

**RAFT-mediated synthesis of graft copolymers
via a thiol-ene addition mechanism**

by

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Thesis presented in partial fulfillment of the requirements for the degree of

Master of Science (Polymer Science)



University of Stellenbosch

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December 2007

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF SCHEMES

LIST OF TABLES

LIST OF ABBREVIATIONS

LIST OF SYMBOLS

CHAPTER 1: INTRODUCTION AND OBJECTIVES

1.1 Introduction	2
1.2 Objectives	3
1.3 Thesis Outline	4
1.4 Bibliography	7

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

2.1 Free Radical Polymerization	10
2.2 Living Radical Polymerization (LRP)	12
2.2.1 Mechanism of LRP	14
2.2.2 Atom Transfer Radical Polymerization (ATRP)	15
2.2.3 Nitroxide Mediated Polymerization (NMP)	16
2.2.4 Degenerative Transfer Using Alkyl Iodides	17
2.2.5 Catalytic Chain Transfer (CCT)	18
2.2.6 Reversible Addition-Fragmentation Chain Transfer (RAFT)	19
2.2.6.1 General	19

2.2.6.2 RAFT End-Group Modification	22
2.3 Thiol-ene Addition Reactions	24
2.4 Polymerization of Allyl Methacrylate	26
2.5 Free Radical Copolymerization	29
2.5.1 Graft Copolymerization	30
2.5.1.1 “Grafting From” Method	31
2.5.1.2 “Grafting Through” Method	31
2.5.1.3 “Grafting Onto” Method	32
2.5.2 Analysis of Branched Polymers	33
2.6 Bibliography	35

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

3.1 Introduction	43
3.2 Experimental	43
3.2.1 Materials	43
3.2.2. Synthesis of Cyanovaleric Acid Dithiobenzoate (CVADTB)	44
3.2.3 Synthesis of Dodecyl Isobutyric Acid Trithiocarbonate (DIBTC)	47
3.2.4 Synthesis of Low Molecular Weight Polystyrene and Poly(butyl acrylate)	50
3.3 Results and Discussion	51
3.3.1 Low Molecular Weight Polystyrene	51
3.3.2 Low Molecular Weight Poly(butyl acrylate)	55
3.4 Conclusions	58
3.5 Bibliography	59

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

4.1 Introduction	63
4.2 Experimental	63
4.2.1 Materials	63
4.2.2 RAFT-Mediated Polymerization of Styrene	64
4.2.3 Modification of RAFT End-Groups	65
4.3 Results and Discussion	66
4.4 Conclusions	75
4.5 Bibliography	76

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

5.1 Introduction	79
5.2 Experimental	79
5.2.1 Materials	79
5.2.2 RAFT-Mediated Synthesis of PAMA Homopolymer	79
5.3 Results and Discussion	80
5.4 Conclusions	90
5.5 Bibliography	91

CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

6.1 Introduction	94
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6.2 Experimental	95
6.2.1 Materials	95
6.2.2 Synthetic Procedure	95
6.3 Results and Discussion	97
6.4 Conclusions	103
6.5 Bibliography	104

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

7.1 Conclusions	107
7.2 Recommendations	108
7.3 Bibliography	110

APPENDIXES

Appendix A: Cyanovaleric Dithiobenzoate	112
Appendix B: Dodecyl Isobutyric Acid Trithiocarbonate	113
Appendix C: RAFT End-Group Modification using NaOH	114
Appendix D: RAFT End-Group Modification using dodecyl amine	115
Appendix E: RAFT End-Group Modification using THF	116

ABSTRACT

The main objective of this project was the controlled synthesis of graft copolymers via a thiol-ene addition mechanism. The Reversible Addition-Fragmentation chain Transfer (RAFT) process was used in all polymerization reactions with the aim to achieve a certain degree of control over the molecular weight. Several synthetic steps were required in order to obtain the final graft copolymer and each step was investigated in detail.

Firstly, two RAFT agents (cyanovaleric acid dithiobenzoate and dodecyl isobutyric acid trithiocarbonate) were synthesized to be used in the various polymerization reactions of styrene and butyl acrylate. This was done successfully and the RAFT agents were used to synthesize low molecular weight polystyrene branches of the graft copolymer. Different molecular weights were targeted. It was found that some retardation phenomena were present especially at high RAFT agent concentrations.

The polystyrene branches that were synthesized contained RAFT end-groups. Various pathways were explored to modify these RAFT end-groups to form thiol end-groups to be used in the thiol-ene addition reaction during the grafting process. The use of sodium methoxide for this purpose proved most successful and no evidence of the formation of disulfide bridges due to the initially formed thiols was detected.

Allyl methacrylate (AMA) was chosen as monomer to be used for the synthesis of the polymer backbone because it has two double bonds with different reactivities. For the first time, RAFT was used to polymerize AMA via the more reactive double bond to obtain linear poly(allyl methacrylate) (PAMA) chains with pendant double bonds. However, at higher conversions, gelation occurred and the molecular weight distributions were uncontrolled. NMR was successfully used to study the tacticity parameters of the final polymer.

Finally, the synthesis of the graft copolymer, PAMA-*g*-polystyrene, was carried out by means of the “grafting onto” approach. The thiol-functionalized polystyrene branches were covalently attached to the pendant double bonds of the PAMA polymer backbone via a thiol-ene addition mechanism in the presence of a free radical initiator. A Multi-Angle Laser Light Scattering (MALLS) detector was utilized in conjunction with Size-Exclusion Chromatography (SEC) to obtain molecular weight data of the graft copolymer. The percentage grafting, as determined by ¹H-NMR, was low.

OPSOMMING

Die hoofdoel van hierdie projek is die beheerde sintese van 'n entkopolimeer via 'n merkaptaan-een addisiereaksie. Die sogenaamde "Reversible Addition-Fragmentation chain Transfer" (RAFT) proses is in al die polimerisasiereaksies gebruik met die doel om 'n mate van beheer oor die molekulêre massa van die polimere te verkry. Verskeie stappe (waarvan elkeen ten volle ondersoek is) was nodig om die finale entkopolimeer te verkry.

Eerstens is twee RAFT-agente (sianovaleriaansuur ditiobensoaat en dodekielisobottersuur tritiokarbonaat) gesintetiseer vir gebruik in verskeie polimerisasiereaksies van stireen en butielakrilaat. Hierdie stap was suksesvol en die RAFT-agente is toe gebruik vir die sintese van lae molekulêre massa polistireensytakke vir die entkopolimeer. Die molekulêre massas van die sytakke is gevarieer en daar is gevind dat verdragings in die polimerisasiereaksies voorgekom het, veral by hoë konsentrasies van die RAFT-agente.

Die polistireensytakke wat gemaak is, besit almal 'n RAFT-eindgroep. Verskeie roetes is bestudeer ten einde die RAFT-eindgroepe tot merkaptaan-eindgroepe te modifiseer om sodoende tydens 'n merkaptaan-een addisiereaksie gebruik te word. Die gebruik van natriummetoksied was hier die suksesvolste en daar was geen teken van die vorming van disulfiedbrûe as gevolg van die oorspronklik gevormde merkaptane nie.

Allielmetakrilaat (AMA) is gekies as die monomeer wat gebruik sou word vir die sintese van die polimeerruggraat omdat die monomeer twee dubbelbindings met verskillende reaktiwiteite besit het. Vir die eerste keer is RAFT gebruik vir die polimerisasie van AMA via die meer reaktiewe dubbelbinding om lineêre poli(allielmetakrilaat) (PAMA) kettings met dubbelbindings in die sygroepe te verkry. Gelvorming en onbeheerde molekulêre massaverspreiding het egter by hoër monomeeromsettings voorgekom. KMR is suksesvol gebruik om die taktisiteitsparameters van die finale polimeer te bestudeer.

Ten slotte is die sintese van die entkopolimeer, PAMA-g-polistireen, uitgevoer deur die aanhegting van voorafgevormde sytakke. Die polistireensytakke met die merkaptaneindgroepe is kovalent geheg aan die dubbelbindings in die sygroepe van die PAMA-polimeerruggraat via 'n merkaptaan-een addisiemeganisme in die teenwoordigheid van 'n vrye radikaalinisieerder. 'n Kombinasie van gelpermeasiechromatografie en multi-hoeklaserligverstrooiing is gebruik om die molekulêre massa van die entkopolimeer te bepaal. Die persentasie sytakke soos bepaal deur ^1H -KMR was laag.

ACKNOWLEDGEMENTS

Prof. Sanderson – for his guidance throughout this project; his scientific knowledge was instrumental in the completion of this thesis

Dr. Mark Frahn – for all his help in the lab and solving so many of my experimental problems

National Research Foundation (NRF) – for funding this project

Margie – for trying to changing my thesis from a grammatical blob to something more civilized

Aneli and Erinda – for their administrative assistance

Adam and Calvin – for making sure that there is always equipment and chemicals available for everybody to run their endless reactions

Free radical group – for making life in the lab a happy experience; I have made so many friends over the last couple of years that I will not try to mention all the names in case I forget one or two!

Marius, Moses and AJ – my friends from my Honours year – a year during which I learned to love polymer science, thanks in a great deal to their enduring friendship

Angie and Vernon – my two best friends and the people who made life bearable when the going got tough (and it got tough many times!) and for their never-ending support

My family – who have stood by me from the beginning of my rather long career as a student, words cannot express my gratitude

LIST OF FIGURES

Figure 3.1: Conversion-time graph for the RAFT-mediated polymerization of styrene in toluene at 100°C with DIBTC as RAFT agent and AIBN as initiator.

Figure 3.2: Semi-logarithmic graph for the RAFT-mediated polymerization of styrene in toluene at 100°C with DIBTC as RAFT agent and AIBN as initiator.

Figure 3.3: Normalized GPC distributions for the RAFT-mediated polymerization of styrene in toluene at 100°C with DIBTC as RAFT agent and AIBN as initiator.

Figure 3.4: Conversion-time graph for the RAFT-mediated polymerization of butyl acrylate in toluene at 90°C with DIBTC as RAFT agent and AIBN as initiator.

Figure 3.5: Normalized GPC distributions for the RAFT-mediated polymerization of butyl acrylate in toluene at 90°C with DIBTC as RAFT agent and AIBN as initiator.

Figure 4.1: ¹H-NMR spectrum of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-group with the use of sodium methoxide.

Figure 4.2: UV spectrum of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-group with the use of sodium methoxide and 1,4-dioxane as solvent.

Figure 4.3: GPC traces of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-groups with the use of sodium methoxide without removal of oxygen prior to the start of the reaction.

Figure 4.4: GPC traces of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-groups with the use of sodium methoxide and removal of oxygen prior to the start of the reaction.

Figure 5.1: GPC results for the DIBTC-mediated homopolymerization of AMA.

Figure 5.2: GPC results of the CVADTB-mediated polymerization of allyl methacrylate using a dual detector system.

Figure 5.3: $^1\text{H-NMR}$ spectrum of PAMA polymerized in the presence of CVADTB, AIBN and THF as solvent at 60°C .

Figure 5.4: Conversion-time graph of the CVADTB-mediated homopolymerization of AMA.

Figure 5.5: Semi-logarithmic plot of monomer consumption over time for the CVADTB-mediated homopolymerization of AMA.

Figure 5.6: Molecular weight versus conversion plot of the CVADTB-mediated homopolymerization of AMA.

Figure 5.7: GPC distributions for the CVADTB-mediated homopolymerization of AMA.

Figure 6.1: GPC data for the graft copolymer synthesized via reaction (1) recorded using a dual detector system.

Figure 6.2: $^1\text{H-NMR}$ of the graft copolymer synthesized via reaction (1).

Figure 6.3: GPC chromatograms of the PAMA backbone, polystyrene branches and final graft copolymer using an RI detector for reaction (1).

Figure A: ^1H -NMR spectrum of CVADTB with chloroform as solvent.

Figure B: ^1H -NMR spectrum of DIBTC with chloroform as solvent.

Figure C: ^1H -NMR spectrum of polystyrene polymerized with DIBTC after end-group modification using NaOH.

Figure D: ^1H -NMR spectrum of polystyrene polymerized with DIBTC after end-group modification using dodecyl amine.

Figure E: ^1H -NMR spectrum of polystyrene polymerized with DIBTC after the modification of the RAFT end-group using THF.

LIST OF SCHEMES

Scheme 1.1: Flow chart of the experimental procedures followed in this study.

Scheme 2.1: Free radical initiator decomposition and subsequent addition to monomer.

Scheme 2.2: Propagation of a radical species through the sequential addition of monomer units.

Scheme 2.3: Free radical termination processes via radical-radical coupling (k_{tc}) and disproportionation (k_{td}).

Scheme 2.4: Reversible end-capping.

Scheme 2.5: Reversible chain transfer.

Scheme 2.6: A copper-based ATRP system with an alkyl chloride initiator.

Scheme 2.7: Schematic representation of the NMP process.

Scheme 2.8: SG1 (N-tert-butyl-N-(1-diethylphosphone-2,2-dimethylpropyl) nitroxide).

Scheme 2.9: Schematic representation of the degenerative transfer process with an alkyl iodide as a transfer agent.

Scheme 2.10: Schematic representation of the RAFT polymerization mechanism.

Scheme 2.11: General RAFT agent structure.

Scheme 2.12: Schematic illustration of the various RAFT end-group modification procedures.

Scheme 2.13: General thiol-ene addition mechanism.

Scheme 2.14: Oxygen scavenging mechanism of thiol-ene systems.

Scheme 2.15: Homopolymerization of allyl methacrylate through the methacryloyl double bonds.

Scheme 2.16: The proposed secondary structures present in PAMA homopolymer.

Scheme 2.17: Branched polymers (1) star (2) comb and (3) hyperbranched polymers.

Scheme 2.18: General structure of a graft copolymer.

Scheme 2.19: The “grafting from” method.

Scheme 2.20: The “grafting through” method.

Scheme 2.21: The “grafting onto” method.

Scheme 2.22: Schematic representation of a typical MALLS experiment setup.

Scheme 2.23: SEC separates on the basis of hydrodynamic volume.

Scheme 3.1: Formation of the Grignard reagent.

Scheme 3.2: Synthesis of dithiobenzoic acid.

Scheme 3.3: Synthesis of bis(thiobenzoyl)disulfide.

Scheme 3.4: Synthesis of cyanovaleric acid dithiobenzoate.

Scheme 3.5: Formation of the sulfide anion.

Scheme 3.6: Addition of carbon disulfide to sulfide anion.

Scheme 3.7: Formation of the isobutyric acid leaving group.

Scheme 3.8: Dodecyl isobutyric acid trithiocarbonate.

Scheme 4.1: Reaction scheme for the RAFT end-group transformation of polystyrene synthesized with DIBTC as RAFT agent with the use of sodium methoxide in dioxane.

Scheme 4.2: Oxidative coupling of the initially formed thiols of RAFT-polymerized polystyrene after treatment with sodium methoxide.

Scheme 5.1: Schematic illustration of the crosslinking reaction that may occur during AMA homopolymerization.

Scheme 5.2: Reaction route for the formation of 6-membered lactone rings during AMA homopolymerization.

Scheme 6.1: Reaction scheme for the synthesis of PAMA-g-polystyrene.

LIST OF TABLES

Table 3.1: Experimental results for the RAFT-mediated homopolymerization of styrene

Table 3.2: Experimental results for the RAFT-mediated homopolymerization of butyl acrylate

Table 4.1: Composition of the various reaction mixtures for the RAFT-mediated homopolymerizations of styrene

Table 4.2: Table summarizing the various attempts at the post-polymerization modification of the RAFT end-groups

Table 4.3: Summary of GPC and $^1\text{H-NMR}$ data for the RAFT end-group modification experiments carried out with sodium methoxide

Table 5.1: Kinetic and characteristic parameters for the RAFT-mediated homopolymerization of AMA

Table 6.1: Reagents and their quantities used in the synthesis of PAMA-g-polystyrene

Table 6.2: Molecular weight data of the PAMA polymer backbone, polystyrene branches and final graft copolymer as determined by GPC with RI and MALLS detectors

LIST OF SYMBOLS

$^{\circ}\text{C}$	Degrees Celsius
dn	Change in refractive index
dc	Change in concentration
$I(\theta)$	Intensity of scattered light at angle θ
k_d	Rate coefficient for initiator dissociation
k_i	Rate coefficient for addition of primary radical to monomer
k_p	Rate coefficient for chain propagation
k_{tc}	Rate coefficient for radical termination by combination
k_{td}	Rate coefficient for radical termination by disproportionation
M	Monomer unit
[M]	Monomer concentration
$[\text{M}]_0$	Initial monomer concentration
$[\text{M}]_t$	Monomer concentration at time t
M_n	Number average molecular weight
$\text{R}\cdot$	Free radical
$\text{R}_n\cdot$	Free radical with degree of polymerization equal to n
t	Time
σ	Isotacticity parameter

LIST OF ABBREVIATIONS

AIBN	Azobisisobutyronitrile
AMA	Allyl Methacrylate
ATRP	Atom Transfer Radical Polymerization
CCD	Chemical Composition Distribution
CCT	Catalytic Chain Transfer
CVADTB	Cyanovaleric Acid Dithiobenzoate
DIBTC	Dodecyl Isobutyric Acid Trithiocarbonate
DMSO	Dimethylsulfoxide
EDMA	Ethylene Glycol Dimethacrylate
ESI-MS	Electrospray Ionization Mass Spectrometry
ESRS	Electron Spin Resonance Spectroscopy
FTIR	Fourier-Transform Infrared Spectroscopy
GFC	Gel Filtration Chromatography
GPC	Gel Permeation Chromatography
LRP	Living Radical Polymerization
MALLS	Multi-Angle Laser Light Scattering
NMP	Nitroxide Mediated Polymerization
NMR	Nuclear Magnetic Resonance Spectroscopy
PAMA	Poly(allyl methacrylate)
PDI	Polydispersity Index
PMMA	Poly(methyl methacrylate)
RAFT	Reversible Addition-Fragmentation Chain Transfer
RI	Refractive Index
SEC	Size Exclusion Chromatography
SG1	N-tert-butyl-N-(1-diethylphosphone-2,2-dimethylpropyl) nitroxide
TEMPO	2,2,6,6-Tetramethylpiperdine-1-oxyl nitroxide
THF	Tetrahydrofuran
UV	Ultraviolet Spectroscopy

CHAPTER 1: INTRODUCTION AND OBJECTIVES

ABSTRACT

A brief introduction to the study is given, followed by an outline of the thesis and a summary of the goals that were set. A flowchart of the synthetic procedures followed throughout the study is also incorporated.

CHAPTER 1: INTRODUCTION AND OBJECTIVES**1.1 Introduction**

The requirements of consumers have increased and progressed rapidly in recent times. This has led to a definite stress being placed on industries to develop products that are capable of performing specific functions under a wide variety of conditions. Consequently, industries have been forced to seek new methods and approaches to expand their range of raw materials. This is most evident in polymer science since modern polymers are mainly synthetic products. It has become the task of today's polymer scientists to synthesize new monomers, improve polymerization techniques, and discover novel polymerization techniques to produce raw materials that will aid industries in satisfying the vast number of requirements of modern consumers.

The development of Living Radical Polymerization (LRP) techniques made possible, for the first time, the synthesis of polymers with controlled molecular weights and predictable architectures via free radical polymerization¹⁻⁴. In this study a specialized LRP method, Reversible Addition-Fragmentation Transfer (RAFT)³, is used to design new polymers. Basic monomers are used and design control is achieved by the polymerization technique itself.

RAFT, used in conjunction with graft copolymerization, opens up numerous avenues for the synthesis of novel branched polymers. In conventional free radical polymerization branching occurs randomly. The amount and type of branching can have a significant effect on the final polymer properties and, since uncontrolled branching during free radical polymerization is difficult to detect and/or measure, it becomes complex to measure the impact of branching on final material properties⁵. In this study, the “grafting onto” approach is used to attach branches to the main polymer chain. The branches are synthesized prior to attachment to the main polymer chain, which means that they can be easily characterized. In addition, the use of RAFT polymerization for the synthesis of both the main polymer chain and the branches prior to the grafting process means that near identical structures can be produced. The result of this capability is that single

CHAPTER 1: INTRODUCTION AND OBJECTIVES

structure parameters can be isolated and studied, and finally varied to investigate their effect on end-material properties.

1.2 Objectives

The principal objective of this study is to produce end-functionalized polymers using the RAFT polymerization process and to use these polymers to synthesize graft copolymers with controlled length and distribution. The use of RAFT as polymerization technique enables us to synthesize both the main chain and the branches of the intended graft copolymer in a controlled manner. The fact that the “grafting onto” approach was used further enables us to fully characterize the main chain and branches prior to the grafting reaction. The objectives are laid out in more detail below:

- Synthesis and purification of different RAFT agents
- Synthesis and characterization of low molecular weight polymers using RAFT
- Investigation into the effect of RAFT agent concentration on the kinetics of polymerization
- Investigation into the modification of RAFT end-groups to produce high yields of thiol end-functionalized polymers
- Purification and characterization of the thiol-end functionalized polymers
- Study of the polymerization kinetics of the RAFT-mediated homopolymerization of allyl methacrylate
- Investigation into the microstructure of poly(allyl methacrylate) (PAMA), i.e. tacticity, degree of gelation, and the possible formation of secondary structures
- Synthesis and characterization of comb-like graft copolymers via a thiol-ene addition reaction

CHAPTER 1: INTRODUCTION AND OBJECTIVES**1.3 Thesis Outline**

A flow diagram of the experimental procedures is given in Scheme 1.1.

Chapter 2: Historical and Theoretical Background

As the title suggests, this chapter deals with the various synthetic techniques, experimental routes and analytical methods that were used in this study. A brief overview of conventional free radical polymerization is followed by a more detailed discussion on LRP techniques. RAFT polymerization is fully discussed with special attention given to the post-polymerization modification of RAFT end-groups⁶. The homopolymerization of allyl methacrylate, including potential pitfalls such as gelation⁷ and the formation of secondary structures⁸, is examined. Finally, thiol-ene addition reactions as a possible method for the synthesis of graft copolymers is discussed, followed by a look at graft copolymerization and the analytical techniques used to study them.

Chapter 3: RAFT-Mediated Synthesis of Low Molecular Weight Polymers

The synthesis of two RAFT agents, cyanovaleric acid dithiobenzoate (CVADTB) and dodecyl isobutyric acid trithiocarbonate (DIBTC), is discussed. Complete experimental routes and full characterizations are given. Two monomers were used in this study – styrene and butyl acrylate: These two monomers were polymerized using a specific RAFT agent at varying concentrations. The polymerization kinetics were studied using gravimetry and gel permeation chromatography (GPC).

Chapter 4: Post-Polymerization Modification of RAFT End-Groups

In this chapter various methods for the modification of RAFT end-groups are discussed. Different analytical techniques such as GPC, Ultraviolet (UV) spectrometry and nuclear magnetic resonance (NMR) spectroscopy were used to fully characterize the polymer after the modification of the RAFT end-group. In conclusion, certain problem areas are highlighted, e.g. the formation of disulfide bridges⁹.

CHAPTER 1: INTRODUCTION AND OBJECTIVES

Chapter 5: RAFT-Mediated Homopolymerization of Allyl Methacrylate

This chapter deals with the polymerization of allyl methacrylate (AMA) as a potential backbone for the attachment of polymer branches in a “grafting onto” reaction. This is made possible by the presence of pendant, unreacted double bonds after polymerization. The final polymer is characterized using NMR and the polymerization kinetics studied via gravimetry and GPC data.

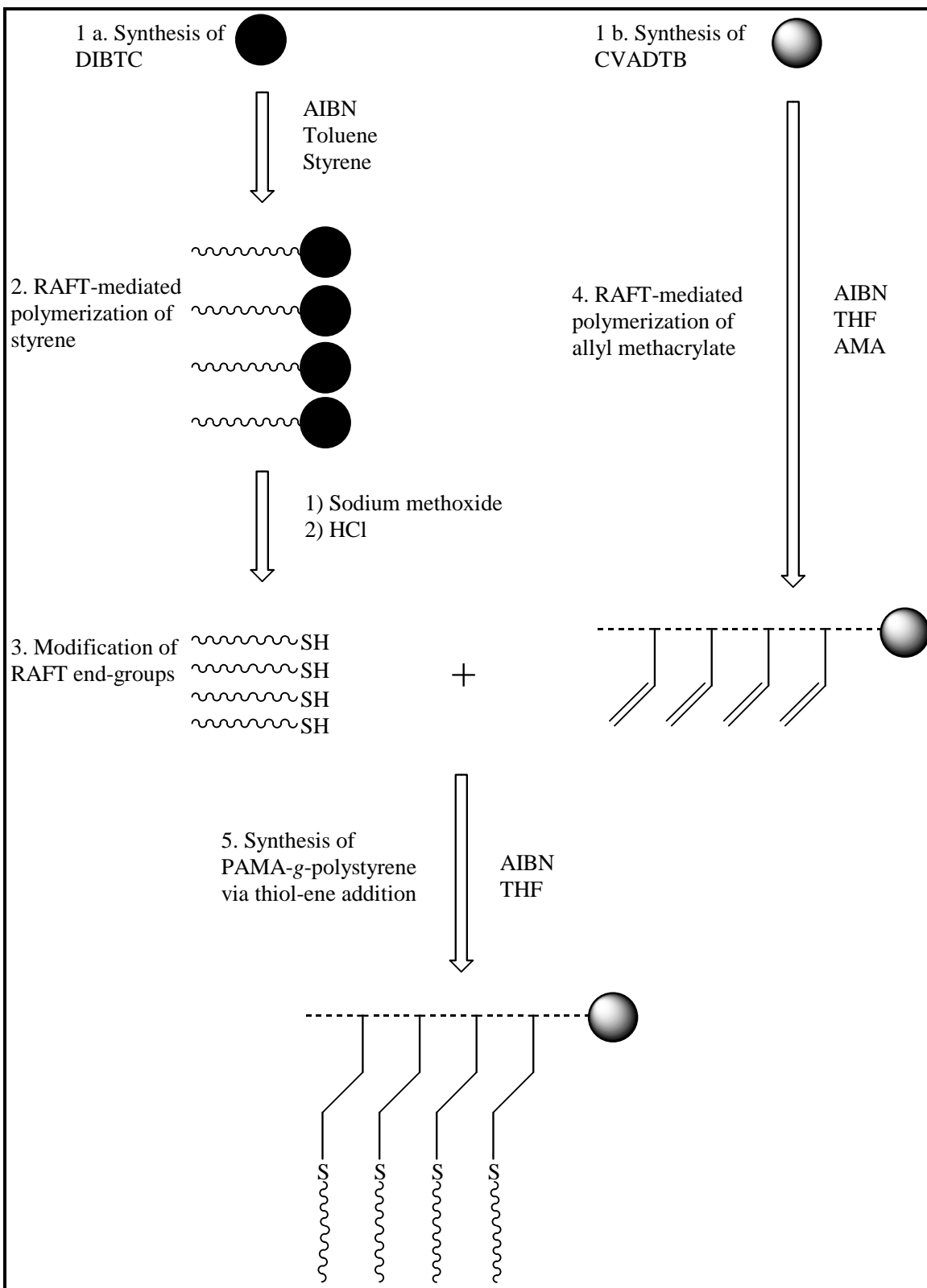
Chapter 6: Synthesis of PAMA-g-Polystyrene

In this chapter the synthesis of the final graft copolymer is discussed. The synthesis of PAMA-g-polystyrene was carried out via the addition of the thiol-end functionalized polystyrene branches to the pendant double bonds of the PAMA backbone. The effect of branch length on the degree of branching is studied.

Chapter 7: Conclusions and Recommendations for Future Research

The achievement of the objectives is evaluated and recommendations are made for future work in this field.

CHAPTER 1: INTRODUCTION AND OBJECTIVES



Scheme 1.1: Flow chart of the experimental procedures followed in this study.

CHAPTER 1: INTRODUCTION AND OBJECTIVES

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CHAPTER 1: INTRODUCTION AND OBJECTIVES

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CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

ABSTRACT

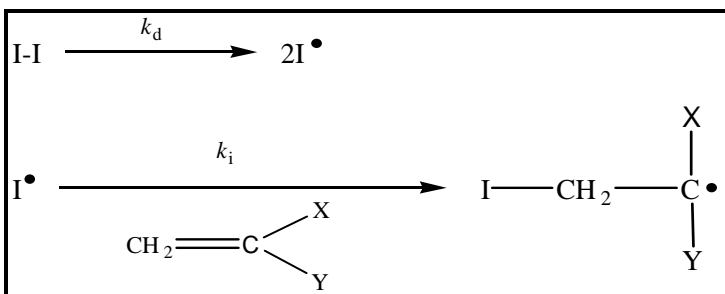
This research encompasses a variety of scientific techniques and experimental pathways and all these are discussed in detail in this chapter. An overview of free radical polymerization is given followed by a discussion on the various LRP techniques, while delving into more detail with RAFT polymerization. Finally, overviews on allyl methacrylate and graft copolymerization are given.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

2.1 Free Radical Polymerization

Free radical polymerization is an example of a chain growth reaction. The three distinct kinetic events of free radical polymerization are: initiation, propagation and termination.

Free radical polymerization is initiated by primary radicals. These primary radicals can be created by the polymerizable monomer itself, as in the case of styrene, i.e. autoinitiation. More commonly, primary radicals are generated via the decomposition of a radical initiator (see Scheme 2.1). The value k_d is unique for all initiators and also dependent on the solvent used and the temperature at which the reaction occurs. Examples of free radical initiators include peroxides, persulfates, azo-compounds and photochemical initiators. The primary radicals that are generated undergo addition to a vinyl monomer, which is normally activated by two groups (X and Y), at least one of which must be electron withdrawing¹.

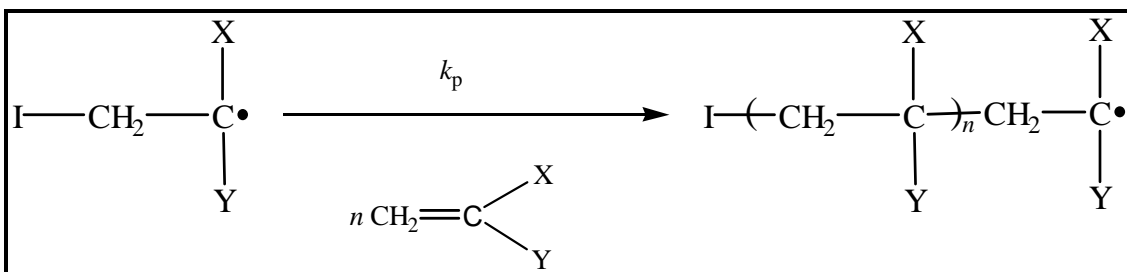


Scheme 2.1: Free radical initiator decomposition and subsequent addition to monomer.

The addition of the primary radicals to the carbon-carbon double bonds of the monomer results in the formation of primary propagating radicals, also known as initiating radicals, that in turn can propagate further. Initiator efficiency is however compromised by chain transfer reactions (discussed later in this section) as well as the solvent cage effect²

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

whereby primary radicals recombine before initiation can occur. After initiation, additional monomer units can be sequentially added to the active radical species. This is known as propagation and is depicted in Scheme 2.2.



Scheme 2.2: Propagation of a radical species through the sequential addition of monomer units.

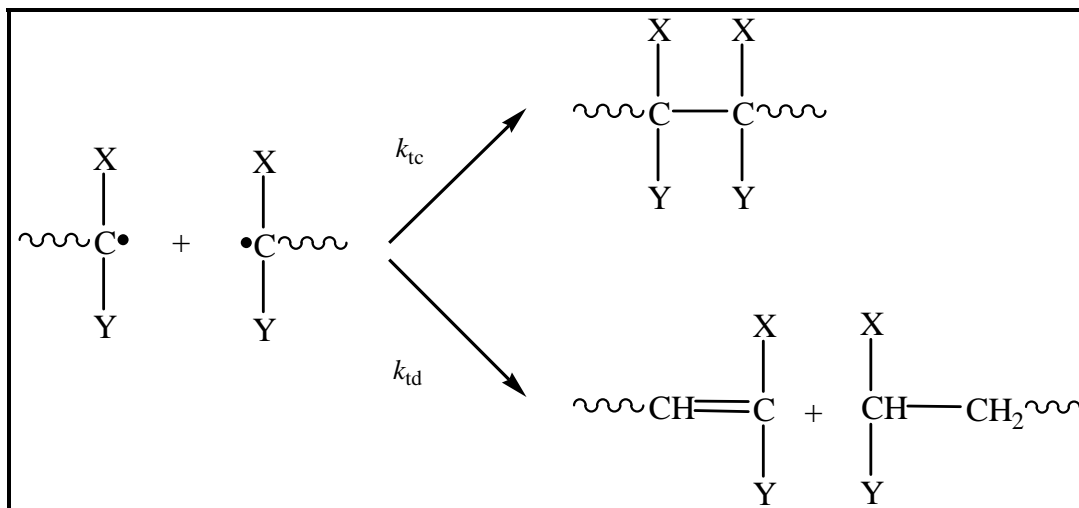
It was discovered that substituents on the propagating radical may stabilize the radical and thereby increase its reactivity. Other factors also play a role in the rate of monomer addition, e.g. bond strength, steric factors and polarity.

Possible chain transfer events may occur during the propagation process. Chain transfer refers to the process whereby the active radical centre is transferred from the polymer end to another molecule present in the system, e.g. monomer, solvent, formed polymer, chain transfer agents present in the system or even the initiator. Chain transfer agents are additives that are added to a system to reduce the molecular weight. Intramolecular chain transfer may also occur and this is known as backbiting. These are important side reactions in free radical polymerizations as they lead to a reduction in molecular weight and a limit is set on the maximum attainable molecular weight.

Termination is defined as the deactivation of propagating radical chain ends via the bimolecular processes of radical combination or radical disproportionation³ (see Scheme 2.3). Termination by combination occurs when a propagating radical species combines with any other radical species, resulting in a single dead polymer chain.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

Termination by disproportionation results in two terminated chains – one chain containing an unsaturated chain end and the other a saturated chain end.



Scheme 2.3: Free radical termination processes via radical-radical coupling (k_{tc}) and disproportionation (k_{td}).

Although these two termination processes are by far the most common for terminating polymerization reactions, termination may also occur by the reaction of a propagating radical with a stable radical such as oxygen or with an inhibitor such as phenol which is a non-radical species.

2.2 Living Radical Polymerization (LRP)

Conventional free radical polymerization is a very important commercial process for preparing high molecular weight polymers for several reasons, which include: reactions can be carried out under mild reaction conditions, trace amounts of impurities can be tolerated and it is suitable for the polymerization of a wide range of vinyl monomers¹.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

However, due to irreversible termination via disproportionation or bimolecular coupling, conventional free radical polymerization is limited in its control over molecular weight, polydispersity, chain architecture, polymer composition and end-group functionality³.

Living ionic polymerization has been successfully employed in the synthesis of well-defined polymers with precisely controlled chain architectures⁴⁻⁶. However, living ionic polymerization requires stringent reaction conditions, e.g. inert atmosphere and the absence of water and other impurities. This technique is also limited to a relatively small number of monomers. For these reasons, it has become desirable to synthesize well-defined polymers by a free radical mechanism and consequently from a larger range of monomers and under milder reaction conditions. This has led to the increase in research on LRP techniques. LRP aims to maintain the desirable attributes of conventional free radical polymerization, while severely suppressing undesirable characteristics such as termination reactions. This enables the synthesis of polymers with precisely controlled molecular weights and complex architectures and compositions, e.g. block copolymers and end-functionalized polymers.

Several LRP techniques exist, but all of them possess one unique characteristic: a dynamic equilibrium between a growing free polymer chain and a dormant species⁷ established via the addition of a specific compound to the conventional free radical polymerization system. This reduces the number of propagating radicals which in turn lowers the probability of irreversible termination. However, the rate of propagation (k_p) must be slower than the rate of deactivation to keep the number of monomer addition steps between the dormant states as few as possible in order to limit termination and chain transfer events.

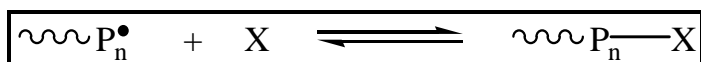
In summary, to achieve control in radical polymerization systems, two criteria must be met: fast initiation in order to allow all polymer chains to grow simultaneously and a low concentration of propagating radicals to limit termination events.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

2.2.1 Mechanism of LRP

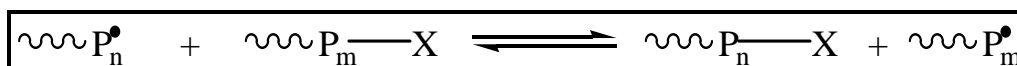
LRP is obtained by two major classes of processes, reversible end-capping and reversible chain transfer.

- 1) **Reversible end-capping:** In this case a dormant species (P_nX) undergoes homolytic bond dissociation to yield an active polymer chain ($P_n\bullet$) which is capable of propagating, and a capping agent ($X\bullet$). It has to be noted that only a single polymer chain interacts with the capping agent at any given time (see Scheme 2.4).



Scheme 2.4: Reversible end-capping.

- 2) **Reversible chain transfer:** This process involves the reversible transfer of the capping agent between more than one polymer chain (Scheme 2.5).



Scheme 2.5: Reversible chain transfer.

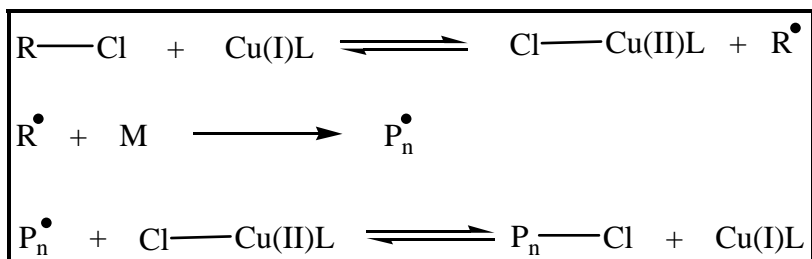
Atom Transfer Radical Polymerization (ATRP) and Nitroxide Mediated Polymerization (NMP) are the two main techniques that employ reversible end-capping.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

Examples of reversible chain transfer processes include degenerative transfer using alkyl iodides, Catalytic Chain Transfer (CCT) and Reversible Addition-Fragmentation chain Transfer (RAFT).

2.2.2 Atom Transfer Radical Polymerization (ATRP)

ATRP was discovered independently by Matyjaszewski⁸ and Sawamoto⁹ in 1995. Matyjaszewski used the term ATRP whereas Sawamoto called the process transition metal catalyzed radical polymerization. The ATRP process is based on the reversible formation of radicals from alkyl halides in the presence of transition metal complexes via a redox reaction. Metals that are most commonly used in ATRP reactions include ruthenium, copper and iron, among others. The ruthenium-based systems require the addition of a Lewis acid to become active¹⁰, whereas the copper-based systems usually contain nitrogen ligands such as bipyridine or multidentate amines¹¹. Scheme 2.6 illustrates the copper-based ATRP process.



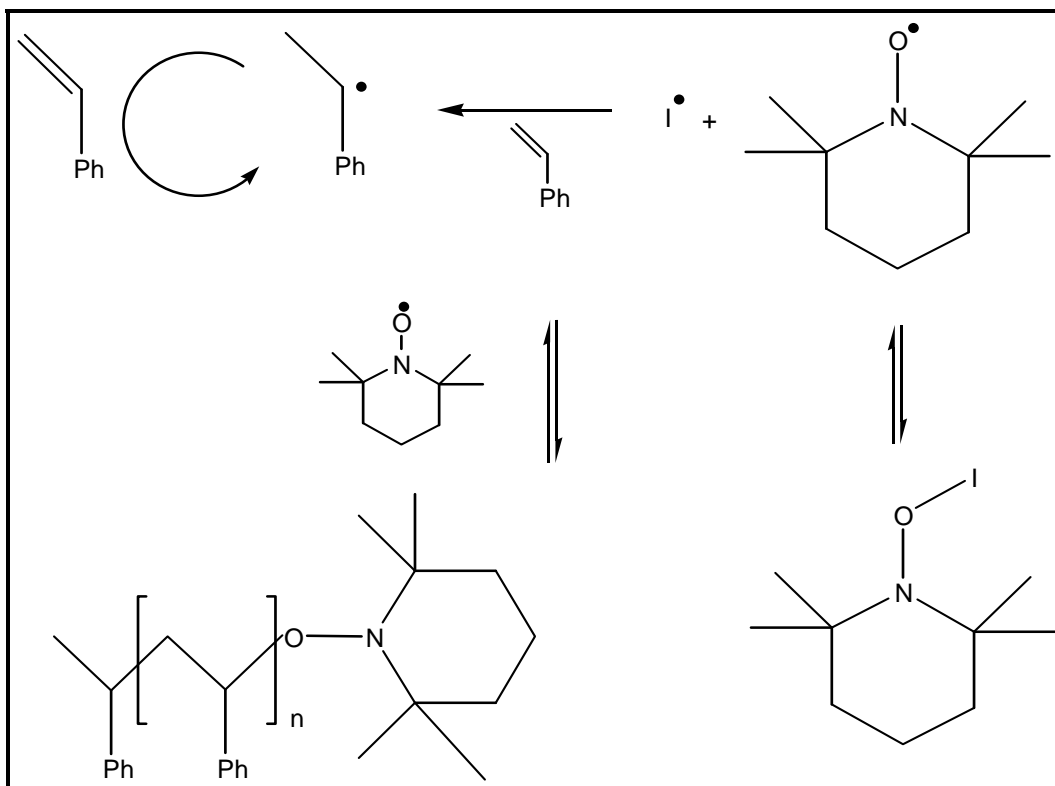
Scheme 2.6: A copper-based ATRP system with an alkyl chloride initiator.

ATRP is a very versatile LRP technique, but it does have several significant drawbacks, e.g. polymers may contain a relatively high amount of metal ions, poor solubility of the

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

initiating systems in certain common polymerization solvents and sensitivity of the metal to other redox reactions in acidic and aqueous media¹¹.

2.2.3 Nitroxide Mediated Polymerization (NMP)

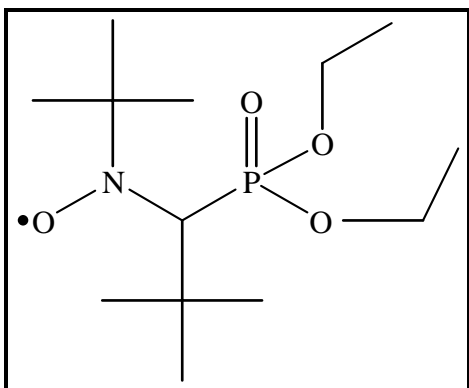


Scheme 2.7: Schematic representation of the NMP process.

NMP is based on the reversible capping of a propagating polymer chain by a stable nitroxide compound to form the corresponding N-alkoxyamine and an alkyl radical (Scheme 2.7). The alkyl radical is capable of initiating polymerization whereas the nitroxide radical can reversibly cap the growing polymer chain, thereby preventing termination. The most common nitroxide used in NMP is 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO).

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

TEMPO does however suffer from two major limitations: (1) styrene and its derivatives are the only monomers that can effectively be controlled by TEMPO, (2) the presence of TEMPO dramatically decreases rates of polymerization and (3) temperatures greater than 100°C are required to break the nitroxide bond. In order to overcome these limitations, Benoit et al.¹² and Hawker et al.¹³ developed nitroxides with a hydrogen atom on one of the α -carbons in contrast to the two quaternary α -carbons present in TEMPO. These nitroxides exhibit living characteristics during the polymerization of acrylates, acrylamides, 1,3-dienes and acrylonitrile based monomers¹³. An example of this new group of nitroxides is N-tert-butyl-N-(1-diethylphosphone-2,2-dimethylpropyl) nitroxide (SG1), as depicted in Scheme 2.8, which has been used for polymerization far below 100°C¹⁴.

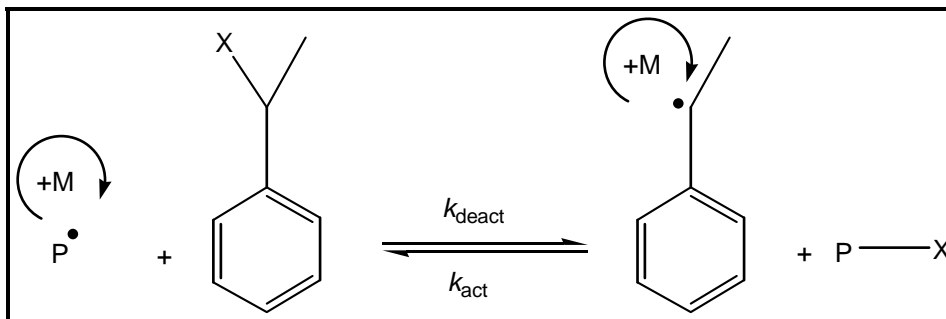


Scheme 2.8: SG1 (N-tert-butyl-N-(1-diethylphosphone-2,2-dimethylpropyl) nitroxide).

2.2.4 Degenerative Transfer Using Alkyl Iodides

This process is termed degenerative due to the fact that the radical activity is reversibly transferred from one polymer chain to another with no effective change in the overall energy. The process is illustrated in Scheme 2.9, where P• represents a propagating polymer chain.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND



Scheme 2.9: Schematic representation of the degenerative transfer process with an alkyl iodide as a transfer agent.

Matyjasewski et al.¹⁵ examined the use of alkyl iodides as transfer agents to produce living polymerizations but, due to the relatively slow rate of chain transfer, control was limited and polydispersities were rarely below 1.5. Alkyl iodides have been successfully used in heterogeneous polymerizations¹⁶.

2.2.5 Catalytic Chain Transfer (CCT)

The CCT process is based on the transfer of a hydrogen atom from a free radical species to an olefin, catalyzed by certain Co(II) chelates¹⁷. It is used for the synthesis of polymers with vinyl end groups which can be used as macromonomers. The chain transfer coefficients of these Co(II) catalysts are high (10^2 - 10^4) compared to those of conventional transfer agents, e.g. thiols (10^{-2} - 10)¹⁸. This, in combination with the fact that the transfer agent is catalytic and not consumed in the process, means that only a minute amount of the transfer agent is required in the reaction.

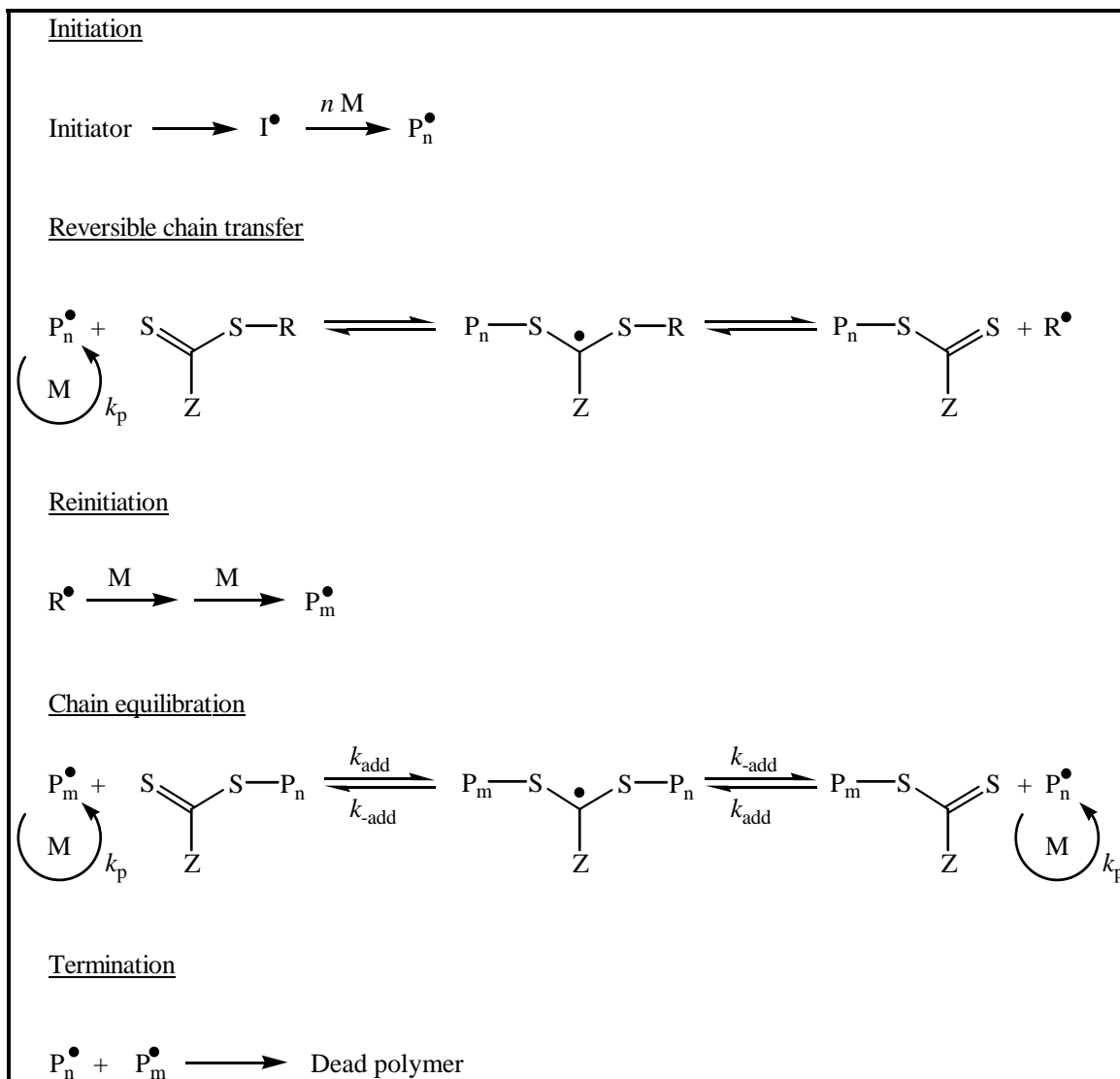
CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

2.2.6 Reversible Addition-Fragmentation Chain Transfer (RAFT)**2.2.6.1 General**

After it was patented by Le et al.¹⁹ in 1998, the RAFT process has proven to be one of the most powerful and versatile of the new LRP techniques. RAFT involves the use of thiocarbonylthio compounds to mediate the polymerization via a reversible chain-transfer process²⁰. The generally accepted mechanism of the RAFT process as described by Moad et al.²¹ is depicted in Scheme 2.10.

The initiation step is the same as in conventional free radical polymerization, i.e. an initiator decomposes to form primary radicals, which add to monomer to produce propagating radicals ($P_n\bullet$). The addition of the propagating radical to the thiocarbonylthio compound leads to the formation of an intermediate radical that can undergo fragmentation to form a dormant polymeric thiocarbonylthio compound and an active radical ($R\bullet$). The radical ($R\bullet$) can add to monomer to form a new polymeric radical ($P_m\bullet$). A rapid equilibrium is established between the dormant thiocarbonylthio compounds and the active propagating radicals. This provides an equal probability for all chains to grow, which leads to the establishment of living characteristics. Although greatly suppressed, termination still occurs via radical-radical coupling. Evidence for this RAFT mechanism has been obtained via Electron Spin Resonance Spectroscopy (ESRS)²², ¹H-NMR and Electrospray Ionization Mass Spectrometry (ESI-MS)²³.

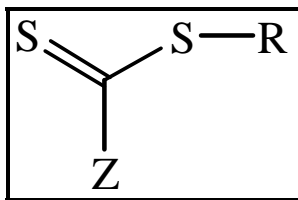
CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND



Scheme 2.10: Schematic representation of the RAFT polymerization mechanism.

The structure of the RAFT agent is vital for the efficiency of the RAFT process. A wide variety of RAFT agents has been reported: dithioesters^{24,25}, dithiocarbamates^{26,27}, trithiocarbonates^{28,29} and xanthates^{30,31}. The general molecular structure of RAFT agents is illustrated in Scheme 2.11.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND



Scheme 2.11: General RAFT agent structure.

The activating or stabilizing Z-group influences the stability of the intermediate radical. The Z-group also modifies the reactivity of the thiocarbonylthio compound towards free radical attack. The rate of addition of radicals to the carbon-sulfur double bond is higher when Z = aryl, alkyl or S-alkyl, and lower when Z = O-alkyl or N,N-dialkyl. If the Z-group contains electron-withdrawing groups, the activity of the RAFT agent is enhanced³². The R-group must be a good homolytic leaving group relative to the attacking radical P_n^\bullet to allow for efficient fragmentation in the desired direction. The rate of fragmentation of the R-group increases with the presence of electron-withdrawing and radical-stabilizing groups on R and also by increasing steric hindrance. Since there is no universal RAFT agent, the choice of R- and Z-groups is very important to ensure a fast approach to the dynamic equilibrium between the active, growing polymer chains and the dormant chains. This equilibrium allows all polymer chains to grow simultaneously, which in turn leads to a narrow molecular weight distribution.

The RAFT process has numerous advantages:

- Reaction conditions are the same as in conventional free radical polymerizations, except for the addition of a predetermined amount of a suitable RAFT agent. The same range of monomers, solvents, initiators and temperatures can be used.
- Polymers with complex molecular architectures (blocks, stars, grafts, telechelics etc.) can be synthesized.
- Molecular weights can be predicted theoretically using a simple equation:

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

$$\overline{M}_{n,\text{theory}} = FW_{\text{RAFT}} + \frac{x[M]_0 FW_M}{[\text{RAFT}]_0} \quad \text{Equation 2.1}$$

where FW_{RAFT} and FW_M are the molar masses of the RAFT agent and the monomer respectively, $[M]_0$ and $[\text{RAFT}]_0$ are the initial concentrations of the monomer and the RAFT agent respectively, and x is the fractional conversion.

- The RAFT process exhibits living characteristics, i.e. molecular weight increases linearly with conversion, active chain ends are preserved and narrow polydispersities are obtained.
- End-group functionalities can be obtained.

Disadvantages of the RAFT process include:

- The synthesis of RAFT agents can be expensive and time-consuming.
- The addition of RAFT agents leads to a decrease in the rate of polymerization.

2.2.6.2 RAFT End-Group Modification

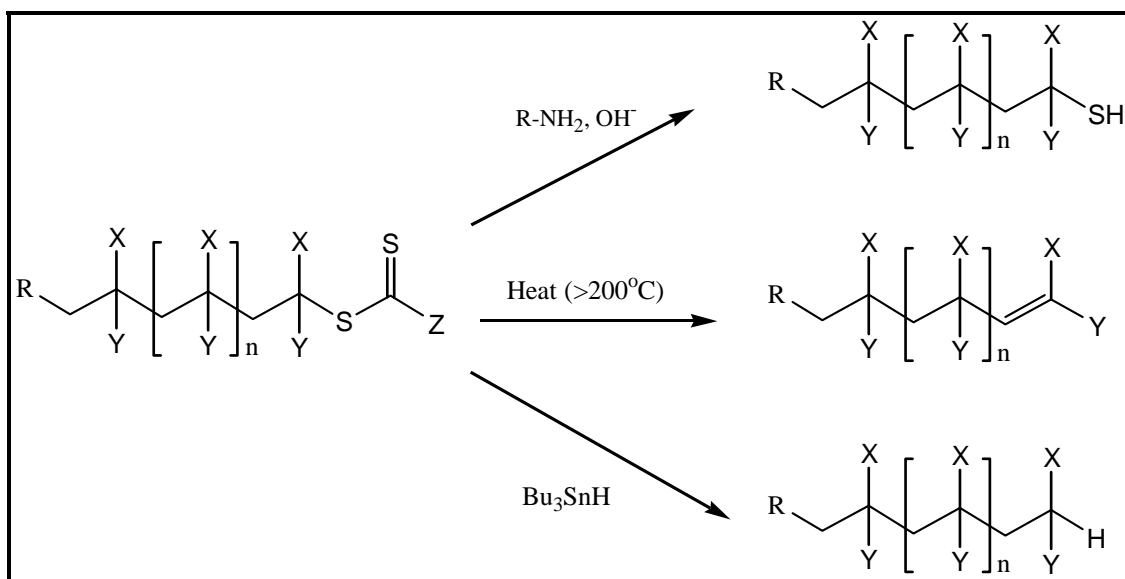
Polymers produced by RAFT polymerization systems retain the thiocarbonylthio moiety present in the initial RAFT agent. By adjusting the molecular structure of the activating and leaving groups, chain-end functionality can be introduced in the polymer. Examples of chain-end functionalities include: (-OH), (-CO₂H), (-CO₂Na) and (SO₃Na)²¹. In certain applications the modification of these RAFT end-groups may be advantageous:

- The reactivity of the RAFT end-groups could pose potential problems in subsequent processing steps and may have to be deactivated/removed.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

- Polymers synthesized by the RAFT process are generally coloured. This is due to the presence of the thiocarbonylthio moieties that act as chromophores. Colour could be disadvantageous for some end-use applications.
- RAFT polymers may have foul odours in some cases or release these foul-smelling sulfur-compounds due to decomposition of the thiocarbonylthio compounds.

These problems can largely be solved by the appropriate choice of RAFT agent, but synthetic barriers may limit the availability of a desired RAFT agent and thus there has been incentive to look for effective methods for the post-polymerization modification of the RAFT end-groups. A variety of methods have been used for the modification of RAFT end-groups as shown in Scheme 2.12.



Scheme 2.12: Schematic illustration of the various RAFT end-group modification procedures.

RAFT end-groups are unstable at very high temperatures. Moad et al.³³ used thermal elimination at temperatures greater than $200^\circ C$ to remove the trithiocarbonate end-groups from polystyrene and poly(butyl acrylate). This process required however that the

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

polymer must be stable at these very high temperatures required for thermolysis. Radical induced reduction of the RAFT end-groups leads to the formation of hydrocarbon end-groups. Tri-*n*-butylstannane has been used for this purpose³⁴. Oxidizing agents (e.g. NaOCl, H₂O₂, tBuOOH)³⁵ and UV irradiation³⁶ have also been successfully employed for the modification of RAFT end-groups.

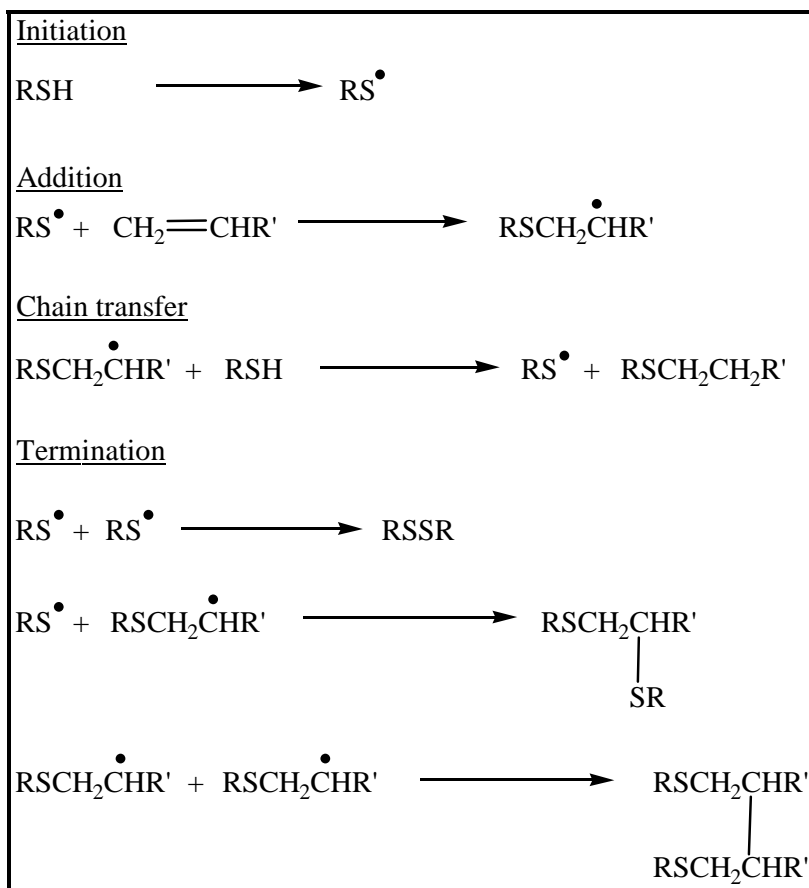
The most common method of transforming the RAFT end-group is via the use of nucleophiles such as primary and secondary amines²⁸, borohydride³⁷ and hydroxide³⁸. In this case the carbon-sulfur bond is cleaved and the RAFT end-group is transformed into a thiol. The advantages of producing a thiol functionality are numerous. Thiols play an important role in biological sciences as they forms conjugates with biopolymers such as proteins. Thiols are also used in the synthesis of condensation polymers, e.g. polythioesters and polythiourethanes. Furthermore, the ability of thiols to form crosslinks and complex metals has also been exploited for various applications^{39, 40}.

2.3 Thiol-Ene Addition Reactions

The addition of thiols to unsaturated compounds was first discovered by Posner⁴¹ in 1905 and initially formulated as a free radical chain reaction by Kharasch et al. in 1938⁴². It has since become a very important chemical reaction in organic synthesis. It was later discovered that thiols add to unsaturated compounds by nucleophilic and electrophilic mechanisms as well. The nucleophilic addition of thiols to substrates requires the presence of a base to catalyze the reaction. Substrates that can undergo nucleophilic thiol-ene addition include polyhalo alkenes and alkynes⁴³. In the case of the electrophilic mechanism, no initiator is present and the thiol-ene addition follows Markovnikov's rule. This reaction requires harsh reaction conditions and a Lewis acid (e.g. AlCl₃⁴⁴) or a protonic acid (e.g. H₂SO₄⁴⁵) is used as a catalyst. The free radical thiol-ene addition reaction follows a stepwise mechanism and the orientation is anti-Markovnikov⁴⁶, as shown in Scheme 2.13. A thiyl radical is created either via excitation by UV radiation or

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

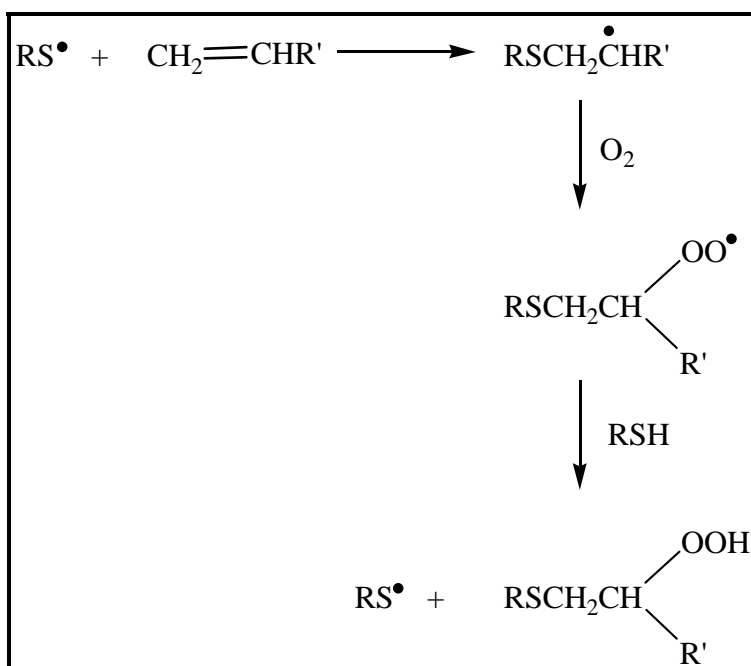
hydrogen abstraction by a free radical initiator. The thiyl radical reversibly adds to the double bond of the unsaturated compound⁴⁷. The formed carbon-centered radical abstracts a hydrogen atom from another thiol molecule and the thiyl radical is regenerated, thus propagating the radical chain. Finally, termination occurs by radical-radical coupling⁴⁸. The rate determining step is generally the chain transfer step and since it involves the cleavage of a carbon-sulfur bond, it is greatly dependent on the structure of the thiol, e.g. aromatic thiols are better chain transfer agents than aliphatic thiols due to the resonance stabilization imparted.



Scheme 2.13: General thiol-ene addition mechanism.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

A major advantage of thiol-ene addition reactions is the insensitivity toward oxygen inhibition, which is generally a problem in free radical reactions. The negligible oxygen inhibition observed in thiol-ene systems is attributed to the formation of peroxy radicals created by the reaction of the carbon centered radical with molecular oxygen⁴⁹. The peroxy radicals abstract hydrogen atoms from other thiol molecules and thus regenerate the thiyl radicals which can in turn add to the unsaturated compounds to continue the two-step chain process (Scheme 2.14).



Scheme 2.14: Oxygen scavenging mechanism of thiol-ene systems.

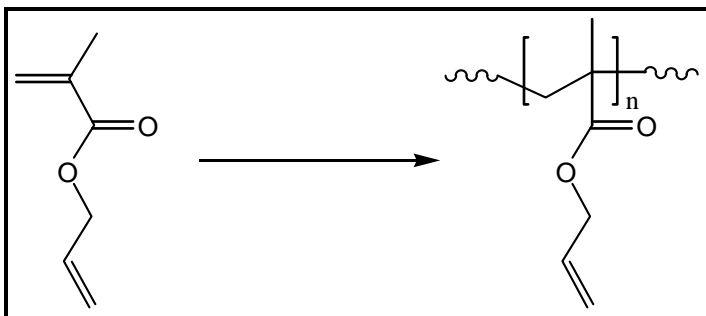
2.4 Polymerization of Allyl Methacrylate

Monomers such as ethylene glycol dimethacrylate (EDMA) and divinyl benzene are examples of monomers that contain two reactive double bonds and are commonly used as cross-linking agents. These monomers are symmetric in structure and therefore both

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

double bonds have the same chemical reactivities. Allyl methacrylate (AMA), however, is an asymmetrical divinyl compound containing two double bonds of different chemical reactivities: a highly reactive methacryloyl double bond and a less reactive allyl double bond. AMA has been used as an alternative cross-linking agent to EDMA in the synthesis of resin foams, coatings and materials with high water absorption⁵⁰. However, due to the different reactivities of the double bonds of AMA, selective polymerization and cross-linking is now possible.

Anionic homopolymerization of AMA occurs mainly through the more reactive methacryloyl double bonds, resulting in linear polymers with pendant allylic double bonds⁵¹ (Scheme 2.15). No cross-linking occurs and the polymers that are obtained have narrow polydispersities, even at high molecular weights.

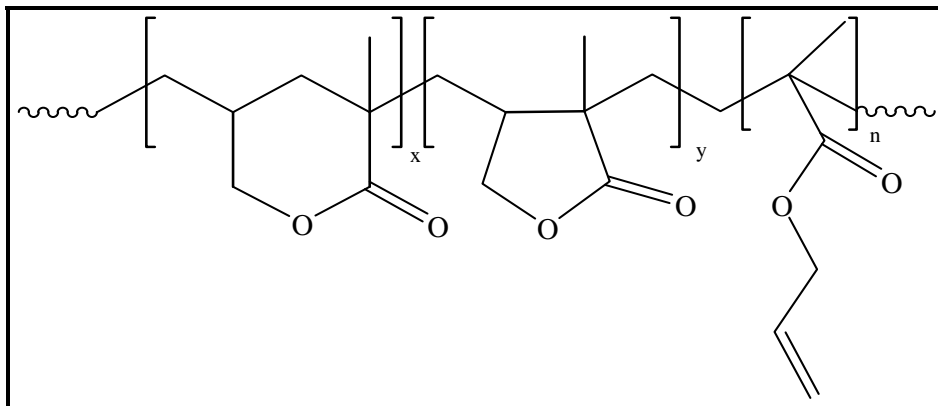


Scheme 2.15: Homopolymerization of allyl methacrylate through the methacryloyl double bonds.

Studies on the free radical polymerization of AMA have been performed in bulk⁵², solution⁵³, and emulsion⁵⁴ systems. The free radical homopolymerization of AMA also leads to the formation of PAMA prepolymers containing pendant allylic double bonds at low conversions. With an increase in conversion however, intermolecular and intramolecular reactions gradually lead to crosslinking and eventually the formation of a gel. Secondary reactions may occur during the free radical polymerization of AMA – these include the formation of five- and six-membered lactone rings⁵⁵ (Scheme 2.16),

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

although NMR spectroscopic investigations by Nagelsdiek et al.⁵⁶ revealed no evidence to support this theory.



Scheme 2.16: The proposed secondary structures present in PAMA homopolymer.

Recently, there have been studies done on the living free radical polymerization of AMA using ATRP during which the gel effect was also observed at higher conversions^{55,56}.

Cohen and Sparrow suggested two ways to delay the onset of crosslinking and gelation⁵⁷:

- During the early stages of polymerization the reactivity of the less reactive allylic double bond has to be decreased, but it must still be capable of crosslinking during later stages of the reaction if required.
- The chain lengths at the early stages of polymerization have to be reduced to delay the onset of crosslinking. This can be done by the addition of a chain transfer agent, such as lauryl mercaptan⁵⁸.

The benefits of having an uncrosslinked, soluble polymer with pendant double bonds are numerous. These polymers can undergo crosslinking on demand (e.g. via irradiation) for the formation of polymer networks or coatings. Grafting onto the double bonds is also a

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

feasible approach by which to synthesize various branched copolymers with specific properties.

2.5 Free Radical Copolymerization

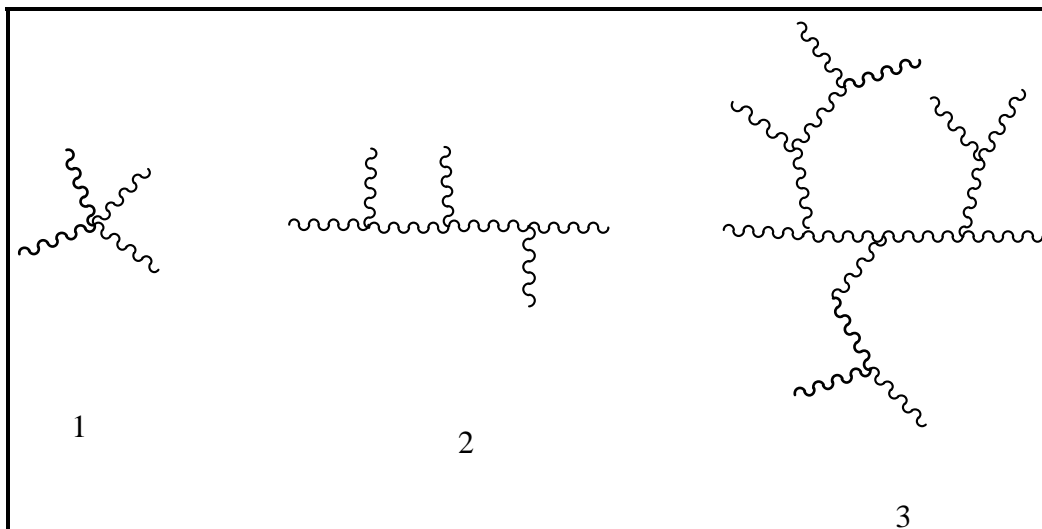
There is, as always, a great need for new polymeric materials with novel properties for use in specific applications. There are three ways to generate such polymers – the first involves the synthesis of new monomers which can be polymerized to form new polymers. Modification of existing monomers/polymers is another way of creating new materials. Both these methods require great amounts of research, development and ultimately money, which can make them economically non-viable.

Copolymerization is a method that uses existing monomers to produce materials with unique properties, making this the most widely used method for producing novel polymers. By varying the combination of comonomers as well as the distribution of the comonomers, known as the chemical composition distribution (CCD), the properties of the copolymer can be varied.

There is a variety of copolymers that can be synthesized by free radical means:

- Random copolymers: ABBABAABABABBAAABBABA
- Block copolymers: AAAAAAAAAABBBBBBBBBBBBBBBB
- Alternating copolymers: ABABABABABABABABABA
- Gradient copolymers: AAAABAABBABBBABBABBBB
- Branched polymers, e.g. comb-, star-, and hyperbranched copolymers (Scheme 2.17)

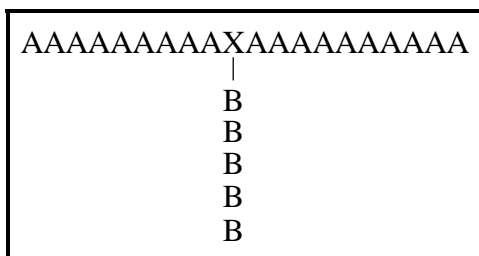
CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND



Scheme 2.17: Branched polymers (1) star (2) comb and (3) hyperbranched polymers.

2.5.1 Graft Copolymerization

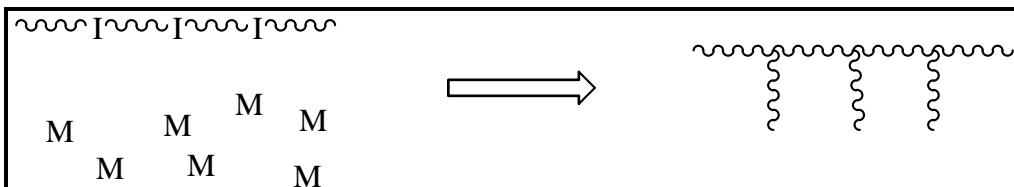
Graft copolymers comprise a main polymer chain to which one or more side chains are covalently bonded. The simplest graft copolymer can be represented by Scheme 2.18, where sequence (A) represents monomer units making up the backbone or main polymer chain, sequence (B) is the side chain or graft and (X) is the unit in the backbone to which the graft is attached.



Scheme 2.18: General structure of a graft copolymer.

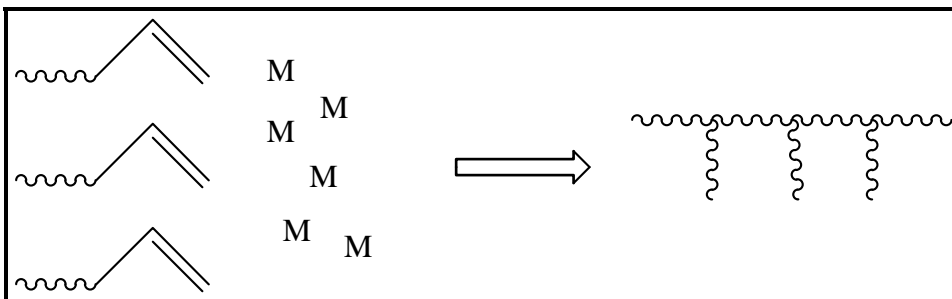
CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

There are three basic methods for the synthesis of graft copolymers:

2.5.1.1 “Grafting From” Method

Scheme 2.19: The “grafting from” method.

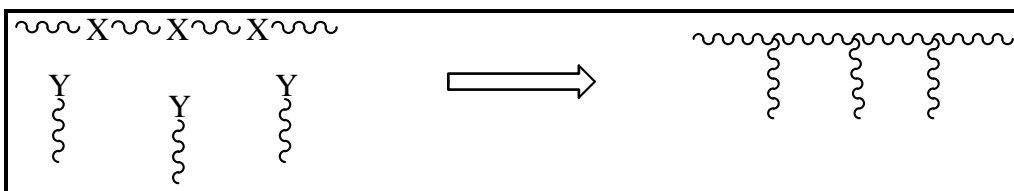
The “grafting from” method involves the synthesis of a polymeric backbone with a functional monomer incorporated into it. These functional monomers must be capable of acting as the active sites from which the polymerization of a second monomer can be initiated. In certain cases the formed branches can be chemically cleaved and characterized⁵⁹.

2.5.1.2 “Grafting Through” Method

Scheme 2.20: The “grafting through” method.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

The “grafting through” method is also known as the macromonomer method as it entails the synthesis of low molecular weight pre-polymers with functional end-groups that are capable of being polymerized. These macromonomers are copolymerized with other monomers to yield graft copolymers. One of the advantages of the “grafting through” method is that the chain lengths of the side chains are entirely dependent on the length of the macromonomer and are thus easily controlled. The frequency of the side chains, however, is dependent on the molar ratios of the comonomers and their reactivity ratios. Various methods have been used to synthesize macromonomers such as ATRP⁶⁰, addition-fragmentation techniques⁶¹ and conventional organic routes⁶².

2.5.1.3 “Grafting Onto” Method

Scheme 2.21: The “grafting onto” method.

In the “grafting onto” method the polymer backbone and side chains are synthesized separately. The actual grafting process occurs via the reaction of a functional group (e.g. –COOH) on the pre-formed side chain, with a complementary functional group (e.g. –OH) distributed along the polymer backbone⁶³. The advantage of this method is that the side chains can often be fully characterized prior to being grafted onto the polymer backbone.

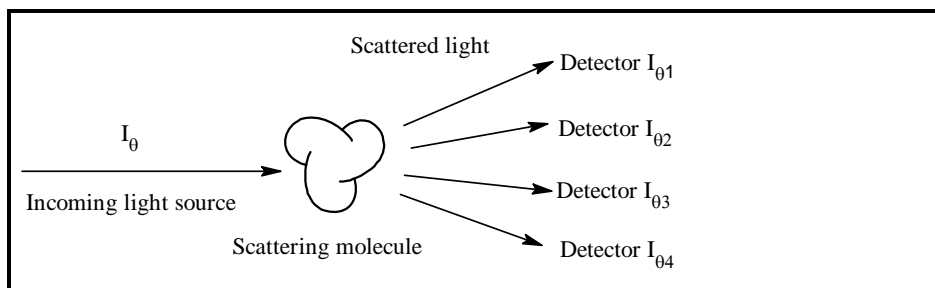
CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

2.5.2 Analysis of Branched Polymers

The intrinsic ability of macromolecules to scatter light has led to the development of various investigation techniques that can determine physical properties of these molecules. The basic premise of these techniques is that when an incoming light source strikes a molecule, it induces an oscillating dipole in the molecule. The molecule subsequently scatters the light in different directions and with different intensities, depending on its size and structure.

Classical light scattering employs a static detector set at an angle θ with respect to the incident beam, whereas dynamic light scattering uses fast photon counters to measure fluctuations in the scattered light (due to constructive and destructive interference) to obtain information concerning the hydrodynamic volume of the molecules.

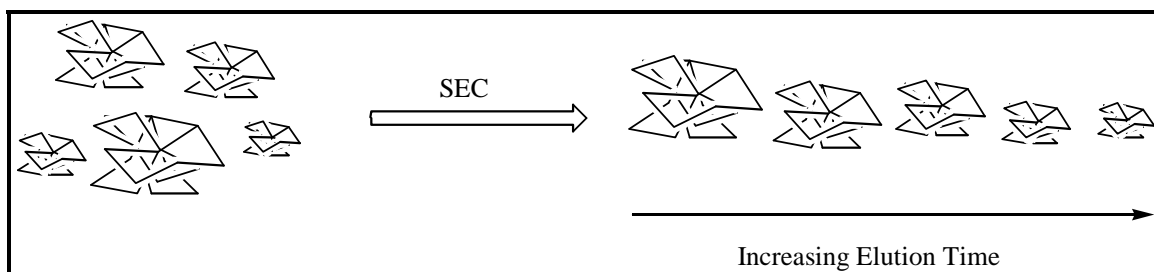
Measuring the variation of scattered light, however, requires the simultaneous detection of scattered light intensities at various angles. This led to the development of multi-angle laser light scattering (MALLS) instruments (Scheme 2.22). A MALLS instrument has a range of detectors set at various different angles along the arc of the scattered plane. MALLS measurements can give information on molecular conformation, absolute molecular weight and root mean square radius.



Scheme 2.22: Schematic representation of a typical MALLS experiment setup.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

Size exclusion chromatography (SEC) used in conjunction with MALLS has opened up new possibilities for the analysis of macromolecules. SEC separates polymers according to their hydrodynamic volume (Scheme 2.23). Large molecules penetrate fewer pores and elute first, whereas smaller molecules are able to penetrate more pores and thereby occupy a larger volume, and this slows their passage through the column and they elute later as their specific volume of elution is reached.



Scheme 2.23: SEC separates on the basis of hydrodynamic volume.

The SEC detectors are normally calibrated with polymers of known molecular weight. This calibration method can fail however when non-linear polymers or polymers consisting of monomeric units different to those of the calibration standards are used. This is where MALLS as a type of absolute detector for SEC comes in useful, since it does not require a calibration curve; only dn/dc values are required, where dn represents the change in refractive index and dc the change in molecular concentration.

A SEC-MALLS setup typically consists of a SEC column, followed by a MALLS instrument and finally a differential refractive index (RI) detector. The SEC column separates the molecules according to molecular weight and each elution fraction is then subjected to MALLS, which assigns an absolute molecular weight to each fraction.

CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

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CHAPTER 2: HISTORICAL AND THEORETICAL BACKGROUND

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CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

ABSTRACT

Two RAFT agents were synthesized for the purposes of this study. Cyanovaleric acid dithiobenzoate (CVADTB) and dodecyl isobutyric acid trithiocarbonate (DIBTC) were produced in good yields and with high purities. DIBTC was used as RAFT agent to polymerize styrene and butyl acrylate. Low target molecular weights were set to study the effect of RAFT agent concentration on polymerization kinetics. Both monomers exhibited living characteristics although some rate retardation phenomena were observed.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

3.1 Introduction

The function of the RAFT agent is to create a dynamic equilibrium between active propagating radicals and dormant chains. Many RAFT agents have been synthesized with great structural variety to mediate free radical polymerization reactions of a wide range of monomers. Initially dithioesters were used as RAFT agents¹, but later trithiocarbonates, dithiocarbamates and xanthates were also synthesized and effectively used for RAFT polymerization, as already described in Chapter 2.

Styrene and butyl acrylate are two commonly studied monomers and thus much is known about their properties. These monomers have been widely used in RAFT polymerization studies in both homogeneous²⁻⁴ and heterogeneous media, i.e. emulsion⁵⁻⁷ and mini-emulsion⁸⁻¹⁰. These factors made styrene and butyl acrylate ideal monomers to use in this model study.

3.2 Experimental

3.2.1 Materials

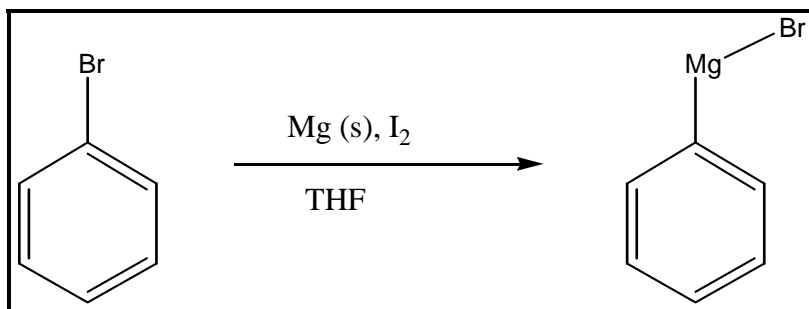
Azo bis(cyanovaleric acid) 75% (Sigma-Aldrich), Aliquot 336 (Fluka), n-dodecyl mercaptan 98%+ (Sigma-Aldrich), diethyl ether 99.5% (Merck), dimethylsulfoxide 99% (Labchem), chloroform 99% (Labchem), hydrochloric acid 33% (Aldrich), bromobenzene 99% (Aldrich), carbon disulfide 99.9% (Aldrich), acetone CP, carbon tetrachloride 99.9% (Aldrich), ethyl acetate CP, isopropanol CP, pentane CP, heptane CP, hexane CP, sodium hydroxide CP, iodine 99% (Aldrich) and magnesium 98% (Aldrich) were used as received. Tetrahydrofuran (THF) was distilled from lithium aluminium

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

hydride (LiAlH_4). Prior to use, the styrene monomer was washed twice with 0.3 M aqueous potassium hydroxide solution to remove inhibitors, followed by distillation under reduced pressure. Butyl acrylate monomer was also purified by vacuum distillation. Both monomers were stored at 2°C over molecular sieve. Toluene was used as the solvent in all the polymerization reactions and purification consisted of distillation under reduced pressure and storage over molecular sieves at low temperature. Azobisisobutyronitrile (AIBN) was recrystallized from methanol and kept at low temperature for later use.

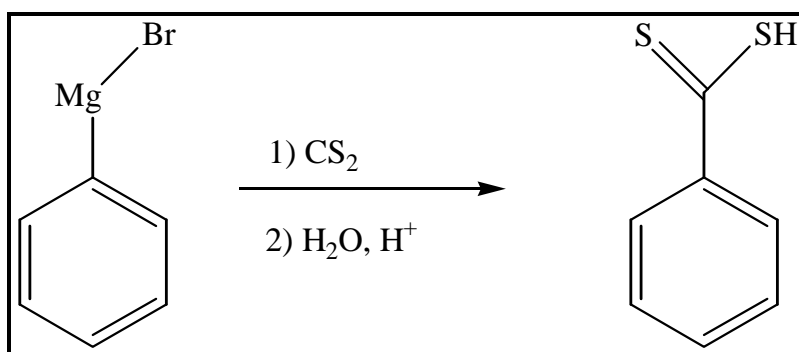
3.2.2 Synthesis of Cyanovaleric Acid Dithiobenzoate (CVADTB)

All the equipment, and the magnesium turnings, was dried in an oven for a minimum period of 12 hours prior to use. The magnesium turnings (5.15 g, 0.21 mol) and a stirrer bar were placed in a 250 ml 3-neck reaction vessel with a single crystal of iodine and a small amount of dry THF. Bromobenzene and the remainder of the THF (44.45 g, 0.62 mol) were placed in two separate dripping funnels. Approximately 10% of the THF and the bromobenzene (39.96 g, 0.25 mol) were added to the reaction mixture. Once the brown/yellow colour of the iodine disappeared, the remainder of the THF and the bromobenzene were added, while cooling the reaction mixture using an ice bath. On completion of the reaction the system was allowed to cool down. It yielded a mixture that had a metallic grey/green colour.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

Scheme 3.1: Formation of the Grignard reagent.

Carbon disulfide (16.15 g, 0.21 mol) was added in a dropwise fashion to a cooled reaction mixture (cooled in an ice bath) using a dripping funnel. The reaction is exothermic, and the reaction mixture turned red upon addition of the carbon disulfide. Upon completion of the reaction (no more heat-generation), water was added to hydrolyze the Grignard reagent. The unreacted magnesium turnings were filtered off prior to the acidification of the reaction mixture with 33% hydrochloric acid. The colour of the mixture changed to purple as the dithiobenzoic acid formed.

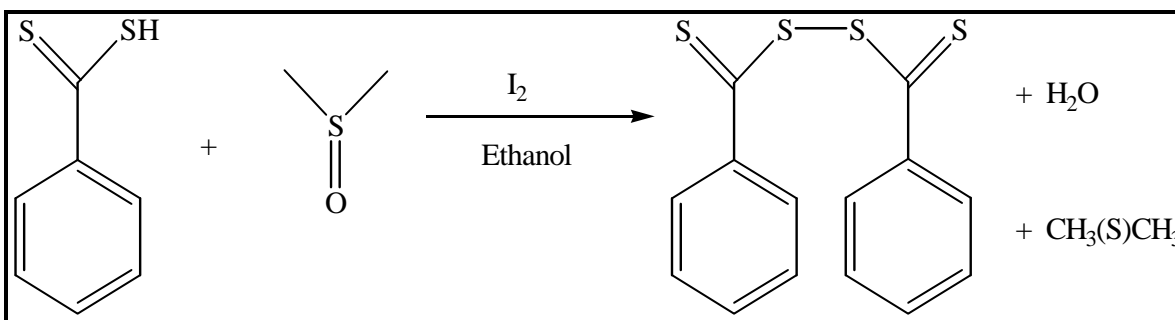


Scheme 3.2: Synthesis of dithiobenzoic acid.

The dithiobenzoic acid was extracted twice with diethyl ether. The diethyl ether was removed with a rotary evaporator to yield a dark red compound. Dithiobenzoic acid

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

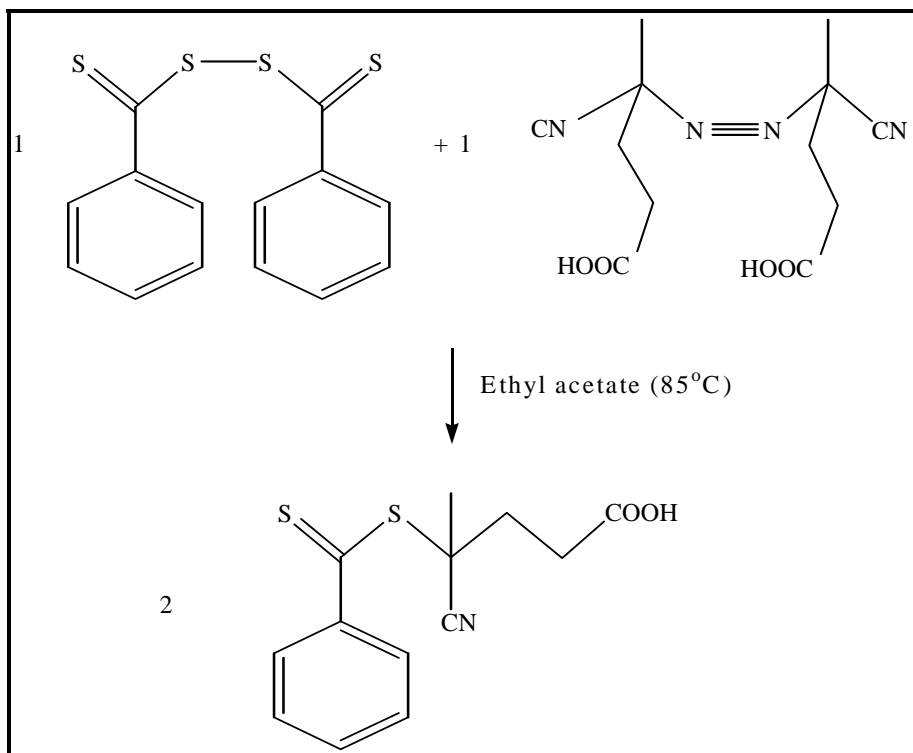
(25.16 g, 0.16 mol) was transferred into a 250 ml three-neck reaction vessel equipped with a dripping funnel. A single crystal of iodine and ethanol (5.92 g, 0.13 mol) was added to the reaction vessel. Twice the molar ratio of dimethyl sulfoxide (25.49 g, 0.32 mol) was slowly added to the reaction mixture via the dripping funnel. The excess DMSO is required to speed up the reaction. The reaction mixture was cooled in an ice bath. The red/purple bis(thiobenzoyl)disulfide crystals that formed and were filtered off and washed with cold ethanol.



Scheme 3.3: Synthesis of bis(thiobenzoyl)disulfide.

The dithioester RAFT agent was synthesized via the technique described by Le et al.^{11,12} Bis(thiobenzoyl)disulfide was reacted with the azo initiator 4,4'-azo-bis(4-cyanovaleric acid) in refluxing ethyl acetate (85°C) under a nitrogen atmosphere for approximately 24 hours.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS



Scheme 3.4: Synthesis of cyanovaleric acid dithiobenzoate.

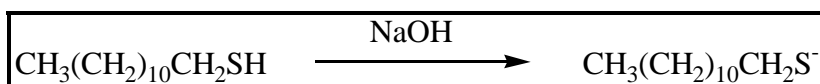
Typical reaction quantities were the following: 5.00 g (0.016 mol) bis(thiobenzoyldisulfide) reacted with 6.00 g (0.016 mol) 4,4'-azobis(4-cyanovaleric acid) to yield 5.20 g (0.018 mol) cyanovaleric acid dithiobenzoate, corresponding to a yield of 56%. ¹H-NMR analysis indicated that purities in excess of 95% were obtained (see Appendix A).

3.2.3 Synthesis of Dodecyl Isobutyric Acid Trithiocarbonate (DIBTC)

S-1-dodecyl-S'-isobutyric acid trithiocarbonate (DIBTC) was synthesized via the method described by Lai et al.¹³ employing phase transfer methodology. 1-Dodecanethiol (8.0 g, 0.040 mol), Aliquot 336 (tricapryl methyl ammonium chloride, 0.65 g, 0.0016 mol) and

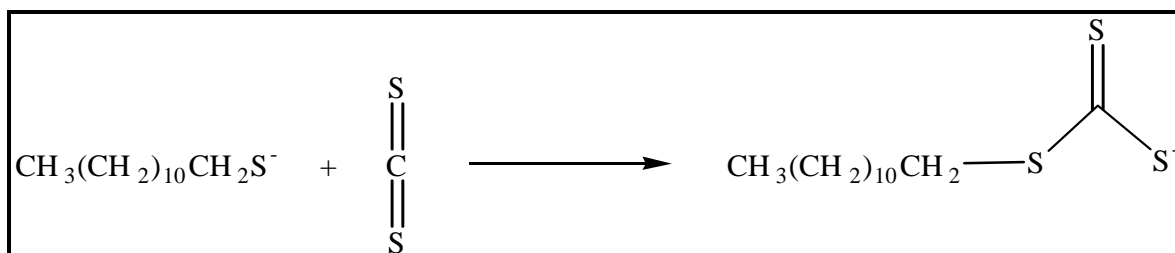
CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

acetone (20.0 g, 0.34 mol) were stirred in a 100 ml-reactor. The reactor was placed in an ice bath and the reaction proceeded under a nitrogen atmosphere. A 50% sodium hydroxide solution (3.5 g, 0.043 mol) was added dropwise over a 20 minute period and the reaction mixture was stirred for an additional 15 minutes.



Scheme 3.5: Formation of the sulfide anion.

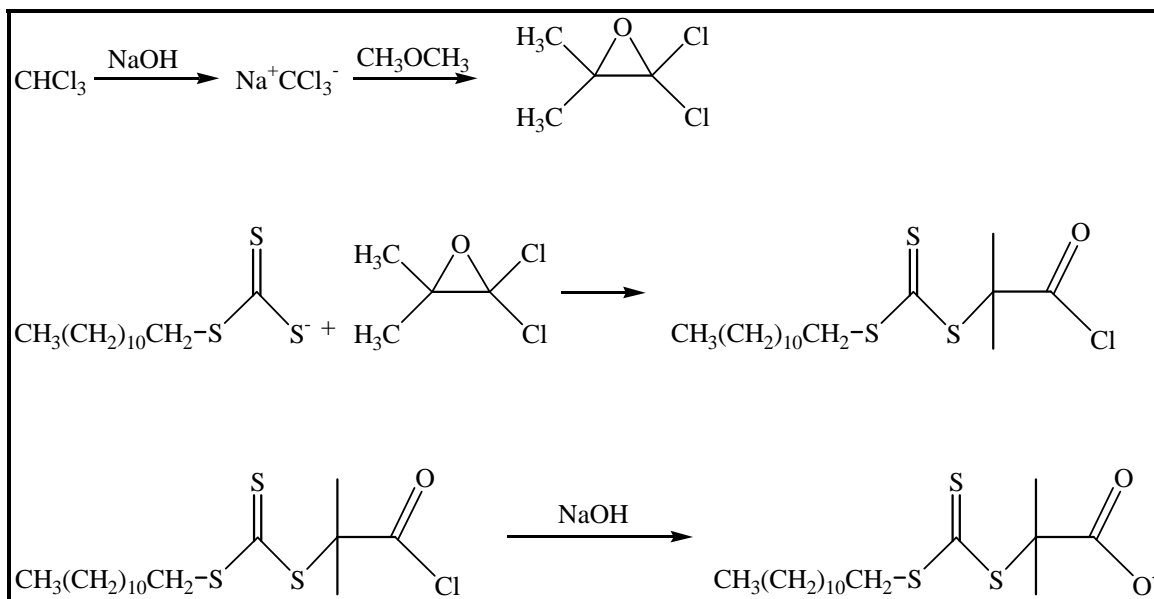
A mixture of carbon disulfide (3.1 g, 0.041 mol) and acetone (4.00 g, 0.069 mol) was added over 30 minutes, during which time the reaction mixture turned yellow.



Scheme 3.6: Addition of carbon disulfide to sulfide anion.

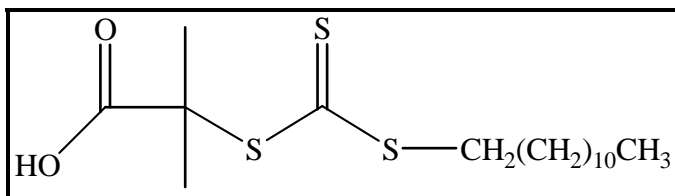
Chloroform (7.0 g, 0.06 mol) was added in one portion. This was followed by the dropwise addition of 50% sodium hydroxide solution (16.0 g, 0.2 mol) over 30 minutes, after which the reaction was allowed to stir overnight.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS



Scheme 3.7: Formation of the isobutyric acid leaving group.

The reaction mixture was placed in a large beaker and stirred at high revolutions. Approximately 60 ml of water was added to the reaction mixture, followed by the addition of 10 ml 33% hydrochloric acid to neutralize the reaction. The reaction mixture was stirred until the acetone evaporated. The solids were collected with a Buchner funnel and stirred in an excess of isopropanol. After 30 minutes the solids were filtered off and the isopropanol solution concentrated by rotary evaporation. The concentrated solution was recrystallized twice from cold hexane to yield 7.2 g (0.020 mol) of the trithiocarbonate RAFT agent, corresponding to a yield of 43%. $^1\text{H-NMR}$ analysis indicated that purity of the product was >95% (see Appendix B).



Scheme 3.8: Dodecyl isobutyric acid trithiocarbonate.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS**3.2.4 Synthesis of low molecular weight polystyrene and poly(butyl acrylate)**

Equation 2.1 (Section 2.2.6.1) can be utilized to target specific molecular weight polymers when using a RAFT polymerization system. For the purposes of this study it was decided to target molecular weights of 4000 g.mol^{-1} and $10\,000 \text{ g.mol}^{-1}$ for monomers, styrene and butyl acrylate.

The styrene polymerizations were carried out at 100°C , with a solvent to monomer ratio of 1:1. The butyl acrylate polymerizations were performed at 90°C , again using a solvent to monomer ratio of 1:1.

All reactions were carried out in a 25 ml pear-shaped reaction vessel and under a nitrogen atmosphere. The reaction vessel was equipped with a stirrer bar, a nitrogen inlet, a rubber septum and a condenser. A temperature regulated bath was used to control the temperature. The reaction mixtures were degassed for 20 minutes prior to the start of the reactions. Samples were taken at regular intervals in order to determine monomer conversion. For this, samples were placed in sample pans before being dried in a vacuum oven for a minimum period of 12 hours

Conversions were determined gravimetrically and molecular weight analysis was carried out by GPC. The GPC instrument consisted of a Waters 717 plus Autosampler, Waters 600E System Controller and a Waters 610 Fluid unit. A Waters 410 refractometer was used at 35°C as detector. THF (HPLC-grade) purged with IR-grade helium was used as eluent at a flow rate of 1 mL.min^{-1} . The columns used were two PLgel $5 \mu\text{m}$ Mixed-C columns and a pre-column (PLgel $5 \mu\text{m}$ guard). The column oven was kept at 30°C and the injection volume was $100 \mu\text{l}$. The system was calibrated with narrow polystyrene standards ranging from 800 to $2 \times 10^6 \text{ g.mol}^{-1}$.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

3.3 Results and Discussion

3.3.1 Low Molecular Weight Polystyrene

The RAFT-mediated styrene polymerizations were carried out at 100°C. At this temperature it can be assumed that a certain degree of thermal initiation takes place, in conjunction with initiation via the free radical initiator AIBN. This high reaction temperature was selected to reduce the reaction time, while still producing polystyrene with low polydispersity (PDI) values.

Table 3.1 summarizes the different reagents that were used for the RAFT-mediated homopolymerization of styrene as well as the molecular weight data as obtained by GPC.

Table 3.1: Experimental results for the RAFT-mediated homopolymerization of styrene

$M_{n,target}^a$	Styrene		Toluene		DIBTC		AIBN		Conv. ^b (%)	M_n		PDI ^e
	Mass (g)	mmol	Mass (g)	mmol	Mass (g)	mmol	Mass (g)	mmol		Calc. ^c	Exp. ^d	
4000	10	96	10	190	1.12	3.0	0.01	0.06	61	2400	2600	1.23
10 000	10	96	10	190	0.40	1.1	0.01	0.06	82	8200	7100	1.21

^a Target molecular weight at 100% conversion

^b Conversion percentage calculated by gravimetry

^c Calculated molecular weight

^d Experimental molecular weight

^e Polydispersity index

The polymerization with the target molecular weight of 10 000 g.mol⁻¹ reached a higher conversion than the polymerization with target molecular weight of 4000 g.mol⁻¹, but in both cases the polydispersities remained low.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

Figure 3.1 clearly shows a linear increase of conversion over time for the polystyrene polymerization with target molecular weight of 10 000 g.mol⁻¹, but a slow conversion rate is visible in the early stages of polymerization with the target molecular weight of 4000 g.mol⁻¹. A similar trend is visible in the semi-logarithmic plot in Figure 3.2.

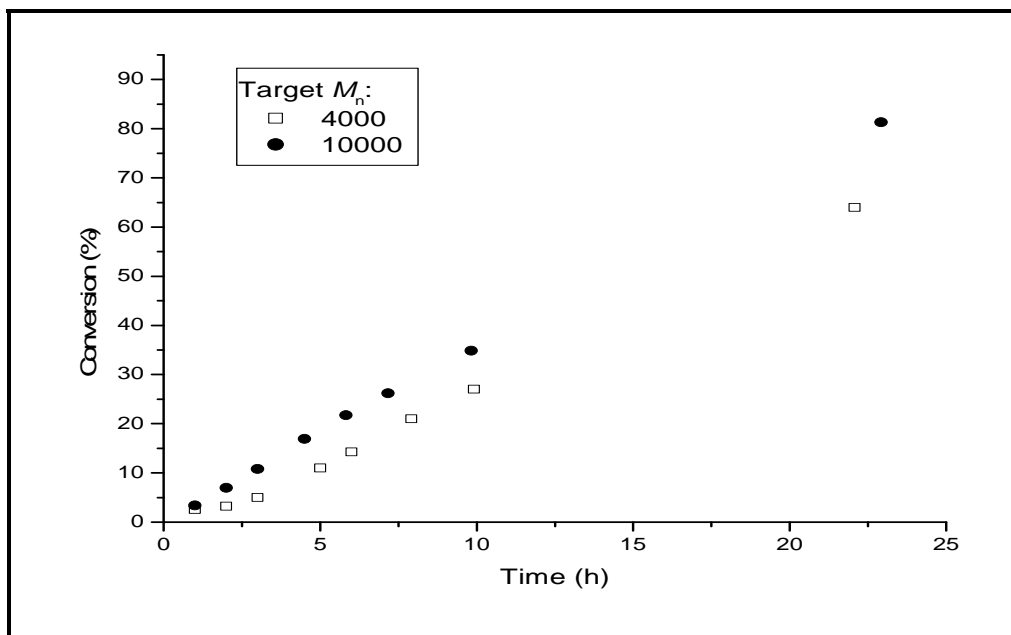


Figure 3.1: Conversion-time graph for the RAFT-mediated polymerization of styrene in toluene at 100°C with DIBTC as RAFT agent and AIBN as initiator.

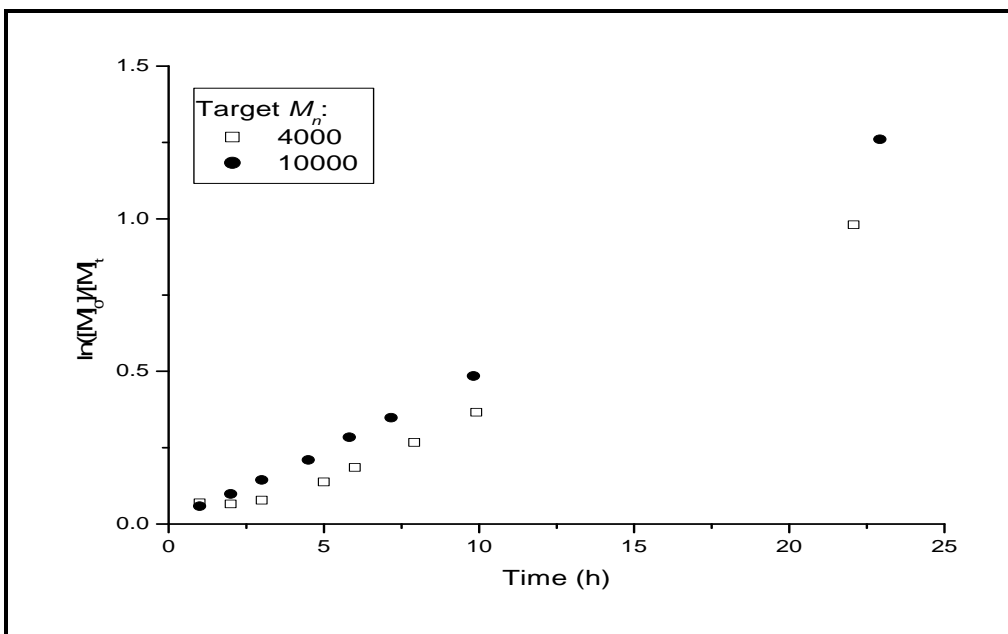
CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

Figure 3.2: Semi-logarithmic graph for the RAFT-mediated polymerization of styrene in toluene at 100°C with DIBTC as RAFT agent and AIBN as initiator.

Various explanations have been given for the retardation phenomena in the RAFT process. Generally speaking, retardation occurs when an unsuitable RAFT agent is used or when the concentration of RAFT agent is very high. Cross-termination between propagating and intermediate radicals was suggested by Monteiro et al.¹⁴ as a possible cause of retardation, whereas Barner-Kowollik et al.¹⁵ believed that the intermediate radical was stable enough to cause no cross-termination. McLeary et al.¹⁶ studied the RAFT polymerization of methyl acrylate with cumyl dithiophenylacetate as RAFT agent. They observed an inhibition period corresponding to the consumption of the initial RAFT agent and termed this period initialization. Other factors that may cause retardation include the inability of the R-group to reinitiate polymerization and the slow fragmentation of the intermediate radical. Sometimes inconsistencies in polymerization rates can also be attributed to extraneous factors such as the presence of oxygen in the reaction mixture as well as impurities in the initial RAFT agent. In the case of styrene, retardation has been observed, especially when high concentrations of dithiobenzoate RAFT agents are used^{14,15,17}.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

Intensive investigations are required to determine the exact causes of retardation for a specific monomer/RAFT agent combination, but for this study it was sufficient that linear trends were observed in the later stages of polymerization and that the polydispersities remained low (<1.35) for the entire duration of the reaction.

Figure 3.3 shows a linear increase in molecular weight with conversion. However, the predicted molecular weights for both experiments are overestimated at higher conversions. This may be due to a decrease in initiator efficiency with conversion¹⁸.

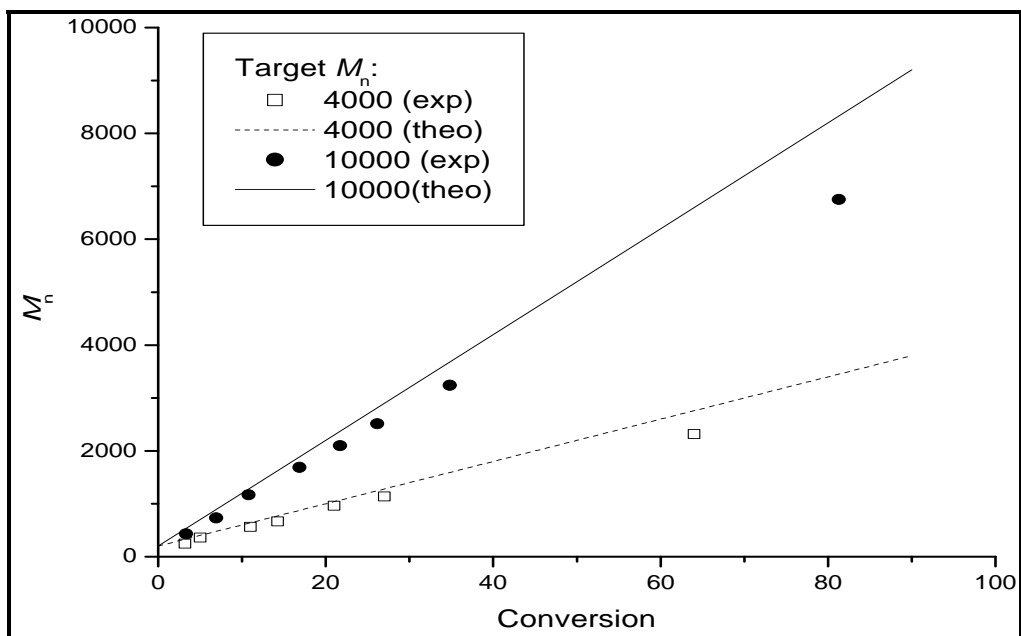


Figure 3.3: Graph of molecular weight versus conversion for the RAFT-mediated polymerization of styrene in toluene at 100°C with DIBTC as RAFT agent and AIBN as initiator.

The narrow, well-defined GPC distributions (Figure 3.4) also give a clear indication of the good level of control that was obtained.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

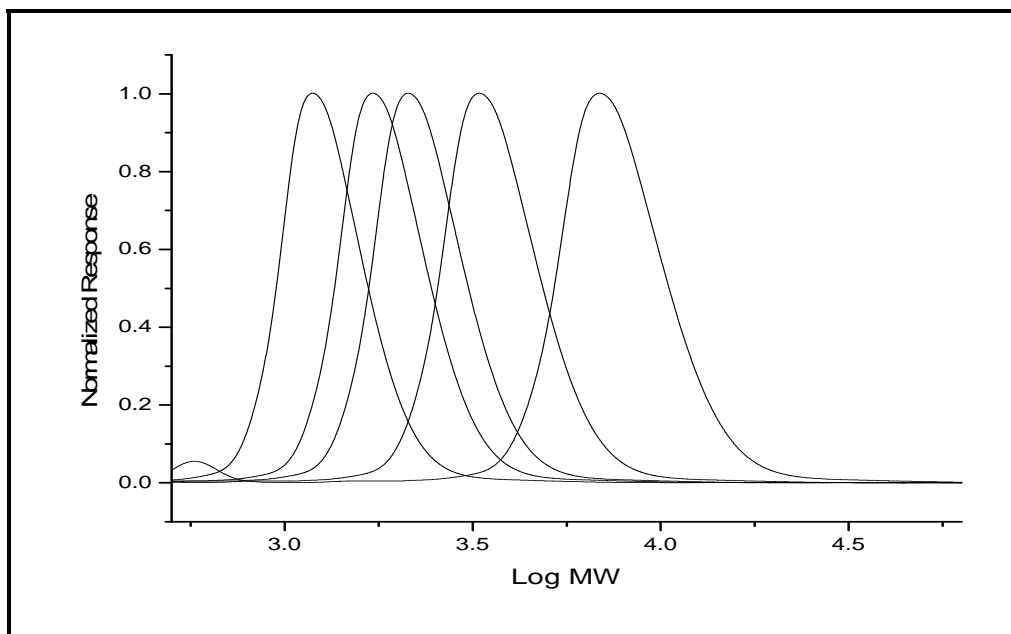


Figure 3.4: Normalized GPC distributions for the RAFT-mediated polymerization of styrene in toluene at 100°C with DIBTC as RAFT agent and AIBN as initiator.

3.3.2 Low Molecular Weight Poly(butyl acrylate)

Table 3.2: Experimental results for the RAFT-mediated homopolymerization of butyl acrylate

$M_{n,target}^a$	Butyl acrylate		Toluene		DIBTC		AIBN		Conv. ^b (%)	M_n		PDI ^e
	Mass (g)	mmol	Mass (g)	mmol	Mass (g)	mmol	Mass (g)	mmol		Calc. ^c	Exp. ^d	
4000	10	78	10	190	1.11	3.1	0.01	0.06	72	2900	2700	1.23
10 000	10	78	10	190	0.39	1.1	0.01	0.06	83	8300	8500	1.21

^a Target molecular weight at 100% conversion

^b Conversion percentage calculated by gravimetry

^c Calculated molecular weight

^d Experimental molecular weight

^e Polydispersity index

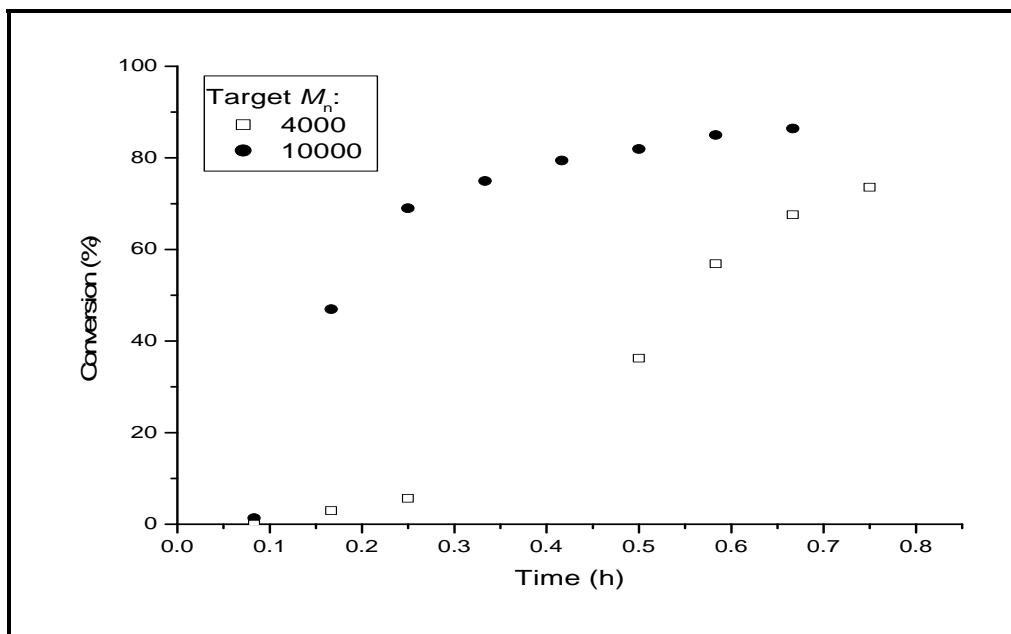
CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

Figure 3.5: Conversion-time graph for the RAFT-mediated polymerization of butyl acrylate in toluene at 90°C with DIBTC as RAFT agent and AIBN as initiator.

The RAFT-mediated polymerization of butyl acrylate with target molecular weight of 10 000 $\text{g}\cdot\text{mol}^{-1}$ shows a rapid increase in conversion over time and reaches a plateau at approximately 80% conversion. The reaction with target molecular weight of 4000 $\text{g}\cdot\text{mol}^{-1}$ has a distinct period of slow conversion early on in the reaction, after which it increases and then finally flattens out at $\sim 70\%$ (see Figure 3.5). As was the case for the RAFT-mediated polymerization of styrene, this retardation phenomenon can be ascribed to various factors such as initialization, etc. These factors were discussed in Section 3.3.1. The retardation is however exacerbated by the fact that AIBN decomposes rapidly at 90°C and butyl acrylate cannot self-initiate as styrene can.

Figure 3.6 illustrates the linear increase in molecular weight for poly(butyl acrylate) for both target molecular weights, indicating good control. This is substantiated by the GPC results given in Figure 3.7. Well defined, symmetrical molecular weight distributions were obtained with low polydispersities (<1.3).

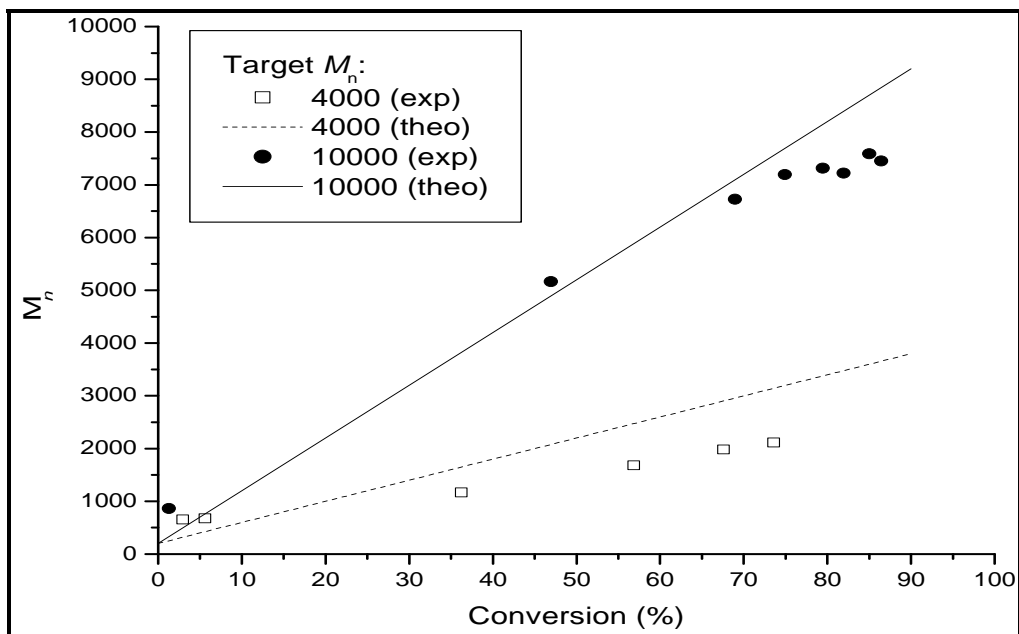
CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS

Figure 3.6: Graph of molecular weight versus conversion for the RAFT-mediated polymerization of butyl acrylate in toluene at 90°C with DIBTC as RAFT agent and AIBN as initiator.

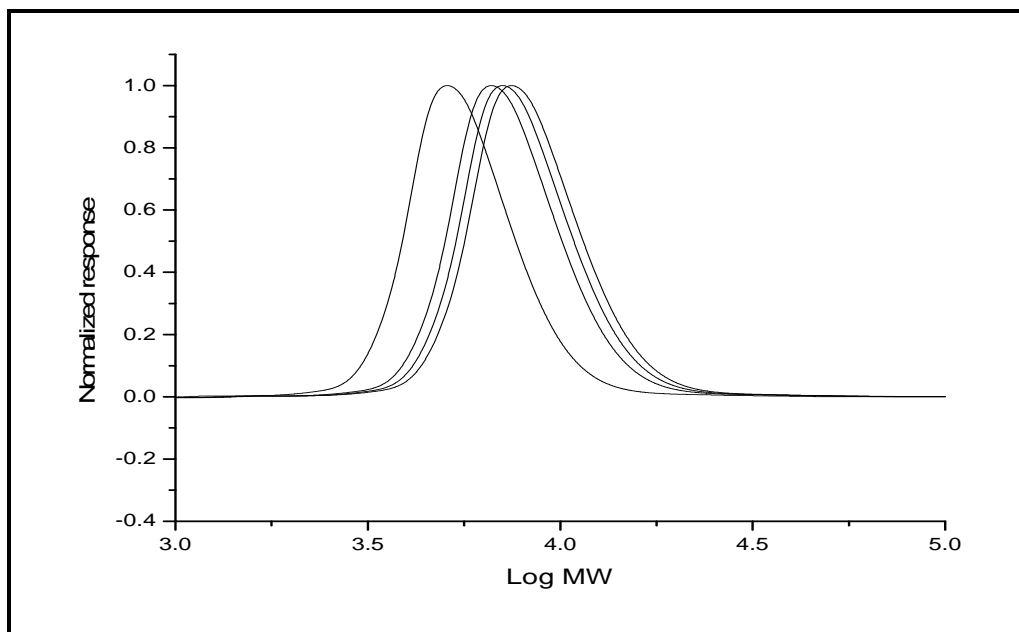


Figure 3.7: Normalized GPC distributions for the RAFT-mediated polymerization of butyl acrylate in toluene at 90°C with DIBTC as RAFT agent and AIBN as initiator.

CHAPTER 3: RAFT-MEDIATED SYNTHESIS OF LOW MOLECULAR WEIGHT POLYMERS**3.4 Conclusions**

There is no universal RAFT agent and the effectiveness of a RAFT agent depends strongly on the monomer that will be polymerized. Therefore the structures of the RAFT agent, i.e. the R- and Z-groups, have to be carefully chosen. It has to be noted though that the majority of polymerization reactions can be carried out with just two RAFT agents: one RAFT agent for the polymerization of acrylamides, acrylates, and styrenic monomers, e.g. DIBTC, and another for the polymerization of vinyl monomers, e.g. CVADTB¹⁹. Therefore the successful synthesis of these two RAFT agents should prove adequate for the polymerization of all monomers used in this study.

The RAFT-mediated polymerization of both monomers proved successful. DIBTC was used as RAFT agent in both polymerization studies and results showed that polymers with low polydispersities and well-defined molecular weight distributions were obtained. Styrene and butyl acrylate showed some form of rate retardation in the early stages of polymerization, especially in the case of the lower target molecular weight polymers, which could be ascribed to a variety of factors. In the case of this study however, it was only required to synthesize polymers with low polydispersities and a known and reproducible molecular weight. In light of these requirements, the RAFT-mediated polymerization of both monomers was therefore considered to be successful.

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CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

ABSTRACT

Various methods for the post-polymerization modification of RAFT end-groups to form thiol end-groups were studied. The use of sodium methoxide proved most successful for this purpose as the modification was virtually complete and impurities were only present at very low levels.

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS**4.1 Introduction**

Due to the mechanism of the RAFT process, only a small fraction of chains are initiated by initiator-derived radicals, whereas the great majority of polymer chains are derived from reinitiation from the R-group of the RAFT agent. However, it is inherent to the RAFT process that all polymer chains should theoretically contain a terminal thiocarbonylthio moiety. The thiocarbonylthio moieties at the ends of the polymer chains may lead to complications in certain applications due to the potential lability of the carbon-sulfur bond. This is especially true in the case of aqueous RAFT polymerization where the presence of water may promote hydrolysis of the RAFT moieties and lead to a loss of active chain ends and diminished control¹. Aminolysis of dithioesters in aqueous RAFT systems has also been cited as a reason for the failure of some of these systems². By making use of these labile carbon-sulfur bonds, various advantageous possibilities also emerge. One of these advantages is the modification of the RAFT end-groups for further chemical reactions, e.g. the synthesis of primary and secondary amine end-functional polymers³ or for the synthesis of thiol end-functional polymers in the production of monolayer-protected clusters of metal nanoparticles⁴⁻⁶. In this project, the aim is to transform the RAFT end-group into a thiol end-group to facilitate the grafting of polymer branches onto a polymer backbone via a thiol-ene addition reaction.

4.2 Experimental**4.2.1 Materials**

Styrene monomer was washed with two aliquots of a 0.3 M aqueous potassium hydroxide solution to remove inhibitors and distilled under reduced pressure prior to use. Toluene

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

CP, methanol CP and 1,4 dioxane 99% (Merck) were distilled and stored over molecular sieves. THF was distilled from LiAlH₄. DIBTC was prepared as described in Chapter 3. Water was distilled and deionized. Sodium bisulfite 99% (Merck), sodium borohydride (NaBH₄) 99% (Merck), sodium methoxide 95% (Aldrich) and concentrated hydrochloric acid 32% (Merck) were used as received.

4.2.2 RAFT-Mediated Polymerization of Styrene

Styrene was polymerized using DIBTC as RAFT agent and toluene as a solvent. The reactions were carried out at 100°C under a nitrogen atmosphere. The target molecular weights (employing Equation 2.1) at 100% conversion were 2000 g.mol⁻¹, 4000 g.mol⁻¹ and 10 000 g.mol⁻¹. The chemical compositions of the reaction mixtures are given in Table 4.1. The reactions were stopped after a specific time period had elapsed, corresponding to 50% conversion, by using the kinetic studies described in Chapter 3. This was done by placing the reaction vessel in an ice bath. The solvent was removed using a rotary evaporator and the polymer was dried in a vacuum oven at room temperature for 24 hours.

Table 4.1: Composition of the various reaction mixtures for the RAFT-mediated homopolymerizations of styrene

$M_{n, target}^a$	Styrene		Toluene		DIBTC		AIBN	
	Mass (g)	mmol	Mass (g)	mmol	Mass (g)	mmol	Mass (g)	mmol
1000	8.0	77	8.0	87	2.32	6.3	0.01	0.06
2000	20.0	192	20.0	217	2.24	6.0	0.02	0.12
5000	20.0	192	20.0	217	0.80	2.2	0.02	0.12

^a Target molecular weight at 50% conversion

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS**4.2.3 Modification of RAFT End-Groups**

The experimental parameters for the various RAFT end-group modification reactions attempted in this study are given in Table 4.2. These reactions were all at least partially unsuccessful, and sodium methoxide was used for all further RAFT end-group modification experiments (as described in detail below).

The RAFT-functionalized polystyrene was reacted with a 30-molar excess of sodium methoxide with dry 1,4-dioxane as solvent. The reactions were carried out in a 50 ml round-bottom reaction flask equipped with a condenser, a nitrogen inlet and a magnetic stirrer bar. The reaction mixtures were degassed for 15 minutes prior to immersion into a temperature-regulated oil bath at 60°C. The reactions were run for approximately 24 hours under a nitrogen atmosphere. After a few hours the reaction mixtures gradually turned from a pale yellow to a rusty orange colour. Upon completion of the reaction the mixtures were allowed to cool down to room temperature before 5 ml of distilled water was added. Concentrated hydrochloric acid (33%) was added in a dropwise fashion until the reaction mixture reached pH ~7. The solids were filtered off using a Buchner filter and the polymer solution poured into a 10X excess of methanol. The polymer precipitated out of solution and filtration yielded a white powder. The polymers were dried in a vacuum oven for 24 hours prior to analysis.

Molecular weight analysis was done via GPC (specifications given in Section 3.2.4). Characterization of the molecular structures of the compounds before and after RAFT end-group modification was obtained via ¹H-NMR and UV analyses. The UV data were obtained with a Perkin Elmer Lambda 20 UV/VIS spectrometer. Autozeroing was performed using THF references. Samples were prepared by dissolving 0.5 g of the polymer in 5 ml of THF and placing the solution in quartz cuvettes. A scan profile was set to scan from 200 to 500 nm in a single ramp profile.

4.3 Results and Discussion

The aim of this experiment was the modification of the RAFT end-group of polystyrene chains synthesized with DIBTC as RAFT agent to obtain thiol-end functionalized polymer chains as illustrated in Scheme 4.1. The thiol end-group is required for the thiol-ene addition reaction later in the grafting process of these polymer chains to a PAMA backbone, as will be described in Chapter 6.

Numerous different techniques have been successfully employed for the modification of RAFT end-groups. These techniques were mentioned in Chapter 2. Various RAFT end-group modification experiments were carried out with mixed results and are summarized in Table 4.2. All reactions were conducted for a minimum period of 24 hours. The presence of impurities and byproducts were determined via $^1\text{H-NMR}$.

Table 4.2: Table summarizing the various attempts at the post-polymerization modification of the RAFT end-groups

Nr.	Compound used for RAFT end-group removal	Conc. (M) ^a	Solvent	Temp. (°C)	Comments
1	NaBH ₄	1.00	Ethyl acetate	Room temp.	No colour change, impurities present
		2.00		50	
2	NaOH	3.00	Methanol	Room temp.	Slight colour change, byproducts
		4.00		50	Colour change from yellow to clear mixture, byproducts
3	CH ₃ (CH ₂) ₁₀ CH ₂ NH ₂	1.00	THF	Room temp.	Complete colour change from yellow to clear, byproducts
		2.00		50	
4	HCl, sonication	1.00	Ethanol	Room temp.	No colour change

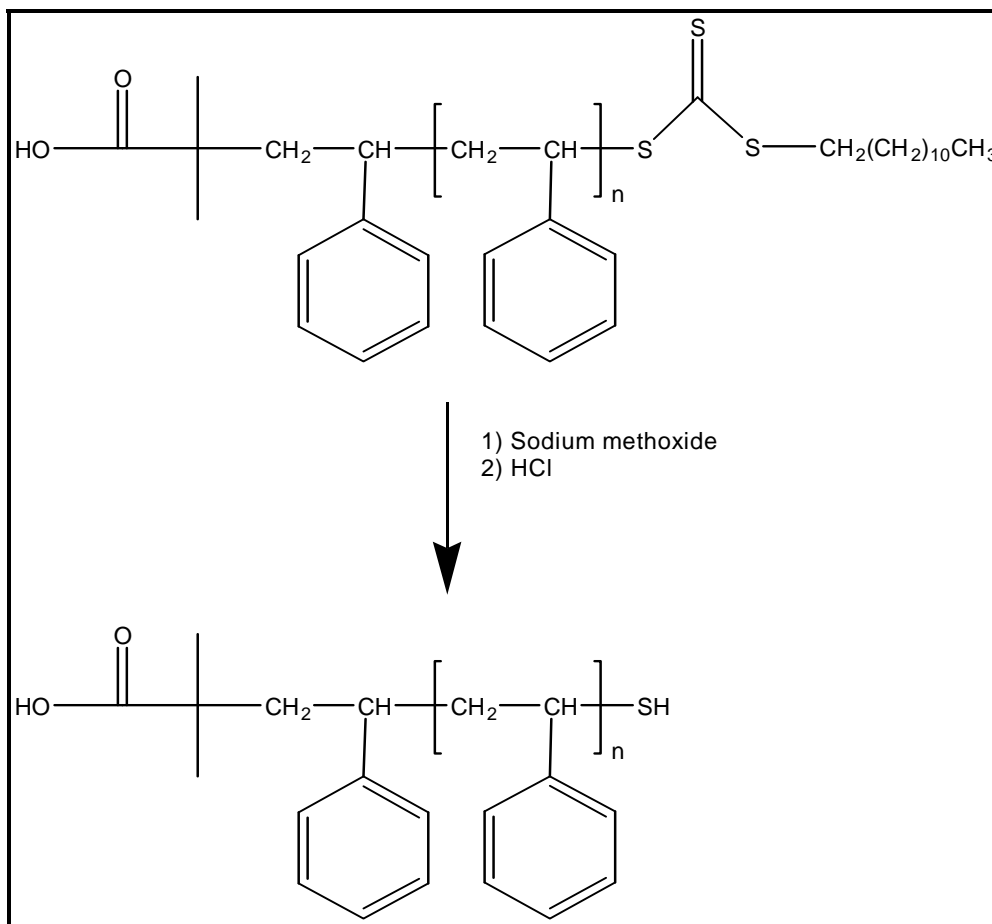
^a Concentration of compound used for RAFT end-group removal

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

The use of NaOH (reaction 2) as described by Schilli et al.⁷, and the use of primary amines (reaction 3) as described by Mayadunne et al.^{8,9}, to modify RAFT end-groups were studied under various reaction conditions. Neither Schilli nor Mayadunne made mention of the presence of impurities in their systems, however in this study it was found that these methods led to several complications. In most cases the yellow colour of the polymer disappeared after treatment with the above chemicals, as would be expected when the trithiocarbonate moiety is removed, but further NMR analysis indicated the presence of byproducts (see Appendix C and Appendix D). No successful methods were found for the isolation and identification of these byproducts. This positively showed that reaction conditions were not desirable. The use of a hydride reducing agent, sodium borohydride⁵, yielded no positive results, not even a colour change. Other, more unusual techniques were also implemented to facilitate the removal of the RAFT end-group, such as the use of ultrasound for ester hydrolysis¹⁰, but similarly proved unsuccessful. The use of thermolysis¹¹ was not considered as it leads to the formation of a carbon-carbon double bond at the end of the polymer chain, instead of the desired thiol functionality.

The method found to be most successful for the post-polymerization removal of the RAFT end-groups entailed the use of sodium methoxide. Initially the end-group modification experiments were carried out with sodium methoxide in a THF medium following the procedure described by Stenzel et al.¹², but contrary to their results the author observed the presence of a large amount of impurities even though the solvent was distilled prior to use (Appendix E). Attempts at the removal of the impurities from the reaction mixture proved ineffective. Instead a 1,4-dioxane medium was used which eliminated this problem and byproducts of the reaction itself, e.g. sodium chloride and methanol are easily and completely removed during workup.

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS



Scheme 4.1: Reaction scheme for the RAFT end-group transformation of polystyrene synthesized with DIBTC as RAFT agent with the use of sodium methoxide in dioxane.

Polystyrene obtained by RAFT polymerization using DIBTC as the RAFT agent has a distinctive yellow colour due to the presence of the trithiocarbonate chromophore. Therefore, the modification of the RAFT end-group should result in a noticeable colour change. This is observed when the polymer is precipitated out of solution after treatment with sodium methoxide as the yellow colour disappears and a completely white polymer remains. The disappearance of colour from the polymer is the first indication that the RAFT end-group was successfully modified to form a thiol end-group. Other techniques were used to confirm this result. $^1\text{H-NMR}$ was found to be the most effective method. The $^1\text{H-NMR}$ spectra of RAFT-polymerized polystyrene are shown in Figure 4.1.

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

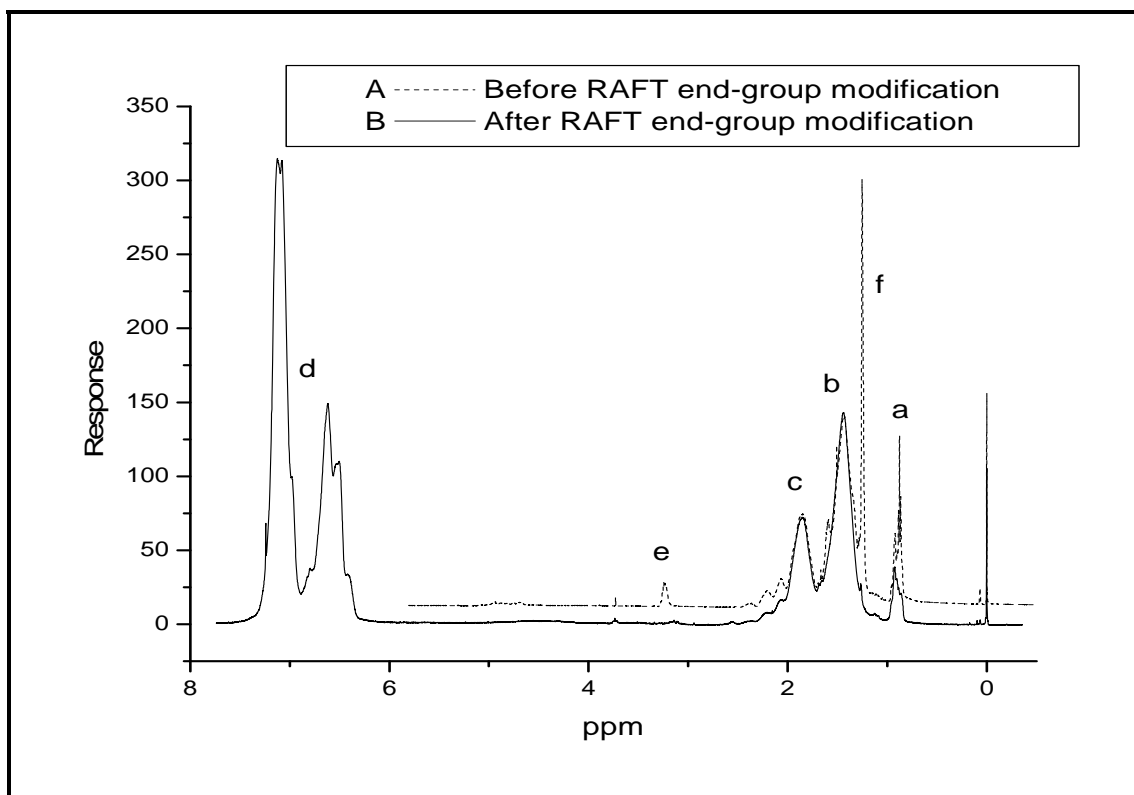
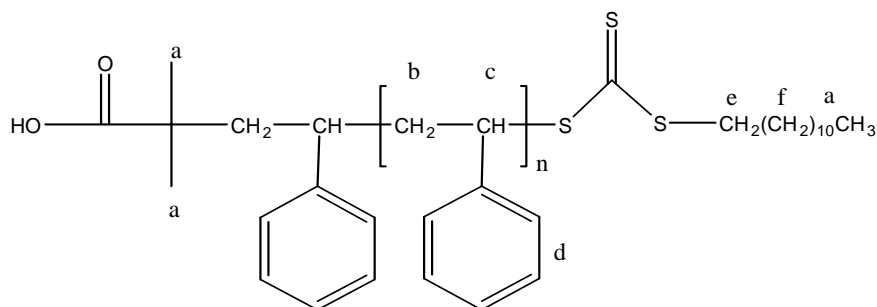


Figure 4.1: $^1\text{H-NMR}$ spectrum of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-group with the use of sodium methoxide.

Spectrum (A) shows the resonance peaks of polystyrene prior to the modification of the RAFT end-groups and spectrum (B) the resonance peaks after modification of the RAFT end-groups. Given that the aim of this experiment was the modification of the RAFT end-groups, monitoring the disappearance of specific resonance peaks corresponding to protons present in the RAFT end-groups should prove conclusively that the experiment was successful. Peak (e) corresponds to the methylene group directly adjacent to the

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

trithiocarbonate moiety in the RAFT end-group. This peak is absent in spectrum (B). Similarly, peak (f), corresponding to the remaining methylene groups in the RAFT end-group, almost completely disappears in spectrum (B). The disappearance of these two peaks after treatment with sodium methoxide indicates that the modification of the RAFT end-group was indeed successful. UV spectroscopy was used as a method to confirm these results.

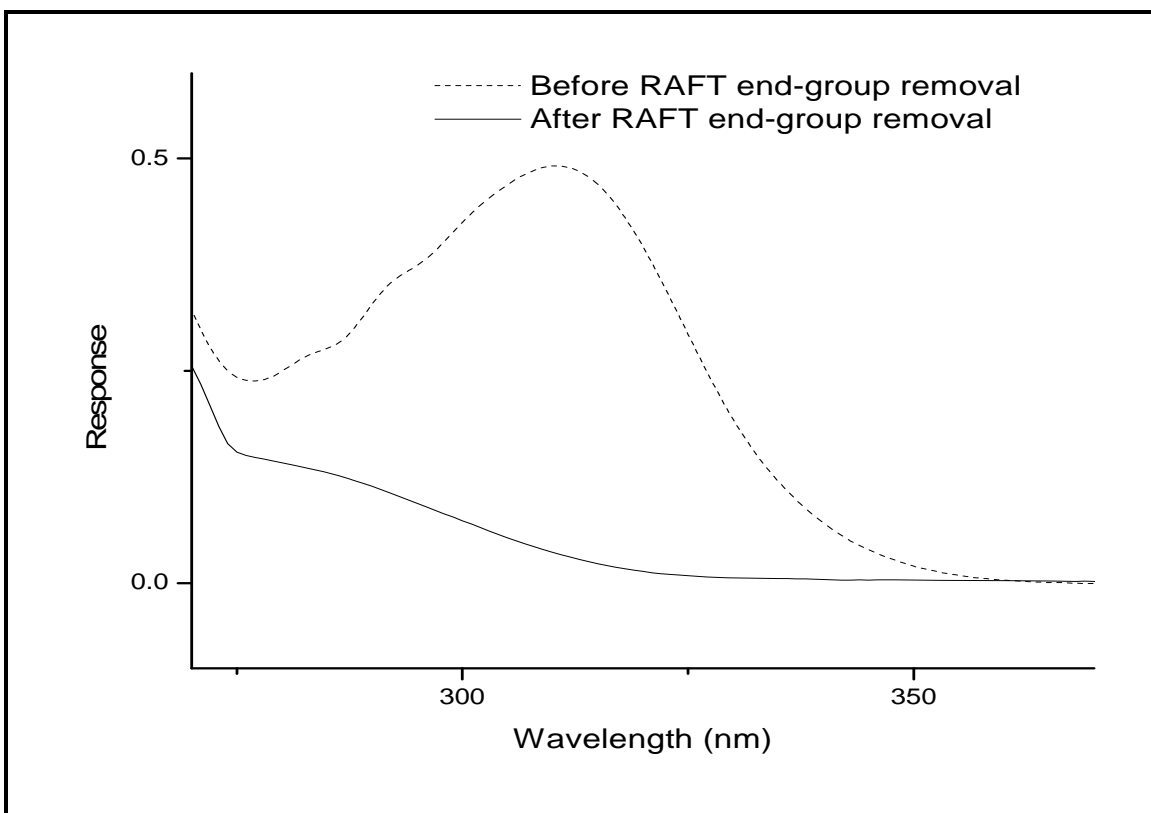


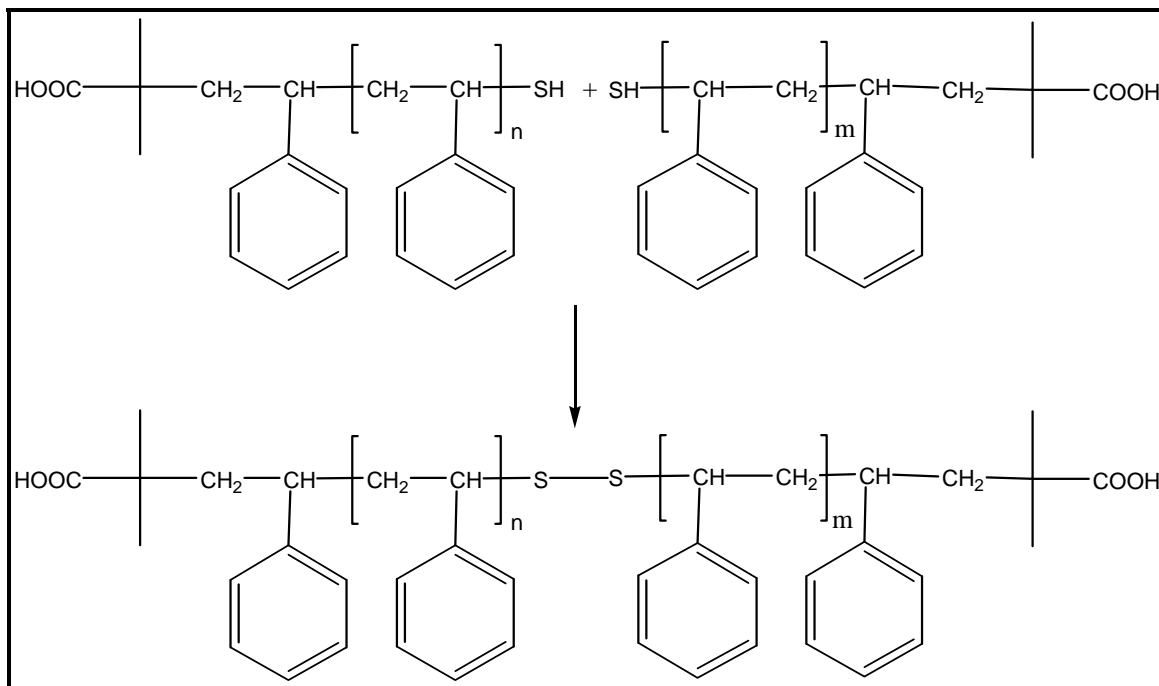
Figure 4.2: UV spectrum of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-group with the use of sodium methoxide and 1,4-dioxane as solvent.

The thiocarbonylthio moiety in the RAFT end-group acts as a UV chromophore and will therefore absorb UV radiation. The UV absorption at approximately 310 nm is indicative of the thiocarbonylthio moiety (Figure 4.2). This absorption disappears after the polymer

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

is treated with sodium methoxide. This once again substantiates earlier indications from the $^1\text{H-NMR}$ spectra, that the RAFT end-group modification was successful.

A serious complication that often arises with the modification of RAFT end-groups after polymerization is the possible oxidative coupling of the initially formed thiols to form disulfide bridges, as illustrated in Scheme 4.2.



Scheme 4.2: Oxidative coupling of the initially formed thiols of RAFT-polymerized polystyrene after treatment with sodium methoxide.

This phenomenon was studied by Wang et al.¹³ and recently confirmed by studies done by Lima et al.¹⁴. They employed a critical-liquid-chromatography technique developed by Jiang et al.¹⁵ to study the end-groups of RAFT polymerized polymethacrylate chains after treatment with 1-hexylamine. The RAFT agent that was used, (4-cyano-1-hydroxypent-4-yl) dithiobenzoate, contains a hydroxyl end-group, and it was found that two of these end-groups were present in some of the polymer chains after treatment with 1-hexylamine, indicating that oxidative coupling did in fact occur. Various methods have

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

been suggested and used with a certain degree of success to prevent oxidative coupling or to treat it after formation of these disulfide bridges. A mixture of zinc and acetic acid was used to eliminate the disulfide bridges, although in certain cases it only managed to diminish them³. Another method was developed by Lima et al.¹⁴ after they established that all RAFT-synthesized polymers that they had studied were susceptible to oxidative coupling after treatment with 1-hexylamine. Prior distillation of solvents and removal of oxygen with freeze-pump-thaw cycles did not prevent the formation of disulfide bridges. They added an antioxidant (an aqueous solution of sodium bisulfite, $\text{Na}_2\text{S}_2\text{O}_4$) to their reaction mixtures, which successfully suppressed the formation of disulfide bridges.

A reference experiment was carried out to determine whether oxidative coupling actually occurred in the system used in the current study. The GPC traces for the experiment are shown in Figure 4.3.

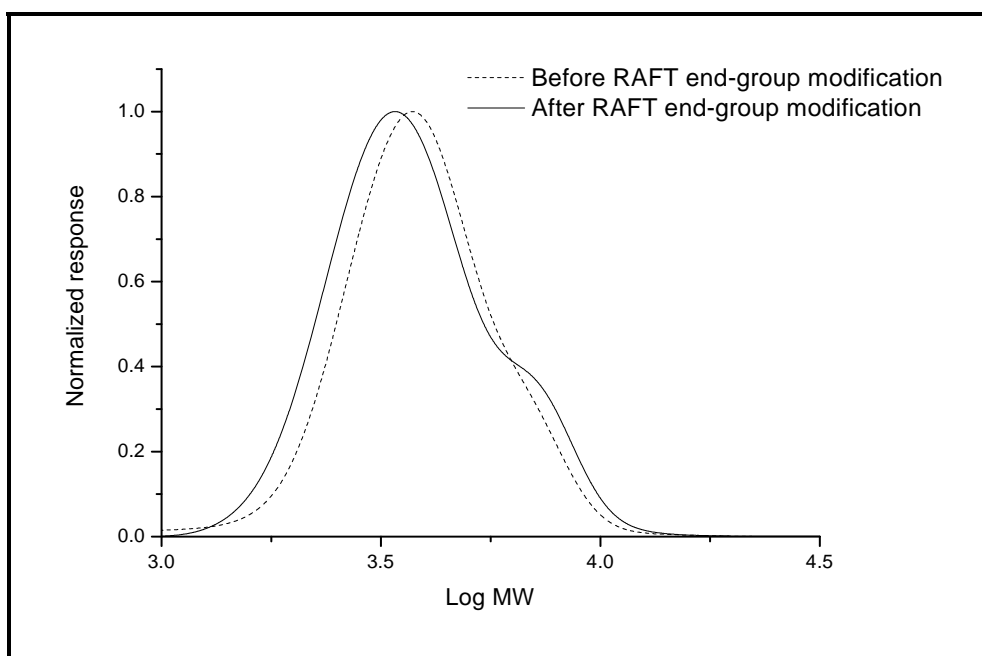


Figure 4.3: GPC traces of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-groups with the use of sodium methoxide without removal of oxygen prior to the start of the reaction.

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

The conditions for the modification of the RAFT end-groups were identical to those described in Section 4.2.3, except that the reaction mixture was not degassed with nitrogen prior to the start of the reaction.

The GPC trace of the polymer after treatment with sodium methoxide has a distinct shoulder at the high molecular weight side (Figure 4.3). The molecular weight of the shoulder is approximately doubled that of the main peak, indicating that oxidative coupling did in fact take place. The use of sodium bisulfite in similar experiments failed to reduce the high molecular weight shoulder and was therefore omitted in all future experiments.

Exclusion of oxygen was then attempted. The modified RAFT end-groups now show no coupling (Figure 4.4.)

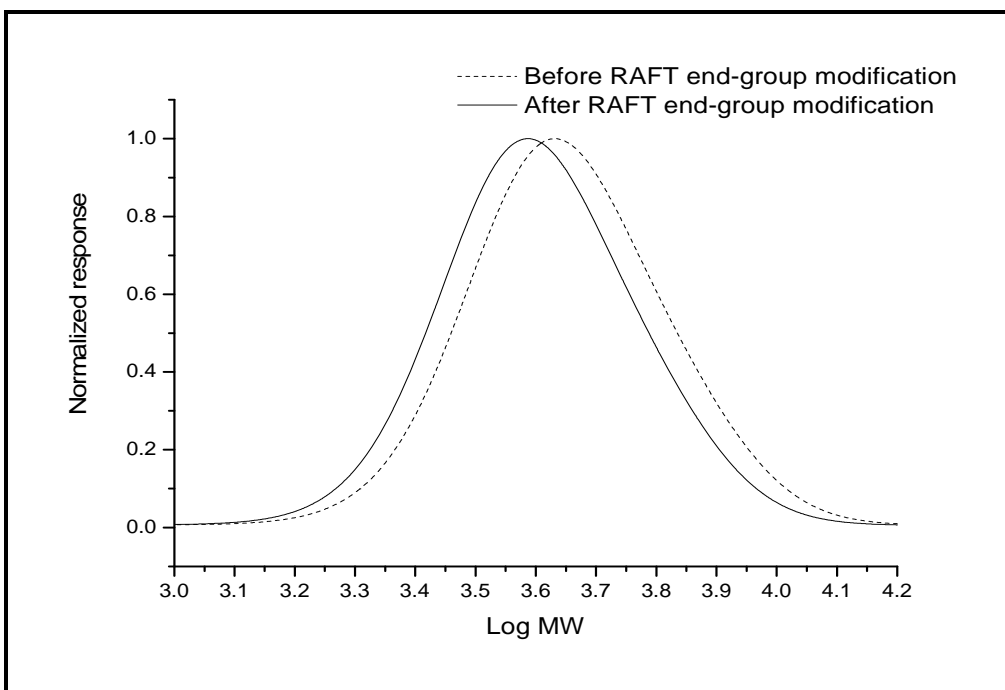


Figure 4.4: GPC traces of polystyrene polymerized with DIBTC before and after the modification of the RAFT end-groups with the use of sodium methoxide and removal of oxygen prior to the start of the reaction.

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

The GPC results of the experiments that were done with prior degassing of the reaction mixture with nitrogen before the onset of the reaction are given in Table 4.3.

Table 4.3: Summary of GPC and ¹H-NMR data for the RAFT end-group modification experiments carried out with sodium methoxide

$M_{n, \text{target}}^{\text{a}}$	M_n^{b}		PDI ^c		End-group modification efficiency (%) ^d
	Before	After	Before	After	
1000	900	750	1.38	1.37	>95%
2000	2100	1900	1.25	1.11	>95%
5000	4100	3800	1.16	1.09	>95%

^a Target molecular weight at 50% conversion

^b Molecular weight before and after RAFT end-group modification obtained via GPC at ~ 50% conversion

^c Polydispersity index before and after RAFT end-group modification

^d Efficiency determined via ¹H-NMR

Two things become immediately apparent when studying the results: There is a distinct decrease in the polydispersity index (PDI) as well as the molecular weight after removal of the RAFT end-group and secondly, both distributions are unimodal. The PDI values of all the polymers were low, indicating that the polymerization was well controlled. The decrease in the PDI is mainly due to the fact that the polymer was precipitated out of solution after treatment with sodium methoxide. The decrease in molecular weight can be ascribed to the modification of the RAFT end-group as it corresponds well with the molecular weight of the end-group. A surprising development is that the GPC distribution after modification of the RAFT end-group remains unimodal. There was no need for the use of either sodium bisulfite or zinc and acetic acid to prevent oxidative coupling of the initially formed thiols (as described in the literature)^{3,14}.

Finally, the end-group modification efficiency was determined by ¹H-NMR. Peak (e) in Figure 4.1 which corresponds to the methylene group directly next to the trithiocarbonate group, was integrated relative to the peaks of the phenyl rings of the styrene units (d). It

CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

was found that the end-group modification efficiency was virtually complete in the cases of all three target molecular weights.

4.4 Conclusions

Polystyrene was successfully polymerized with DIBTC as RAFT agent to yield a polymer with a narrow molecular weight distribution. Various chemical routes were explored for the post-polymerization modification of the RAFT end-groups. The use of sodium methoxide for this purpose proved most successful as the other methods quoted in the literature^{5,7-11} either completely failed to modify the end-groups or produced too many byproducts and impurities. GPC, UV and ¹H-NMR were used as analytical techniques to study the polymer chains after end-group modification. The end-group modification was virtually complete irrespective of the molecular weight of the polystyrene chains. Impurities and byproducts were only present at very low levels. Polymer chains with thiol end-groups were obtained. It was found that oxidative coupling of the initially formed thiols only occurred when the reaction mixture was not degassed with nitrogen before the onset of the reaction. There was no need for the addition of antioxidants or reducing agents. This simplifies the reaction and leads to less impurities in the final polymer. In conclusion, a simple yet effective method was developed to modify the RAFT end-groups into thiol end-groups via the use of sodium methoxide for future use in thiol-ene addition reactions.

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CHAPTER 4: POST-POLYMERIZATION MODIFICATION OF RAFT END-GROUPS

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CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

ABSTRACT

Cyanovaleric acid dithiobenzoate (CVADTB) was used as RAFT agent in the homopolymerization of allyl methacrylate. Linear polymer chains were obtained at low conversions, but at higher conversions gel formation occurred.

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE**5.1 Introduction**

Bifunctional monomers such as divinyl benzene and the dimethacrylate of ethylene glycol have two double bonds with equal reactivities. These monomers are generally used to prepare crosslinked polymers in a single step¹. Monomers with two double bonds of different reactivities can be crosslinked in two separate steps: the more reactive double bond is selectively polymerized to obtain a linear polymer chain with pendant double bonds, followed by the crosslinking of these pendant double bonds². In this case, the pendant double bonds of PAMA are studied as potential grafting sites.

5.2 Experimental**5.2.1 Materials**

AMA 98% (Fluka) was washed twice with a 0.3 M aqueous potassium hydroxide solution to remove inhibitors, followed by distillation under reduced pressure. DIBTC and CVADTB were synthesized as described in Chapter 3. AIBN was recrystallized from methanol and stored at low temperature. THF was distilled from lithium aluminium hydride.

5.2.2 RAFT-Mediated Synthesis of PAMA Homopolymer

All reactions were carried out in a 100 ml three-neck, round bottom reaction flask at 60°C or 80°C (see Table 5.1) under a nitrogen atmosphere. A round bottom flask was equipped

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

with a condenser, a nitrogen inlet, a magnetic stirrer bar and a rubber septum for sample extraction. A temperature-controlled oil bath was used to regulate the temperature of the reaction mixtures. The reaction mixtures were degassed with nitrogen for 15 minutes prior to the start of the reaction to remove oxygen. Samples were drawn at regular intervals using a glass syringe and placed in sample pans before being dried in a vacuum oven for a minimum period of 12 hours. The quantities of the different reagents for the RAFT-mediated polymerizations of AMA are given in Table 5.1.

Conversions were determined gravimetrically and molecular weight analysis was done via GPC (specifications given in Section 3.2.4). $^1\text{H-NMR}$ was used to study the microstructure of the synthesized polymers.

5.3 Results and Discussion

To the best of the author's knowledge, the living/controlled homopolymerization of allyl methacrylate to produce linear polymers with pendant double bonds has only been carried out by the living techniques of anionic polymerization³ and ATRP^{1,4,5}. It would therefore be an interesting study to determine whether the effectiveness of RAFT polymerization for this particular monomer mirrors that of ATRP.

Table 5.1 summarizes the various RAFT-mediated homopolymerizations of AMA that were carried out.

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE
Table 5.1: Kinetic and characteristic parameters for the RAFT-mediated homopolymerization of AMA

	AMA		THF		RAFT agent ^a			AIBN		Conv. at gel point (%) ^b	M_n^c at gel point	PDI ^d at gel point
	Mass (g)	mmol	Mass (g)	mmol	Type	Mass (g)	mmol	Mass (g)	mmol			
1	20.0	159	46.67	647	a	0.117	0.32	0.010	0.06	-	-	-
2	20.0	159	46.67	647	b	0.260	2.06	0.010	0.06	42	3600	1.62
3	20.0	159	46.67	647	b	0.127	1.01	0.010	0.06	27	4800	1.47
4	20.0	159	46.67	647	b	0.116	0.40	0.010	0.06	17	4600	1.34
5 ^c	20.0	159	46.67	647	b	0.116	0.40	0.010	0.06	12	3800	1.55

^a RAFT agent (a) is DIBTC and RAFT agent (b) is CVADTB

^b Conversion percentage at gel point

^c Molecular weight at gel point as determined by GPC

^d Polydispersity index at gel point as determined by GPC

^e All reactions were done at 60°C, except reaction (5) which was done at 80°C

First, the trithiocarbonate RAFT agent DIBTC was used for the RAFT-mediated polymerization of AMA, but large uncontrolled, multimodal distributions were observed. This can be explained by the incorrect choice of the R-group. The importance of choosing the correct R- and Z-groups to form a particular RAFT agent has already been discussed in Section 2.2.6.1. The R-group must be a good homolytic leaving group compared to the propagating radical to ensure that fragmentation occurs efficiently in the desired direction.

Chong et al.⁶ studied the efficiency of benzyl dithiobenzoate as a RAFT agent where R = benzyl. This RAFT agent functions well where the propagating radical is styrenic or acrylic, but is virtually inert when the propagating radical is methacrylic. The reason for this is that the R-group is a poor homolytic leaving group in comparison with the propagating methacrylic radical. This leads to uncontrolled polymerization. The same reasoning can be used to explain the large uncontrolled distributions observed in the GPC

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

data for the RAFT-mediated homopolymerization of AMA with DIBTC as RAFT agent, as observed in Figure 5.1.

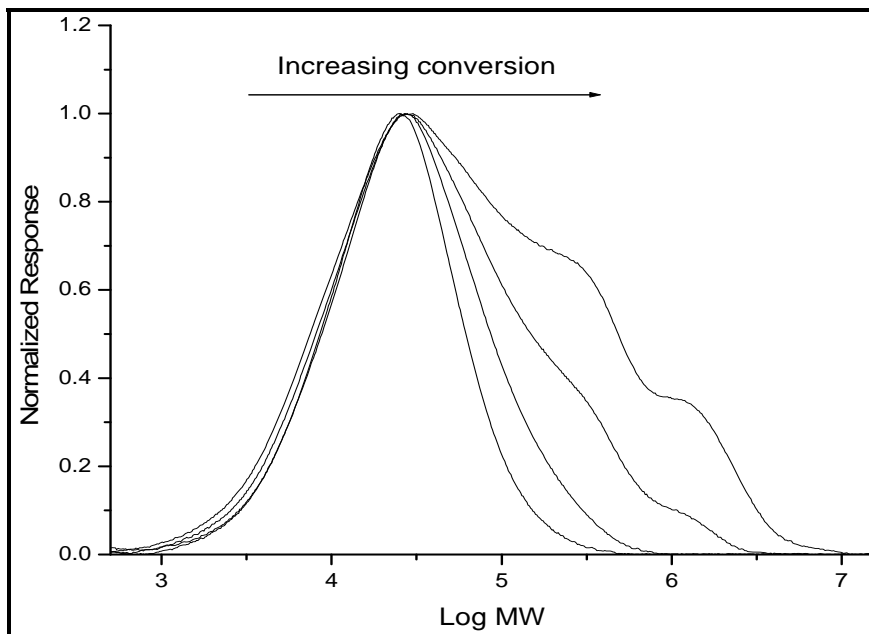


Figure 5.1: GPC results for the DIBTC-mediated homopolymerization of AMA.

The PDI increased from 2.5 at the onset of polymerization to 8.4 on completion of the reaction. This implies side reactions involving the allyl groups and less normal RAFT chain growth.

CVADTB was used as RAFT agent in all further AMA polymerization reactions and a certain degree of success was obtained.

In the case of the CVADTB-mediated polymerization of AMA it was necessary to determine whether and to what degree the RAFT agents were incorporated into the polymer chains. GPC analyses were done using a refractive index (RI) detector in conjunction with a UV detector. The UV detector was set at a wavelength of 320 nm as

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

only the RAFT agent absorbs UV light at this wavelength and not the monomer itself. This makes it possible to distinguish between polymer chains that have RAFT end-groups and polymer chains that do not.

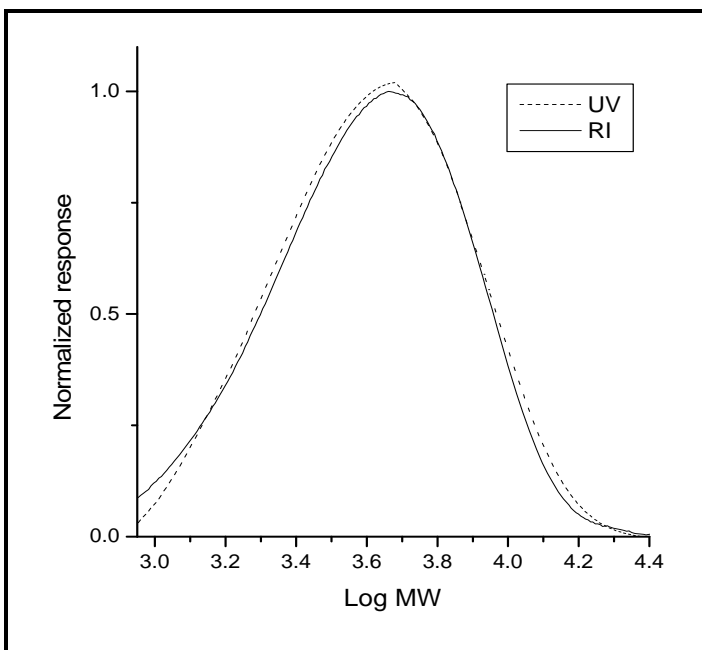


Figure 5.2: GPC results of the CVADTB-mediated polymerization of allyl methacrylate using a dual detector system.

The UV and RI signals show a good overlay, indicating that the majority of the polymer chains contain the RAFT moiety and that the polymerization was indeed RAFT-mediated (Figure 5.2). The free radical polymerization² and copolymerization⁷ of allyl methacrylate leads to the formation of linear polymers with pendant allyl double bonds in the early stages of the reaction, i.e. at low conversion. This is due to the significantly lower reactivity of the allyl double bond compared to the high reactivity of the resonance-stabilized methacryloyl double bond. With the progress of polymerization the number of intermolecular and intramolecular bonds increases gradually until a crosslinked gel

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

eventually forms⁷. Figure 5.3 shows the ¹H-NMR spectrum of homopolymerized PAMA at low conversion.

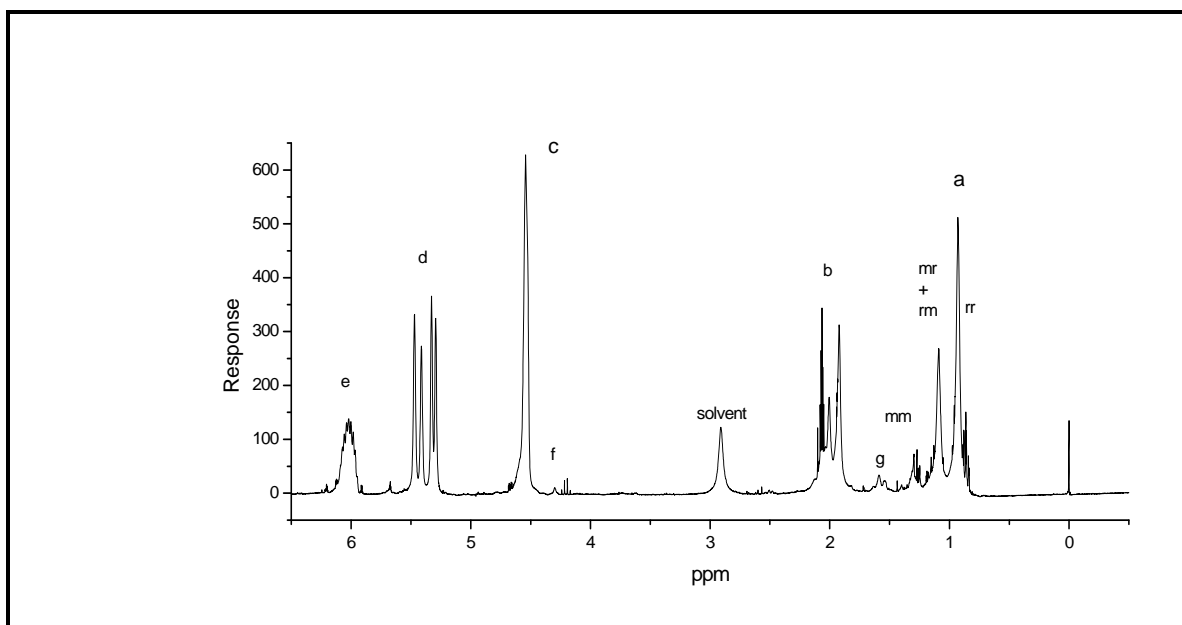
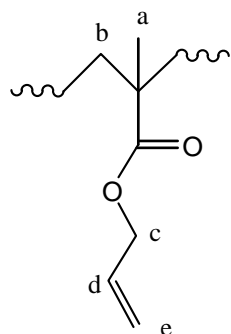
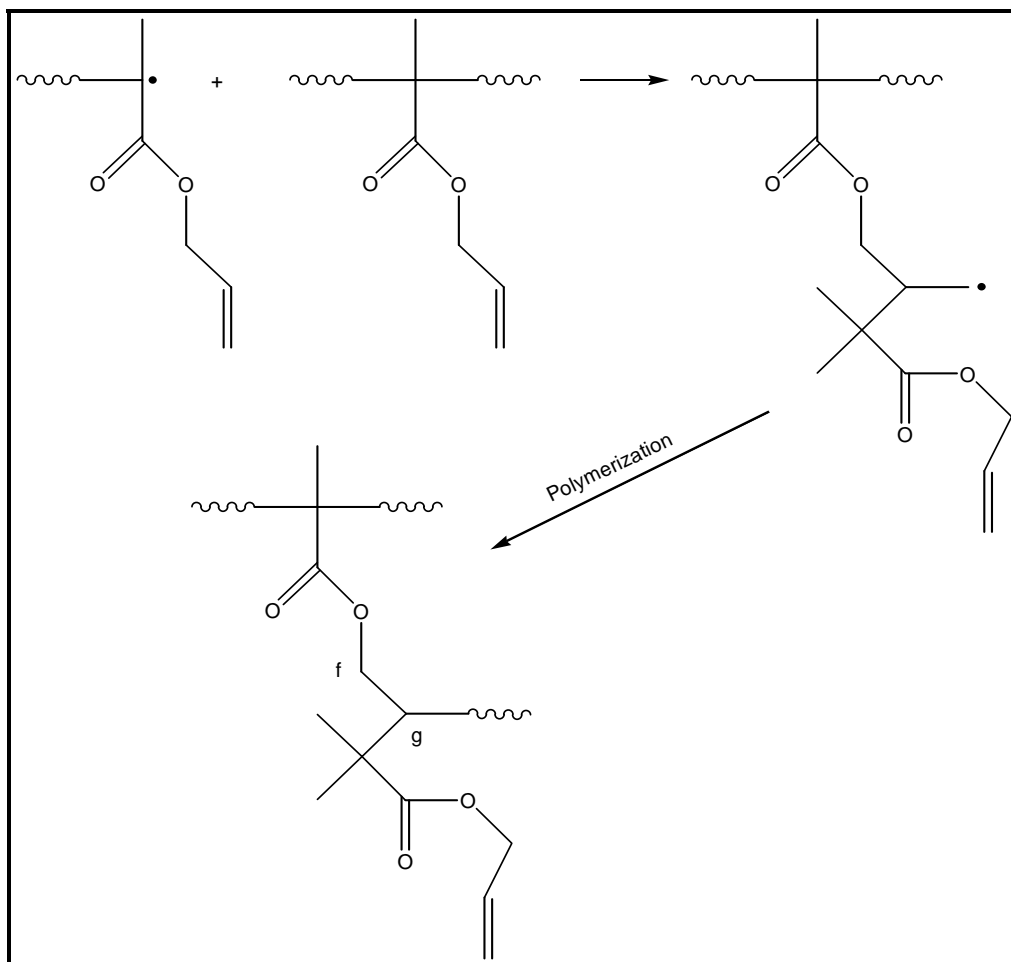


Figure 5.3: ¹H-NMR spectrum of PAMA polymerized in the presence of CVADTB, AIBN and THF as solvent at 60°C.

The ¹H-NMR spectrum clearly shows the complete absence of unreacted methacryloyl double bonds whereas the resonance signals corresponding to the allyl double bonds are present. This indicates that the PAMA homopolymer is predominantly linear at low conversions.

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

Peak (f) and peak (g) correspond to the same proton resonances as peaks (c) and (d) respectively, but in the case of peaks (f) and (g) there are no pendant double bonds present. This indicates either the formation of 5- and 6-membered lactone rings and/or the presence of intermolecular crosslinking, as depicted in Scheme 5.1 and Scheme 5.2.

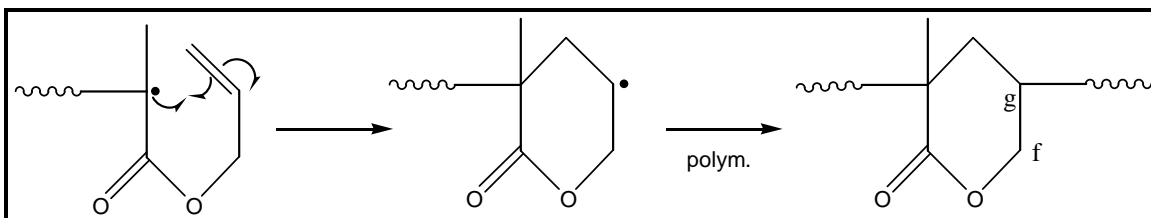


Scheme 5.1: Schematic illustration of the crosslinking reaction that may occur during AMA homopolymerization.

Scheme 5.1 depicts the crosslinking reaction in which the free radical attacks the allyl carbon at the α -position. Another possibility is when radical attack occurs at the β -position. By using the integral values for these resonances it was possible to determine a

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

value for the allyl fraction; it was found that $F_{\text{allyl}} = 0.93$. This value corresponds well with the value obtained by Matsumoto et al.⁸ who determined it iodometrically.



Scheme 5.2: Reaction route for the formation of 6-membered lactone rings during AMA homopolymerization.

The presence of 5- and 6-membered lactone rings (Scheme 5.2) is very difficult to prove in the case of PAMA. Scheme 5.2 depicts the formation of 6-membered lactone rings and, similarly, the formation of 5-membered rings is also possible. Nagelsdiek et al.⁴ found no evidence for the formation of these lactone rings, whereas Paris et al.⁵ used Fourier-Transform Infrared (FTIR) spectroscopy in conjunction with curve-fitting analysis to prove otherwise. For the purpose of the present study it was sufficient to conclude that cyclopolymerization and crosslinking reactions were kept to a minimum at low conversions and that the polymer chains contained predominantly pendant allyl double bonds.

The stereochemical configuration of the monomer units along the polymer chain was also analyzed. The resonance signals of the α -CH₃ split into three distinct peaks at 0.87, 1.10 and 1.25 ppm. These peaks correspond to syndiotactic (*rr*), heterotactic (*rm*, *mr*) and isotactic (*mm*) triads. The isotacticity parameter for PAMA (σ_{AMA}) was determined using the integral values for these resonance signals. The isotacticity parameter, as defined by Bovey⁹ and Coleman¹⁰, is the probability of producing a meso dyad between an *i*-ending propagating radical and an incoming *j*-monomer. The value for PAMA $\sigma_{\text{AMA}} = 0.19$

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

corresponds well with that of poly(methyl methacrylate) (PMMA), $\sigma_{\text{MMA}} = 0.23$, as obtained by de la Fuente et al.¹¹.

Table 5.1 shows that all CVADTB-mediated reactions led to gelation at low conversions and no definite relationship could be established between the concentration of RAFT agent used and the molecular weight that was attained before the onset of gelation. The experiments all yielded low molecular weight PAMA, but reaction (4) had the lowest PDI and was thus chosen as the model reaction for all further discussions.

Figure 5.4 illustrates the increase in monomer conversion over time.

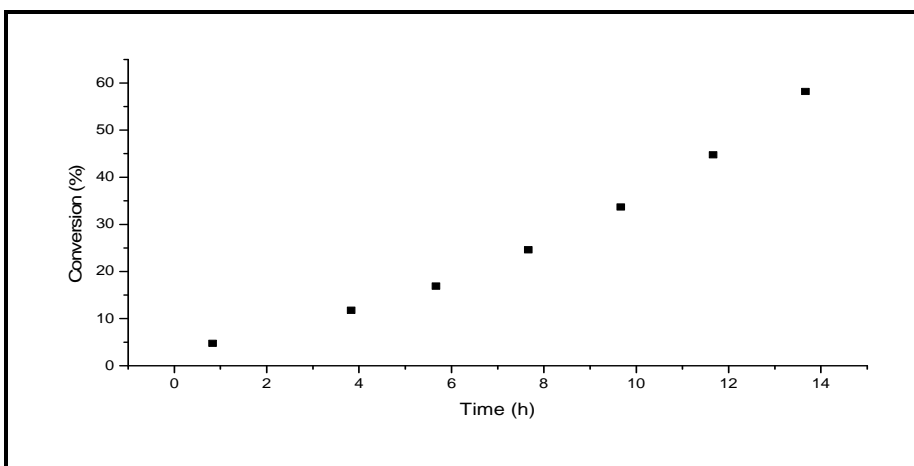


Figure 5.4: Conversion-time graph of the CVADTB-mediated homopolymerization of AMA.

Initially the conversion rate is slow, but at a conversion of approximately 25% there is a sudden increase in the conversion rate. This can be attributed to the formation of microgel particles^{2,12}. These particles form due to the formation of intramolecular and intermolecular bonds. Radicals are trapped inside the gel particles and as a result the number of radicals in the system increases dramatically, which in turn leads to an increase in the rate of conversion. As the polymerization progresses there is an increase in intramolecular and intermolecular bonds and a crosslinked gel eventually forms at 60%

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

conversion. It was also observed that when left standing in air at room temperature for only a few hours, PAMA started crosslinking, and therefore samples were stored under a nitrogen atmosphere.

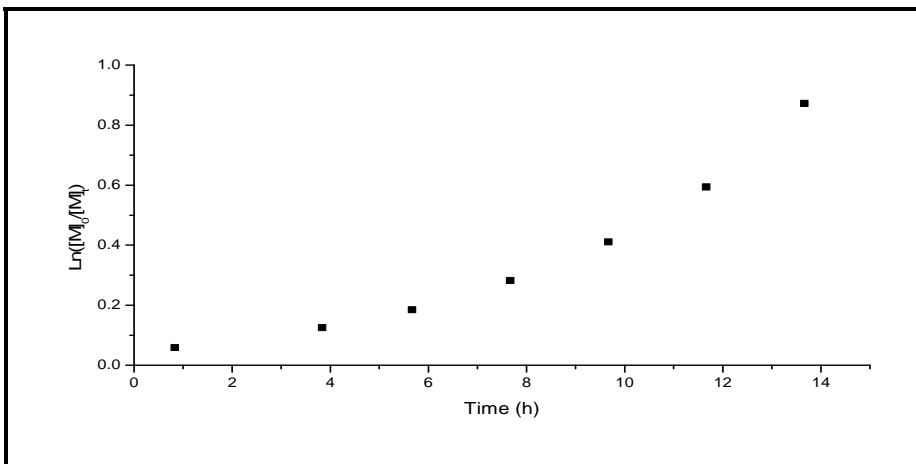


Figure 5.5: Semi-logarithmic plot of monomer consumption over time for the CVADTB-mediated homopolymerization of AMA.

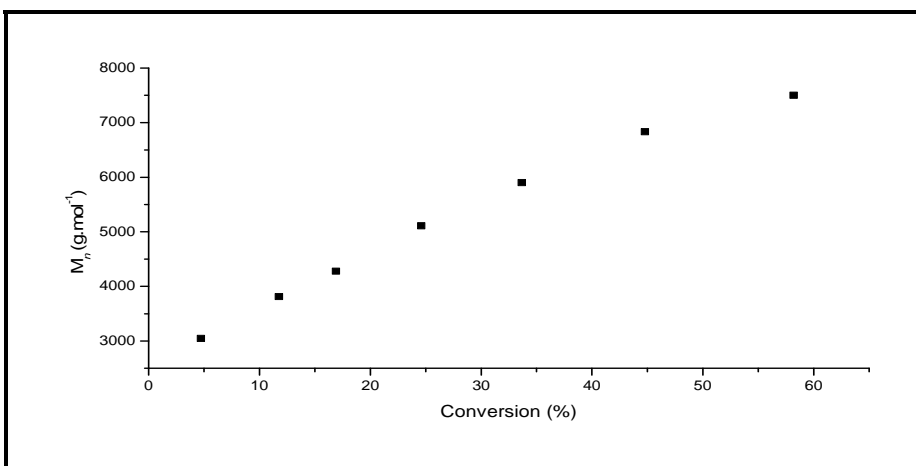


Figure 5.6: Molecular weight versus conversion plot of the CVADTB-mediated homopolymerization of AMA.

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

Figure 5.5 also shows a definite increase in monomer consumption at a reaction time of approximately 7 hours. Once again this can be attributed to an increase in the number of radicals in the system due to the formation of microgel particles. At the specific conversion where the effect of the microgel particles is first observed, there is a marked decrease in the rate of gain in molecular weight as seen in Figure 5.6. Paris and de la Fuente⁵ attributed this phenomenon to the fact that high molecular weight sol polymers have a greater chance of being consumed by the gel network due to reactions between radicals and pendant double bonds. This corresponds well with the observed GPC curves, as illustrated in Figure 5.7. During the GPC process the larger gel particles are filtered out in a pre-column and therefore they do not appear in the molecular weight data, which now presents a decrease in rate of gain in molecular weight as gel formation occurs. The reason for the decrease is also attributed to the decrease in hydrodynamic volume as the polymer intramolecularly crosslinks and is mirrored in a slower rate of molecular weight increase and an increase in PDI.

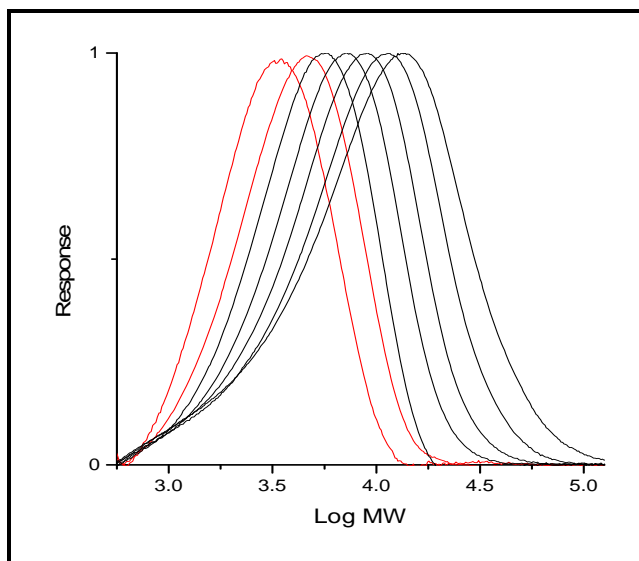


Figure 5.7: GPC distributions for the CVADTB-mediated homopolymerization of AMA.

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

The symmetry of the GPC curves is somewhat lost at higher conversions, but at low conversions well-defined, symmetric peaks are observed. Finally, the PDI of the polymers remained below 1.4 at low conversions. At higher conversions the PDI increased dramatically to values greater than 7.

5.4 Conclusions

The polymerization of allyl methacrylate with DIBTC as RAFT agent proved unsuccessful. Polymerization with CVADTB as RAFT agent yielded better results. However, linear polymers with pendant double bonds and narrow molecular weight distributions ($PDI < 1.5$) were only obtained at low conversions. At higher conversions the formation of microgel particles leads to decreased control as observed by the broadening of molecular weight distributions. Since the aim of this project is to synthesize graft copolymers with linear poly(allyl methacrylate) as the backbone, it would be necessary to terminate these reactions at low conversions before the onset of gelation.

CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

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CHAPTER 5: RAFT-MEDIATED HOMOPOLYMERIZATION OF ALLYL METHACRYLATE

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CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

ABSTRACT

A range of PAMA-g-polystyrene copolymers were synthesized with branches of different molecular weights. Abnormal GPC behaviour of the branched copolymer was studied using an RI and a MALLS detector.

6.1 Introduction

Graft copolymers are currently used in a many areas such as polymeric emulsifiers, compatibilizers, impact-resistant plastics and thermoplastic elastomers¹. The main reason for the upsurge in research into synthesizing new graft copolymers is the wide variety of structural variables that can be employed to fine-tune the final material properties. These variables include branch length and backbone length, comonomer composition and branch distribution. This enables scientists to create materials with new properties or improve the performance of existing materials.

The “grafting through” method makes use of macromonomers that are copolymerized with other monomers to create graft copolymers. The “grafting through” method has been successfully applied using RAFT² or a combination of RAFT and ATRP¹.

The “grafting from” approach entails the polymerization of branches from active sites on a polymeric backbone. The advantage of this method is that high graft densities can be obtained due to the absence of steric hindrances from previously attached branches, which causes problems in the “grafting onto” approach. This approach does however complicate the analysis of the branches. The “grafting from” technique is currently the most widely used RAFT-mediated grafting technique. Baum and Brittain,^{3,4} and Tsujii et al.⁵ were the first to apply RAFT to “grafting to” copolymerization. RAFT polymerizations from surface-functionalized silica particles³⁻⁵, plasma treated Teflon surfaces⁶ and ozonolyzed polyimide surfaces⁷ were also successfully carried out.

In this study, the aim was to use a thiol-ene addition reaction to facilitate the “grafting onto” method for covalently attaching preformed thiol-functionalized polystyrene branches to the pendant double bonds of a PAMA backbone. The ability of thiols to bind to gold surfaces has been exploited previously to synthesize polymer brushes using RAFT⁸⁻¹⁰. This field has sparked great interest recently due to the potential

CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

use of thiol-stabilized gold nanoparticles in applications related to optics and electronics¹¹.

6.2 Experimental

6.2.1 Materials

THF was distilled from LiAlH₄. Toluene was distilled under reduced pressure and stored over molecular sieve. AIBN was recrystallized from methanol and stored at low temperature for later use. Polystyrene was synthesized as described in Section 3.2.4 and modified as described in Section 4.2.3. PAMA was synthesized as described in Section 5.2.2.

6.2.2 Synthetic Procedure

Styrene polymerized in the presence of DIBTC as RAFT agent was used as the branches of the graft copolymer and PAMA was used as the backbone. In order to obtain predominantly linear PAMA chains with pendant allyl double bonds the reaction was stopped at an early stage of polymerization, i.e. 4.5 hours. This was done in order to circumvent the problems of gelation¹² and other secondary reactions normally associated with the later stages of the radical polymerization of allyl methacrylate¹³.

The graft copolymerization reactions were conducted in a 100 ml three-neck reaction flask equipped with a condenser, a rubber septum, a gas inlet and a magnetic stirrer bar. The graft copolymerization mixtures consisted of thiol end-functionalized polystyrene

CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

branches and PAMA chains as polymer backbones for the “grafting onto” reaction. Polystyrene was added in a 25-molar excess with respect to the PAMA homopolymer. The reactions were conducted with THF as solvent and AIBN as free radical initiator. A typical reaction mixture is given in Table 6.1.

Table 6.1: Reagents and their quantities used in the synthesis of PAMA-g-polystyrene

Reagent	Mass (g)	mmol
PAMA ($M_n = 3200$)	0.11	0.03
Polystyrene ($M_n = 4800$)	4.00	0.83
THF	30.00	420
AIBN*	0.06	0.37

*AIBN was added at the start of every reaction and every 24 hours thereafter in aliquots of 0.02 g.

The reaction mixtures were degassed for 25 minutes prior to the start of the reaction. All reactions were run at a temperature of 60°C under a nitrogen atmosphere for 72 hours and then stopped by placing them in an ice bath. The reaction mixtures were decanted into a Petri dish and dried in a vacuum oven at room temperature for 24 hours. The ungrafted polystyrene chains were found to be slightly more soluble (they took longer to dissolve) in acetone than the graft copolymer and this fact was exploited to remove these chains. After the polymer mixture was dried, it was stirred in acetone for a short period of time to selectively remove the ungrafted polystyrene chains. This was repeated several times until no more ungrafted polystyrene chains were observed in the GPC spectra.

Molecular weights and molecular weight distributions were determined using a GPC system comprising a Waters 410 Differential Refractometer, Waters 717_{plus} Autosampler, Waters 600E System Controller and Wyatt DAWN DSP Multiangle Laser Light Scattering (MALLS) detector. The molecular weights and polydispersity data were

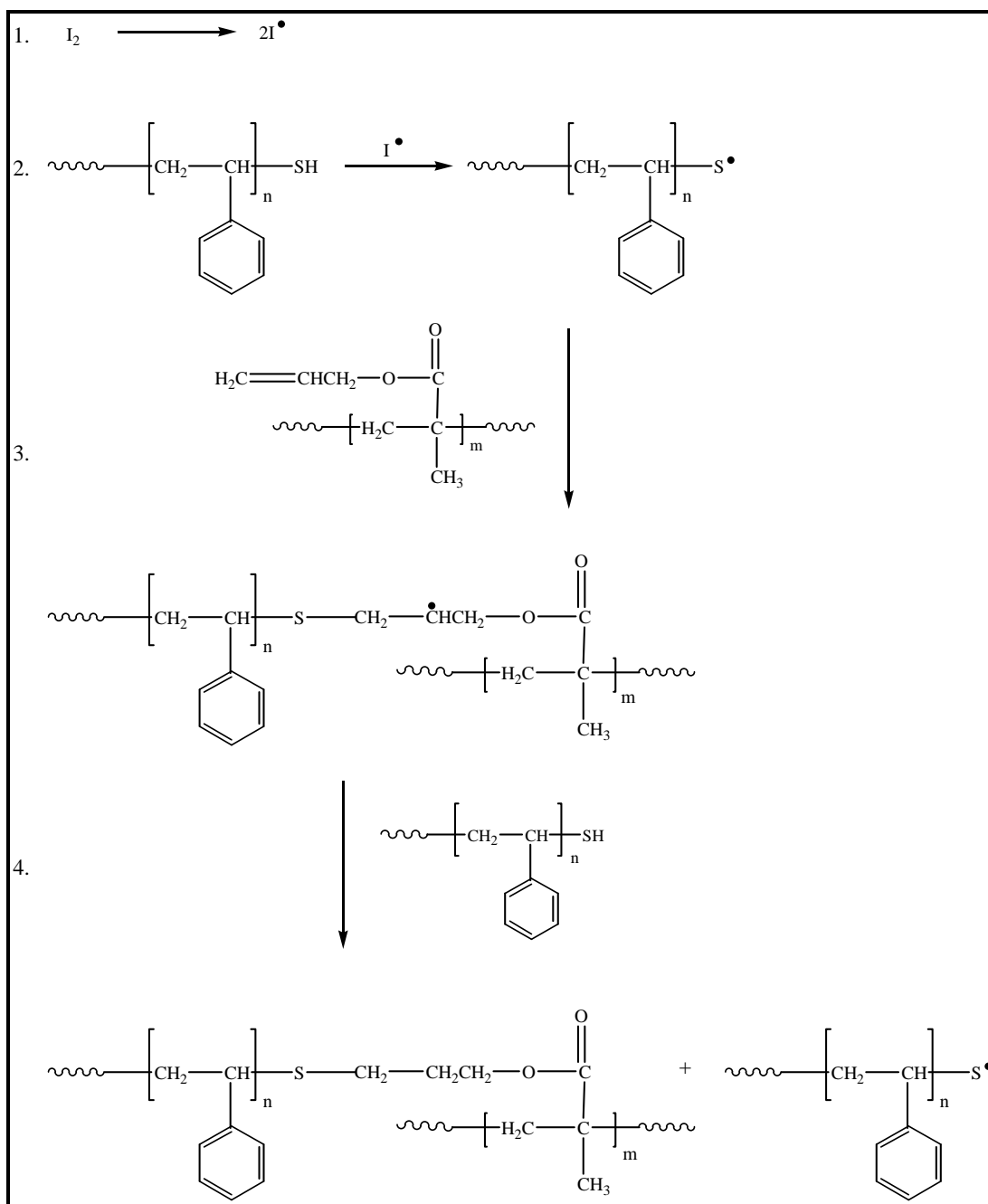
CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

calculated using the Wyatt ASTRA^{4,50} software package. The dn/dc values were determined over a range of concentrations (0.5, 1, 2, 3, 4, 5 mg/l). The flow rate was set at 1 ml/min.

6.3 Results and Discussion

The general proposed reaction scheme for the synthesis of PAMA-*g*-polystyrene is given in Scheme 6.1. First, AIBN decomposes to create initiating radicals (step 1). These radicals then react with the thiol-functionalized polystyrene to create thiyl radicals (step 2), which, in turn, add to the PAMA chains via the pendant allyl double bonds (step 3). Thus there is a sulfur linkage created between the polystyrene branch and the PAMA backbone. Finally, a hydrogen atom is abstracted by the carbon-centered radical from another thiol-functionalized polystyrene chain and an additional thiyl radical is created (step 4).

CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE



Scheme 6.1: Reaction scheme for the synthesis of PAMA-g-polystyrene.

GPC was used initially to determine whether the grafting reaction was successful. A UV detector was used in conjunction with an RI detector. The UV detector was set at a wavelength of 254 nm as only the polystyrene side chains absorb UV light at this

CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

wavelength, and not the PAMA backbone. The GPC results for reaction (1) are given as an example in Figure 6.1.

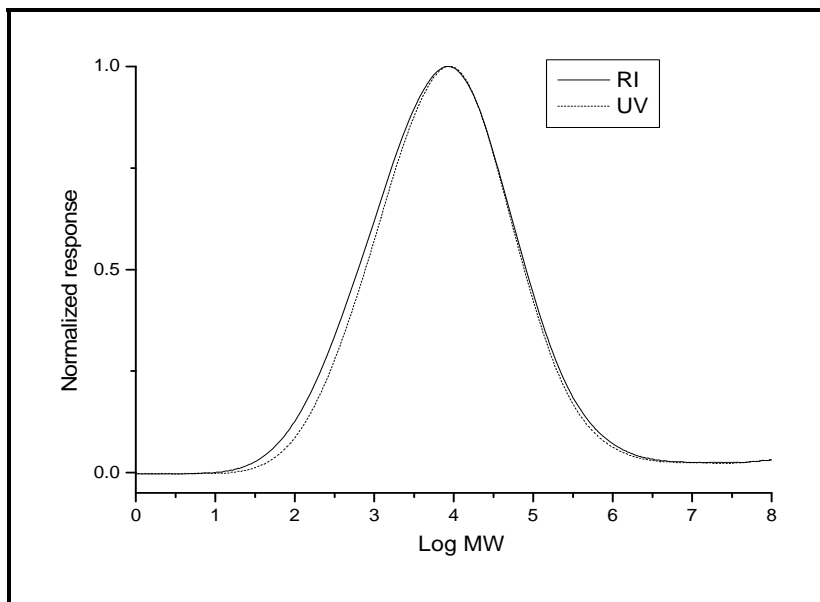


Figure 6.1: GPC data for the graft copolymer synthesized via reaction (1) recorded using a dual detector system.

The RI and UV signals show a good overlay indicating that the polystyrene side chains were successfully attached to the PAMA backbone. The UV signal does however deviate slightly from the RI signal at lower molecular weights signifying that a certain percentage of these low molecular weight PAMA chains remained ungrafted or have low extents of grafting, so making the RI signal greater than the UV signal.

The $^1\text{H-NMR}$ spectrum of the graft copolymer that was synthesized in reaction (1) is shown in Figure 6.2.

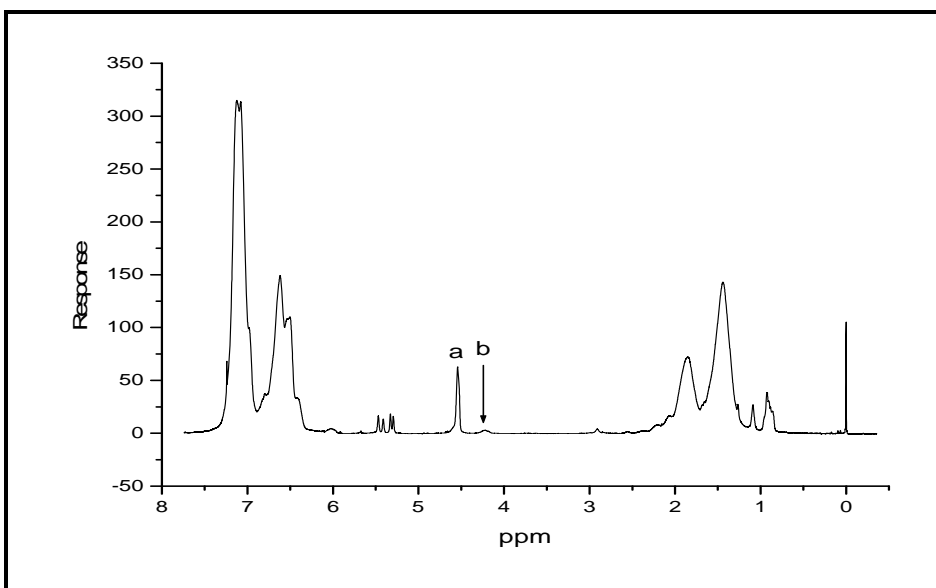
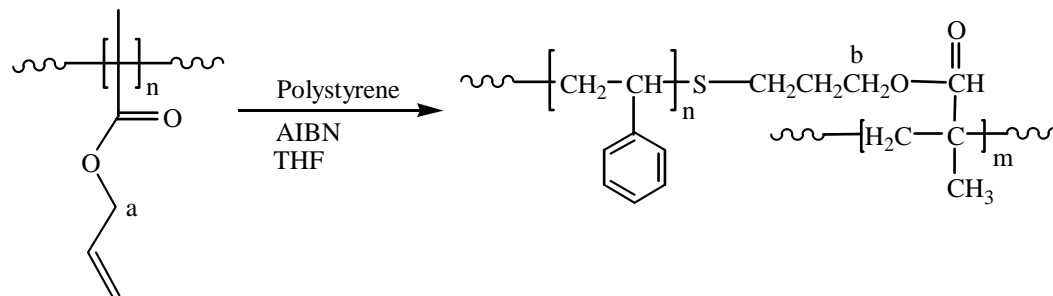


Figure 6.2: $^1\text{H-NMR}$ of the graft copolymer synthesized via reaction (1).

The resonance peaks (a) and (b) were used to determine the grafting percentage of the final graft copolymer as there is too much peak overlap in the rest of the spectrum. Peaks (a) and (b) refer to the same methylene group as illustrated in Figure 6.2, but in the case of peak (b) there is no adjacent double bond. In Section 5.3 it was reported that in the homopolymerization of AMA, peak (b) arises due to the formation of lactone rings or during crosslinking. It was also shown that the occurrence of these reactions is very low in the early stages of polymerization and the extent of these reactions can be calculated using the integrals of peaks (a) and (b). Thus it can be deduced that any subsequent growth of peak (b) relative to peak (a) can be attributed mainly to the attachment of the polystyrene chains to the PAMA backbone. The grafting percentages for the various reactions are given in Table 6.2. It is clear from the results that the grafting percentage

CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

increases as the molecular weight of the branches decreases. Steric hindrance of previously attached chains could therefore be shown to be a cause of this phenomenon.

Table 6.2 summarizes the GPC results of the PAMA backbone, the thiol-terminated polystyrene branches and the final graft copolymer using a RI detector. Also included is the absolute molecular weight as determined via GPC with a MALLS detector as well as the grafting percentage.

Table 6.2: Molecular weight data of the PAMA polymer backbone, polystyrene branches and final graft copolymer as determined by GPC with RI and MALLS detectors

Reaction	PAMA		Polystyrene		PAMA-g-PS (RI) ^a		PAMA-g-PS (MALLS) ^b		Grafting ^c (%)
	M_n	PDI	M_n	PDI	M_n	PDI	M_n	PDI	
1	3200	1.45	4800	1.11	8700	1.52	17300	1.32	6
2	3200	1.45	1900	1.11	8200	1.48	20200	1.43	25
3	3200	1.45	750	1.37	7900	1.43	16800	1.30	49

^a Molecular weight data of the graft copolymer using an RI detector

^b Molecular weight data of the graft copolymer as determined using a MALLS detector

^c Grafting percentage as determined by ¹H-NMR

Table 6.2 shows that the molecular weights of the graft copolymers as determined by the RI detector are significantly lower than the molecular weights obtained by the MALLS detector. This is because GPC separates polymer molecules on the basis of hydrodynamic volume, and it has been reported that branched polymers have smaller hydrodynamic volumes compared to their linear counterparts for a given molecular weight¹⁴. The phenomenon is exacerbated by the retardation experienced by branched polymers during the GPC process. Polymers with fewer branches experience less

CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

retardation and elute earlier than expected. This is then observed as an apparent increase in molecular weight, as illustrated in Figure 6.3.

Figure 6.3 shows the GPC chromatograms of the PAMA backbone, the polystyrene branches and the final PAMA-g-polystyrene copolymer of reaction (1). There is no significant broadening of the molecular weight distribution of the graft copolymer when compared with the molecular weight distributions of the polymer backbone and branches. It can be deduced that inter- and intramolecular crosslinking reactions between the PAMA backbones were largely avoided.

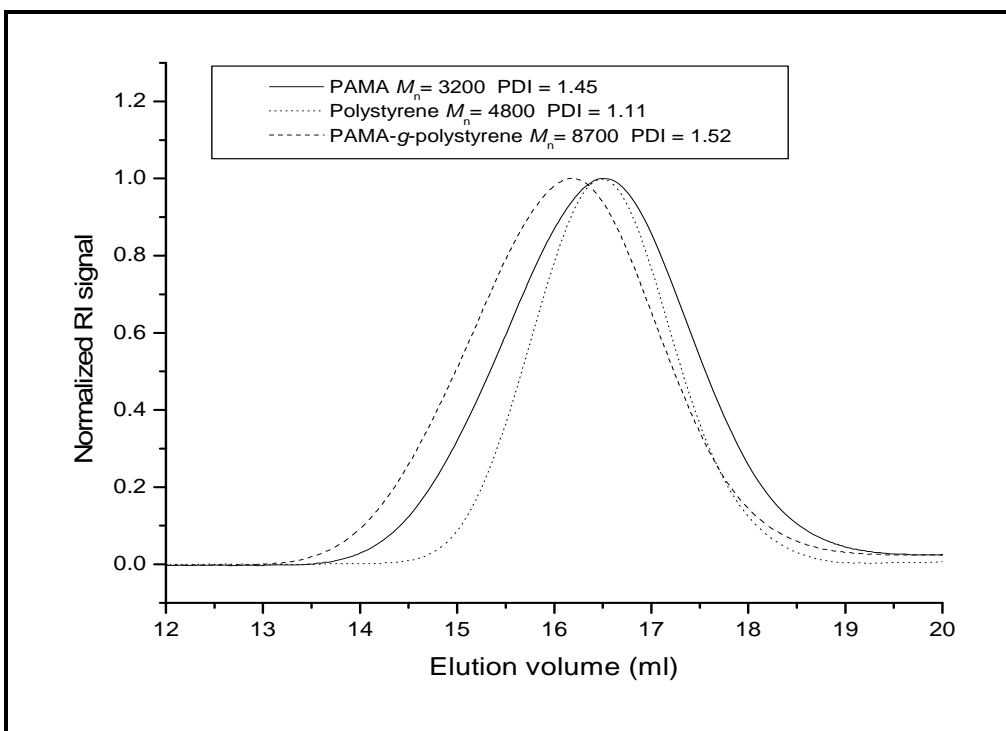


Figure 6.3: GPC chromatograms of the PAMA backbone, polystyrene branches and final graft copolymer obtained using an RI detector for reaction (1).

6.4 Conclusions

PAMA-g-polystyrene was successfully synthesized using a thiol-ene addition mechanism. The low branching percentage was attributed to steric hindrance due to previously attached chains. Abnormal GPC behaviour was observed when using a RI detector, but the MALLS detector gave more realistic results.

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CHAPTER 6: SYNTHESIS OF PAMA-G-POLYSTYRENE

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CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

ABSTRACT

General conclusions are drawn and suggestions are made for future work in similar fields.

7.1 Conclusions

A few general conclusions can be drawn from the work done in this study:

- Chapter 3 dealt with the successful synthesis of two RAFT agents, CVADTB and DIBTC, and described the effect of RAFT agent concentration on the synthesis of low molecular weight polymers. Some retardation phenomena were observed, especially at higher RAFT agent concentrations.
- In Chapter 4 the post-polymerization modification of RAFT end-groups to obtain thiol end-groups was studied using various techniques proposed in literature. The most successful of these methods was found to be the one in which use was made of sodium methoxide in a dry 1,4-dioxane medium. This method generated only a very low amount of impurities and the formation of disulfide bridges between the initially formed thiols was successfully suppressed. Thus, the method of Stenzel and Davis¹ was successfully modified to effectively remove RAFT end-groups.
- Chapter 5 described the RAFT-mediated homopolymerization of allyl methacrylate. No references pertaining to this procedure were found in the literature. There were however some problems associated with the procedure such as the formation of gels at higher conversions (~40%). The homopolymerization of allyl methacrylate using ATRP achieved higher conversions before the onset of gelation (~65%)². The microstructure of PAMA at low conversions, including its tacticity, was comprehensively analyzed.
- In Chapter 6 the thiol-ene addition reaction as an approach to synthesizing graft copolymers was investigated. The pendant double bonds of PAMA were used as active sites onto which the preformed polystyrene branches were covalently attached. Comparative molecular weight data were obtained and studied using

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

GPC with an RI and a MALLS detector. It was found that the molecular weight as determined with the RI detector was much lower than the molecular weight as determined by the MALLS detector. This was explained by the fact that polymers with fewer branches experience less retardation during the GPC process and therefore elute earlier than expected.

7.2 Recommendations

The design of new graft polymers could yield great reward due to the wide range of structural variables that can be fine-tuned to obtain specific final polymer properties. This benefit, used in conjunction with the ability of living radical polymerization techniques to produce controlled architectures, opens up a great many avenues for researchers to explore. It is in this light that some recommendations for future work in this field are made:

- A great number of RAFT agents have already been synthesized and still more are continually being designed in order to better understand the RAFT mechanism and to obtain superior polymerization characteristics for a wide variety of monomers. This study highlights the need for a suitable RAFT agent to polymerize allyl methacrylate, hence research should be carried out into this.
- The retardation phenomenon that is often observed in RAFT polymerization systems, especially at high concentrations of RAFT agent³, has been studied in detail, but many questions still remain, and hence a more exhaustive investigation into the workings of the RAFT mechanism is required to answer them.
- The modification of RAFT end-groups to produce thiol end-groups as described in this study was successful and yielded products with few impurities. However,

CHAPTER 7: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

there are still many RAFT systems where the modification of RAFT end-groups has proved troublesome^{4,5}. Better end-group modification techniques that produce fewer impurities are needed. Also, methods of preventing RAFT end-group hydrolysis in aqueous systems need to be explored.

- Allyl methacrylate has been effectively polymerized using ATRP⁶ and living anionic polymerization⁷, but to the author's knowledge this is the first time that this monomer has been polymerized using RAFT. The fact that allyl methacrylate contains two double bonds with different reactivities makes it an attractive prospect as a crosslinking agent. The use of CVADTB generated linear polymer chains with pendant, unreacted double bonds, but only at low conversions. Detailed investigations are needed to produce linear PAMA chains with high molecular weights by delaying the onset of gelation, e.g. through copolymerization.
- A reliable method for the synthesis of branched copolymers using a "grafting onto" approach via a thiol-ene addition reaction has been established. Much work still has to be done however, in terms of varying the backbone length, branch length, branch distribution, etc., and studying their effects on final material properties.
- The analysis of architecturally tailored comb polymers is still in its infancy. A comprehensive investigative approach has been developed by the Key Centre for Polymer Colloids (Sydney) that can be used to deconvolute GPC data of comb polymers to obtain information on their hydrodynamic volumes⁸. This could be used to try to explain the abnormal GPC behaviour, e.g. retardation that is experienced by comb polymers.

7.3 Bibliography

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APPENDIXES

Appendix A: Cyanovaleric Acid Dithiobenzoate

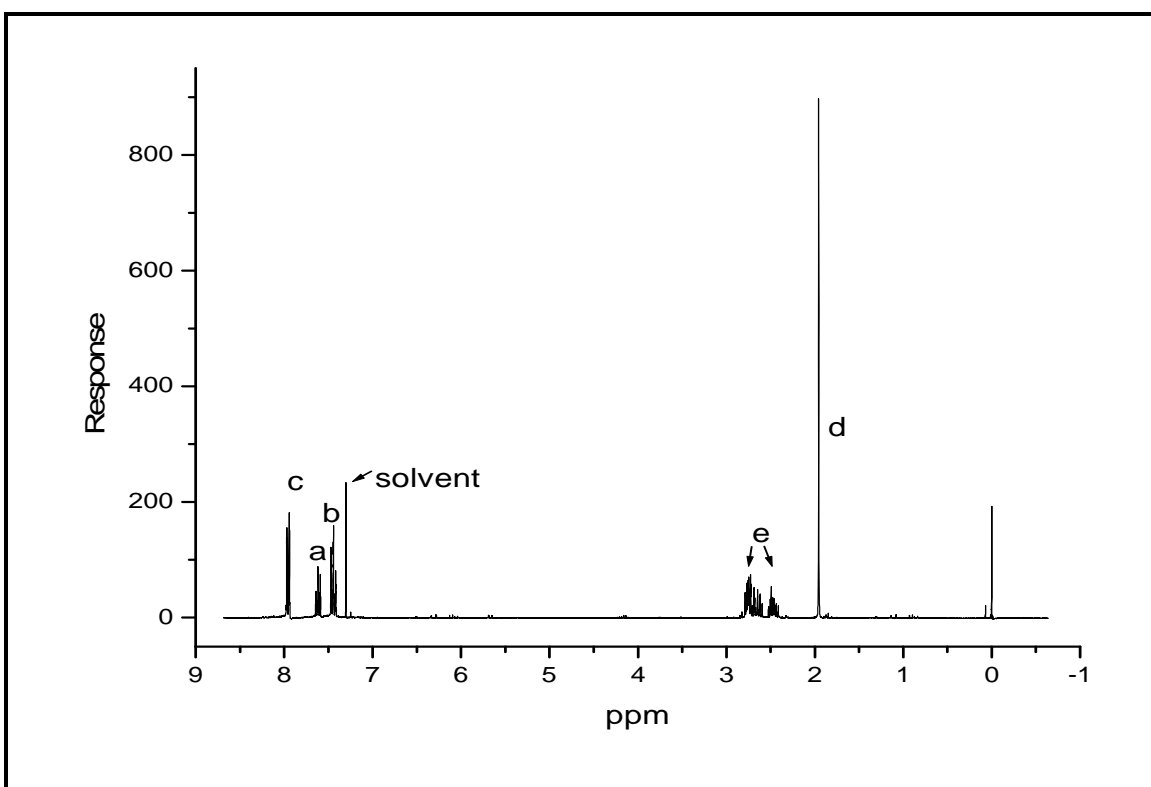
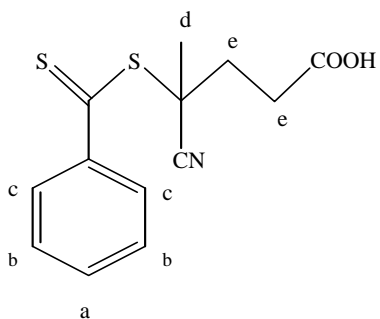


Figure A: ^1H -NMR spectrum of CVADTB with chloroform as solvent.

Appendix B: Dodecyl Isobutyric Acid Trithiocarbonate

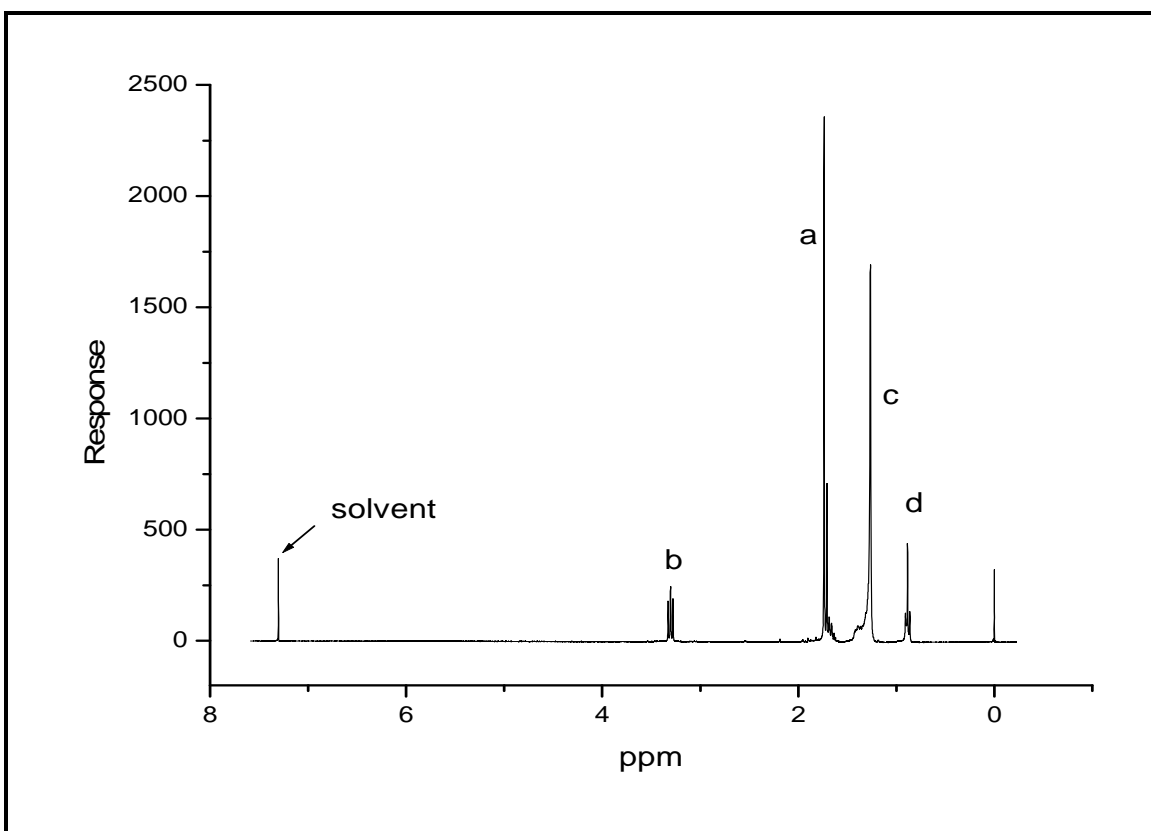
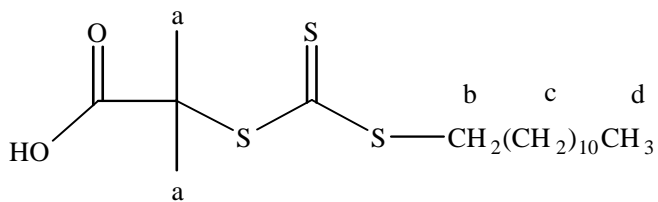


Figure B: ¹H-NMR spectrum of DIBTC with chloroform as solvent.

Appendix C: RAFT End-Group Modification using NaOH

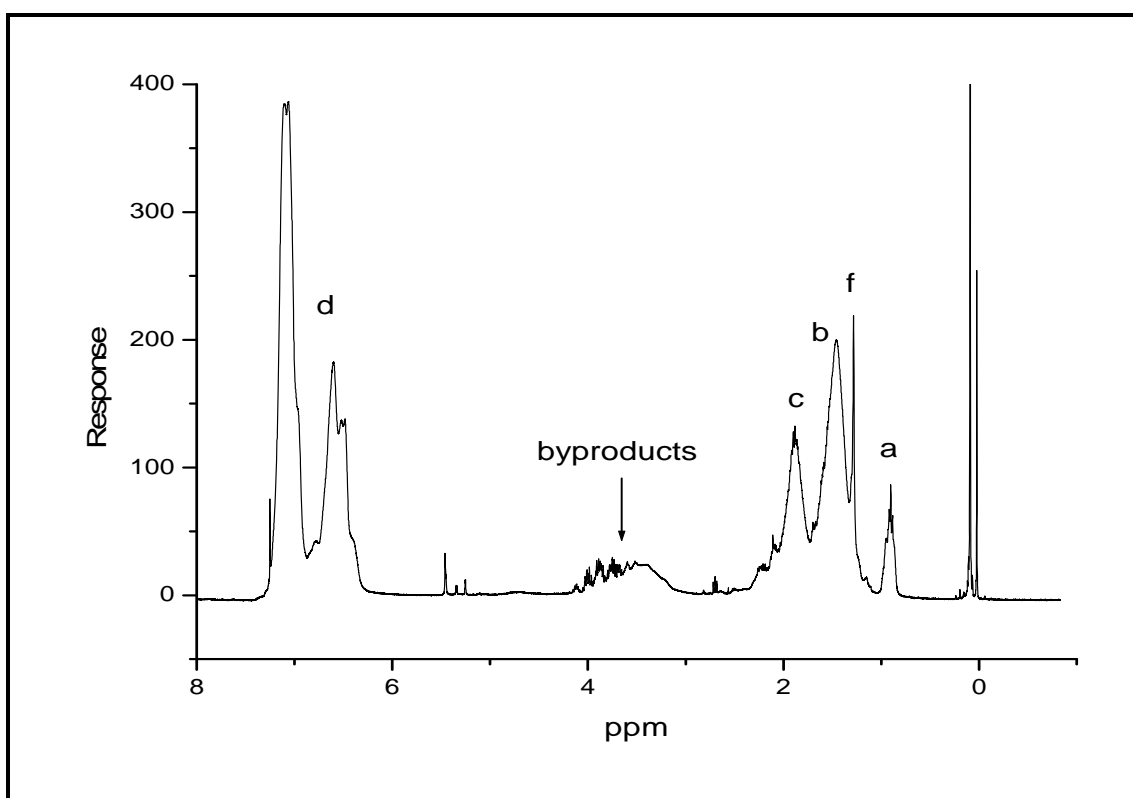
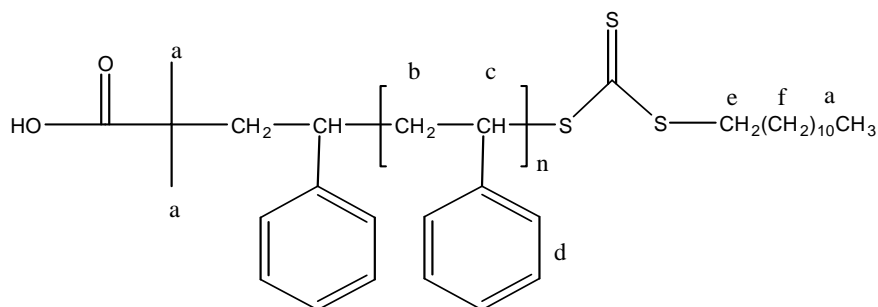


Figure C: ¹H-NMR spectrum of polystyrene polymerized with DIBTC after end-group modification using NaOH.

Appendix D: RAFT End-Group Modification using Dodecyl

Amine

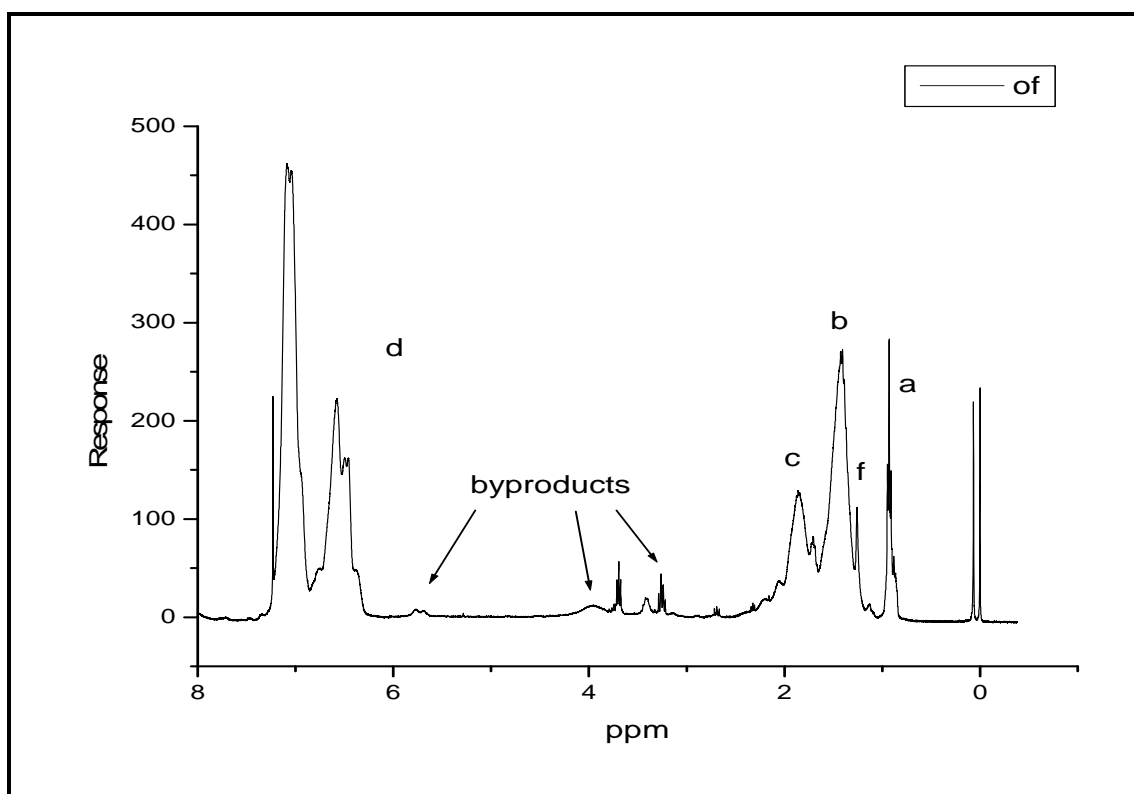
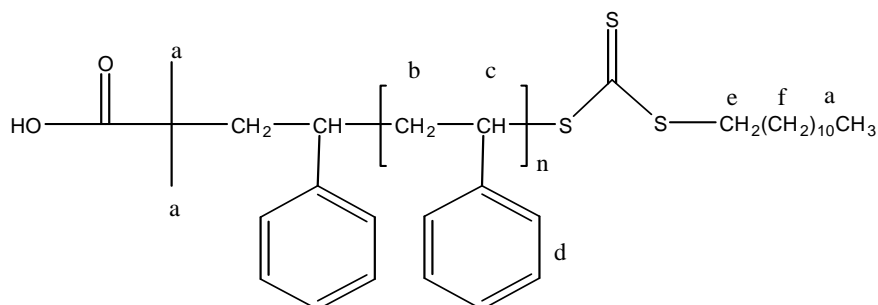


Figure D: $^1\text{H-NMR}$ spectrum of polystyrene polymerized with DIBTC after end-group modification using dodecyl amine.

Appendix E: RAFT End-Group Modification using THF

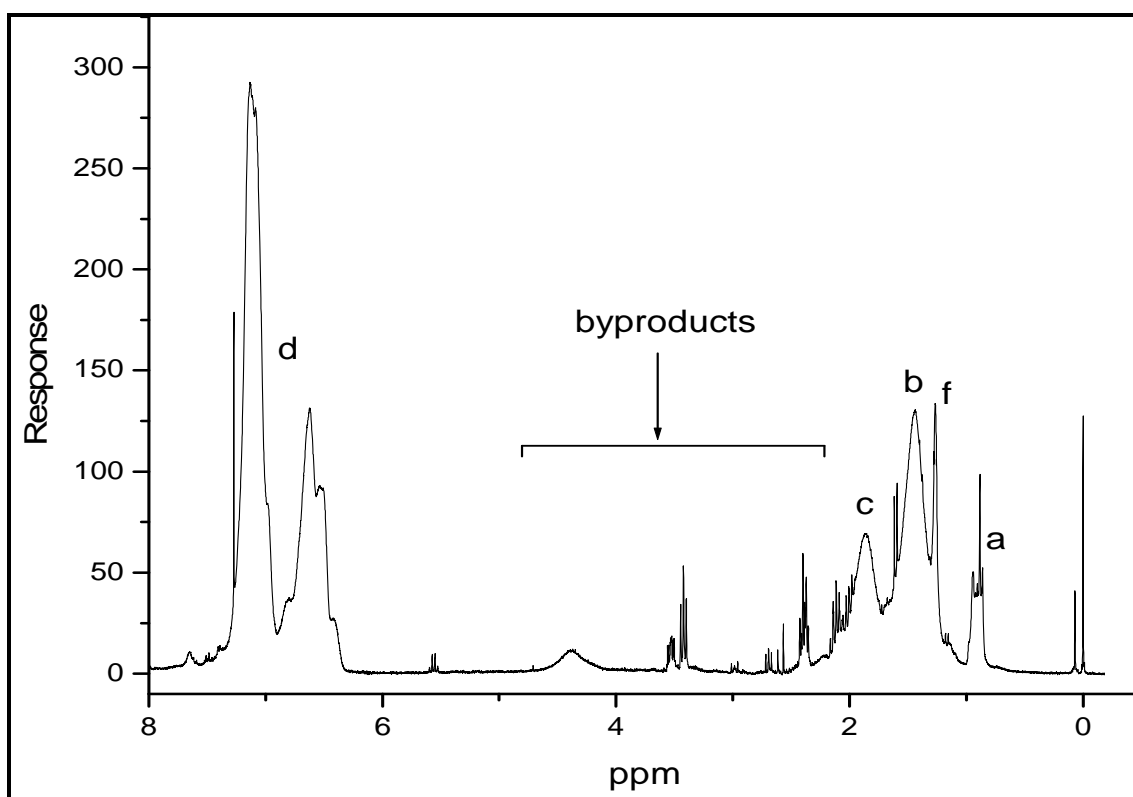
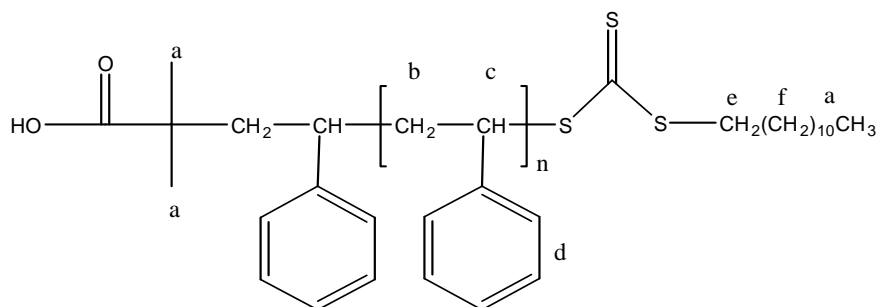


Figure E: $^1\text{H-NMR}$ spectrum of polystyrene polymerized with DIBTC after the modification of the RAFT end-group using THF.