mbar; 40°C), the crude product that was obtained was subjected to column chromatography using a mixture of heptane, pentane and ethyl acetate (2; 2; 6), to afford an oily red compound (Scheme 3.11).



**Scheme 3.11** The preparation of 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid.

After further drying the oily red compound for a period of 4 h to 6 h under strong vacuum, the product turned into red crystals. The crude yield was 3 g (0.0105 mol)(75%).

$^1\text{H}$  NMR: 7.97 (d, 2H, *o*-ArH); 7.59 (t, 2H, *m*-ArH); 7.38 (t, 1H, *p*-ArH) ppm), 2.71 to 2.22 ppm (m, 4H,  $\text{CH}_2$   $\text{CH}_2$ ); 1.92 ppm (s, 3H,  $\text{CH}_3$ ).

FT-IR (KBr disc.  $\text{cm}^{-1}$ ): ~3140-2480 (COO-H); 2235 (-CN); 1700 (C=O); 1425 (C=C aromatic); 1050 (C=S) and 574 (C-S stretching).

UV(C=S): ( $n \rightarrow \pi^*$ ;  $\lambda = 514$  nm) and ( $\pi \rightarrow \pi^*$ ;  $\lambda = 303$  nm).

Chloroform-*d* was used for  $^1\text{H}$ -NMR and dichloromethane for UV analyses.

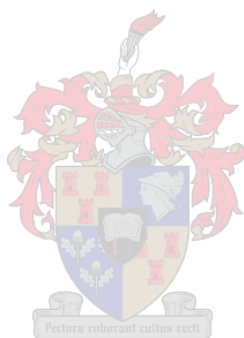
The details of  $^1\text{H}$  NMR, FTIR and UV spectra are reported in the Appendix (Figures 10 through 12 and Table 4).

### 3.9.2 4-cyano-4-[(4-methylphenyl)carbothioyl]sulfanyl]pentanoic acid and 4-cyano-4-[(4-methoxyphenyl)carbothioyl]sulfanyl]pentanoic acid

4-cyano-4-[(4-methylphenyl)carbothioyl]sulfanyl]pentanoic acid and 4-cyano-4-[(4-methoxyphenyl)carbothioyl]sulfanyl]pentanoic acid were synthesized in a similar fashion to

4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid (see Section 3.9.1), the only difference being that ethyl acetate and toluene were used as solvent for the reaction in the ratio of 100/50 mL. The purification of these compounds was done by using liquid chromatography on a silica column, with a 3:3:4 ratio of pentane: heptane: ethyl acetate. The fact that both final products 4-cyano-4-[[4-methylphenyl]carbothioyl]sulfanyl}pentanoic acid and 4-cyano-4-[[4-methoxyphenyl]carbothioyl]sulfanyl}pentanoic acid crystallized easily suggest that recrystallization could be used as another method of purification.

The bis(4-methylphenyl)dithioperoxyanhydride and bis(4-methoxyphenyl)dithioperoxy-anhydride previously prepared (Section 3.8.3) were reacted with 1.5 molar equivalents of the corresponding azo compound 4,4'-azobis (4-cyanopentanoic acid) at 85°C in the absence of oxygen. This led to the syntheses of 4-cyano-4-[[4-methoxyphenyl]carbothioyl]sulfanyl}-pentanoic acid and 4-cyano-4-[[4-methylphenyl]carbothioyl]sulfanyl}pentanoic acid in good yields: 3.5 g (0.0119 mol) (85%) and 3.46 g (0.0112 mol) (80%) respectively. The aforementioned compounds were analysed by <sup>1</sup>H NMR, FT-IR and UV. See Table 3.4.



**Table 3.4: <sup>1</sup>H NMR, FT-IR and UV characterization of 4-cyano-4-[[4-(4-methylphenyl)carbothioyl]sulfanyl]pentanoic acids**

| 4-cyano-4-[[4-(4-methylphenyl)carbothioyl]sulfanyl]-pentanoic acid (1) |                          |           | 4-cyano-4-[[4-(4-methoxyphenyl)carbothioyl]sulfanyl]-pentanoic acid (2) |      |      |     |
|--|--------------------------|-----------|---|------|------|-----|
|  |                          |           |   |      |      |     |
| (1)  | COOH                     | CN        | C=O   | C=C  | C=S  | C-S |
| IR (cm <sup>-1</sup> )   | 3080-2860                | 2250      | 1706  | 1438 | 1046 | 582 |
| <sup>1</sup> H-NMR   | a                        | m         | c   | d    | b    |     |
| δ (ppm)  | 1.92                     | 2.68-2.48 | 7.21  | 2.42 | 7.88 |     |
| UV (nm)  | A (n → π*)    B (π → π*) |           |   |      |      |     |
| (C=S)  | 511                      | 314       |   |      |      |     |
| (2)  | COOH                     | CN        | C=O   | C=C  | C=S  | C-S |
| IR (cm <sup>-1</sup> )   | 3133-2705                | 2241      | 1715  | 1608 | 1028 | 582 |
| <sup>1</sup> H-NMR   | a                        | m         | d   | c    | b    |     |
| δ (ppm)  | 1.92                     | 2.74-2.57 | 3.85  | 6.86 | 7.97 |     |
| UV (nm)  | A (n → π*)    B (π → π*) |           |   |      |      |     |
| (C=S)  | 347                      | 314       |   |      |      |     |

Chloroform-d was used for <sup>1</sup>H-NMR and dichloromethane for UV analyses.

The spectra of <sup>1</sup>H NMR, FT-IR and UV are reported in the Appendix (Figures 13 through 15 and Table 5, for the compound (1) and Figures 16 through 18 and Table 6 for the compound (2)).

### 3.10 1-methyl-1-phenylethyl benzenecarbothioate and its derivatives

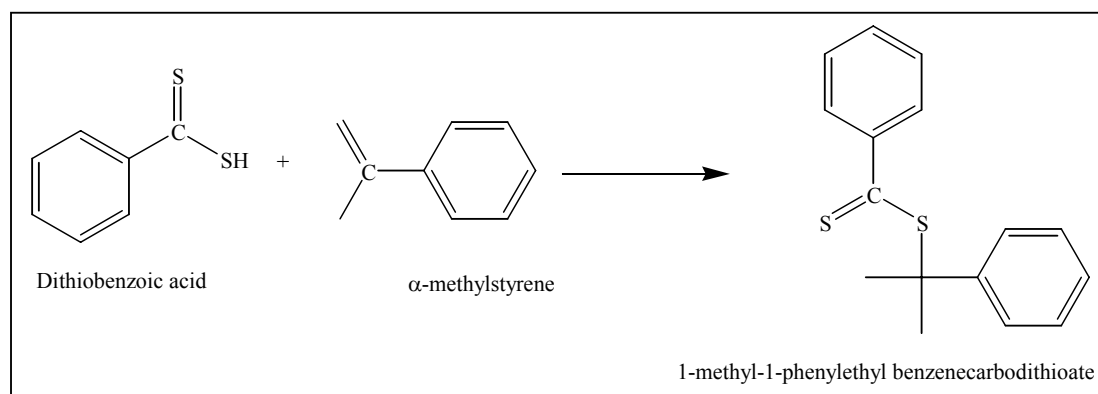
Monomers having one or more carbon-carbon double bonds such as  $\alpha$ -methylstyrene will allow the addition of a dithioacid synthesized by the Grignard method to yield dithioesters.<sup>18</sup> The synthetic mechanism of the addition of dithioacids to alkenes proceeds either by a nucleophilic or electrophilic addition and both are oriented by the nature of the alkene used.<sup>18,19</sup> The nucleophilic

addition of  $\alpha$ -methylstyrene to benzenecarbodithioic acid and its derivatives prepared from Grignard reagents is given Scheme 3.12 (Section 3.10.1).<sup>1</sup>

Four compounds: 1-methyl-1-phenylethyl benzenecarbodithioate, 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate, 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate and 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate were carried out according the method patented by *Le et al.*<sup>1</sup> These 1-methyl-1-phenylethyl benzenecarbodithioate derivatives were purified by liquid chromatography over a silica column using hexane as eluent. The products were allowed to crystallize in a freezer at  $-4^{\circ}\text{C}$  and were analysed by NMR, FT-IR and UV spectroscopy.

### 3.10.1 1-methyl-1-phenylethyl benzenecarbodithioate

A mixture of  $\alpha$ -methyl styrene (10 g, 0.084 mol) and 10 g (0.065 mol) of the benzenecarbodithioic acid synthesized previously (Section 3.6.1) was placed in 250 mL three-necked flask, fitted with a reflux condenser, a stopper and a septum. Carbon tetrachloride (40 mL) was added with paratoluene sulfonic acid monohydrate (98.5%) as catalyst. The reaction mixture was first degassed for 15 min, and then stirred and heated at  $70^{\circ}\text{C}$  while purging with nitrogen for 24 hours. The reaction was then allowed to cool to room temperature. After removal the solvent under vacuum at  $40^{\circ}\text{C}$ , the viscous pink oil that resulted was subjected to column chromatography on silica gel using hexane as eluent. After purification, the residue obtained was kept in a freezer at  $-4^{\circ}\text{C}$ . The product turned to a violet colour. By following the same reaction with TLC, it was found that the reaction was completed after a period of 7 to 8 hours and 10.62 g (0.039 mol) of 1-methyl-1-phenylethyl benzenecarbodithioate was obtained (60% yield). Scheme 3.12 summarizes the synthesis of 1-methyl-1-phenylethyl benzenecarbodithioate.



**Scheme 3.12 Synthesis of 1-methyl-1-phenylethyl benzenecarbodithioate.**

The product was identified by  $^1\text{H}$  NMR, FT-IR and UV:



$^1\text{H}$  NMR spectrum: ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.98 ( $-\text{C}(\text{CH}_3)_2$ ); for cumyl ring: 7.56 (d, 2H, *o*-ArH); 7.33 (d, 2H, *m*-ArH); 7.24 (t, 1H, *p*-Ar -H); for dithiobenzoate ring: 7.88 (d, 2H, *o*-ArH); 7.33 (t, 2H, *m*-ArH); 7.24 (t, 1H, *p*-Ar -H).

FT-IR (KBr disc. ( $\text{cm}^{-1}$ )): 1602 ( $\text{C}=\text{C}$  aromatic); 1054 ( $\text{C}=\text{S}$ ); 541 ( $\text{C}-\text{S}$  stretching); 1350 ( $-\text{C}(\text{CH}_3)_2$ ).

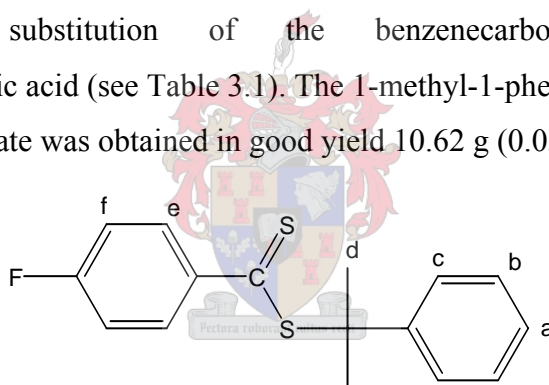
UV( $\text{C}=\text{S}$ ): ( $n \rightarrow \pi^*$ ;  $\lambda = 523$  nm) and ( $\pi \rightarrow \pi^*$ ;  $\lambda = 303$  nm).

Chloroform-*d* was used for  $^1\text{H}$ -NMR and dichloromethane for UV analyses.

The details of the  $^1\text{H}$  NMR, FT-IR and UV analyses of 1-methyl-1-phenylethyl benzenecarbodithioate are shown in the Appendix, Figures 28 through 30 and Table 10.

### 3.10.2 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate

The synthesis of 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate (Scheme 3.13) was realized similarly to the synthesis of 1-methyl-1-phenylethyl benzenecarbodithioate Section 3.10.1. The only difference was the substitution of the benzenecarbodithioic acid by the 4-fluorobenzenecarbodithioic acid (see Table 3.1). The 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate was obtained in good yield 10.62 g (0.036 mol)(63%).



#### Scheme 3.13 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate

$^1\text{H}$  NMR, FT-IR and UV were used to identify the 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate. (See the Appendix, Figures 37 to 39 and Table 13.)

$^1\text{H}$  NMR spectrum: ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.03 (t, 1H, a); 7.94 (m, 4H, b, e); 7.35 (d, 2H, c); 1.98 (s, 6H, d); 7.59 (d, 2H, f).

FT-IR (KBr disc. ( $\text{cm}^{-1}$ )): 1598 ( $\text{C}=\text{C}$  aromatic); 1050 ( $\text{C}=\text{S}$ ) and 569 ( $\text{C}-\text{S}$  stretching); 1370 ( $-\text{C}(\text{CH}_3)_2$ ); 1244 ( $\text{C}-\text{F}$ ).

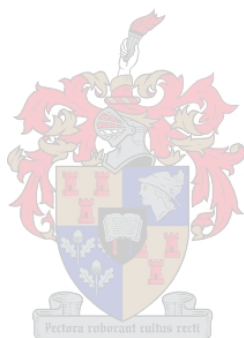
UV( $\text{C}=\text{S}$ ): ( $n \rightarrow \pi^*$ ;  $\lambda = 523$  nm) and ( $\pi \rightarrow \pi^*$ ;  $\lambda = 308$  nm).

Chloroform-*d* was used for  $^1\text{H}$ -NMR and dichloromethane for UV analyses.

### 3.10.3 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate and 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate

Using the synthetic procedure in Section 3.10.1, the benzenecarbodithioic acid was replaced by the 4-methylbenzenecarbodithioic acid (see Table 3.1). The reaction of  $\alpha$ -methyl styrene (10 g, 0.084 mol) with 10 g (0.06 mol) of 4-methylbenzenecarbodithioic acid gave, in a one-step procedure at 70°C, 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate in good yield: 11 g (0.038 mol)(65%).

Similarly, reacting  $\alpha$ -methyl styrene (10 g, 0.084 mol) and 10 g (0.054 mol) of 4-methoxybenzenecarbodithioic acid, the 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate was prepared in a yield of 11.48 g (0.037 mol)(70%). <sup>1</sup>H NMR, FT-IR and UV analyses of the 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate and 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioates are shown in the Table 3.5.



**Table 3.5:** <sup>1</sup>H NMR, FT-IR and UV analyses of 1-methyl-1-phenylethyl 4-methyl- and 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioates

| 1-methyl-1-phenylethyl 4-methylbenzene-carbodithioate (1) |            | 1-methyl-1-phenylethyl 4-methoxybenzene-carbodithioate (2) |            |      |      |      |      |
|---|------------|--|------------|------|------|------|------|
|   |            |  |            |      |      |      |      |
| (1)   | C=C        | CH <sub>3</sub>  | C=S        |      |      |      |      |
| IR (cm <sup>-1</sup> )                                    | 1590       | 1362   | 1041       |      |      |      |      |
| <sup>1</sup> H-NMR  | a          | b  | c          | d    | e    | f    | g    |
| δ (ppm)   | 7.03       | 7.47   | 7.12       | 1.87 | 7.76 | 7.15 | 2.22 |
| UV (nm)   | A (n → π*) |  | B (π → π*) |      |      |      |      |
| (C=S)   | 523        | 316  |            |      |      |      |      |
| (2)   | C=C        | CH <sub>3</sub>  | C=S        | C-S  |      |      |      |
| IR (cm <sup>-1</sup> )                                    | 1590       | 1380   | 1168       | 586  |      |      |      |
| <sup>1</sup> H-NMR  | a          | b  | c          | d    | e    | f    | g    |
| δ (ppm)   | 6.80       | 7.53   | 7.21       | 1.95 | 7.94 | 7.30 | 3.79 |
| UV (nm)   | A (n → π*) |  | B (π → π*) |      |      |      |      |
| (C=S)   | 520        | 335  |            |      |      |      |      |

Chloroform-d was used for <sup>1</sup>H-NMR and dichloromethane for UV analyses.

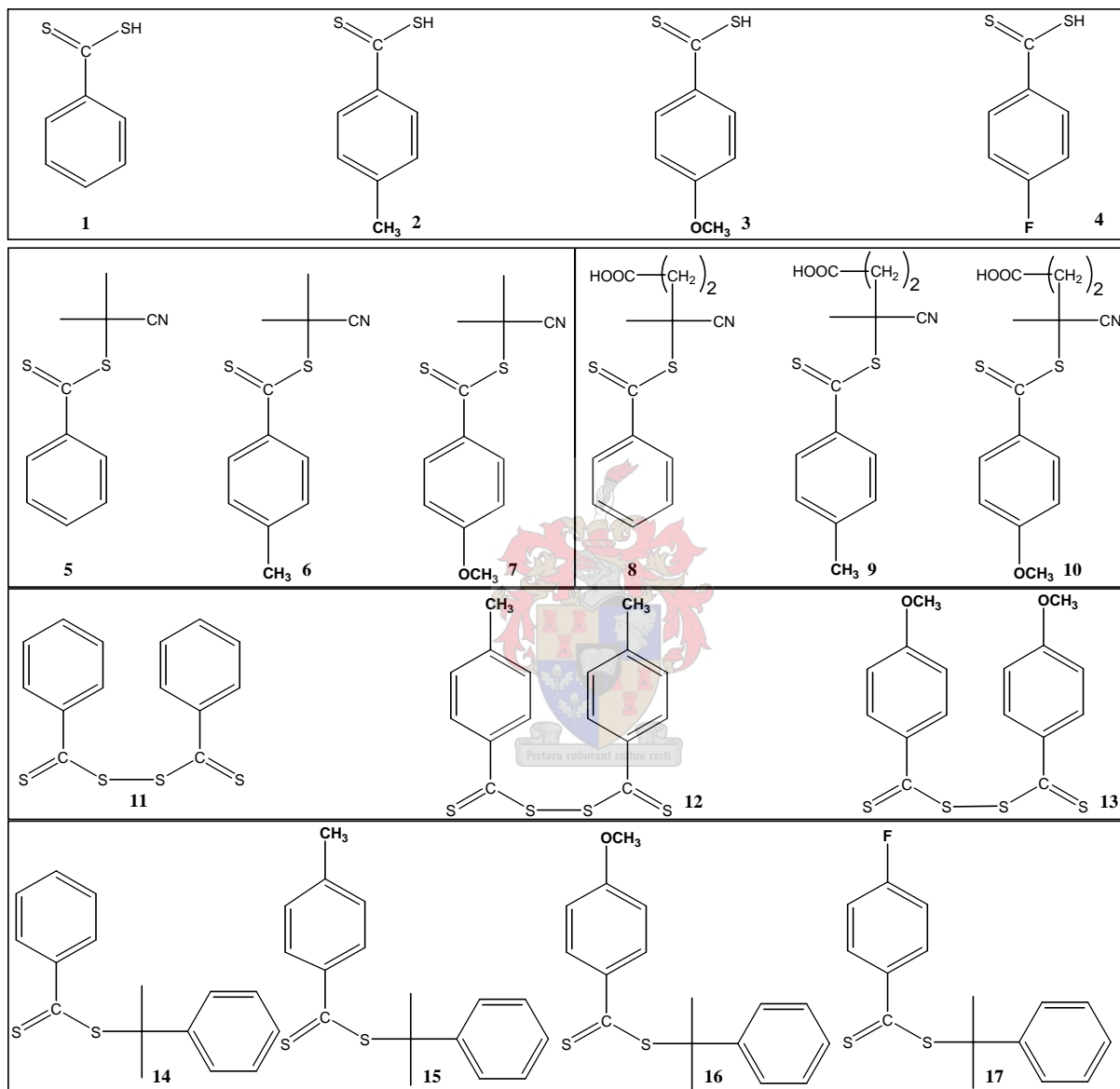
Their spectra are shown in the Appendix (Figures 31 through 33 and Table 11, for the characterization of 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate (compound 1), and Figures 34 through 36 and Table 12 for that of the 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate compound 2).

### 3.11 Summary of all dithiobenzoate compounds

#### synthesized in this chapter

The thirteen typical thiocarbonyl thio compounds prepared are shown in Table 3.6

Table 3.6: Summary of all dithiobenzoate compounds synthesized in this chapter



Nomenclature:

1. benzenecarboxylthioic acid
2. 4-methylbenzenecarboxylthioic acid
3. 4-methoxybenzenecarboxylthioic acid
4. 4-fluorobenzenecarboxylthioic acid
5. 1-cyano-1-methylethyl benzenecarboxylthioate

6. 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate
7. 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate
8. 4-cyano-4-[(phenylcarbonothioyl)sulfanyl]pentanoic acid
9. 4-cyano-4-[[4-methylphenyl]carbonothioyl]sulfanyl]pentanoic acid
10. 4-cyano-4-[[4-methoxyphenyl]carbonothioyl]sulfanyl]pentanoic acid
11. bis(4-methylphenyl)dithioperoxyanhydride
12. bis(4-methoxyphenyl)dithioperoxyanhydride
13. bis(4-fluorophenyl)dithioperoxyanhydride
14. 1-methyl-1-phenylethyl benzenecarbodithioate
15. 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate
16. 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate
17. 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate

*"This information was obtained using the ACD/I-Lab Web service (ACD/IUPAC Name Free 8.05)".*  
[http://www.iupac.org/nomenclature/ACD/calc\\_3dparty.html](http://www.iupac.org/nomenclature/ACD/calc_3dparty.html)

### 3.12 Conclusions

The author has successfully prepared thirteen typical RAFT agents via Grignard reagents, in good yields. 4-cyano-4-[[4-methoxyphenyl]carbothioyl]sulfanyl]pentanoic acid, 4-cyano-4-[[4-methylphenyl]carbothioyl]sulfanyl]pentanoic acid, 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate, 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate, bis(4-methylphenyl)dithioperoxyanhydride, and 1-cyano-1-methylethyl 4-methylbenzene-carbodithioate are typical novel chain transfer agents that were prepared in this study. In our laboratory, we have found that the synthesis of 4-methoxy- and 4-methylbenzenecarbodithioic acids can be performed faster than the synthesis of benzenecarbodithioic acid.

### 3.13 References

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*“Learning is a treasure that will follow its owner everywhere” Chinese proverb.*

## *CHAPTER 4: An examination of the living character of styrene polymerisation mediated by functionalized dithiobenzoates*

In Chapter 3, thirteen dithiobenzoate RAFT agents were synthesized. In this chapter the living character of styrene polymerisation as a function of these chain transfer agents is examined. The polymerisations were conducted in bulk, making use of the self-initiation of styrene at 100°C. Monomer conversion was determined gravimetrically, and molar masses and molar mass distributions of styrene polymerisations were measured by size exclusion chromatography. Good control was obtained over the homopolymerisation of styrene monomer using the thirteen RAFT agents synthesized in Chapter 3 although polydispersities around 1.5 to 1.6 were obtained in some cases.

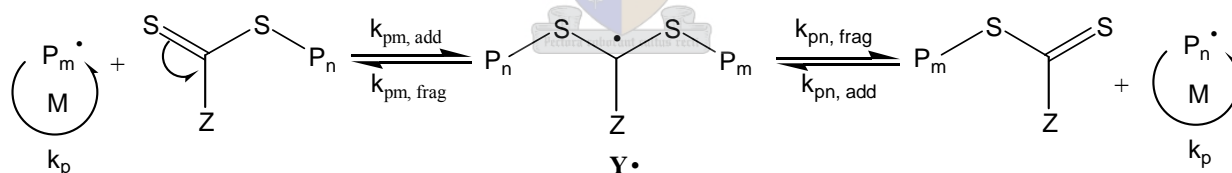
## 4.1 Homopolymers

Homopolymerisation can be considered as the process in which a polymer is formed from the successive addition of identical units called monomers. The regulation of homopolymerisation by the mediation of RAFT agents should allow the preparation of polymers with narrow molar mass distributions and predetermined molar masses. Therefore, the properties of the homopolymer formed (in this study) should depend on the type and concentration of the monomer, transfer agent and polymerisation conditions. The fact the monomer and reaction conditions stay constant, the properties of the homopolymer only depends on the type and concentration of the RAFT agent.

The present study focuses on the use of different RAFT agents in order to prepare polymers with narrow molar mass distributions and to study the kinetics of these polymerisation reactions, with subtle changes of the RAFT agent structure.

## 4.2 Homopolymers via monofunctional RAFT agents

Homopolymers synthesized through the use of monofunctional RAFT agents all have the RAFT functional group at the one end of the chain and an initiating fragment at the other end. In other words, the formed polymer is located between the (C=S)S moiety and the activating group R (Scheme 4.1). This process can be extended by the addition of other monomer units and thus, step-by-step, a polymer is produced<sup>1</sup> (see Scheme 4.1).



**Scheme 4.1 Homopolymer synthesis via a monofunctional RAFT agent. The RAFT moiety remains at the chain end throughout the polymerisation.**

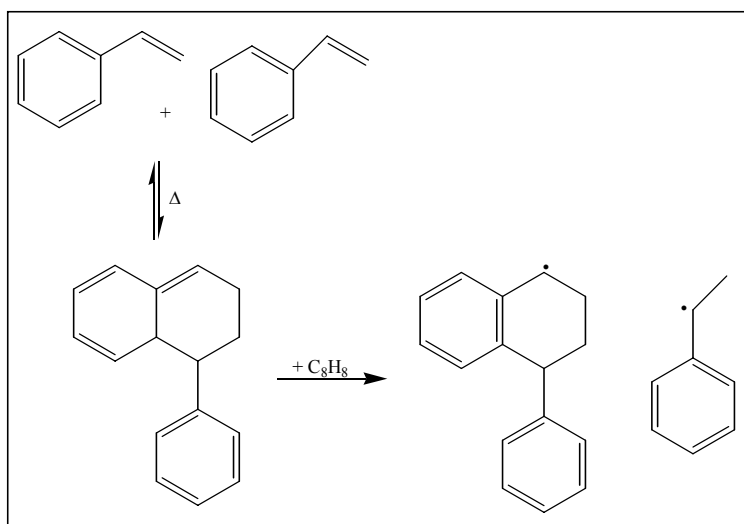
Polymerisation using RAFT agent precursors may be more complex because it is believed that two processes can occur. This will be discussed later (see Scheme 5.1 in Section 5.4).

It should be kept in mind that the polymerisation of styrene mediated by the RAFT process includes several reactions, which are: self-initiation of styrene,<sup>2</sup> and a series of addition, fragmentation and propagation steps.<sup>1</sup> The basis of the RAFT process is governed by the rapid addition-fragmentation equilibrium process between propagating ( $P_m\bullet$ ) and intermediate ( $Y\bullet$ ) radicals and dormant species (see Schemes 4.1 and 2.8, and Sections 2.6.2 and 2.6.2.1).



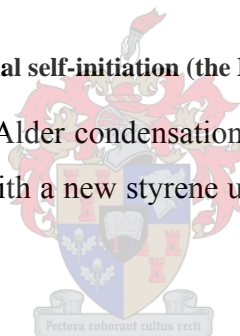
### 4.3 Thermal initiation of styrene

At high temperatures the thermal initiation of styrene is characterized by the formation of active species, namely styrene dimers and styrene trimers. The mechanism of the formation of these active species, accepted in the literature,<sup>2</sup> is as follows (Scheme 4.2):



Scheme 4.2 Styrene polymerisation via thermal self-initiation (the Mayo mechanism).<sup>2</sup>

Two styrene monomers undergo Diels Alder condensation, associating under thermal conditions to form an unstable dimer, which reacts with a new styrene unit via hydrogen transfer to generate two radicals, as shown in Scheme 4.2.



## 4.4 Experimental

### 4.4.1 Materials

#### 4.4.1.1 Styrene

Styrene (St) was washed with an aqueous solution of potassium hydroxide (0.3 M KOH) three times and then, after rinsing with deionised water, the monomer was distilled under reduced pressure and stored below 4°C.

#### 4.4.1.2 The RAFT agents

The RAFT agents used were synthesized and purified according to the method of *Le et al*<sup>1</sup> (see Chapter 3).

## 4.4.2 Characterization

The molar masses and molar mass distributions of the polymers were determined by GPC (SEC).

### 4.4.2.1 Size-exclusion chromatography

Molar mass distributions were measured via size-exclusion chromatography (SEC). Dried polystyrene samples were dissolved in THF (8 mg/mL) and filtered through a 0.45  $\mu\text{m}$  nylon filter. Analyses were carried out with a SEC system comprising a Waters 610 Fluid Unit, Waters 410 Differential Refractometer at 30°C, a Waters 717<sub>plus</sub> Autosampler and Waters 600E System Controller. Two Plgel 5 $\mu\text{m}$  Mixed-C columns and a precolumn (Plgel 5 $\mu\text{m}$  Guard) were used and the column oven was set at 30°C. Millennium<sup>32</sup> was used for data acquisition and data analysis. THF was used as solvent and the flow rate was 1.0 mL/min. The volume of the injected samples was 100  $\mu\text{L}$ . The system was calibrated with narrow polystyrene standards ranging from 800 to  $2 \times 10^6$  g/mol.

## 4.5. Synthetic procedures

### 4.5.1 Precautions taken

For the number of chains to be constant throughout the reaction, the contribution from the initiator should be negligible compared to the concentration of the RAFT agent. In other words, in order for all polymer chains to carry the RAFT moiety up to high monomer conversions, the initiator concentration thus needs to be considerably smaller than the RAFT agent concentration. Termination of the chain process can occur by a combination of two radicals, a process that has a very high rate constant (often approaching diffusion control). Thus, the precaution was taken to keep the concentration of radicals very low, leading to low actual rates of radical combination.

### 4.5.2 Thermally initiated polymerisation of styrene

Styrene (40 g; 0.384 mol) and 0.0005 mol of the selected RAFT agent were accurately weighed and then transferred to a 100 mL three-necked round-bottom flask equipped with a condenser, and stirred at 300 rpm using a magnetic stirrer. The homogeneous mixture was purged with nitrogen for 10 minutes to eliminate oxygen, and then the reaction flask was immersed in an oil bath and heated to 100°C. No radical initiator was used in this case of thermal polymerisation. The reaction was carried out under nitrogen at a constant temperature of 100°C. Samples were taken with a syringe, for gravimetric conversion determination, at suitable time intervals (1 h), and for GPC analyses. A

few drops of methanol were added to precipitate the samples taken. Finally, these samples were dried at room temperature for several days (4 to 7) or in a vacuum oven at ambient temperature for two to four days. The formed polymers were then weighed for gravimetric studies and placed in small vials. This procedure was employed for all polymers prepared via the thirteen RAFT agents described in Chapter 3.

## 4.6 Results and discussion

### 4.6.1 Styrene polymerisation in the absence of a RAFT agent

Figure 4.1 shows the increase in conversion with time for the thermally initiated polymerisation of styrene at 100°C in the absence of a RAFT agent.

After seven hours of reaction time the conversion was approximately 35%.

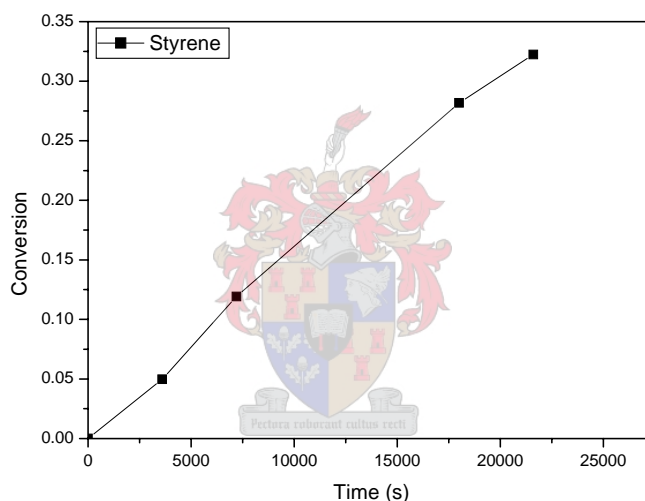


Figure 4.1 Styrene polymerisation via thermal self-initiation at 100°C in absence of any RAFT agent.

### 4.6.2 Styrene polymerisation via living polymerisation

#### 4.6.2.1 Kinetic behaviour of living polymerisation

As discussed in Section 2.3, there exists some experimental criteria by which to diagnose a controlled/living polymerisation,<sup>3</sup> for example, narrow molar mass distribution, linear relationship between number average molar mass and monomer conversion, and constant concentration of active centres during the polymerisation. In order to investigate some of these criteria, the polymerisation of styrene in the presence of the thirteen respective RAFT agents was studied. The polymerisation kinetics was investigated by the gravimetric method.

The conversion of styrene to polystyrene was determined at 100°C. The ratio of monomer to RAFT agent was chosen to be:

$$[M]_0/[RAFT]_0 = 9.615 \times 10^{-3} / 1.25 \times 10^{-5} = 770; \text{ mass of styrene (M) = 40g and mol(RAFT) = 0.0005 mol.}$$

All the experiments were performed in bulk and the primary radicals were generated by thermal initiation of styrene. To check reproducibility each reaction was run two times.  $M_{n\text{exp}}$  and  $M_{n\text{th}}$  are the experimental and theoretically calculated molar masses calculated using equation Eq.2.5<sup>7</sup> (Section 2.6.5), and given by:

$$M_{n\text{th}} = M_{\text{RAFT}} + 104 ([\text{Monomer}]_0 \times \text{conversion}) / [\text{RAFT}]_0$$

Results of the experiments are shown in Figures 4.2 to 4.40 in this chapter and Tables 1 to 13 in the Appendix.

#### 4.6.2.2 1-cyano-1-methylethyl benzenecarbodithioate and its derivatives

The derivatives of the 1-cyano-1-methylethyl benzenecarbodithioate are all RAFT agents prepared from two radical additions of 2,2'-azobis(isobutyronitrile) in the presence of bis(4-methylphenyl)dithioperoxyanhydride and bis(4-methoxyphenyl)dithioperoxyanhydride in order to prepare RAFT agents with isobutyronitrile as the R group (see Sections 3.10.1 through 3.10.2).

##### a) 1-cyano-1-methylethyl benzenecarbodithioate: RAFT agent 1

The bulk polymerisation of styrene, mediated with 1-cyano-1-methylethyl benzenecarbo-dithioate (RAFT agent 1), was performed to determine whether the RAFT agent 1 was capable of mediating a controlled polymerisation. Results are given in Figures 4.2 through 4.4 and Table 1 in the Appendix.

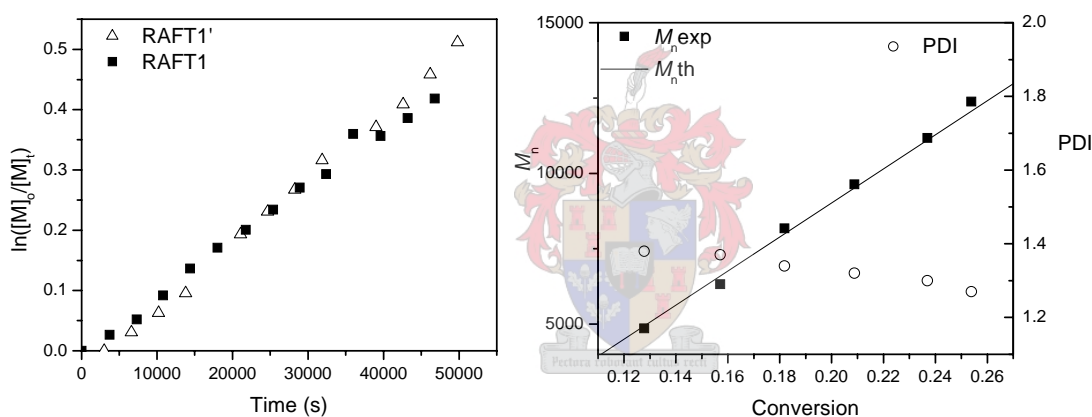
The semi-logarithmic function of monomer concentration ( $\ln ([M]_0/[M]_t)$ ) versus time shown in Figure 4.2 indicates that there is a first order monomer consumption rate. It should however be noted that this linearity does not provide any information about the living character of the system but shows that there is a steady state radical concentration. In addition, it shows that the number of growing chains is constant throughout the polymerisation. Finally, it does not, however, eliminate the existence of transfer reactions. Figure 4.2 also shows that the reaction was repeated and that the results obtained with RAFT agent 1' were similar to the first experiment (RAFT agent 1).

Figure 4.3 shows the linearity of the  $M_n$  increase as a function of monomer conversion. This testifies that there are a constant number of growing chains during the polymerisation. One of the similarities observed in the experiments 1 to 13 (where RAFT agents 1 to 13 were used) in this

study is that the experimentally determined molar masses ( $M_{n,exp}$ ) were close to the theoretical calculated ( $M_{n,th}$ ) values for the RAFT systems. This indicates that all of the initial RAFT agent was consumed during the polymerisation.

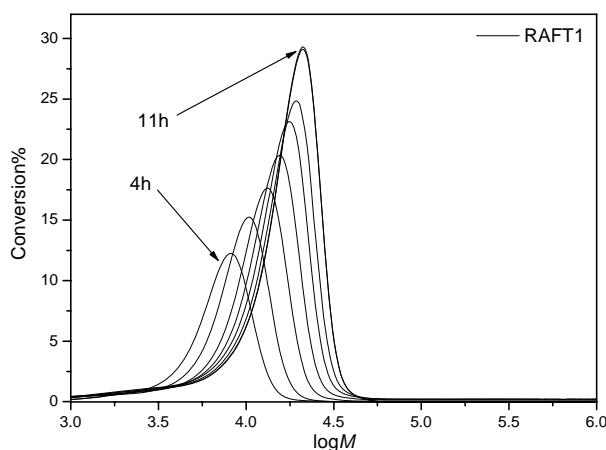
The data in Figure 4.3 for the bulk polymerisation of styrene in the presence of RAFT agent 1 also demonstrates that the PDI of the polystyrene formed remained below the benchmark of 1.5. Indeed, the polydispersity evolution with monomer conversion was first higher (1.37) then decreased with time (1.25). This proves that the polymerisation of styrene with the RAFT agent 1 was under control.<sup>4</sup>

Figure 4.4 shows SEC chromatograms for the 1-cyano-1-methylethyl benzenecarbodithioate (RAFT agent 1) mediated styrene polymerisation. It is clearly seen that there is a shift in the average molar mass from a low molar mass towards a high molar mass. This is one indication of the living character of the system. Moreover, the polystyrene formed was characterized by narrow molar mass distributions although some tailing was present.



**Figure 4.2** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 1 at 100°C. RAFT agent 1' demonstrates that the reaction was reproducible.

**Figure 4.3** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)



**Figure 4.4** MMDs of samples scaled for conversion taken from experiment (1) where RAFT agent 1 was used.

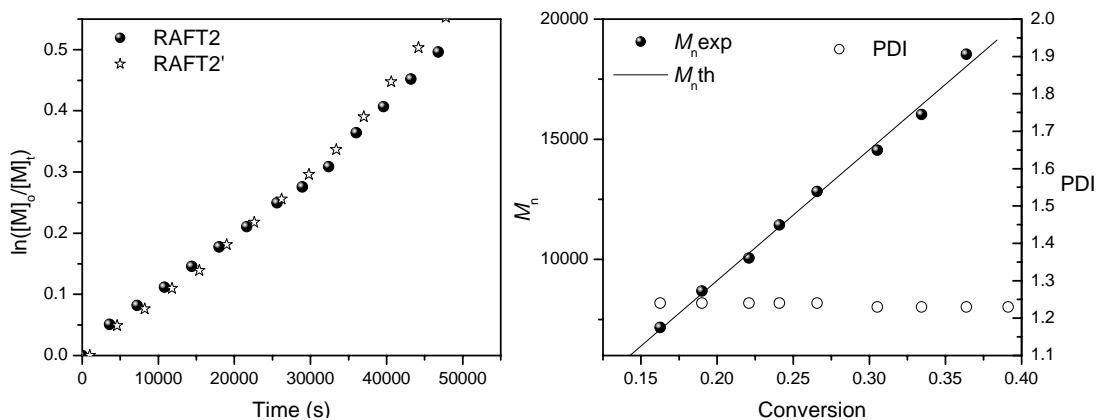
The following experiments were carried out by replacing the 1-cyano-1-methylethyl benzenecarbodithioate by its derivatives: 1-cyano-1-methylethyl 4-methylbenzenecarbo-dithioate (RAFT agent 2) and 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate (RAFT agent 3).

#### **b) 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate: RAFT agent 2**

Figure 4.5 shows a typical semi-logarithmic kinetic plot of the homopolymerisation of styrene at 100°C in the presence of 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate (RAFT agent 2). The observed kinetics is similar to that observed in Figure 4.2. In other words, the linearity indicates that there were a constant number of active radicals during the polymerisation. Figure 4.5 also shows that the results of a duplicate experiment (RAFT agent 2') correspond very well with those of the original one (RAFT agent 2).

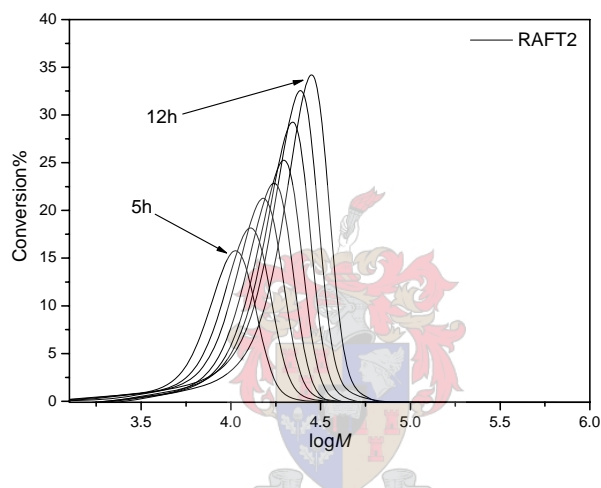
In Figure 4.6, the plots of  $M_n$  and polydispersity as a function of conversion are shown. The experimental  $M_n$  determined molar masses ( $M_{n,exp}$ ) coincide reasonably well with the theoretically calculated ( $M_{n,th}$ ) values for the RAFT system. The linear increase of  $M_n$  as a function of monomer is indicative of the living character of the polymerisation. The polydispersities of the resulting polystyrene were almost constantly low, with values from 1.22 to 1.23 (see Table 2 in the Appendix). This provides evidence that the RAFT agent 2 was efficient for the polymerisation of styrene.

Figure 4.7 shows the MMD peaks as a function of conversion. It is clearly seen that the MMDs determined by GPC were narrow, although some tailing was still occurring. This confirms that the polymers prepared had living characteristics.



**Figure 4.5** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 2 at 100°C. RAFT agent 2' demonstrates that the reaction was reproducible.

**Figure 4.6** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)



**Figure 4.7** MMDs of samples scaled for conversion taken from experiment (2) where RAFT agent 2 was used.

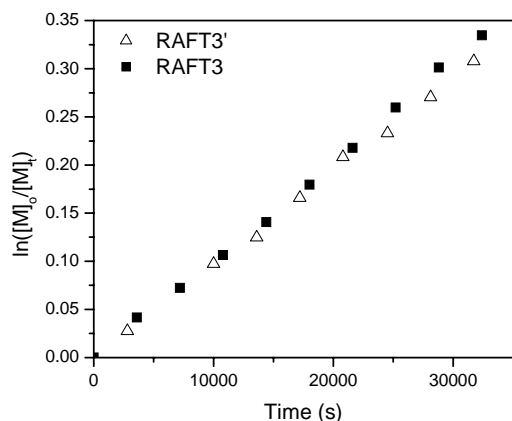
### c) 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate: RAFT agent 3

1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate is the final compound of the family of 1-cyano-1-methylethyl benzenecarbodithioate. The results of this experiment are reported in Figures 4.8 through 4.10 and Table 3 in the Appendix.

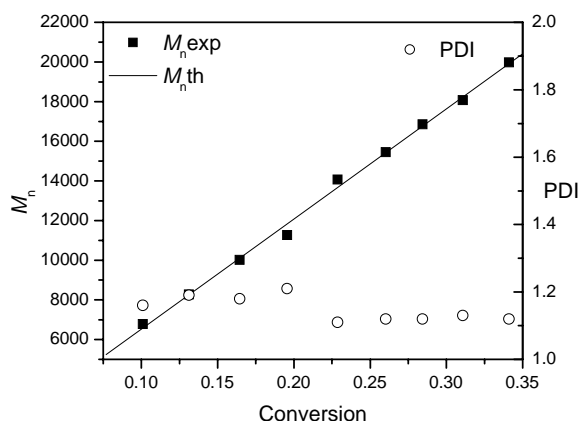
Figure 4.8 shows a kinetic plot of monomer conversion. Pseudo-first-order kinetics is observed in the case where the 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate was used as RAFT agent 3. In other words, a strictly linear consumption of monomer is obtained with conversion (time). A duplicate experiment fits the original one almost perfectly.

Figure 4.9 shows the evolution of the number average molar mass ( $M_n$ ) and polydispersity as a function of conversion for RAFT agent 3. From this figure it is seen that  $M_n$  increased linearly with conversion. Polydispersity values were very low (PDI: 1.2 to 1.1), this provides evidence that the RAFT agent 3 was very efficient for the polymerisation of styrene.

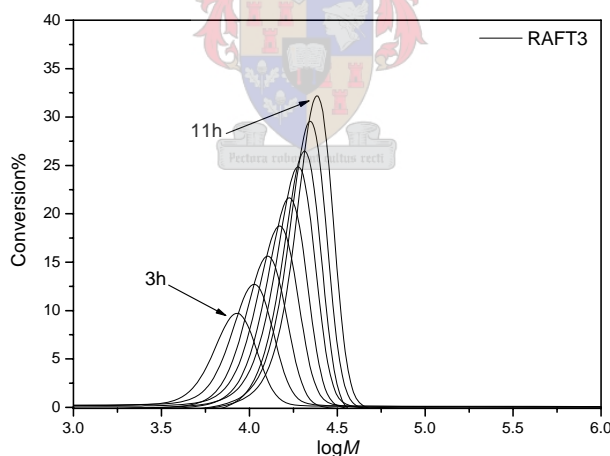
Figure 4.10 shows the shift of the MMD peak as a function of conversion. The RAFT polymerisations of styrene using the RAFT agent 3 yielded polymers with controllable molar masses and narrow MMDs. Figure 4.10 shows tailing mainly towards the lower molar mass. This implies that termination reactions, though not entirely suppressed, were less than in the cases where RAFT agents 1 and 2 were used. A comparison between the RAFT agents will be given in Chapter 5.



**Figure 4.8** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 3 at 100°C. RAFT agent 3' demonstrates that the reaction was reproducible.



**Figure 4.9** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)



**Figure 4.10** MMDs of samples scaled for conversion taken from experiment (3) where RAFT agent 3 was used.

After studying the family of 1-cyano-1-methylethyl benzenecarbothioate, the series comprising 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid and its derivatives was studied.

#### 4.6.2.3 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid and its derivatives

4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid and its derivatives concern all RAFT agents prepared from the addition of 4,4'-azobis(4-cyanopentanoic acid) in the presence of a diphenyldithioperoxyanhydride<sup>1</sup> or bis(4-methylphenyl)dithioperoxyanhydride and bis(4-

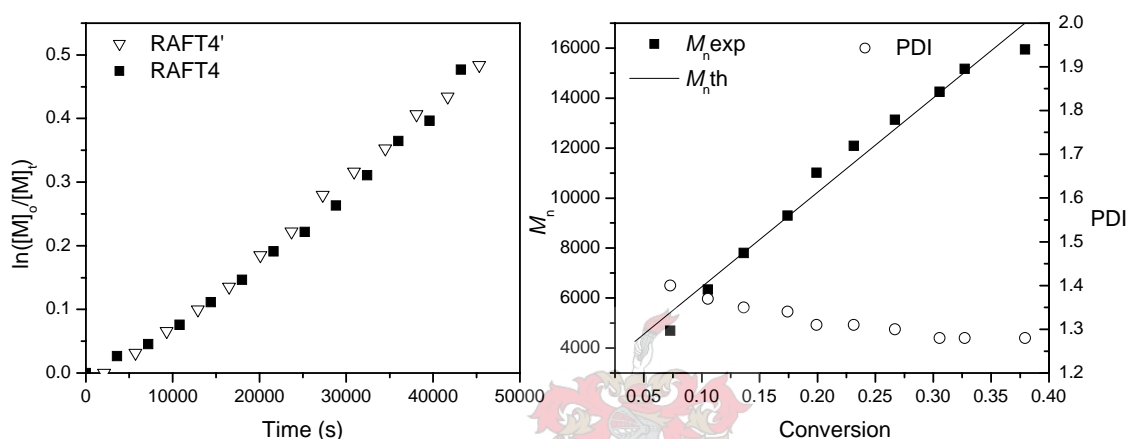


methoxyphenyl)dithioperoxyanhydride in order to prepare RAFT agents with cyanopentanoic acid as R group.

#### a) 4-cyano-4-[(phenylcarbothiioyl)sulfanyl]pentanoic acid: RAFT agent 4

As in the above series (4.6.2.2), the characteristic of constant growth throughout the polymerisation is observed here by the linear relationship between  $\ln([M]_0/[M]_t)$  and time (Figure 4.11).

Figure 4.12 shows the evolution of the number average molar mass ( $M_n$ ) and polydispersity as a function of conversion for 4-cyano-4-[(phenylcarbothiioyl)sulfanyl]-pentanoic acid as RAFT agent 4.



**Figure 4.11** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 4 at 100°C. RAFT agent 4' demonstrates that the reaction was reproducible.

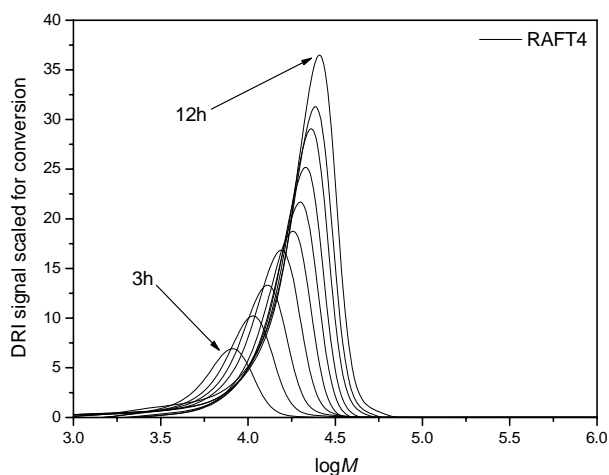
**Figure 4.12** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)

Using RAFT agent 4, the RAFT mediated polymerisation of styrene was found to be controlled, as shown by a linear evolution (with a slight downward curvature) of molar mass with conversion, narrow molar mass distribution and predetermined molar mass (Figures 4.12 and 4.13). The slight downward curvature noted could be explained by the formation of new chains.

The fact that in this experiment, at lower conversion, the PDI is high (1.4-1.37 at 7% and 10%, shown in Table 4.4 in the Appendix) is probably due to termination reactions between radical species present in the reaction system or because of the preference of the expelled radical to add to RAFT agent rather than to monomer. The presence of oxygen in the reaction flask at the commencement of the reaction (which was not completely removed by the nitrogen bubbling) could have reacted with radicals species produced by the Mayo mechanism or intermediate RAFT radicals (Figure 4.12).

Figure 4.13 shows the evolution of the MMD peak toward higher molar masses. From the shift of the MMD peak as a function of conversion, shown in Figure 4.13, one can conclude that this is

indeed a LRP. The presence of tailing towards low molar mass is indicative of some termination reactions among short chains.



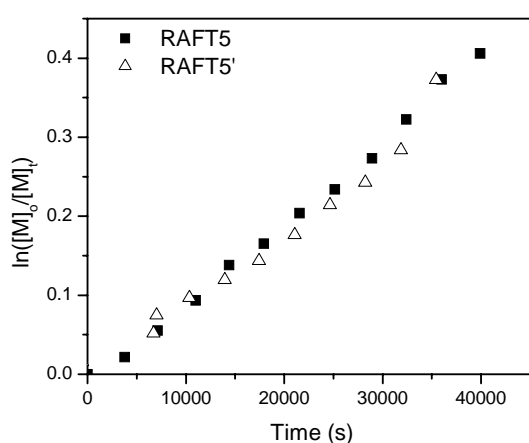
**Figure 4.13** MMDs of samples scaled for conversion taken from experiment (4) where RAFT agent 4 was used.

**b) 4-cyano-4-[[4-(4-methylphenyl)carbothioyl]sulfanyl]pentanoic acid: RAFT agent 5**

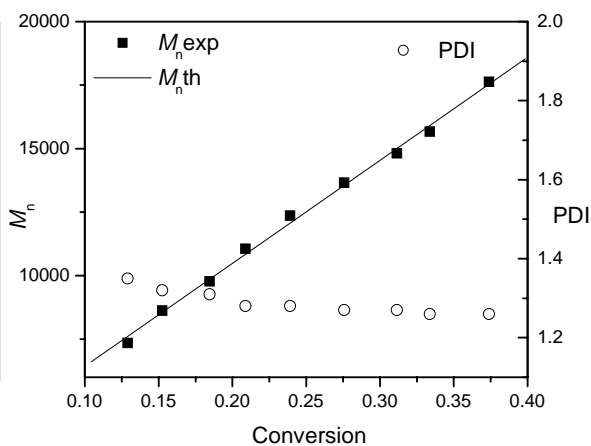
Figure 4.14 shows the plot of  $\ln ([M]_0/[M]_t)$  versus time for the polymerisation of styrene using RAFT agent 5. The semi-logarithmic plot of the monomer concentration versus polymerisation time was slightly curved, indicating the formation of new chains, as mentioned in the previous case.

Figure 4.15 shows a plot of molar mass and polydispersity versus conversion for the thermal polymerisation of styrene using the RAFT agent 5. It is also seen that the polydispersity indices are relatively low ( $1.35 < PDI < 1.26$ ). The observation of higher values early in the reaction and lower values later is consistent with a living polymerisation.<sup>4</sup> This suggests that RAFT agent 5 was therefore efficient in the homopolymerisation of styrene.

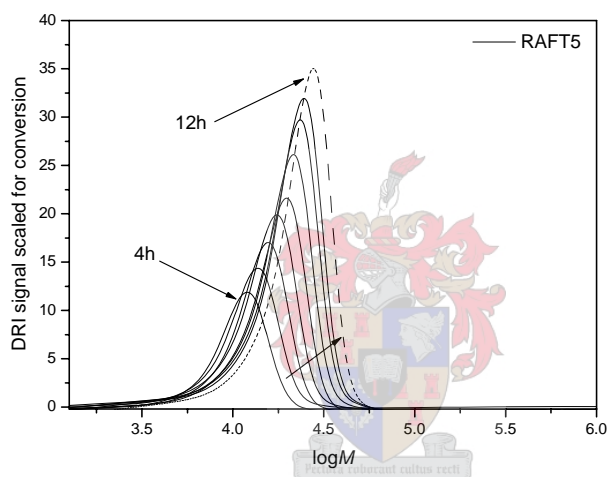
Figure 4.16 shows the evolution of the MMD peak toward higher molar masses. Figure 4.16 shows that the evolution of the number average molar mass ( $M_n$ ) linearly increases with fractional conversion throughout the polymerisation. This is a key characteristic of living radical polymerisation.



**Figure 4.14** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 5 at 100°C. RAFT agent 5' demonstrates that the reaction was reproducible.



**Figure 4.15** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,theo}$  are the experimental and theoretically calculated molar masses.)



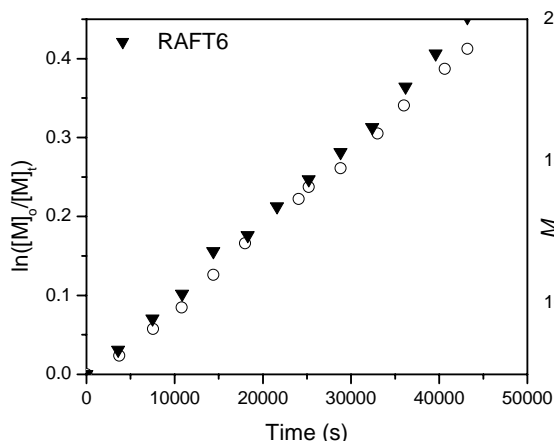
**Figure 4.16** Normalized MMDs of samples taken from experiment (5) where RAFT agent 5 was used.

### c) 4-cyano-4-[[4-(4-methoxyphenyl)carbothioyl]sulfanyl]pentanoic acid: RAFT agent 6

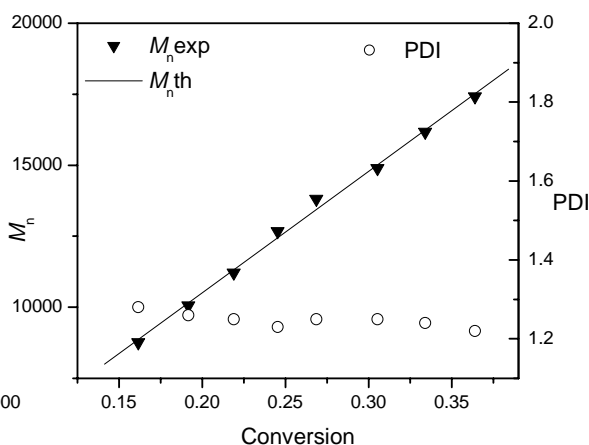
The kinetic study was implemented at 100°C in the bulk polymerisation of styrene using the 4-cyano-4-[[4-(4-methoxyphenyl)carbothioyl]sulfanyl]pentanoic acid (RAFT agent 6). Results are shown in Figure 4.17. The linear time dependence of  $\ln([M]_0/[M]_t)$  is consistent with a controlled polymerisation that is first-order in monomer.

Figure 4.18 shows a plot of molar mass and polydispersity versus conversion for the thermal polymerisation of styrene using the RAFT agent 6. The polystyrene formed with RAFT agent 6 appears to be of low polydispersity and has a unimodal molar mass distribution (see Figures 4.18 and 4.19, and Table 6 in the Appendix). Both  $M_{n,exp}$  and  $M_{n,theo}$  values match well (see Figure 4.18). This indicates that the polymerisations have living characteristics.

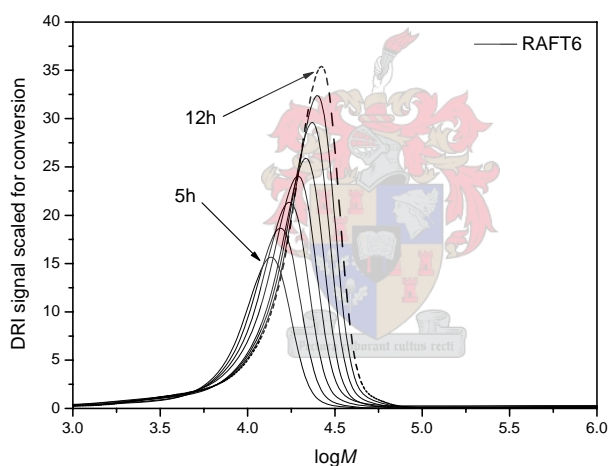
Figure 4.19 shows the evolution of the MMD peak toward higher molar masses. Here the tailing towards high molar masses is not significant. There is still significant low molar mass tailing.



**Figure 4.17** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 6 at 100°C. RAFT agent 6' demonstrates that the reaction was reproducible.



**Figure 4.18** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)



**Figure 4.19** MMDs of samples scaled for conversion taken from experiment (6) where RAFT agent 6 was used.

#### 4.6.2.4 Disulfides

The disulfides are symmetric compounds represented by diphenyldithioperoxyanhydride and its derivatives. In this family we have bis(4-methylphenyl)dithioperoxyanhydride and bis(4-methoxyphenyl)dithioperoxyanhydride. To investigate their reactivities they were also used as chain transfer agents in the bulk polymerisation of styrene.

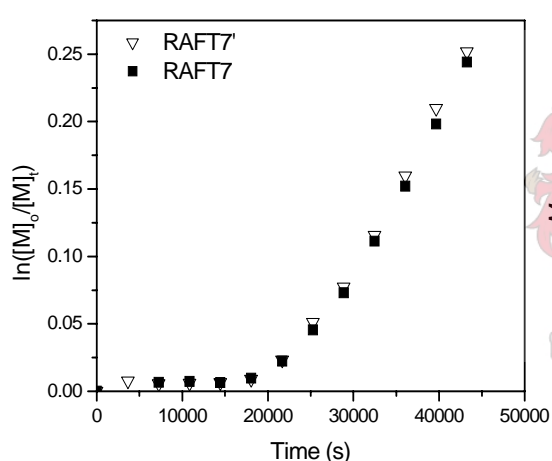
### a) Diphenyldithioperoxyanhydride: RAFT agent precursor 7

Figures 4.20, 4.23 and 4.26 show the kinetic plots of the bulk polymerisation of styrene using the RAFT agent precursors 7 through 9. These figures show first that the conversion of styrene was low at the early stage of the reactions. This inhibition is probably due to:

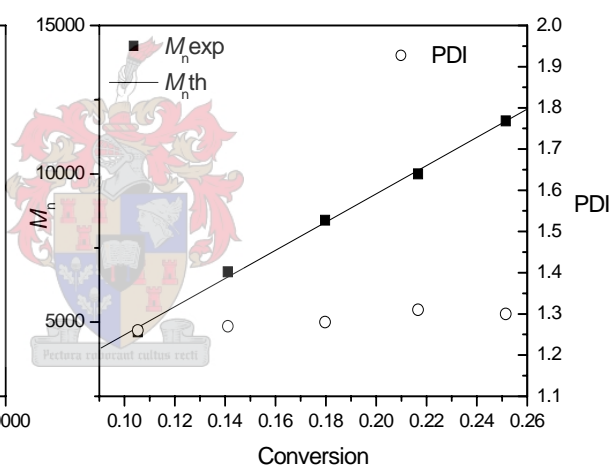
- Slow fragmentation of initial intermediate radicals of disulfide in order to form the new RAFT agent with styryl as a leaving group (Scheme 5.1).
- Slow propagation of benzyl sulfur radical as initial leaving group

More details about the above are given later (Section 5.4, Chapter 5).

Second, after this inhibition period, the plot of  $\ln([M]_0/[M]_t)$  versus time reached higher conversions, indicating the bulk polymerisation of styrene was first-order with respect to the monomer concentration; this is shown in Figures 4.20, 4.23 and 4.26. These figures also demonstrate that the reactions were in good agreement with duplicate experiments.



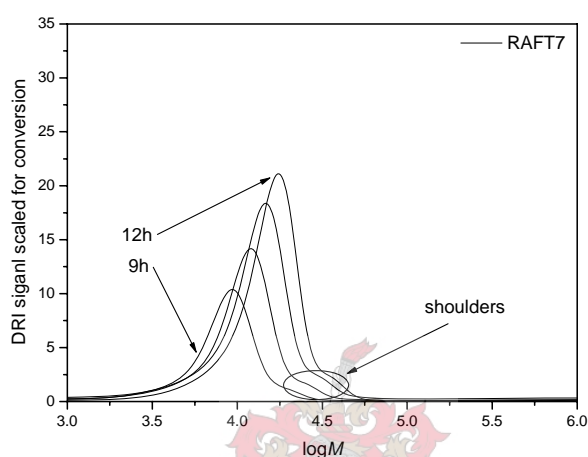
**Figure 4.20** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent precursor 7 at 100°C. RAFT agent precursor 7' demonstrates that the reaction was reproducible.



**Figure 4.21** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)

Figures 4.21, 4.24, and 4.27 show the plots of  $M_n$  and polydispersity versus conversion for the thermal polymerisation of styrene using RAFT agent precursors 7, 8 and 9. In all cases the molar mass  $M_n$  increases linearly with monomer conversion and the measured molar masses ( $M_{n,exp}$ ) are close to the theoretically predicted ( $M_{n,th}$ ) values. This testifies to the living character of the polymerisation. The polydispersities indices of the resulting polystyrene were relatively low using diphenyldithioperoxyanhydride as chain transfer agent (RAFT agent precursor 7) in the RAFT polymerisation of styrene proved that the polymerisation of styrene was controlled.

The MMD peaks as a function of conversion are shown in Figure 4.22. The RAFT polymerisations of styrene using the RAFT agent precursor 7 as chain transfer agent yielded polymers with controllable molar masses and narrow MMD. The shifting of MMD towards the higher molar mass, as shown in Figures 4.22 is another indication of the living character. However, the presence of shoulders to high molar mass in Figure 4.22 indicates that termination reactions of long chains still occur despite the use of the RAFT agent precursor 7. The presence of tailing in the lower molar mass regions (Figure 4.22) could be due to termination of short species. This is explained in Chapters 5 and 6, in Sections 5.4 and 6.2.

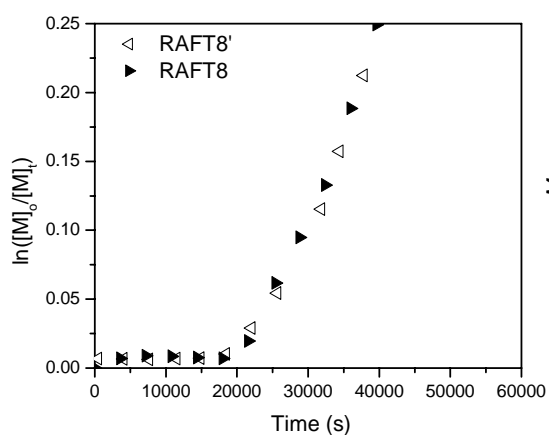


**Figure 4.22** Normalized MMDs of samples taken from experiment (7) where RAFT agent precursor 7 was used.

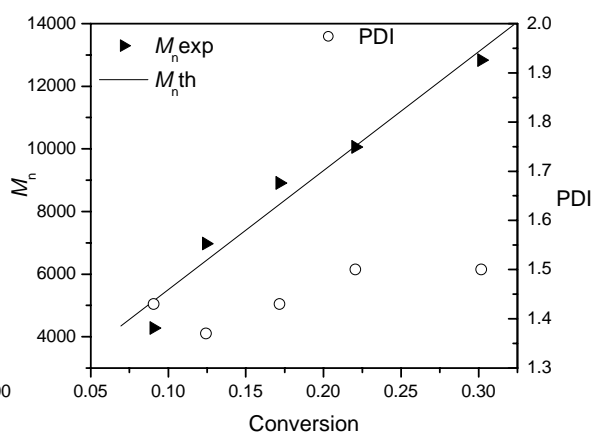
### b) Bis(4-methylphenyl)dithioperoxyanhydride: RAFT agent precursor 8

The plot of  $\ln ([M]_0/[M]_t)$  versus time, and the number average molar mass and polydispersity for the styrene polymerisation using the RAFT agent precursor 8 are shown in Figures 4.23 and 4.24 respectively.

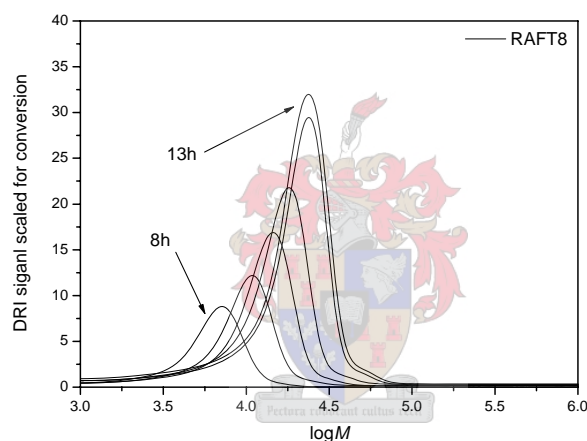
The evolution of MMD peaks as a function of conversion is shown in Figure 4.25. At higher conversions, while the polymerisation is taking place, some low molar mass tailing can be observed in the chromatograms depicted in Figure 4.25. The low molar mass tailing is also reflected in the somewhat higher polydispersity index ( $PDI = 1.5$ ) of the polymer product produced in the experiment where bis(4-methylphenyl)dithioperoxyanhydride (RAFT agent precursor 8) was used as mediator. See Table 8 in the Appendix. Thus, using bis(4-methylphenyl)dithioperoxyanhydride as chain transfer agent, the RAFT polymerisation of styrene was found to be controlled. This was confirmed by the shifting of MMD towards the higher molar mass, as shown in Figures 4.25.



**Figure 4.23** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent precursor 8 at 100°C. RAFT agent precursor 8' demonstrates that the reaction was reproducible.



**Figure 4.24** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)

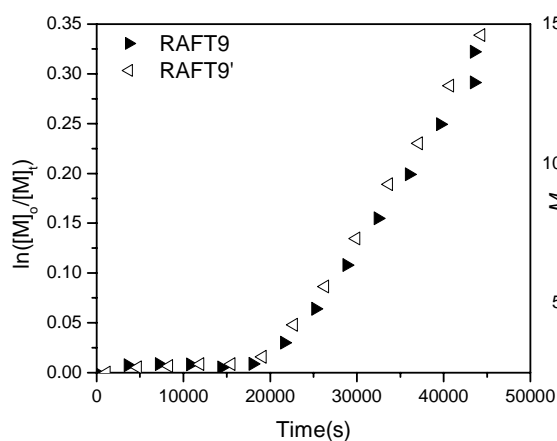


**Figure 4.25** Normalized MMDs of samples taken from experiment (8) where RAFT agent precursor 8 was used.

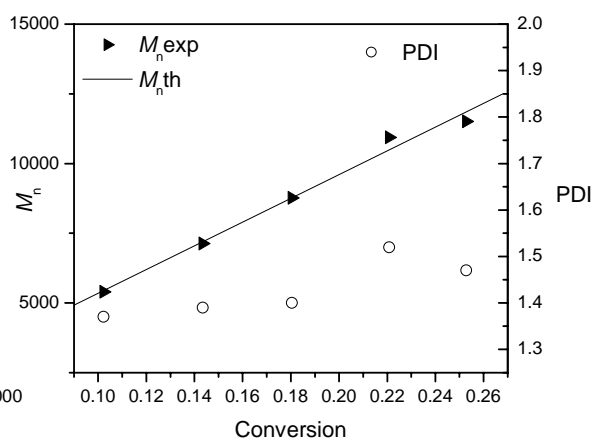
### c) Bis(4-methoxyphenyl)dithioperoxyanhydride: RAFT agent precursor 9

This RAFT agent precursor 9 showed similar behaviour to that exhibited by RAFT agent precursors 7 and 8. However, the polydispersities of the resulting polymer with RAFT agent precursor 9 were larger than values of polymers prepared with RAFT agent precursors 7 and 8; values were 1.30 for RAFT agent precursor 7, 1.50 for RAFT agent precursor 8 and 1.47 to 1.52 for RAFT agent precursor 9 (Figure 4.27). These results are summarized in Table 9 in the Appendix.

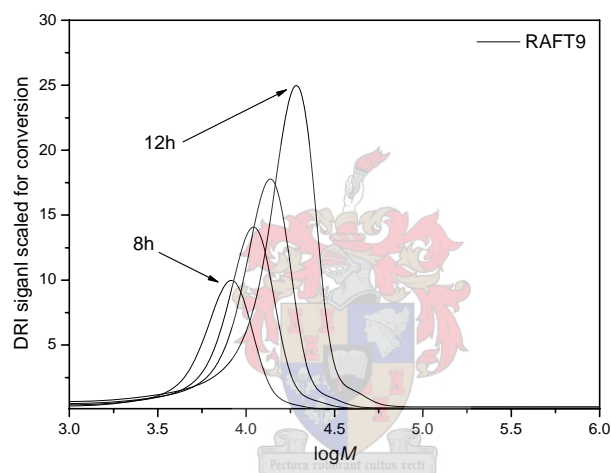
The shift towards the high molar mass is clearly observed in Figure 4.28. This indicated the living character of these RAFT agents.



**Figure 4.26** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent precursor **9** at 100°C. RAFT agent precursor **9'** demonstrates that the reaction was reproducible.



**Figure 4.27** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)



**Figure 4.28** Normalized MMDs of samples taken from experiment (**9**) where RAFT agent precursor **9** was used.

#### 4.6.2.5 1-methyl-1-phenylethyl benzenecarbodithioate and its derivatives

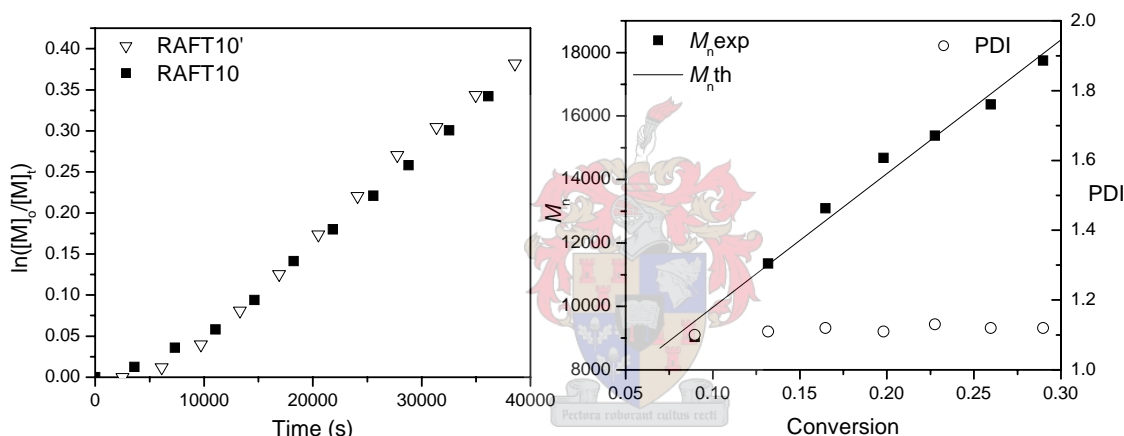
The polymerisation of styrene was also conducted using 1-methyl-1-phenylethyl benzenecarbodithioate and its derivatives as RAFT agents. These polymerisation reactions showed a short inhibition period (2-3 hours) (see Figures 4.29, 4.32, 4.35 and 4.38) compared to the cases of disulfides (Sections 4.6.2.4a-c). This short inhibition period is often observed in RAFT polymerisation and is particularly common when 1-methyl-1-phenylethyl benzenecarbodithioate is used as the CTA.<sup>5,6</sup> After this period, the rate of polymerisation increases significantly with an increase in polymerisation time. Figures 4.30, 4.33, 4.36 and 4.39 show the relationships between molar mass and monomer conversion in these experiments. The PDI values of the polymers being prepared using those chain transfer agents show similar trends; they are relatively low.



The four cumyl functional RAFT agents studied here are: 1-methyl-1-phenylethyl benzenecarbodithioate, 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate, 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate and 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate.

### a) 1-methyl-1-phenylethyl benzenecarbodithioate: RAFT agent 10

Results of the homopolymerisation of styrene via 1-methyl-1-phenylethyl benzenecarbo-dithioate (RAFT agent 10) are displayed in Figures 4.29 through 4.31 and Table 10 in the Appendix. The plot of  $\ln([M]_0/[M]_t)$  versus time is shown in Figure 4.29. In this figure the straight line indicates first-order kinetics with respect to monomer and that the concentration of propagating radicals remains constant during the polymerisation. It can also be seen that the monomer conversion increases with reaction time. Figure 4.29 shows that the reaction was also reproducible; this is shown by the good agreement between duplicate experiments.



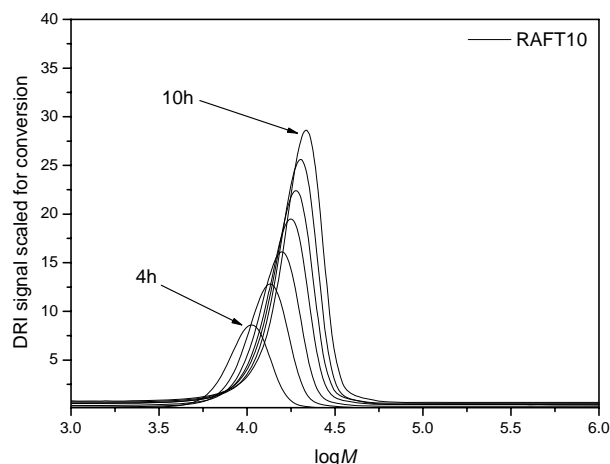
**Figure 4.29** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 10 at 100°C. RAFT agent 10' demonstrates that the reaction was reproducible.

**Figure 4.30** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)

In Figure 4.30 the number average molar mass,  $M_n$ , and polydispersity, PDI, for a styrene polymerisation using the chain transfer agent 10 are shown as a function of conversion. In this figure, the  $M_n$  of the resulting polystyrene increased from 9 000 to 18 000, proportionally, with increasing monomer conversion from 9% to 29%. The molar mass distributions possess polydispersity indexes that are below 1.2. These results indicate that the controlled radical polymerisation of styrene can be carried out with RAFT agent 10.

Figure 4.31 shows the shift of the MMD peaks as a function of conversion. The SEC trace shows an increase in molar mass of a unimodal nature, thus it could be concluded that this is indeed a LRP. The tailing noted in the low molar mass region is believed to be due to linear dormant chains and polymer from radical-radical termination of linear propagating radicals. Figure 4.31 also shows an

insignificant tailing towards the high molar mass. This might be indicative of uncontrolled polymerisation reactions taking place too.



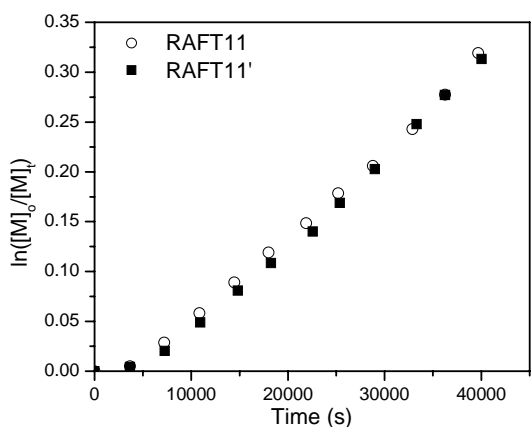
**Figure 4.31** MMDs of samples scaled for conversion taken from experiment (10) where RAFT agent 10 was used.

#### **b) 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate: RAFT agent 11**

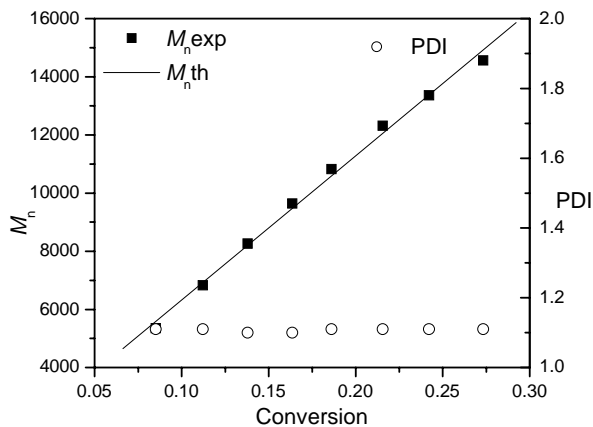
As in the experiments mediated by the previously discussed RAFT agents (1 through 10), the linear relationship obtained between the semi-logarithmic plots of fractional conversion versus time observed in Figure 4.32 indicates that the number of propagating species remained constant during the polymerisation of styrene using 1-methyl-1-phenylethyl 4-methylbenzenecarbo-dithioate as RAFT agent 11.

Figure 4.33 shows the evolution of the molar mass of the polymer,  $M_n$ , and the PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by the RAFT agent 11. As expected for a living free-radical polymerisation, the molar mass of the polymer grows linearly with increasing conversion (Figure 4.33). The constant values of PDI (1.11) obtained demonstrate therefore that RAFT agent 11 is an effective CTA for the thermally initiated RAFT polymerisation of styrene.

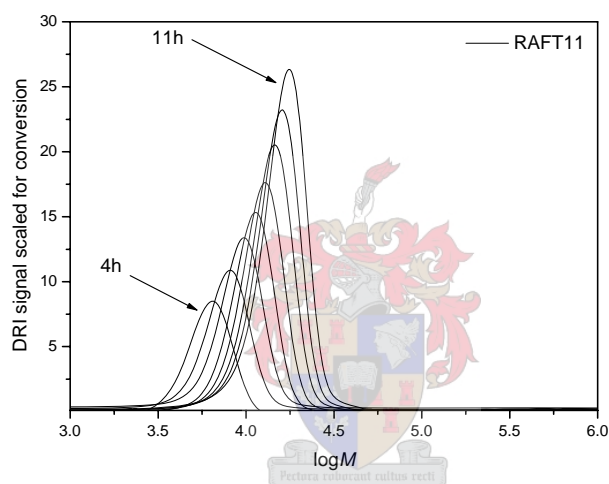
Figure 4.34 shows the narrow distributions of the MMD peak toward high molar masses. This confirms the living nature of the polymerisation. The tailings noted in the low and high molar mass regions are reduced but terminations are still occurring.



**Figure 4.32** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 11 at 100°C. RAFT agent 11' demonstrates that the reaction was reproducible.



**Figure 4.33** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)



**Figure 4.34** MMDs of samples scaled for conversion taken from experiment (11) where RAFT agent 11 was used.

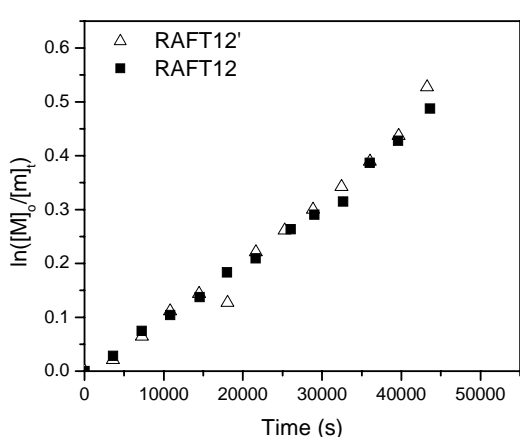
### c) 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate: RAFT agent 12

Figure 4.35 shows that, using 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate (RAFT agent 12), the first-order kinetic plot is linear until fairly high conversions, indicating that the concentrations of active species were constant for a significant part of the polymerisation of styrene.

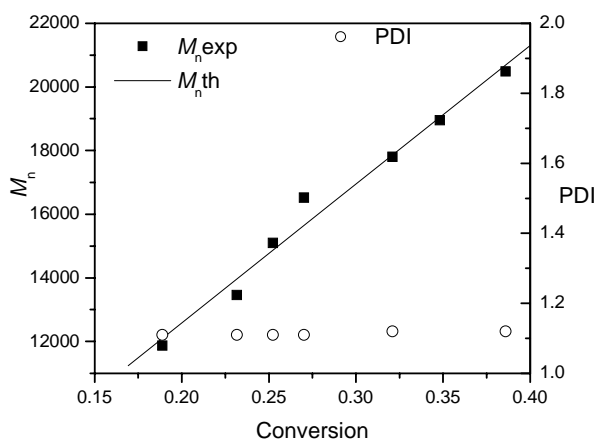
Figure 4.36 shows the evolution of the molar mass of the polymer,  $M_n$ , and the PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agent 12. The results shown in Figure 4.36 and Table 12 in the Appendix indicate an increase in molar mass with conversion. This is characteristic of living radical polymerisation.

Figure 4.37 shows the narrow distributions of the MMD peak toward high molar masses. The distributions shown in Figure 4.37 further support the living nature of the polymerisation, as

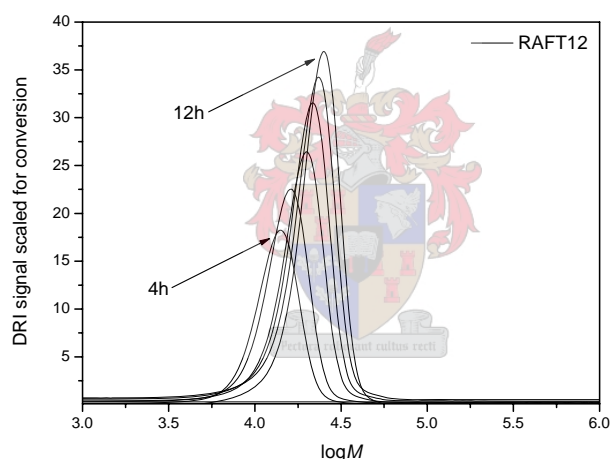
evidenced by the shift of the MMD peak toward larger molar masses. However, the presence of tailing proves that terminations of short species still occur.



**Figure 4.35** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 12 at 100°C. RAFT agent 12' demonstrates that the reaction was reproducible.



**Figure 4.36** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,th}$  are the experimental and theoretically calculated molar masses.)

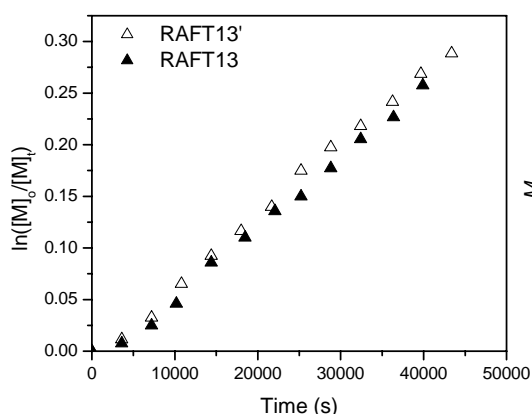


**Figure 4.37** MMDs of samples scaled for conversion taken from experiment (12) where RAFT agent 12 was used.

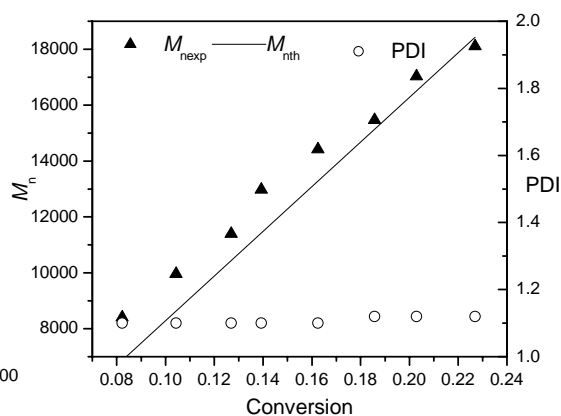
#### d) 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate: RAFT agent 13

The first-order kinetic plot of the polymerisation of styrene using 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate (RAFT agent 13) is shown in Figure 4.38. A linear plot of  $\ln([M]_0/[M]_t)$  versus time using RAFT agent 13 was obtained, indicating that the number of propagating species remained constant.

SEC traces for the polymerisation of styrene in the presence of 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate (RAFT agent 13) can be seen in Figures 4.37 and 4.40.



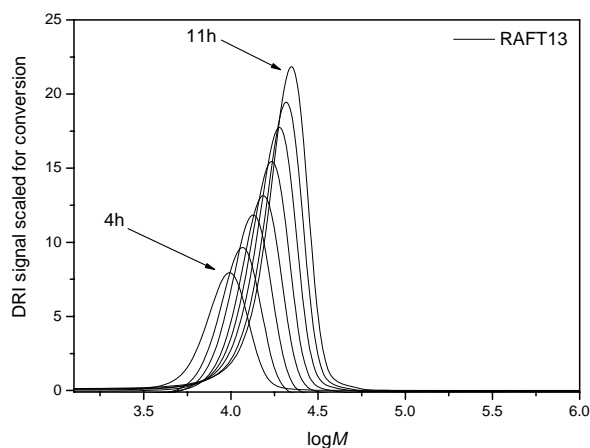
**Figure 4.38** Semi-logarithmic plot of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent 13 at 100°C. RAFT agent 13' demonstrates that the reaction was reproducible.



**Figure 4.39** Plots of  $M_n$  and polydispersity as a function of conversion. ( $M_{n,exp}$  and  $M_{n,theo}$  are the experimental and theoretically calculated molar masses.)

Figure 4.39 clearly indicates the living nature of the system, as evidenced by the steady increase in molar mass as a function of conversion. The predicted number average molar mass was calculated according to the equation Eq.2.5 mentioned in Section 2.6.5. The experimental  $M_n$  values are similar to the theoretically calculated  $M_n$  values. This is a strong indication of the controlled nature of the system, which is further strengthened by the low polydispersity index values obtained ( $1.1 < PDI < 1.2$ ).

Figure 4.40 shows the shift of the MMD peaks as a function of conversion; this clearly proves the living nature of the polymerisation. Some tailing though reduced compared to RAFT agents 11 and 12 are seen towards the lower and higher molar mass regions; this is due to reduced terminations of short and long species respectively.



**Figure 4.40** MMDs of samples scaled for conversion taken from experiment (13) where RAFT agent 13 was used.

## 4.7 Conclusions

In Chapter 2 the features of living radical polymerisation were discussed. These are essentially internal first-order kinetics with respect to monomer, and narrow molar mass distribution. Thus, in a series of thirteen experiments, the ability of thirteen thiocarbonyl thio compounds to control the homopolymerisation of styrene was studied. From the data presented in this chapter, it can be said without any doubt that the polymerisation of styrene was controlled using the aforementioned RAFT agents 1 through 6, 10 through 13 and RAFT agent precursors 7 through 9. The relatively narrow MMDs obtained from all the RAFT mediated reactions are evidence of this (Figures 4.4, 4.7, 4.10, 4.13, 4.16, 4.19, 4.22, 4.25, 4.28, 4.31, 4.34, 4.37, and 4.40). Moreover, the linear increase in  $M_n$  as a function of monomer conversion, observed in Figures 4.3, 4.6, 4.9, 4.12, 4.15, 4.18, 4.21, 4.24, 4.27, 4.30, 4.33, 4.36 and 4.39, is another indication of the living character of the polymerisation. All these results, added to the fact that polymers with low polydispersity indices significantly below 1.5 were prepared with RAFT agents 1 through 6, 10 through 13 and RAFT agent precursor 7, and the good agreement observed between experimental and calculated molar masses confirm that these RAFT agents were efficient in controlling the styrene polymerisation.

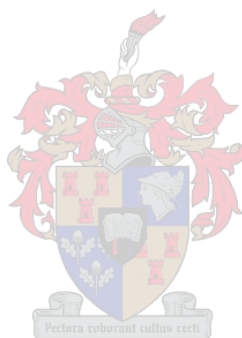
Except with RAFT agent precursors 8 through 9, low values of polydispersity indices obtained with the other RAFT agents and the narrow molar mass distributions with conversion, indicate that these RAFT agents have a higher initial chain transfer constant. This is most likely due to the good homolytic leaving ability of the cyanoisopropyl, cyanovaleric acid and cumyl group compared to the benzyl sulfur group. More details are given in Chapters 5 and 6.

In the styrene polymerisations using RAFT agent precursors 7 through 9 there is no polymerisation during the first 6 h (zero conversion). This strong inhibition in the early stages of the polymerisation

is considered to be a result of a low fragmentation rate of the RAFT radical precursor (intermediate radical) leading to the formation of active chain transfer agents. This is discussed in Chapters 5 and 6. The appearance of a high molar mass shoulder at higher conversions (Figures 4.22, 4.25 and 4.28) indicates that some termination reactions occur. These termination reactions usually occur when two growing macroradicals combine. The increase in PDI in the later stages of the styrene polymerisations where RAFT agent precursors 7 through 9 were employed justifies the presence of dead chains.

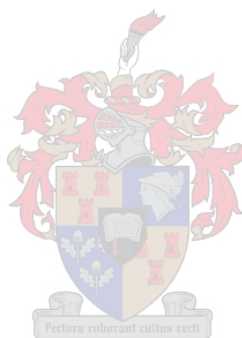
The semi-logarithmic plots of fractional conversion versus time of the reaction of the thirteen respective selected RAFT agents show good agreement with those of duplicate experiments.

After studying the general behaviour of the thirteen chain transfer agents used in this study, an attempt was made to understand how the respective Z and R groups of the RAFT agents affect the rate of polymerisation of styrene. This will be discussed in Chapters 5 and 6 respectively.



## 4.8 References

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*“If we knew what it was we were doing, it would not be called research would it?” Albert Einstein.*

## *CHAPTER 5: The activity of the dithiobenzoates and derivatives as a function of phenyl Z group modification*

In Chapter 4, the living radical polymerisation of styrene was successfully performed in the presence of thirteen dithiobenzoates compounds. In Chapter 4 the effect of the phenyl substituent (Z group) of the thirteen chain transfer agents are investigated by grouping the RAFT agents according to the same R group. Two different classes of RAFT agents were therefore identified. The first one comprises three series of monofunctional RAFT agents, which differ according to their respective R groups, including:

- Series A: Cyanoisopropyl (R group)
- Series B: Cyanovaleric acid (R group)
- Series C: Cumyl (R group).



The second class comprises disulfides or precursors of RAFT agents (compounds that can be converted into or used to form active RAFT agents).

The kinetics of diphenyldithioperoxyanhydride and derivatives, contrary to 1-methyl-1-phenylethyl benzenecarbodithioate and derivatives, were characterized by strong inhibition periods.

SEC was the technique applied in order to be able to compare the molar masses and the polydispersity indexes of the homopolymers produced by these RAFT agents.

The comparison studies between electron donating and electron withdrawing substituents (Z phenyl derivatives) show an almost similar trend in the control of the polymerisation of styrene.

## 5.1 Introduction

In Chapter 2 it was shown that the rate of addition of radicals to dithioesters is strongly influenced by the substituent group Z of the RAFT agent.<sup>1</sup> Consequently, the substituents that stabilize intermediate radicals are responsible for the slow rate of fragmentation of these intermediate radicals. In other words, the substituent group Z is also expected to influence the rate of fragmentation of the intermediate radicals (**2**) and (**4**) (Scheme 2.8). This part of the current study focuses on the examination of the effect of the Z substituent in the RAFT polymerisation of styrene. Here the R groups were selected to be the same. R varied in four different series: including cyanoisopropyl, cyanovaleric acid, cumyl groups and benzyl sulfur and its derivatives. Figures 5.1 through 5.12 compare the effects of ten RAFT agents with four types of Z groups and summarize their reactivities. The ratios of monomer to RAFT agent were chosen to be all the same, which is:

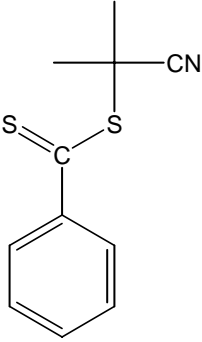
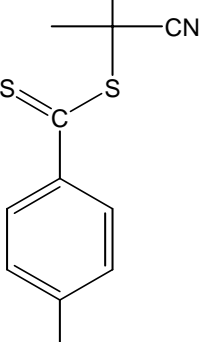
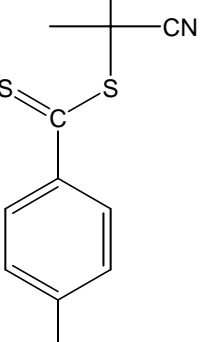
$$[\mathbf{M}]_0/[\mathbf{RAFT}]_0 = 9.615 \times 10^{-3} / 1.25 \times 10^{-5} = 770.$$

Series A displays the activity of 1-cyano-1-methylethyl benzenecarbodithioate and its derivatives in the polymerisation of styrene. Table 5.1 shows the compounds, which comprise the series A.

## 5.2 Series A: 1-cyano-1-methylethyl benzenecarbodithioate and its derivatives: Z-(C=S)-SC(CH<sub>3</sub>)<sub>2</sub>CN

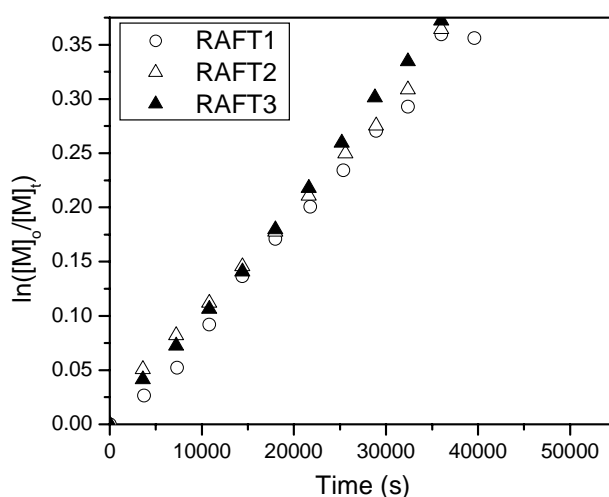
1-cyano-1-methylethyl benzenecarbodithioate with Z as phenyl ring (RAFT agent 1), 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate having Z as 4-methylphenyl (RAFT agent 2) and 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate with Z as 4-methoxyphenyl (RAFT agent 3) are the RAFT agents that comprise the series A, see Table 5.1.

**Table 5.1: 1-cyano-1-methylethyl benzenecarbodithioate and derivatives**

| RAFT agent 1: 1-cyano-1-methylethyl benzenecarbodithioate                         | RAFT agent 2: 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate                 | RAFT agent 3: 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate                  |
|---|---|---|
|  |  |  |

For the comparison studies, 1-cyano-1-methylethyl benzenecarbodithioate as RAFT agent 1 was chosen because it is one of the most studied RAFT agents.<sup>2,3</sup> It has also been reported to be an efficient RAFT agent in the polymerisation of styrene and other monomers such as methyl methacrylate (MMA).<sup>4,5</sup> In addition, its phenyl Z group provides retardation in polymerisation rates.<sup>6</sup> The use of its derivatives (Z group) such as 4-methyl thiobenzoyl and 4-methoxy thiobenzoyl with electron donating substituents (see Table 5.1 above) in the para-position on the phenyl ring might increase the polymerisation rates.

Figure 5.1 is the result of studying the relationship between  $\ln([M]_0/[M]_t)$  and polymerisation time for the RAFT agents 1 through 3.



**Figure 5.1** Semi-logarithmic plots of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agents 1 through 3 at 100°C.

Inspection of Figure 5.1 indicates that the three polymerisations proceed at almost the same overall rate of reaction, with only slight differences, which can be explained either by the errors margins or

by the difference of the Z groups (phenyl thiobenzoyl, 4-methylphenyl thiobenzoyl and 4-methoxyphenyl thiobenzoyl). The polymerisation reactions mediated by the RAFT agents 3 and 2 seem to proceed slightly faster than the one with RAFT agent 1. The information about the above Z groups discussed in Section 2.7, is very useful for rationalizing and predicting the course of the reactions. Indeed, compounds with electronic effects (inductive effect or resonance effect), such as 4-methoxyphenyl and 4-methylphenyl, have the ability to influence chemical reactions such as electrophilic substitution reactions by enhancing yields in those reactions compared to the case where phenyl is used.

According to the electronic effects of the three Z groups in the present case, one would expect to see a significant difference in overall rates of polymerisation; in other words, the order of decreasing polymerisation rate is expected to be RAFT agent 3 > RAFT agent 2 > RAFT agent 1. In contrast to the prediction, almost the same polymerisation rate was obtained with the three RAFT agents during the polymerisation of styrene. Thus, after 10 h of reaction, under the same polymerisation conditions the following was obtained: a conversion of 31% with RAFT agent 3, 31% with RAFT agent 2 and 30% of with RAFT agent 1. (See Figure 5.1, and Tables 1-3 in the Appendix). The finding displayed in Figure 5.1 suggests that, in the reactions the performed, substituents' electronic effect on the Z group does not play a significant role in the current Z group studied.

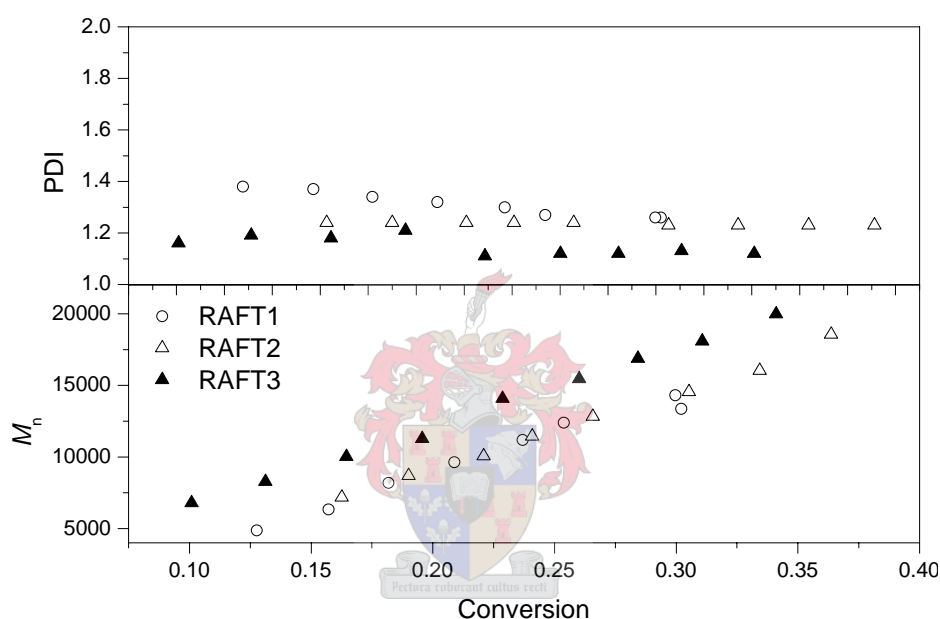
The results of the polymerisation of styrene for the series of 1-cyano-1-methylethyl benzenecarbodithioate and its derivatives show also that the final conversion was relatively low in all cases compared to the polymerisation of styrene by the thermal autoinitiation in the absence of RAFT agent (Figure 4.1 in Section 4.6.1). Indeed, after 7 hours of reaction, the percentage conversions in the reactions were 21% with RAFT agent 1, 22% with RAFT agent 2 and 23% with RAFT agent 3 (see Tables 1 through 3 in the Appendix) whereas 35% was obtained by the thermal autoinitiation of styrene after the same reaction time (7 h) (see Figure 4.1).

In conventional free radical polymerisation, the rate of initiation is much smaller than the rates of propagation and termination. When a polymeric chain is initiated, it propagates and terminates very fast before a new chain is initiated. In the RAFT process, the initiation rate is larger than the average propagation rate. Compared to the propagation, most of the polymeric chains are initiated at the same time, and they growth simultaneously. At the same time, the extent of irreversibly terminated chains is small. Thus, the introduction of the RAFT agent in the polymerisation of styrene might be to modify the relative rates of propagation and initiation.

After 7 h comparisons could not be made between both living radical polymerisation and free radical polymerisation because it became difficult to take samples from the thermal polymerisation

of styrene, due to fact that the reaction medium became increasingly viscous. In fact, in bulk polymerisation the viscosity is considered as a major drawback because it increases with conversion/time (see Section 2.11.4). Thus, one can understand why, after 11 h to 16 h of RAFT reaction, it became difficult to take samples from the reaction flask using a syringe. Further, there was no evidence of autoacceleration (Section 2.12) resulting in a viscosity increase during polymerisation and this is consistent with the obtained results (low yields mentioned above).

Figure 5.2 shows the evolution of the molar mass of the polymer,  $M_n$ , and the PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C in a reaction mediated by the three RAFT agents 1-3 respectively.



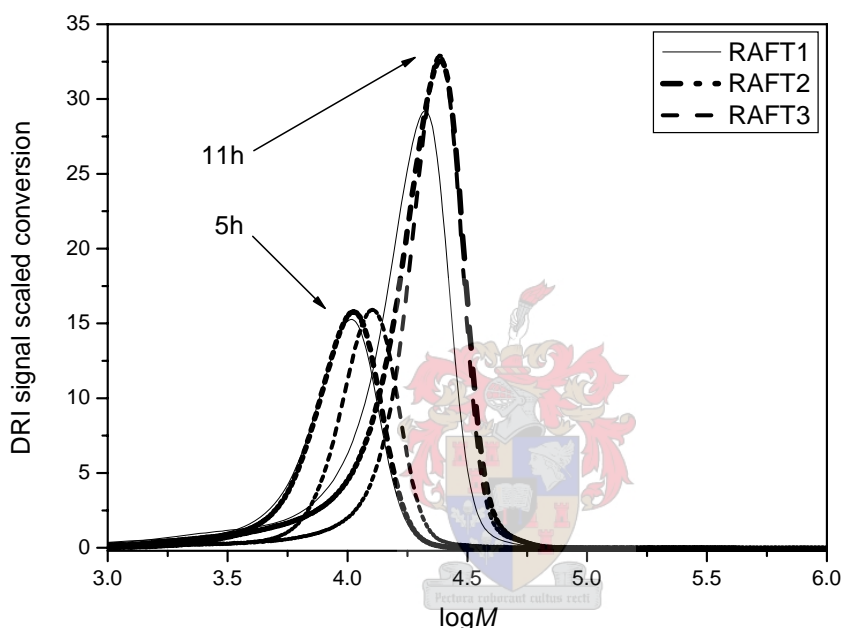
**Figure 5.2** Evolution of the number average molar mass,  $M_n$ , and the polydispersity index, PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agents 1 through 3.

As expected for a living free radical polymerisation, the molar mass of the polymer grows linearly with increasing conversion (see Figure 5.2). From this figure, a linear increase of the molar mass,  $M_n$ , with conversion is observed, keeping a low polydispersity ( $\text{PDI} < 1.3$ ). These are good indications of a living process. However, the molar mass,  $M_n$ , of styrene is slightly higher in the reaction with RAFT agent 3 in contrast to reactions with RAFT agents 2 and 1, which yield identical molar mass versus conversion traces (Figure 5.2). This is a surprising result, because all three RAFT agents were used in the same concentrations ( $[\text{RAFT}]_0 = 1.25 \times 10^{-5} \text{ M}$ ) and all are supposed to have an efficient chain transfer equilibrium.

Figure 5.2 also shows that the polydispersity evolution with monomer conversion is in agreement with later results (Figure 5.5) for other RAFT systems.<sup>7</sup> Indeed, an initial decrease in the PDI was observed at low conversions, followed by a constant value of PDI towards higher monomer

conversion; PDIs 1.37 to 1.25 for RAFT agent 1, 1.24 to 1.23 for RAFT agent 2 and 1.21 to 1.12 for RAFT agent 3. It should be noted that the polydispersities of the resultant polymers remained low ( $PDI < 1.3$ ) during the polymerisations. Thus, findings suggest that RAFT agents 3 and 2 have higher transfer coefficients than the RAFT agent 1 or less termination during the initial stages (less low molar mass tailing).

Figure 5.3 shows the shift of the MMD peaks as a function of conversion. The SEC trace showed an increase in molar mass with unimodal nature. Thus it can be concluded that this is indeed a LRP. The narrowing MMD peaks support the idea that the RAFT agents 3 and 2 have higher transfer coefficients than the RAFT agent 1.



**Figure 5.3** MMDs for the homopolymerisation of styrene at 100°C mediated by RAFT agents 1 through 3.

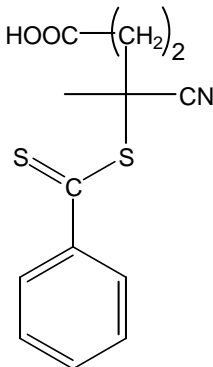
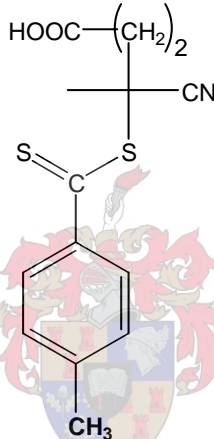
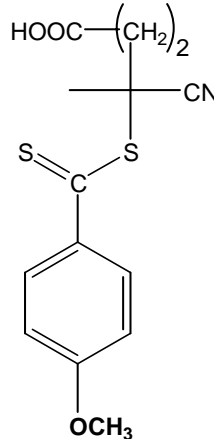
The tailing noted in the low and high molar masses indicates that transfer and termination reactions still occur, but not to the extent that control of MMD is significantly affected. RAFT agent 3 shows the least low molar mass tailing.

Thus far, it has been demonstrated that the electronic effect along the Z group only has a small effect on the polymerisation rate when the substituted and unsubstituted phenyl Z group is used. At this point the following questions could be posed: What could mainly influence the polymerisation rate in these cases? Would the previous observations change if the cyanoisopropyl radical (as the leaving R group) for the series A was replaced by the cyanovaleric acid radical? These are the questions that will be answered in the next series B, C and D (Sections 5.3 through 5.5).

### 5.3 Series B: 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid and its derivatives: Z-(C=S)-(S)-C(CH<sub>3</sub>)-(CN)CO<sub>2</sub>H

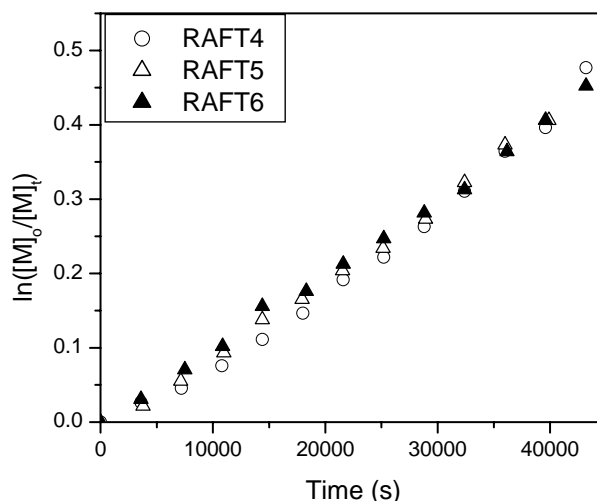
4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid (RAFT agent 4), 4-cyano-4-[[4-(4-methylphenyl)carbothioyl]sulfanyl]pentanoic acid (RAFT agent 5) and 4-cyano-4-[[4-(4-methoxyphenyl)carbothioyl]sulfanyl]pentanoic acid (RAFT agent 6) are the CTAs that comprise the series (B). All have the same cyanovaleric acid as leaving group (see Table 5.2).

**Table 5.2: 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid and its derivatives**

| RAFT agent 4: 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid                | RAFT agent 5: 4-cyano-4-[[4-(4-methylphenyl)carbothioyl]sulfanyl]pentanoic acid    | RAFT agent 6: 4-cyano-4-[[4-(4-methoxyphenyl)carbothioyl]sulfanyl]pentanoic acid     |
|--|--|--|
|  |  |  |

To determine the efficacy of the RAFT agents 4 through 6, the results obtained from the reactions with RAFT agents 5 and 6 were compared with those of RAFT agent 4, which is one of the most frequently used RAFT agent in polymerisation systems.<sup>8-10</sup> The conditions under which the homopolymerisation of styrene mediated by the three RAFT agents 4 through 6 was carried out were the same as in the previous case. The results are reported in Figures 5.4 through 5.6.

The semi-logarithmic function of monomer concentration ( $\ln([M]_0/[M]_t)$ ) versus time is shown in Figure 5.4.



**Figure 5.4** Semi-logarithmic plots of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agents 4 through 6 at 100°C.

As seen in the previous series A, here Figure 5.4 also indicates that the three polymerisations proceed at almost the same overall rates of reaction, with only slight differences. It should be noted that the number of growing chains with these three RAFT agents 4 through 6 is constant throughout the polymerisations.

Moreover, it is noteworthy that the rates of polymerisation within the series B are identical; these results are similar to those recorded for the series A. Thus, the difference in electronic delocalisation that occurred along each specific thiobenzoyl Z phenyl and its derivatives was unable to allow the formation of intermediate radical species with significant differences in terms of the intermediate radical's lifetime, concentration and reactivity. If it had been the case, we might have observed differences in the polymerisation rates of styrene for the three reactions. The results obtained here could however not be justified in terms of stability of the leaving radical, because the cyanovaleric acid radical (R group) was also kept constant within the series B, as compared to the series A with the cyanoisopropyl radical.

The evolution of number average molar mass,  $M_n$ , for the three RAFT agents 4, 5 and 6 with conversion for the bulk polymerisation of styrene is characterized by ideal linear increases of  $M_n$  as a function of monomer conversion (Figure 5.5). Moreover, the PDIs of the polymers remained below the benchmark of 1.5, showing that control was achieved in the three RAFT systems. This is a good example of what should be expected in ideal RAFT systems. Moreover, in the series B, all three RAFT agents 4 through 6 presented an excellent trend of the evolution of polydispersity versus conversion: PDI values were first high, then decreased with increasing conversion (Figure 5.5).<sup>7</sup>



It was found that the rate at which polydispersity decreases with conversion was lower with RAFT agent 6 (PDI: 1.28 to 1.22), followed by the RAFT agent 5 (PDI: 1.35 to 1.26), then RAFT agent 4 (PDI: 1.40 to 1.28). See Figure 5.5, and Tables 4 through 6 in the Appendix.

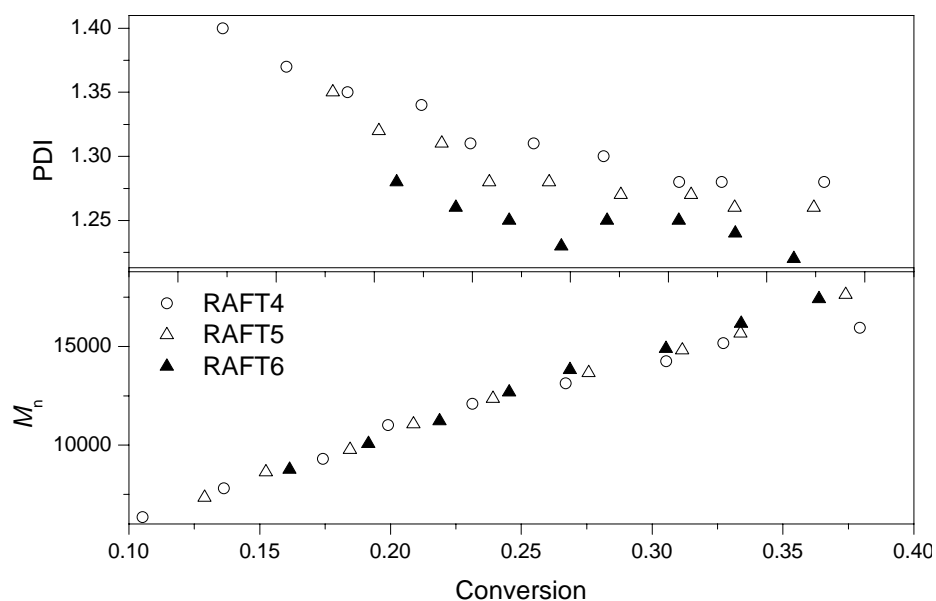


Figure 5.5 Evolution of the number average molar mass,  $M_n$ , and the polydispersity index, PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agents 4 through 6.

Figure 5.6 shows the shift of the MMD peaks as a function of conversion.

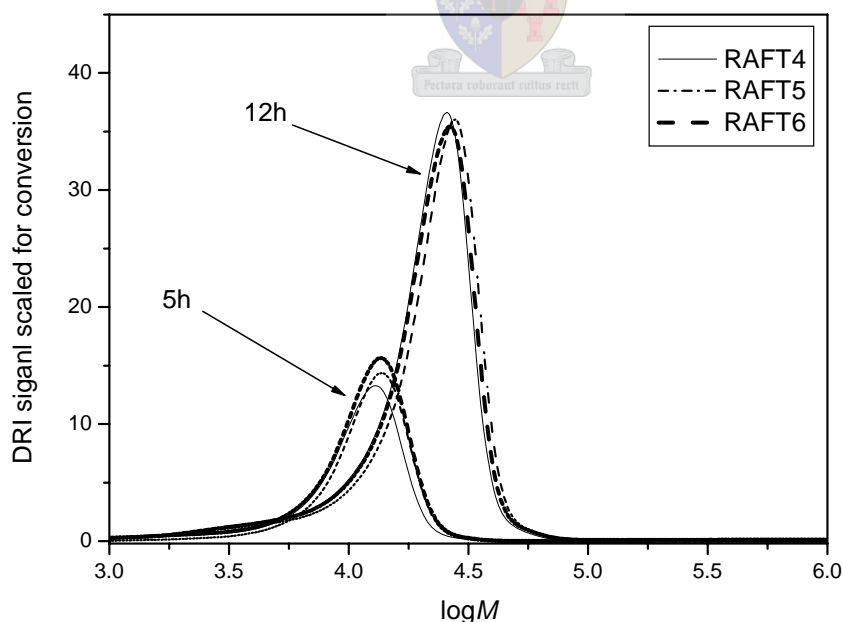


Figure 5.6 MMDs for the homopolymerisation of styrene at 100°C mediated by RAFT agents 4 through 6.

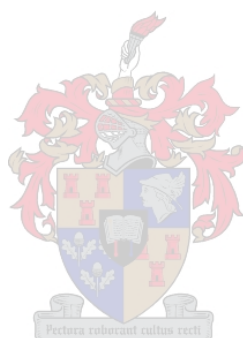
From this figure it is seen that when conversion increased, the SEC peaks shifted towards the region of higher molar masses. These results are indications that the polymerisation of styrene via the three RAFT agents 4 through 6 was controlled. Contrary to the previous series A, the MMD peaks

suggest that the three RAFT agents 4-6 have the same transfer coefficients. Both termination and transfer reactions were present since there is noticeable tailing toward lower and higher molar masses.

Series C of the Z studies concerns diphenyldithioperoxyanhydride and its derivatives.

## 5.4 Series C: Diphenyldithioperoxyanhydride and its derivatives: Z-(C=S<sub>2</sub>)<sub>2</sub>-Z

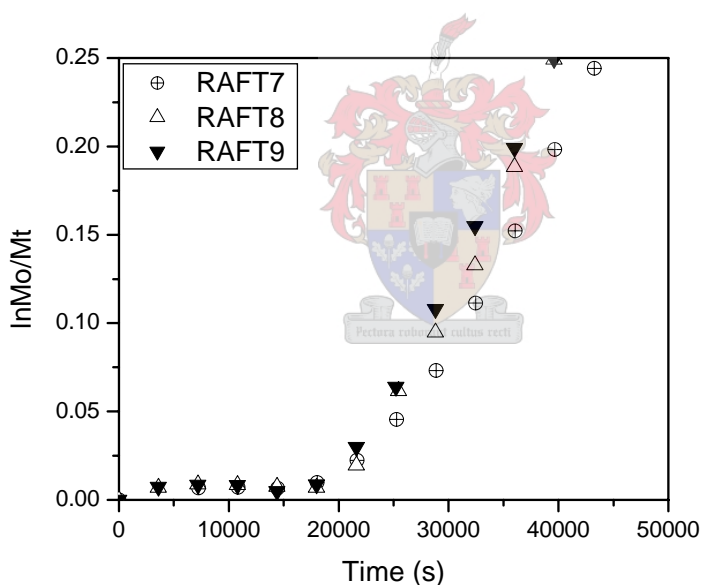
Series C displays the activity of disulfides or precursors of RAFT agents in the polymerisation of styrene. For convenience, the following naming convention will be used: RAFT agent precursor 7 is diphenyldithioperoxyanhydride, RAFT agent precursor 8 is bis(4-methylphenyl)dithioperoxyanhydride and RAFT agent precursor 9 is bis(4-methoxyphenyl)dithioperoxyanhydride. These precursors of RAFT agents are the compounds that comprise the series C. (See Table 5.3).



**Table 5.3: Diphenyldithioperoxyanhydride and its derivatives**

| RAFT agent precursor 7:<br>Diphenyldithioperoxy-<br>anhydride | RAFT agent precursor 8: bis(4-<br>methylphenyl)dithioperoxy-<br>anhydride | RAFT agent precursor 9: bis(4-<br>methoxyphenyl)dithio-<br>peroxyanhydride |
|---|---|--|
|   |   |  |

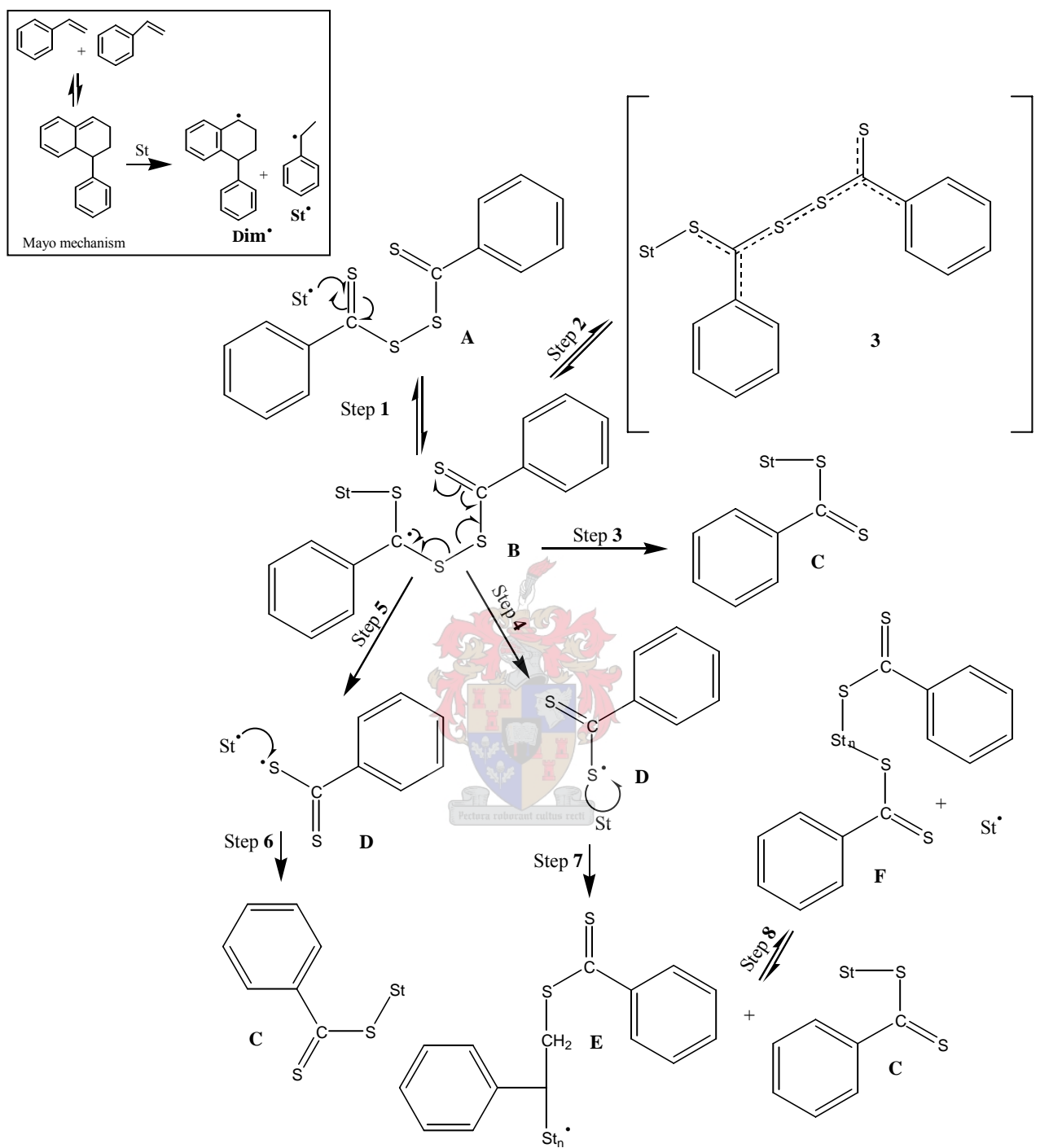
Results are presented in Figures 5.7 through 5.9. The semi-logarithmic function of monomer concentration  $\ln([M]_0/[M]_t)$  versus time is shown in Figure 5.7. Two distinct steps can be seen in all three reactions. The first step lasts approximately six hours. In this step, the slope of each of the polymerisation reactions is equal to zero. A slope of zero means that effectively there is no polymerisation.



**Figure 5.7** Semi-logarithmic plots of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agent precursors 7 through 9 at 100°C.

To understand the effect of the Z group on the effectiveness of the RAFT agent precursors 7-9, the mechanism of the RAFT must be known. The proposed mechanism for styrene polymerisation in the presence of the above RAFT agent precursors (7 through 9) is shown in Scheme 5.1. Despite the symmetric nature of the RAFT agent precursors 7 through 9, the author believes that the RAFT process is a selective process where one, and only one, radical has the ability to initiate the mechanism (step 1, Scheme 5.1). Thus, the mechanism starts by the attack of a selective free radical initiator ( $St\cdot$ ) from the Mayo mechanism (Scheme 4.2 in Section 4.3),<sup>11</sup> leading to formation of intermediate radical (B), which may fragment into two species: a new RAFT agent C (step 3) and a

new radical  $\text{RCS}_2\cdot$  (species D in steps 4 and 5 in Scheme 5.1). It has been assumed that the dimer radical (**Dim** $\cdot$ ) reacts with monomer with the same rate constant as the monomeric radical ( $\text{St}\cdot$ ).<sup>12</sup>



**Scheme 5.1 Mechanism of disulfides mediated polymerisation.**

The radical ( $\text{RCS}_2\cdot$ ) probably does not propagate but adds a new styrene radical to form a second RAFT agent (**C**) (step 6). These reactions occur at diffusion-controlled rates. However, to avoid any termination, the reactions between two radicals ( $\text{RCS}_2\cdot$ ) for example can be slowed down only if benzyl sulfur ( $\text{RCS}_2\cdot$ ) radicals are stabilized by electronic effects<sup>13</sup> or by steric effects.<sup>12</sup>

In the present case, these aforementioned factors are not strong enough to prevent diffusion-controlled recombination of benzyl sulfur radicals ( $\text{RCS}_2\text{-S}_2\text{CR}$ ) or benzyl sulfur radicals with styrene radicals.

Thus, if the reaction between the benzyl sulfur radicals ( $\text{RCS}_2\bullet$ ) and styrene radicals is faster than radical combinations then the result is two identical chain transfer agents (**C**). It is now evident that, to undergo the RAFT process, the two chain transfer agents generated require two other styrene radicals (Scheme 5.1). On the other hand, if the benzyl sulfur radical ( $\text{RCS}_2\bullet$ ) propagates (step 7), in other words, if the reaction between benzyl sulfur radical ( $\text{RCS}_2\bullet$ ) and styrene monomer is faster than radical termination,<sup>13</sup> the resultant adduct will propagate, leading to the formation of a coupled compound<sup>14</sup> (**F**) (step 8 in Scheme 5.1).

The author also believes that after the attack of a selective free radical initiator from the Mayo mechanism<sup>11</sup> to one of the double bonds of the RAFT agent **A** (Scheme 5.1), the intermediate radical (**3**) in step 2 is formed, which then fragments back to the styryl radical and RAFT agent **A**. Then, the styryl radical species can reinitiate the polymerisation by adding to a styrene monomer to form polymeric radicals, which are able to react with the RAFT agent.

Based on the above observations, and to facilitate discussion, the following terms are defined:

1. *Substitution period* is the period in which the precursor is converted into an active RAFT agent.
2. *Precursor* is a compound capable of being converted to another. For instance in Scheme 5.1, compound A is used to form compound C.
3. *Transfer period* is the period in which compound A is converted into the intermediate radical 3. This implies that there is no splitting of the S-S bond after the formation of the intermediate radical B (See Scheme 5.1).
4. 1 and 3, and 1, 5 and 6 are termed *conversion steps* (See Scheme 5.1).
5. 1 and 2 are termed *transfer steps* (See Scheme 5.1).
6. *Initialization period* is the period in which the starting RAFT agent is consumed.

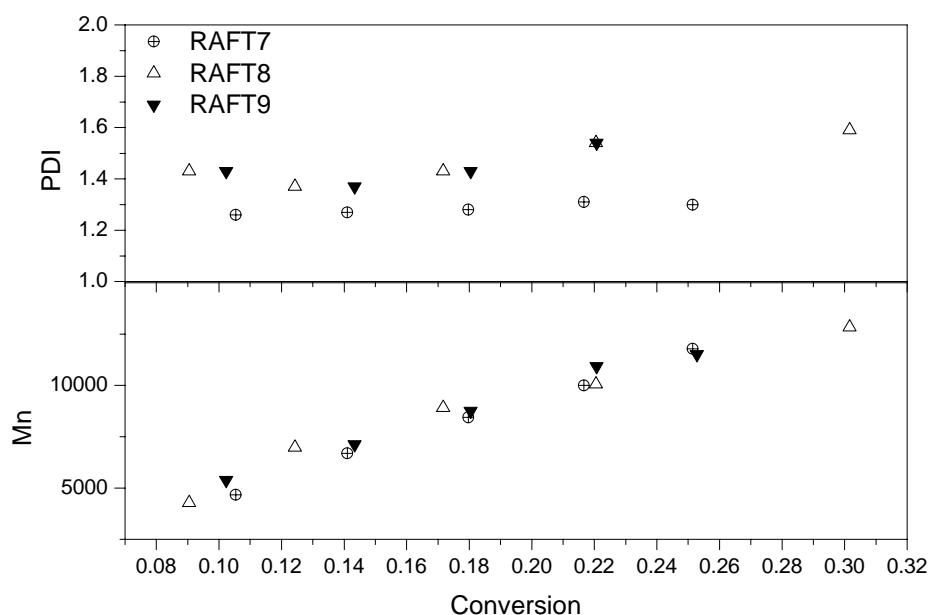
It is clear that the polymerisation of styrene using the disulfide (RAFT agent precursor) starts with the *substitution* period allowing the formation of an active RAFT agent (compound C in Scheme 5.1) and is followed by the consumption of the active RAFT agent (initialisation). Thus, the understanding of both the *substitution* and *initialization periods* is useful in the case of the disulfide in order to explain the strong inhibition (period of no polymerisation) noted (6 h).

In the above mechanism (Schemes 5.1) the polymerisation rate of styrene mediated by the disulfides as dormant chains relies on the lifetime of the so-called intermediate macroRAFT radical and on the sulfur centred radical (species **B**,  $\text{RCS}_2\bullet$  and **3** in Scheme 5.1). Therefore, the lack of polymerisation noted in Figure 5.1 could also be explained by the slow fragmentation of the disulfide intermediate radicals. The possibility that intermediate radicals undergo cross-termination is not high due to the fact that the concentrations of the initially formed intermediate radicals are too low to allow significant amounts of cross-termination. Likewise, fellow researchers, Vosloo *et al.*,<sup>15</sup> have suggested that the species (**D**) may undergo side reactions, other than directly producing RAFT end-capped chains.

After this period of no polymerisation which lasts  $\sim 6$  h (Figure 5.7), the rates of monomer consumption of the three aforementioned RAFT agent precursors (7 through 9) are identical. The inhibition step does not significantly affect the final product, but strongly influences the kinetics of polymerisation. The polymerisation depends therefore on the lifetime of the intermediate radical, on its concentration and on the absence of termination of propagating radicals, and on the first monomer addition. This is in agreement with what was found by Calitz *et al.*<sup>16</sup> They demonstrated that the amount of short chains produced during the early stages of the reactions are proportional to the concentration of intermediate radicals in the reaction flask.

The inspection of Figure 5.7 shows also a slightly lower conversion with the RAFT agent precursor 7. This lower conversion is probably due to the resonance structures of the phenyl ring, which has a stabilizing effect on the intermediate radical species formed in the RAFT process (this was discussed in Section 2.7).

Figure 5.8 shows the evolution of the number average molar mass,  $M_n$ , versus the monomer to polymer conversion for the three RAFT agent precursors 7 through 9.

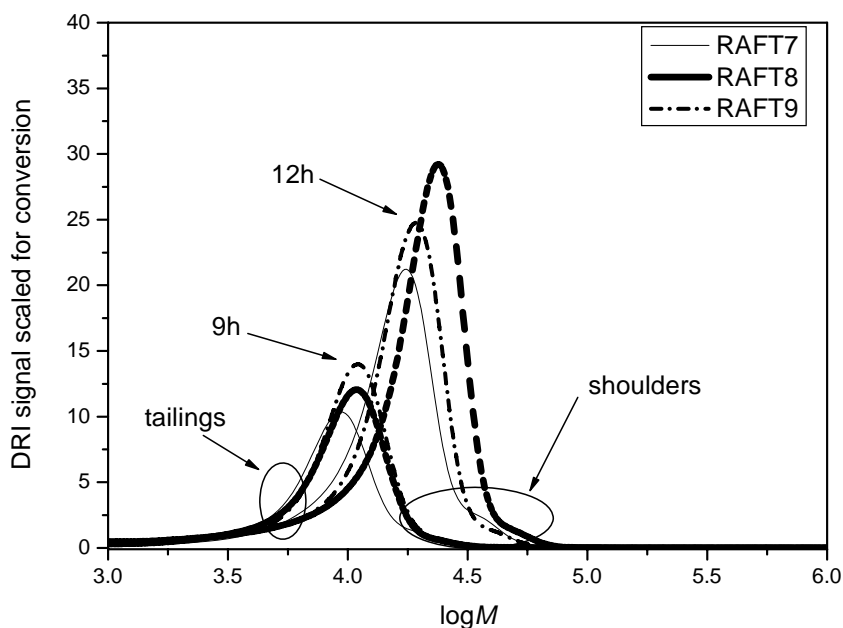


**Figure 5.8** Evolution of the number average molar mass,  $M_n$ , and the polydispersity index, PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agent precursors 7 through 9.

Inspection of Figure 5.8 clearly indicates that the molar mass increases with monomer conversion. Moreover, all three RAFT agent precursors show a similar behaviour and comparable slopes of the  $M_n$  versus conversion traces. This suggests that the degrees of polymerisation of the chains formed in each specific case are similar.

After a sufficient period of time, the proportion of transferred (dormant) chains is high enough so that chain transfer occurs between propagating radicals and dormant chains. Assuming that the reversible transfer reaction is fast enough, all polymer chains will be growing at the same rate of polymerisation (Figure 5.7). As the polymerisation proceeds, new chains are created in a proportion that is negligible if the concentration of initiator generated from the self-initiation of styrene (in the present case) is negligible compared to the concentration of the chain transfer agent used.

Figure 5.9 shows the shift of the MMD peaks as a function of conversion.



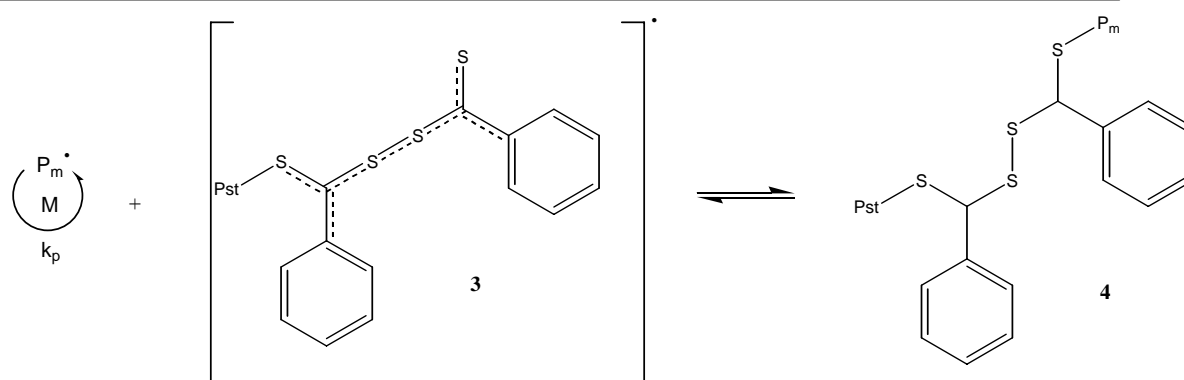
**Figure 5.9** MMDs for the homopolymerisation of styrene at 100°C mediated by RAFT agent precursors 7 through 9.

Analysis of the SEC chromatograms of polymers generated using the three RAFT agent precursors 7 through 9 (Figure 5.9 and Figures 4.22, 4.25 and 4.28) present two major drawbacks, which are: tailing at low conversion and a bimodal distribution at higher conversion. The small peak (shoulder) that appears on the high molar mass side of the distributions (Figure 5.9) has its own molar mass that is almost double that of the main peak: 33900 compared to 17800. Molar mass of the small peak (shoulder):  $10^{(4.530)} = 33900$ ; molar mass of the main peak  $10^{(4.25)} = 17800$ , and the ratio is  $33900/17800 = 2$ .

This calculation suggests therefore that the presence of the small peak might be formed via the bimolecular termination between polystyrene propagating radicals or benzyl sulfur radical ( $RS\bullet$ ) with polystyrene propagating radical ( $St\bullet$ ).

The presence of the shoulder (Figure 5.9) could also be explained by the formation of a polymer with two chains obtained after the addition of a radical (styrene) or propagating radical to the intermediate radical 3 in Schemes 5.1 through 5.2. If this product **4**, splits into two radicals it will again form a double chain compound.





Scheme 5.2 Formation of polymer with two chains

The higher values of polydispersities (1.26 to 1.30 with RAFT agent precursor 7 and  $> 1.5$  for RAFT agent precursors 8 through 9) at the latter stage of the polymerisation with RAFT agent precursors 8 and 9 provide evidence of the bimodality. However, the presence of tailing in the lower molar mass region demonstrates that termination, as a chain-breaking reaction, was not ideally eliminated.

In summary, despite the constant number of chains formed throughout the polymerisation reactions other chains start growing at a later stage of the polymerisation, leading to chains with different lengths.

## 5.5 Series D: 1-methyl-1-phenylethyl benzenecarbodithioate and its derivatives: Z-(C=S)-(S)-C(CH<sub>3</sub>)<sub>2</sub>Ph

The final series of the Z group studies concerns the series of 1-methyl-1-phenylethyl benzenecarbodithioate and its derivatives (see Table 5.4). The conditions of the homopolymerisation of styrene mediated by the four aforementioned RAFT agents were again identical to the three previous series above.

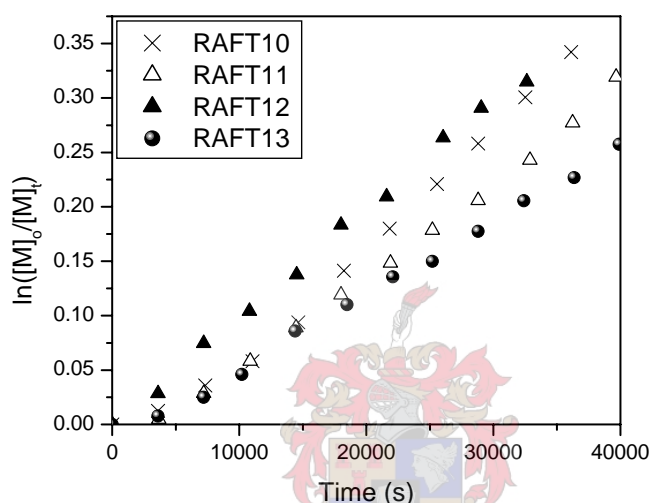
**Table 5.4: 1-methyl-1-phenylethyl benzenecarbodithioate and its derivatives**

|  |   |
|--|---|
| RAFT agent <b>10</b> : 1-methyl-1-phenylethyl benzenecarbodithioate          | RAFT agent <b>11</b> : 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate |
|  |   |
| RAFT agent <b>12</b> : 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate | RAFT agent <b>13</b> : 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate |
|  |   |

This is an interesting series as the author has already analysed the case where the reactivities of the activating compounds 4-methylphenyl and 4-methoxyphenyl were compared to that of phenyl. In the former cases it was found that when phenyl Z groups are used then the electronic effects (inductive and resonance) do not have a strong effect on the polymerisation rate, even if they stimulate the addition of a propagating radical to the double bond of the RAFT agent. The question is now posed: Would it be the same if a compound with the properties of electron deactivation along the phenyl ring, such as a fluoro substituent, is used? To answer this question, the phenyl Z groups employed in the previous three series A, B, C were kept similar to that used in the current series D, and cyanoisopropyl and cyanovaleric acid radicals were replaced by the cumyl group. Four different RAFT agents: 1-methyl-1-phenylethyl benzenecarbodithioate (RAFT agent 10), 1-methyl-1-phenylethyl 4-methyl-benzenecarbodithioate (RAFT agent 11), 1-methyl-1-phenylethyl 4-methoxybenzene-carbodithioate (RAFT agent 12) and 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate (RAFT agent 13) were selected, with the aim of assessing their effectiveness in mediating the free-radical polymerisation of styrene. Among them, the 1-methyl-1-phenylethyl benzene-carbodithioate is the most studied RAFT agent,<sup>2</sup> and its cumyl leaving group has been reported to be excellently suited to reinitiate the polymerisation of various monomers.<sup>7,17</sup> It

has also been demonstrated that its phenyl Z group leads to significant stabilization of the resulting intermediate macroRAFT radicals, giving therefore strong rate retardation effects.<sup>7,18-20</sup> Thus, a comparative study of the other three RAFT agents to the behaviour of RAFT agent 10 turned out to be interesting.

The semi-logarithmic function of monomer concentration ( $\ln([M]_0/[M]_t)$ ) versus time shown in Figure 5.10 indicates that the rate of monomer consumption using all four RAFT agents 10 through 13 respectively comprised two steps, as in the case of the series C. An initialisation period of two hours was noticed for all the four chain transfer agents (Figures 5.10 and 4.31, 4.34, 4.37 and 4.40).



**Figure 5.10** Semi-logarithmic plots of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agents 10 through 13 at 100°C.

The initialisation period at the beginning of the reaction might be caused by the slow consumption of the initial RAFT agent. This was observed before the equilibrium between intermediate  $[Y\bullet]$ , propagating radicals  $[P\bullet]$  and the concentration of the RAFT agent that occurs in the RAFT mechanism had been reached. In our laboratory, McLeary *et al.*,<sup>3</sup> in an *in situ*  $^1\text{H-NMR}$  study of styrene polymerisations mediated with 1-cyano-1-methylethyl benzenecarbodithioate, have shown that during the initialisation period the addition-fragmentation process is extremely selective and, because of this, significant quantities of RAFT adducts of degrees of polymerisation larger than unity were formed only after complete conversion of the initial RAFT agent to its single monomeric adduct. The mechanism depicted in Scheme 5.3 concerns the consumption of 1-methyl-1-phenylethyl benzenecarbodithioate to produce the dithiobenzoate species with a single styrene unit<sup>3</sup> (species **6**).

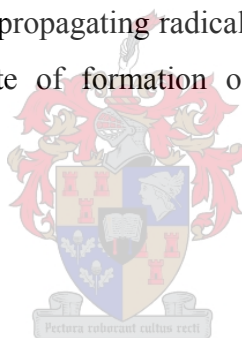
The first reaction starts by the addition of a styrene radical generated from the Mayo mechanism (Scheme 4.2 in Section 4.3) and is followed by the fragmentation of the intermediate radical into species **3** and a radical  $R\bullet$ . Note that this expelled radical is crucial in the reinitiating step because it

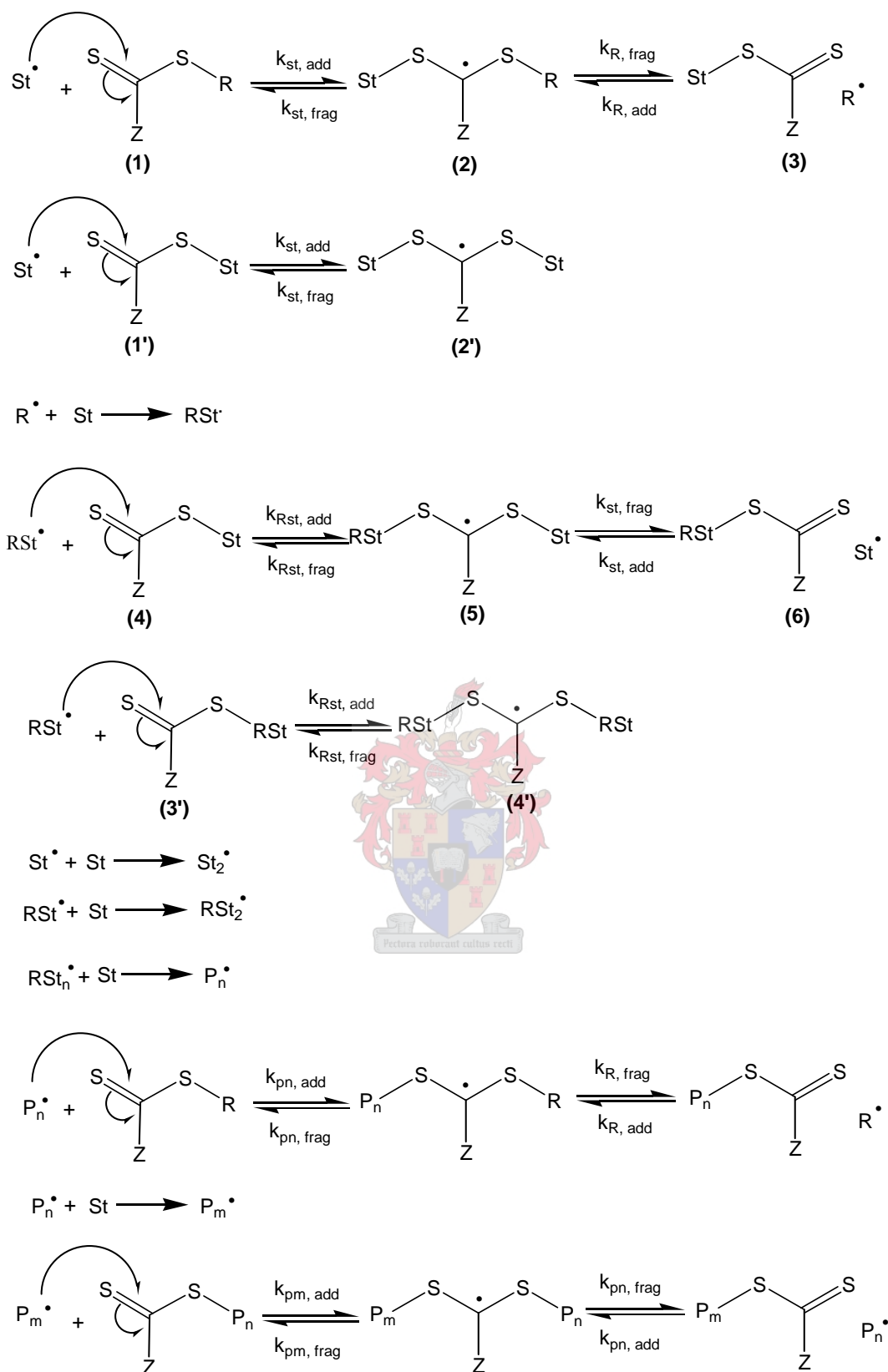
allows the formation of growing chains, which should continue the process  $R^\bullet + St \longrightarrow RSt^\bullet$  (Scheme 5.3). It should be noted that, before the equilibrium, several distinct types of intermediate radicals are generated, each of which has different stabilities and fragmentation rate coefficients. Among all of them, only one is considered to be important, preferably the one that gives a potential tertiary leaving group, to a polymeric RAFT agent and tertiary leaving group.

From this mechanism, it emerges that:

- The speed of consumption of the monomer by the leaving group of the RAFT agent can be responsible for the initialisation. Therefore, the faster the monomer is consumed, the shorter the initialisation.
- The formation of single monomer adducts to RAFT species can explain the initialisation period (species 6 in Scheme 5.3).

After this short initialisation period, the slopes of the polymerisation reaction rates shown in Figure 5.10 remain proportional to the overall propagating radical concentrations in the four reactions (for RAFT agents 10 through 13). The rate of formation of styryl radicals is therefore the rate-determining step in this series (D).





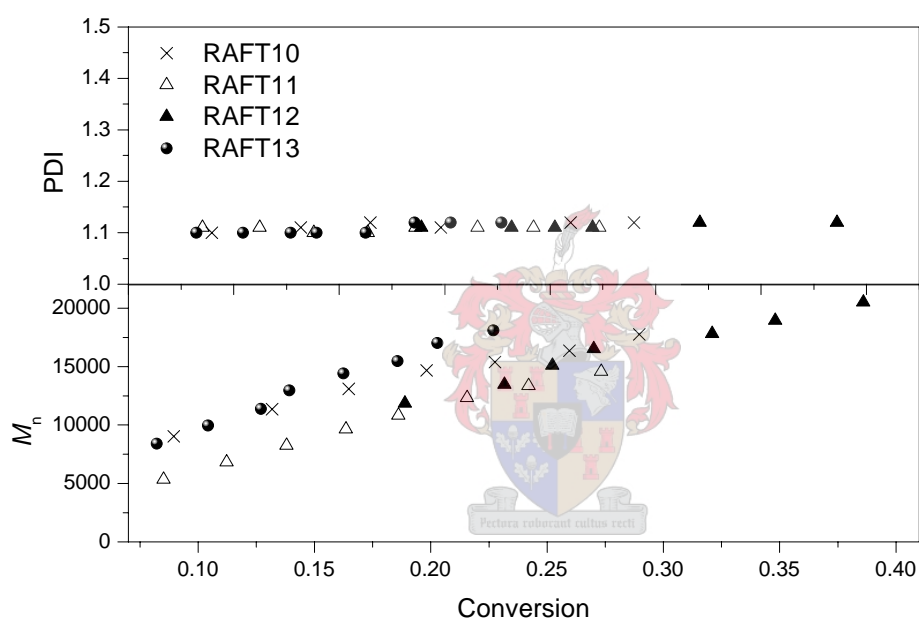
**Scheme 5.3** The steps involved in the initialization period of the RAFT reaction in which thirteen different RAFT agents were used as mediators in the polymerisation of styrene monomer.

The kinetic plots for the homopolymerisation of styrene (Figures 5.10) show that the polymerisation rate increases in the following order of RAFT agent: (12) > (10) > (11) > (13). After 10 h the conversions were 32% for RAFT agent (12); 29% for RAFT agent (10), 24% for RAFT agent (11)

and 20% for RAFT agent (13) (see Tables 10-13 in the Appendix). Contrary to the previous series (A, B, and C) these results suggest that by varying the electronic properties of the Z group via substitution of the phenyl with electron withdrawing or electron donating substituents the efficiency of the RAFT agent in styrene polymerisation is affected. Therefore, the proposed trend of **Z reactivity** obtained for the homopolymerisation of styrene in this present study is: **CH<sub>3</sub>-O-Ph > Ph > CH<sub>3</sub>-Ph > F-Ph**.

Despite the difference observed in the conversion of monomer by the four RAFT agents (10 through 13), Figures 5.11 through 5.12 show that molar masses were controlled in all cases.

Figure 5.11 shows the relationships of the number average molar mass,  $M_n$ , and polydispersity index, PDI, with monomer conversion.



**Figure 5.11** Evolution of the number average molar mass,  $M_n$ , and the polydispersity index, PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agents 10 through 13.

From this figure it is seen that the evolution of number average molar mass with conversion is linear. In addition, a similar trend in the control of the polymerisation of styrene is also observed (with  $PDI \approx 1.1$ ). From the results shown in Figure 5.11, RAFT mediated polymerisation of styrene with the RAFT agents 10 through 13 have demonstrated the conditions of a living polymerisation. Indeed they offer low polydispersity polymers (below the benchmark 1.5), and have a linear molar mass-conversion profile.

In Figure 5.12, the MMDs of samples of reactions with RAFT agents 10 through 13, taken at the same time (6 h and 10 h), are shown. The SEC chromatograms of the generated polymers exhibit extremely narrow peaks. As shown in Figure 5.12, it is difficult to affirm that the narrowing of the

molar mass distribution of the polymer after 6 h or 10 h depends on the electronic properties of the Z group, because the difference found is insignificant (in terms of narrow peaks).

It is difficult to give a clear order in the determination of the most efficient RAFT agent by comparing the narrow MMDs and the values of the PDI for all four RAFT agents 10 through 13 in styrene polymerisation, because both criteria were found to be almost the same in the reactions with the four RAFT agents 10 through 13. See Figures 5.11 through 5.12.

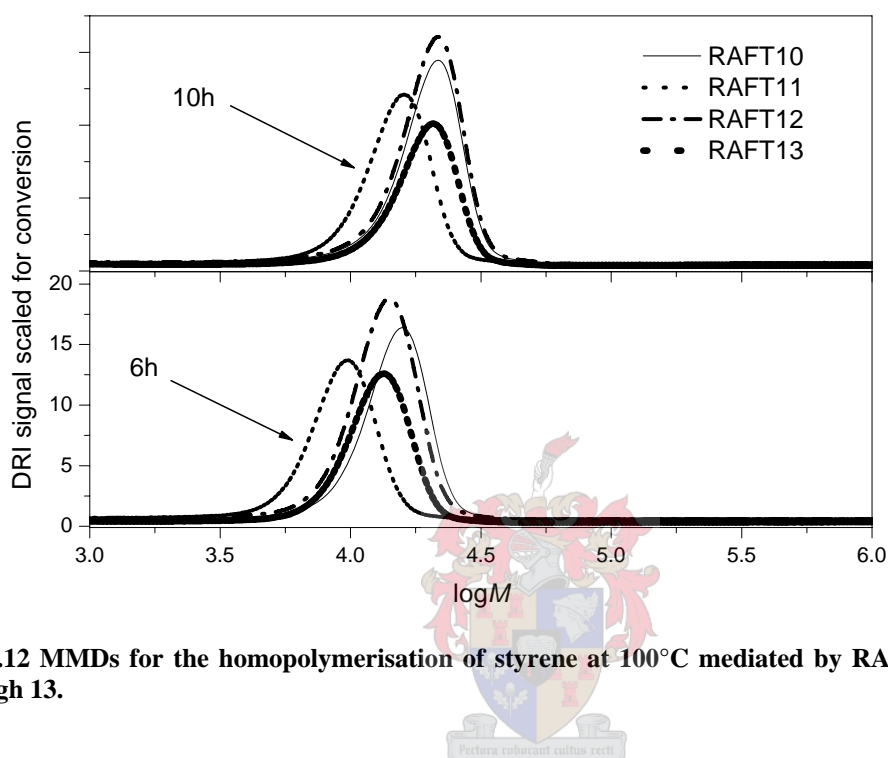


Figure 5.12 MMDs for the homopolymerisation of styrene at 100°C mediated by RAFT agents 10 through 13.

## 5.6 Conclusions

The difference in the relative rates of polymerisation within each series compared to the rate of polymerisation of conventional free radical polymerisation (Figure 4.1) proves that retardation occurs in the RAFT process mediated by para-substituted dithiobenzoates. Assuming that all growing chains have the same degree of polymerisation in the RAFT process and knowing that the RAFT process is a chain transfer process, where the fragmentation should occur fast enough and the intermediate radical should be accompanied by no side reactions, the rate of polymerisation should not be retarded in the RAFT technique. Thus, as was discussed in Section 2.14, the rate of retardation can be explained either by the intermediate radical termination or by the slow fragmentation of the first adduct (**2**)<sup>21</sup> formed from the initial RAFT agent used and by slow fragmentation of the macroRAFT adduct (**5**)<sup>21</sup> formed from the polymeric RAFT agent (species **2**) in Scheme 5.1), or the RAFT mechanism illustrated in Scheme 2.8. Other factors, such as the specificity for the propagating radical ( $P_n\bullet$ ) or the expelled radical ( $R\bullet$ ) to add to the RAFT agent rather than monomer, can also explain the phenomenon of retardation. It has been suggested that

irreversible termination events of the macroRAFT radicals, leading to the formation of a three-armed star polymer, may also be responsible for radical loss processes in RAFT polymerisations.

The inhibition in the early stages of the polymerisation of styrene using the 1-methyl-1-phenylethyl benzenecarbodithioate and its derivatives is considered to be a result of a low reinitiation rate of the leaving group (cumyl radical) or a slow fragmentation rate of the intermediate radical. However, the strong inhibition observed in the case of disulfides is attributed to the need for three radicals in order to allow the consumption of the initial RAFT agent.

Analysis of the MMDs of the polystyrene prepared via the use of disulfides (as chain transfers) shows that two types of chains were formed. Indeed, at the beginning of the polymerisation, the concentration of monomers is high, such that chain propagation is the main reaction; thus if termination of the intermediate radical occurs, the radicals have little chance to couple with the intermediate radicals. As the polymerisation proceeds, the concentration of monomer radicals decreases and the additional intermediate radical termination begins to be a competitive reaction of chain propagation, resulting in a decrease in polymerisation. This theory is still being debated.

The presence of tailing noted in all the thirteen reactions where the RAFT agents 1 through 13 were employed indicates that transfer and termination reactions occurred.

In this chapter, the effect of changing the phenyl Z substituents of the RAFT agents on the course of the RAFT process was studied. It was found that the electron withdrawing or donating group does not significantly affect the activity of the RAFT agents even if the rates of polymerisation in Series D do show a slight dependence on the Z group. This is why it is difficult to deduce a general trend in all four of the series, A, B, C and D, where R was kept constant.

Obtaining a better understanding of both initialisation and retardation remains relevant in order to try to ultimately enhance the efficiency of the RAFT process. Further studies that focus on the R group of the RAFT agent are presented in Chapter 6.



## 5.7 References

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*“Science has ‘explained’ nothing; the more we know the more fantastic the world becomes and the profounder the surrounding darkness” Aldous Huxley.*

## *CHAPTER 6: The activity of the dithiobenzoates and derivatives as a function of R group modification*

The aim of the work described in this chapter is to study the role of the R group on the activity of 12 of the 13 dithiobenzoates studied in Chapter 5. By grouping all the 12 RAFT agents according to the same Z group, three different classes of RAFT agents were identified:

1. The first series E consisted of RAFT agents having the phenyl as the Z group:  
 $\text{Ph}-(\text{C}=\text{S})-(\text{S})-\text{R}$ .
2. In the second series F, the Z group was the 4-methylphenyl:  $\text{CH}_3\text{-Ph}-(\text{C}=\text{S})-(\text{S})-\text{R}$
3. The last series G comprised the 4-methoxyphenyl as the Z group:  $\text{CH}_3\text{-O-Ph}-(\text{C}=\text{S})-(\text{S})-\text{R}$ .

Among all the RAFT agents studied, the fast consumption of the initial RAFT agent was found in the decreasing order for the following RAFT agents with  $\text{R} = -\text{C}(\text{Me})(\text{CN})(\text{CH}_2)_2\text{COOH} \approx -\text{C}(\text{Me})_2\text{CN}$ ,  $-\text{C}(\text{Me})_2\text{Ph}$ , and  $-\text{CS}_2\text{Ph}$ .

The dithiobenzoates with  $\text{R} = -\text{C}(\text{Me})_2\text{Ph}$ ;  $-\text{C}(\text{Me})_2\text{CN}$  and  $-\text{C}(\text{Me})(\text{CN})(\text{CH}_2)_2\text{COOH}$  were found to give very low polydispersities, good molar mass control and narrow MMDs during the polymerisation of styrene, contrary to the precursors of RAFT agents (disulfides). This implies that these compounds are effective RAFT agents with higher transfer coefficients than achieved with the disulfides.

## 6.1 Introduction

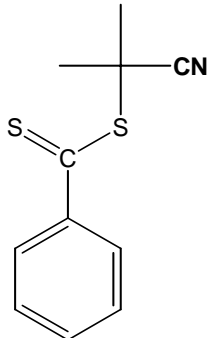
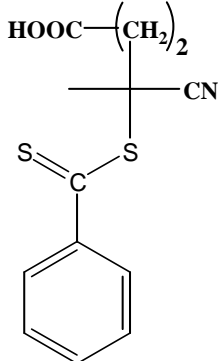
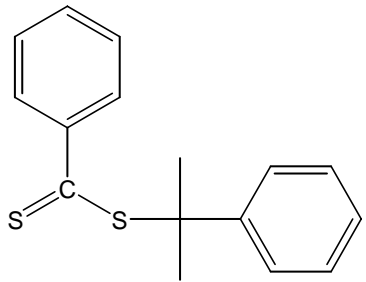
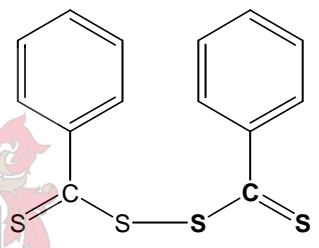
The RAFT process controls the synthesis of well-defined polymers with narrow molar mass distributions. This is largely dependent on the choice of the Z and R groups of the respective RAFT agents.<sup>1</sup> Thus, the effect of R as a leaving group on the fragmentation step occurring in the RAFT process is as crucially important as the Z group effect. It was said in Section 2.8 that a high rate constant for fragmentation of intermediate radicals (2) and (4) to the polymeric thiocarbonyl thio species (3), (5) (Scheme 2.8) is achieved by selecting a R group as a good homolytic leaving radical group but also as a potential reactive species having the ability to reinitiate polymerisation efficiently. If this is not the case then the RAFT agent will be inert and the polymerisation will not display living characteristics. To assess the effect of the R group on the activity of thiocarbonyl thio compounds in the polymerisation of styrene via RAFT polymerisation, ten RAFT agents taken from the thirteen described in Chapters 3, 4 and 5 were grouped according to their identical Z groups. The first series E consisted of RAFT agents having phenyl as Z group (Ph-(C=S)-(S)-R). In the second series F, Z was the 4-methylphenyl group (CH<sub>3</sub>-Ph-(C=S)-(S)-R) and in the last series G, Z was the 4-methoxyphenyl group (CH<sub>3</sub>-O-Ph-(C=S)-(S)-R). The ratio of monomer to RAFT agent here (Chapter 6) remains the same as in Chapters 4 and 5:

$$[M]_0/[RAFT]_0 = 9.615 \times 10^{-3} / 1.25 \times 10^{-5} = 770.$$

## 6.2 Series E: RAFT agents with phenyl as Z group: Ph-(C=S)-(S)-R

To understand the reasons for the change in polymerisation rate during the RAFT process, four RAFT agents were first examined. These had been previously reported to be efficient transfer agents in the polymerisation of various monomers, such as methyl acrylate and styrene.<sup>1,2</sup> These RAFT agents are shown in Table 6.1. They differ from each other in the R leaving group. In the RAFT agents 1, 4 and 10 and RAFT agent precursor 7 we have the following R groups: cyanoisopropyl, cyanovaleric acid, benzyl sulfur and cumyl. See also Scheme 6.1.

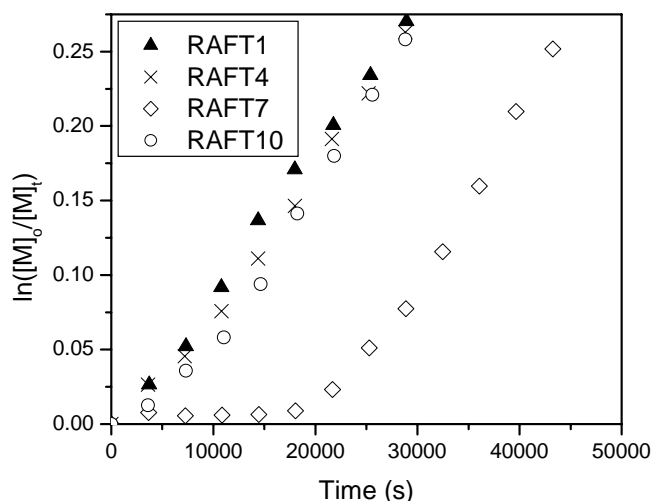
**Table 6.1: RAFT agents with phenyl as Z group**

|  |   |
|--|---|
| RAFT agent <b>1</b> : 1-cyano-1-methylethyl benzene-carbodithioate                 | RAFT agent <b>4</b> : 4-cyano-4-[(phenylcarbothioyl)-sulfanyl]pentanoic acid        |
|   |   |
| RAFT agent <b>10</b> : 1-methyl-1-phenylethyl benzene-carbodithioate               | RAFT agent precursor <b>7</b> : Diphenyldithioperoxy-anhydride                      |
|  |  |

Examination of the diagnostic criteria of the livingness of the polymerisation of styrene using the above three RAFT agents 1, 4 and 10 and RAFT agent precursor 7 showed the consumption of monomer with time (Figure 6.1). The linearity observed in Figure 6.1 implies that the concentration of growing radicals is constant during the polymerisation.

It is also important to note that there was no apparent inhibition in the early stages of the reactions with both RAFT agents 1 and 4. This implies that the propagation of the cyanoisopropyl and cyanovaleric acid radicals with a single monomer unit was very quickly converted to new chain transfer, R group.<sup>3,4</sup>

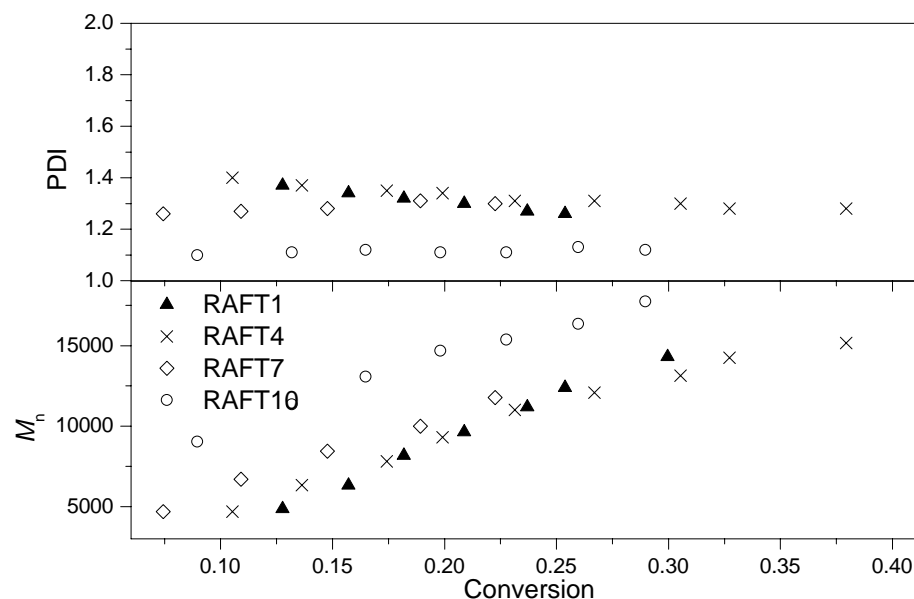
In contrast, RAFT agents 1, 4 and 10 and RAFT agent precursor 7 showed different characteristics. Close inspection of Figure 6.1 as well as the enlargement of Figure 4.30 of RAFT agent 10 (see Chapter 4) indicates that at the early stage of the polymerisation there is a strong reduction in the rate of polymerisation when the RAFT agent precursor 7 was used and a short inhibition period in the case of RAFT agent 10.



**Figure 6.1** Semi-logarithmic plots of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agents 1, 4, 10 and RAFT agent precursor 7 at 100°C.

In the case of the RAFT agent precursor 7 a period of 6 h was noted and 2 h for RAFT agent 10. The short period noted in the case of the RAFT agent 10 is termed *initialisation period*,<sup>4</sup> which corresponds to the period in which the starting RAFT agent is completely converted into its single monomer adduct. McLeary *et al.*<sup>4</sup> have demonstrated that the large differences in addition and fragmentation rate coefficients for the different intermediate radicals are the key to understanding the behaviour of the reaction during the initialisation period. However, the strong inhibition in the rate of polymerisation observed in the case of the RAFT agent precursor 7 could be explained by the need of three radicals for the RAFT agent precursor 7 to be converted into an active RAFT agent, which is then consumed (initialisation). Therefore in order to allow the polymerisation to start, the RAFT agent precursor 7 needs three radicals compared to the cases of other chain transfer agents that require only one radical. This was discussed in Section 5.4 and the mechanism depicted in Scheme 5.1. See also Scheme 6.1. Moreover, the slow fragmentation of the intermediate radical (species 2 in Scheme 6.2) could also be at the origin of this phenomenon. However, it is difficult to suggest that termination reactions of the intermediate radicals in the case of cumyl could cause the inhibition simply because McLeary *et al.*<sup>3,4</sup> have recently demonstrated experimentally that the concentration of intermediate radicals is small during the initialisation period.

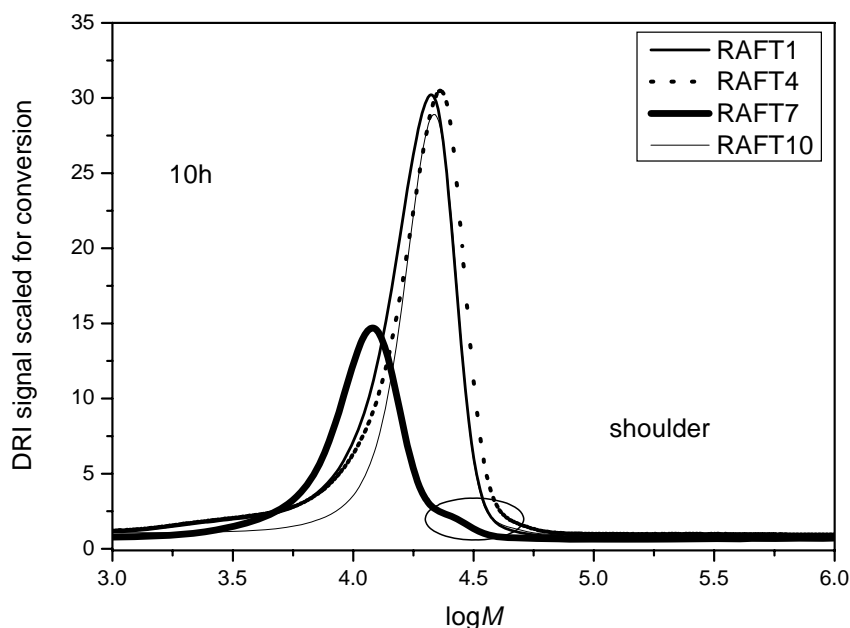
Figure 6.2 shows a plot of molar mass and polydispersity versus conversion for the thermal polymerisation of styrene at 100°C using the three RAFT agents 1, 4, 10 and RAFT agent precursor 7.



**Figure 6.2** Evolution of the number average molar mass,  $M_n$ , and the polydispersity index, PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agents 1, 4 and 10 and RAFT agent precursor 7.

In terms of polydispersity values, Figure 6.2 shows that the polymerisation was more controlled in the reaction with the RAFT agent 10 (PDI = 1.1). The plots of the molar mass versus conversion for the three RAFT agents 1, 4 and 10 and RAFT agent precursor 7 are linear. This highlights the living character of the styrene polymerisation. The deviation noted in Figure 6.2 when the RAFT agent 10 was used cannot be explained by the use of the phenyl group because the phenyl was used as the Z group for all three RAFT agents (1, 4 and 10 and RAFT agent precursor 7). Moreover, the use of the cumyl as a leaving group can also not explain this deviation because it has been reported that the cumyl group is an excellent leaving group in the RAFT polymerisation of various monomers such as styrene and it appears to be efficient in the current case. The reasons for this deviation are under investigation.

Figure 6.3 shows the experimentally determined molar mass distributions for the homopolymer prepared after 10 h with the three RAFT agents 1, 4 and 10 and RAFT agent precursor 7, respectively. In this figure there is a progressive narrowing of molar mass distribution of the polymers. This implies that the polymerisations proceed in a controlled manner, in the order 7, 1, 4 and 10.



**Figure 6.3** MMDs for the homopolymerisation of styrene at 100°C mediated by RAFT agents 1, 4 and 10 and RAFT agent precursor 7

In the polymerisation of styrene mediated by RAFT agent precursor 7, controlled polymerisation is achieved, but a shoulder in Figure 6.3 indicates the existence of termination products. This is at higher conversion (10 h, 29%), and presumably attributed to the product formed by bimolecular termination between polystyrene propagating radicals or between benzyl sulfur radical ( $\text{RCS}_2\bullet$ ) and styrene radical ( $\text{St}\bullet$ ) (see also Section 5.4). Finally, the formation of this shoulder could also be due to the reaction of the intermediate radical with a styryl radical. This theory is still under debate.

The presence of tailing in the lower molar mass regions in the reactions with all three RAFT agents 1, 4 and 10 and RAFT agent precursor 7 could be explained by the formation of new chains or by termination reactions that still occur in all the four cases although much less with RAFT agent 10 (see also Section 5.4).

### 6.3 Series F: RAFT agents with 4-methylphenyl as Z group: $\text{CH}_3\text{-Ph-(C=S)-(S)-R}$

The following discussion concerns the examination of the effect of the R group on the activity of thiocarbonyl thio compounds having 4-methylphenyl as Z group (see Table 6.2). 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate (RAFT agent 2), 4-cyano-4-[[[(4-methylphenyl)carbothioyl]sulfanyl]pentanoic acid (RAFT agent 5), bis(4-methylphenyl)-dithioperoxyanhydride (RAFT agent precursor 8), and 1-methyl-1-phenylethyl 4-methylbenzenecarbo-dithioate (RAFT agent 11) were the CTAs employed in this series (F).

To date, there is no literature reporting the study of such chain transfer agents.

**Table 6.2: RAFT agents with 4-methylphenyl as Z group**

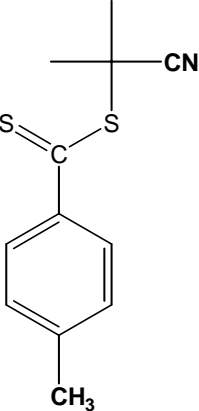
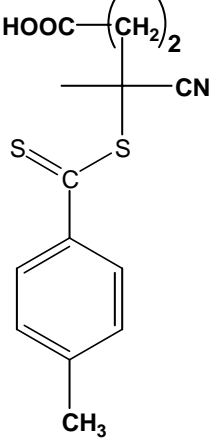
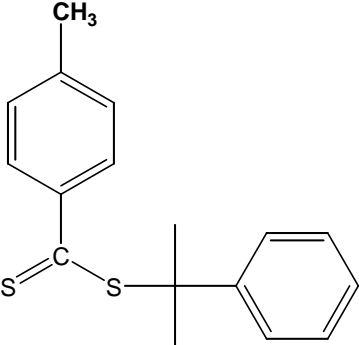
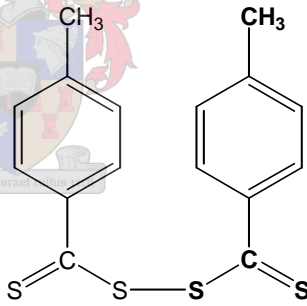
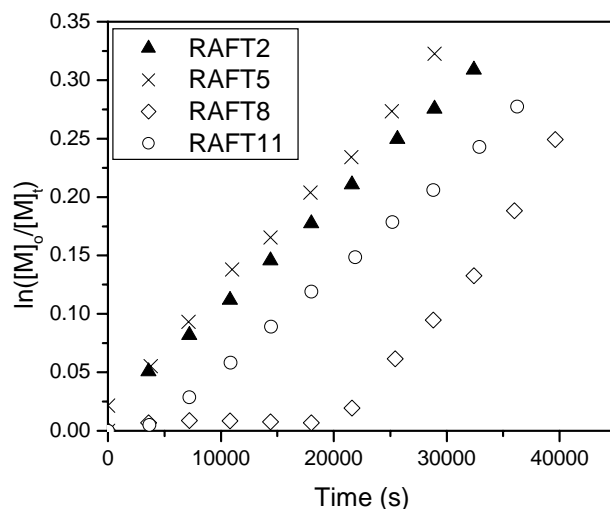
|   |  |
|---|--|
| RAFT agent <b>2</b> : 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate           | RAFT agent <b>5</b> : 4-cyano-4-[[4-methylphenyl]carbothioyl]sulfanyl}pentanoic acid |
|    |    |
| RAFT agent <b>11</b> : 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate         | RAFT agent precursor <b>8</b> : bis(4-methylphenyl)dithioperoxyanhydride             |
|  |  |

Figure 6.4 shows the plots of  $\ln ([M]_0/[M]_t)$  versus time for the polymerisation of styrene using RAFT agents 2, 5 and 11 and RAFT agent precursor 8. It is evident that the kinetics of the polymerisation reactions in which RAFT agents with R groups =  $-\text{C}(\text{Me})_2\text{CN}$  and  $-\text{C}(\text{Me})(\text{CN})(\text{CH}_2)_2\text{COOH}$  were used have shorter initialisation periods than polymerisation systems where the other R groups were employed. The results suggest that the expelled  $-\text{C}(\text{Me})_2\text{CN}$  and  $-\text{C}(\text{Me})(\text{CN})(\text{CH}_2)_2\text{COOH}$  radicals are good leaving groups and have the ability to reinitiate the polymerisation of styrene faster than  $-\text{C}(\text{Me})_2\text{Ph}$  or  $-\text{CS}_2\text{Ph}-\text{CH}_3$ .



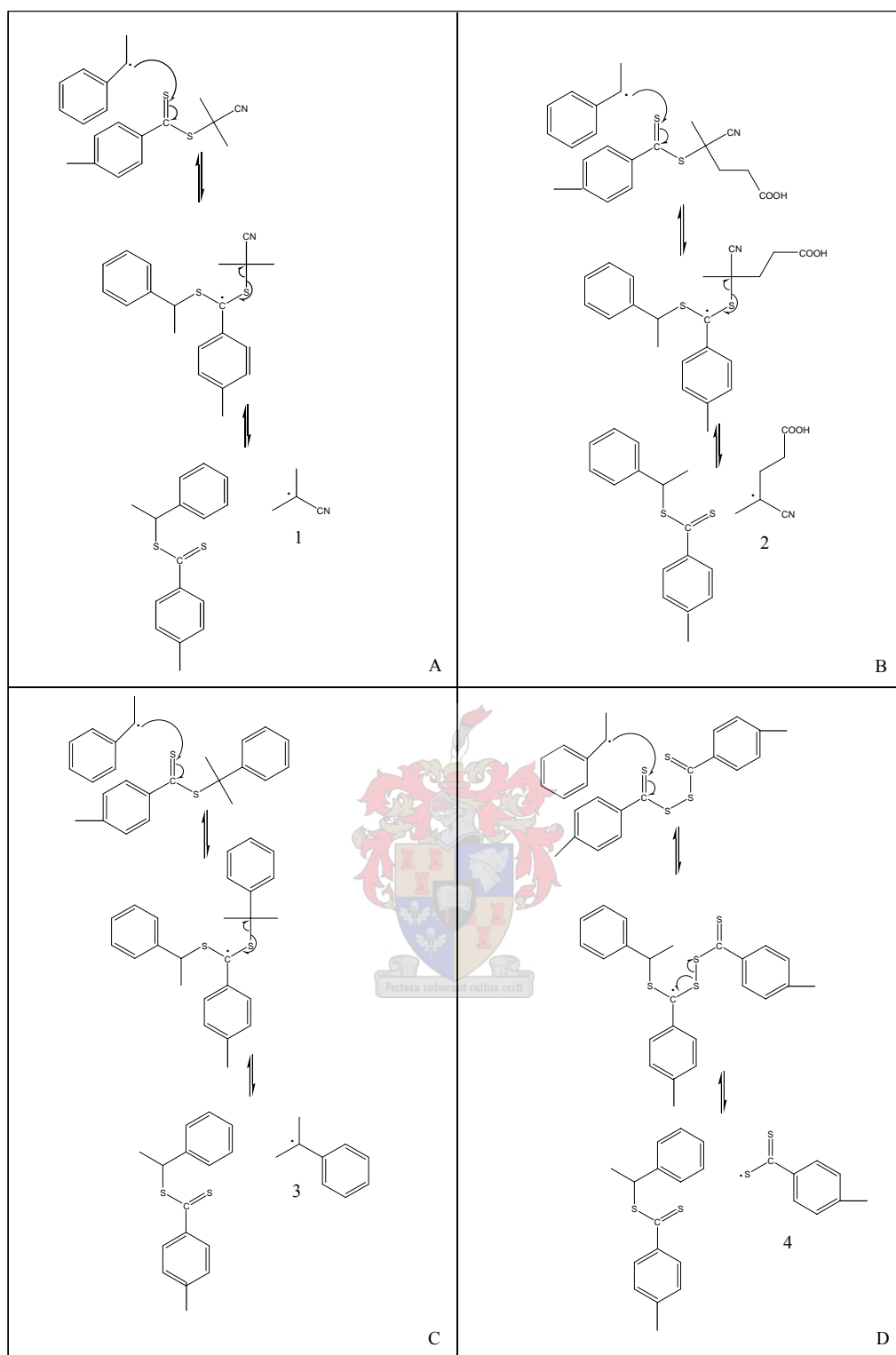


**Figure 6.4** Semi-logarithmic plots of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agents 2, 5 and 11 and RAFT agent precursor 8 at 100°C.

In general, during the RAFT process, the re-initiating effect is governed by the specific interaction between the expelled radicals with monomer (styrene) in order to form propagating radicals (step 2 in the RAFT mechanism, Chapter 2). Thus, according to the molecular size, the more bulky radical group will diffuse and terminate more slowly,<sup>5,6</sup> in an attempt to find a styrene monomer in the reaction. From this statement, one can expect that the rapid formation of propagating radical within the series (F) will be in the following order:

4-methylbenzyl sulfur radical (4) ~ cumyl radical (3) > cyanovaleric acid radical (2) ≈ cyanoisopropyl radical (1) (see Scheme 6.1).

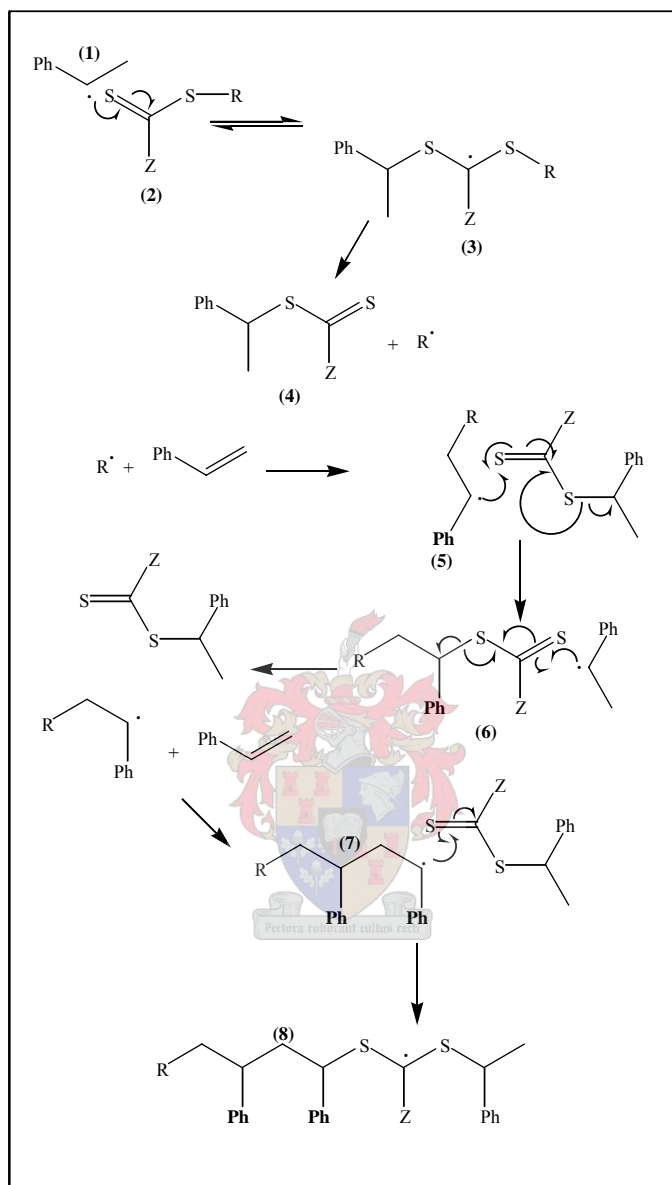
However, contrary to the expected trend mentioned above, the author found that RAFT agents with the cyanoisopropyl radical and cyanovaleric acid radical as leaving groups induced the polymerisation more rapidly than in the cases of RAFT agents with a cumyl radical and a 4-methylbenzyl sulfur radical (Scheme 6.1). It can be envisaged that the intermediate macroRAFT radical (species (2) in the RAFT mechanism (Scheme 2.8) is more stable in the cases where the RAFT agent precursor 8 and RAFT agent 11 are employed instead of the RAFT agents 2 and 5. Possibly, the electron withdrawing CN group in the  $\alpha$ -position to the dithioester bond is responsible for this instability of the resulting intermediate radical formed in the RAFT agents 2 and 5. Therefore, the intermediate radical lifetime can be at the origin of the observed retardation.



**Scheme 6.1** Initial leaving groups formed during the polymerisations of styrene mediated by RAFT agents 2, 5, 10 and RAFT agent precursor 8.

In our laboratory, Calitz *et al.*<sup>7</sup> demonstrated with ESR and NMR that the intermediate radical in styrene polymerisation in the presence of 1-methyl-1-phenylethyl benzenecarbodithioate at 90°C in 50% benzene solution undergoes cross-termination. Vosloo *et al.*<sup>2</sup> have also suggested that the benzyl sulfur radical can undergo side reactions. (See Scheme 6.1). It has to be noted that the benzyl

sulfur radical and the 4-methylbenzyl sulfur radical only differ by the presence of the methyl group in the para-position of the phenyl group. (See RAFT agent precursors 7 and 8 in Tables 6.1 and 6.2).



**Scheme 6.2** Schematic representation of the addition/fragmentation reactions of a dormant chain.

After the initialisation period, a comparative study of the effectiveness of all four chain transfer agents in controlling the polymerisation of styrene shows that the gradient of the slope of the reaction with RAFT agent precursor 8 is a lot bigger than the other. This is probably because the leaving group is big and more stable. The reaction will thus go faster. The leaving group in the other reactions first have to add some monomer units before it gets big enough.

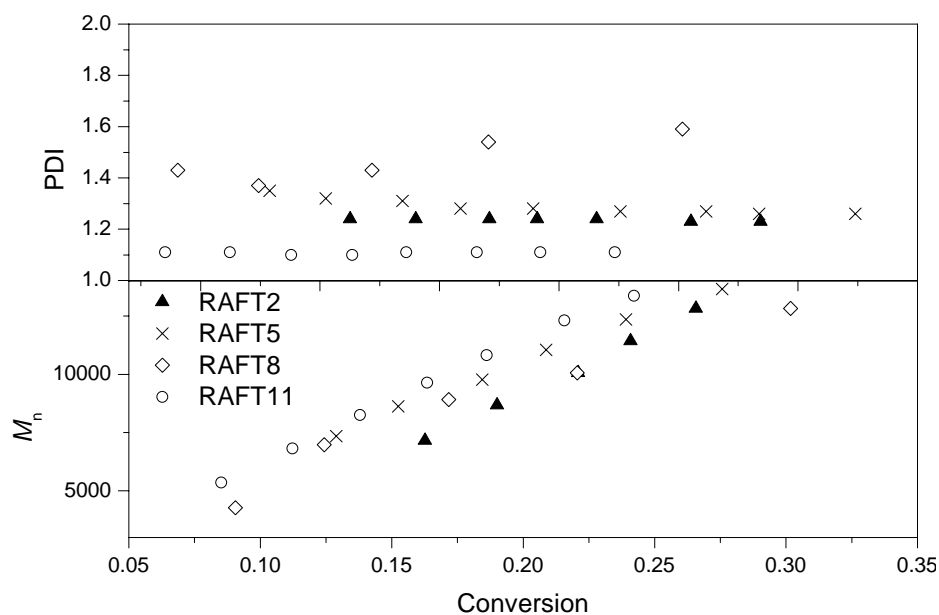
The difference noted during the start of each of the four reactions above (where RAFT agents 2, 5 and 11 and RAFT agent precursor 8 were used) is due to the need to convert the RAFT agent into a

macroRAFT agent. After the initialisation period, the propagating rate becomes constant and depends not on the initial leaving radical R• group but on the polystyryl radicals (species 7 and 8 in Scheme 6.2). The conversions of styrene polymerisation with RAFT agent precursor 8 and RAFT agent 11 appear to be lower for the same reaction times. For example, after 10 h of reaction, a conversion of 31% for RAFT agent 2, 31% for RAFT agent 5, 17% for RAFT agent precursor 8, and 24% for RAFT agent 11 were recorded. The results show that RAFT agents 2 and 5 have higher transfer constants than RAFT agent precursor 8 and RAFT agent 11. These results are similar to what was found by Chiefari *et al.*,<sup>8</sup> Monteiro and De Brouwer.<sup>9,10</sup> Indeed, they reported that 1-cyano-1-methylethyl benzenecarbodithioate has a higher transfer constant than 1-methyl-1-phenylethyl benzenecarbodithioate and that the degree of retardation in styrene polymerisation caused by 1-methyl-1-phenylethyl benzenecarbodithioate is less with 1-cyano-1-methylethyl benzenecarbodithioate.

Here the polymerisation could be retarded due to the slow fragmentation of the intermediate RAFT radical in the cases where the RAFT agent precursor 8 and RAFT agent 11 were used (Schemes 6.2 and 5.1, in Chapter 5). It has been speculated that irreversible termination of the macroRAFT radicals leading to the formation of three-armed, star polymers may also be responsible for a radical loss process in RAFT polymerisations. This theory is still being debated. Other factors have been discussed in the Series E.

Figure 6.5 shows a plot of molar mass and polydispersity versus conversion for the thermal polymerisation of styrene at 100°C using the RAFT agents 2, 5 and 11 and RAFT agent precursor 8. The measured polydispersity indices are below 1.5 for RAFT agents 2, 5 and 11 and decrease with conversion: PDI: 1.1 for RAFT agent 11; 1.24 to 1.23 for RAFT agent 2; 1.32 to 1.26 for RAFT agent 5; and 1.43 to 1.37 to 1.52 for RAFT agent precursor 8.

On comparing the polydispersity values of the three RAFT agents mentioned above (2, 5 and 11 and RAFT agent precursor 8), it can be concluded that the RAFT agents 2, 5 and 11 have a higher transfer coefficient than the RAFT agent precursor 8. Moreover, the RAFT agent 11 seems to be more efficient in the control of molar mass distribution (PDI: 1.1).

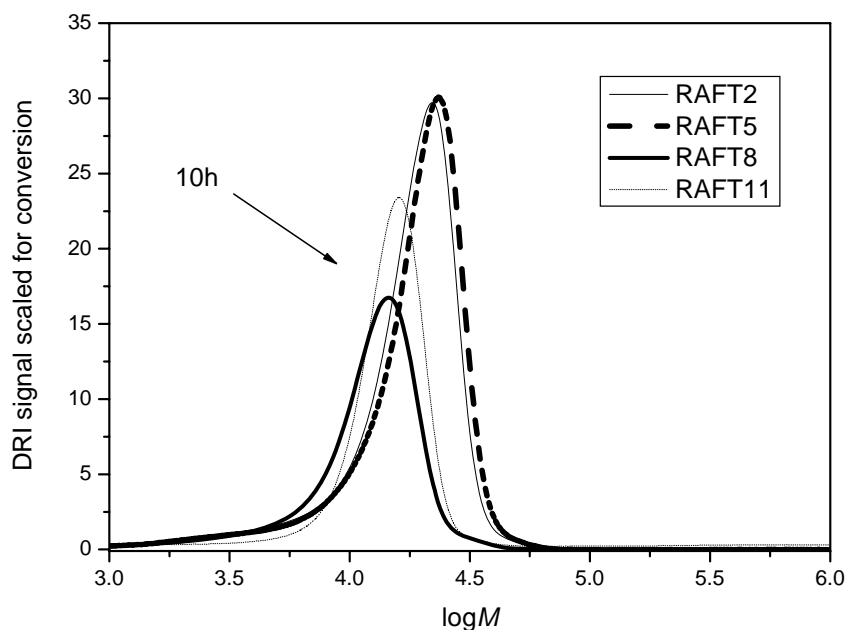


**Figure 6.5 Evolution of the number average molar mass,  $M_n$ , and the polydispersity index, PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agents 2, 5 and 11 and RAFT agent precursor 8.**

Figure 6.6 shows the molar mass distributions (MMDs) for the homopolymerisations of styrene at 100°C mediated by the three RAFT agents 2, 5 and 11 and RAFT agent precursor 7. The narrow MMDs observed imply that these “four” RAFT agents were efficient for the homopolymerisations of styrene. The narrower MMD peaks of the RAFT agents 5, 2 and 11 suggest that they have higher transfer coefficients than the RAFT agent precursor 8.

The observed linear relationship in the pseudo first-order rate plot in Figure 6.5, in conjunction with the MMDs in Figure 6.6, confirm the living characteristic of the reaction. Moreover Figure 6.6 clearly shows the successful formation of polymers with narrow molecular distribution—another indication of a living feature. The current research has shown that the speed of the formation of the polymer in each respective case was realized in the following order:





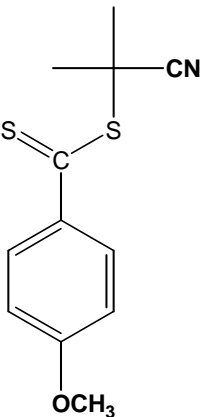
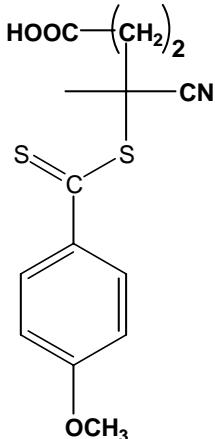
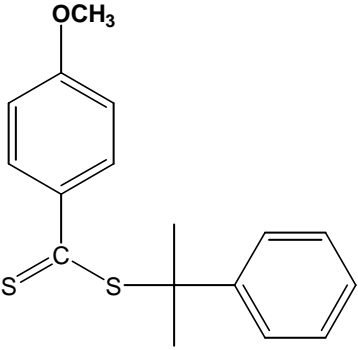
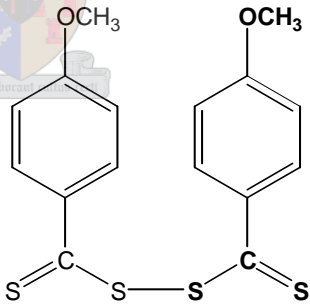
**Figure 6.6** MMDs for the homopolymerisations of styrene at 100°C mediated by RAFT agents 2, 5 and 11 and RAFT agent precursor 8.

The following section addresses, in a similar approach to the previous two series (E and F), the influence of the R substituent on the activity of chain transfers in which the 4-methylphenyl (Z group) was replaced by the 4-methoxyphenyl (Z group). (See Table: 6.3).

## 6.4 Series G: RAFT agents with 4-methoxyphenyl as Z group: CH<sub>3</sub>-O-Ph-(C=S)-(S)-R

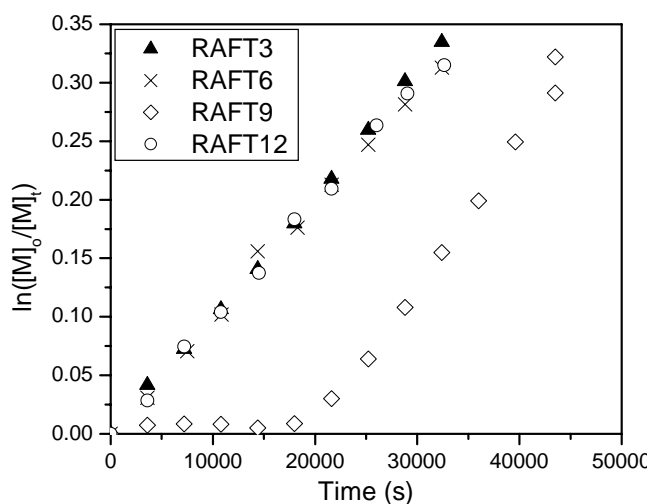
1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate (RAFT agent 3), 4-cyano-4-[[4-methoxyphenyl]carbothioyl]sulfanyl}pentanoic acid (RAFT agent 6), 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate (RAFT agent 12), and bis(4-methoxyphenyl)dithioperoxy-anhydride (RAFT agent precursor 9) were the CTAs used in Series G. (See Table 6.3). As in the case of Series F, nothing has yet been reported in the literature on the study of such chain transfer agents.

**Table 6.3: RAFT agents with 4-methoxyphenyl as Z group**

|   |   |
|---|---|
| RAFT agent <b>3</b> : 1-cyano-1-methylethyl 4-methoxybenzenecarbodithioate          | RAFT agent <b>6</b> : 4-cyano-4-[[4-methoxyphenyl]carbothioyl]sulfanyl}pentanoic acid |
|    |     |
| RAFT agent <b>12</b> : 1-methyl-1-phenylethyl 4-methoxybenzenecarbodithioate        | RAFT agent precursor <b>9</b> : bis(4-methoxyphenyl)dithioperoxyanhydride             |
|  |   |

To examine the effect of the RAFT agents with 4-methoxyphenyl as Z group on the RAFT polymerisation, the styrene polymerisations with different RAFT agents were carried out in bulk under the same conditions as the experiments in Series E and F above. The results of these experiments (molar masses, polydispersities and conversions) are summarized in Figures 6.7 through 6.9 and Tables 3, 6, 9 and 12 in the Appendix.

Figure 6.7 shows the plots of  $\ln ([M]_0/[M]_t)$  versus time for the polymerisation of styrene using RAFT agents 3, 6 and 12 and RAFT agent precursor 9.



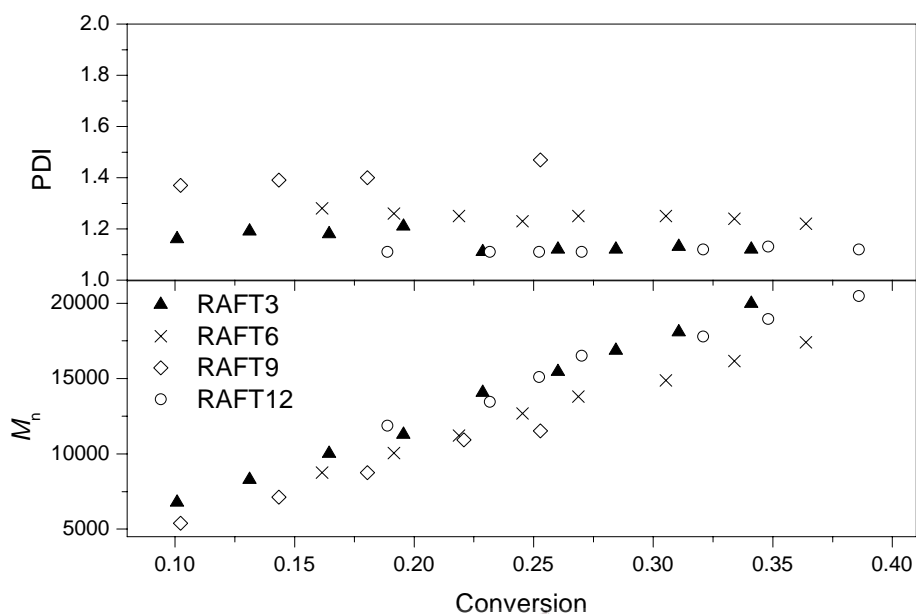
**Figure 6.7** Semi-logarithmic plots of fractional conversion versus time for styrene mediated homopolymerisation by RAFT agents 3, 6 and 12 and RAFT agent precursor 9 at 100°C.

The kinetics seen in Figure 6.7 are in agreement with what was found in Figure 6.1, for Series E: Ph-(C=S)-(S)-R. Figure 6.7 also indicates that the three polymerisations with RAFT agents 3, 6 and 12 proceed at similar overall rates of reaction, implying that constant growing chains were produced during the polymerisations. However, the polymerisation reaction mediated by the RAFT agent precursor 9 starts slower than in the cases of the other RAFT agents (3, 6 and 12) due its strong inhibition. Then, after this inhibition, the plot  $\ln([M]_0/[M]_t)$  versus polymerisation time affords a straight line, indicating further that the chain radical concentration remains constant during the polymerisation of styrene after the inhibition. The explanations given about the inhibition (substitution/initialization periods) observed in polymerisations with both series E and F remain useful in the present series G, in particularly for the RAFT agent precursor 9.

In Figure 6.8, the evolution of the number average molar mass,  $M_n$ , linearly increases with conversion throughout the polymerisation. This is a key characteristic of living radical polymerisation. It is well known that number average molar mass is inversely proportional to the concentration of RAFT agent.<sup>11,12</sup> This principle suggests that for the same concentration of RAFT agent, we expect a constant number of growing chains during the polymerisation. Hence, the three RAFT agents 3, 6 and 12 and the RAFT agent precursor 7 should yield polymers with the same molar mass distributions, as indeed observed in Figure 6.8. It is also seen in Figure 6.8 that the rate of polydispersity narrowing with conversion (time) was lower with RAFT agent 3, PDI = 1.10; RAFT agent 12, PDI = 1.10; and RAFT agent 6, PDI = 1.25 than with RAFT agent precursor 9, PDI = 1.37 to 1.52.



On comparing the polydispersity values of the three RAFT agents above (3,6 and 12) and the RAFT agent precursor 9, it can be concluded that the RAFT agents 3, 12 and 6 have a higher transfer coefficient than the RAFT agent precursor 9.



**Figure 6.8** Evolution of the number average molar mass,  $M_n$ , and the polydispersity index, PDI, with monomer conversion in the bulk polymerisation of styrene at 100°C mediated by RAFT agents 3, 6 and 12 and RAFT agent precursor 9.

The evolution of the molar mass distributions for all the four systems is shown in Figure 6.9. From this figure it is seen that the curves representing RAFT agents 3, 6 and 12 and RAFT agent precursor 9 are unimodal and shift to higher molar masses with increasing monomer-to-polymer conversion, and their peaks are relatively narrow, indicative of efficient control. The close inspection of Figure 6.9 indicates that the order of decreasing narrow peaks is 3 ~ 6 ~ 12 and 9. This implies that the RAFT agents 3, 6 and 12 are more efficient than the RAFT agent precursor 9 in the polymerisation of styrene.

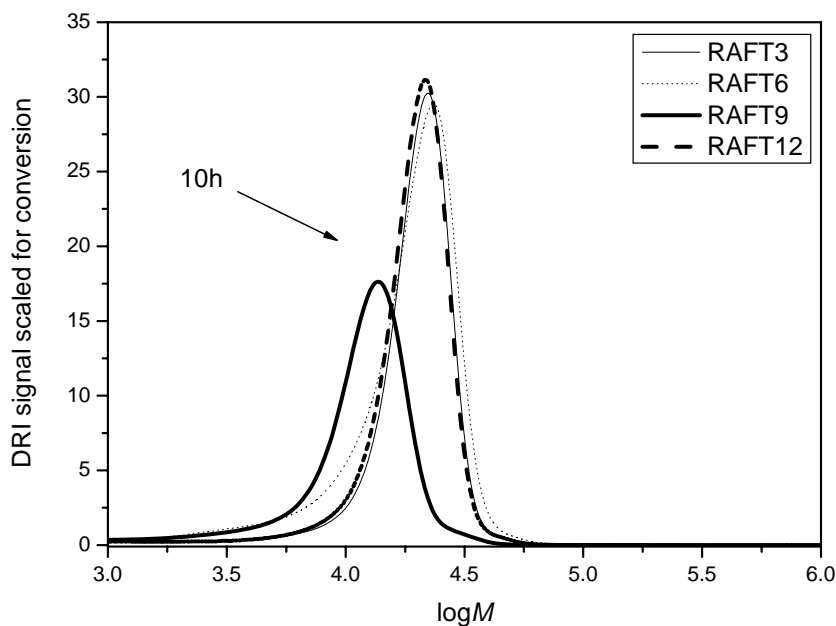


Figure 6.9 MMDs for the homopolymerisations of styrene at 100°C mediated by RAFT agents 3, 6 and 12 and RAFT agent precursor 9.

## 6.5 Conclusions

The effect of changing the R group of RAFT agents in the polymerisation of styrene was studied. Results suggested that the R group has a significant effect on the initialisation period. In other words, in the early stages of the polymerisation, the rate of consumption of the initial RAFT agent depends of the fragmentation rate of the first intermediate radical with the initial leaving R group and on the specific interaction between the initial leaving R group and the monomer. Among the RAFT agents studied, fast consumption of the initial RAFT agent was found in the reactions with RAFT agents where R was:  $-\text{C}(\text{Me})(\text{CN})(\text{CH}_2)_2\text{COOH} \sim -\text{C}(\text{Me})_2\text{CN} > -\text{C}(\text{Me})_2\text{Ph} > -\text{CS}_2\text{Ph}$  (and derivatives).

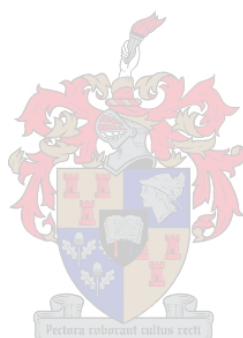
Thus, the nature of the R leaving group plays an important role in the early stages of polymerisation reactions.

The finding demonstrates that the leaving group (R) group should not only be a tertiary bulky group such as the cumyl but should also have more electronic effects such as the cyanovaleric acid or cyanoisopropyl groups. Thus, it is proposed that the electron withdrawing CN group in the  $\alpha$ -position to the dithioester bond is responsible for the instability of the resulting intermediate radical formed in RAFT agents with:

R =  $-\text{C}(\text{Me})_2\text{CN}$  and R =  $-\text{C}(\text{Me})(\text{CN})(\text{CH}_2)_2\text{COOH}$ .

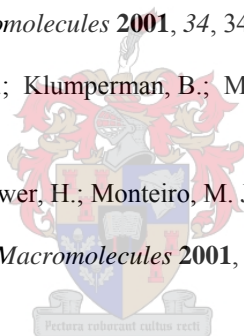
In this work, strong inhibition periods and slow polymerisation rates were obtained in reactions with the use of the disulfides (RAFT agent precursors 7, 8 and 9). This could be explained by slow fragmentation of the intermediate radical leading to the formation of active RAFT agents.

For the styrene polymerisations reported in this chapter, the three dithiobenzoates with R = -C(Me)<sub>2</sub>Ph; -C(Me)<sub>2</sub>CN and -C(Me)(CN)(CH<sub>2</sub>)<sub>2</sub>COOH were found to give very low polydispersities, good molar mass control and narrow MMDs. This implies that these compounds are very effective RAFT agents with high transfer coefficients. However, in the case of precursors of RAFT agents (disulfides), the rate of increase in polydispersity with conversion/time was larger in the later stages of the polymerisations, suggesting that these compounds have low transfer coefficients.



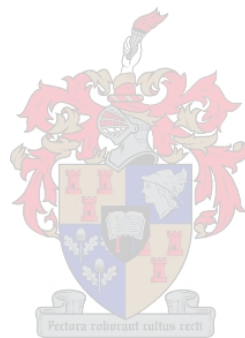
## 6.6 References

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*“The limits of the possible can only be defined by going beyond them into the impossible” Arthur C. Clarke.*

## *CHAPTER 7: Conclusions and recommendations*



## 7.1 Conclusions

RAFT polymerisations were carried out in the presence of 13 thiocarbonyl thio compounds of the general structure  $Z-(C=S)S-R$ , with styrene. The synthesis of homopolymers of polystyrene via reversible addition-fragmentation chain transfer (RAFT) polymerisation has resulted in polymers with narrow molar mass distributions (in most cases  $PDI < 1.5$ ).

The Grignard method was successfully used to prepare benzenecarbodithioic acid and its derivatives carrying para-substituents (one electron-withdrawing and two donating groups) under moderate conditions. It was found that the Grignard reaction was fast, when electron-donating groups in the para-position of the phenyl ring were employed, contrary to the case where phenyl itself or compounds with electron withdrawing groups in the para-position of phenyl were used. The thirteen chain transfer agents were successfully prepared in good yields via Grignard reactions following the methods of *Le et al.* (see Chapter 3). However, the synthesis of bis(4-fluorophenyl)dithioperoxyanhydride was not achieved by this method.

The overall aim of this research was also to understand the influence of the thirteen different RAFT agents on the RAFT process, in terms of the kinetics and mechanism of homopolymerisation of styrene.

The effect of changing the phenyl Z substituents of the RAFT agents used in this work showed that the electron withdrawing or donating group in the para-position of the phenyl ring does not significantly affect the activity of the RAFT agent. However, the type of leaving group of the initial RAFT agent influences the polymerisation kinetics substantially. There was no inhibition period when cyanoisopropyl and cyanovaleric acid leaving groups were used compared to the cases where cumyl and benzyl sulfur radical (and derivatives) leaving groups were used. In the case of the cumyl radical leaving group, the inhibition of 2 hours that was observed could be caused by the slow fragmentation of the first adduct (**2**) formed from the initial RAFT agent (see the RAFT mechanism in Scheme 2.8) or by the slow reinitiation of the polymerisation by the cumyl radical. However, the long inhibition (6 hours) in the case of the disulfides (RAFT agent precursors) could not only be explained by the factors mentioned above but also by the fact that they have to be converted into active RAFT agents.

All the RAFT agents displayed rate retardation compared to styrene polymerisation via conventional free radical polymerisation. The presence of a RAFT agent in the polymerisation process slowed the propagation rate via a decreased propagating radical concentration. The cause of the experimentally observed retardation effects may be fragmentation of the intermediate RAFT radical in the pre-equilibrium or intermediate termination.

All of the thirteen RAFT agents used in this work provided good molar mass control and low polydispersities. A disadvantage of the RAFT polymerisation of styrene mediated by disulfides is side reactions, which are noticeable as bimodal distributions in the GPC chromatograms of the polymers, particularly at high conversions. This is most likely due to the bimolecular termination between polystyrene propagating radicals or benzyl sulfur radicals ( $\text{RCS}_2\bullet$ ) with polystyrene propagating radicals ( $\text{St}\bullet$ ). The termination between benzyl sulfur polystyryl radical ( $\text{RCS}_2\text{-(St)}_n\text{-St}\bullet$ ) with benzyl sulfur radical ( $\text{RS}\bullet$ ) or polystyrene propagating radical ( $\text{(St)}_n\text{-St}\bullet$ ), or vice versa, is not excluded. The higher value of polydispersities ( $> 1.5$ ) in the latter stage of the polymerisation with RAFT agent precursors 8 and 9, and  $> 1.3$ , for RAFT agent precursor 7, provides evidence of the bimodality. The relatively high polydispersity at low conversion is attributed to the relatively low chain transfer constants of RAFT agent precursors 7, 8 and 9 (PDI: 1.26 at 10%, 1.43 at 9% and 1.37 at 10%, respectively). By contrast, RAFT agents 10-13 gave rise to polymers of very low polydispersity at very low conversion, which implies that these RAFT agents have higher transfer constants than RAFT agent precursors 7 through 9 do (see Tables 10 through 13 in the Appendix) or suffer less side reactions (intermediate radical could be short lived).

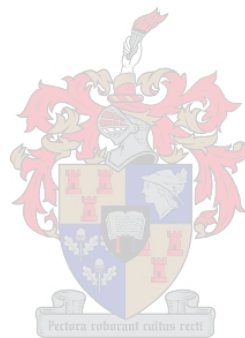
## 7.2 Recommendations for future research

As the disulfide mediated reactions provide the results that differ most from the expected results (long inhibition period of six hours), future research should include following the polymerisation reactions of styrene mediated by the disulfides by both NMR and ESR techniques.

- The ESR technique can be used to identify radical types and quantify radical concentrations in RAFT mediated radical polymerisations.
- NMR spectroscopy can be used to identify and quantify the species present in RAFT mediated free radical polymerisation reactions.

The interpretation of data provided by these two techniques should allow the mechanism of disulfide mediated RAFT processes to be even more fully understood.

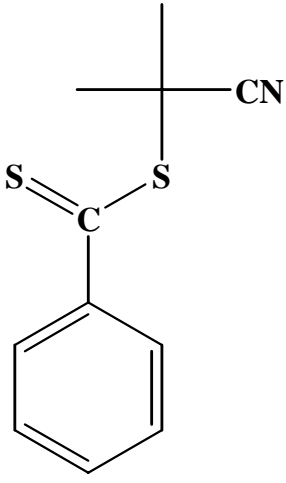
# Appendix





## RAFT agent 1: 1-cyano-1-methylethyl benzenecarbodithioate

Table 1: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 1

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                 |          |       |      |                |
|--|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                    |          |       |      |                |
| RAFT 1   | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 4        | 4860  | 1.37 | 13             |
|  | 5        | 6320  | 1.34 | 16             |
|  | 6        | 8180  | 1.32 | 18             |
|  | 7        | 9640  | 1.30 | 21             |
|  | 8        | 11200 | 1.27 | 24             |
|  | 9        | 12400 | 1.26 | 25             |
|  | 10       | 13300 | 1.26 | 30             |
|  | 11       | 14300 | 1.25 | 30             |

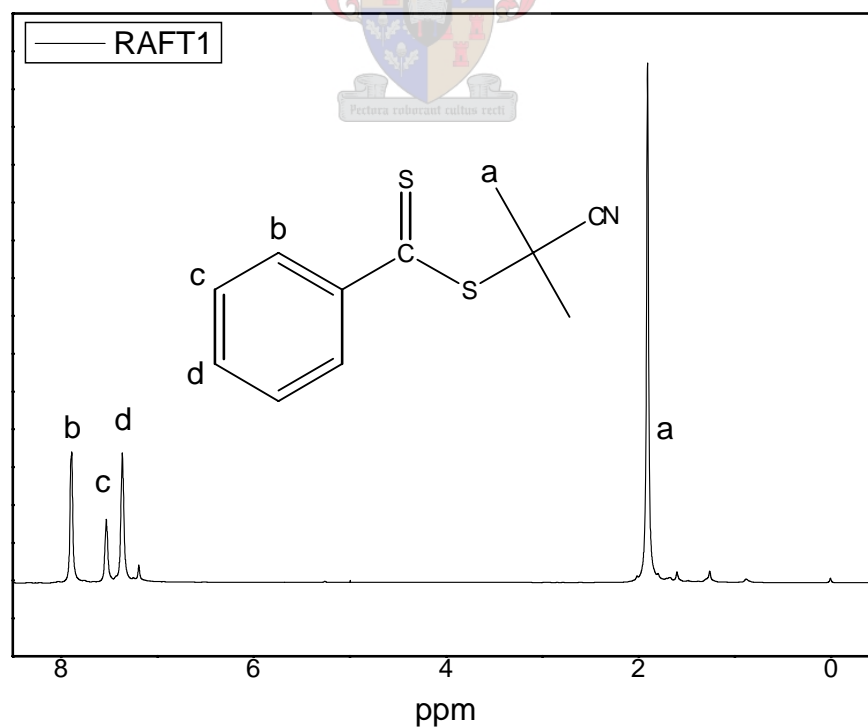


Figure 1. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 1 in chloroform- $d$ .

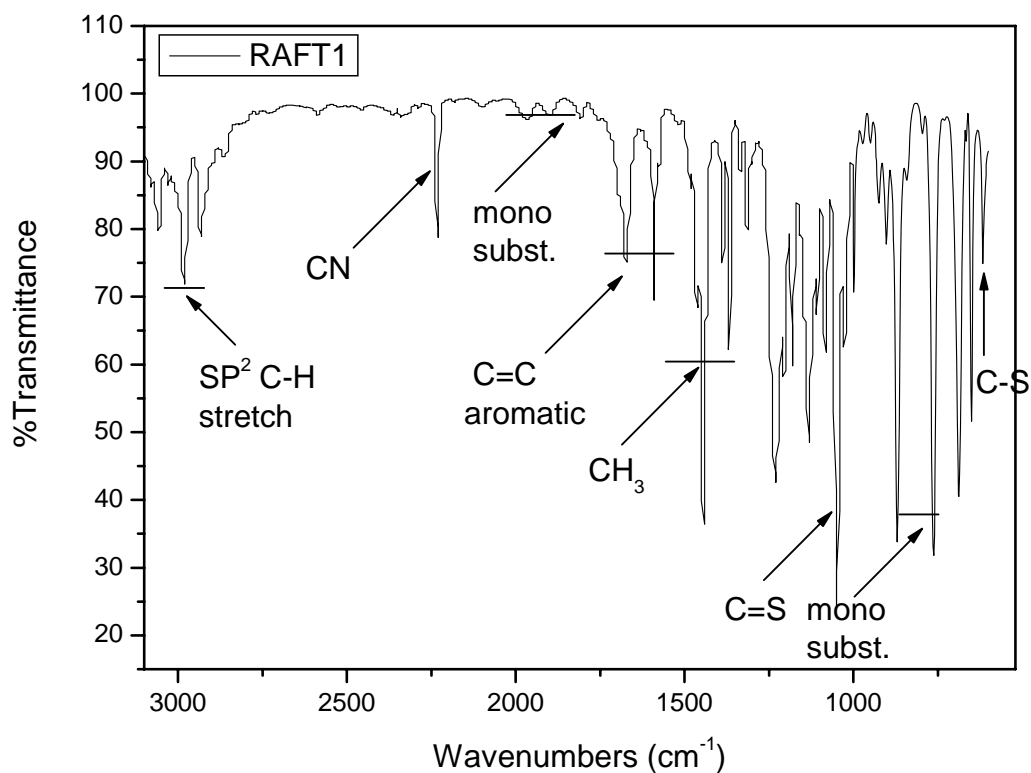


Figure 2. The infrared spectrum of RAFT agent 1 in KBr.

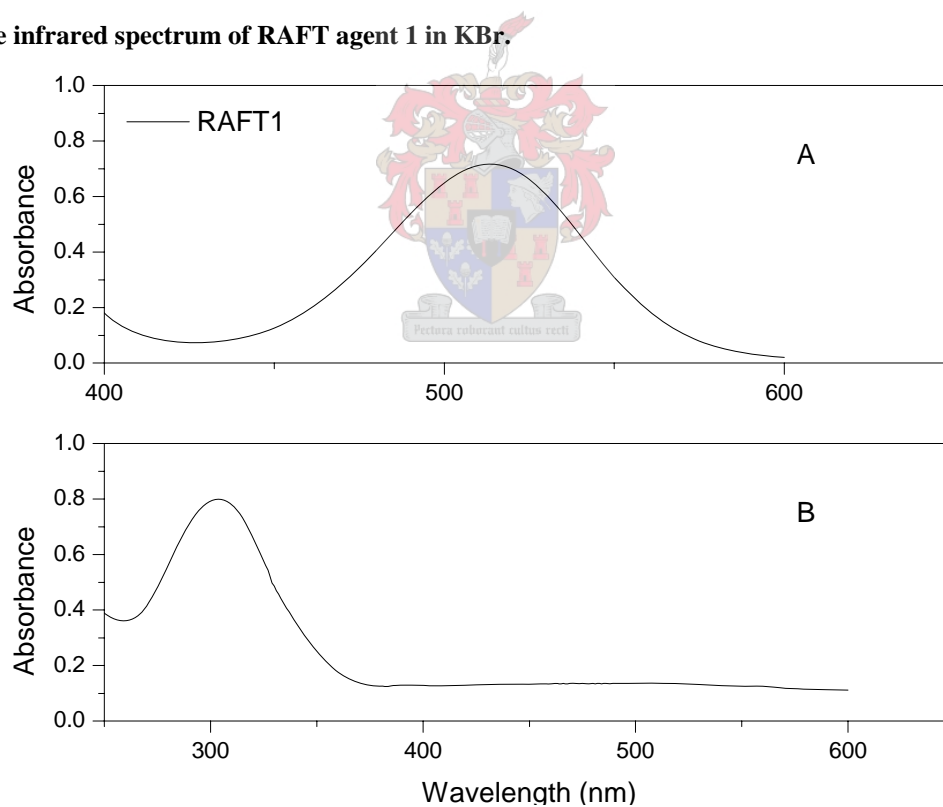
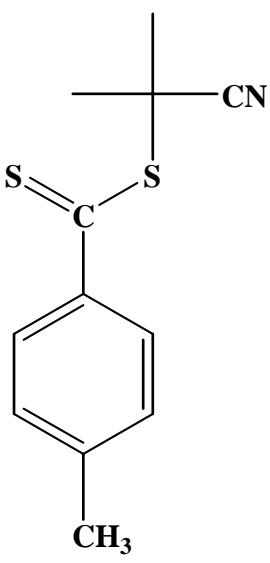


Figure 3. Absorbance spectrum of RAFT agent 1 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 514.6$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 303.4$  nm.

## RAFT agent 2: 1-cyano-1-methylethyl 4-methylbenzenecarbodithioate

Table 2: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 2

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                |          |       |      |                |
|---|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                   |          |       |      |                |
| RAFT 2  | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 5        | 7170  | 1.24 | 16             |
|   | 6        | 8680  | 1.24 | 19             |
|   | 7        | 10000 | 1.24 | 22             |
|   | 8        | 11400 | 1.24 | 24             |
|   | 9        | 12800 | 1.24 | 26             |
|   | 10       | 14500 | 1.23 | 31             |
|   | 11       | 16000 | 1.23 | 33             |
|   | 12       | 18500 | 1.23 | 36             |

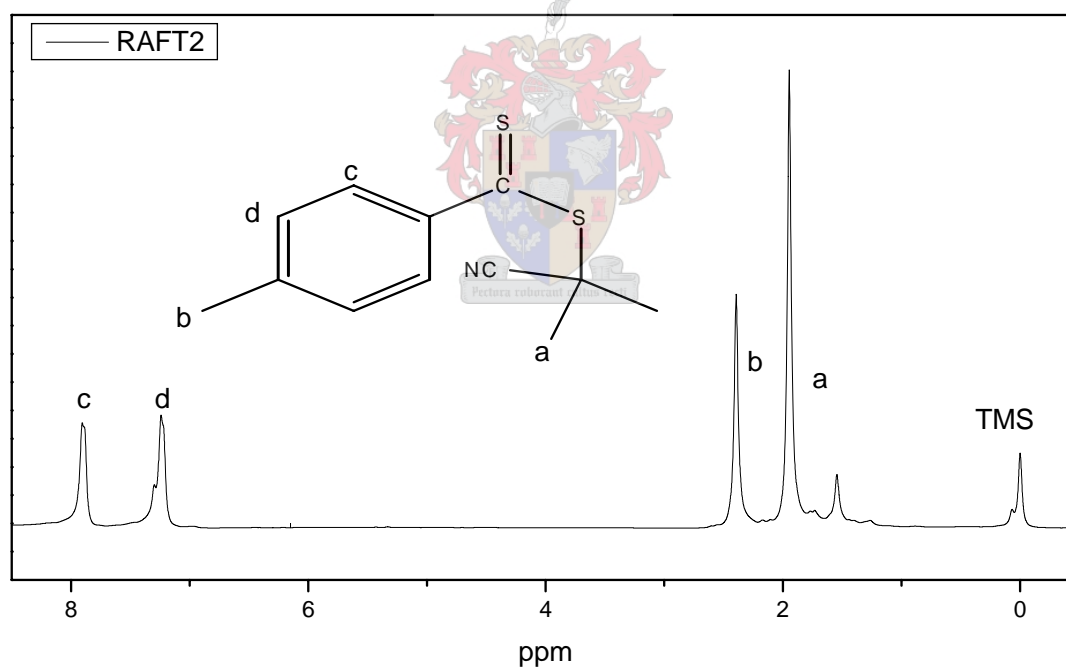


Figure 4. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 2 in chloroform-d.

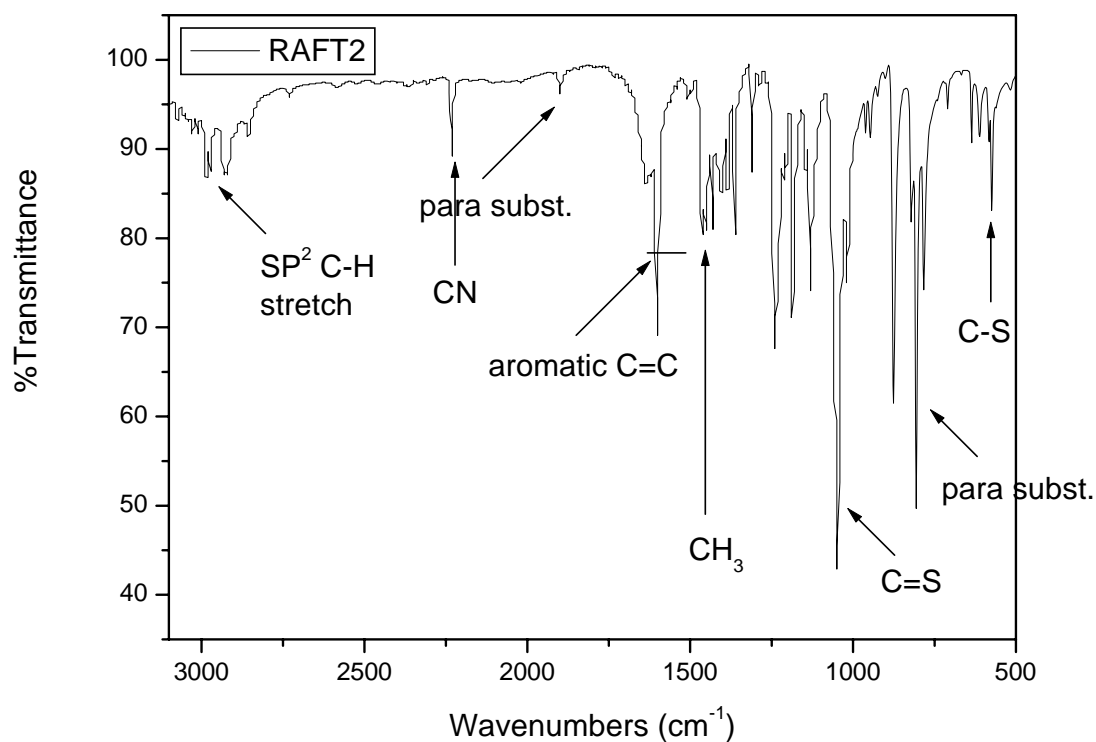


Figure 5. The infrared spectrum of RAFT agent 2 in KBr.

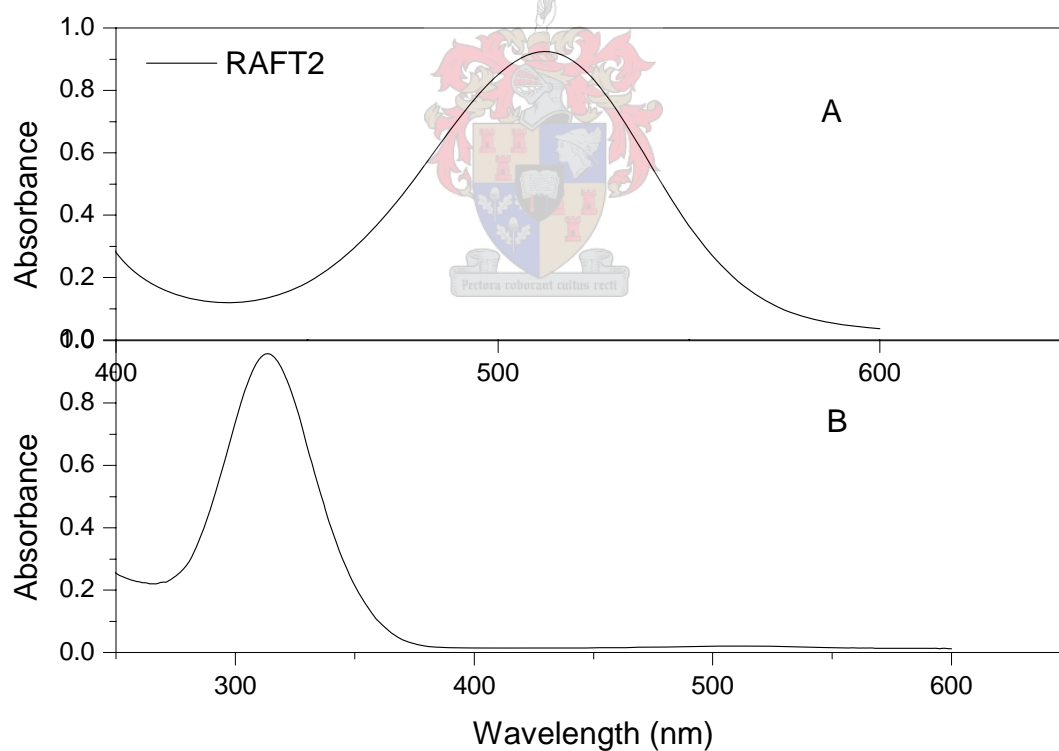
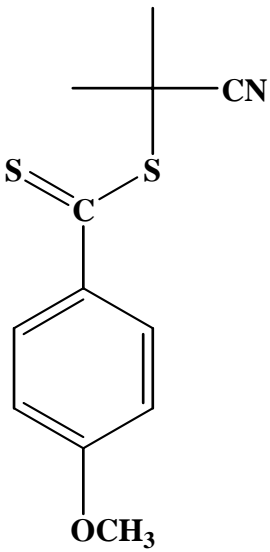


Figure 6. Absorbance spectrum of RAFT agent 2 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 513.1$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 313.8$  nm.

## RAFT agent 3: 1-cyano-1-methylethyl 4-methoxybenzenecarbo-dithioate

Table 3: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 3

| [RAFT] <sub>0</sub> = 1.275x10 <sup>-5</sup> M                                     |          |        |      |                |
|--|----------|--------|------|----------------|
| [M] <sub>0</sub> = 9.615 x10 <sup>-3</sup> M                                       |          |        |      |                |
| RAFT 3   | Time (h) | $M_n$  | PDI  | Conversion (%) |
|  | 3        | 6770   | 1.16 | 10             |
|  | 4        | 8280   | 1.19 | 13             |
|  | 5        | 10000  | 1.18 | 16             |
|  | 6        | 11300  | 1.21 | 19             |
|  | 7        | 14100  | 1.11 | 23             |
|  | 8        | 15400  | 1.12 | 26             |
|  | 9        | 16900  | 1.12 | 28             |
|  | 10       | 18100  | 1.13 | 31             |
|  | 11       | 200000 | 1.12 | 34             |

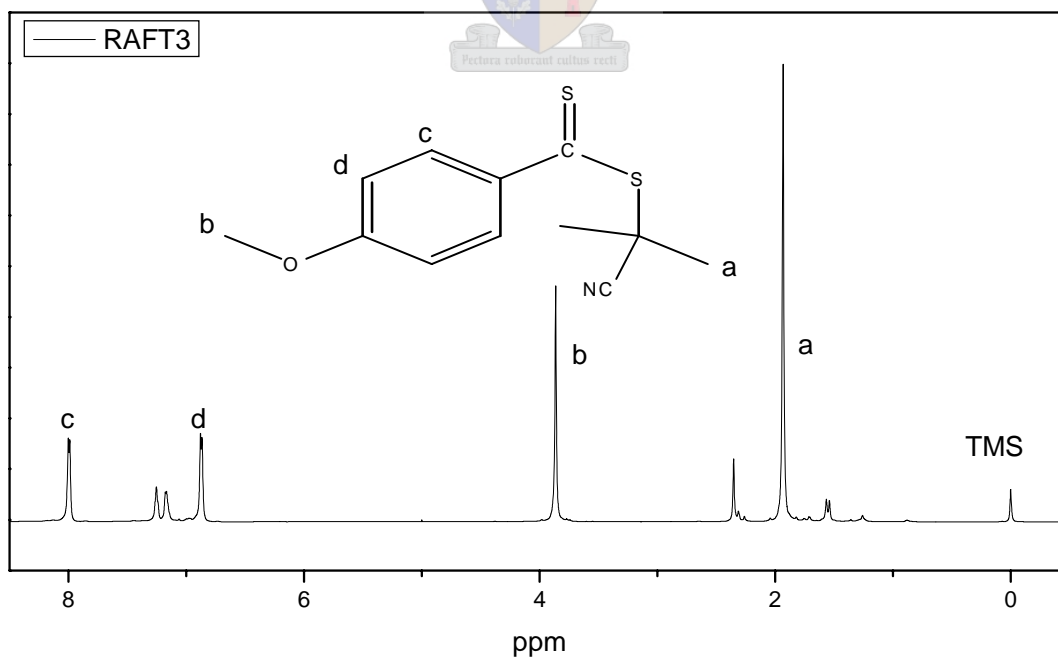


Figure 7. The 300-MHz <sup>1</sup>H NMR spectrum of RAFT agent 3 in chloroform-d.

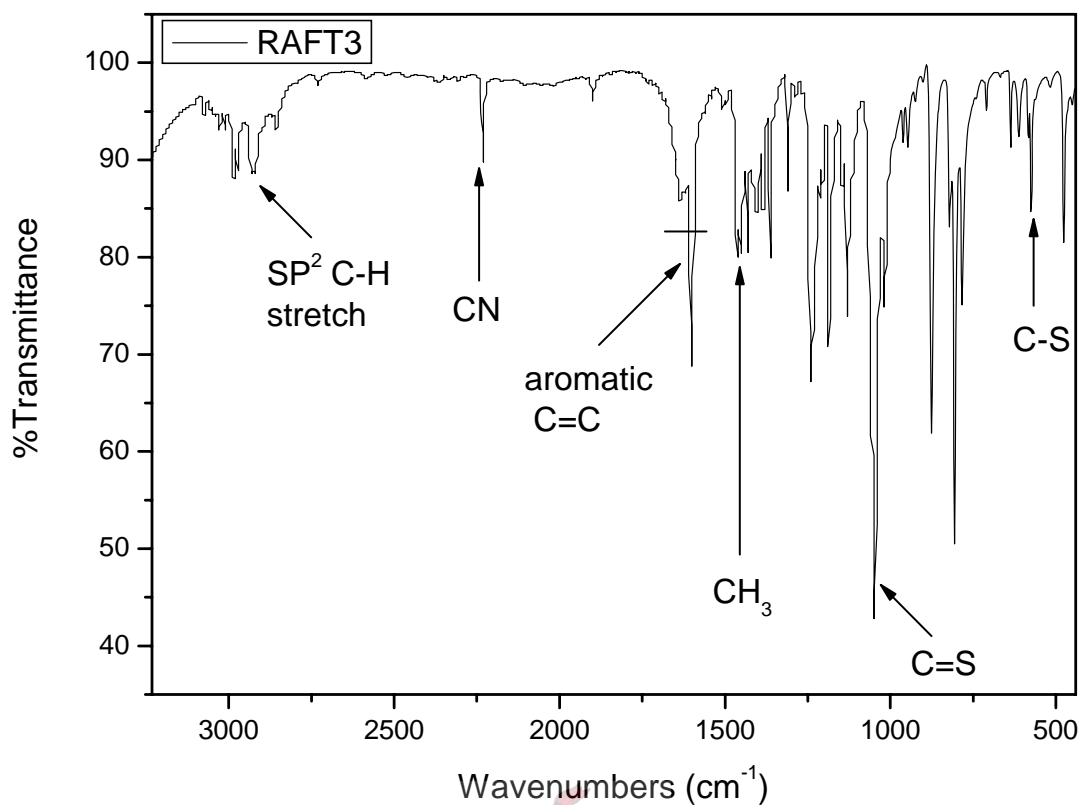


Figure 8. The infrared spectrum of RAFT agent 3 in KBr.

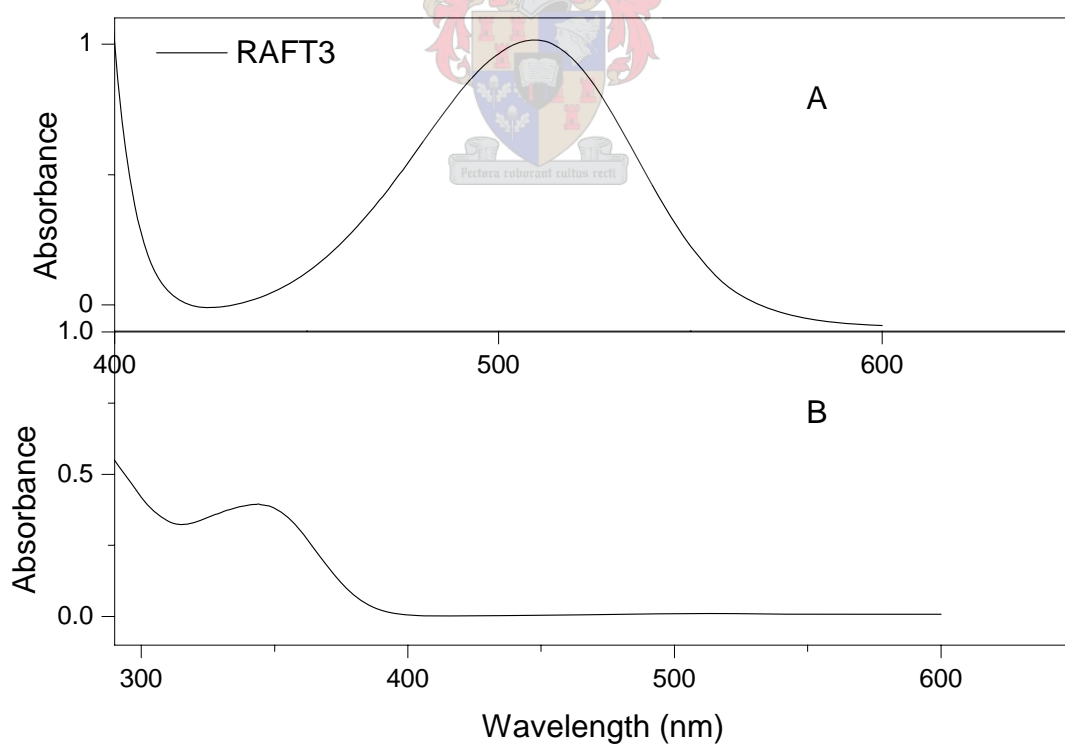
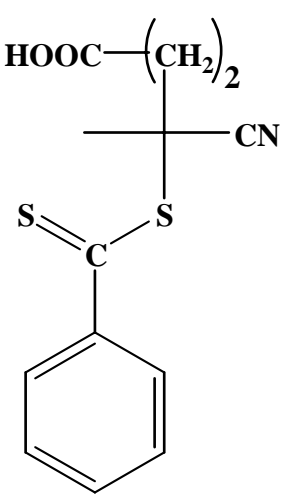


Figure 9. Absorbance spectrum of RAFT agent 3 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 508.6$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 347.0$  nm.

## RAFT agent 4: 4-cyano-4-[(phenylcarbothioyl)sulfanyl]pentanoic acid

Table 4: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 4

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                 |          |       |      |                |
|--|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                    |          |       |      |                |
| RAFT 4   | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 3        | 4690  | 1.40 | 7              |
|  | 4        | 6340  | 1.37 | 10             |
|  | 5        | 7800  | 1.35 | 14             |
|  | 6        | 9300  | 1.34 | 17             |
|  | 7        | 11000 | 1.31 | 20             |
|  | 8        | 12100 | 1.31 | 23             |
|  | 9        | 13100 | 1.30 | 27             |
|  | 10       | 14200 | 1.28 | 30             |
|  | 11       | 15200 | 1.28 | 33             |

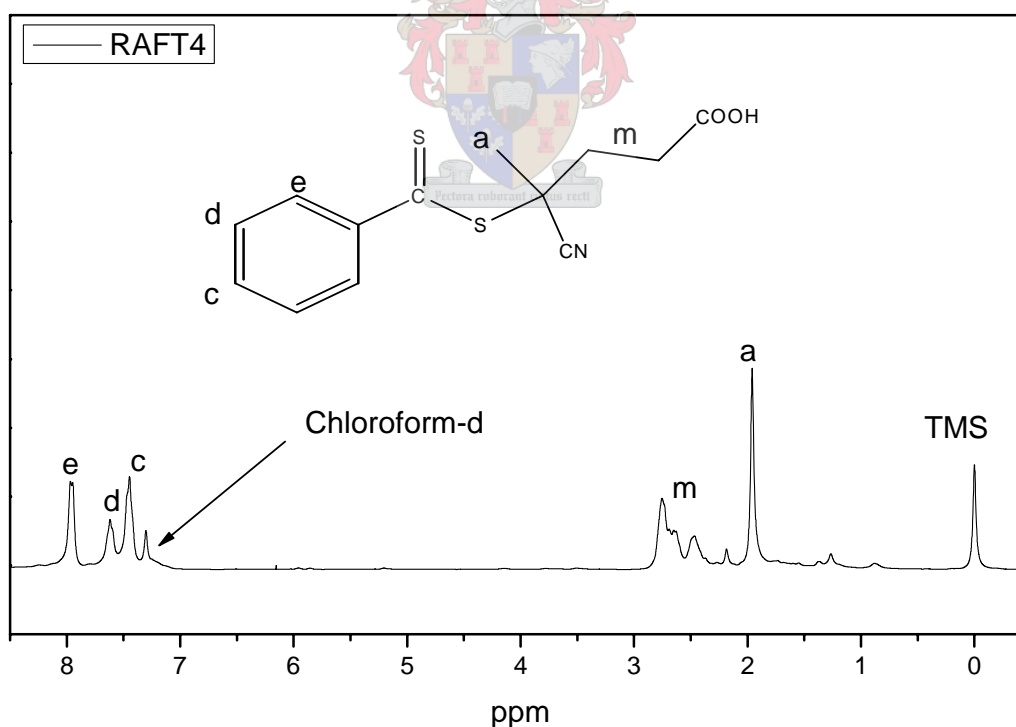


Figure 10. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 4 in chloroform-d.

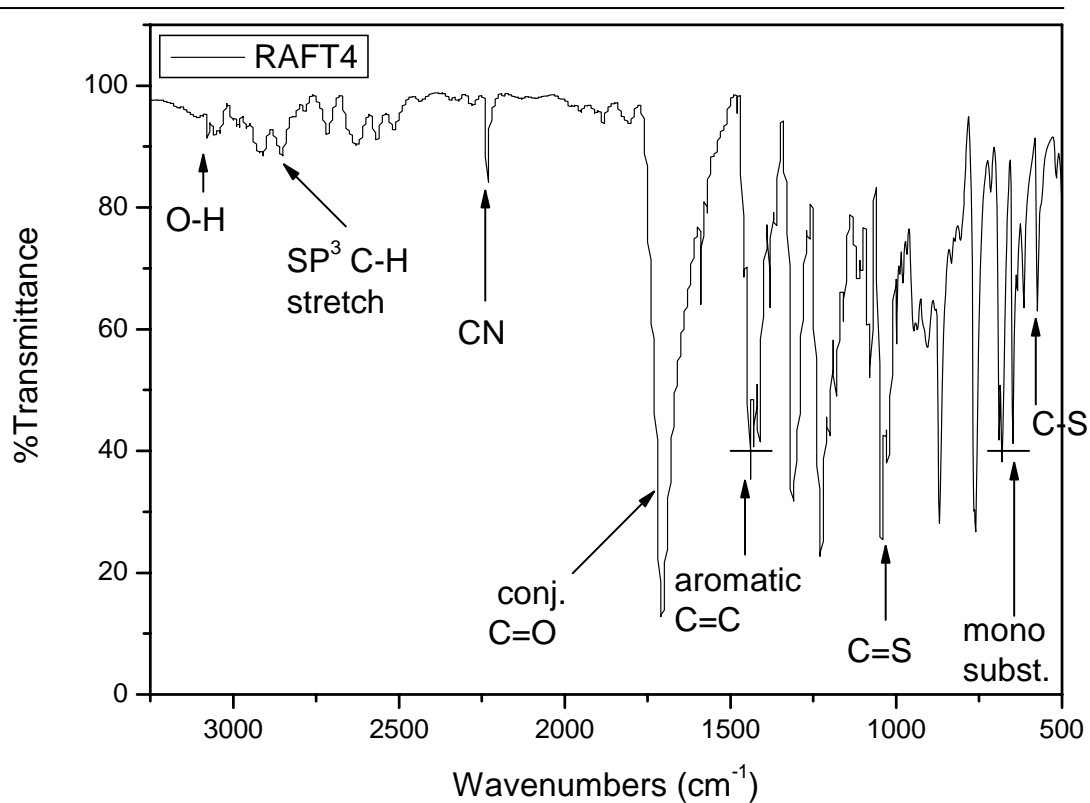


Figure 11. The infrared spectrum of RAFT agent 4 in KBr.

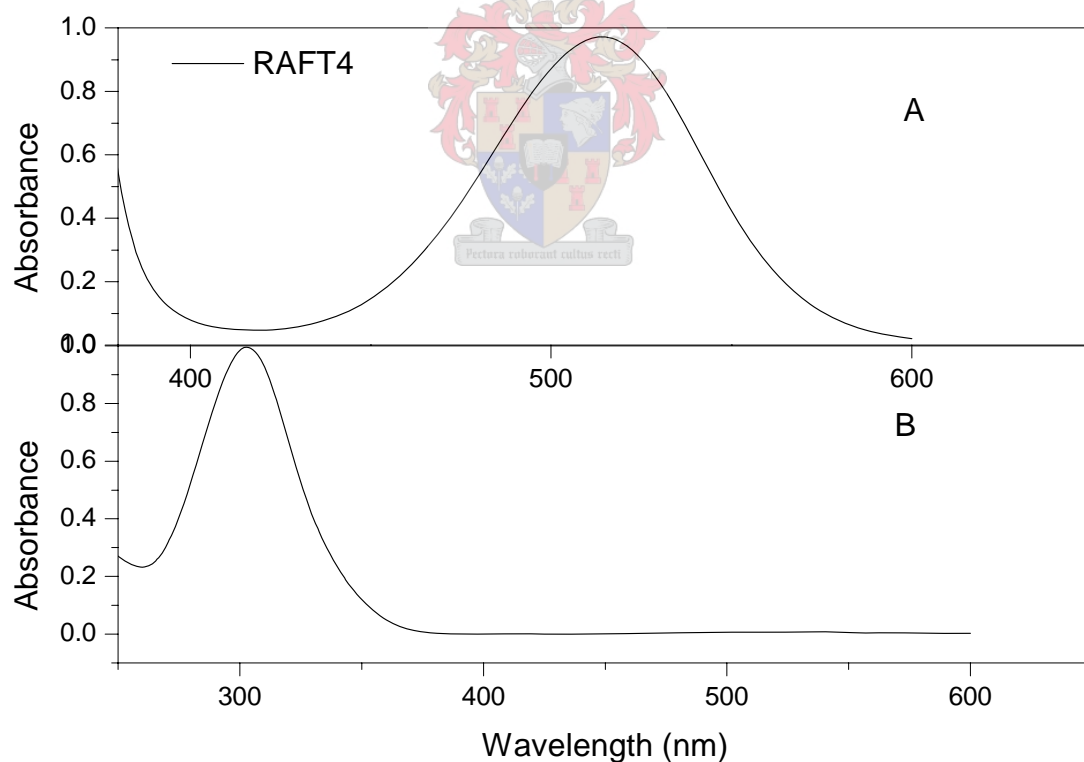
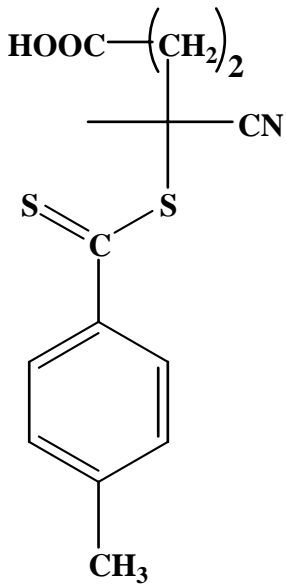


Figure 12. Absorbance spectrum of RAFT agent 4 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 514.6$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 303.4$  nm.



## RAFT agent 5: 4-cyano-4-[[[(4-methylphenyl)carbothioyl]sulfanyl]-pentanoic acid

Table 5: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 5

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                 |          |       |      |                |
|--|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                    |          |       |      |                |
| RAFT 5   | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 4        | 7350  | 1.35 | 13             |
|  | 5        | 8624  | 1.32 | 15             |
|  | 6        | 9775  | 1.31 | 18             |
|  | 7        | 11100 | 1.28 | 21             |
|  | 8        | 12400 | 1.28 | 24             |
|  | 9        | 13700 | 1.27 | 27             |
|  | 10       | 14800 | 1.27 | 31             |
|  | 11       | 15700 | 1.26 | 33             |
|  | 12       | 17600 | 1.26 | 37             |

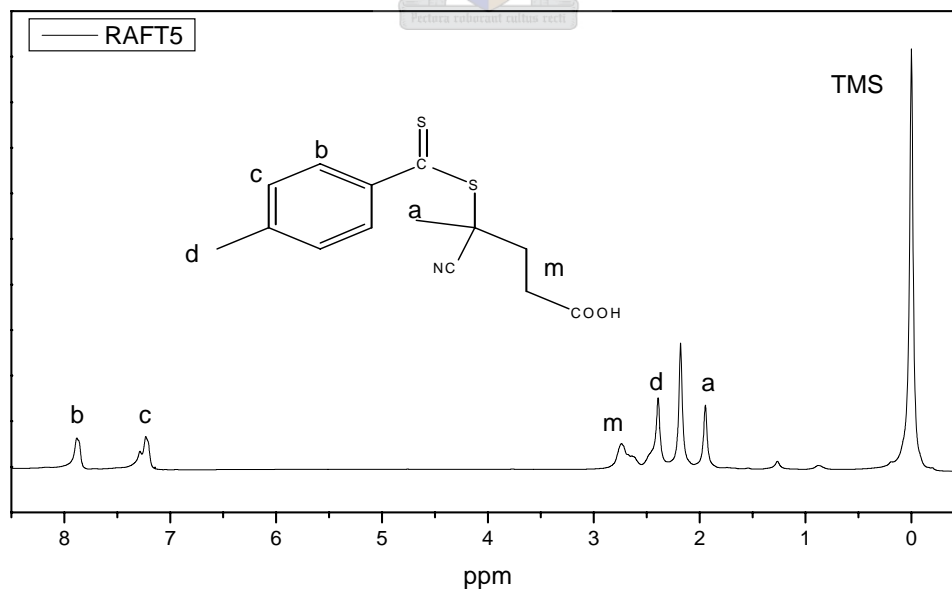


Figure 13. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 5 in chloroform-d.

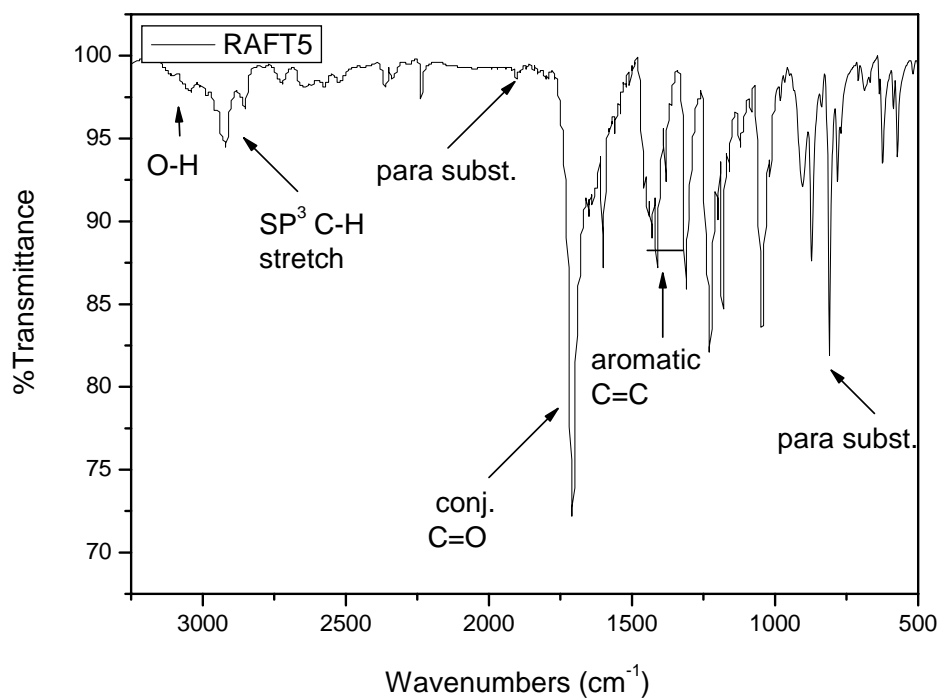


Figure 14. The infrared spectrum of RAFT agent 5 in KBr.

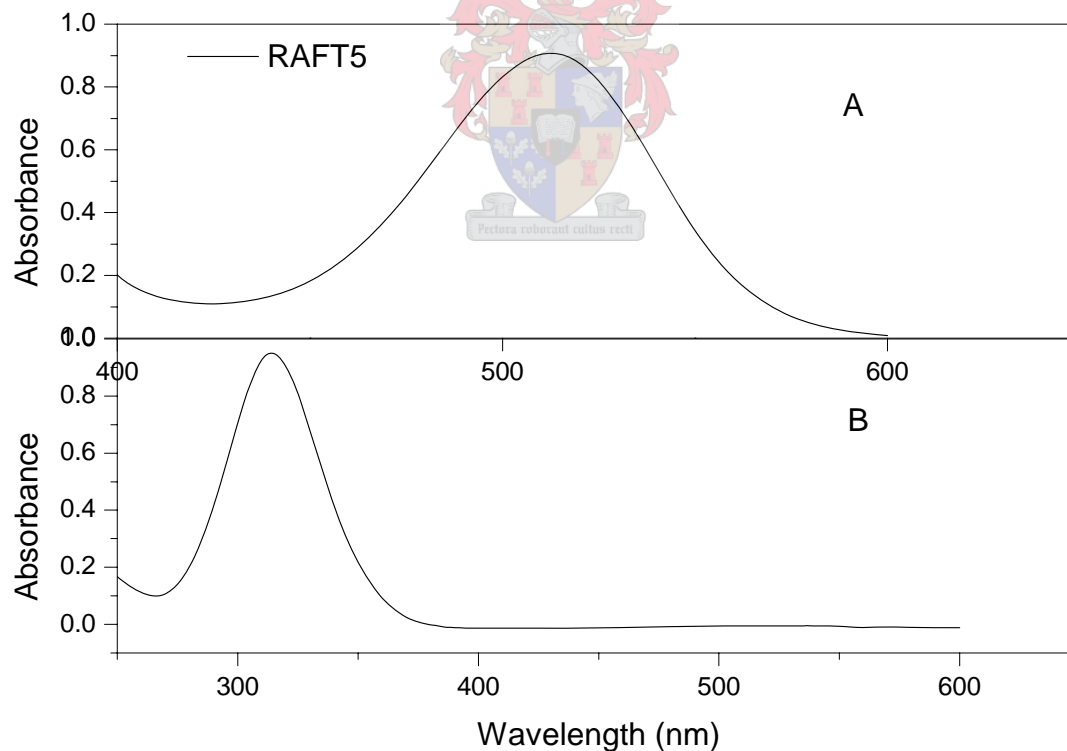


Figure 15. Absorbance spectrum of RAFT agent 5 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 511.5$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 313.8$  nm.

## RAFT agent 6: 4-cyano-4-[[[(4-methoxyphenyl)carbothioyl]sulfanyl]-pentanoic acid

Table 6: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 6

| [RAFT] <sub>0</sub> = 1.275 × 10 <sup>-5</sup> M |          |       |      |                |
|--|----------|-------|------|----------------|
| [M] <sub>0</sub> = 9.615 × 10 <sup>-3</sup> M    |          |       |      |                |
| RAFT 6   | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 5        | 8760  | 1.28 | 16             |
|  | 6        | 10060 | 1.26 | 19             |
|  | 7        | 11200 | 1.25 | 22             |
|  | 8        | 12700 | 1.23 | 24             |
|  | 9        | 13800 | 1.25 | 27             |
|  | 10       | 14900 | 1.25 | 30             |
|  | 11       | 16200 | 1.24 | 33             |
|  | 12       | 17400 | 1.22 | 36             |

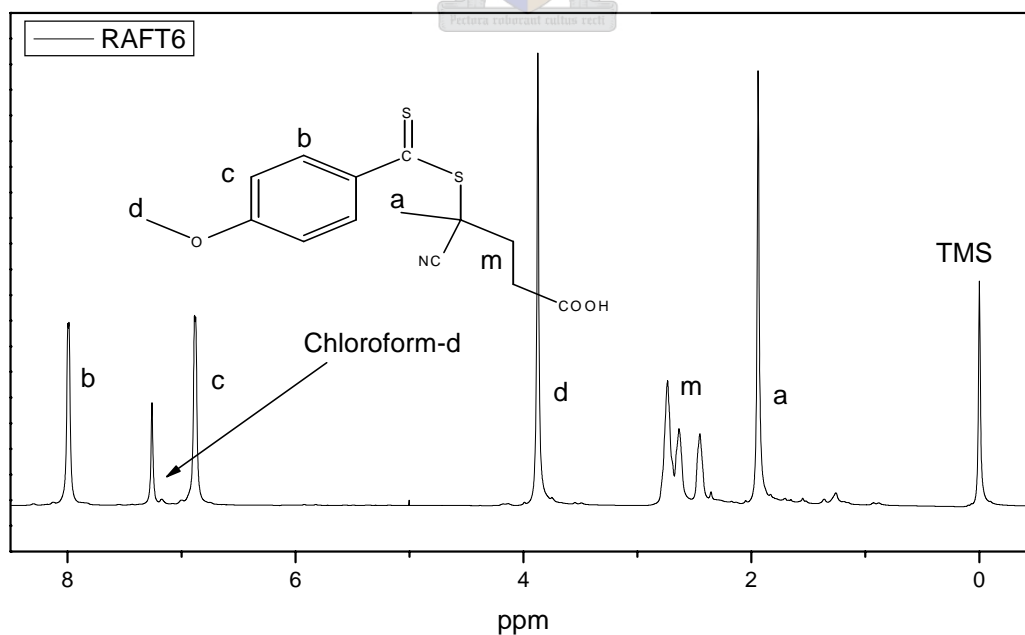


Figure 16. The 300-MHz <sup>1</sup>H NMR spectrum of RAFT agent 6 in chloroform-d.

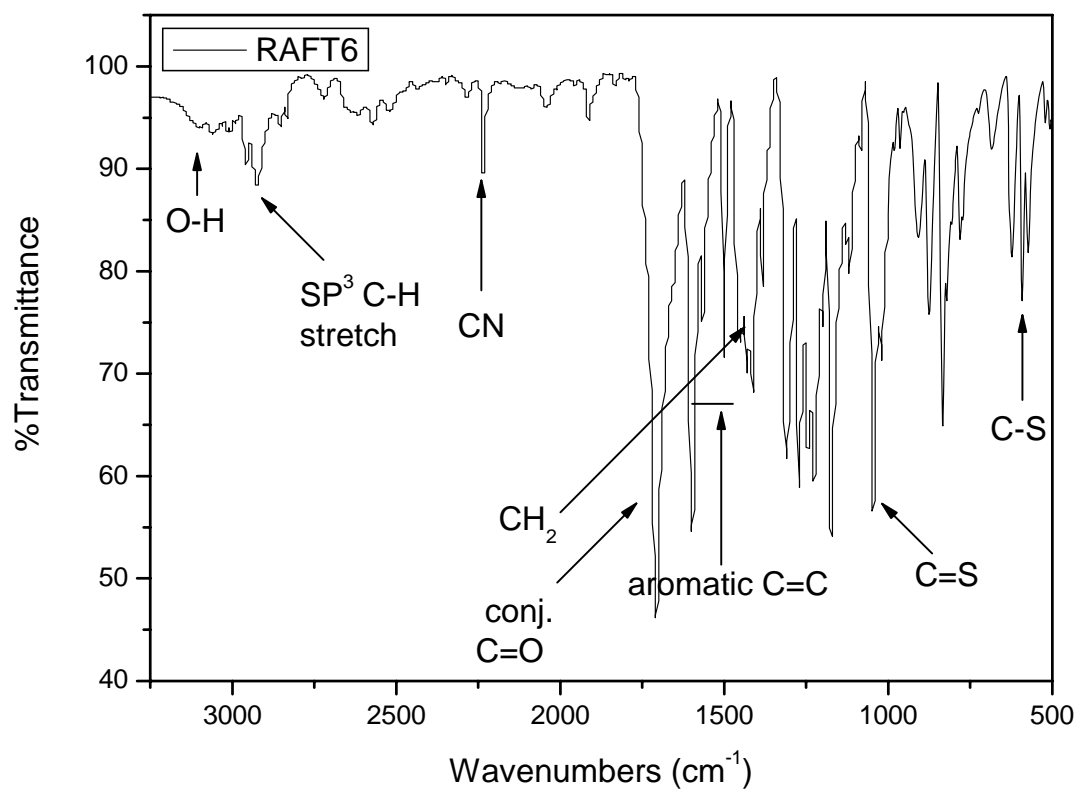


Figure 17. The infrared spectrum of RAFT agent 6 in KBr.

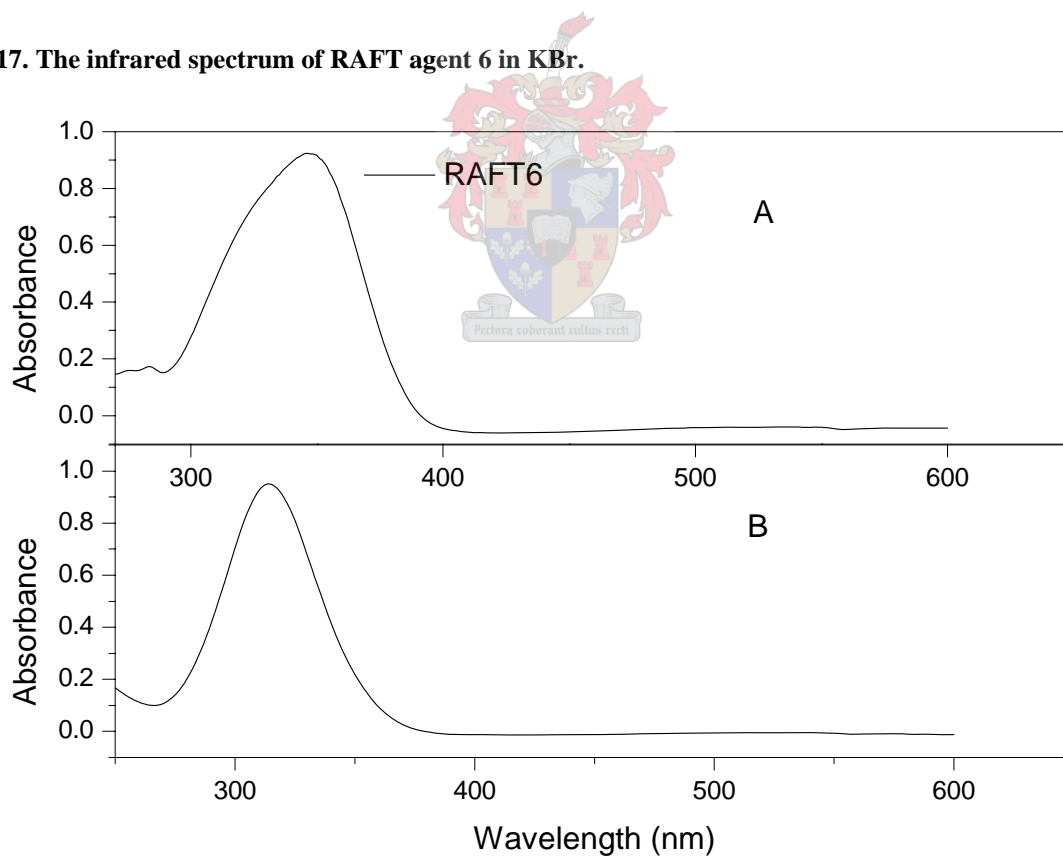
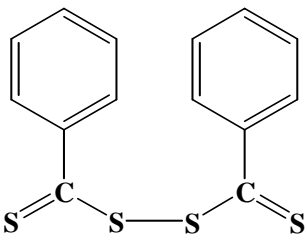


Figure 18. Absorbance spectrum of RAFT agent 6 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 347.3$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 313.8$  nm.

## RAFT agent precursor 7: Diphenyldithioperoxyanhydride

Table 7: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent precursor 7

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$  |          |       |      |                |
|---|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$   |          |       |      |                |
| RAFT 7<br> | Time (h) | $M_n$ | PDI  | Conversion (%) |
|   | 8        | 4680  | 1.26 | 10             |
|   | 9        | 6700  | 1.27 | 14             |
|   | 10       | 8400  | 1.28 | 18             |
|   | 11       | 10000 | 1.31 | 22             |
|   | 12       | 11800 | 1.30 | 25             |

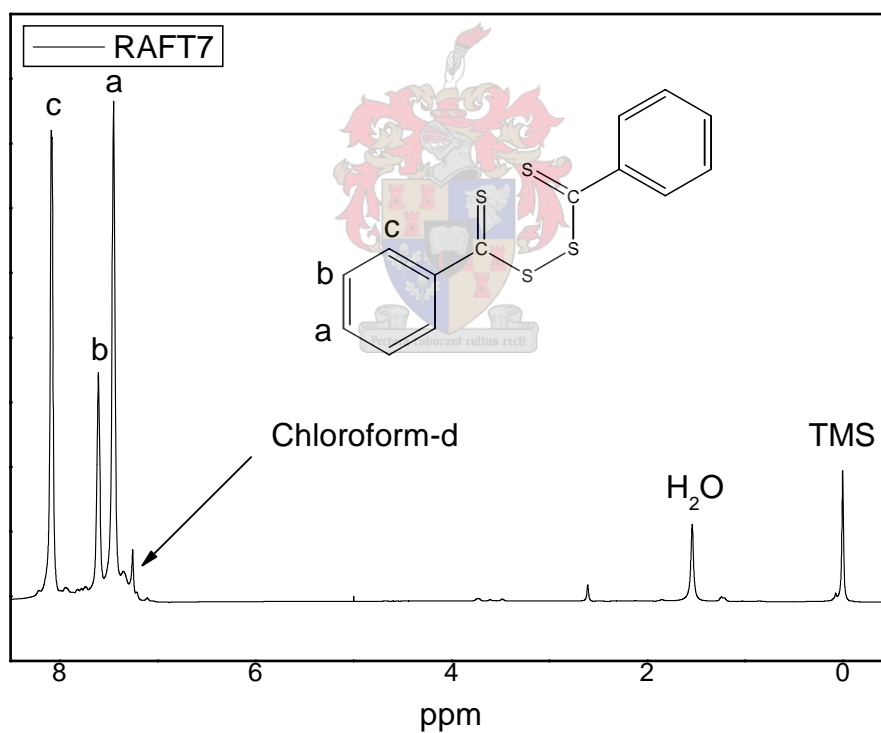


Figure 19. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent precursor 7 in chloroform-d.

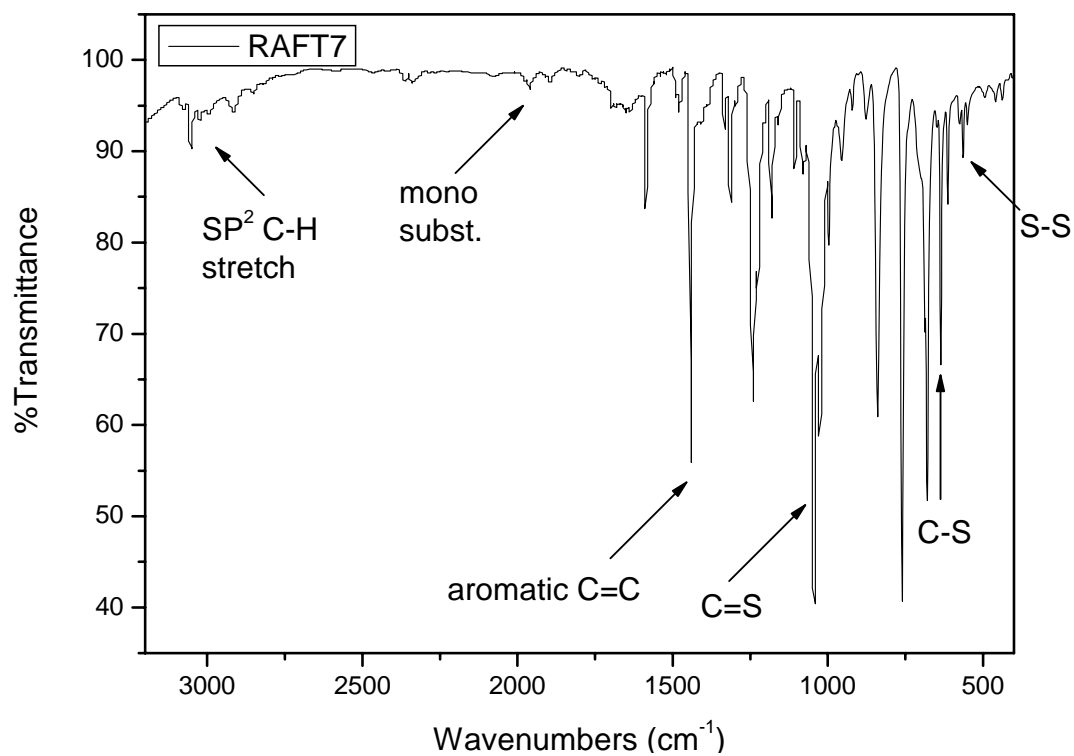


Figure 20. The infrared spectrum of RAFT agent precursor 7 in KBr.

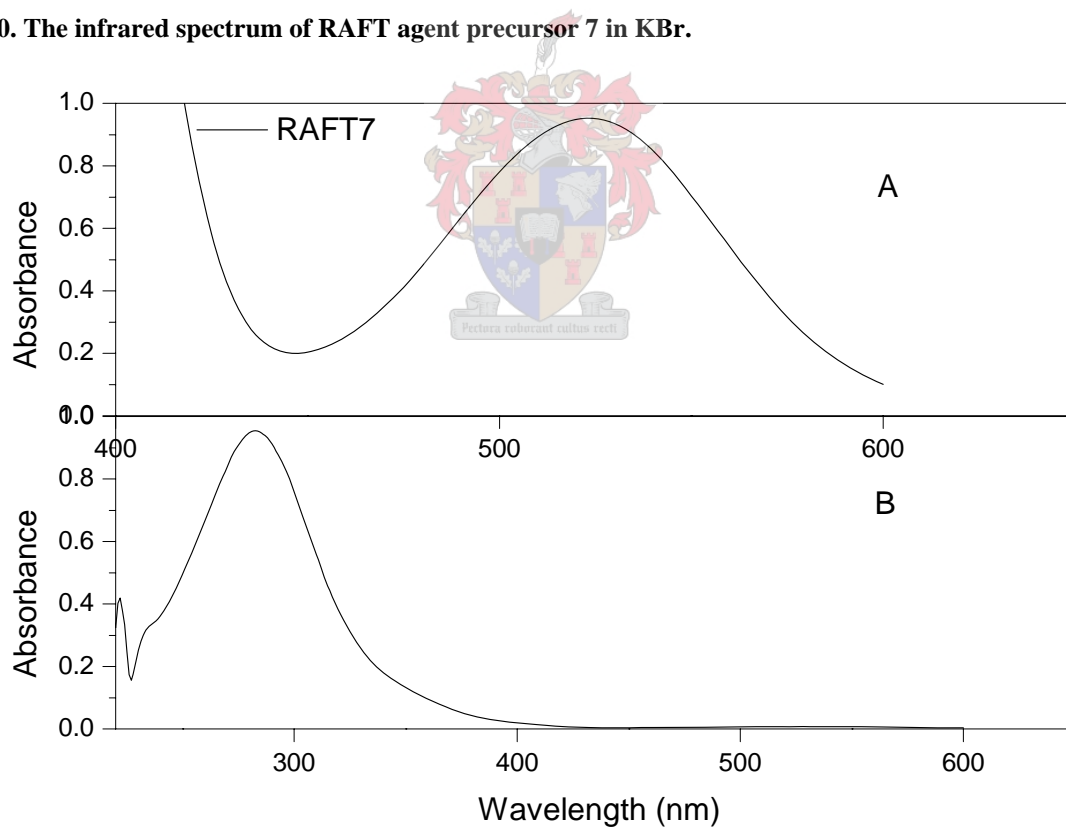
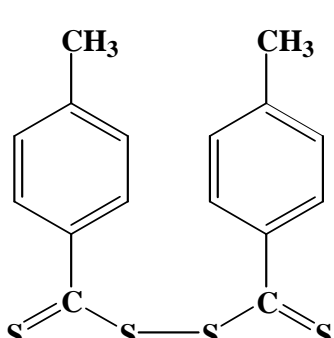


Figure 21. Absorbance spectrum of RAFT agent precursor 7 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 525.4$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 282.3$  nm.

## RAFT agent precursor 8: Bis(4-methylphenyl)dithioperoxyanhydride

Table 8: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent precursor 8

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                |             |       |      |                   |
|---|-------------|-------|------|-------------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                   |             |       |      |                   |
| RAFT 8  | Time<br>(h) | $M_n$ | PDI  | Conversion<br>(%) |
|  | 8           | 4280  | 1.43 | 9                 |
|   | 9           | 6980  | 1.37 | 12                |
|   | 10          | 8910  | 1.43 | 17                |
|   | 11          | 10100 | 1.50 | 22                |
|   | 12          | 12800 | 1.50 | 30                |

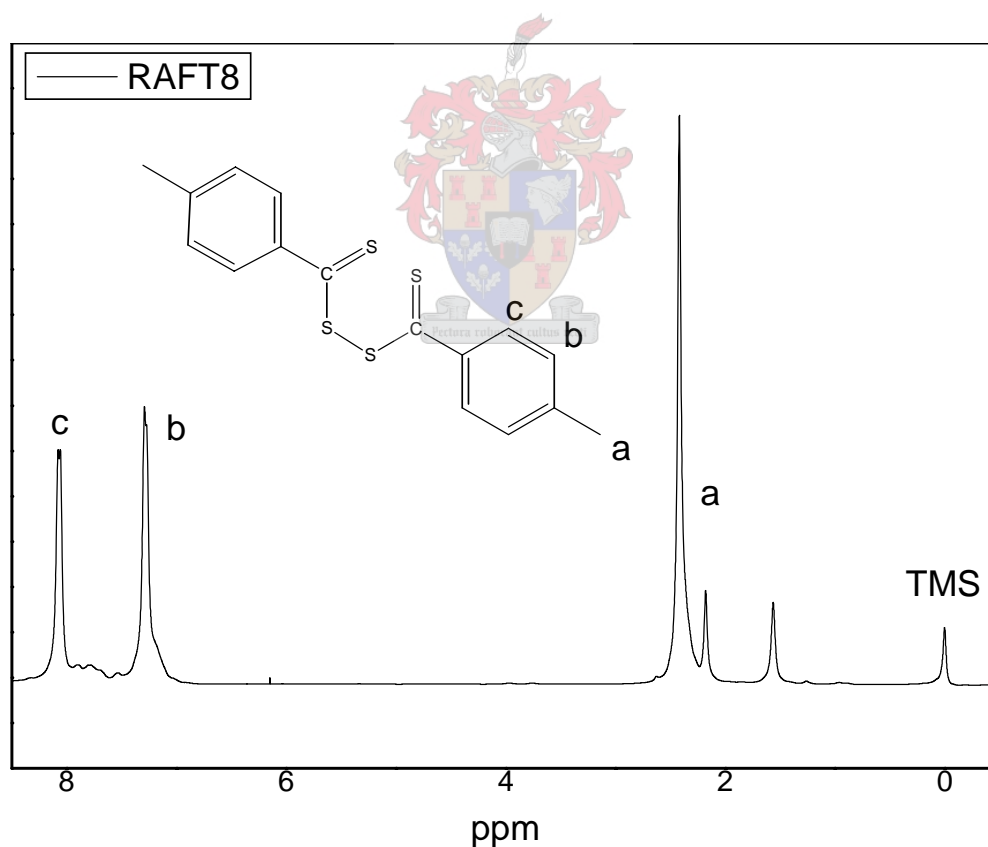


Figure 22. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent precursor 8 in chloroform-d.

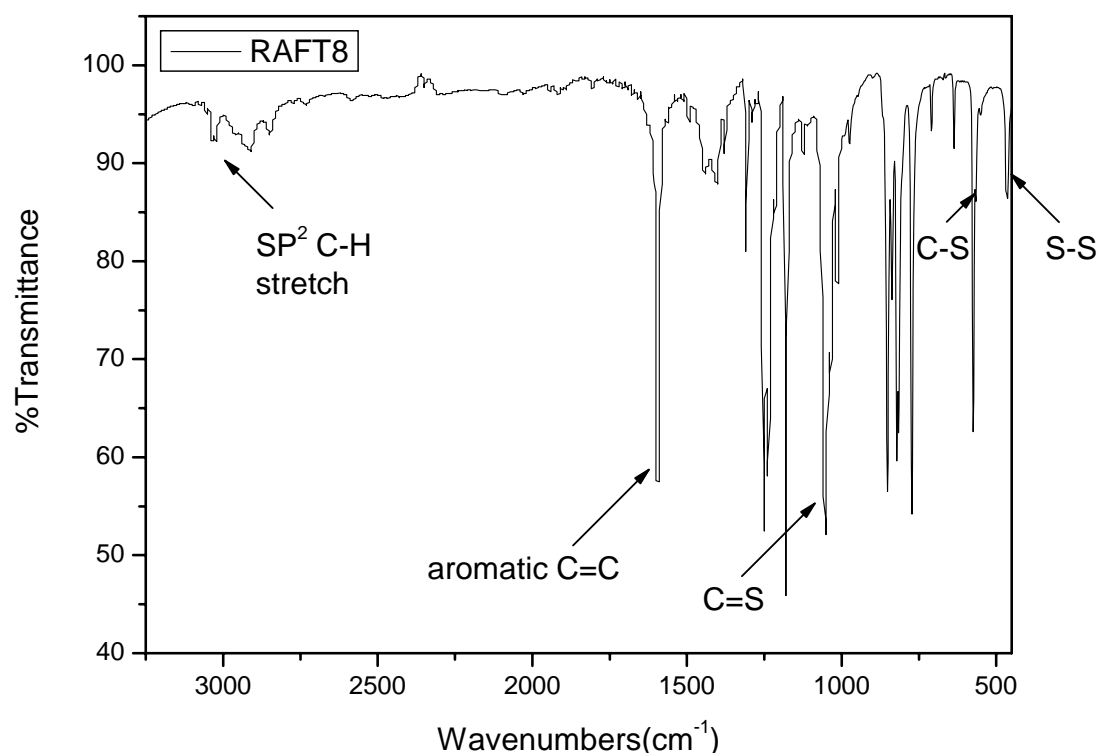


Figure 23. The infrared spectrum of RAFT agent precursor 8 in KBr.

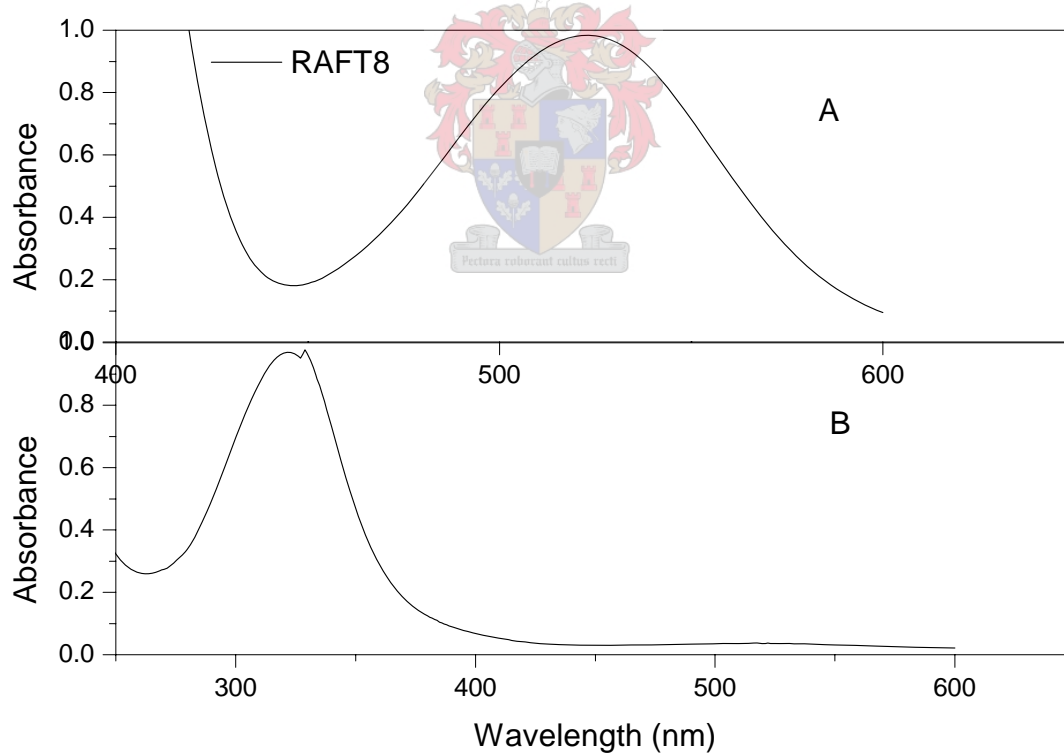
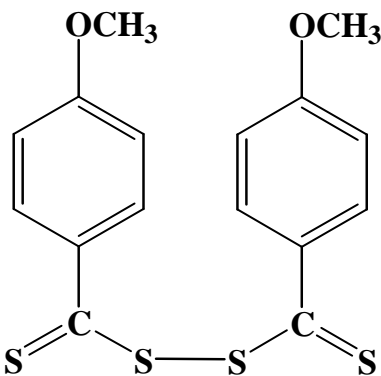


Figure 24. Absorbance spectrum of RAFT agent precursor 8 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 523.2$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 323.1$  nm.



## RAFT agent precursor 9: Bis(4-methoxyphenyl)dithioperoxyanhydride

Table 9: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent precursor 9

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                |             |       |      |                   |
|---|-------------|-------|------|-------------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                   |             |       |      |                   |
| RAFT 9  | Time<br>(h) | $M_n$ | PDI  | Conversion<br>(%) |
|  | 8           | 5390  | 1.37 | 10                |
|   | 9           | 7130  | 1.39 | 14                |
|   | 10          | 8760  | 1.4  | 18                |
|   | 11          | 10900 | 1.52 | 22                |
|   | 12          | 11500 | 1.47 | 25                |

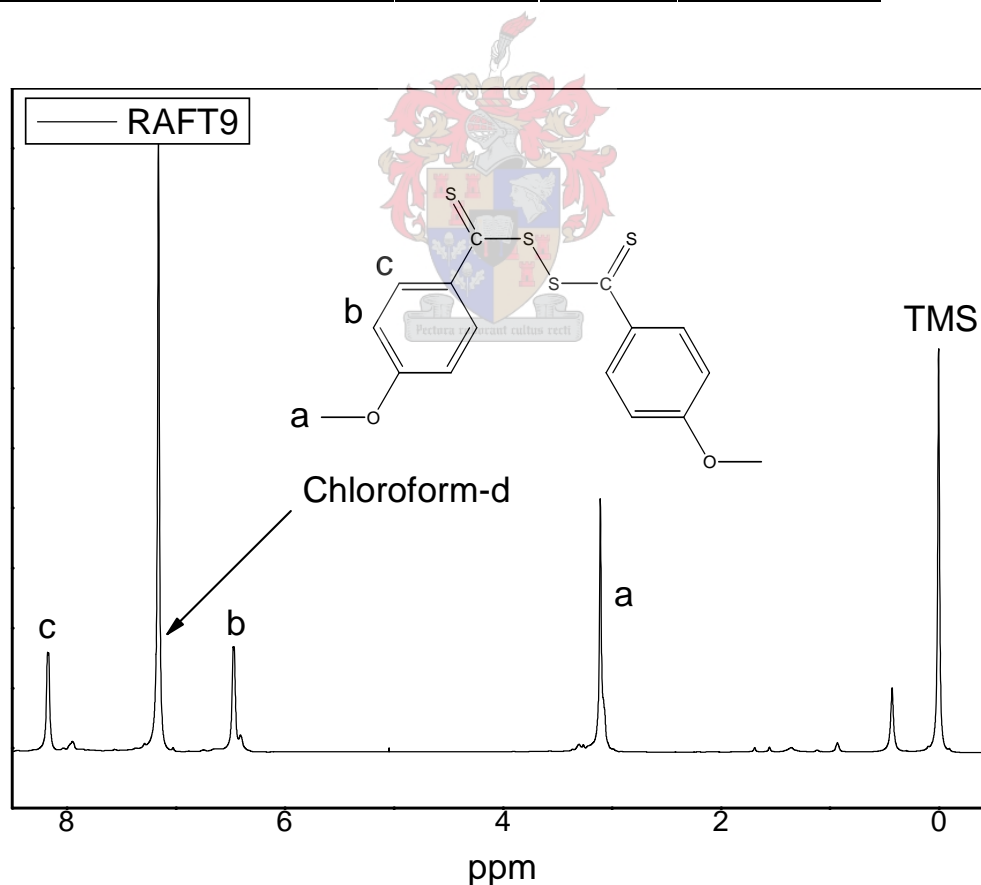


Figure 25. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent precursor 9 in chloroform-d.

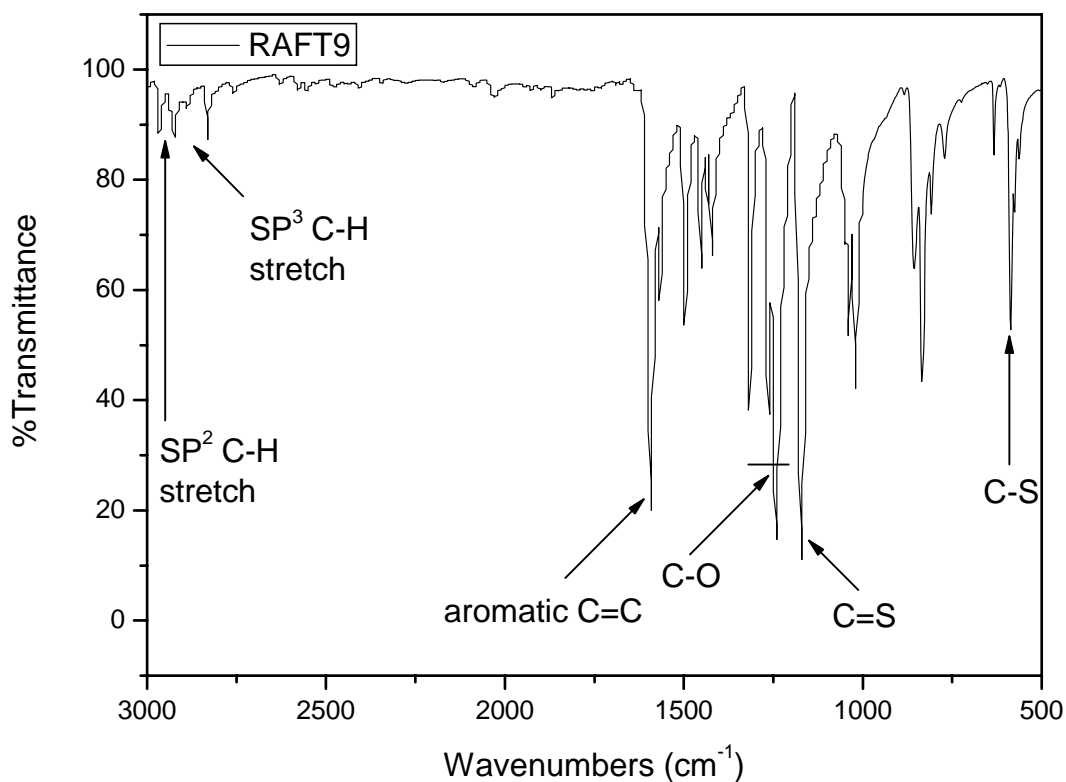


Figure 26. The infrared spectrum of RAFT agent precursor 9 in KBr.

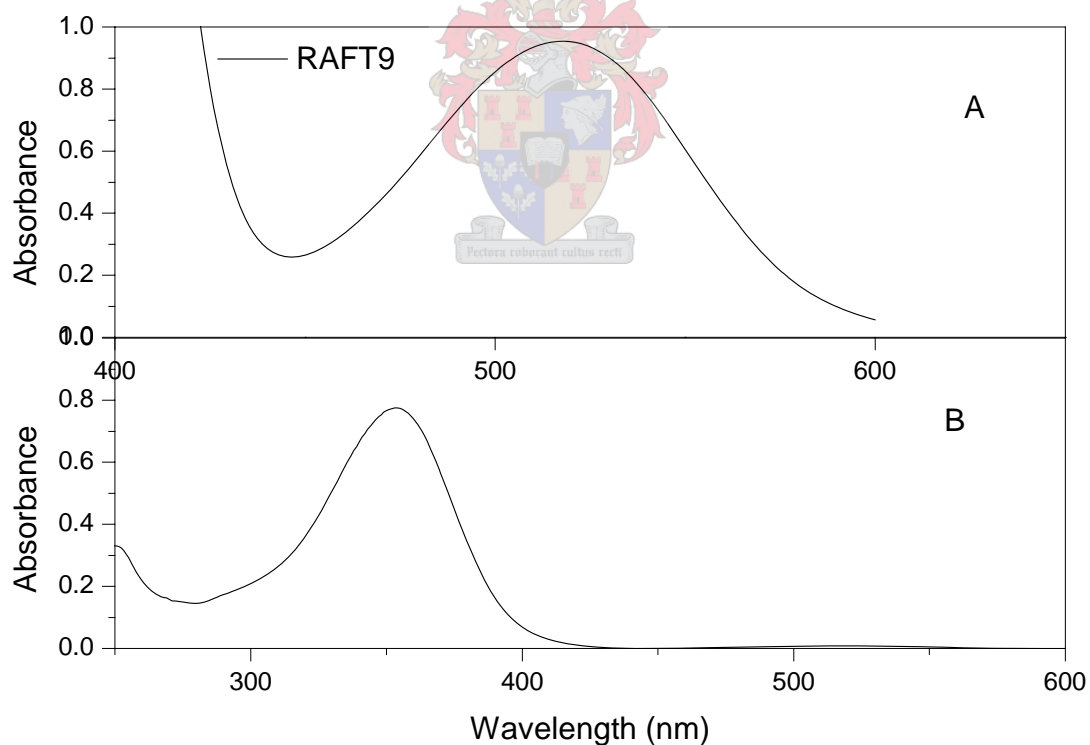
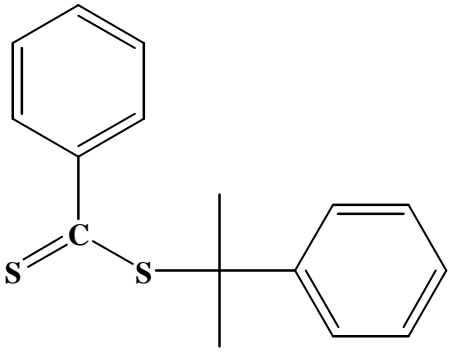


Figure 27. Absorbance spectrum of RAFT agent precursor 9 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 518.1$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 352.9$  nm.

## RAFT agent 10: 1-methyl-1-phenylethyl benzenecarbodithioate

Table 10: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 10

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                |             |       |      |                   |
|---|-------------|-------|------|-------------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                   |             |       |      |                   |
| RAFT 10   | Time<br>(h) | $M_n$ | PDI  | Conversion<br>(%) |
|  | 4           | 9000  | 1.10 | 9                 |
|   | 5           | 11300 | 1.11 | 13                |
|   | 6           | 13100 | 1.12 | 16                |
|   | 7           | 14700 | 1.11 | 20                |
|   | 8           | 15400 | 1.13 | 23                |
|   | 9           | 16700 | 1.12 | 26                |
|   | 10          | 17700 | 1.12 | 29                |

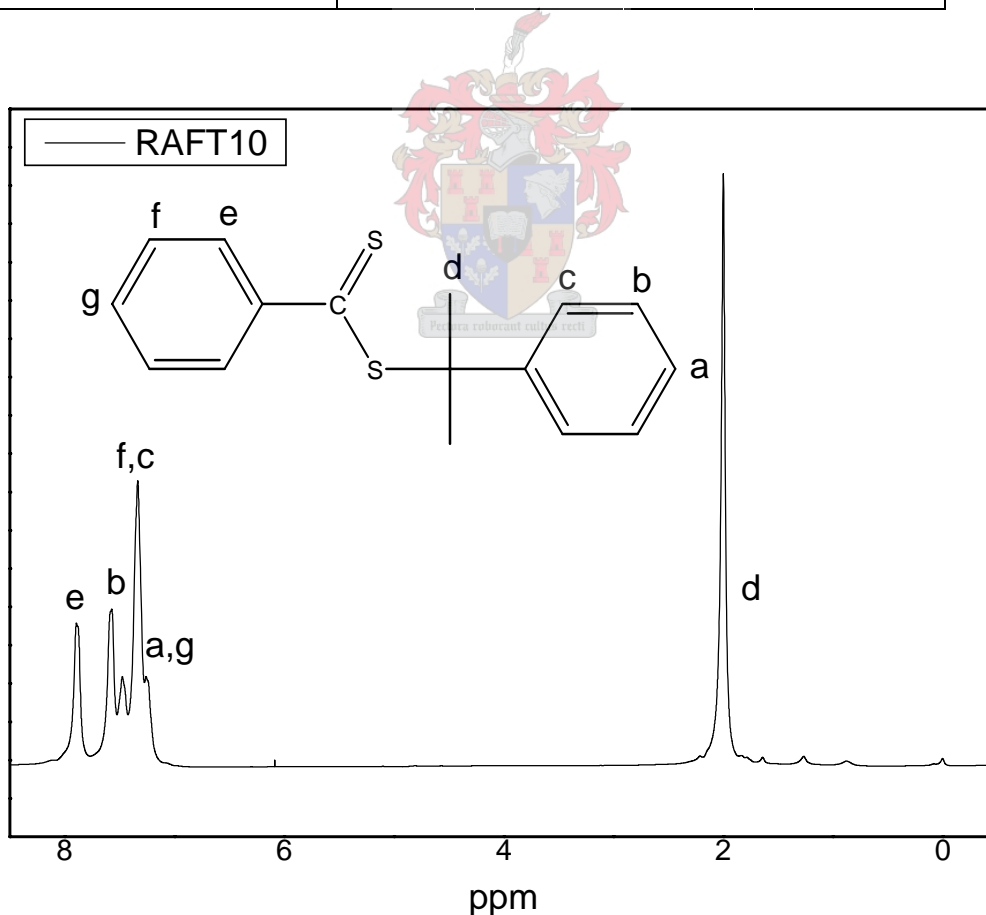


Figure 28. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 10 in chloroform-d.

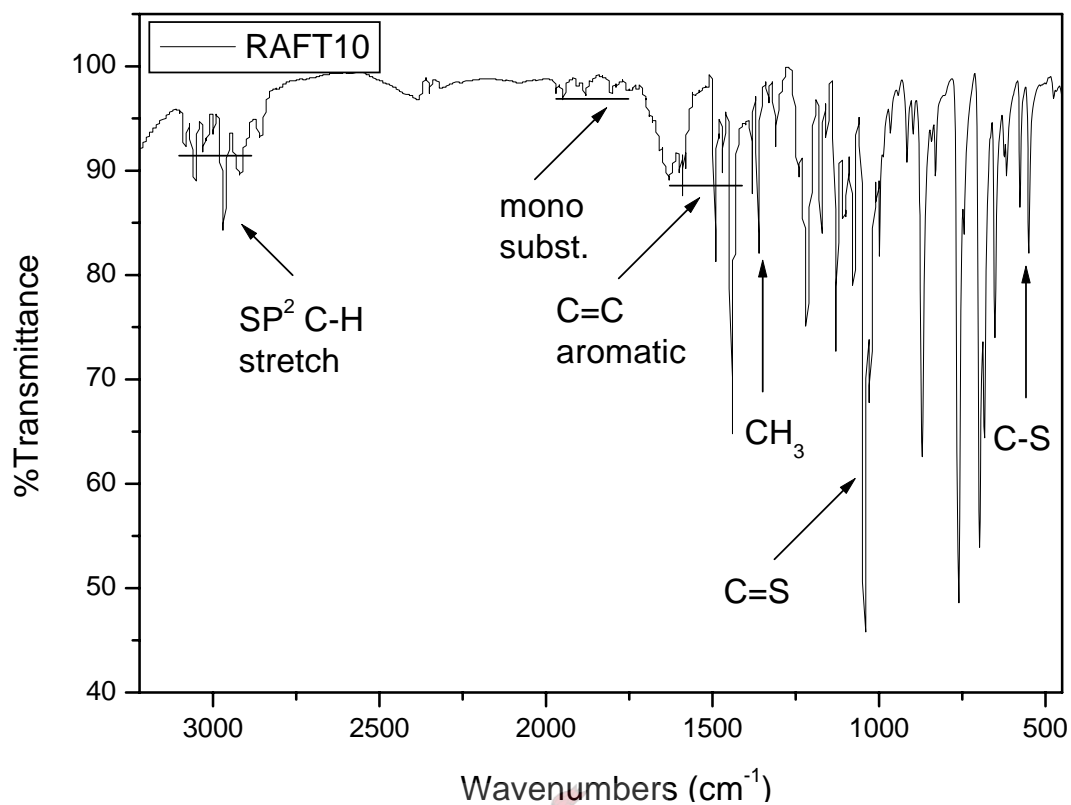


Figure 29. The infrared spectrum of RAFT agent 10 in KBr.

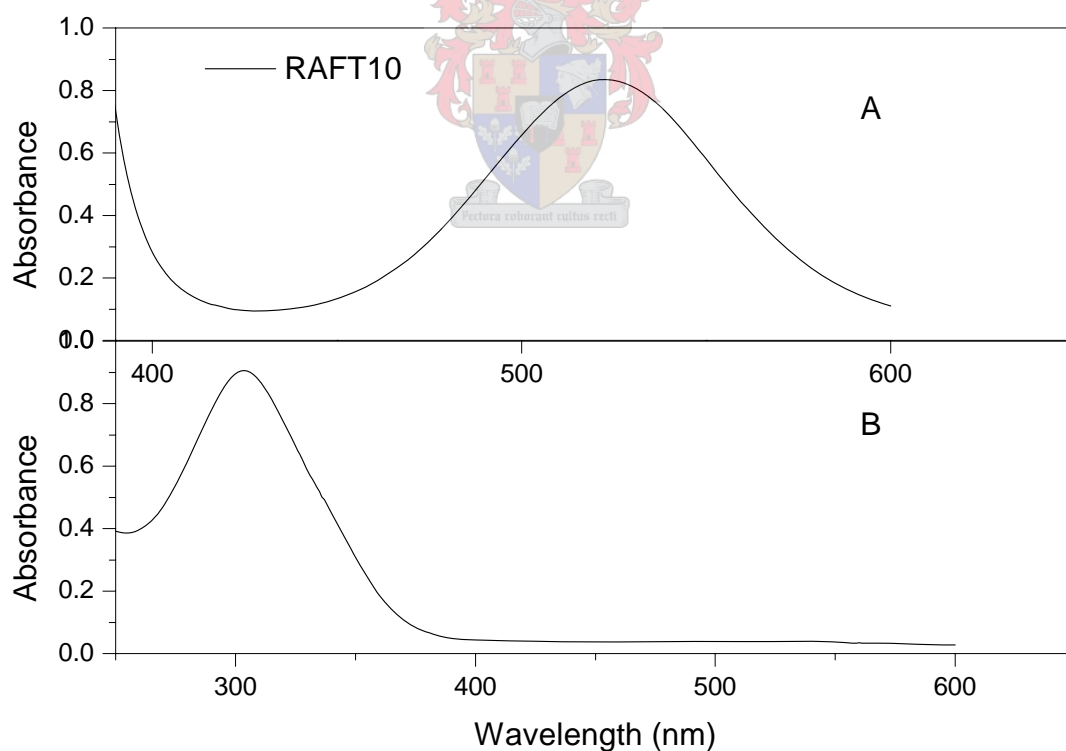
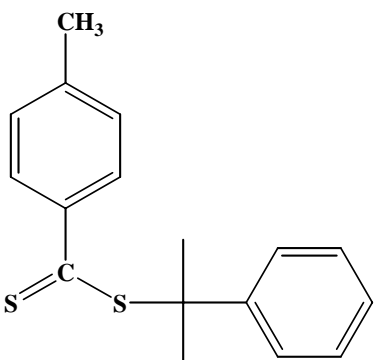


Figure 30. Absorbance spectrum of RAFT agent 10 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 522.7$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 303.3$  nm.

## RAFT agent 11: 1-methyl-1-phenylethyl 4-methylbenzenecarbodithioate

Table 11: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 11

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                |          |       |      |                |
|---|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                   |          |       |      |                |
| RAFT 11   | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 4        | 5360  | 1.11 | 8              |
|   | 5        | 6820  | 1.11 | 11             |
|   | 6        | 8260  | 1.10 | 14             |
|   | 7        | 9640  | 1.10 | 16             |
|   | 8        | 10800 | 1.11 | 19             |
|   | 9        | 12300 | 1.11 | 21             |
|   | 10       | 13400 | 1.11 | 24             |
|   | 11       | 14600 | 1.11 | 27             |

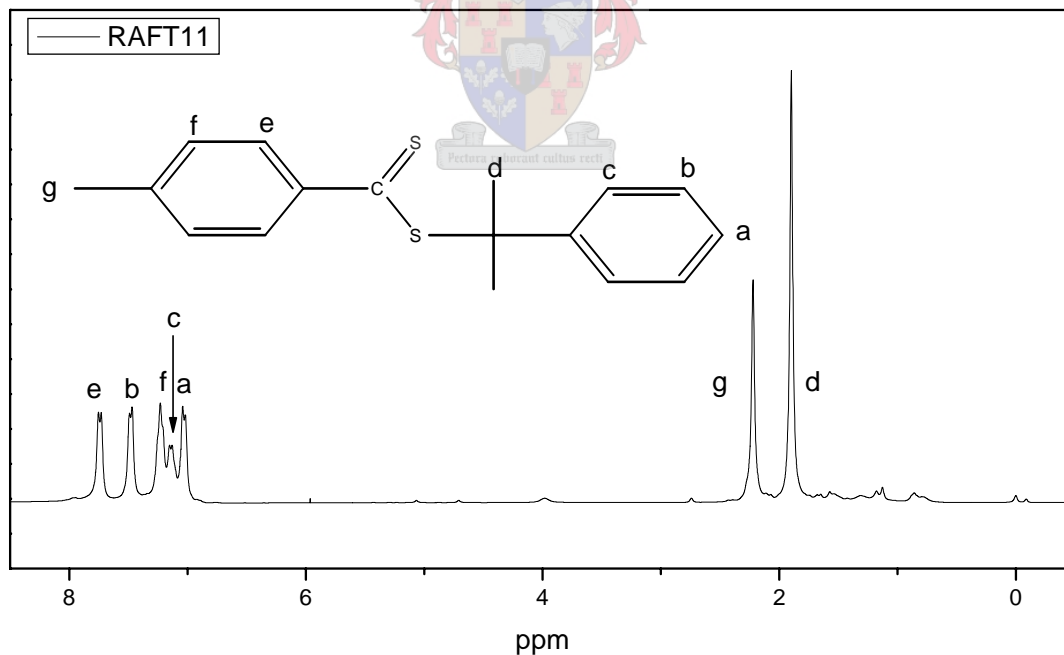


Figure 31. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 11 in chloroform-d.

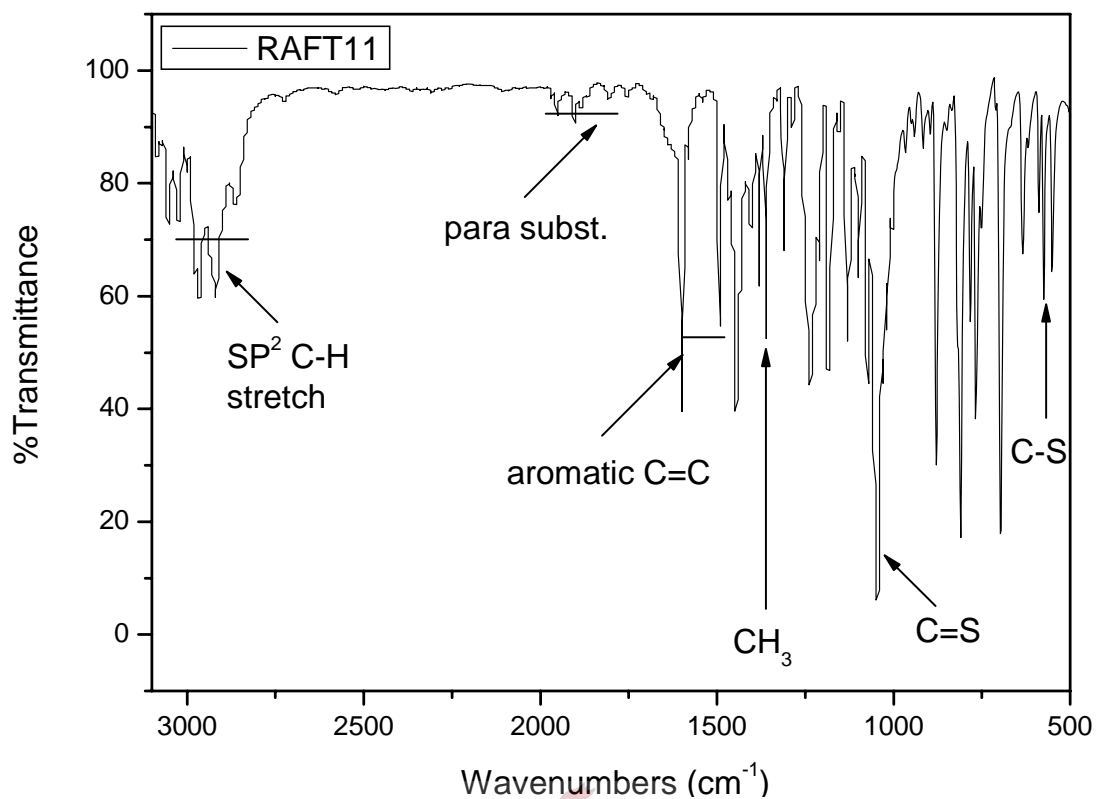


Figure 32. The infrared spectrum of RAFT agent 11 in KBr.

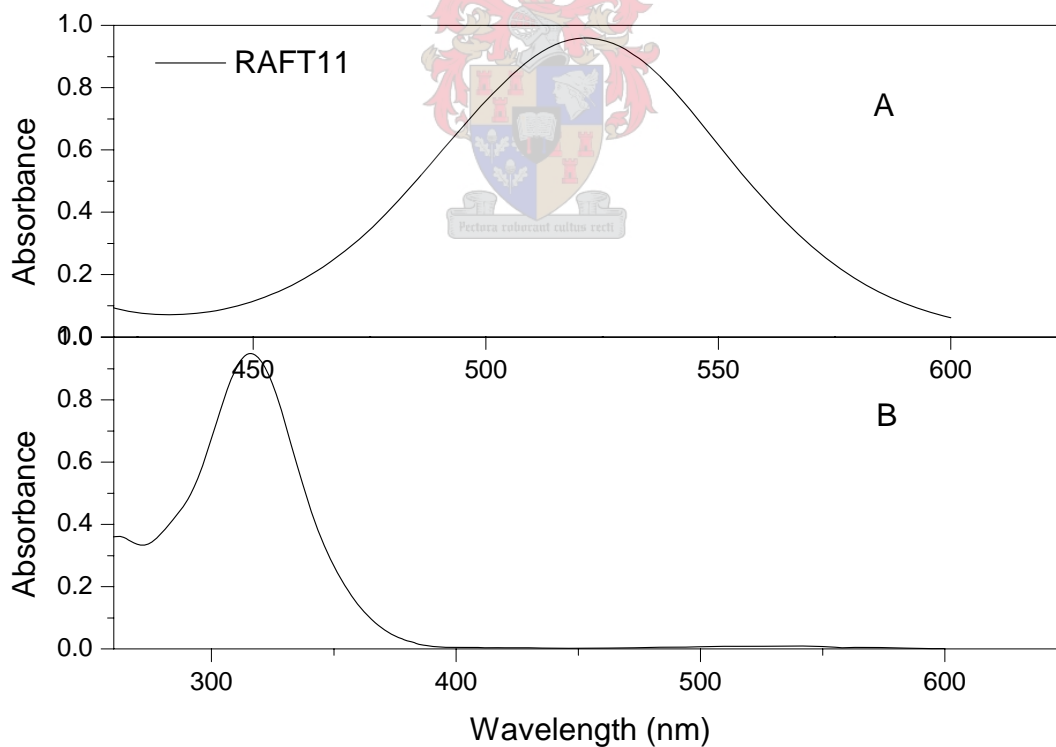
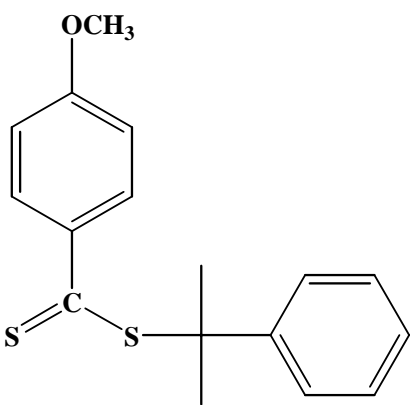


Figure 33. Absorbance spectrum of RAFT agent 11 in dichloromethane. A is  $n \rightarrow \pi^*$  at  $\lambda = 522.8$  nm and B is  $\pi \rightarrow \pi^*$  at  $\lambda = 316.5$  nm.

## RAFT agent 12: 1-methyl-1-phenylethyl 4-methoxybenzenecarbo-dithioate

Table 12: Number average molar mass,  $M_n$ , and polydispersity, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 12

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$   |          |       |      |                |
|--|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$  |          |       |      |                |
| RAFT 12<br> | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 6        | 11870 | 1.11 | 19             |
|  | 7        | 13500 | 1.11 | 23             |
|  | 8        | 15100 | 1.11 | 25             |
|  | 9        | 16500 | 1.11 | 27             |
|  | 10       | 17800 | 1.12 | 32             |
|  | 11       | 18900 | 1.13 | 35             |
|  | 12       | 20500 | 1.12 | 36             |

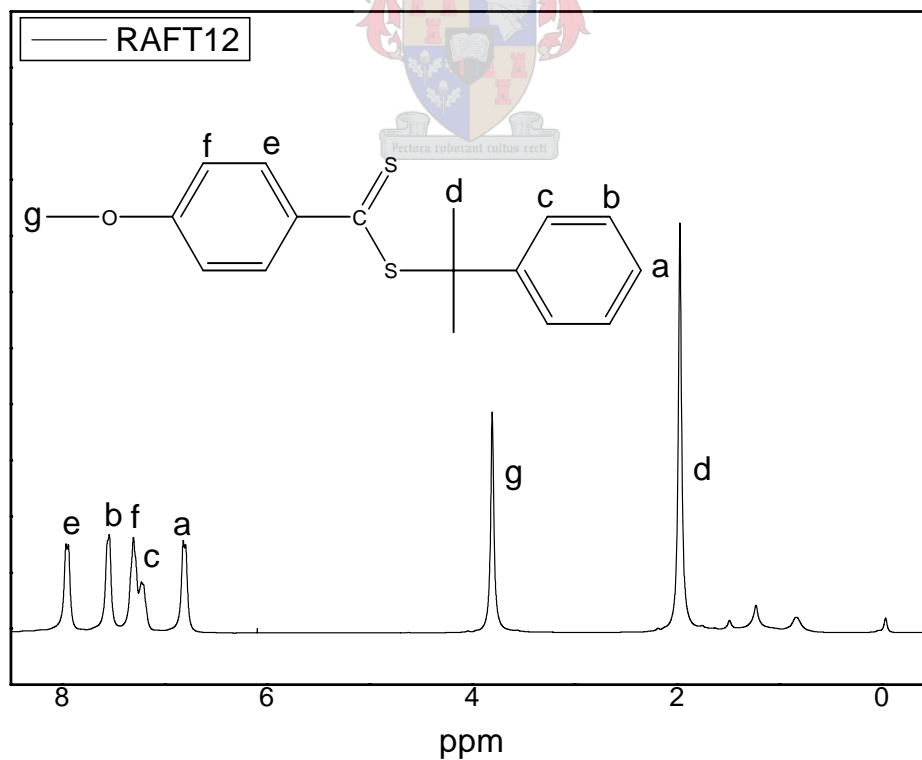


Figure 34. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 12 in chloroform-d.

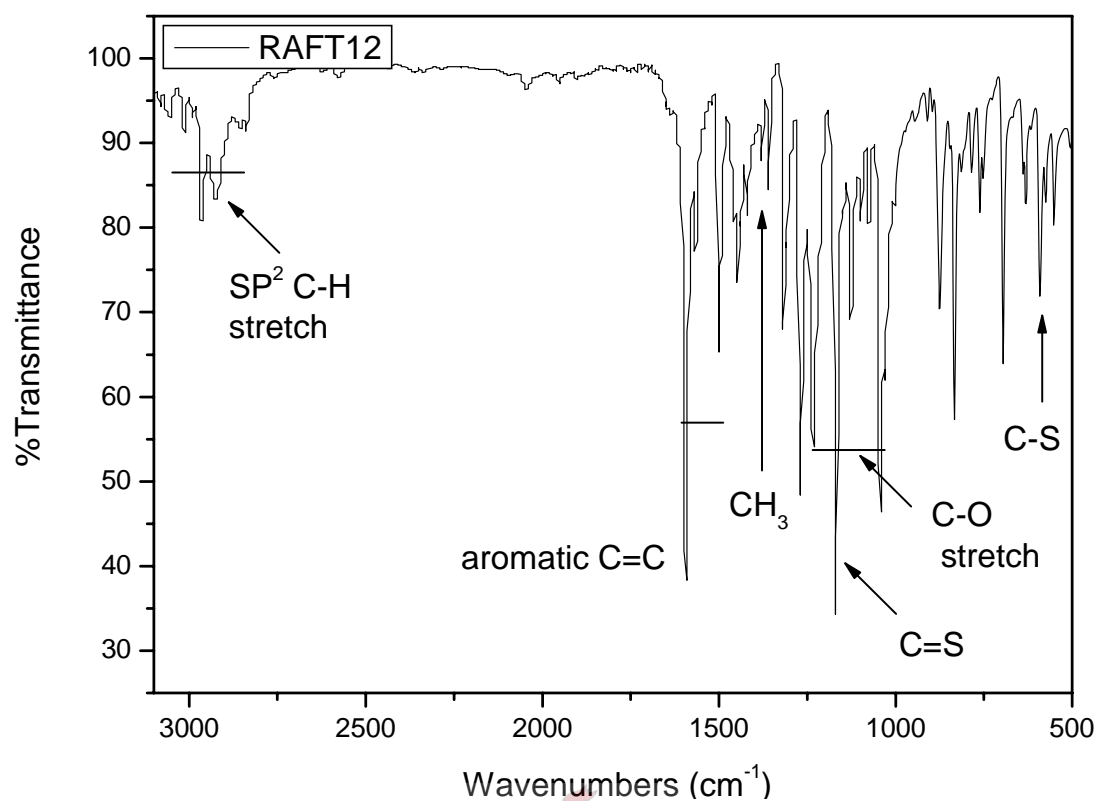


Figure 35. The infrared spectrum of RAFT agent 12 in KBr.

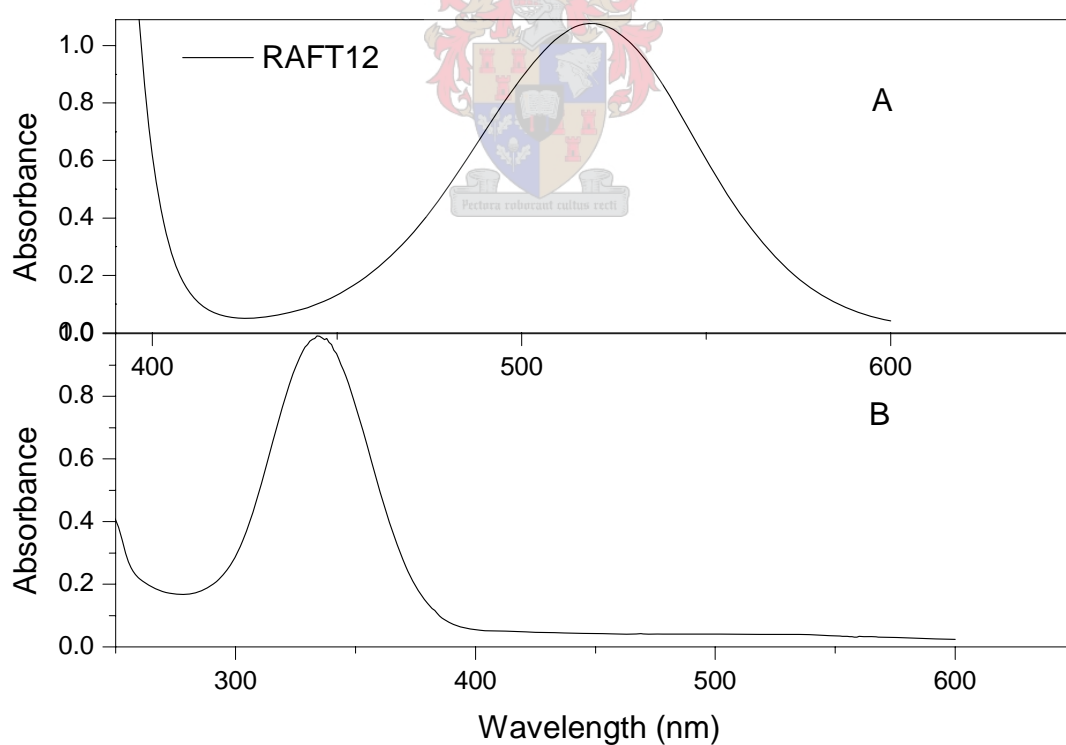
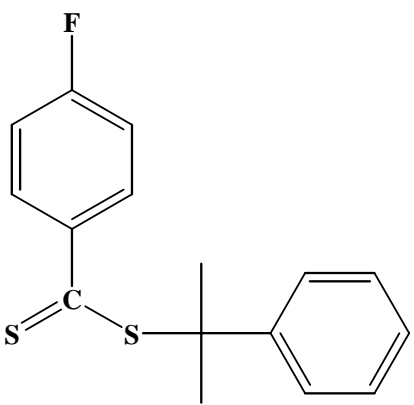


Figure 36. Absorbance spectrum of RAFT agent 12 in dichloromethane. A is n → π\* at  $\lambda = 518.9$  nm and B is π → π\* at  $\lambda = 334.9$  nm.



## RAFT agent 13: 1-methyl-1-phenylethyl 4-fluorobenzenecarbodithioate

Table 13: Number average molar mass,  $M_n$ , and polydispersities, PDI, obtained in the free radical (bulk) polymerisation of styrene at 100° C using RAFT agent 13

| $[\text{RAFT}]_0 = 1.275 \times 10^{-5} \text{ M}$                                |          |       |      |                |
|---|----------|-------|------|----------------|
| $[\text{M}]_0 = 9.615 \times 10^{-3} \text{ M}$                                   |          |       |      |                |
| RAFT 13   | Time (h) | $M_n$ | PDI  | Conversion (%) |
|  | 4        | 8410  | 1.10 | 8              |
|   | 5        | 9960  | 1.10 | 10             |
|   | 6        | 11400 | 1.10 | 13             |
|   | 7        | 13000 | 1.10 | 14             |
|   | 8        | 14400 | 1.10 | 16             |
|   | 9        | 15470 | 1.12 | 18             |
|   | 10       | 17000 | 1.12 | 20             |
|   | 11       | 18100 | 1.12 | 23             |

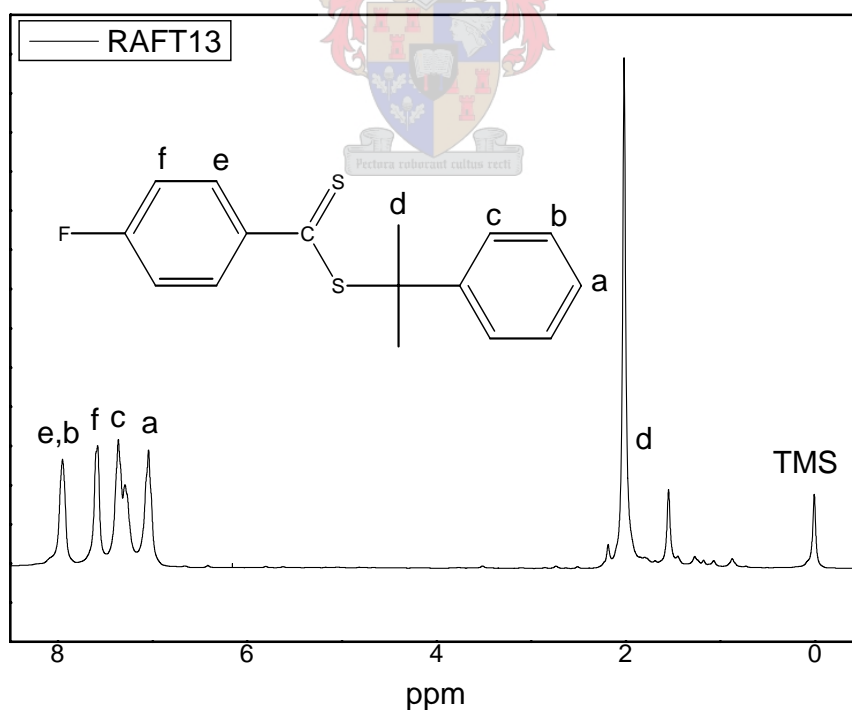


Figure 37. The 300-MHz  $^1\text{H}$  NMR spectrum of RAFT agent 13 in chloroform-d.

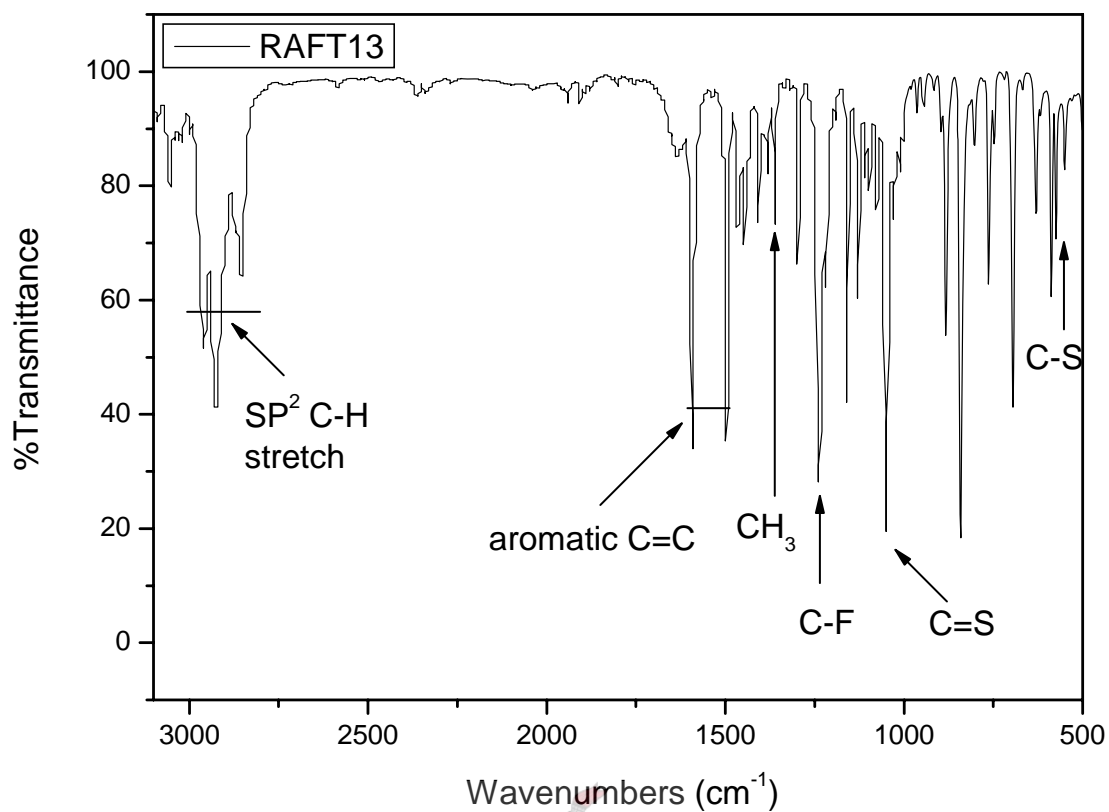


Figure 38. The infrared spectrum of RAFT agent 13 in KBr.

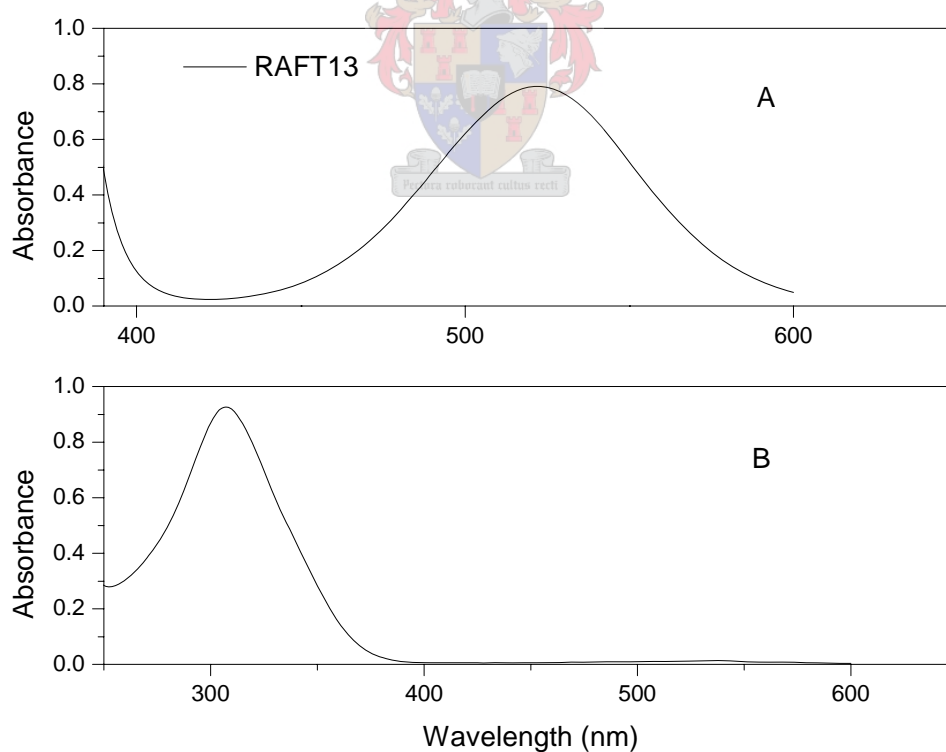


Figure 39. Absorbance spectrum of RAFT agent 13 in dichloromethane. A is n → π\* at  $\lambda = 523.4$  nm and B is π → π\* at  $\lambda = 308.0$  nm.

