

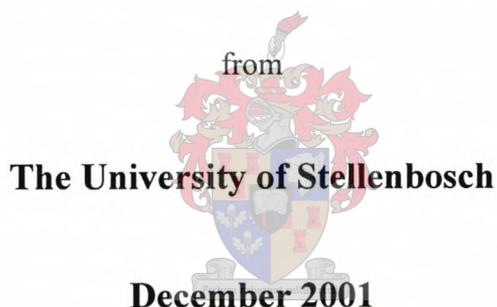
Controlled Free Radical Polymerization in Miniemulsion using Reversible Addition- Fragmentation Chain Transfer (RAFT)

by

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Master of Science (Polymer Science)



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Declaration

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

Abstract

A novel approach to conducting controlled free radical polymerization in aqueous systems using Reversible Addition-Fragmentation Chain Transfer (RAFT) has been studied. When conducting RAFT in aqueous systems, reaction conditions must be chosen such that monomer transport across the aqueous-phase is either eliminated or facilitated. This is to prevent the formation of the red layer associated with RAFT in emulsions. The formation of the red layer is ascribed to the inability of water-insoluble, dithiobenzoate-encapped oligomers to be sufficiently transported across the aqueous phase. The novel approach in this study focussed on eliminating monomer transport and comprises two fundamental steps: the synthesis of dithiobenzoate-encapped oligomers in bulk followed by miniemulsification of these oligomers to yield a polymerizable miniemulsion. Dithioesters that act as chain transfer agents in the RAFT-process were synthesized *in situ*, thereby eliminating laborious and time-consuming organic purification procedures of dithioesters.

In situ formation of the RAFT-agents involved conducting the reaction between di(thiobenzoyl) disulfide and conventional azo-initiators of differing structures in the presence of monomer. The structure of the chosen azo-initiator played a role in the efficiency of the RAFT process when the reaction was conducted in the presence of monomer to control the free radical polymerization process.

Synthesis of the oligomers was performed by heating di(thiobenzoyl) disulfide and a selected azo-initiator, in the presence of monomer for a specific reaction duration in bulk. After the reaction was stopped, these oligomers were then miniemulsified by adding water, surfactant and cosurfactant, followed by the application of shear to form the resulting miniemulsion.

The free radical polymerization of the dithiobenzoate-encapped oligomers in the miniemulsion proceeded in a controlled manner with molecular weight increasing in a linear fashion with increasing conversion, while polydispersities remained low. The familiar red layer formation associated with RAFT polymerization in conventional emulsions was not observed under these conditions.

The effects of changing the cosurfactant (hydrophobe) as well as changing the degree of polymerization of the emulsified oligomers were also investigated and described.

Opsomming

Hierdie studie is geloods om 'n nuwe benadering tot die beheerde vry-radikaal polimerisasie in water gebaseerde sisteme te ondersoek. Daar is spesifiek gekyk na die uitvoer van die RAFT (Reversible Addition-Fragmentation Chain Transfer) prosesse in emulsies. Wanneer RAFT in emulsies toegepas word, moet die toestande waaronder die reaksie uitgevoer word, versigtig opgestel word. Die toestande moet so gekies word dat die vervoer van monomere deur die waterfase óf geëlimineer word óf gefasiliteer word. Dit word gedoen om die faseskeiding in die vorm van 'n rooi laag, wat so kenmerkend van RAFT-polimerisasie in emulsies is, te voorkom. Hierdie faseskeiding vind plaas omdat die vervoer van ditiobensoaat endgroep-bevattende oligomere deur die waterfase tydens interval II, moeilik is a.g.v. hul lae oplosbaarheid in water.

Die nuwe benadering wat hier bestudeer is, het twee basiese stappe. Eerstens word die ditiobensoaat endgroep-bevattende oligomere in bulk gesintetiseer. Dit word gevolg deur die emulsifisering van die oligomere. Hierna vind verdere polimerisasie van die oligomere plaas deur die dormante oligomere te heraktiveer.

Die ditiio-esters wat as kettingoordrag agente optree in die RAFT prosesse, word *in situ* gesintetiseer. Hierdie modifikasie sny tydrowende organiese suiweringsmetodes uit.

Die *in situ* RAFT agente word gesintetiseer deur di(tienbensoïel) disulfied met verskillende konvensionele azo-inisieerders te laat reageer. Die struktuur van die spesifieke azo-inisieerder het wel 'n rol gespeel in die effektiwiteit van die RAFT prosesse om molekulêre massa te beheer as bg. reaksie in die teenwoordigheid van monomere uitgevoer is.

Die sintese van die oligomere is gedoen deur di(tienbensoïel) en 'n azo-inisieerder te verhit in die teenwoordigheid van monomere. Die reaksie is gedoen in bulk en die graad van polimerisasie van die oligomere is beheer deur die reaksie te stop by verskillende tydskritte. Nadat die bulk reaksie gestop is, is hierdie oligomere ge-emulsifiseer deur die oligomere te meng met 'n seep, hidrofoob en water. Hierdie mengsel word dan onderwerp aan 'n vermengingskrag om 'n polimeriseerbare mini-emulsie te vorm.

Die voortsetting van die polimerisasie van die oligomere in die mini-emulsie het op 'n beheerde wyse verloop, m.a.w. molekulêre massa wat lineêr toeneem met stygende omsetting. Polidispersiteit indekse van die polimere het deurentyd laag gebly in die stabielste sisteme. Onder hierdie toestande was daar geen kenmerkende rooi laagvorming te bespeur nie.

Die effekte wat die verandering van die hidrofoob, asook die verandering van die graad van polimerisasie van die oligomere op die sisteem gehad het, is onder andere ook ondersoek en beskryf.

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List of Symbols

DP_n	Degree of polymerization
$\Delta\bar{G}_1$	Partial molar free energy of mixing of monomer in droplets
j_{crit}	Critical chain length for solubility
j_2	Ratio of the molar volumes of monomer to cosurfactant
k_d	Rate coefficient for dissociation of initiator
k_p	Rate coefficient for propagation of growing polymer chain
$k_{t, com}$	Rate coefficient for termination by radical recombination
$k_{t, dis}$	Rate coefficient for termination by disproportionation
k_{deact}	Rate coefficient for deactivation of propagating chain
k_{exch}	Rate coefficient for exchange between active and dormant species
k_{act}	Rate coefficient for activation of dormant species
k_{tr}	Chain transfer coefficient
m/v	Percentage expressed as grams of dissolved compound per 100ml of solvent
\bar{M}_n	Number average molecular weight
\bar{M}_w	Weight average molecular weight
$[M]_0$	Initial monomer concentration
$[M]_t$	Monomer concentration at time t
\bar{n}	Average number of radicals per particle
n	Number of radicals per particle
R	Universal gas constant
R	Droplet radius
$[R\bullet]$	Concentration of active species
T	Temperature in Kelvin
V_{1M}	Molar volume of monomer
v_{max}	Maximum reaction rate
ϕ_1 and ϕ_2	Volume fractions of monomer and cosurfactant respectively

χ	Interaction parameter
γ	Interfacial tension
λ	Wavelength

List of Abbreviations

1-HD	1-Hexadecanol
ACHN	1,1'-Azobis(cyclohexanecarbonitrile)
Ag-TFA	Silver(I)-trifluoroacetate
AIBN	Azobisisobutyronitrile
ATRP	Atom Transfer Radical Polymerization
CFRP	Controlled Free Radical Polymerization
CMC	Critical Micelle Concentration
COBF	Bis(borondifluorodimethylglyoximate)cobaltate(II)
CTA	Chain Transfer Agent
DDI	Distilled and Deionized Water
DMSO	Dimethylsulfoxide
DSD	Droplet Size Distribution
ESR	Electron Spin Resonance
GPC	Gel Permeation Chromatography
HPLC	High Performance Liquid Chromatography
IR	Infrared
MALDI-TOF	Matrix-Assisted Laser Desorption/Ionization-Time Of Flight
<i>n</i> -HD	<i>n</i> -Hexadecane
NMR	Nuclear Magnetic Resonance
PDI	Polydispersity Index
RAFT	Reversible Addition-Fragmentation Chain Transfer
SANS	Small-Angle Neutron Scattering
SEM	Scanning Electron Microscopy
SLS	Sodium Lauryl Sulfate
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl
THF	Tetrahydrofuran
UV	Ultra Violet

VOC

Volatile Organic Content

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Chapter 1: Introduction and Objectives

1.1 Introduction

Along with the increasing scientific and technological capabilities of the global society, a growing demand for materials with novel properties for specific applications is evident. In the realm of synthetic polymers, three possibilities present themselves for overcoming the challenge of synthesizing such new materials. The first possible solution involves the design and synthesis of new monomers. These monomers may, when polymerized, yield materials with completely new properties. The second, more viable solution may be the changing and controlling of the microstructure of polymers synthesized using existing, inexpensive and readily-available monomers. When, for example, a diblock co-polymer is synthesized, simply varying the lengths of the different blocks can change the properties of the resulting material. A third possibility might be the modification (chemical or other) of natural or synthetic polymers.

The research described in this dissertation focuses on the second option, namely the carefully controlled synthesis of polymers using existing monomers. This dissertation specifically discusses the control of free radical polymerization reactions conducted in aqueous media.

1.2 Synthesizing Polymers in a Controlled Manner

1.2.1 Free Radical Polymerization in Emulsions

The process of free radical polymerization has many attractive features, including: tolerance of trace amounts of impurities and water, reactions can be carried out at conventional temperatures, and a wide range of monomers can be used.¹ These are just some of the reasons why industry prefers to synthesize polymers by free radical means.

It has become necessary for world industry to conform to the global trend towards being more sensitive to the environment and its needs. Therefore, any process contaminating the surroundings and atmosphere with volatile organic compounds is likely to come under the scrutiny of environmental and legislative bodies. The main advantage of emulsion polymerization is that the monomer is dispersed in water. Hence, since water is environmentally friendly and because of other advantages associated with emulsion polymerization (see Section 2.2), the process is extensively employed in industry. In Western countries alone, the current production of all polymers is in excess of 10^8 tonnes per year, of which approximately 30% is made by free-radical means; emulsion methods are used for effecting 40–50% of these free-radical polymerization reactions.²

1.2.2 Living/Controlled Free Radical Polymerization

In order to obtain control over chain architecture, a so-called “living system” must be established. In a living polymerization system, the probabilities of termination and chain transfer side reactions are kept to a minimum. Such a system exhibits some distinctive characteristics, such as:¹

- Molecular weight increases with conversion in a predictable manner.
- Polymers with low polydispersities ($<1,3$) are produced.
- Polymerization proceeds until all monomer is consumed and commences again upon addition of new or more monomer.
- Polymers with endgroup functionalities can be synthesized.
- Polymers with complex architectures can be synthesized.

Living polymerization has been achieved using ionic polymerization techniques.³⁻⁵ In these polymerization techniques the carbanion or carbocation of the growing polymer chain is protected against destructive side reactions by a counter-ion. Ionic polymerization requires very stringent reaction conditions, such as high vacuum or inert atmosphere and an absence of water or other impurities. These factors make it difficult to conduct ionic polymerization on an industrial scale. Improvements in ionic techniques are, however, continuously being reported.⁶

Free radical polymerization, on the other hand, requires conditions that are much less demanding. The main problems associated with it are: Termination of growing chains through bimolecular coupling and/or disproportionation as well as chain transfer to various components, such as solvent and monomer. Unfortunately these problems are inherent to the mechanism of free radical polymerization. (Bimolecular coupling can be reduced by keeping the effective concentration of the propagating radicals as low as possible. Many of the controlled free radical polymerization techniques rely on this principle.) The attractive features of free radical polymerization make it a widely used process in industry, especially in emulsions. The past decade has seen researchers strive to eliminate, or at least limit, the termination and chain transfer reactions in free radical polymerization while still maintaining the advantages of the process. This has given rise to a new field of research, termed “living or controlled” free radical polymerization (CFRP).⁷ This process usually involves the addition of a specific compound to a conventional free radical polymerization reaction. Equilibrium is then established between propagating active species and dormant species, with fast exchange between these species.

1.2.2.1 Reversible Addition-Fragmentation Chain Transfer

Various techniques have been developed to control free radical polymerization reactions. This so-called control is obtained by reducing the concentration of the active radicals and thereby reducing the probability of termination. Probably the most robust and versatile (in terms of compatibility with a wide range of monomers) of these techniques is the reversible addition-fragmentation chain transfer (RAFT) process.^{1, 8-10} This process involves the addition of dithioester compounds to a free radical polymerization process. Propagating chains are reversibly capped by a dithio-moiety with subsequent fragmentation of a radical capable of propagating (see Section 2.4.6).

1.2.3 Controlled Free Radical Polymerization in Aqueous Media

The acceptance of any of the controlled free radical (CFRP) techniques developed depends to a great extent on its ability to be conducted in an aqueous environment.

As mentioned previously (see Section 1.2.1), a large number of industrial polymerization processes are conducted in emulsions. This is mainly because of the inherent advantages of emulsions, including: high reaction rates, the potential for formation of high molecular weight compounds and the ease of handling of the final latex (see Section 2.2). The environment also benefits from emulsion polymerization due to the absence of volatile organic solvents.

1.3 Research leading up to the project

Attempts have been made to conduct RAFT polymerization in conventional emulsions.¹¹⁻¹² All cases reported phase separation in the form of a red layer, which, upon analysis, was found to consist of monomer-swollen dithiobenzoate-encapped oligomers.¹³ It was suspected that the phase separation occurred because of the inability of these oligomers to be transported through the aqueous phase to polymerization loci.

It therefore became clear that the transport of these RAFT-oligomers through the aqueous phase either had to be eliminated or facilitated. Research efforts, worldwide, have focused on the former and two modifications of the aqueous environment were explored.

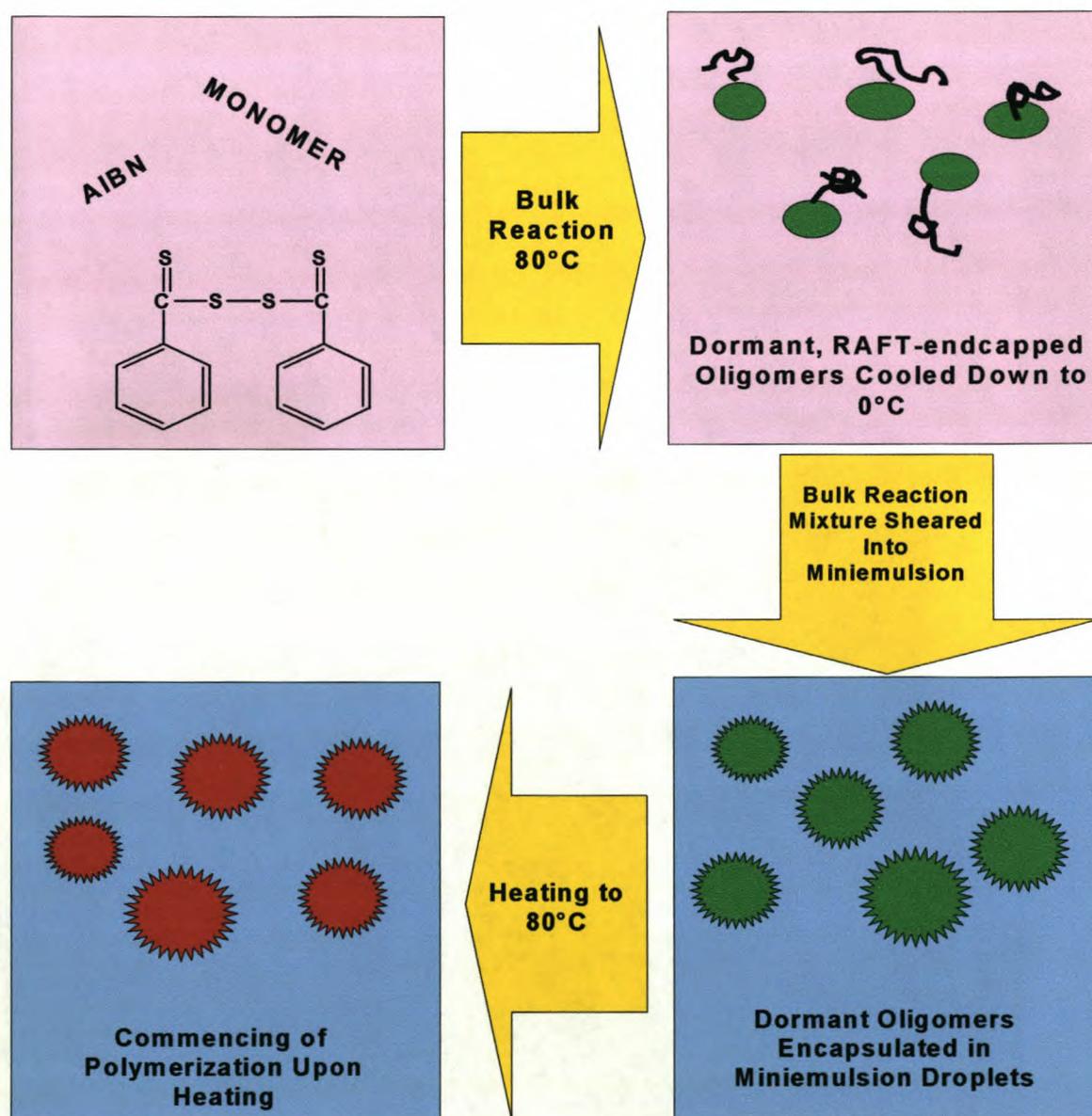
The first was to conduct the RAFT polymerization in a conventional emulsion and to introduce the monomer to the system by starved feed.^{8, 14} This allows the monomer to directly diffuse to the polymerization loci, thus eliminating the formation of monomer droplets. Transport from droplets to homogeneous nucleation sites is subsequently minimized.

The second route was to conduct the RAFT polymerization in a miniemulsion system.^{8, 13} In miniemulsion systems the presence of a cosurfactant (hydrophobe) reduces the rate of monomer diffusion through the aqueous phase.¹⁵ This causes the monomer droplets to become the main polymerization loci. Diffusion of monomer from droplets through the aqueous phase (responsible for the constant reaction rate in

Interval II found in conventional emulsion polymerization reactions) is not observed to a large extent in a miniemulsion system.

1.4 Objectives

This project involves a novel approach to CFRP in emulsions; it entails the synthesis of the dithiobenzoate-endcapped oligomers in bulk and subsequent emulsification of the bulk reaction mixture into a miniemulsion system. A schematic representation of the study that was undertaken is shown in Scheme 1.1.



Scheme 1.1: Flow diagram of the novel approach that was followed in this study.

The oligomers were to be synthesized in bulk with the RAFT agent being formed *in situ*, utilizing the reaction between bis(dithiobenzoyl) disulfide and 2,2'-azobisisobutyronitrile (AIBN). After a specific period of time the bulk reaction mixture is cooled in an ice-bath to yield dormant, oligomeric polymer chains that can be re-initiated upon heating. The bulk reaction mixture is then added to the other components needed for a miniemulsion system (surfactant, cosurfactant and water), and sheared to prepare a miniemulsion, which is heated to re-initiate the polymerization process.

The objectives of the present project were as follows:

- ✓ Establishing a living system (see Section 2.4) by employing an *in situ* RAFT-agent formation.
- ✓ Establishing an emulsifier system that endows stability in terms of coagulation and phase separation upon the oligomer-containing miniemulsion system.
- ✓ Reinitiation of the oligomers in the miniemulsion droplets to yield a polymerization reaction exhibiting living characteristics.
- ✓ Gaining new insights into the mechanism of RAFT polymerization in aqueous systems.

In the course of the study the following were studied:

- ✓ The efficiency of an *in situ* RAFT-agent formation.
- ✓ The effect of the presence of oligomers on the miniemulsion system.
- ✓ The re-initiation efficiency of the polymerization reaction in the oligomer-containing miniemulsion upon heating.
- ✓ The effect of different lengths of oligomers on the polymerization reaction.
- ✓ The effect of different emulsifier systems on the stability of the polymerization system.

1.5 Layout of the Thesis

This thesis is constituted as follows:

➤ Chapter 1: Introduction

A brief introduction is given on free radical polymerisation, emulsion polymerization and synthesizing polymers in a controlled manner. Research that lead up to this project is also discussed. Objectives of the study and an outline of the dissertation are given.

➤ Chapter 2: Historical and theoretical background

A theoretical and historical discussion is given on all aspects related to the study. This should enable the reader to clearly understand all concepts relevant to the study and those used in discussions.

➤ Chapter 3: Synthesis of RAFT-agents

The organic synthesis of two dithioester chain transfer agents (2-cyanobut-2-yl dithiobenzoate and 1-cyano-1-cyclohexyl dithiobenzoate) is discussed.

➤ Chapter 4: Solution polymerization studies

The efficiency of the RAFT process when performing the *in situ* RAFT-agent formation is investigated. This was done by reacting di(thiobenzoyl) disulfide with selected azo-initiators in the presence of monomer in solution.

➤ Chapter 5: Synthesis of oligomers

The synthesis of dormant, oligomeric dithiobenzoate-endcapped polystyrene chains is described. The polymerization reaction is performed in bulk and the RAFT-agent is formed *in situ*.

➤ Chapter 6: Miniemulsion polymerisation

This chapter describes how the dormant oligomers were miniemulsified and reinitiated to yield polymers of which the molecular weights increased in a linear manner with increasing conversion.

➤ Chapter 7: Conclusions

General conclusions to the study are made. This is done with the initial objectives in mind. Recommendations for future work are also given.

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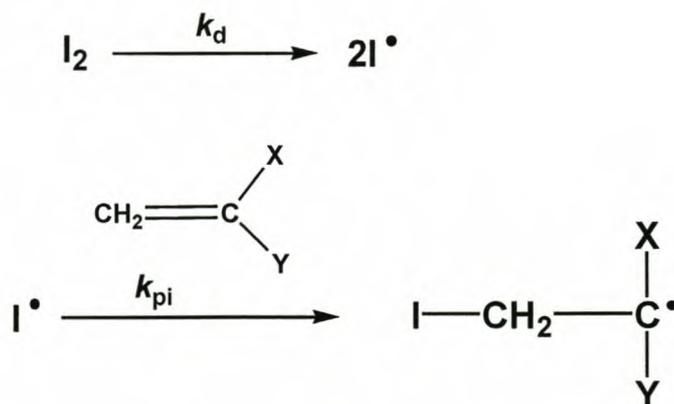
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Chapter 2: Historical and Theoretical

2.1 Free Radical Polymerization

The process of free radical polymerization is extensively employed in industry to prepare synthetic polymers. This is mainly because the process is not negatively affected by the presence of water and trace amounts of impurities and oxygen. Free radical polymerization can also be conducted in aqueous media. The reaction conditions for free radical polymerization reactions are therefore much less demanding and economically more viable than they are for ionic and coordination polymerization reactions. Free radical polymerization is a form of a free radical chain reaction. The important kinetic events include the initiation reaction, the propagation step (and the competing chain transfer reaction) and the chain termination processes.

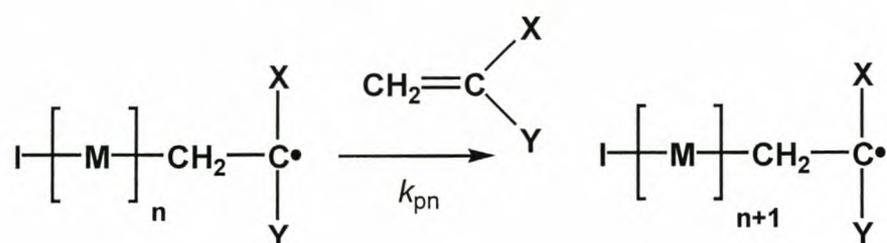
The initiation reaction generates primary radicals which may then undergo reactions, such as with monomer in the propagation reaction. These primary radicals are often chemically generated from the decomposition of a free radical source. Examples of initiators for free radical polymerization reactions include azo-compounds, peroxides, persulfates, photochemical initiators and redox couples. These primary radicals mainly undergo addition to the least substituted end of asymmetrically substituted α -olefins¹ (Scheme 2.1).



Scheme 2.1: *Decomposition of an initiator molecule to yield free radicals, which undergo addition to monomer.*

Addition to the carbon-carbon double bonds leads to the formation of propagating radicals. Initiator efficiency is, however, never 100%. This can be due to one or more of the following reasons: chain transfer to monomer, solvent, polymer and other compounds, as well as the recombination of primary radicals due to the solvent cage effect.²

Once the initial radical formation has occurred, further reaction or propagation involving the addition of monomer units to the active radical species can take place (Scheme 2.2).

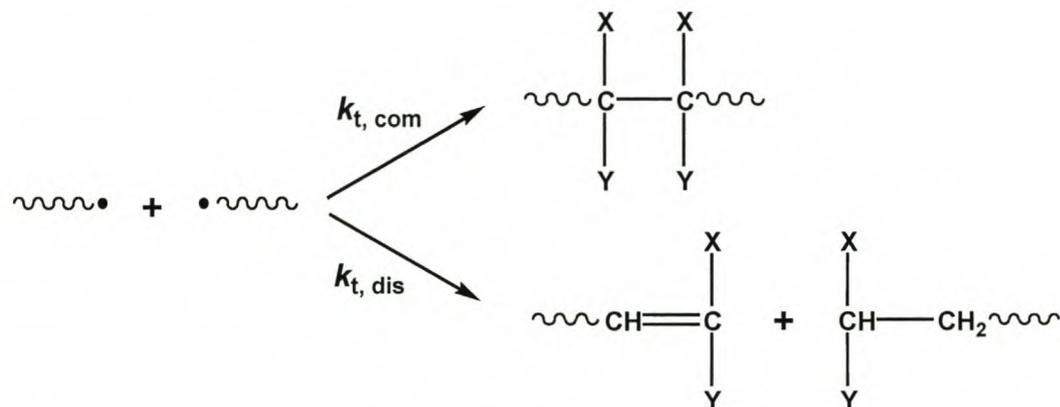


Scheme 2.2: Propagation through sequential monomer addition to form a growing polymer chain.

During the course of propagation, chain transfer can occur. This is an important side reaction in free radical polymerization as it leads to a reduction in molecular weight and a limit is set on the maximum attainable molecular weight. Chain transfer events entail the transfer of the unpaired electron of the propagating radical to monomer, solvent, formed polymer or any other component present in the system. Chain transfer to monomer competes with propagation and can lead to shorter chains that have a greater chance of termination. Chain transfer is the primary source of monomeric radicals which may desorb from latex particles in emulsion systems.

Termination is usually defined as the process which leads to the cessation of growth of one or more polymer chains.³ Termination involves the recombination or disproportionation of propagating radicals, depending on the nature of the monomer (Scheme 2.3). Propagating radicals can recombine with any other radical species, including another propagating radical or initiator-derived radicals.

Termination events thus kill radical activity, and the chain reaction ceases. This is one of the primary mechanisms for limiting the lengths of growing polymer chains, and for loss of control in controlled (“living”) polymerization techniques.



Scheme 2.3: *The possible chain death fates of propagating polymeric radicals: termination via bimolecular coupling (com) or the formation of an unsaturated endgroup through disproportionation (dis).*

2.2 Emulsion Polymerization

Emulsion polymerization is a heterogeneous free radical process conducted in an aqueous environment. This technique has found widespread application in numerous industries, including the food industry, cosmetics, agro-chemicals, pharmaceuticals, paints and bitumen. A few of the advantages associated with emulsion polymerization are as follows:

- Polymerization in aqueous reaction media supports the current worldwide trend towards making industries more environmentally friendly.
- The aqueous phase is very efficient in absorbing and dissipating the heat of the polymerization exotherm.
- An emulsion system is extremely robust and relatively insensitive to impurities.
- Polymers with high molecular weight can be synthesized.
- Reaction rates in an emulsion system are high.

- High conversions can be reached, leaving very little free residual monomer in the final latex.
- Upon completion of polymerization the low viscosity of the emulsion ensures easy further processing.

An emulsion system usually begins with a dispersion of monomer droplets stabilized by surfactant molecules in a continuous aqueous phase. Polymerization is initiated by a conventional primary radical source, such as potassium persulfate. A buffer may be included in such a system, if deemed necessary, to compensate for changes in pH due to the hydrolysis of persulfate initiators. Further additives, such as chain transfer agents, may be included for specific purposes – in this case to reduce the molecular weights of the polymer chains produced in the polymerization process.

2.3 Miniemulsion polymerization

2.3.1 General

Ugelstad *et al* were the first to report on the polymerization of submicron-size styrene droplets synthesized using an emulsifier system consisting of a surfactant (SLS) and a cosurfactant (cetyl alcohol).⁴ Miniemulsions are classically defined as relatively stable aqueous dispersions of oil droplets within the size range 50nm – 500nm.⁵ Miniemulsions are prepared by shearing a system containing oil, water, a surfactant and a cosurfactant (hydrophobe). The cosurfactant is usually an oil-soluble, long chain alkane (e.g. *n*-hexadecane) or fatty alcohol (e.g. 1-hexadecanol). Whereas the surfactant suppresses the coalescence of particles by electrostatic repulsion or steric hindrance, the function of the cosurfactant is two-fold:

(a) The cosurfactant retards, or even prevents, Ostwald-ripening (τ_1 -process).⁶ This relates to an osmotically-controlled steady state. Ostwald-ripening refers to the process of monomer diffusion from smaller droplets to larger droplets, causing the droplet size distribution (DSD) to decrease and the average droplet size to increase.⁶ This phenomenon is inherent to emulsion systems and is caused by the higher vapour

pressure of the smaller droplets, due to the variation of Gibbs free energy with droplet size. Any system strives toward a state of minimum free energy. This is the main driving force behind droplet degradation through monomer diffusion. The degradation phenomenon is governed by the diffusion rate of the least soluble component present in a droplet.⁷ For this reason the cosurfactant efficiency increases as its water solubility decreases, due to a slower diffusion rate.

(b) The cosurfactant prevents the coalescence of droplets through collisions (τ_2 -process). This relates to a collision-rate-controlled steady state. It is especially the fatty alcohols that are considered to provide additional stabilization.^{7, 8} The OH-group of the alcohol will allow it to form an ordered interfacial complex with the ionic surfactant and this complex can act as a barrier to prevent coalescence through droplet collisions. It has been postulated that this complex might be liquid-like and carry an electrical charge.⁹

This two-fold stability function enables the system to approach a state of steady droplet size. Miniemulsions can achieve a minimum droplet size for a specific amount of surfactant.¹⁰

The efficiency of a cosurfactant can be calculated by means of a thermodynamic equation (2.1) derived by Ugelstad *et al.*⁶ The swelling capacity of the droplets in the presence of a cosurfactant can be calculated by setting $\Delta\bar{G}_1=0$ in equation 2.1:

$$\Delta\bar{G}_1 = 0 = RT \left(\ln \phi_1 + \left(1 - \frac{1}{j_2} \right) \phi_2 + \phi_2^2 \chi + \frac{2V_{1M}\gamma}{rRT} \right) \quad (2.1)$$

where $\Delta\bar{G}_1$ is the partial molar free energy of mixing of monomer in the droplets, R is the universal gas constant, T is the temperature in Kelvin, ϕ_1 and ϕ_2 are the volume fractions of the monomer and cosurfactant respectively, r is the radius of the droplets, χ is the interaction parameter, γ is the interfacial tension, V_{1M} is the molar volume of the monomer and j_2 is the ratio of the molar volume of the monomer to the molar volume of the cosurfactant.

Advantages of miniemulsion polymerization relative to conventional emulsion polymerization include: ^{8, 11-13}

- Miniemulsions are far more robust to variations in recipe e.g. initiator and oil-phase inhibitor concentrations.
- Miniemulsions have a lower sensitivity to contaminant levels.
- In miniemulsions, no competition exists between particle growth and particle nucleation for available surfactant molecules.
- Miniemulsions have superior shear stability due to the absence of small numbers of polymerized droplets found in conventional emulsions.
- Hydrophobic comonomers can be used as cosurfactants.
- Copolymers produced in miniemulsion polymerization have very uniform copolymer compositions. This is because the supply of hydrophobic co-monomer is not limited by mass transfer problems.
- Miniemulsions produce polymers with a low volatile organic content (VOC).
- The nature of the nucleation process ensures that there is no oscillatory behaviour in particle size compared to conventional emulsions in a continuous stirred tank reactor.
- Direct control over the final particle number may be achieved by controlling the initial droplet number.
- Inert species like dyes and pigments can be introduced to the initial system prior to miniemulsification and, because of encapsulation, they will be incorporated in the final latex.

There are, however, some disadvantages associated with miniemulsions:¹²

- The use of hexadecane as the cosurfactant might cause the VOC to increase.
- Similarly, use of the more hydrophilic cetyl alcohol as the cosurfactant may cause problems with respect to water resistance.

2.3.2 Mechanism and kinetics

In an ideal miniemulsion system it should be possible to obtain a 1:1 transformation of droplets to particles. This means that each monomer droplet acts as a pseudo-bulk nanoreactor. This is, however, not always the case and miniemulsions have to be prepared very carefully to avoid aqueous phase and micellar nucleation as well as monomer transport through the aqueous phase.

Micellar nucleation can be minimized by ensuring that the aqueous phase concentration of the surfactant stays below its critical micelle concentration (CMC). This is often difficult to achieve and impractical. Therefore, a high shear rate that leads to a very fine droplet dispersion is crucial. This very fine dispersion corresponds to a large droplet surface area.^{9, 14} The larger surface area of the minidroplets leads to more surfactant molecules being adsorbed. This leaves little or no free surfactant molecules to stabilize micellar nucleation.

Preventing homogeneous nucleation in a miniemulsion system poses a completely different challenge. Nucleation in the aqueous phase can be reduced by providing enough free radical “sinks”, such as droplets and particles.⁸ The purpose of these “sinks” is to restrict the lifetime of an oligomeric radical in the aqueous phase to a value that is less than the time needed for the radical to grow beyond its limit of water solubility. This will prevent the radical from becoming surface active and precipitating as a growing polymer chain. A large droplet surface area aids in achieving this goal as it provides a large area for radical adsorption. In essence, miniemulsion polymerization strives to bypass interval II in conventional emulsion polymerization.

To illustrate the kinetics of a typical miniemulsion, a calorimetric curve for a miniemulsion system utilizing a water-soluble initiator is shown in Figure 2.1.

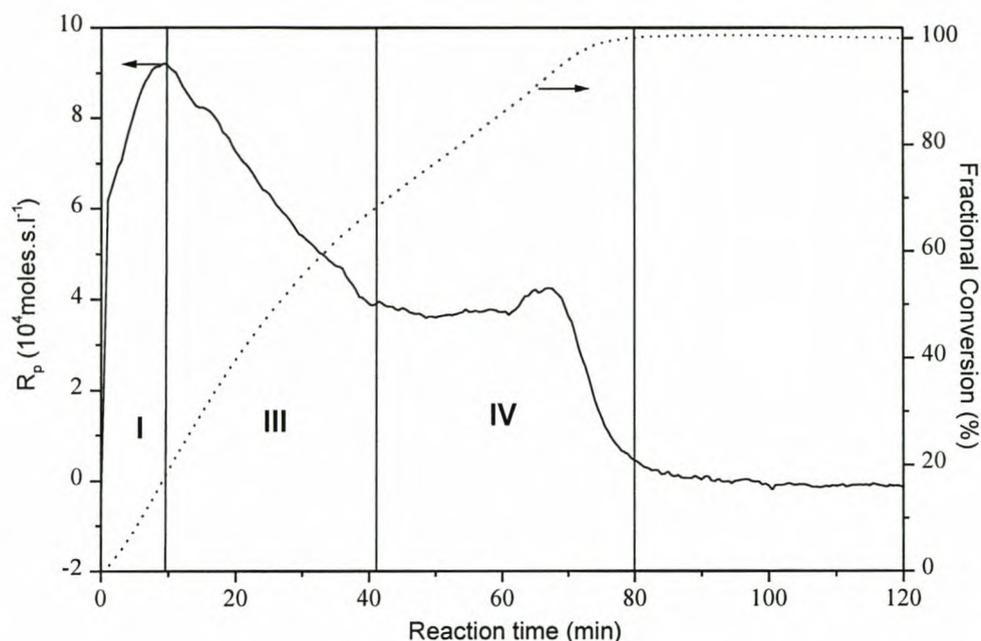


Figure 2.1: Calorimetric curve of a typical miniemulsion. (Kindly supplied by Dr Nina Bechthold from the Max Planck Institute for Colloids and Interfaces, Forschungscampus Golm, Am Mühlenberg, 14424 Golm/Potsdam, Germany.)

From the curve it can be seen that the miniemulsion polymerization process can be divided into three distinct intervals. These intervals are named to correspond to the kinetically similar regions in conventional emulsion polymerization as proposed by Harkins.¹⁵

Interval I:

The first interval is associated with particle nucleation. Particle nucleation comprises the time needed to establish an equilibrium radical concentration within each minidroplet. The duration of this interval is much shorter in miniemulsions than it is in conventional emulsion polymerizations. During this interval (assuming zero-one conditions) the average radical concentration per particle (\bar{n}) increases towards a value of 0.5.⁵ The end of interval I is reached after about 20% conversion and is indicated by the reaction rate maximum (v_{\max}), which indicates the establishment of an equilibrium concentration of radicals per particle. Droplet nucleation is not a very efficient process and the first interval would not be observed if the persulfate radical

was able to enter directly into the droplets. A number of reasons for the slow radical entry into the droplets have been postulated:^{5, 16}

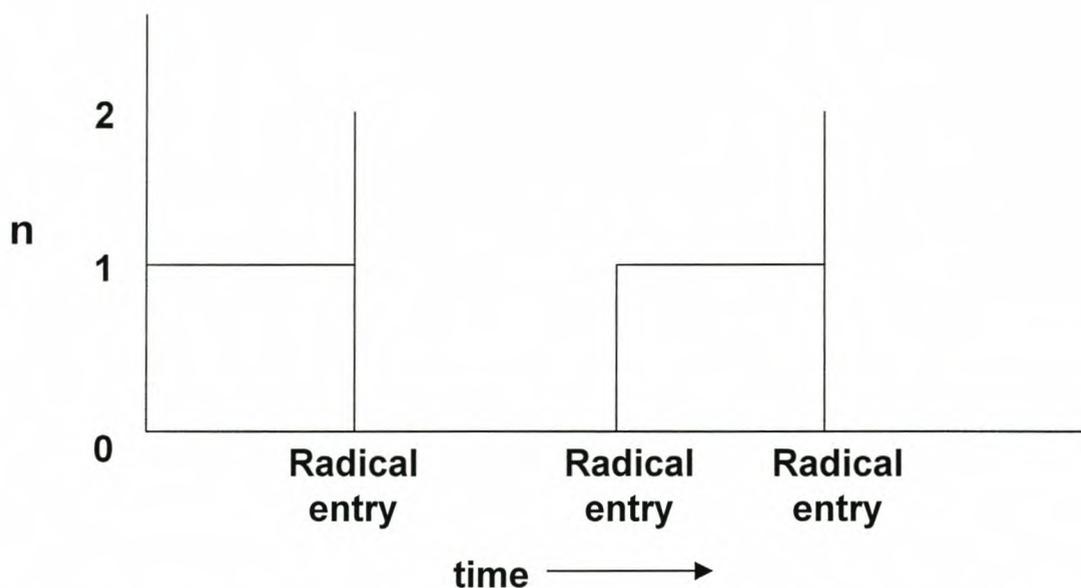
- (i) The barrier created at the oil/water interface can cause electrostatic repulsion between the negatively charged SLS surfactant and a negatively charged radical.
- (ii) A negatively charged radical, being hydrophilic, will possess a shell of water molecules around it. This shell can prevent the radical from entering the hydrophobic monomer droplet.
- (iii) In light of the aforementioned point (ii) it makes sense to note that the persulfate radical anion will only be able to penetrate the droplet once it has reacted with a few monomer units encountered in the aqueous phase. In a miniemulsion system the concentration of monomer in the continuous water phase is very low due to the cosurfactant. It will therefore take a certain amount of time for the radical to grow to form an oligomeric radical capable of droplet penetration. There exists a direct proportionality between the rate of radical entry into droplets and the rate of oligomer growth in the aqueous phase.¹⁷
- (iv) Particles act as more efficient radical “sinks” than droplets. This is due to the difference in internal viscosities of particles and droplets. When a radical enters a droplet that contains no polymer, it can desorb again before propagation can take place. A droplet that contains polymer will have a higher internal viscosity. This will cause a longer residence time for a radical and a better chance of propagation to occur.

Results of experimental work have shown that the mutual contributions of (ii) and (iii) seem to best explain the slow radical flux through the interface.^{7, 18}

Interval III :

A \bar{n} value of 0.5 implies the onset of interval III.⁵ During this interval, kinetics similar to those in bulk or suspension polymerization are observed. Only the monomer inside the droplet is available for polymerization and the monomer

concentration decreases exponentially during this interval. The average number of radicals per particle, \bar{n} , is kept at 0.5 and this means that Smith-Ewart case 2 kinetic behaviour is exhibited. A schematic representation of this behaviour is shown in Scheme 2.4.



Scheme 2.4: Schematic representation of the number of radicals per particle with time in Smith-Ewart case 2 type of kinetic behaviour.

From Scheme 2.4 it can be seen that the lifetime of a radical in a particle is the time interval between successive radical entries. Entry of a second radical results in instantaneous termination and \bar{n} is kept at 0.5.

The value of $\bar{n} = 0.5$ during interval III is not affected by an increase in initiator concentration and only the number of polymerization sites defines the duration of the reaction.¹⁹ Smaller particles therefore imply a shorter reaction time.

Interval IV :

During this interval there is a steep rise in \bar{n} and a typical gel peak, due to the Trommsdorff-Norrish effect, is observed.⁵ This effect is caused by an increase in the internal viscosity of the particles. At this relatively high conversion the chains ends are unable to reach each other by means of diffusion to undergo bimolecular

termination. This enables a droplet to provide residence to more than one radical at a time and, since monomer can still diffuse freely to the hindered polymeric radicals, there will be an increase in propagation rate. This increase in propagation rate and corresponding decrease in termination rate causes the observed gel peak.

2.3.3 Oil-Soluble Initiators in Miniemulsions

In miniemulsions using water-soluble initiators, the formation of primary radicals from the initiator molecules will primarily occur in the aqueous phase. The primary radicals are generated in pairs, but the diffusion of the radicals away from each other is very rapid in the water phase, which reduces geminate recombination of these radical pairs, thus leading to higher initiator efficiency. Primary radicals then continue to propagate until they reach a sufficient degree of polymerization to undergo entry into the droplets (individually, rather than in pairs).

This scenario changes when an oil-soluble initiator is employed. The primary locus of initiator decomposition to yield pairs of primary radicals shifts to within the oil droplets. The ability of the primary radicals to initiate polymerization reactions is dependent on their ability to diffuse apart after decomposition of the initiator molecule to avoid radical-radical termination, and is generally poor inside the droplets. This will be especially important in a zero-one type system, although this is also a very important consideration for pseudo-bulk systems. Many oil-soluble initiators (like AIBN) are sparingly soluble in water, and the aqueous phase is where much of the effective generation of primary radicals takes place. This is because the generated radicals diffuse more quickly in the aqueous phase, while generated radicals in the droplets have a lower diffusion rate. In other words the oil-soluble initiator efficiency is higher in the aqueous phase than it is in the oil phase. This results in most of the radicals that initiate polymerization actually originating in the aqueous phase, even though an oil-soluble initiator was employed. Single radicals then enter the droplets (as for an aqueous phase initiator system) from the aqueous phase to initiate polymerization.

2.4 Controlled Free Radical Polymerization

Irreversible termination remains a drawback that is inherent to the mechanism of free radical polymerization. Propagating polymer chains will inevitably terminate via bimolecular combination or through disproportionation. This leads to poor control over molecular weight, molecular weight distribution, chain architecture and functionalized endgroups.

In today's world of ever expanding technological frontiers, the demand for materials with tailor-made properties for specific applications is rapidly increasing. Conventional free radical polymerization, due to the mechanism of the process, cannot provide us with the route to meet these challenges. The relatively new field of controlled free radical polymerization (CFRP) can, however, provide us with a solution. Through the use of controlled free radical polymerization one is able to maintain the desirable characteristics of free radical polymerization, such as convenient reaction conditions and compatibility with a wide range of monomers, while virtually eliminating unwanted reactions such as radical-radical recombination. This means that polymers with low polydispersities ($<1,2$), predictable molecular weights, and complex architecture and compositions can now be synthesized. In the past this was only possible by means of ionic polymerization techniques that required high vacuum conditions and had no tolerance for impurities. There has subsequently been an upsurge in the field of controlled free radical polymerization research.

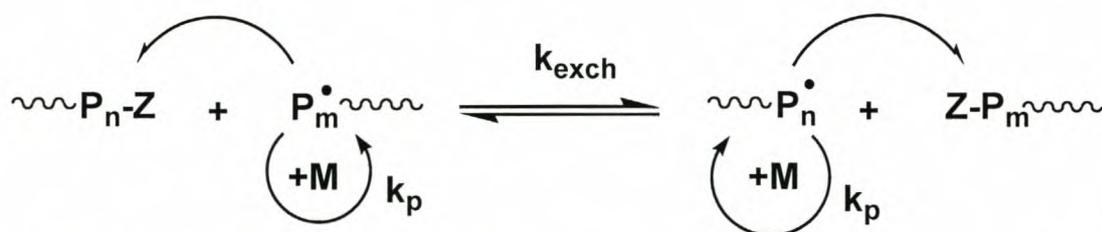
Several CFRP techniques have been developed over the past decade and they all possess one distinguishing feature. This feature is the establishment of an equilibrium between the propagating active species and a "dormant" or unreactive species.²⁰ This is achieved by conducting the polymerization reaction in the presence of reagents with very specific chemical structures. This leads to a very low concentration of propagating chains and therefore a low probability for termination. Chains can grow continuously and predictable molecular weights can be obtained. However, exchange between the active and dormant species must be sufficiently rapid, such that the rate of deactivation (k_{deact}) is faster than the rate of propagation (k_p), to ensure that the active species does not undergo irreversible termination through radical-radical

coupling.²¹ If the rate of deactivation is too slow compared to the rate of propagation, chains are allowed to propagate for too long at a time. This increases the probability of chain transfer and irreversible termination. Monomer addition between the dormant states of a polymer chain must be kept as few as possible to keep the probability of transfer and termination as low as possible.

2.4.1 Mechanism of Controlled Free Radical Polymerization

CFRP is usually obtained in three ways:²² degenerative transfer, reversible formation of persistent radicals and through homolytic cleavage of covalent species (catalyzed or non-catalyzed). These are shown schematically in Schemes 2.5-2.7.

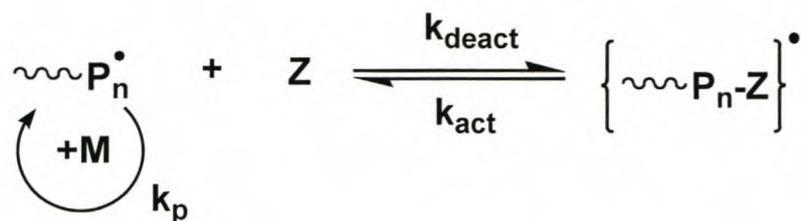
The degenerative transfer mechanism (Scheme 2.5) relies on the slow decomposition of a conventional radical initiator in the presence of an efficient chain transfer agent.²³



Scheme 2.5: CFRP via degenerative transfer.

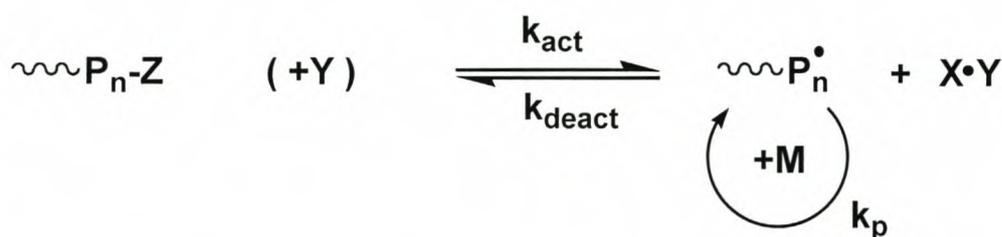
The number of chains is defined by the concentration of R-Z species and the concentration of the transfer agent must be high, relative to the initiator concentration.

The second route to CFRP is via the reversible trapping of growing radicals with compounds that have an even number of electrons. This leads to persistent radicals that cannot react with alkenes, but reversibly dissociate to provide growing radicals (Scheme 2.6). It has been postulated that this mechanism operates in the presence of phosphites, stilbenes, aluminium and chromium (II) compounds.²⁴



Scheme 2.6: CFRP via the reversible trapping of growing radicals.

The third and seemingly most successful route is via the homolytic cleavage of a weak covalent bond in the dormant species (Scheme 2.7).



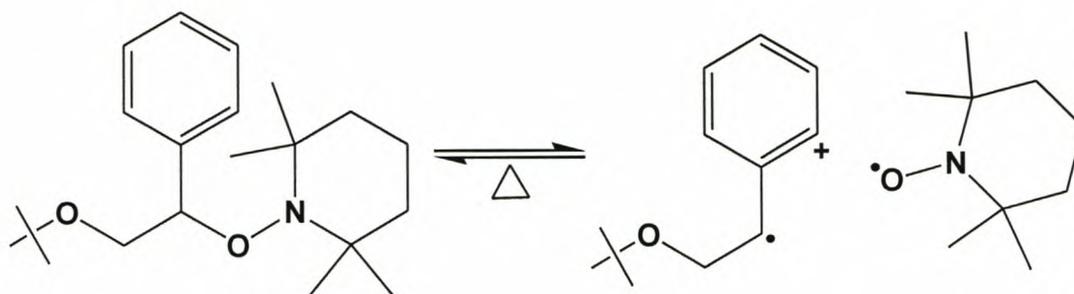
Scheme 2.7: CFRP via the homolytic cleavage of a weak covalent bond in the dormant species.

This process can be spontaneous upon heating²⁵ or be catalyzed.²⁶

A number of methods to obtain CFRP have been developed and will be briefly discussed in Sections 2.4.2-2.4.6.

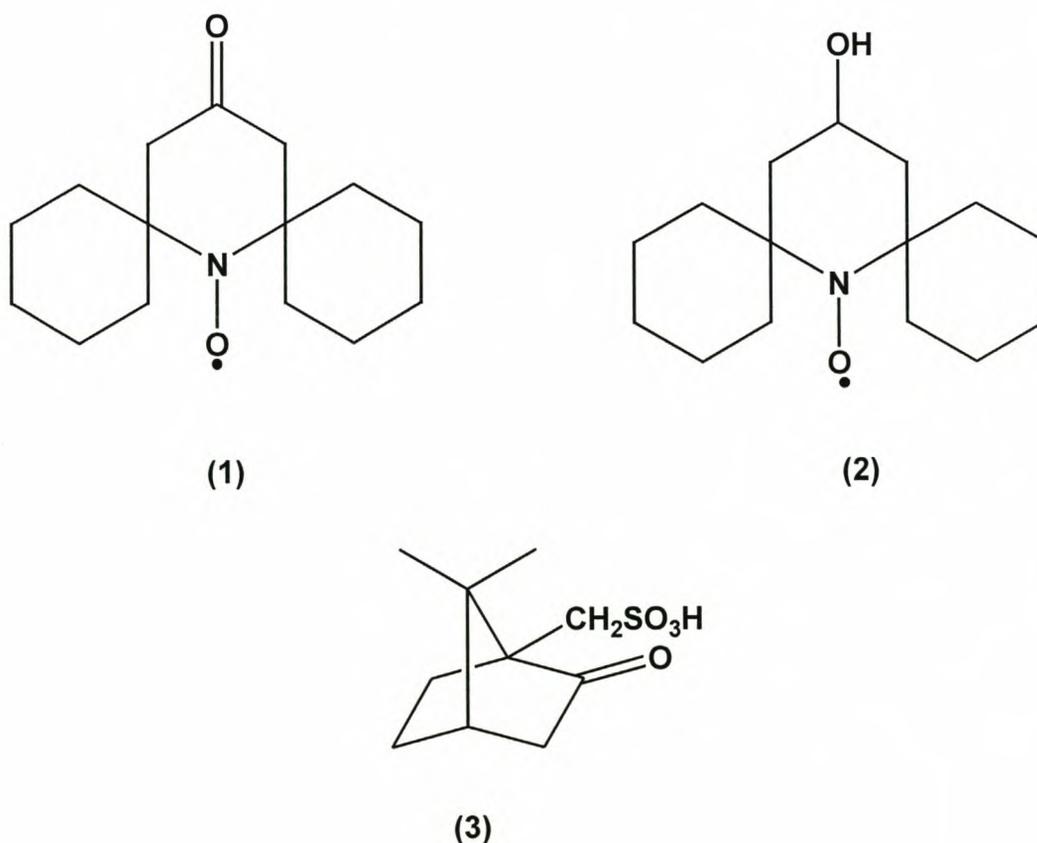
2.4.2 Nitroxide-mediated controlled free radical polymerization

This technique is based on the reversible capping of the growing polymer chain by a nitroxide compound. The carbon-oxygen bond formed during the capping reaction is weak; it has a bond dissociation energy of 25-30 kcal.mol⁻¹. This bond can dissociate at about 125°C to allow the polymer chain to grow.²⁷ Alkoxyamines are commonly used as nitroxides for obtaining CFRP. Scheme 2.8 illustrates the thermal dissociation of 1-*tert*-butoxy-2-phenyl-2-(1-oxy-2,2,6,6-tetramethylpiperidinyl)ethane to give 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) and an alkyl radical.



Scheme 2.8: *Reversible thermolysis of an alkoxyamine to produce TEMPO.*

The alkyl radical can initiate polymerization while the nitroxide radical will reversibly cap the growing polymer chain and prevent termination. The capping of the polymer chain with the nitroxide has been proved by ^1H NMR spectroscopy.²⁸ Nitroxide-mediated radical polymerization is only successful when styrene monomer or styrene derivatives are used. The high temperatures (110°C-140°C) at which the reaction has to be conducted are also a drawback, especially when emulsion systems are involved. Improvements in this regard have been made recently.²⁹ Living radical polymerization of styrene at lower temperatures (70°C-110°C) has been achieved by utilizing nitroxides with dispiro structures (**1** and **2**).





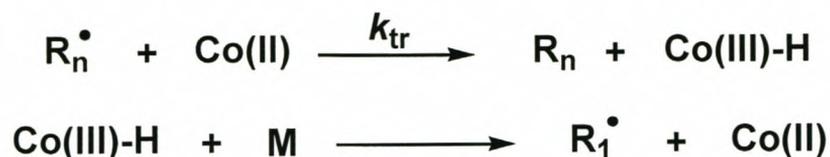
Scheme 2.10: A representation of the degenerative transfer process.

The transfer agent reacts with a propagating radical to form a dormant chain and a new radical species that can initiate further polymerization. The propagating radical species can then react with a dormant chain, which will enable it to propagate further; thus equilibrium between growing and dormant chains is established. This process differs quite significantly from degradative chain transfer where the dormant chain cannot be reactivated after reacting with the transfer agent. In degenerative chain transfer reactions the total concentration of polymer chains is equal to the sum of the concentrations of the transfer agent and consumed initiator. If the initial initiator concentration is kept sufficiently low and the targeted molecular weights are not too high, this process can reduce termination to a negligible level.³¹

2.4.5 Organometallic Compounds as Catalytic Chain Transfer Agents

Co(II) catalysts have high chain transfer constants (in the order of $10^3 - 10^4$) and minute quantities are necessary to achieve control in free radical polymerization reactions.³²

The chain transfer reaction involves a growing polymer chain that encounters a Co(II) complex. This encounter results in β -H abstraction that, in turn, leads to the formation of a dead polymer chain with an unsaturated endgroup and a Co(III)-H species. Reaction of the Co(III)-H species with monomer forms a monomeric radical capable of propagation and the Co(II) catalyst is regenerated. This is shown schematically in Scheme 2.11.



Scheme 2.11: Achieving controlled free radical polymerization by the use of catalytic chain transfer to synthesize macromonomers, using a Co(II) catalyst.

An example of an Co(II) complex is bis(boron difluorodimethylglyoximate)cobaltate(II) or COBF. The structure of the catalyst is shown in Figure 2.2.

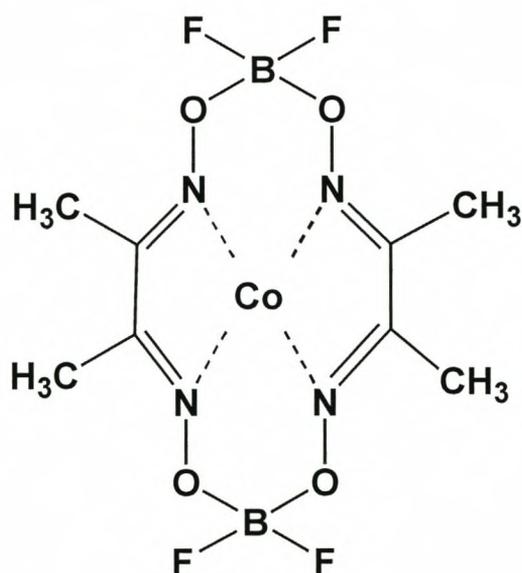
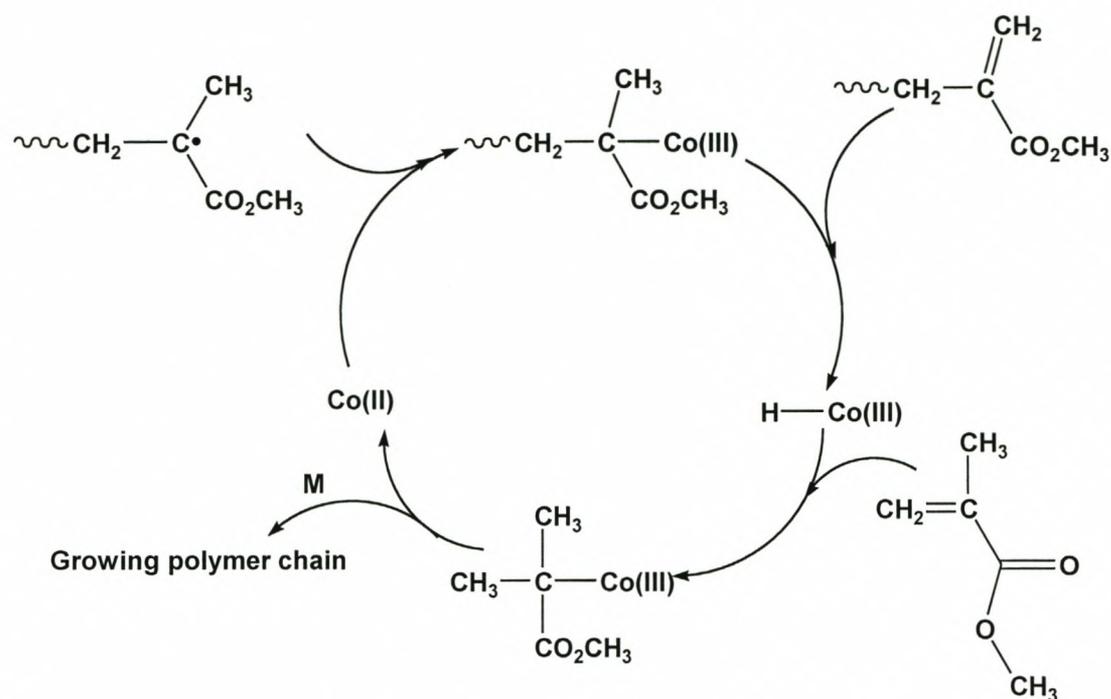


Figure 2.2: Structure of the catalytic chain transfer agent COBF.

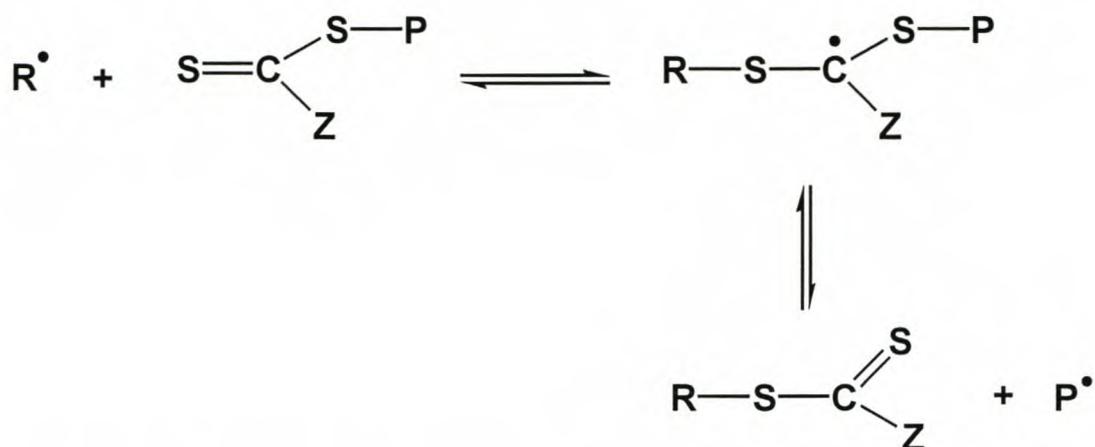
The process of achieving CFRP through the use of organometallic compounds as catalytic chain transfer agents is a cyclic process. This is depicted in Scheme 2.12, in which methyl methacrylate is used as an example.³³



Scheme 2.12: CFRP in which an organometallic system is used as a means for catalytic chain transfer.

2.4.6 Reversible Addition-Fragmentation Chain Transfer (RAFT)

The process of reversible addition-fragmentation chain transfer involves the homolytic cleavage of a weak carbon-sulfur bond and the reversible end-capping of propagating polymer chains with a dithioester moiety.²⁰ The mechanism of this is shown in Scheme 2.13.



Scheme 2.13: Mechanism of the RAFT process.

The dithioester is of the general structure Z-C(S)-S-R. In the early stages of polymerization there is addition of an initiating radical to the dithioester via the carbon-sulfur double bond. This leads to the formation of an intermediate radical that undergoes fragmentation, to yield a new radical species capable of propagating, as well as a dormant end-capped chain. The equilibrium between the propagating and dormant chains give all the polymer chains equal probability to grow, leading to living characteristics and narrow polydispersities. Dithio-endgroup detection by means of ^1H NMR spectroscopy³⁴ and detection of the intermediate radical by ESR spectroscopy³⁵ supports this mechanism.

The correct choice of the substituents R and Z in the dithioester Z-C(S)-S-R is crucial to ensure the efficient function of the compound in a polymerization reaction. Z is the so-called stabilizing group and it strongly affects the addition of radicals to the carbon-sulfur double bond. Aryl or alkyl substituents as choices for Z give the best results. R must be a good leaving group upon homolytic cleavage of the weak covalent carbon-sulfur bond. The correct choice of the stabilizing and leaving groups will ensure a fast addition-fragmentation rate to yield polymers with low polydispersities. In the absence of chain transfer the total number of polymer chains formed will be equal to (or less than) the sum of the moles of dithio compound employed and the moles of initiator-derived radicals.³⁶

The RAFT process is extremely versatile and has many advantages:^{20, 37, 38}

- The RAFT process conveys living characteristics to conventional free radical polymerization reactions.
- Polymers with complex architectures (stars, blocks and grafts) and compositions (e.g. gradient) can be synthesized.
- Telechelic polymers can be readily synthesized.
- The process is compatible with a wide range of monomers, including functional monomers.
- Polymers with low polydispersities (<1,2) are obtained.
- The process can be successfully employed under conventional free radical reaction conditions in terms of initiators, solvents and temperatures.
- The degree of polymerization is the ratio of the number of monomer units consumed to the concentration of dithio molecules.
- The Trommsdorff-Norrish gel effect is not observed, since k_{act} and k_{deact} decrease by roughly the same amount. There is never an inequality in terms of rates of propagation and termination.
- Molecular weights increase in a linear and predictable manner with conversion.
- Molecular weight is controlled by the stoichiometry of the reaction and can be predicted theoretically using Equation 2.2:

$$MW_{prod} = \frac{[monomer]}{[CTA]} \times MW_{mon} + MW_{cta} \quad (2.2)$$

where [monomer] is the moles of consumed monomer, [CTA] is the moles of employed transfer agent, MW_{mon} and MW_{cta} are the molecular weights of the monomer and the chain transfer agent respectively. A conversion factor can be introduced if all of the monomer is not consumed.

- Transfer constants³⁹ of the compounds with the general formula Z-C(S)-S-R are very high (>20) whereas macromonomers have very low transfer constants (<2). This leads to starved feed conditions not being necessary to obtain materials with low polydispersities.

- Compounds of the general formula Z-C(S)-S-R do not undergo copolymerization with monomers.
- Controlled, multimodal molecular weight distributions can be obtained by introducing the chain transfer agent in a controlled manner over the duration of a polymerization reaction.

Disadvantages associated with this technique include:

- Synthesis and purification of the dithio-compounds are both time-consuming, costly and laborious.
- Polymerization reaction rates decrease when conducted in the presence of the RAFT-agents.
- RAFT cannot be used directly in conventional emulsion polymerization reactions due to phase separation of the oligomeric dithio-encapped chains.

From the discussion above it can be seen that RAFT presents itself as a very attractive alternative to pursue in the field of controlled free radical research. From an industrial viewpoint RAFT is an exciting development; it requires no special reaction conditions and leaves no contaminants upon completion of the polymerization process. This is especially important in the synthesis of dispersants and rheology modifiers.

2.4.7 Controlled Free Radical Polymerization in Aqueous Media

The vast majority of industrial polymerization reactions are done in emulsion systems. This is in accord with the ever-increasing global trend to meet the needs of the environment and its residents. Therefore, any novel radical polymerization process that appears to be able to improve an existing status quo must succeed in doing so in emulsion systems. Without success in emulsion systems, the chance of any new process being widely accepted in industry is very slim indeed.

The obvious challenge in the ever-expanding field of controlled free radical research is to make a novel technique succeed in an aqueous medium. This has been the focus of many studies and good results have been obtained with ATRP^{40, 41}, nitroxides⁴²,

degenerative transfer^{43, 44}, catalytic chain transfer⁴⁵ as well as for the RAFT process.⁴⁶⁻

⁴⁸ There remains much research still to be done to obtain an understanding of the reaction kinetics and mechanisms of the different techniques. Reaction conditions for the different techniques under investigation must also be optimized.

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$$k_{tr} = k_{add} \times \frac{k_{\beta}}{k_{-add} + k_{\beta}} \quad (2.3)$$

where k_{add} is the rate constant for addition to the chain transfer agent and k_{-add} and k_{β} are the rate constants for fragmentation in the reverse and forward directions respectively.

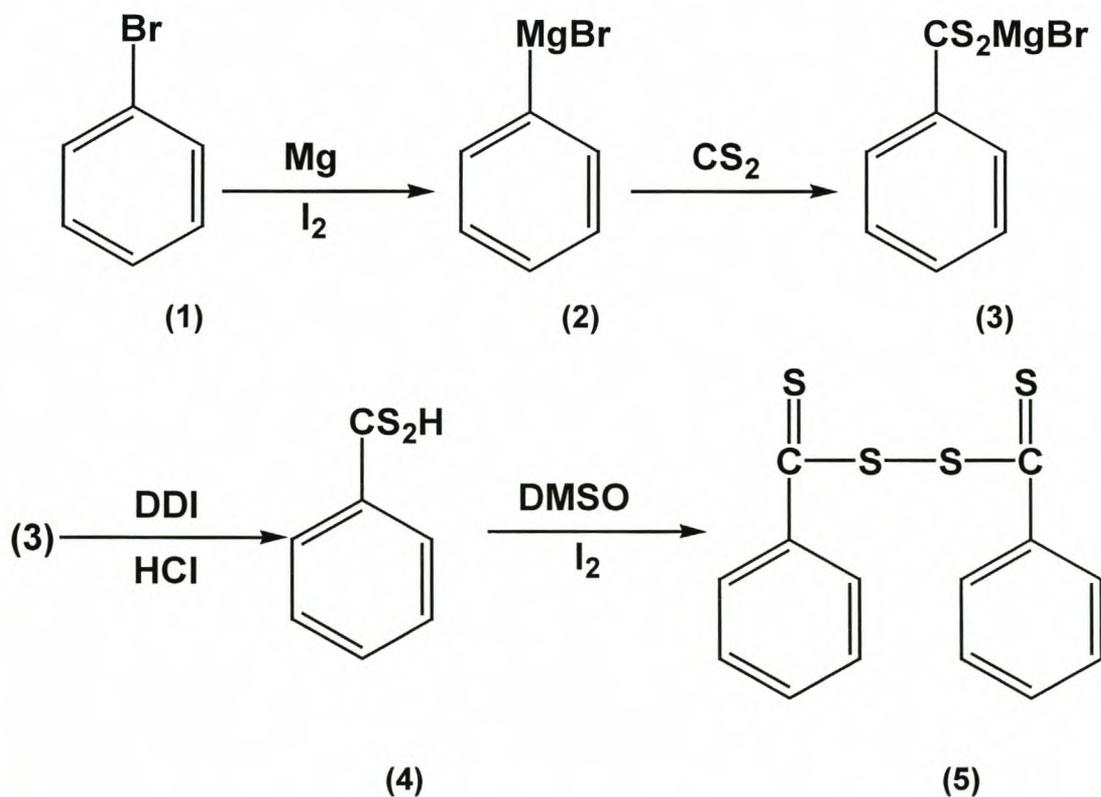
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Chapter 3: Synthesis and Characterization of RAFT-agents

3.1 Synthesis of the RAFT-agents

The following RAFT-agents were synthesized: 2-cyanobut-2-yl dithiobenzoate and 1-cyano-1-cyclohexyl dithiobenzoate.

The RAFT-agents to be used in this study were prepared by first synthesizing dithiobenzoic acid (**4**). This was followed by the preparation of di(thiobenzoyl) disulfide (**5**) and the selected RAFT-agents (Sections 3.1.1 and 3.1.2) as described in the patents of Rizzardo *et al*¹ and Le *et al*.² A schematic representation of the reaction route used for the synthesis of the di(thiobenzoyl) disulfide (**5**) is given in Scheme 3.1.



Scheme 3.1: Reaction route used for the synthesis of di(thiobenzoyl) disulfide.

Magnesium turnings (2g), together with a catalytic amount of iodine crystals, were added to a 250ml three-necked reaction vessel fitted with a condenser, two dripping funnels and a magnetic stirrer. The condenser and dripping funnels were fitted with CaCl₂ drying tubes to ensure the absence of water. One dripping funnel was charged with bromobenzene (Fluka, 12,56g) and the other with dry, distilled tetrahydrofuran (THF, 60ml).

The reaction was initiated by slight heating (20°C). The colour of the reaction mixture changed from dark purple to clear metallic, indicating the onset of the Grignard reaction. The temperature was kept at 0°C using an ice bath. The contents of both dripping funnels were added over the course of 30 minutes, while carefully controlling the reaction temperature.

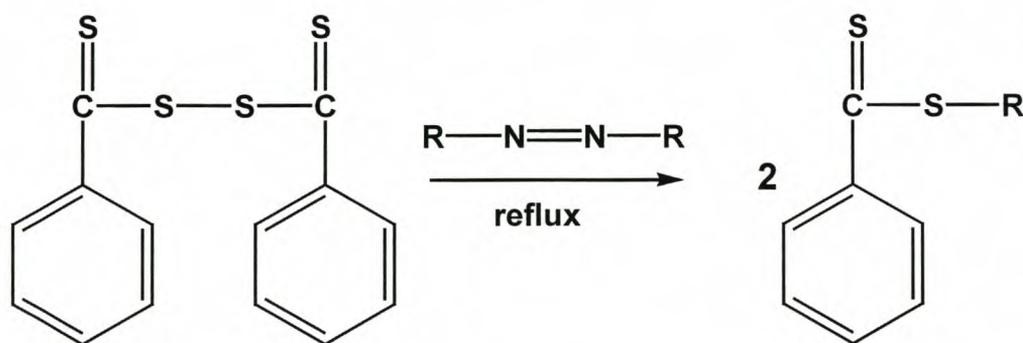
CS₂ (Aldrich, 6,10g) was then added to an empty dripping funnel, from which it was carefully added to the reaction mixture. The exothermic reaction was controlled using an ice bath. Distilled, deionized water (DDI) was then added by means of a dripping funnel, leading to the formation of the MgBr-salt of dithiobenzoic acid. DDI was added until there was no change in reaction temperature, indicating completion of the exothermic reaction. The reaction mixture was then filtered and the THF evaporated from the filtrate under reduced pressure on a rotary evaporator.

Concentrated HCl was added dropwise to the reaction mixture until the brown-red mixture took on a purple, plum colour. This colour change is indicative of the formation of dithiobenzoic acid (**4**) from its MgBr-salt. The mixture was washed with equal aliquots of diethyl ether until the ether extract no longer showed red traces of dissolved dithiobenzoic acid. The ether was removed by rotary evaporation and the product dissolved in 100ml ethanol. Dimethyl sulfoxide (DMSO, Saarchem, 12,50g) and a catalytic amount of iodine crystals were added to the ethanol mixture and stirred at room temperature, using a magnetic stirrer. This was done in a one-neck reaction vessel fitted with a condenser. After stirring for one hour the reaction mixture was placed in a

refrigerator (2°C) overnight. The mixture was then filtered and the di(thiobenzoyl) disulfide (**5**) was obtained as a purple, crystalline material.

The di(thiobenzoyl) disulfide can be readily recrystallized from lukewarm ethanol for purification purposes. The disulfur bond present in the compound makes it extremely susceptible to decomposition caused by UV-irradiation and heat. To prevent degradation during storage, the compound should be stored in the dark and at low temperatures.

The di(thiobenzoyl) disulfide was converted to the selected dithioester by heating (**5**) in the presence of an azo-compound.³ A general reaction procedure to illustrate this is shown in Scheme 3.2. Usually (**5**) is heated with 1.5 molar equivalents of the azo-compound to compensate for the solvent cage effect.⁴ This cage effect can cause up to 30-50% of the azo-compound derived radicals to react (for example, recombine) within the solvent cage and may therefore cause a shortage of radicals supplied to the reaction.

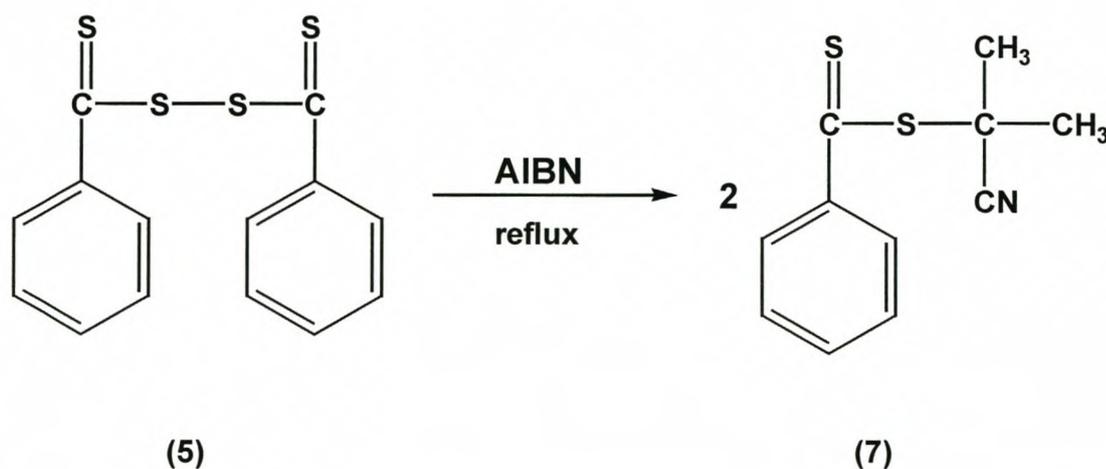
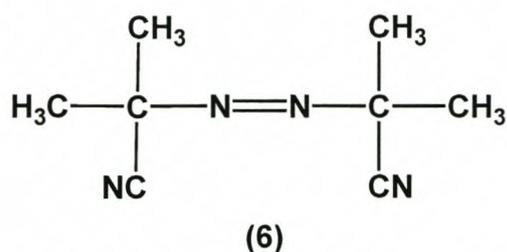


Scheme 3.2: Schematic representation of the preparation of dithioesters by heating di(thiobenzoyl) disulfide in the presence of an azo-compound.

The reaction involves a free radical mechanism and must be conducted in the absence of oxygen. This can be achieved by either refluxing the reaction mixture or by degassing the mixture using N₂.

3.1.1 Synthesis of 2-cyanobut-2-yl dithiobenzoate

2-cyanobut-2-yl dithiobenzoate (**7**) was synthesized by heating di(thiobenzoyl) disulfide (**5**) (0,101g, $3,28 \times 10^{-4}$ moles) in the presence of azobisisobutyronitrile (AIBN, 0,081g, $4,939 \times 10^{-4}$) (**6**) as shown in Scheme 3.3. To facilitate discussion, (**7**) will be referred to as AIBN-RAFT.



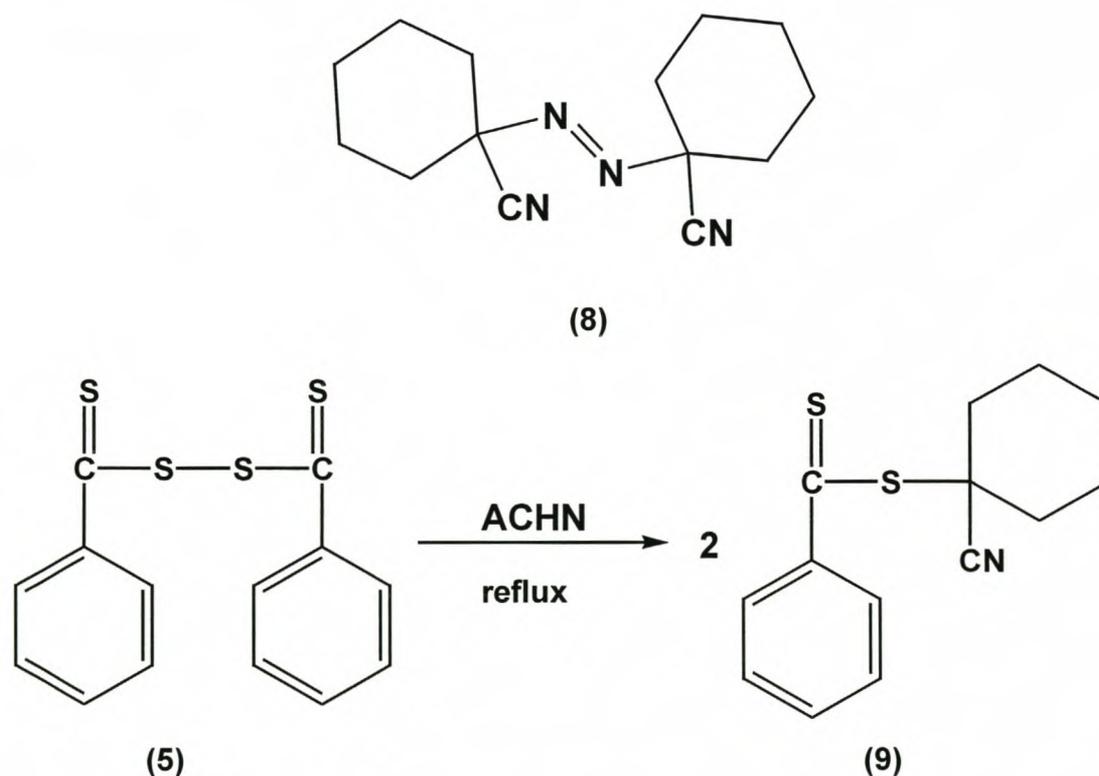
Scheme 3.3: Preparation of 2-cyanobut-2-yl dithiobenzoate by heating di(thiobenzoyl) disulfide in the presence of AIBN.

AIBN was first recrystallized from methanol at 2°C. The synthesis was conducted at 80°C for 20 hours under reflux with ethyl acetate as solvent. The reaction time used in this synthesis corresponds to 4-5 times the half-life of the selected azo-compound at the specific reaction temperature.

The solvent was removed under reduced pressure to yield the product (**7**) as a red, viscous oil. The compound was purified by column chromatography with silica gel (Kieselgel 60, 0,063-0,2mm, 70-230 mesh ASTM) as the stationary phase. A mixture of *n*-heptane (90% v/v) and ethyl acetate (10% v/v) was used as the mobile phase.

3.1.2 Synthesis of 1-cyano-1-cyclohexyl dithiobenzoate

1-cyano-1-cyclohexyl dithiobenzoate (**9**) was synthesized by heating di(thiobenzoyl) disulfide (**5**) in the presence of 1,1'-azobis(cyclohexanecarbonitrile) (**8**) (ACHN, Aldrich, 0,120g), as depicted in Scheme 3.4. To facilitate discussion, (**9**) will be referred to as ACHN-RAFT.



Scheme 3.4: Schematic representation of the preparation of 1-cyano-1-cyclohexyl dithiobenzoate by heating di(thiobenzoyl) disulfide in the presence of ACHN.

1,1'-azobis(cyclohexanecarbonitrile) (ACHN) has a half-life of 1400 minutes at 80°C, which is considerably longer than the half-life of 65 minutes for AIBN at the same temperature. This necessitates a longer reaction time for the formation of (9). The reaction was conducted under the same conditions as used for the preparation of (7), except that the reaction time was increased to 48 hours.

After removal of the ethyl acetate solvent under reduced pressure on a rotary evaporator, the product was isolated as an orange, viscous oil. The same purification procedure was followed as for (7).

3.2 Characterization of the RAFT-agents

Both ^1H NMR and ^{13}C NMR spectroscopy were used to characterize the two dithioesters (7 and 9) and the di(thiobenzoyl) disulfide (see appendix I). Results showed that the title compounds were indeed successfully synthesized and that they were pure. This underlined the fact that the purification methods used for the individual title compounds were indeed successful.

3.3 Conclusions

In this chapter it was described how the simple heating of di(thiobenzoyl) disulfide in the presence of different azo-initiators leads to the formation of the corresponding dithioesters. The high yields obtained in these reactions confirmed the efficiency of this approach to synthesize dithioesters. These dithioesters can be used as chain transfer agents in polymerization reactions to control the free radical polymerization process.

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Chapter 4: Solution Polymerization Studies

4.1 Background

As mentioned in Section 3.1.1, the dithioesters used as RAFT-agents are usually obtained as viscous oils. This necessitates the use of column chromatography for purification, which can be laborious and time consuming.

In various patents^{1,2} it is stated that the reaction of di(thiobenzoyl) disulfide with any azo-compound can be conducted in the presence of monomer, yielding a system in which living characteristics are conveyed to the free radical polymerization process. Living characteristics comprise a linear relationship between molecular weight and conversion while maintaining low polydispersities (<1,3). Irreversible termination is also kept to a minimum and thus chain growth can commence upon further addition of monomer after the reaction is complete.

It was decided that, in the present study, the *in situ* formation of the RAFT-agent in the system was the route to be followed. This was because of the number of inherent advantages associated with the process. These advantages include the relatively simple purification process for crystalline materials (azo-compounds and di(thiobenzoyl) disulfide) and the ease of handling crystalline materials compared to viscous oils. Scheme 3.2 (see Section 3.1) illustrates the general reaction that was conducted in the presence of monomer.

Although it was assumed, for experimental purposes, that the reaction depicted in Scheme 3.2 proceeds to completion, enough unreacted azo-compound was usually present to initiate the polymerization reaction. The amount of unreacted azo-initiator can be calculated using the equation corresponding to a decomposition curve for the initiator at a specific temperature. This is shown in Figure 4.1, using AIBN and starting at $6,85 \times 10^{-4}$ moles at 80°C , as an example.

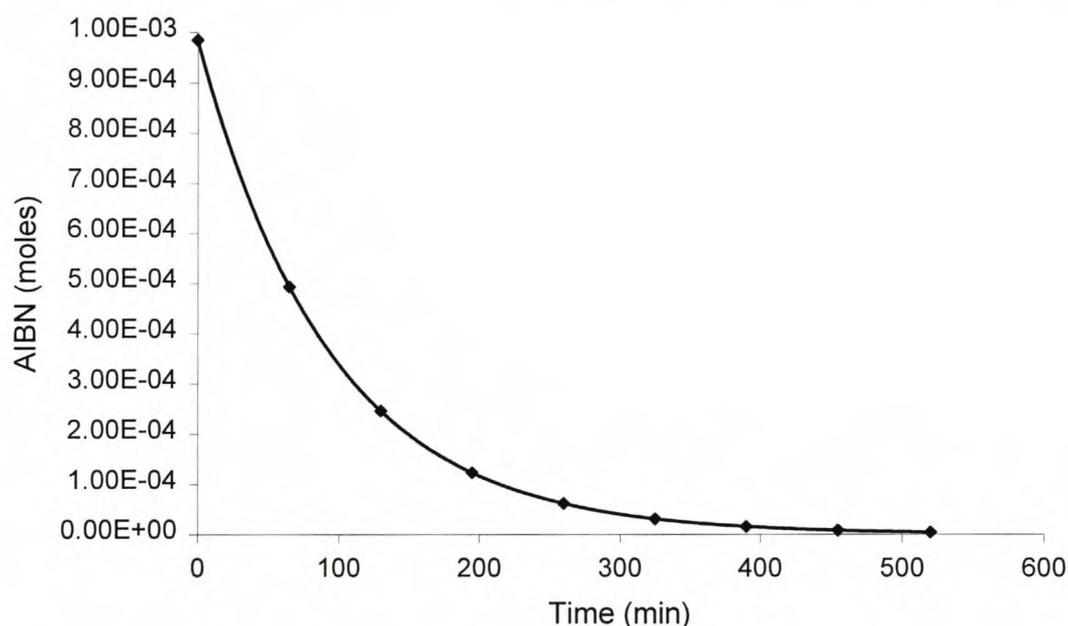


Figure 4.1: Curve illustrating the exponential decomposition rate of AIBN at 352K (80 °C)

4.2 Experimental

Styrene was selected as monomer for all studies in this project. In all experiments the styrene monomer was first washed with two equal aliquots of a 0.3 M aqueous KOH solution to remove inhibitors. This procedure was followed by distillation under reduced pressure. The styrene was kept over molecular sieves at 2°C for later use. All AIBN was recrystallized from methanol at 2°C , ACHN (Aldrich) was used as received and the di(thiobenzoyl) disulfide was recrystallized from ethanol. Distilled ethyl acetate was used as polymerization solvent in a 3:1 ratio with styrene monomer. In all cases the ethyl acetate/styrene mixtures were degassed by bubbling N_2 through the mixture for 30

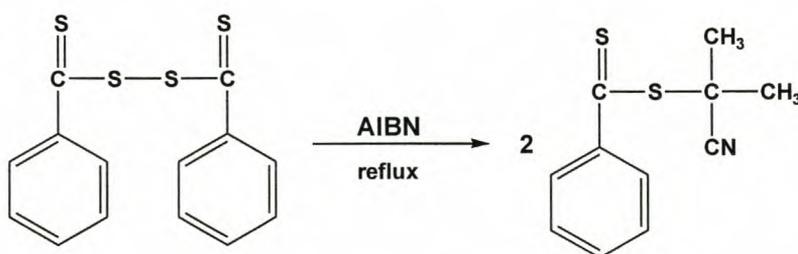
minutes at room temperature. After adding the azo-compound and di(thiobenzoyl) disulfide N_2 was again bubbled through the mixture for another 30 minutes at room temperature. All reactions were conducted under N_2 at $80^\circ C$ in a three-neck reaction vessel fitted with a condenser, thermometer and rubber septum.

Samples were precipitated using a 2.5% (m/v) hydroquinone (Aldrich) in methanol solution and dried under vacuum. Conversions were calculated gravimetrically and molecular weights determined by gel permeation chromatography (GPC).

The GPC instrument consisted of a Waters 717_{plus} Autosampler, Waters 600E System Controller and a Waters 610 fluid unit. The Waters 410 differential refractometer at $35^\circ C$ was used as detector. THF (HPLC-grade) sparged with IR-grade helium was used as eluent at a flow rate of $1\text{ml}\cdot\text{min}^{-1}$ and 60 minutes per sample. The column oven was kept at $35^\circ C$ and the injection volume was $100\mu\text{l}$. Four Phenogel columns ($300\text{mm}\times 7,80\text{mm}$) with respective pore sizes of 100\AA , 10^3\AA , 10^4\AA and 10^5\AA were used in series (GPC calibrated using six narrow polystyrene molecular weight standards in the range of $4\,000 - 2\,000\,000\text{g}\cdot\text{mol}^{-1}$ supplied by Pressure Chemical).

4.2.1 *In situ* formation of AIBN-RAFT

The general reaction depicted in Scheme 3.2, was conducted in the presence of styrene monomer (Scheme 4.1):



Scheme 4.1: Reaction conducted in the presence of styrene monomer to lead to the *in situ* formation of AIBN-RAFT.

By utilizing Equation 2.2 (see Section 2.4.6) it becomes possible to target a specific molecular weight to be reached after full conversion. It was decided to target a molecular weight of $8,3 \times 10^3 \text{g}\cdot\text{mol}^{-1}$. For this, the following quantities were used: styrene 50,0g, ethyl acetate 150,0g, di(thiobenzoyl) disulfide 0,919g, AIBN 0,903g. Samples were drawn at regular intervals to follow conversion and molecular mass. Results are shown in Table 4.1

Conversion (%)	Time (h)	\bar{M}_n	\bar{M}_w	PDI
15,1	0,18			
17,2	0,35			
19,2	0,53			
21,0	1,83	4975	5147	1,03
31,0	2,67	5720	6199	1,08
44,8	4,07	6882	7863	1,14
76,0	21,22	8839	11339	1,28
80,5	28,72	8932	11495	1,29
83,8	45,42	9126	11773	1,29
86,0	51,87	9203	11891	1,29

Table 4.1: *Experimental results of the in situ AIBN-RAFT solution polymerization of styrene in ethyl acetate. (Blank entries imply samples with molecular weights below the lowest molecular weight GPC standard.)*

The conversion profile (Figure 4.2), as well as the relationship between molecular weight and conversion (Figure 4.3), are shown below.

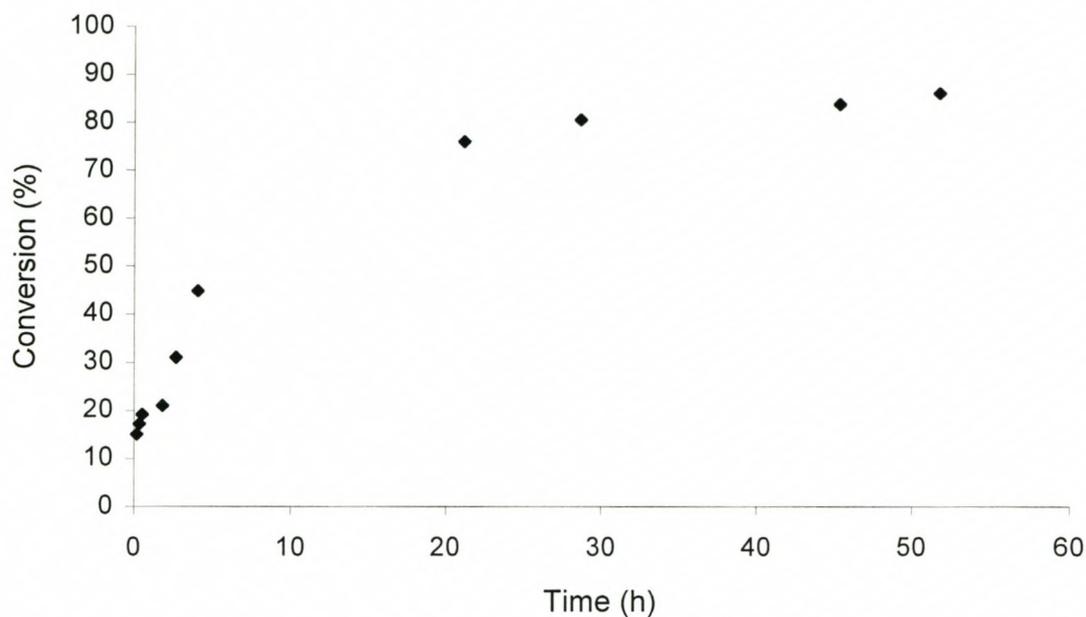


Figure 4.2: Conversion profile of the in situ AIBN-RAFT solution polymerization of styrene in ethyl acetate.

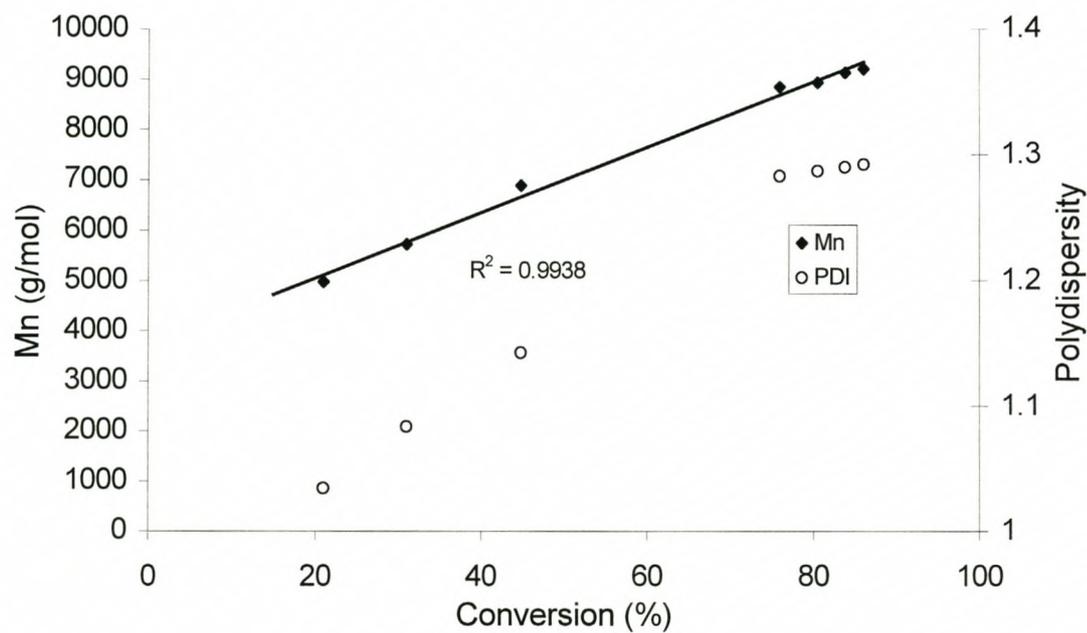


Figure 4.3: Graphic representation of the linear relationship between \bar{M}_n and conversion for the in situ AIBN-RAFT solution polymerization of styrene in ethyl acetate.

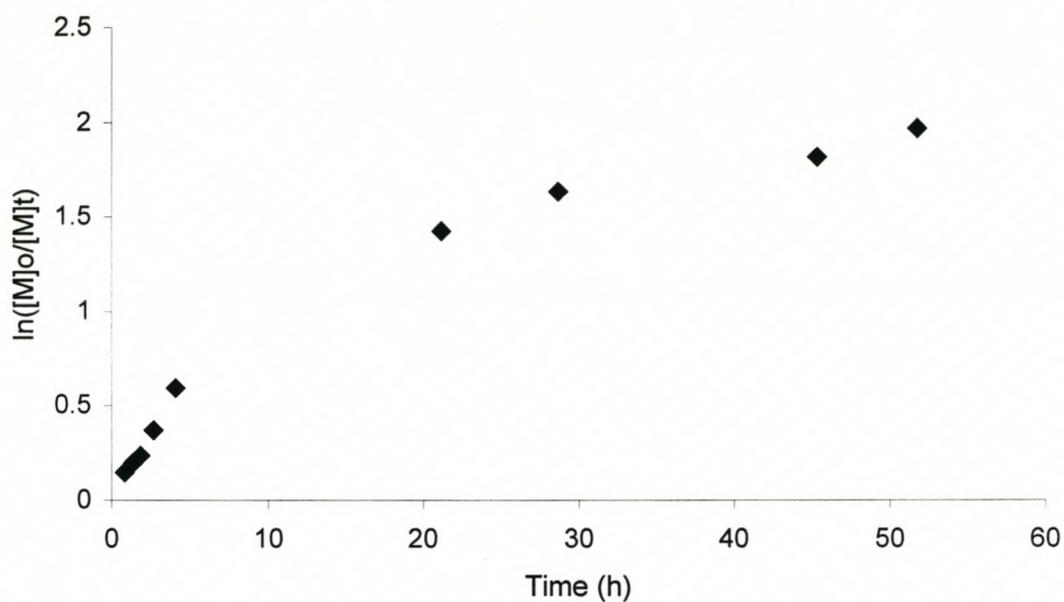
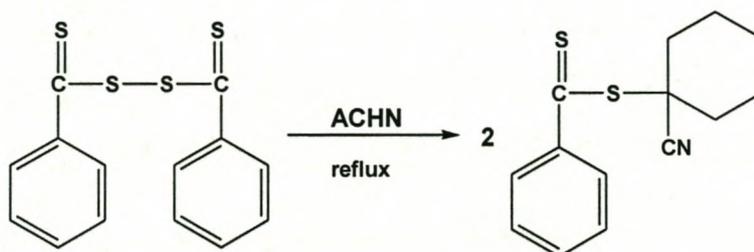


Figure 4.4: Graphic representation of the kinetic behaviour of the in situ AIBN-RAFT polymerization of styrene in ethyl acetate.

4.2.2 In situ formation of ACHN-RAFT

For this experiment the following reaction was conducted in the presence of styrene monomer (Scheme 4.2):



Scheme 4.2: Reaction conducted in the presence of styrene monomer to lead to the in situ formation of ACHN-RAFT.

As mentioned previously, ACHN has a longer half-life (37 times) than that of AIBN at 80°C.³⁻⁵ The following quantities of reagents were used: styrene 50,0g, ethyl acetate 150,0g, di(thiobenzoyl) disulfide 0,153g, ACHN 0,183g. Experimental results are shown in Table 4.2, and Figures 4.5, 4.6 and 4.7.

Conversion (%)	Time (h)	\overline{M}_n	\overline{M}_w	PDI
11,6	0,55			
11,7	0,73			
16,7	1,27			
25,2	9,77	15212	19337	1,27
50,0	21,80	26383	40584	1,54
62,1	26,57	28831	45171	1,57
70,1	33,05	31203	51059	1,64
90,5	45,42	34722	57295	1,65
99,9	54,13	33415	58382	1,75

Table 4.2: *Experimental results of the in situ ACHN-RAFT solution polymerization of styrene in ethyl acetate.*

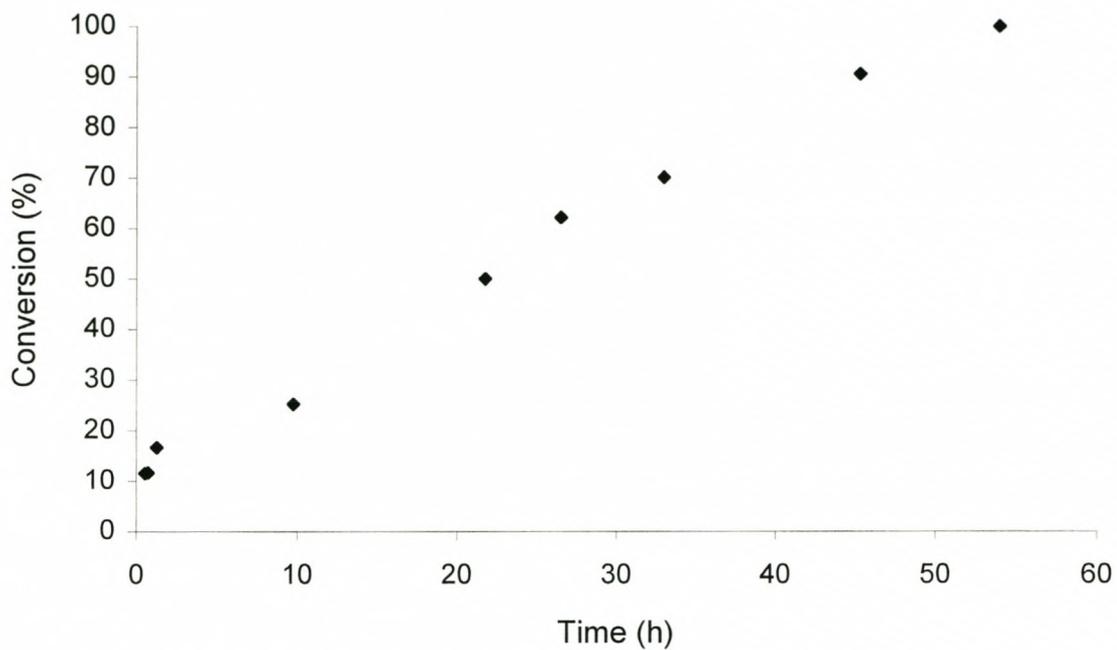


Figure 4.5: Conversion profile for the in situ ACHN-RAFT solution polymerization of styrene in ethyl acetate.

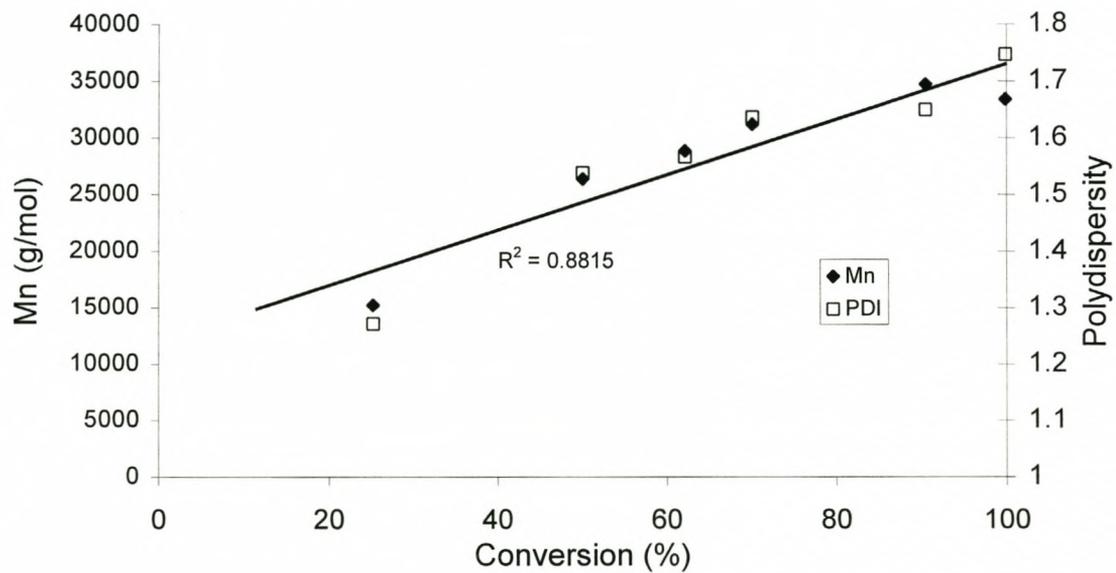


Figure 4.6: Graphic representation of the relationship between \bar{M}_n and conversion for the in situ ACHN-RAFT solution polymerization of styrene in ethyl acetate.

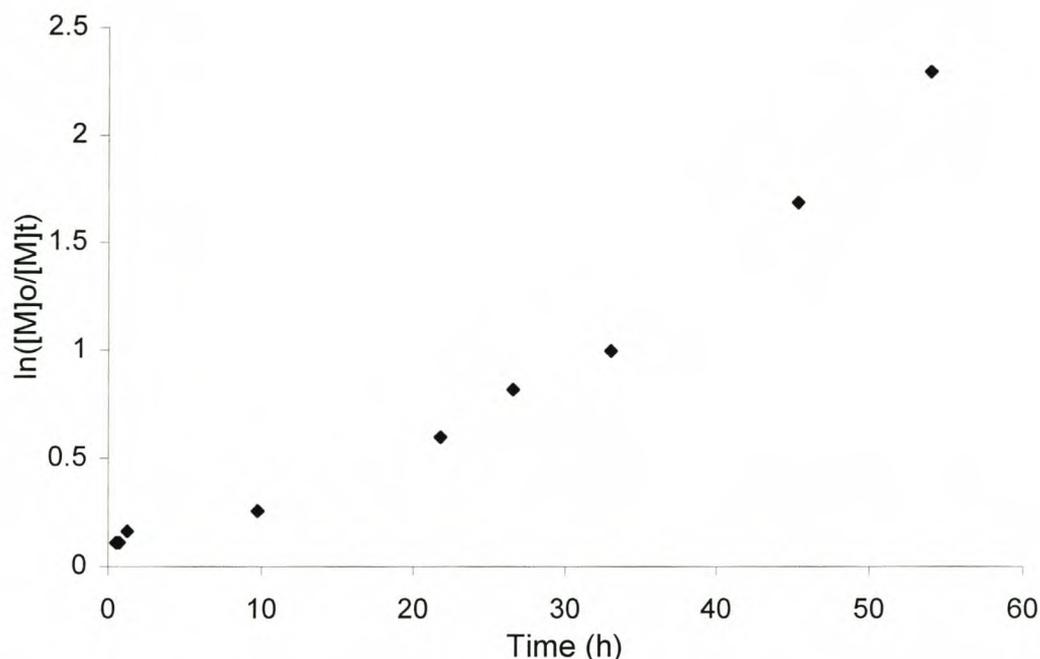


Figure 4.7: Graphic representation of the kinetic behaviour for the in situ ACHN-RAFT solution polymerization of styrene in ethyl acetate.

4.3 Discussion

From the results it is evident that the AIBN initiated system gave the best results, in terms of low polydispersities throughout the polymerization reaction and linear relationship between molecular weight and conversion. The initiation period in these systems will be shorter than in the case of the ACHN systems owing to the difference in half-lives (AIBN 65 minutes at 80°C and ACHN 1400 minutes at 80°C) of the initiators. The living characteristics of the AIBN system can clearly be seen from the characteristic conversion profile as well as the linear relationship between number average molecular weight and conversion. The molecular weight obtained in the AIBN system is also well within range of the targeted molecular weight. The discrepancy between theoretical and experimental molecular weight can be ascribed to experimental error and incomplete removal of oxygen from the system.

The results from the ACHN initiated system were not good. A poor linear relationship between number average molecular weight and conversion, together with the obtained conversion profile, underlines the fact that living characteristics was not endowed upon this system. The considerably longer half-life of ACHN could have the effect of insufficient azo-derived radicals forming early in the reaction to form dithioesters. The azo-initiator has a two-fold role in this system. One function is to initiate polymerization and the other function is to react with di(thiobenzoyl) disulfide to form RAFT-agents. A longer half-life (as with ACHN) will not have an effect on the initiation of the polymerization process – although it will be slower. Where the impact of an azo-initiator with a longer half-life will be seen is in the inability to form RAFT-agents fast enough to sustain a living system. For the RAFT-process to be efficient, the number of RAFT molecules must be higher than the number of initiator-derived radicals. If this is not the case then the probability of growing chains encountering each other and not a dithioester is high and irreversible termination might occur. This will lead to the formation of high molecular weight compounds that will influence the value of \bar{M}_w profoundly. This is indeed observed in the polydispersity values that increase throughout the duration of the reaction.

From the logarithmic kinetic curves for the two different azo-initiators a few aspects become evident. Neither of the curves display a well defined linear relationship between $\ln([M]_0/[M]_t)$ and time, as is expected for a truly living system. This can be ascribed to the inherent complications associated with the *in situ* RAFT-agent formation; in that one can only make an educated guess at exactly how many RAFT-agents there are present at any given time. For calculation purposes it must be assumed that the reaction between the azo-initiator and di(thiobenzoyl) disulfide proceeds rapidly and to completion, with some fraction of initiator derived radicals initiating the polymerization reaction. The logarithmic curve for the AIBN-RAFT system shows a slow initial reaction rate, which then increases in a fairly abrupt and linear way, slowing slightly at high conversion. This may indicate that the AIBN generated radicals react faster with the di(thiobenzoyl) disulfide than with the styrene units to initiate polymerization. As the reaction continues

the di(thiobenzoyl) disulfide becomes depleted and chain initiation becomes more probable. Enough RAFT-agents are formed at this stage to ensure that the polymerization proceeds in a controlled manner. The decomposition of AIBN is fast enough to maintain low polydispersities.

The ACHN system exhibits a reaction rate that continues to rise even at complete conversion. The long half-life of this azo-initiator has the effect of initiator-derived radicals being formed throughout the course of the polymerization reaction. Initially there is not an abundance of initiator-derived radicals available as was the case with the fast decomposing AIBN. The competition between styrene units and di(thiobenzoyl) disulfide molecules for primary radicals is high and not as many RAFT-agents will form initially. Furthermore, new chains are being initiated as the polymerization reaction proceeds and this can be observed by the number average molecular weight dropping below the linear trend at full conversion. This can also be seen by the increasing rate of reaction.

4.4 Conclusions

In situ RAFT-agent formation in a solution polymerization seems to give good results. It does, however, bring with it a couple of inherent complications. The most interesting is the partitioning of the azo-initiator derived radicals between two possible fates. These competing fates are: reaction with a monomer unit to initiate polymerization or reaction with a di(thiobenzoyl) disulfide to form a dithioester chain transfer agent. This partitioning of radicals will differ for different azo-initiators and for different monomers, and is expected to depend on the relative rate coefficients for reaction of the initiator-derived radical with each species, the concentration of each species and the molecular structure of the initiator. Results are expected to improve as the employed initiator's half-life decreases, such as is observed when the results for the systems initiated by ACHN and AIBN are compared. A shorter half-life, combined with initiator-derived radicals that have a greater affinity for di(thiobenzoyl) disulfide than for styrene, will ensure that an adequate number of chain transfer agents form initially to take part in the polymerization process. It will also prevent the continuous initiation of new chains.

4.5 Bibliography

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Chapter 5: Synthesis and Characterization of Oligomers

5.1 Background

Previous attempts to use RAFT successfully in emulsion polymerization had the common problem of phase separation in the form of a conspicuous red layer.^{1, 2} The red colour is indicative of dithiobenzoate-endgroup-containing compounds. Analysis of the red layer showed it to consist of monomer-swollen oligomers with dithiobenzoate endgroups.² As stated in Chapter 1, these dithiobenzoate-endcapped oligomers phase separate from the aqueous phase due to their high water insolubility. This insolubility of the oligomers makes transport from droplets to aqueous nucleation sites through the water phase highly unlikely. Red layer formation is then observed, in the course of the reaction, as the oligomers phase separate to form a new phase.

The obvious underlying challenge is to bypass any aqueous phase transport. Towards this aim, researchers have explored two routes. The first was polymerization in miniemulsion systems.^{2, 3} As explained in Section 2.3, the monomer droplets are the main loci for polymerization in miniemulsions and therefore no transport through the water phase to aqueous nucleation sites is required. The second route involved the introduction of monomer through the use of starved feed protocols.³ This method allows monomer to be consumed by growing polymer chains at the same rate as the monomer is fed into the system. Subsequently, no monomer droplets are formed and water phase transport is thus eliminated.

A third, novel technique developed in this study entailed the synthesis of the water-insoluble, dithiobenzoate-endgroup-containing oligomers prior to emulsification. This synthesis was performed under bulk conditions, and the polymerization reaction stopped

after a specific duration that corresponds to a predefined conversion and molecular weight. This was achieved by cooling the bulk reaction mixture after a specific time to yield dormant, oligomeric, dithiobenzoate-endcapped polymer chains. The RAFT-agent was formed *in situ*, which lead to unreacted azo-initiator and excess monomer remaining at the end of the reaction. The dormant oligomers and the excess monomer were then miniemulsified by mixing the bulk reaction mixture with water, surfactant and cosurfactant, and then applying shear. Upon further heating, polymerization recommenced due to the thermal cleavage of the carbon-sulfur bond in the dormant oligomers and the presence of the unreacted azo-initiator. In Section 4.2.1 it was shown that AIBN gave the best experimental results for the *in situ* RAFT-agent formation, hence it was decided to use AIBN for all further studies in this project.

5.2 Experimental

In all experiments the styrene monomer was washed with two aliquots of equal amounts of a 0.3M aqueous KOH solution to remove all inhibitors. This procedure was followed by distillation under reduced pressure. The styrene was kept over molecular sieves at 2°C for later use. AIBN was recrystallized from methanol at 2°C and di(thiobenzoyl) disulfide was recrystallized from ethanol.

Styrene bulk reaction mixtures were degassed by bubbling N₂ through for 30 minutes at room temperature. Upon addition of the AIBN and di(thiobenzoyl) disulfide, N₂ was bubbled through the mixture for another 30 minutes at room temperature before heating to the reaction temperature. All reactions were carried out under N₂ at 80°C in a three-necked reaction vessel equipped with condenser, N₂ inlet and a rubber septum for withdrawing samples. Reaction mixtures were cooled by submerging the vessels in ice-water. Molecular weights were determined by GPC and Matrix-Assisted Laser Desorption/Ionization Time-Of-Flight Mass Spectrometry (MALDI-TOF MS). For MALDI-TOF MS analysis, silver(I)-trifluoroacetate (Ag-TFA) was used as the matrix and

THF was used to dissolve both the matrix and the sample. Samples for the MALDI-TOF analysis were prepared as follows: 10mg of the sample was dissolved in 1ml THF, 1mg matrix in 1ml THF and 10mg dithranol in 1ml THF. These three solutions were mixed in a ratio of 1:1:8 (sample:Ag-TFA:dithranol). 2 μ l of this final solution was loaded into a single well of a gold-coated MALDI plate and dried before putting it into the vacuum chamber of the instrument. The MALDI-TOF MS was carried out on a PerSeptive Biosystems Voyager-DE Pro mass spectrometer operating in linear mode. The instrument was equipped with a nitrogen laser ($\lambda=337$ nm) and calibrated using a mixture of insulin (bovine, peak at 5 734,59Da), thioredoxin (E. Coli, peak at 11 674,48Da) and apomyoglobin (horse, peak at 16 952,56Da).

5.3 Results and Characterization

Two different oligomeric lengths were selected to determine the effect of oligomer length on the performance of the resulting miniemulsion. The selection was done in terms of the duration of the bulk polymerization reaction. The bulk reactions were allowed to run for 60 minutes and 80 minutes respectively, with each time interval corresponding to a different molecular weight. Results are shown in Table 5.1.

Reaction time bulk (min)	\bar{M}_n	\bar{M}_w	PDI
60	3423	4199	1,23
80	7071	9821	1,39
100	7969	11867	1,49

Table 5.1: GPC results of samples drawn from the bulk reaction after specific time intervals.

Results of the MALDI-TOF MS analysis of the oligomers synthesized in bulk for 60 and 80 minutes are shown in Appendix I. From the spectra it is possible to determine the molecular weights of the oligomers as well as proving unambiguously that the oligomers are endcapped with dithiobenzoate-endgroups. To prove the presence of a dithiobenzoate-endgroup, any mass peak in the MALDI-TOF spectrum should fit the following expression (Eq. 5.1):⁴

$$M_{\text{peak}} = M_{\text{initiator}} + n \times M_{\text{monomer}} + M_{\text{endgroup}} + M_{\text{counter-ion}} \quad (5.1)$$

where: M_{peak} = value of the selected weight peak

$M_{\text{initiator}}$ = molecular weight of the initiating group

M_{monomer} = molecular weight of the monomer

n = number of monomer repeat units

M_{endgroup} = molecular weight of chain endgroup

$M_{\text{counter-ion}}$ = molecular weight of counter-ion used for ionization

When n is made the subject of the equation, the number of monomer repeat units can be derived from Equation 5.2:

$$\frac{M_{\text{peak}} - M_{\text{initiator}} - M_{\text{endgroup}} - M_{\text{counter-ion}}}{M_{\text{monomer}}} = n \quad (5.2)$$

The molecular weights of the initiating group and monomer are known. When looking for a specific endgroup the molecular weight of the endgroup is substituted into Equation 5.2. The obtained value for n should be a positive integer.

The general structure of the oligomers is shown in Figure 5.1.

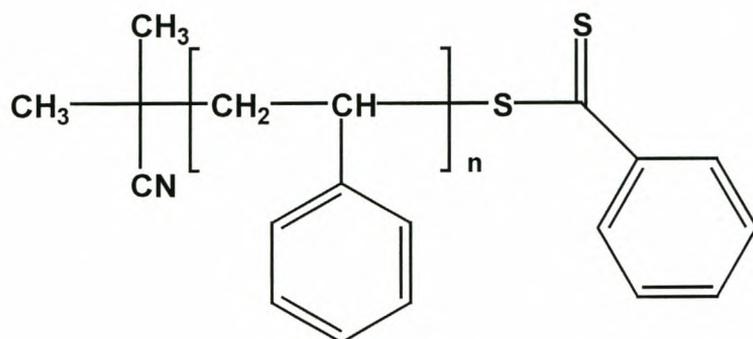


Figure 5.1: General structure of the oligomers synthesized in bulk.

It can be seen from Figure 5.1 that the oligomers contain an AIBN initiating group as well as a dithiobenzoate endcap.

From the MALDI-TOF spectra (Appendix 1) for the oligomers synthesized in bulk for 60 minutes, it can be seen that the peak molecular weight lies at 4185,84g.mol⁻¹.

When the variables in Equation 5.2 are assigned values, the number of monomer units in the oligomers can be determined. This was done by simple calculations from a periodic table.

$$M_{\text{peak}} = 4185,84\text{g.mol}^{-1}$$

$$M_{\text{initiator}} = 68,09\text{g.mol}^{-1}$$

$$M_{\text{dithiobenzoate endgroup}} = 153,25\text{g.mol}^{-1}$$

$$M_{\text{counter-ion}} = 107,86\text{g.mol}^{-1} (\text{Ag}^+)$$

From the increments between successive mass peaks it is evident that styrene units are measured at a molecular weight of 104,13g.mol⁻¹.

When the above values for M_{peak} , $M_{\text{initiator}}$, $M_{\text{dithiobenzoate endgroup}}$ and $M_{\text{counter-ion}}$ are substituted into Equation 5.2, a value of 37,04 for the number of styrene repeat units (n) is obtained.

When the same is done for the oligomers synthesized in bulk for 80 minutes, a value of 76,97 is obtained for n .

Both of the obtained values for n show very slight ($\sim 0,03$) deviations from being absolute positive integers. This can be attributed to experimental error and instrument setup.

5.4 Conclusions

In situ RAFT-agent formation can be successfully applied in a bulk system for the purposes of the study. The low molecular weights of the oligomers at the time that the bulk reaction was stopped ensured that no viscosity problems that could hamper the RAFT process would be encountered. With MALDI-TOF MS analysis it was possible to show that the oligomers did contain dithiobenzoate endgroups and that emulsification of the oligomers could be done with this assurance in mind.

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Chapter 6: RAFT Polymerization in Miniemulsion

6.1 Background

As explained in Section 2.3, polymerization reactions in miniemulsion strive to bypass interval II found in conventional emulsion polymerization. The probability of transport through the aqueous phase will be further lowered due to the presence of the oligomers. The reason for this is that the water-insoluble, dithiobenzoate endgroup-containing oligomers will ensure that the RAFT-agents are available in the polymerization loci from the onset of the reaction. By employing the bulk polymerization reaction initially, the polystyrene oligomers reach a critical chain length (j_{crit}) that is beyond the limit of water solubility for polystyrene. In the literature there is as yet no consensus on the exact value of j_{crit} for polystyrene. Fitch states that this critical value for styrene is five units.¹ Exit, however, is unlikely even for a dimeric polystyrene radical, and irreversible entry is usually expected to occur for dimeric or trimeric radicals with the SO_4^- group attached. Thus, for uncharged species, even a dimer is expected to be insoluble in the aqueous phase.² The result is that the exit of these dormant oligomers from droplets is highly unlikely, leaving the RAFT-agents inside the droplets to take part in polymerization reactions. The possibility exists that the dithioester might be transferred to a propagating oligomeric radical that is below the critical length of polystyrene for water solubility. This may enable transport of the dithio-moiety through the water phase. Although only used as a diagnostic tool, the addition of a water-soluble radical trap to the system may help prevent the transport of these radicals through the aqueous phase and thereby eliminate the possibility of subsequent homogeneous nucleation.³

The oligomers can further stabilize the system against phase separation through equilibrium swelling with monomer. This stabilizing effect of adding polystyrene to styrene miniemulsions, has been investigated thoroughly.⁴⁻⁶ The fact that polystyrene is soluble in styrene monomer brings about so-called “enhanced droplet nucleation”.

Polystyrene present in a monomer droplet will be swollen with monomer. This prevents the droplet from degrading through Ostwald ripening. Degradation will occur, but only up to a specific point where the equilibrium swelling of the polymer prevents the monomer from diffusing out of the droplet. In this way the droplet number is preserved sufficiently long for nucleation to occur. The enhancement in nucleation of the droplets increases as the molecular weight of the added polymer decreases. This is because a droplet can only be preserved by a polymer with a radius of gyration that is equal or less than the diameter of the droplet itself. The addition of polymer with low molecular weight will therefore preserve a larger proportion of the droplet population than would be the case with a higher molecular weight polymer.

6.2 Experimental

In all miniemulsion experiments the styrene monomer was first washed with two equal aliquots of a 0.3M aqueous KOH solution to remove inhibitors. The monomer was then distilled under reduced pressure. The styrene was kept over molecular sieves at 2°C for later use. Distilled styrene was never kept for longer than one week. AIBN was recrystallized from methanol at 2°C. The water used was distilled and deionized. Sodium lauryl sulfate (BDH), 1-hexadecanol (cetyl alcohol, Acros Organics) and *n*-hexadecane (Acros Organics) were used as received. Polystyrene dithiobenzoate endcapped oligomers were synthesized as described in Section 5.2. Samples were precipitated using a 2,5% (m/v) hydroquinone (Aldrich) in methanol solution. Molecular weights were determined using GPC. Shear was applied using a Silverson L4R high-shear mixer.

The amounts of AIBN and di(thiobenzoyl) disulfide used in the bulk reaction corresponded to the molar amount of AIBN-RAFT necessary to produce polymer chains with a molecular weight of 20 000g.mol⁻¹. For this theoretical calculation of molecular weight, as described in Section 2.4.6 (Equation 2.2), it must be assumed that the reaction between the AIBN and di(thiobenzoyl) disulfide goes to completion. This assumption does not take into account the intrinsic complications of the *in situ* formation of the

AIBN-RAFT. In such a system there will be less chain transfer agents present at any given time than expected. This is because the transfer agents are continuously being formed and not added as a separate reagent in a known quantity at the onset of the polymerization reaction. This discrepancy will be governed by the decomposition rate of the azo-initiator, as described in Section 4.1. This will result in a higher experimental molecular weight than predicted theoretically. Furthermore, it has been assumed that chains are not initiated at a greater rate than that of the RAFT-agents forming. This means that, at the least, as an AIBN molecule decomposes one of the primary radicals can initiate a polymer chain and the other primary radical must react with a di(thiobenzoyl) disulfide molecule to form an AIBN-RAFT agent to control the growth of the chain. The faster RAFT-agents form initially, compared to chain initiation, the more efficient the process will be. These assumptions have not been tested and further work is required in this area.

Take for example the oligomers formed after the bulk reaction has continued for 60 minutes. If the bulk reaction mixture consists of 26,25g styrene and a molecular weight of 20 000g.mol⁻¹ is to be obtained, $1,31 \times 10^{-3}$ moles of chain transfer agent should be employed (Equation 2.2). If it is assumed that a molar amount, that corresponds to double that of the molar amount of di(thiobenzoyl) used, of AIBN-RAFT is formed after completion of the reaction between AIBN and di(thiobenzoyl) disulfide, the required amounts of the two reagents can be calculated. 1,5 times the molar amount of AIBN is used to compensate for the cage-effect.

These calculations lead to the prediction that 0,162g AIBN and 0,201g di(thiobenzoyl) disulfide are necessary for the reaction to obtain polymers with the desired molecular weight. According to the decomposition behaviour described in Section 4.1, roughly 93% of the AIBN would have decomposed after 60 minutes at 80°C. This results in fewer RAFT-agents than expected to be present and will lead to a higher than predicted experimental molecular weight. The polymerization may commence upon heating simply because of the thermal homolytic cleavage of the carbon-sulfur bonds, while the non-

decomposed AIBN may act as an additional source of primary radicals to attack the carbon-sulfur double bonds.

6.2.1 SLS/*n*-hexadecane emulsifier system

In this system an anionic surfactant (SLS) was employed with a hydrophobe (*n*-hexadecane) as a cosurfactant. Recently, small-angle neutron scattering (SANS) has shown hexadecane (*n*-HD) to be homogeneously dispersed throughout a droplet and not possessing any interfacial activity.⁷ Miniemulsion systems employing alkanes as cosurfactants are better stabilized against Ostwald ripening compared to systems employing the corresponding long chain fatty alcohol.⁸ The reason for this is that the alkane is less soluble in water than the corresponding long chain fatty alcohol, which can be regarded as having some amphiphilic character.

All miniemulsions employing SLS and *n*-hexadecane as emulsifier combination were prepared as follows. The SLS was dissolved in water and the *n*-hexadecane was dissolved in the styrene bulk reaction mixture (described in Chapter 5). The two mixtures were then combined and subjected to high shear for one hour.

The following quantities were used in the two different miniemulsion reactions:

SLS/*n*-HD system containing oligomers synthesized in bulk for 60 minutes:

Step 1:

- 26,25g styrene
- 0,162g AIBN
- 0,201g di(thiobenzoyl) disulfide

The above reagents were reacted for 60 minutes in bulk. The next step was to prepare the miniemulsion after the above reaction mixture was cooled. The miniemulsion consisted of the following components:

Step 2:

- Bulk reaction mixture from Step 1
- 150g DDI
- 0,433g SLS
- 1,359g *n*-HD

SLS/*n*-HD system containing oligomers synthesized in bulk for 80 minutes:

Step 1:

- 29,07g styrene
- 0,179g AIBN
- 0,223g di(thiobenzoyl) disulfide

The above reagents were reacted for 80 minutes in bulk. The next step was to prepare the miniemulsion after the above reaction mixture was cooled. The miniemulsion consisted of the following components:

Step 2:

- Bulk reaction mixture from Step 1
- 150g DDI
- 0,433g SLS
- 1,359g *n*-HD

The experimental results for this system are shown in Table 6.1 and Figures 6.1 - 6.5.

A control miniemulsion experiment was also done in which the system contained no di(thiobenzoyl) disulfide and no preceding bulk reaction step. This means that no compounds that can act as chain transfer agents in the RAFT-process could be formed.

The control consisted of the following components:

- 22,07g styrene
- 150g DDI
- 0,136g AIBN
- 0,433g SLS
- 1,359g *n*-HD

The results for the control experiment are shown in Table 6.2.

6.2.2 SLS/1-hexadecanol emulsifier system

As stated before, long chain fatty alcohols have an amphiphilic character. This is due to the presence of a hydrophobic hydrocarbon tail and a hydrophilic OH-group. The cetyl alcohol acts as a cosurfactant and with the anionic surfactant the cetyl alcohol can form an interfacial complex to help reduce the rate of coalescence.^{9, 10}

All miniemulsions employing the cetyl alcohol/SLS emulsifier combination were prepared as follows. The SLS and cetyl alcohol (1-HD) were mixed at 70°C for 2 hours to form an aqueous gel. The gel was allowed to cool to room temperature, after which the styrene bulk reaction mixture was added to it. Shear was then applied for one hour.

The following quantities were used in the two different miniemulsion reactions:

SLS/1-HD system containing oligomers synthesized in bulk for 60 minutes:

Step 1:

- 26,66g styrene
- 0,164g AIBN
- 0,204g di(thiobenzoyl) disulfide

The above reagents were reacted for 60 minutes in bulk. The next step was to prepare the miniemulsion after the above reaction mixture was cooled. The miniemulsion consisted of the following components:

Step 2:

- Bulk reaction mixture from Step 1
- 150g DDI
- 0,433g SLS
- 1,455g 1-HD

SLS/1-HD system containing oligomers synthesized in bulk for 80 minutes:

Step 1:

- 24,69g styrene
- 0,152g AIBN
- 0,189g di(thiobenzoyl) disulfide

The above reagents were reacted for 80 minutes in bulk. The next step was to prepare the miniemulsion after the above reaction mixture was cooled. The miniemulsion consisted of the following components:

Step 2:

- Bulk reaction mixture from Step 1
- 150g DDI
- 0,433g SLS
- 1,455g 1-HD

The experimental results for this system are shown in Table 6.3 and Figures 6.6 - 6.10.

The control miniemulsion experiment, without chain transfer agents and no preceding bulk step, for the SLS/1-HD system consisted of the following components:

- 20,58g styrene
- 150g DDI
- 0,433g SLS
- 0,127g AIBN
- 1,455g 1-HD

The results for the control experiment can be seen in Table 6.4.

6.2.3 In Situ RAFT-agent formation in miniemulsion without preceding bulk reaction step

In the following experiments the bulk reaction step was omitted, and the RAFT-agent was made *in situ* in the miniemulsion. This means that no oligomers were present at the onset of the polymerization reaction. Since aqueous phase transport should be expected to be eliminated when working with miniemulsions, these experiments were also expected to yield good results.

The experimental results are shown in Table 6.5 and Figures 6.19 - 6.23.

The following quantities were used in the two different miniemulsion reactions:

SLS/*n*-HD miniemulsion system:

- 150g DDI
- 0,433g SLS
- 1,359g *n*-HD

- 22,61g styrene
- 0,139g AIBN
- 0,173g di(thiobenzoyl) disulfide

All reagents were simultaneously sheared into a miniemulsion with no preceding bulk step.

SLS/1-HD miniemulsion system:

- 150g DDI
- 0,433g SLS
- 1,455g 1-HD
- 20,74g styrene
- 0,128g AIBN
- 0,159g di(thiobenzoyl) disulfide

All reagents were simultaneously sheared into a miniemulsion with no preceding bulk step.

6.3 Results

Results of the polymerization of the oligomers in miniemulsions are shown below for the SLS/*n*-HD and SLS/1-HD emulsifier systems containing the two different oligomers. Results are also shown for experiments where the *in situ* RAFT-agent formation was performed in the miniemulsion, with no preceding bulk reaction. The effect of a water-soluble, ionic salt (Frémy's salt) on an oligomer-containing miniemulsion is also described.

6.3.1 SLS/n-HD emulsifier system with oligomers

SLS/n-Hexadecane + 60min oligomers			
Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
18,4	5368	5824	1,09
24,3	7023	7822	1,11
32,9	10726	13058	1,22
40,4	13054	16935	1,30
51,2	16179	22238	1,37
61,6	17167	24144	1,41
66,9	18987	27707	1,46
SLS/n-Hexadecane + 80min oligomers			
Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
20,0	4558	4616	1,01
31,3	8407	10047	1,20
34,5	12169	15914	1,31
43,4	13534	17781	1,31
50,7	16634	23146	1,39
62,8	19718	30252	1,53
70,9	21478	33903	1,58

Table 6.1: Experimental results of the styrene miniemulsions employing a SLS/n-hexadecane emulsifier system.

Time (h)	Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
1,02	14,1	32138	56794	1,77
1,98	33,5	28152	53071	1,89
3,10	52,4	33502	71266	2,13
4,68	77,9	41969	117391	2,80

Table 6.2: Experimental results for the SLS/n-HD system containing no chain transfer agents.

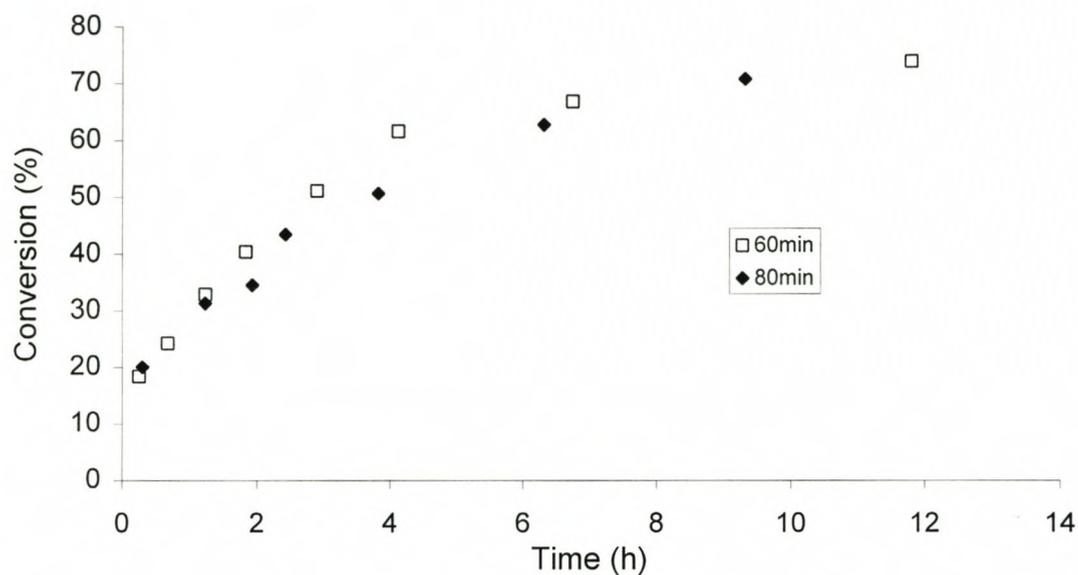


Figure 6.1: Conversion profiles for the SLS/n-HD miniemulsion polymerization of styrene in the presence of two different RAFT-endcapped polystyrene oligomers.

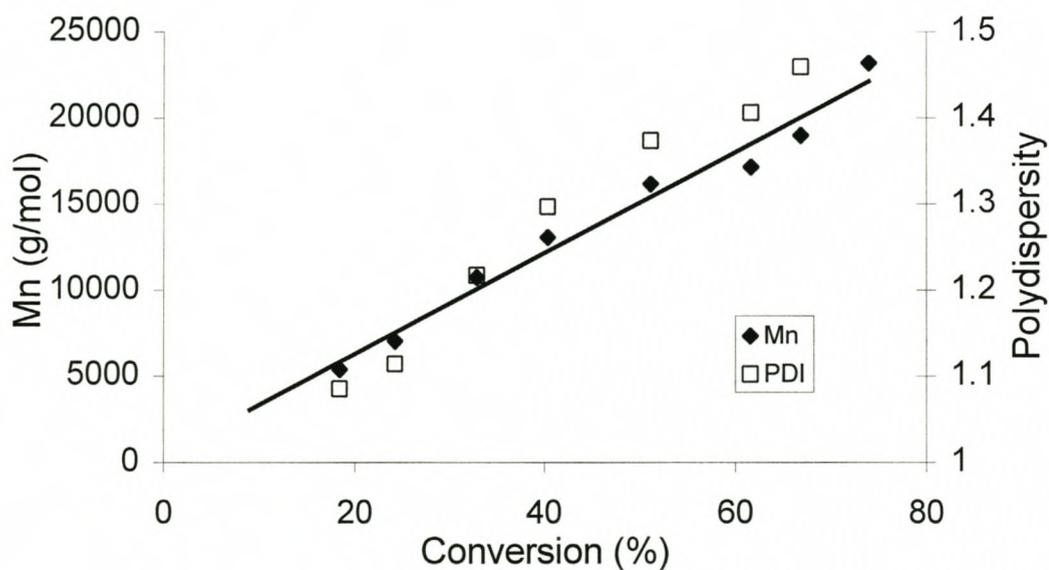


Figure 6.2: Graph showing the relationship between molecular weight and conversion for the SLS/n-HD system containing the oligomers synthesized in bulk for 60 minutes.

Fig. 6.2 shows a good linear relationship ($R^2=0,9765$) between molecular weight and conversion. Polydispersity, however, rises throughout the course of the reaction.

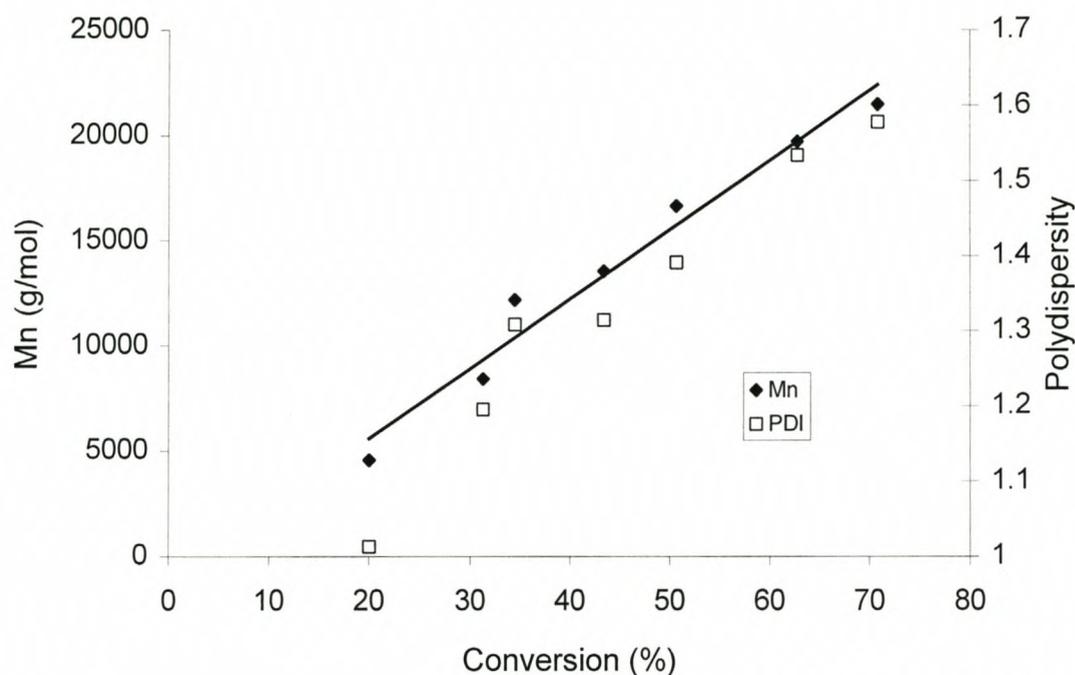


Figure 6.3: *Graph showing the relationship between molecular weight and conversion for the SLS/n-HD system containing oligomers synthesized in bulk for 80 minutes.*

Although the linear relationship ($R^2=0,9688$) between molecular weight and conversion in Figure 6.3 is not as well defined as it was in Figure 6.2, it is still good. Polydispersity is also higher for the 80 minutes oligomers than for the 60 minutes oligomers.

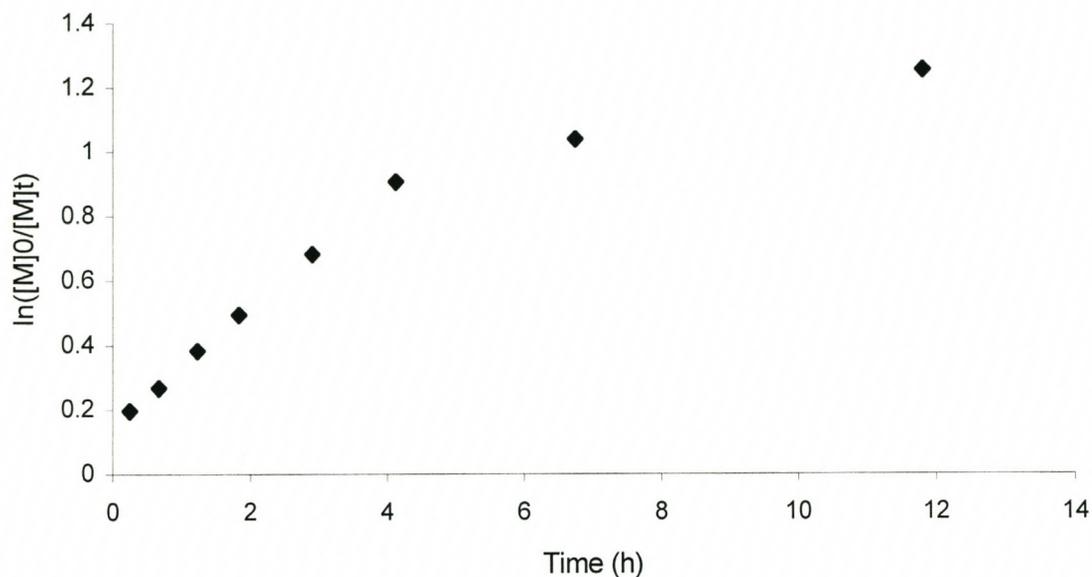


Figure 6.4: *Graph illustrating the kinetic behaviour of the SLS/n-HD system containing the 60min oligomers.*

Figure 6.4 shows a nearly perfect linear relationship for the first part of the reaction. The rate slows in the latter stages, which may indicate radical termination events taking place.

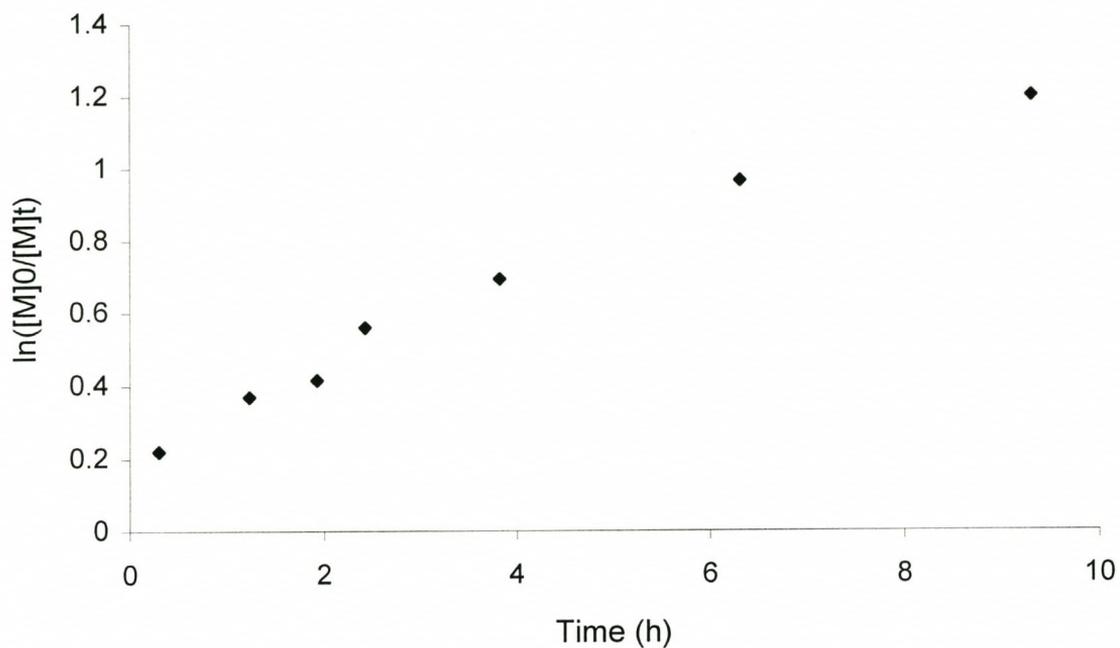


Figure 6.5: Graph illustrating the kinetic behaviour of the SLS/n-HD system containing the 80min oligomers.

Figure 6.5 also shows a reasonably good linear relationship ($R^2=0,9825$) although it is not as well defined in the initial stages as was seen in Figure 6.4.

6.3.2 SLS/1-HD emulsifier system with oligomers

SLS/1-Hexadecanol + 60min oligomers			
Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
23,5	5085	5362	1,06
23,4	5184	5480	1,08
30,9	8601	17704	2,06
35,7	10252	19846	1,94
42,7	12120	24561	2,03
49,6	15494	33624	2,17
64,7	19034	44169	2,32
SLS/1-Hexadecanol + 80min oligomers			
Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
26,9	6272	6856	1,09
27,6	6779	7472	1,10
31,0	9130	12101	1,33
39,8	11343	16077	1,42
43,7	13855	21990	1,59
51,3	15591	26897	1,73
63,1	17793	33048	1,83
68,8	19581	39287	2,00

Table 6.3: Experimental results of the styrene miniemulsions employing a SLS/1-hexadecanol emulsifier system.

Time (h)	Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
1,28	24,9	31273	86514	2,77
2,12	38,9	33492	85039	2,54
4,00	63,3	47780	139566	2,92
5,38	86,9	66343	237580	3,58

Table 6.4: Experimental results for the SLS/1-HD system containing no chain transfer agents.

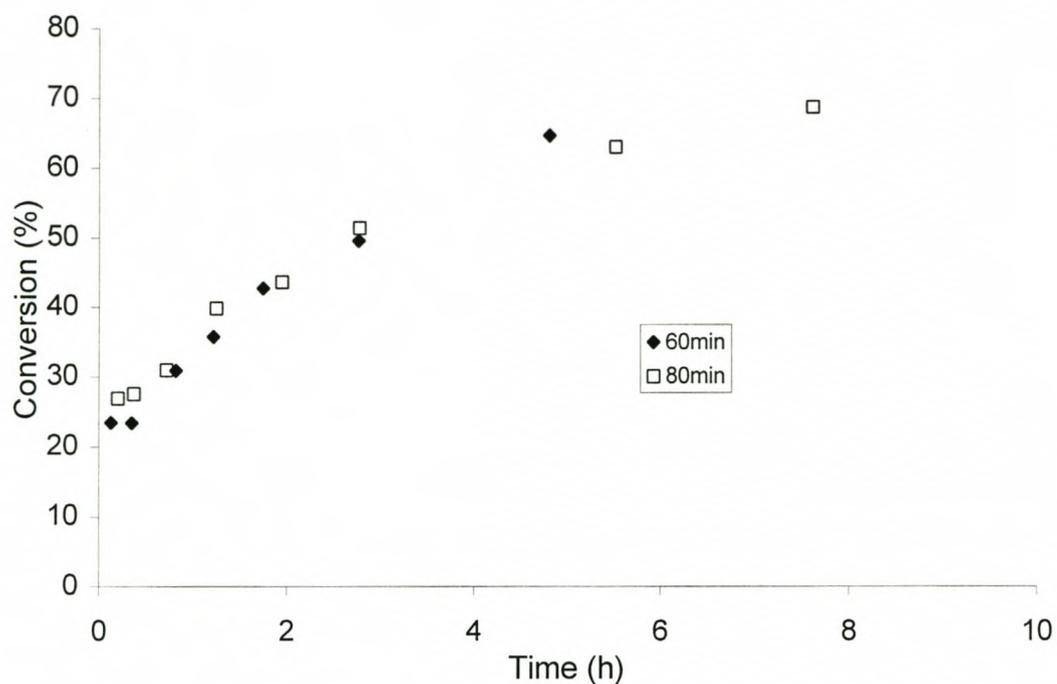


Figure 6.6: Conversion profiles for the SLS/1-HD miniemulsion polymerization of styrene in the presence of two different RAFT-endcapped polystyrene oligomers.

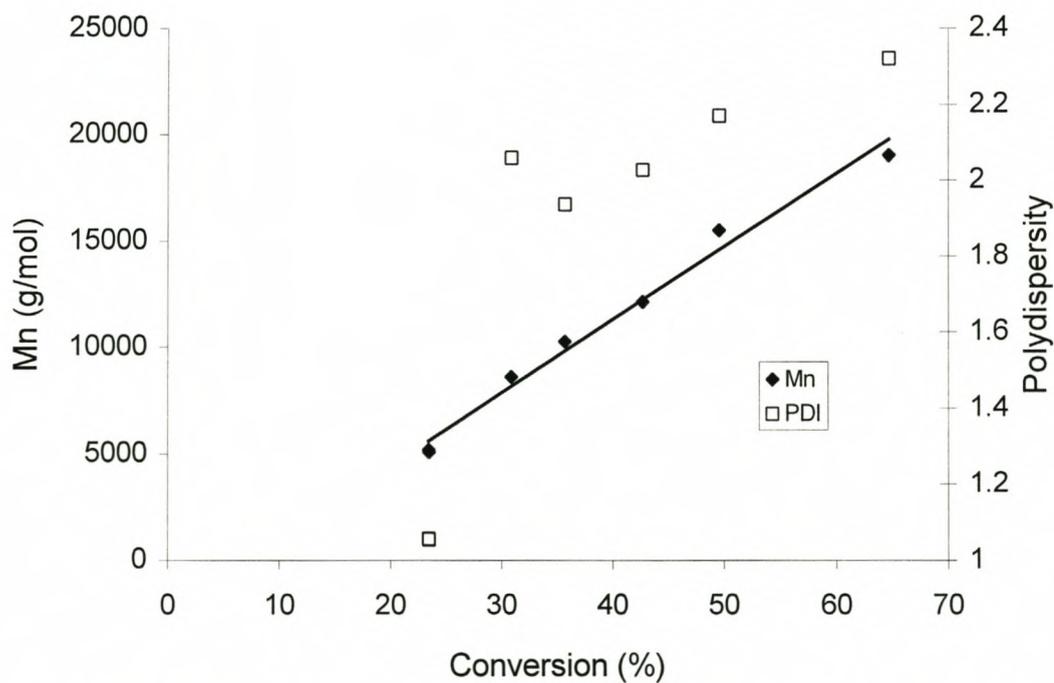


Figure 6.7: Graph showing the relationship between molecular weight and conversion for the SLS/1-HD system containing oligomers synthesized in bulk for 60 minutes.

A good linear relationship ($R^2=0,9860$) can be seen between molecular weight and conversion in Figure 6.7. The polydispersity values are, however, high and continuously rising throughout the course of the reaction.

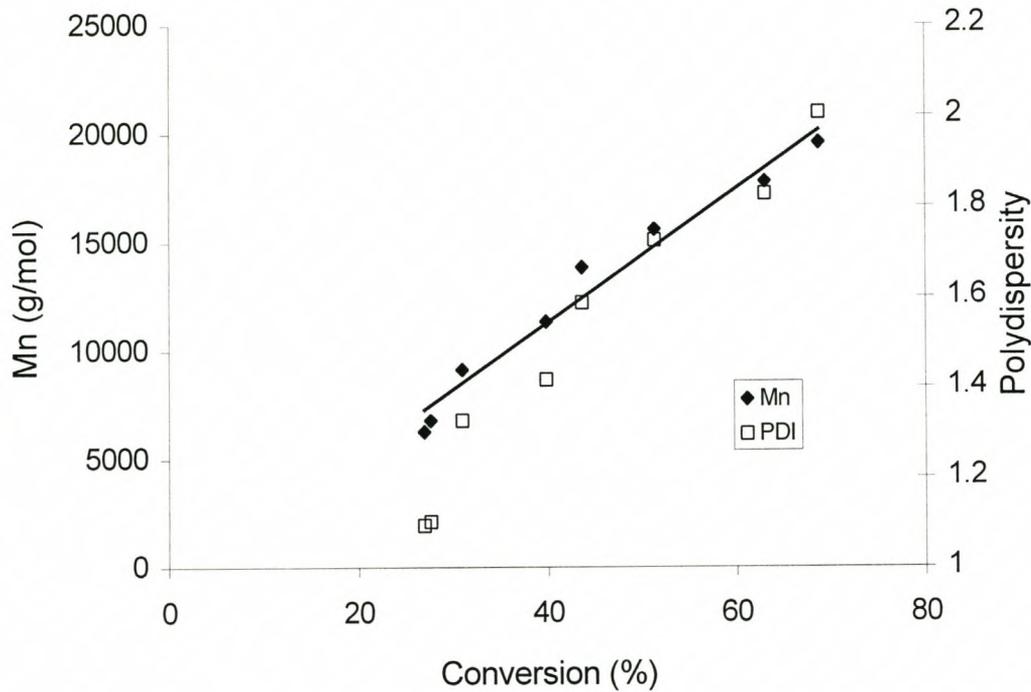


Figure 6.8: Graph showing the relationship between molecular weight and conversion for the SLS/1-HD system containing oligomers synthesized in bulk for 80 minutes.

Figure 6.8 shows a reasonable linear relationship ($R^2=0,9698$) between molecular weight and conversion. Polydispersity values are also high in this case.

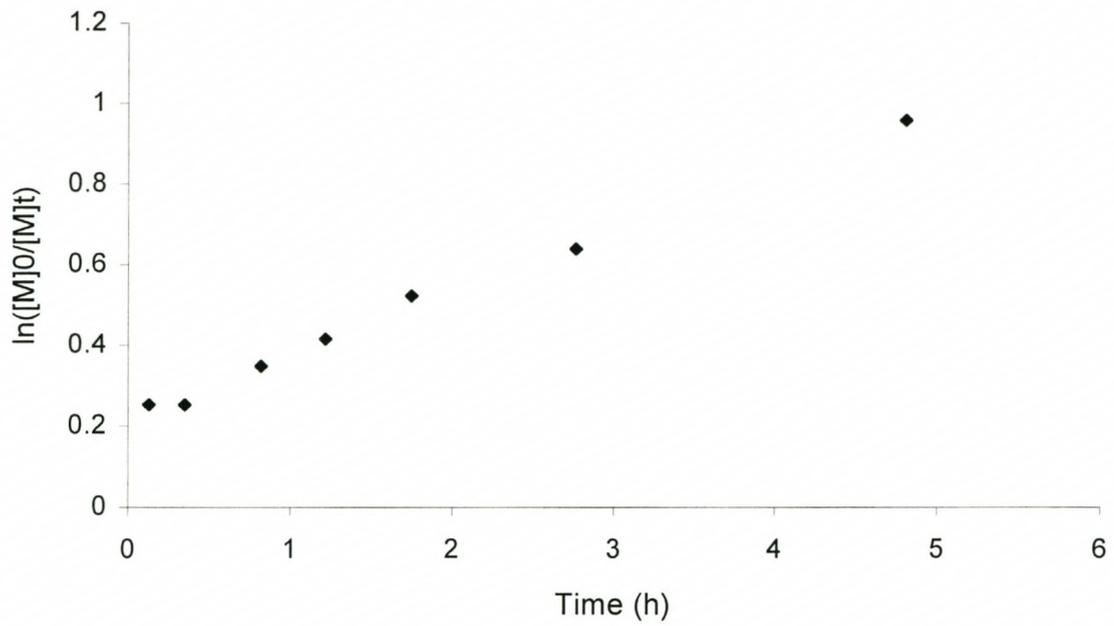


Figure 6.9: Graph illustrating the kinetic behaviour of the SLS/1-HD system containing the 60min oligomers.

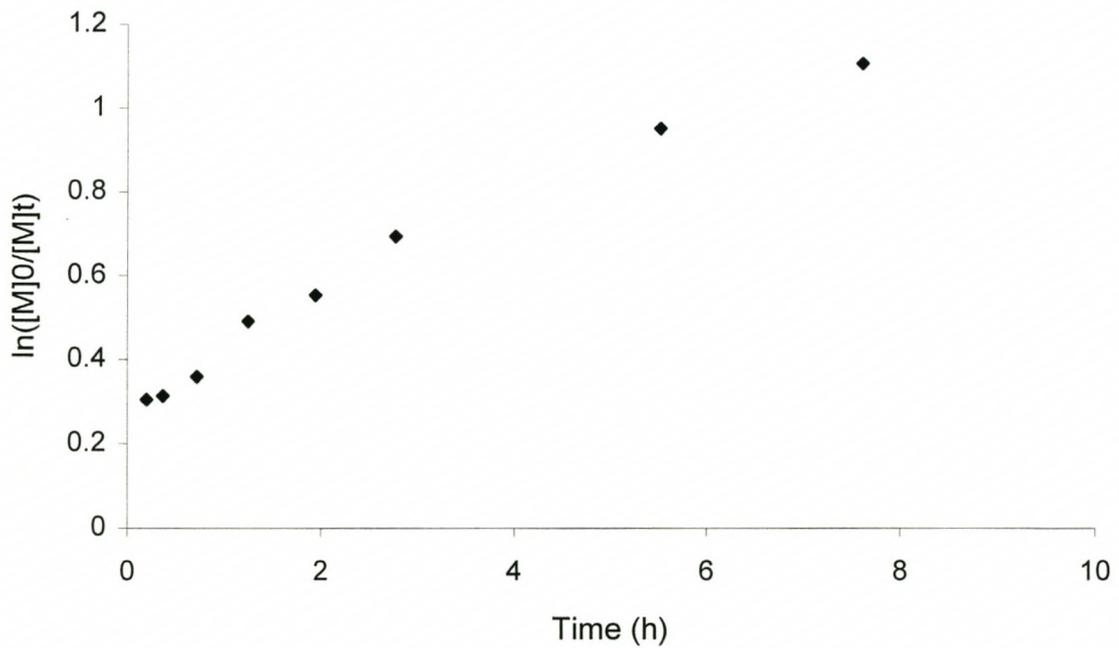


Figure 6.10: Graph illustrating the kinetic behaviour of the SLS/1-HD system containing the 80min oligomers.

Both Figure 6.9 and Figure 6.10 show reasonably linear relationships between $\ln([M]_0/[M]_t)$ and time that show signs of the reaction slowing during its latter stages. From the above curves of the number average molecular weight and polydispersity versus conversion it can be seen that the linear relationship between \bar{M}_n and conversion becomes poorer as the molecular weight of the oligomers increases. The polydispersities of the systems employing 1-hexadecanol as cosurfactant are also much higher than the same systems employing *n*-hexadecane.

The possibility that some aqueous phase activities are taking place presents itself in the form of a bimodal particle size distribution, as measured by light scattering. The suspicion of nucleation in the aqueous phase was enhanced by the increase in polydispersity of the particle size distribution when the cosurfactant was changed from *n*-hexadecane to 1-hexadecanol. Fatty alcohols do not stabilize as efficiently against monomer diffusion from droplets as the corresponding alkanes do. This is because, due to their amphiphilic character, the fatty alcohols are slightly more soluble in water than the alkanes. The diffusion rate of monomer out of droplets is governed by the diffusion rate of the least water-soluble component in the droplet. In miniemulsions the component with the lowest water-solubility is the cosurfactant (hydrophobe). Relatively speaking, fatty alcohols will be more water-soluble than their corresponding alkanes. Therefore aqueous phase nucleation sites in the SLS/1-hexadecanol systems will be better supplied with free monomer than the corresponding SLS/*n*-hexadecane systems.

Another observation was the impact of the oligomers on particle size. Particle size increased significantly when the oligomers were added to the miniemulsions, compared to control miniemulsions without chain transfer agents. Particle size analysis of a SLS/*n*-hexadecane miniemulsion, for example, showed a particle diameter of 240-340nm. When the bulk reaction mixture was added and emulsified, with all parameters kept constant, particle size increased by up to 600nm, to yield particles close to 1 micron in diameter.

6.3.3 Investigation of Changing Concentration of Active Species

In a free radical polymerization reaction conducted in a controlled manner, the number of active species (i.e. propagating chains) should be kept to a minimum. After establishing equilibrium between active and dormant species in a CFRP environment, the number of propagating radicals should also be constant. Therefore, in an ideal free radical polymerization reaction where the RAFT technique is used to obtain CFRP, a graph showing active radical concentration against conversion or time should show a straight, horizontal line throughout the course of the reaction. The data obtained from the four different reactions described earlier (see Sections 6.2.1 and 6.2.2) were manipulated and plotted as the product of active radical concentration and k_p (k_p is constant throughout the conversion range and is therefore proportional to the active radical concentration) versus percentage conversion. The curves were obtained by determination of the slope (i.e. differentiation) of the $\ln([M]_0/[M]_t)$ vs conversion curves. The first derivative of $\ln([M]_0/[M]_t)$ gives $k_p[R^*]$ (where $[R^*]$ is the concentration of the active species). k_p stays constant and this enables one to determine the concentration of active species. The curves are shown in Figures 6.11 - 6.14.

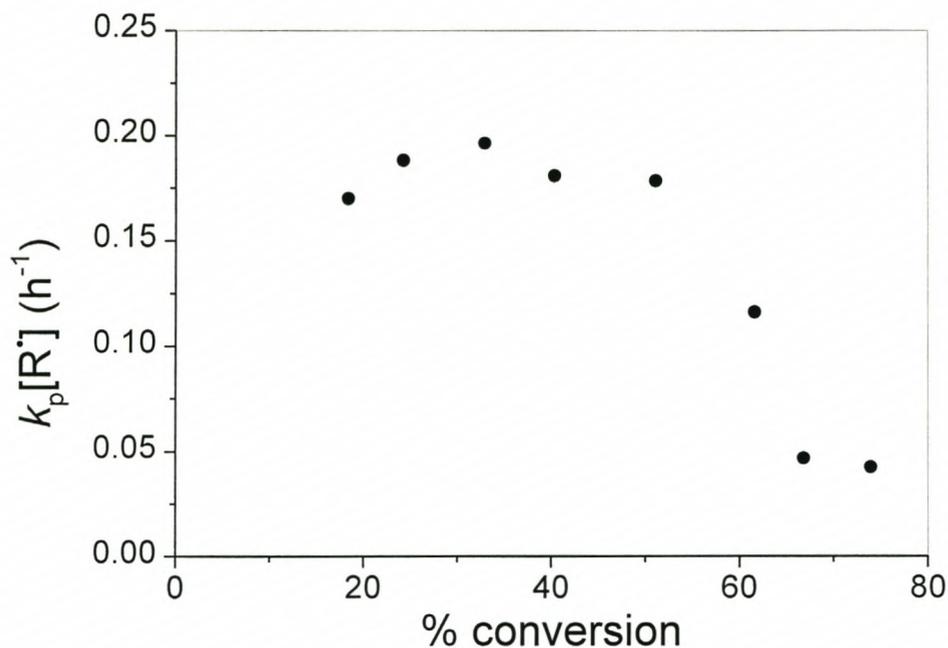


Figure 6.11: Graph showing active radical concentration versus conversion for the SLS/n-HD system containing oligomers synthesized in bulk for 60 minutes.

Figure 6.11 shows an initial rise in the concentration of active radicals, which culminates in a pseudo steady state from roughly 22-55% conversion. There is an abrupt drop in active radicals after about 55% conversion. The initial rise can be attributed to the undecomposed AIBN decomposing in the miniemulsion step.

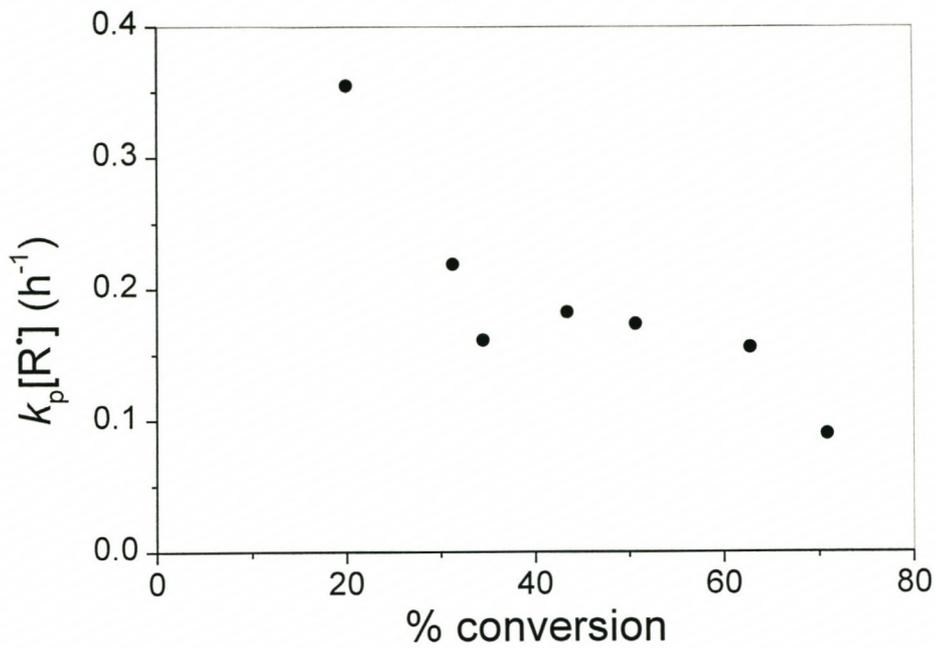


Figure 6.12: Graph showing active radical concentration versus conversion for the SLS/n-HD system containing oligomers synthesized in bulk for 80 minutes.

Figure 6.12 shows an initial drop in the number of active radicals and a relationship that resembles reasonable steady-state characteristics is observed.

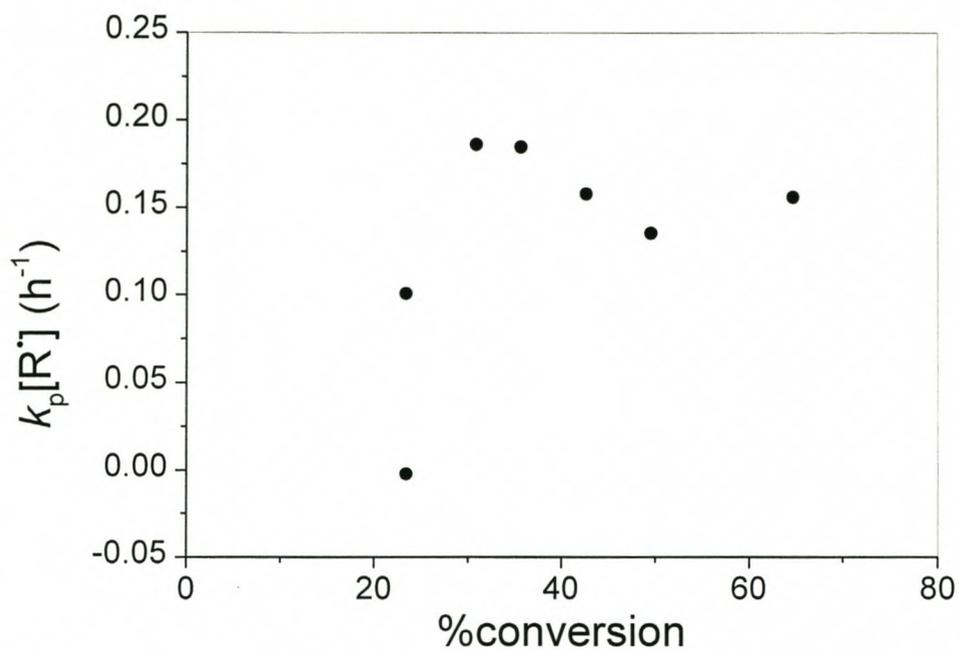


Figure 6.13: Graph showing active radical concentration versus conversion for the SLS/1-HD system containing oligomers synthesized in bulk for 60 minutes.

Figure 6.13 shows the data from the first of the two experiments (see Section 6.2.2) in which 1-hexadecanol was used as the cosurfactant. An initial steep rise in the number of active radicals is observed. A very short period of steady-state behaviour can be observed after the initial rise, after which the concentration of active radicals decreases.

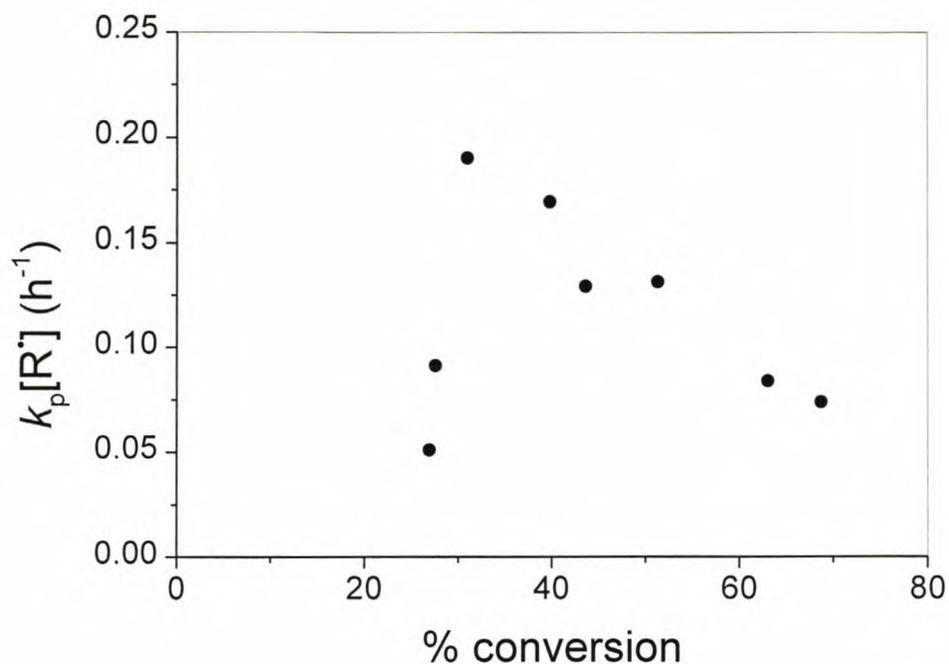


Figure 6.14: Graph showing active radical concentration versus conversion for the SLS/1-HD system containing oligomers synthesized in bulk for 80 minutes.

A trend similar to that observed in Figure 6.13 is also seen in Figure 6.14. There is an initial steep rise, followed by a drop in active radical concentration into a steady-state region. Higher conversions also correspond to a decrease in active radical concentration.

There are some similarities between Figures 6.11 - 6.14. Usually the trend involves an initial rise in active radical concentration, a region resembling steady-state behaviour and a final decrease in the number of radicals in the latter stages of the polymerization reaction. As stated before, the initial increase in concentration of active radicals can be attributed to the thermal decomposition of the unreacted, undecomposed AIBN remaining from the bulk polymerization step. This is seen at about 20% conversion and not at 0% conversion, because the reactions start with oligomers. The regions resembling steady-state behaviour will represent the stage of the polymerization reaction during which the free radical polymerization reaction proceeds in a controlled manner. The decrease in the concentration of active radicals in the latter stages of the reactions suggests that termination might be occurring. This will be discussed in further detail.

At this stage it is important to mention that the graphic representation of the number of radicals versus conversion includes *all* active (propagating) radicals in the system concerned. This means that the active radicals can be partitioned between the aqueous and oil phases. In theory, all active radicals should be located in the droplets when polymerizing in miniemulsions. This is, however, not always the case and some aqueous phase side-reactions may occur.

One of the characteristics of the RAFT-process is that the reversible deactivation reaction is much faster than the propagation reaction of the growing polymer chain. The deactivation reaction is also faster than the reactivation of the dormant chain. This means that at higher conversions the deactivation reaction will be the first component of the RAFT-process to be affected. As conversion increases, higher internal viscosities of the droplets will cause the deactivation reaction of the RAFT-process to become diffusion controlled. This will cause the ratio of the rate coefficients of the deactivation and reactivation reactions to change. Propagation will therefore not necessarily be faster, just more likely (relatively) than before. This change in the ratio of the rate coefficients will cause a rise in the concentration of the active species, which will therefore increase the probability of irreversible termination through bimolecular coupling. The change in the ratio of rate coefficients will probably also lead to broadening of the molecular weight distributions.

6.3.4 Investigation into Molecular Weight Distributions

In an ideal system where the free radical polymerization process is conducted in a controlled manner, the molecular weight distribution should become narrower as the polymerization reaction progresses. The curves shown in Figures 6.15 - 6.18 show the generated signal obtained from the GPC vs the logarithm of the molecular weight distribution of the two different emulsifier systems described above (Sections 6.2.1 and 6.2.2) containing the different oligomers. The different reactions are referred to as follows:

- Reaction A: SLS/*n*-hexadecane (*n*-HD) system containing oligomers synthesized in bulk for 60 minutes.
- Reaction B: SLS/*n*-HD system containing oligomers synthesized in bulk for 80 minutes.
- Reaction C: SLS/1-hexadecanol (1-HD) system containing oligomers synthesized in bulk for 80 minutes.
- Reaction D: SLS/1-HD system containing oligomers synthesized in bulk for 60 minutes.

In each set of samples from the different reactions, numerically increasing sample names correspond to increasing conversions within the specified reaction.

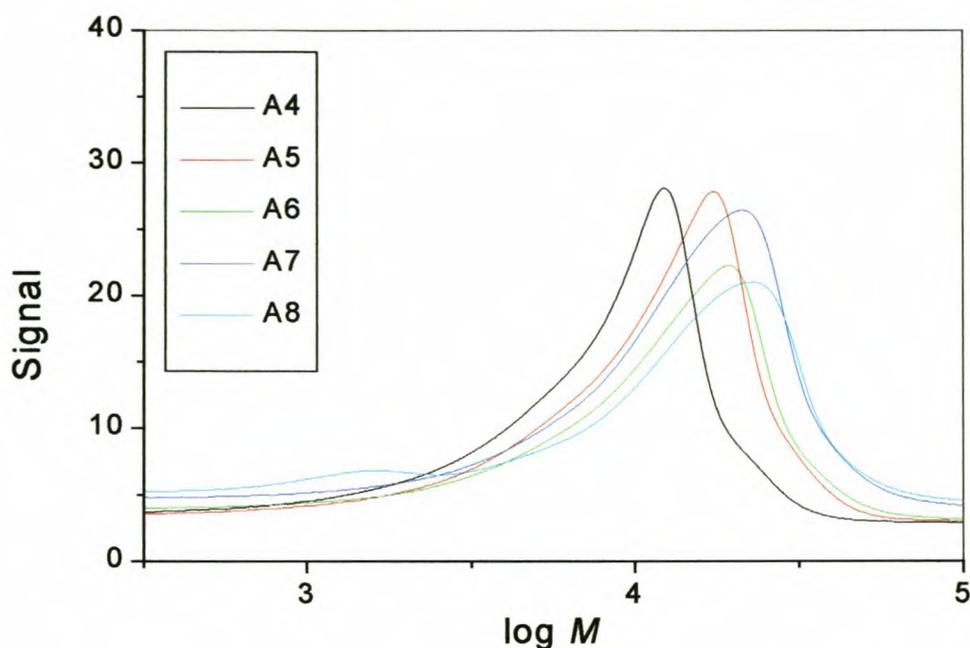


Figure 6.15: Molecular weight distribution for the SLS/n-HD system containing the oligomers synthesized in bulk for 60 minutes.

In Figure 6.15 all curves show tailing towards the lower molecular weight region. This could be indicative of some fraction of the oligomers not being reinitiated in the miniemulsion polymerization step. Sample A8 shows a significant distribution in the lower molecular weight region. This may also be an indication that at higher conversions shorter chains form by transfer and then terminate, since deactivation might at this stage have become diffusion controlled. This deactivation also relates to the drop in concentration of active species observed in Figure 6.11, as well as the drop in reaction rate seen in Figure 6.4.

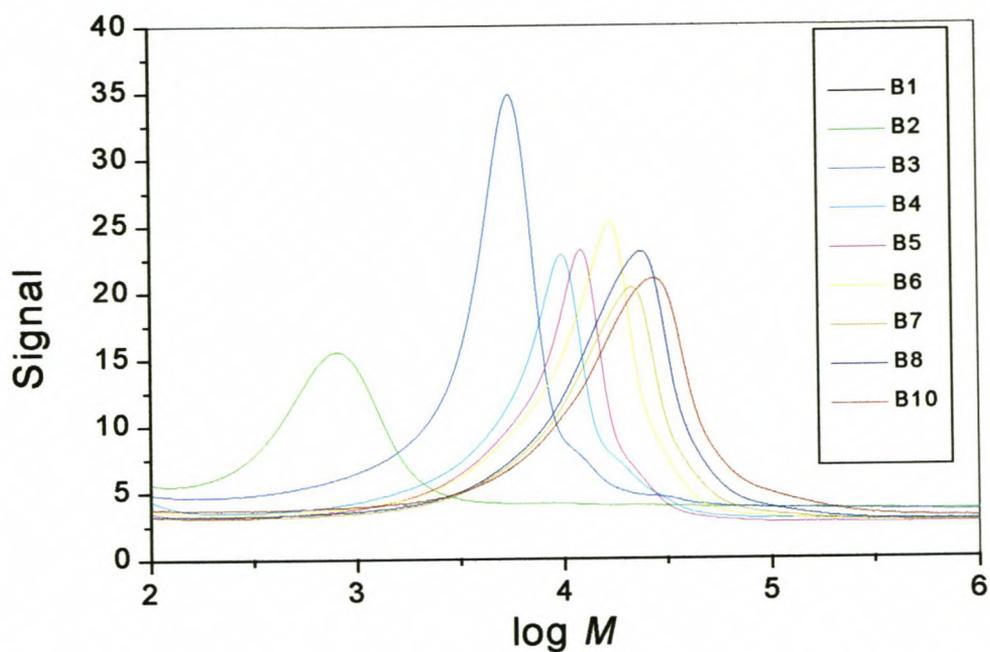


Figure 6.16: Molecular weight distribution for the SLS/n-HD system containing oligomers synthesized in bulk for 80 minutes.

In Figure 6.16 the tailing towards the lower molecular weight region is not as pronounced as in Figure 6.15, although tailing is still evident. The later samples (B10, B8, etc.) also develop a significant high molecular weight shoulder.

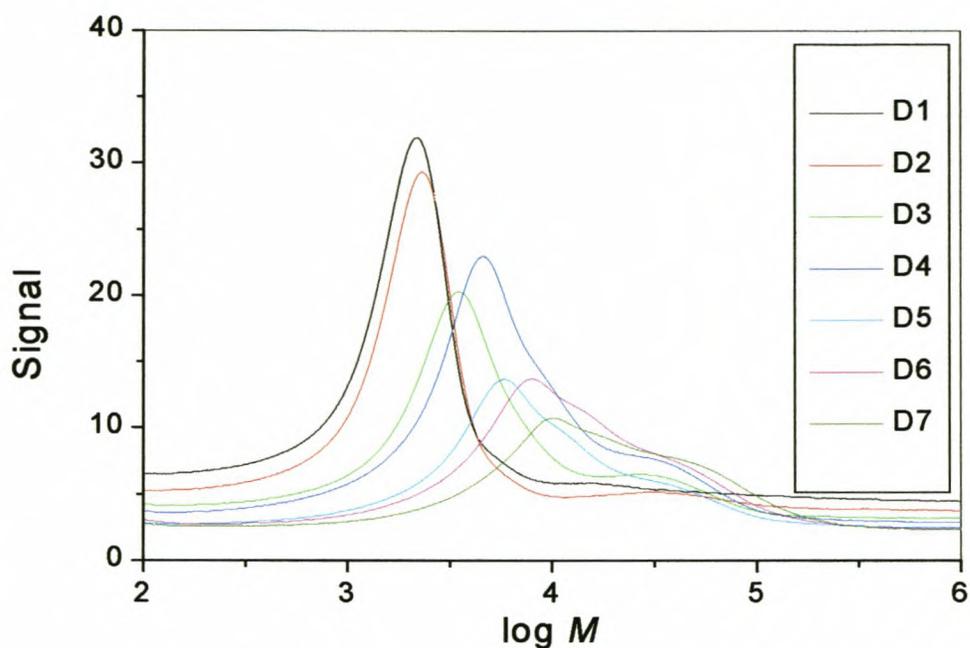


Figure 6.17: Molecular weight distributions for the SLS/1-HD system containing oligomers synthesized in bulk for 60 minutes.

Figure 6.17 shows a prominent tailing towards the high molecular weight region. This might be indicative of uncontrolled polymerization reactions taking place, leading to high molecular weight compounds. Such reactions can take place in the aqueous phase, where polymerization reactions at aqueous phase nucleation sites, from which any chain transfer agents are absent, proceed in an uncontrolled manner. It may also be an indication of loss of control in the minidroplets themselves at high conversions.

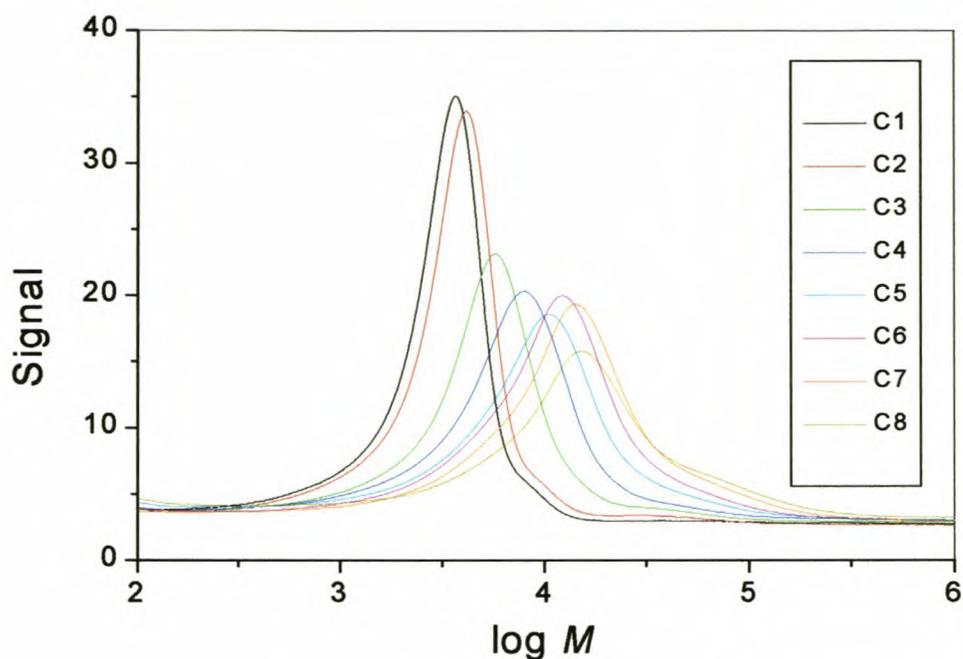


Figure 6.18: *Molecular weight distribution for the SLS/1-HD system containing oligomers synthesized in bulk for 80 minutes.*

A very pronounced tailing towards the high molecular weight region through the sample set can be seen in Figure 6.18. This might also be attributed to the fact that polymerization reactions leading to high molecular weight compounds at aqueous phase nucleation sites will be more probable in the systems employing 1-hexadecanol as cosurfactant and SLS as surfactant than the systems using SLS and *n*-hexadecane.

Figures 6.15 - 6.18 it show that the peak molecular weight increases as the polymerization reaction progresses. This necessarily implies that the oligomers can be reinitiated after miniemulsification and propagate in a controlled manner. Tailing towards both low and high molecular weight regions is also be observed, which indicates that termination of various kinds might be occurring or that transfer is taking place.

6.3.5 *In Situ* RAFT-agent formation in miniemulsion without preceding bulk reaction step

SLS/<i>n</i>-Hexadecane			
Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
8,0	1127	1284	1,14
19,1	3485	4564	1,31
35,0	6726	9887	1,47
40,9	8519	13274	1,56
57,5	11369	17325	1,52
57,8	10952	17133	1,56
58,1	11343	17260	1,52
58,1	11691	17564	1,50
SLS/1-Hexadecanol			
Conversion (%)	\bar{M}_n	\bar{M}_w	PDI
20,6	3061	3900	1,27
36,9	5980	8719	1,46
41,9	7534	11083	1,47
48,3	9684	13912	1,43
58,4	12524	17690	1,41
59,2	12650	19311	1,53
61,7	11068	19787	1,79
58,5	13456	19057	1,42

Table 6.5: Experimental results for the miniemulsions using different emulsifier systems with no bulk reaction prior to emulsification.

The following graphs compare the conversions of the different emulsifier systems as well as the obtained relationships between molecular weight and conversion. Kinetic behaviour of the different systems is also illustrated in the graphs of $\ln([M]_0/[M]_t)$ versus time.

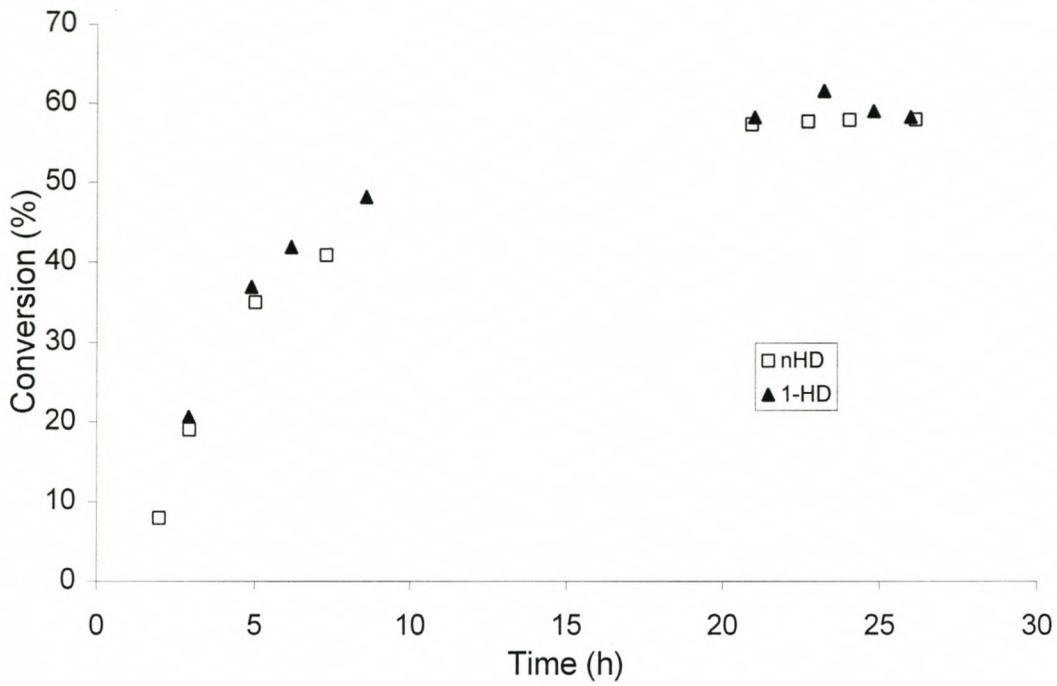


Figure 6.19: Comparative conversion curves for the two different emulsifier systems with no bulk reaction step prior to emulsification.

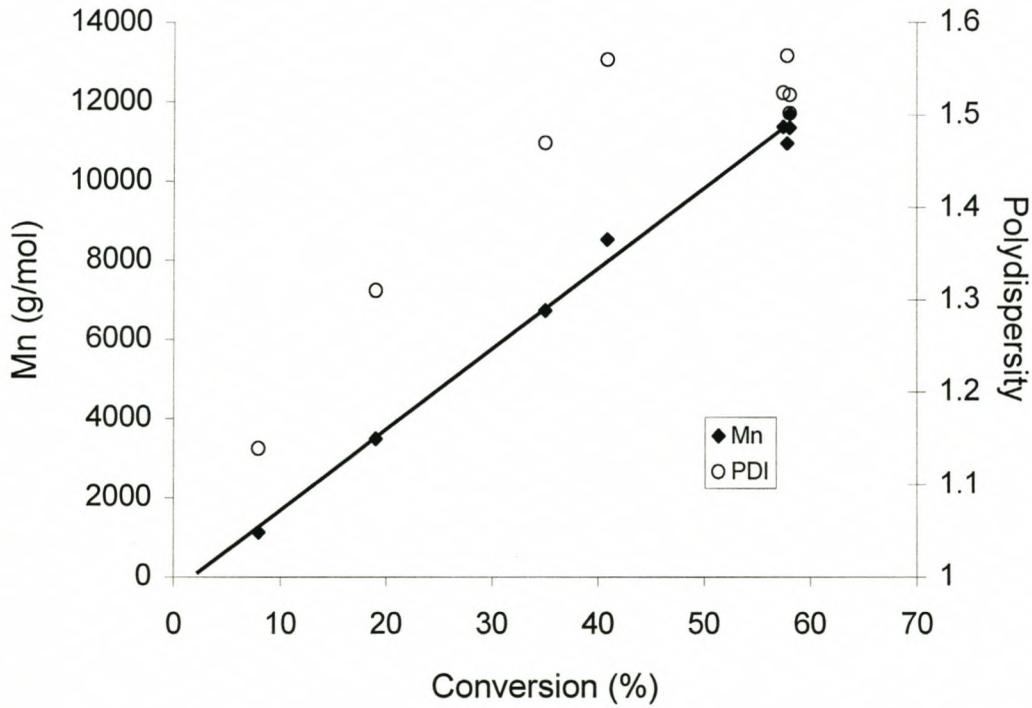


Figure 6.20: Graphs showing \bar{M}_n and polydispersity versus conversion for the SLS/n-HD emulsifier system with no preceding bulk reaction step.

A very good linear relationship ($R^2=0,9947$) between molecular weight and conversion can be seen in Figure 6.20, with polydispersity decreasing during the latter stages of the reaction. It can also be seen that there is a cessation in chain growth at a relatively low conversion.

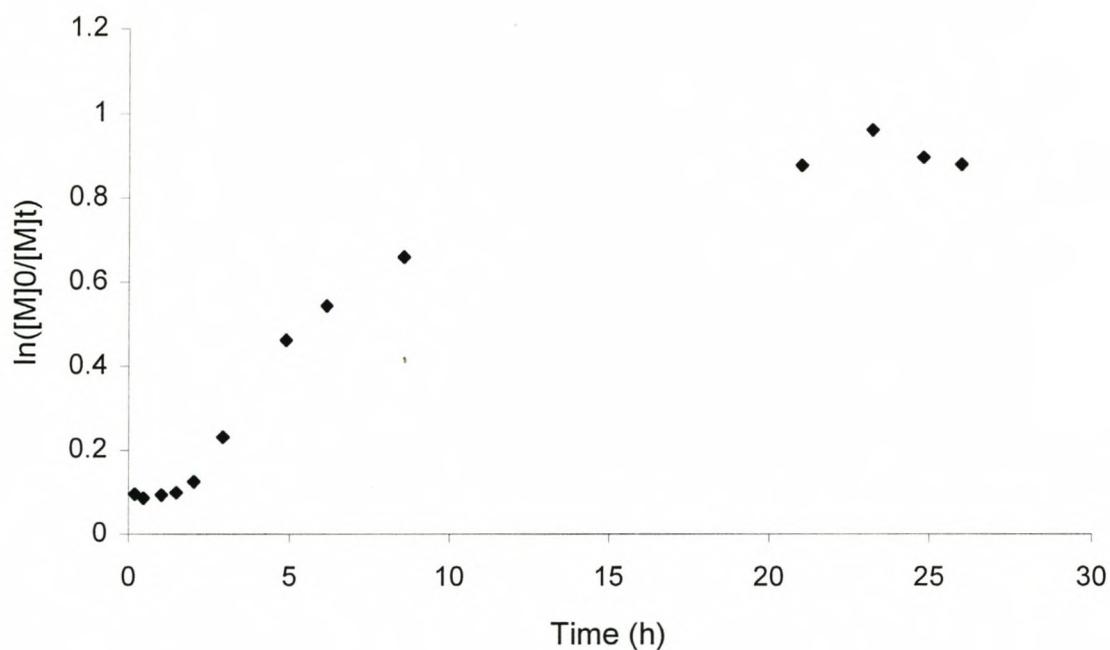


Figure 6.21: Graph illustrating the kinetic behaviour of the SLS/1-HD emulsifier system with no bulk reaction prior to emulsification.

Figure 6.21 reflects the cessation of chain growth observed in Figure 6.20 in that the rate of reaction drops rapidly as the reaction proceeds in the latter stages.

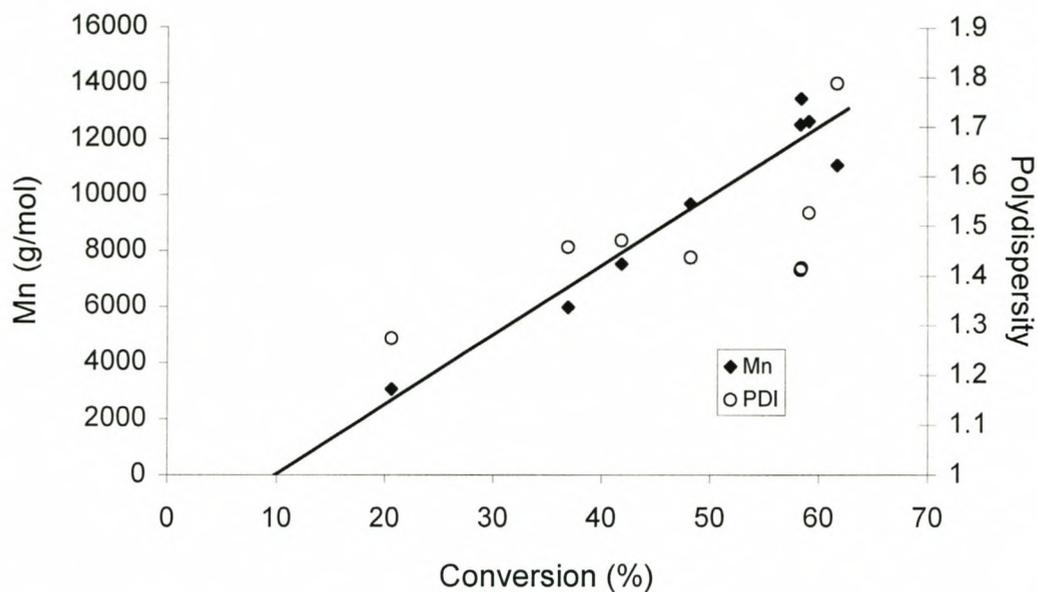


Figure 6.22: Graph showing \bar{M}_n and polydispersity versus conversion for the SLS/1-HD emulsifier system with no preceding bulk reaction step.

Figure 6.22 shows a poor linear relationship ($R^2=0,9313$) between molecular weight and conversion and the final polydispersity value is high.

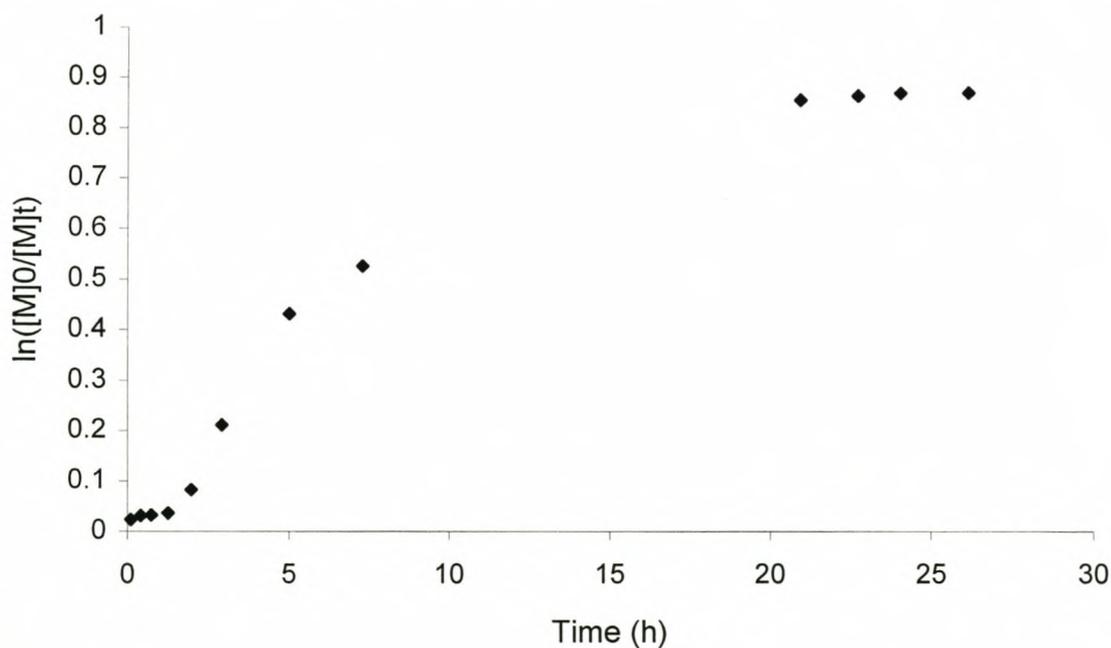


Figure 6.23: Graph illustrating the kinetic behaviour of the SLS/n-HD emulsifier system with no bulk reaction prior to emulsification.

Figure 6.23 also shows the reaction slowing towards the latter stages of the reaction. This is indicative of the apparent cessation of chain growth, also observed in Figure 6.22.

The above figures reveal that although a good linear relationship is maintained between molecular weight and conversion in both cases, the reactions do not go to high conversions. Chain growth ceases at roughly 60% conversion. Particle size also increased significantly when the RAFT-agent formation was performed in the miniemulsion, indicating that the presence of the chain transfer agent influences the particle size profoundly.

6.3.6 Effect of aqueous phase radical trap on the miniemulsion system

The purpose of this experiment was to determine whether an aqueous phase radical trap, in the form of a water-soluble salt, would have an effect on the reaction. Use of such a trap should help to prevent polymerization reactions taking place in the aqueous phase and would help ensure that the polymerization loci were predominantly in the minidroplets.² The SLS/*n*-hexadecane emulsifier system containing oligomers synthesized in bulk for 80 minutes was chosen for this investigation. Frémy's salt (potassium nitrosodisulfonate) was the radical trap selected. The salt was added after shearing to prevent partitioning of the salt into the droplets. The quantity used corresponded to a 1% (m/v) solution, based on the aqueous phase volume.

Upon heating, phase separation in the form of a red layer took place from the onset of the reaction. This separate phase kept growing in volume throughout the course of the polymerization reaction. The polymer chains in the red layer, however, were capable of growth and were supplied with monomer by diffusion of monomer from the minidroplets. This corresponded to a drop in particle size from 1,2 μ m to 180nm over the course of the reaction, suggesting that this red layer was dominant.

6.4 Conclusions

The first important observation was that the oligomers synthesized in bulk could indeed be successfully miniemulsified and polymerization commenced upon heating of the miniemulsion. This was also clearly evident from the overlay plots of molecular weight distributions for the different reactions (Figures 6.15 – 6.18). No red layer formation was observed and the postulated reasons for this were discussed in Section 6.1. The possible explanations were concerned with the prevention of aqueous phase transport and they included the nature of miniemulsions themselves, swelling of the oligomers with monomer and encapsulation of the RAFT-agents in the minidroplets.

In all the reactions continued in the miniemulsion step, good linear relationships of number average molecular weight with increasing conversion were obtained. Polydispersity, however, did not decrease, as would be the case in an ideal CFRP environment. This rise in polydispersity was more pronounced in the miniemulsions using 1-hexadecanol as a cosurfactant. Polydispersity was also higher when oligomers of higher molecular weight were miniemulsified and further polymerized. These two observations pointed to the possibility that aqueous phase polymerization reactions could not be ruled out completely, even though the reactions were being conducted in miniemulsions. As has been mentioned, fatty alcohols do not stabilize as efficiently against monomer diffusion as the corresponding alkanes. In other words, any polymerization reaction taking place in the aqueous phase would be better supplied with monomer in a system employing 1-hexadecanol as cosurfactant than in a system employing *n*-hexadecane. Such an aqueous phase nucleation site may exhibit conventional emulsion polymerization characteristics, leading to high molecular weight compounds being formed. This would cause a rise in polydispersity, as was indeed observed when the two different emulsifier systems were compared.

Furthermore, the “enhanced droplet nucleation” phenomenon described in Section 6.1 becomes more pronounced as the molecular weight of the added polymer decreases. The radius of gyration of oligomers synthesized in bulk will increase as their molecular weight

increases. Smaller radii of gyration enable the oligomers to preserve a larger part of the droplet population through equilibrium swelling with monomer. Therefore, when the oligomers synthesized in bulk for 80 minutes were used instead of the oligomers synthesized for 60 minutes, more droplets could degrade through monomer diffusion to larger droplets. This effect could also supply aqueous phase reactions with monomer and cause polydispersity to rise.

Plots of $[R^*]k_p$ vs conversion showed that the rate of termination suddenly increases at higher conversions. Although it has not been proved unambiguously, it might be indicative of the deactivation reaction of the RAFT-process becoming diffusion controlled at higher conversions. This might also help to explain the loss of control with increasing conversion.

6.5 Bibliography

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Polymer Type in Sodium Lauryl Sulfate/Cetyl Alcohol Miniemulsions"
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Chapter 7: Conclusions and Future Work

7.1 Conclusions

The first important observation made in this study was that the heating of different azo-initiators in the presence of di(thiobenzoyl) disulfide resulted in the formation of the corresponding dithioesters. These dithioesters were formed in high yields, indicating a very efficient reaction process.

Dithioesters act as chain transfer agents in the reversible addition-fragmentation chain transfer (RAFT) process in conventional free radical polymerization reactions to reversibly terminate growing polymer chains, and thereby endow living characteristics on the polymerization reaction. This led to the belief that the reaction between azo-initiators and di(thiobenzoyl) disulfide could be conducted in the presence of monomer and yield dithioesters in sufficient quantities to control the free radical process. The *in situ* formation of the RAFT-agent in the polymerization system has a number of advantages. These include:

- Di(thiobenzoyl) disulfide and most azo-initiators are crystalline materials which can be handled easily. The corresponding dithioesters, on the other hand, are viscous oils that are difficult to handle and weigh accurately.
- No purification of the corresponding dithioester oils is necessary. Oils need to be purified by column chromatographic techniques which can be time consuming and laborious. Di(thiobenzoyl) disulfide and azo-initiators can be readily purified by recrystallization from solvents.
- All of the dithioesters formed in the course of the reaction are available to take part in the polymerization reaction. Column chromatography of the dithioesters causes some of the product to be lost on the column.

This reaction between di(thiobenzoyl) disulfide and AIBN proved to be effective in controlling a conventional free radical polymerization reaction, when conducted in the presence of monomer, as proved by the results of the solution polymerization studies. Molecular weights increased in a predictable and linear manner with conversion, while polydispersities remained low ($<1,3$).

The results obtained from the solution polymerization studies paved the way to proceed with the synthesis of the oligomers in bulk. A bulk polymerization is in essence also a solution polymerization, with the monomer acting as the solvent. The synthesis of the oligomers in bulk involved stopping the reaction at low conversions. This meant that viscosity problems usually associated with bulk reactions at high conversions were not encountered.

The second stage of the polymerization reaction involved the shearing of the bulk reaction mixture (i.e. excess monomer, non-decomposed azo-initiator, unreacted di(thiobenzoyl) disulfide, unattached formed RAFT-agents and dormant dithiobenzoate-endcapped oligomers) into a miniemulsion, using a high shear mixer. Upon heating of the resulting miniemulsion, polymerization took place. Molecular weight increased in a linear manner with conversion, although high conversions ($>70\%$) could not be reached. Results were also dependent on both the type of cosurfactant used and the molecular weight of the emulsified oligomers. Results improved as the molecular weights of the oligomers decreased. Results (with special reference to polydispersities) improved when alkanes were used as cosurfactants instead of the corresponding fatty alcohols.

7.2 Achievement of Objectives

Even though the *in situ* RAFT-agent formation brought with it various inherent challenges, the approach still yielded a system in which molecular weight increased in a predictable and linear manner with conversion. This paved the way to continue with the synthesis of the oligomers in bulk, using the *in situ* RAFT-agent formation.

An emulsifier system was also established which provided stabilization against coagulation as well as phase separation. The changing of the cosurfactant was also observed to play a very important role in the performance of the system. Miniemulsions employing alkanes as cosurfactants performed better than miniemulsions employing the corresponding fatty alcohols.

After being miniemulsified, the oligomers could indeed be reinitiated and molecular weight also increased in a linear fashion with increasing conversion. No phase separation in the form of a red layer was observed. Reasons and possible explanations for any deviations from predicted behaviour and results were proposed to help further understand the mechanism of the RAFT-process.

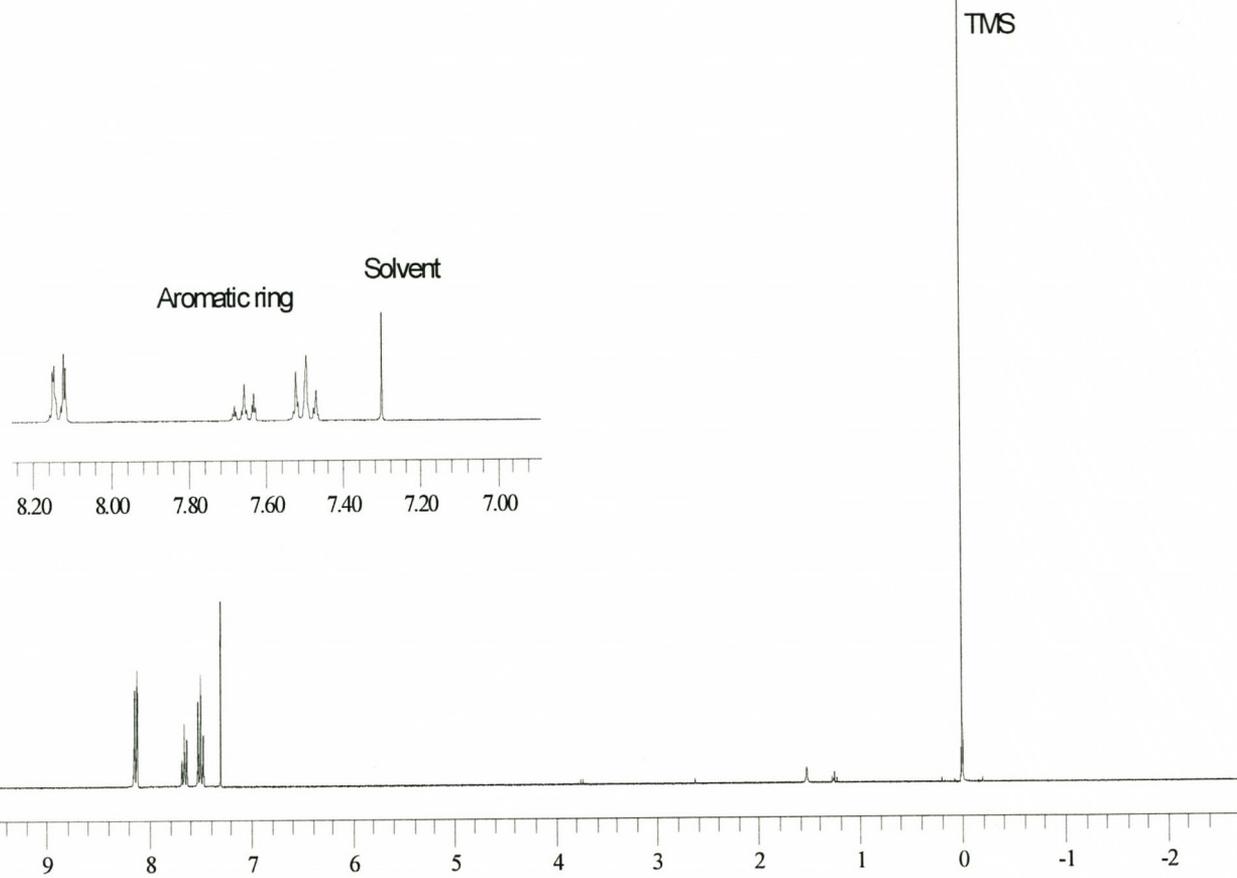
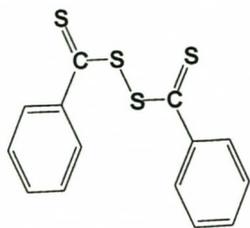
7.3 Future work and recommendations

A novel approach was taken to face the challenge of conducting RAFT-polymerization reactions in emulsions. With this approach came a range of new aspects and questions that need to be further investigated to understand the fundamentals of RAFT and conducting of the process in aqueous media. Aspects that require further investigation include:

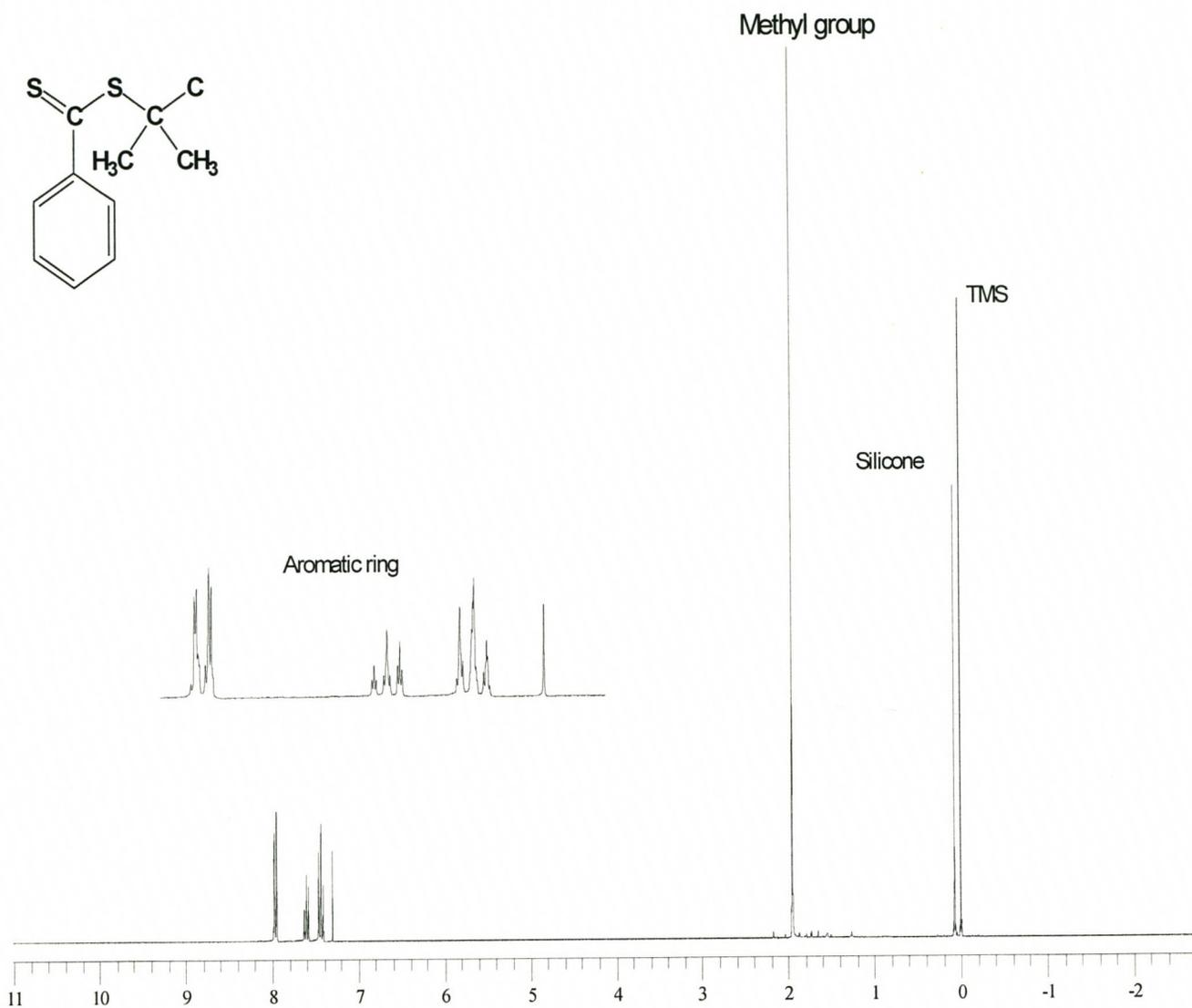
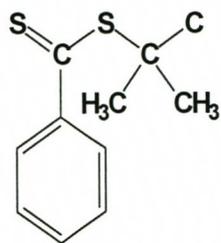
- ✓ The nature of all the competing reactions when the RAFT-agents are made *in situ* in the reaction system should be determined. The primary radicals derived from the decomposing azo-initiator have two possible reaction routes to follow. The radical can either react with a di(thiobenzoyl) disulfide molecule to form a RAFT-agent, or the radical can react with a monomer unit to initiate polymerization. For the reaction of di(thiobenzoyl) disulfide with any azo-initiator in the presence of monomer to be effective, the RAFT-agents have to form at a greater rate initially than the rate of initiation of polymer chains. The reaction rates of these competing reactions and the effect of the structure of the azo-initiator on the rate of RAFT-agent formation should be investigated.

- ✓ As the presence of the transfer agent seems to have a strong effect on the particle size of the miniemulsion, this needs to be investigated. This should be done with extensive electron microscope imaging, to determine the distribution of the particle population. The effect of the transfer agent on the stabilization of the miniemulsion should also be further investigated.
- ✓ The new technique needs optimizing, to minimize the exposure to oxygen and other potential chain-killing impurities. This might lead to higher conversions being reached.
- ✓ The reasons for the limiting conversions need to be determined.
- ✓ Changes in rate behaviour and loss of control should be investigated further.
- ✓ Modeling of the RAFT process when conducted in aqueous systems.
- ✓ Use of the dithiobenzoate-endcapped oligomers to stabilize miniemulsions instead of using a conventional hydrophobe.

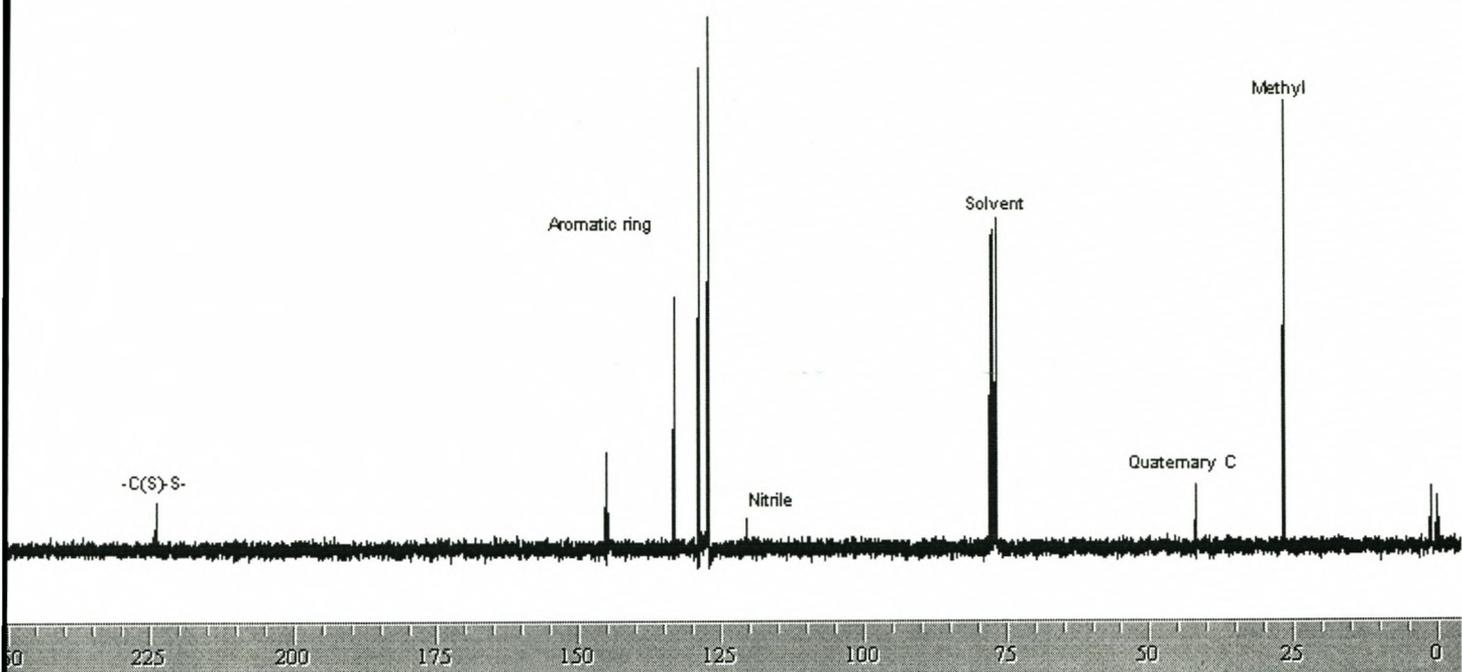
Appendix I



Spectrum I-1: ¹H-NMR spectrum of di(thiobenzoyl) disulfide.



Spectrum I-2: ¹H-NMR spectrum of AIBN-RAFT.



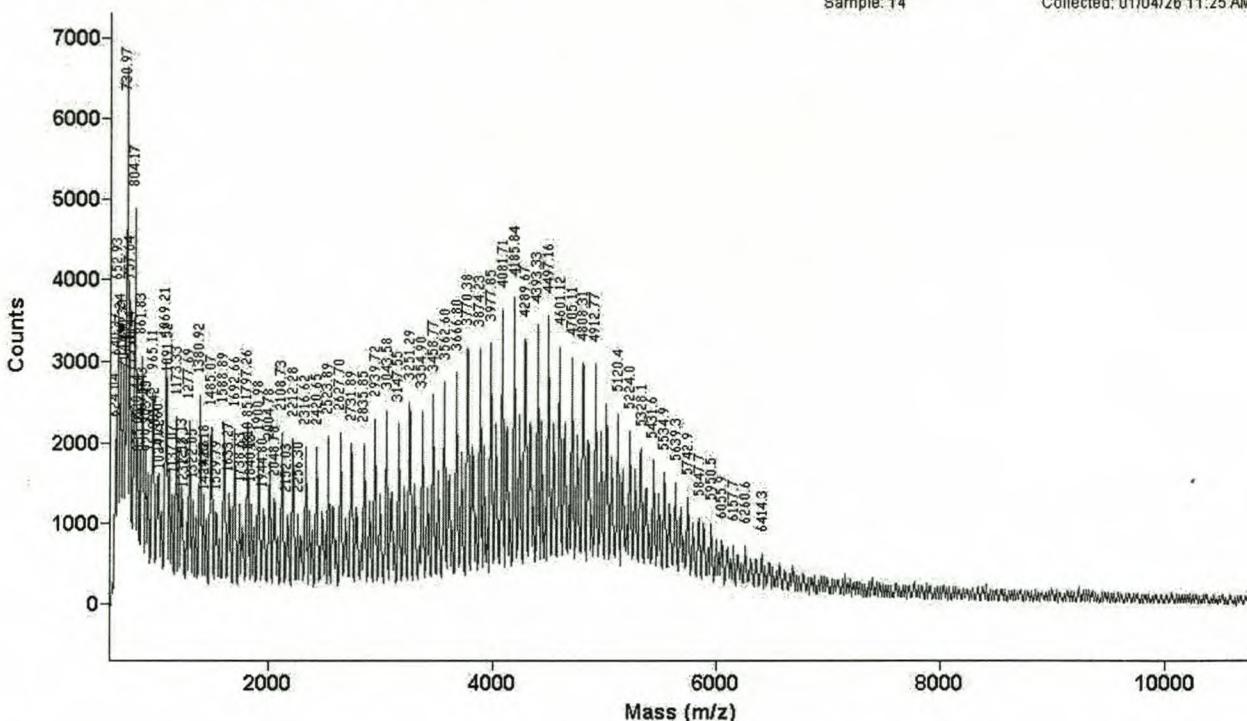
Spectrum I-3: ^{13}C -NMR spectrum of AIBN-RAFT.

PerSeptive Biosystems

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Comment: 60 min in Dithranol + Ag(I)trifluoroacetate

Method: HCD1001
Mode: Linear
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Grid Voltage: 94.500 %
Guide Wire Voltage: 0.050 %
Delay: 250 ON
Sample: 14

Laser: 2200
Scans Averaged: 256
Pressure: 2.66e-07
Low Mass Gate: 600.0
Timed Ion Selector: 28.6 OFF
Negative Ions: OFF
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Spectrum I-6: MALDI-TOF MS spectrum of the oligomers synthesized in bulk for 60 minutes.

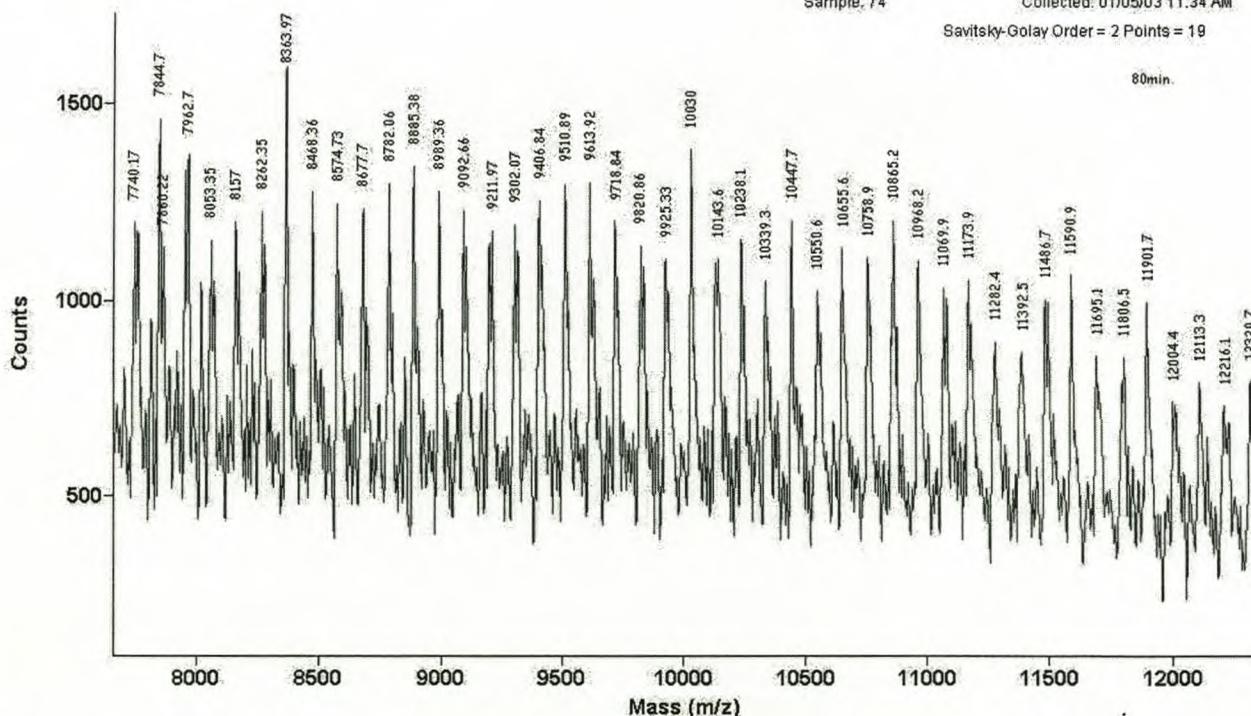
PerSeptive Biosystems

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Comment: 80 min in Dithranol + Ag(I)trifluoroacetate

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Grid Voltage: 92.000 %
Guide Wire Voltage: 0.050 %
Delay: 300 ON
Sample: 74

Laser: 2244
Scans Averaged: 256
Pressure: 2.70e-07
Low Mass Gate: 1000.0
Timed Ion Selector: 24.9 OFF
Negative Ions: OFF
Collected: 01/05/03 11:34 AM

Savitsky-Golay Order = 2 Points = 19



Spectrum I-7: MALDI-TOF MS spectrum of the oligomers synthesized in bulk for 80 minutes.